

Quintet–Triplet Electronic Transitions and Nephelauxetic Effects in CrF_6^{4-} . Results of an SCF MO Calculation

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The 18 triplets of the octahedral cluster CrF_6^{4-} are computed by using the solutions of SCF MO calculations on the $t_{2g}^3 e_g^2 {}^5T_{2g}$ state at five metal–ligand distances. The diagonal (first order) calculation is compared with the results of a CI description limited to the d^4 configuration. A third representation which includes CI and a correlation energy correction, CEC, locates the five lower triplets within 0.25 eV of their observed values. The last calculation locates the lower ${}^3A_{2g}$ below the ${}^3A_{1g}$, in contrast with a previous assignment. It is shown that the crystal-field matrices can be better fitted to the published spectrum of CrF_6^{4-} in KCrF_3 if the positions of the triplets predicted by our calculation are adopted. Electron delocalization calculated from our MO wavefunction is larger in the $e_g(\sigma)$ block than in the $t_{2g}(\pi)$ block. A reasonably good estimate of the delocalization effect can be made from appropriate relations among repulsion integrals. However, the trend followed by these relations when R_{ML} changes is opposite to that shown by the delocalization. Furthermore, the trend of the estimates which neglect the metal–ligand overlap integrals is incorrect. Finally, the covalency of this cluster is explored from a purely empirical point of view. The significance of the spin–orbit and Racah–Trees interactions in the empirical generation of a best set of Racah parameters for Cr^{2+} is examined. Our optimum sets of cluster and free-ion empirical parameters do not show the usually observed covalent reduction.

I. Introduction

The cluster CrF_6^{4-} is known to be a tetragonally distorted octahedron. In CrF_2 (1), three different metal–fluoride distances are found: 1.98, 2.01, and 2.43 Å. The double fluorides KMfF_3 have, generally, the perovskite lattice (2). Edwards and Peacock (3) have shown that in KCrF_3 two of the six M – F distances are shorter (2.00 Å) than the other four (2.14 Å). Oelkrug (4) quoted tetragonal distortions in $\text{CrF}_2 \cdot 2\text{H}_2\text{O}$, NaCrF_3 , and Na_2CrF_4 .

In an octahedral site, a d^4 system shows only one spin-allowed electronic transition, ${}^5E_g \rightarrow {}^5T_{2g} = 10 Dq$. The reported absorp-

tion spectra of Cr^{2+} in fluoride lattices present two or three broad bands in the 5- to 15,000- cm^{-1} region. These bands are interpreted in terms of the tetragonal splitting of the 5E_g and ${}^5T_{2g}$ states.

The spin-forbidden quintet–triplet transitions are less well known. Earnshaw *et al.* (5) found two sharp peaks at 16,700 and 20,000 cm^{-1} in the reflectance spectrum of KCrF_3 . They assigned them, tentatively, to the ${}^5E_g \rightarrow {}^3E_g$, ${}^3T_{2g}$ transitions, respectively. Holloway and Kestigian (6) observed four very narrow lines in the absorption spectrum of CrF_2 at 16,970 (3E_g), 18,640 (a^3T_{2g}), 19,164 (${}^3A_{1g}$), and 20,200 cm^{-1} (a^3A_{2g}). To our knowledge, Oelkrug's report (4) on the

quintet–triplet transitions of the CrF_6^{4-} cluster is the most complete. Oelkrug describes (4) the room-temperature spectra of KCrF_3 , NaCrF_3 , CrF_2 , $\text{CrF}_2 \cdot 2\text{H}_2\text{O}$, and Na_2CrF_4 , as well as the 78-K spectrum of KCrF_3 . In these experiments only six or seven triplets can be observed. Oelkrug assigned them to some of the 18 theoretically predicted triplets in octahedral symmetry (7).

Quantum-mechanical calculations on the electronic structure of the system CrF_6^{4-} are limited, as far as we know, to the recent work of Adachi *et al.* (8). They perform discrete variational $X\alpha$ cluster calculations on a series of fluoride compounds, including KCrF_3 . Their calculation of 10 Dq in this crystal (0.91 vs 1.4 eV experimental) is in moderately good agreement with the observed value. They do not include the quintet–triplet transitions in their discussion.

Under these circumstances, we believe that a theoretical calculation of the electronic structure of the cluster CrF_6^{4-} can be useful in the interpretation of its optical spectra. We have completed such a calculation within an open-shell SCF MO methodology developed by Richardson and collaborators (9). We report in this paper results of our calculations related to the behavior of the triplets, the nephelauxetic effects (10), and the covalency of CrF_6^{4-} .

The theoretical problems involved in the understanding of the system CrF_6^{4-} begin with a correct prediction of the observed tetragonal distortion. In this prediction the detailed consideration of the lattice potential and the spin–orbit and Jahn–Teller interactions is, probably, essential. However, in dealing with the quintet–triplet electronic transitions, a simpler theoretical calculation may be of interest since these transitions have been analyzed in terms of the octahedral crystal-field matrices and all the mentioned refinements have been neglected (4).

As in (8), we have assumed octahedral

symmetry in our calculation. Within this approximation we have computed all the triplet states as functions of the metal–ligand separation, R_{ML} , with MOs obtained from the SCF on the $t_{2g}^2 e_g^{2.5} T_{2g}$ state. The (diagonal) first-order calculation has been extended to include the configuration interaction, CI, limited to the d^4 configuration. We have found it necessary to include in our calculation the effects of the correlation energy correction, CEC, recently reported (11). This CEC propagates into the cluster the atomic energy corrections defined as $E(\text{SL}, \text{approx Hartree–Fock}) - E(\text{SL}, \text{experimental})$.

Using our wavefunction we have analyzed the dependence of the nephelauxetic effects (12) on (a) the MO symmetry and (b) the metal–ligand distance. Also, we have obtained the central-field covalency, CFC, and the symmetry-restricted covalency, SRC (12). These quantities are normally estimated from crystal-field theory and some difficulties are encountered, particularly in the SRC case (13). In this paper we compare our SCF MO predictions concerning the covalency of the cluster with the information gained from the optical spectrum. In order to get this information we have obtained an optimized set of electronic repulsion parameters for Cr^{2+} , using the spectrum recently reported by Ekberg (14) and considering the spin–orbit and Racah–Trees (15) interactions. The significance of such refinements has been pointed out, among others, by Ferguson and Wood (16) and by Witzke (17). When this set of free-ion parameters is used the nephelauxetic effect detected by Oelkrug (4) vanishes. This noticeable change illustrates the importance of an accurate selection of the empirical parameters and it is discussed in connexion with the SCF MO results.

In the next section we present our analysis of the spectrum of the Cr^{2+} ion. Section III is dedicated to the SCF MO calculation

on CrF_6^{4-} . The last section contains the discussion.

II. Cr^{2+} Interelectronic Repulsion Parameters

The spectrum of Cr^{2+} has been reported by Moore (18) and more recently by Ekberg (14), who locates the b^3P level some 6000 cm^{-1} below Moore's value.

The interelectronic repulsion integrals are obtained, usually, by fitting the Slater theoretical formulas to the observed spectrum, through a least-squares method. As an improvement, Griffith suggests (19) the

use of a weighting factor f_i , associated to each level, defined as the multiplicity of the level: $f_i = (2S_i + 1)(2L_i + 1)$. However, it has been a very common practice to make $f_i = 1$ for each term.

We have fitted the theoretical formulas to Ekberg's spectrum with $f_i = 1$ (giving $B = 826$, $C = 3166 \text{ cm}^{-1}$) and with $f_i = (2S_i + 1)(2L_i + 1)$ (giving $B = 801$, $C = 3278 \text{ cm}^{-1}$). The rms deviation, δ , is 556 cm^{-1} in the first case and 636 cm^{-1} in the second. We will employ results of calculations with $f_i = 1$, since $f_i = (2S_i + 1)(2L_i + 1)$ neither produces important changes in Racah parameters nor improves the agreement.

TABLE I
DIFFERENT CALCULATIONS OF THE RACAH PARAMETERS OF Cr^{2+}

Slater formulas for the d^4 triplets ^a :	Observed (cm^{-1}) ^b			
$^5D: 6A - 21B$	0			
$^3H: 6A - 17B + 4C$	17,064			
$^3G: 6A - 12B + 4C$	20,521			
$^3F: 6A - 5B + 11C/2 \pm 3(68B^2 + 4BC + C^2)^{1/2}/2$	42,951, 18,177			
$^3D: 6A - 5B + 4C$	25,420			
$^3P: 6A - 5B + 11C/2 \pm (912B^2 - 24BC + 9C^2)^{1/2}/2$	43,377, 17,152			
Best Racah parameters: First row entries are obtained without Racah-Trees correction ^c ; second row, with such correction				
	Without spin orbit		With spin orbit	
	Triplets	Tri. + singlets	Triplets	Tri. + singlets
B	826	842	819	833
	848	863	846	858
C	3,165	3,117	3,149	3,113
	3,046	2,979	3,046	3,005
ζ^d	—	—	342	315
			227	205
α^e	56	71	58	67
δ^e	556	925	449	720
	182	441	154	327
C/B	3.83	3.70	3.84	3.74
	3.59	3.45	3.60	3.50

^a Taken from Ref. (19), p. 86.

^b Ref. (14).

^c Polarization correction of the form: $\alpha L(L + 1)$, Ref. (15).

^d Spin-orbit coupling constant, ζ_{3d} , Ref. (19), p. 109.

^e Root-mean-square deviation.

Next, we considered the polarization correction of Trees and Racah (15) which is introduced by adding a term of the form $\alpha L(L+1)$ to the theoretical formulas. α is a fitting parameter.

The spin-orbit interaction has been included also. The appropriate matrix elements for this coupling have been calculated by Racah (20) and Dunn and Li (21).

Finally, we obtained the empirical parameters by considering all the terms of the d^4 configuration and, also, by taking only the triplets.

Results of all these calculations are collected in Table I, where we include the theoretical formulas and Ekberg's spectrum.

From Table I a number of interesting consequences can be drawn. First, we note that by comparison with the triplets-only calculation, inclusion of the highly excited singlets increases B and decreases C , lowering the C/B ratio. This is so whether the

spin-orbit coupling is neglected or not. As expected, the rms deviation is almost doubled when all the terms are taken into account.

Second, the spin-orbit interaction reduces B and C uniformly although very slightly, leaving the C/B ratio almost unchanged. Also, this coupling reduces the rms deviation by about 20% even though many more transitions are included in the calculation. The effect of this interaction on the value of α is negligible.

Finally, the Racah-Trees correction (15) turns out to be the most relevant refinement among all those considered here. It raises B by 3% and reduces C by 3%, improving the agreement by nearly 70%. This effect has been observed in other ions by Trees and Jorgensen (15). It is worthwhile to note the effect of the polarization correction on the spin-orbit constant: a reduction of about 35%.

The total consideration of all our results

TABLE II
STO ORBITAL EXPONENTS (IN PARENTHESES) AND AO EXPANSION COEFFICIENTS
FOR Cr³⁺ AND F^{-a} (22)

	1s(23.39)	2s(8.9)	3s(4.06)	4s(1.75)
1s _M	1.			
2s _M	-0.36240564	1.06364368		
3s _M	0.14156036	-0.47925202	1.09703726	
4s _M	-0.04246753	0.14647754	-0.38365720	1.05957517
	2p(9.70)	3p(3.74)	4p(1.48)	
2p _M	1.			
3p _M	-0.30745939	1.04619852		
4p _M	0.07726496	-0.28882174	1.03743504	
	3d ₀ (2.20)	3d ₁ (4.95)		
3d _M	0.58216579	0.54596792		
3d _I		1.		
	1s _F (8.7)	2s _F (2.425)		2p _F (2.425)
1s _F	1.			2p _F
2s _F	-0.21754530	1.02338944		1.

^a AOs are the rows and STOs are the columns.

suggests that in Cr^{2+} we need the polarization and spin-orbit interactions to obtain the best atomic parameters. We choose the triplets-only calculation since no quintet-singlet transition is reported in CrF_6^{4-} (4). Our best set is, then, $B = 846$, $C = 3046$, $\zeta = 227$, and $\alpha = 58 \text{ cm}^{-1}$, with $\delta = 154 \text{ cm}^{-1}$. This set differs from Oelkrug's values (4): $B = 815$, $C = 3400 \text{ cm}^{-1}$. Oelkrug's values reproduce the spectrum in Moore's compilation (18) with $\delta = 1967 \text{ cm}^{-1}$ and Ekberg's spectrum (14) with $\delta = 981 \text{ cm}^{-1}$.

III. SCF MO Calculations on CrF_6^{4-}

A. First-Order Calculation

We follow the methodology described by

Richardson and collaborators (9), and use the same multicenter Slater-type basis (22) and numerical procedures, which have given quite satisfactory results for similar systems before (23, 24). The STO exponents and the AO coefficients are presented in Table II.

SCF MO calculations were done at five internuclear distances, 3.26, 3.425, 3.59, 3.99, and 4.39 AU. These distances span the range observed for most Cr-F bonds. The calculations on the ground state, $t_{2g}^3 e_g^- {}^5E_g$, give a theoretical equilibrium distance of $R_e = 2.00 \text{ \AA}$. This figure agrees well with the equatorial metal-ligand distances observed in the tetragonally distorted CrF_6^{4-}

TABLE III
MULTIELECTRON MO WAVEFUNCTIONS OF THE d^4 PROBLEM IN
OCTAHEDRAL SYMMETRY USED IN THIS WORK^a

${}^5E \theta (M_s = 2)$	
1.	$t^3({}^4A_2)e : \xi\eta\zeta\epsilon $
${}^3T_1 z (M_s = 1)$	
1.	$t^4 : \xi\eta\zeta^2 $
2.	$t^3({}^2T_1)e : 2^{-1/2}(\xi^2\zeta\theta - \eta^2\zeta\theta)$
3.	$t^3({}^2T_2)e : 2^{-1/2}(\xi\xi^2\epsilon - \zeta\eta^2\epsilon)$
4.	$t^2({}^3T_1)e^2({}^1A_1) : -2^{-1/2}(\xi\eta\theta^2 + \xi\eta\epsilon^2)$
5.	$t^2({}^3T_1)e^2({}^1E) : -2^{-1/2}(\xi\eta\epsilon^2 - \xi\eta\theta^2)$
6.	$t^2({}^1T_2)e^2({}^3A_2) : -2^{-1/2}(\xi\bar{\eta}\theta\epsilon + \eta\bar{\xi}\theta\epsilon)$
7.	$te^3 : \zeta\theta^2\epsilon $
${}^3T_2 \zeta (M_s = 1)$	
1.	$t^3({}^2T_1)e : 2^{-1/2}(\xi^2\zeta\epsilon - \eta^2\zeta\epsilon)$
2.	$t^3({}^2T_2)e : 2^{-1/2}(\xi^2\zeta\theta - \eta^2\zeta\theta)$
3.	$t^2({}^3T_1)e^2({}^3A_2) : 2^{-1}(\xi\bar{\eta}\theta\epsilon + \bar{\xi}\eta\theta\epsilon - \xi\eta\theta\bar{\epsilon} - \xi\eta\bar{\theta}\epsilon)$
4.	$t^2({}^3T_1)e^2({}^1E) : 2^{-1/2}(\xi\eta\bar{\theta}\epsilon - \xi\eta\theta\bar{\epsilon})$
5.	$te^3 : \zeta\theta\epsilon^2 $
${}^3E \theta (M_s = 1)$	
1.	$t^3({}^4A_2)e : (3^{1/2})(2^{-1})(- \xi\eta\zeta\bar{\epsilon} + (\bar{\xi}\eta\zeta\epsilon + \xi\bar{\eta}\zeta\epsilon + \xi\eta\bar{\zeta}\epsilon)/3)$
2.	$t^3({}^2E)e : 2^{-1}(3^{-1/2})(2 \xi\eta\zeta\epsilon - \xi\bar{\eta}\zeta\epsilon - \xi\eta\bar{\zeta}\epsilon - \xi\eta\zeta\theta + \xi\bar{\eta}\zeta\theta)$
3.	$t^2({}^1E)e^2({}^3A_2) : 2^{-1/2}(\eta^2\theta\epsilon - \xi^2\theta\epsilon)$
${}^3A_2 (M_s = 1)$	
1.	$t^3({}^2E)e : 2^{-1}(\xi\bar{\eta}\zeta\epsilon - \bar{\xi}\eta\zeta\epsilon - 3^{-1/2}(2 \xi\eta\bar{\zeta}\theta - \xi\bar{\eta}\zeta\theta - \bar{\xi}\eta\zeta\theta))$
2.	$t^2({}^1A_1)e^2({}^3A_2) : 3^{-1/2}(\xi^2\theta\epsilon + \eta^2\theta\epsilon + \zeta^2\theta\epsilon)$
${}^3A_1 (M_s = 1)$	
1.	$t^3({}^2E)e : 12^{-1/2}(3^{1/2}(\xi\bar{\eta}\zeta\theta - \bar{\xi}\eta\zeta\theta) + 2 \xi\eta\zeta\epsilon - \xi\bar{\eta}\zeta\epsilon - \bar{\xi}\eta\zeta\epsilon)$

^a t and e stand for t_{2g} and e_g , respectively; ξ for $\xi\alpha$ and $\bar{\xi}$ for $\xi\beta$; α , β are spin functions. $\xi^2 \equiv \xi\bar{\xi}$.

(1). Analysis of the nuclear potential obtained in these calculations will be reported elsewhere. We will concentrate now on the optical transition energies.

All the theoretically predicted triplets were computed, at the above-mentioned five distances, from the MO's obtained in the SCF calculations on the $t_{2g}^3 e_g^2 {}^3T_{2g}$ state. The necessary multielectron MO wavefunctions were obtained by standard methods (25) and they are collected in Table III. As in CrF_6^{3-} (26), our best calculated transition energies are those in the *SPDD* basis (24, 26). In this basis the valence shell is composed of Cr^{2+} $3s$, $3p$, $3d_M$, and $3d_I$ orbitals.

B. Configuration Interaction

Configuration interaction (CI) has proved to be quite important in a correct description of the optical transition energies in clusters similar to CrF_6^{3-} (24, 26). Matrix elements required for the d^4 problem in terms of the appropriate 10 independent integrals (9) were computed and are collected in Table IV.

C. Correlation Energy Correction

We have incorporated in our calculation this correction (11) in the same way as in NiF_6^{3-} and CrF_6^{3-} . The required atomic CEC

TABLE IV
CI MATRIX ELEMENTS OF THE d^4 PROBLEM (TRIPLETS ONLY) UNDER OCTAHEDRAL SYMMETRY IN TERMS OF THE TEN INDEPENDENT INTEGRALS INTRODUCED IN REF. (9)^a

${}^3T_{1g}$							
1.							
2.	$-2^{1/2}i$						
3.	$-6^{1/2}i$	$3^{1/2}P'$					
4.	$-2^{1/2}\bar{K}$	$-i$	$3^{1/2}i$				
5.	$2^{1/2}K'$	i	$3^{1/2}i$	$-2P'$			
6.	0	$3^{1/2}i$	$5i$	0	$3^{1/2}K'$		
7.	0	$(3/2)^{1/2}K'$	$2^{-1/2}(3\bar{K}-K)$	$-6^{1/2}i$	$6^{1/2}i$		$2^{1/2}i$
${}^3T_{2g}$							
1.							
2.	$3^{1/2}P'$						
3.	$2^{1/2}i$	$6^{1/2}i$					
4.	$-i$	$3^{1/2}i$	$2^{1/2}K'$				
5.	$(3/2)^{1/2}K'$	$2^{-1/2}(\bar{K}+K)$	$12^{1/2}i$	$6^{1/2}i$			
3E_g							
1.							
2.	$-2K'$						
3.	0	$6^{1/2}i$					
${}^3A_{2g}$							
1.							
2.	$-4(3)^{1/2}i$						

^a $K = K(e\theta, t\xi)$; $\bar{K} = \bar{K}(et) = (K(\theta\xi) + K(e\xi))/2$; $K' = K - \bar{K}$; $P' = \bar{P}(et) - P(e\theta, t\xi)$; $P = J - K/2$; $\bar{P} = J - \bar{K}/2$; $\bar{J}(et) = (J(\theta\xi) + J(e\xi))/2$.

matrix was computed from Ekberg's spectrum (14). In Table V we present the atomic CEC matrix and the $\langle iSL|t^x e^y, jS\Gamma\rangle$ coefficients needed in the CrF_6^{4-} case. As in Ref. (11) we have used the CEC with and without delocalization.

IV. Discussion of Results

A. SCF MO Transition Energies

In Table VI we collect the results of our SCF MO calculations of the quintet-triplet transition energies. All entries correspond to vertical transitions computed at our theoretical minimum. Only the triplets ob-

served by Oelkrug (4) have been considered. We will discuss the problems of the 10 Dq in a later paper.

The numbers in Table VI illustrate the variations in the theoretical predictions produced by different refinements. CI lowers the triplets by more than 3000 cm^{-1} . The ${}^3A_{1g}$ is not affected by CI within the d^4 configuration and it lies above the lower ${}^3A_{2g}$ in the calculation which includes CI. In this cluster the effects of the CEC are larger than those of CI, as far as the presently discussed triplets are concerned: the CEC (not delocalized) lowers their positions by 9600 cm^{-1} and the CEC (delocalized) by 8500 cm^{-1} , on the average. This behavior is

TABLE V
ATOMIC CEC OF Cr^{2+} AND $\langle iSL|t^x e^y, jS\Gamma\rangle$ COEFFICIENTS

$\text{Cr}^{2+}; {}^5D \rightarrow$	3H	3G	a^3F	b^3F	3D	a^3P	b^3P
CEC(iSL) cm^{-1}	-4608	-6896	-6745	-15853	-10038	-7036	-16210
1.	2.	3.	4.	5.	6.	7.	${}^3T_{1g}$
0.031687	0.314145	0.633735	0.362744	-0.407556	0.314145	0.319870	b^3P
-0.341085	0.144660	0.491742	-0.250556	0.732923	0.144660	-0.006627	b^3F
0.447213	-0.547723	0.0	0.316228	0.316228	0.547723	0.0	3G
-0.465825	-0.281203	-0.157663	0.487050	0.171724	-0.281202	0.577315	a^3F
-0.376637	0.398063	-0.375814	0.459648	0.072996	0.398064	-0.428246	a^3P
0.429335	0.561282	-0.364998	-0.061413	0.303585	0.070914	0.516185	3H
0.373472	0.166793	0.239275	0.503361	0.264085	-0.581230	-0.338386	3H
1.	2.	3.	4.	5.	${}^3T_{2g}$		
0.323468	0.726057	0.186754	0.264110	0.513400	b^3F		
-0.534522	-0.308607	0.617213	0.218218	0.436436	3D		
-0.119523	0.414039	0.621059	-0.292769	-0.585540	3G		
0.628784	-0.373508	0.363028	0.513400	-0.264110	a^3F		
0.447214	-0.258199	0.258199	-0.730297	0.365148	3H		
1.	2.	3.	3E_g	1.	2.	${}^3A_{2g}$	
0.755929	-0.377965	0.534522	3D	0.457452	-0.889234	b^3F	
-0.169031	0.676123	0.717138	3G	0.889234	0.457452	a^3F	
-0.632456	-0.632456	0.447213	3H				
1.	5E_g	1.	${}^5T_{2g}$	1.	${}^3A_{1g}$		
1.	5D	1.	5D	1.	3G		

TABLE VI
VERTICAL TRANSITION ENERGIES IN CrF_6^{4-} FROM SCF ON ${}^5T_{2g}$ CALCULATED AT THE THEORETICAL
EQUILIBRIUM GEOMETRY

Transition	Observed ^a	First order	CI	CI + CEC	CI + CEC (deloc.)
$t^3e^1.{}^5E_g \rightarrow$					
a^3E_g	16,840	23,410	20,200	15,270	16,130
b^3T_{1g}	17,900	25,410	21,090	15,180	16,250
a^3T_{2g}	18,600	27,460	21,940	15,750	16,900
a^3A_{2g}	20,100	28,480	24,200	17,230	18,570
${}^3A_{1g}$	20,600	24,390	24,390	17,490	18,800
rms deviation	—	7,250	3,570	2,680	1,530

Note. All numbers in cm^{-1} .

^a Reference (4).

quite similar to that shown by the spin-forbidden transitions of NiF_6^{4-} and CrF_6^{3-} (11), where CI and the CEC reduce the first-order transition energies by about 2000 and 4500 cm^{-1} , respectively. In CrF_6^{4-} the CEC (not delocalized) locates all the triplets in Table VI below their observed values. That was also the case in the t^3e^1 doublets 2E_g , ${}^2T_{1g}$ of CrF_6^{3-} (11). The CEC (delocalized) reduces this too-large correction and improves the spectral calculation, as can be seen in the rms deviation appearing in the last row of Table VI. The order of the triplets after CI coincides with the order in the best calculation. Here we have a case, then, where the delocalization effects of the CEC play a significant role in the spectral calculation.

The total energy of the triplet states considered in Table VI shows a dependence of R_{ML} almost identical to that of the ground state. This parallel behavior is altered rather slightly by the contributions of CI and the CEC. The noticeable exception to this regularity is the ${}^3A_{2g}$. In the first-order calculation the total energy of this state is constantly higher than the energy of the ${}^3A_{1g}$ by about 4000 cm^{-1} from $R_{\text{ML}} = 1.7$ to 2.1 Å.

After CI the minimum of the lower ${}^3A_{2g}$, in the $E_T - R_{\text{ML}}$ diagram, is slightly dis-

placed to larger metal–ligand distances, and it crosses the unchanged ${}^3A_{1g}$.

The effect of the CEC (not delocalized) on the variation of the total energies of the triplets with R_{ML} is necessarily small since this CEC is independent of R_{ML} . It gives rise to a closer packing of the triplets in the range 15,000–20,000 cm^{-1} . In particular, the CEC does not change the inversion of the ${}^3A_{1g}$, ${}^3A_{2g}$ states produced by CI. On the other hand, the CEC (delocalized) changes with R_{ML} (11), but the pattern of the $E_T - R_{\text{ML}}$ diagram in our best calculation is very similar to that obtained in the CI + CEC (not delocalized) calculation. The crossing point of the ${}^3A_{1g}$, ${}^3A_{2g}$ states moves to the region of smaller R_{ML} when the CEC is included, making more evident the inversion of these triplets produced by CI. At this point we recall that the variation of the total energy of the ground and the triplet states of CrF_6^{4-} with R_{ML} could be modified if the effects of the ions surrounding the CrF_6^{4-} cluster were properly taken into account. For instance, Pueyo and Richardson (26) found that the equilibrium value of R_{ML} in CrF_6^{3-} changes from 1.79 to 1.92 Å when the lattice potential of the K_2NaCrF_6 is incorporated into the SCF calculation. Although this effect could be smaller in other lattices (28), its significance in the spin-allowed

electronic transitions (and perhaps in the curvature of the $3d^{n-1}4s^1$ multiplets) should always be large enough to be considered. On the other hand, in spin-forbidden, largely intraconfigurational (even after CI) electronic transitions, such as those analyzed in this work, we can assume that the contributions of the external potential are small. A systematic study of the effects of the crystal lattice in this type of SCF calculation is now in progress in our laboratory.

The effects of CI and the CEC on these triplets of CrF_6^{4-} can be appreciated in a very simple way in Table VII. In this table we collect the values of the Racah parameters B and C obtained by systematic linearization of the electrostatic matrices (27) to the theoretical spectrum calculated at different distances. In the CI calculation these parameters are almost independent of R_{ML} in the equilibrium region. That is an indication of the intraconfigurational character of these quintet-triplet transitions after CI.

The CEC (not delocalized) reduces B by 37% and C by about 25% giving rise to C/B ratios noticeably larger than those of the CI calculation. In the best spectral calculation we observe that (a) B and C have values intermediate between those of the CI and the CI + CEC (not delocalized) calculations and (b) the C/B ratios turn out to be similar to those of the CI calculation.

From Table VII we would like to make the following points. First, the theoretical C/B ratios change with R_{ML} in contrast with the predictions of the simpler crystal-field theory. Second, the ratio $B/B(\infty)$ differs from the ratio $C/C(\infty)$, particularly in the CI + CEC calculations. Finally, in the CI and the CI + CEC (not delocalized) calculations the values of B and C obtained at the equilibrium configuration are smaller than the correspondent Cr^{2+} values by a factor of 0.8–0.9 (notice that the Racah-Trees and the spin-orbit interactions are not included now). In the best calculation, however, B and C are more similar to the cor-

TABLE VII
BEST RACAH PARAMETERS OBTAINED BY
SYSTEMATIC LINEARIZATION OF THE
ELECTROSTATIC MATRICES TO THE
THEORETICAL SPECTRUM

		CI				
B	1036	1040	1037	1030	1149 ^a	
C	3722	3731	3755	3816	4270	
		CI + CEC				
B	637	645	659	677	826 ^b	
C	2826	2827	2828	2835	3165	
		CI + CEC (deloc.)				
B	810	805	808	770	826 ^b	
C	3121	3050	2984	2960	3165	

Note. The linear equations $\bar{v}_i = a_i\Delta + b_iB + c_iC$ have been used in the calculations. All entries in cm^{-1} .

^a Cr^{2+} Hartree-Fock values.

^b Best experimental values neglecting the Racah-Trees and the spin-orbit interactions.

respondent Cr^{2+} values. That is simply due to the fact that our best calculation is the closest to the observed spectrum. As we will see below, the reduction in B, C is not observed when the comparison is made in terms of experimental free-ion and cluster parameters.

B. Empirical Nephelauxetic Effect

The present SCF MO calculation of the lower triplets of CrF_6^{4-} is in general agreement with the assignment made by Oelkrug (4) using crystal-field theory. Our calculation differs from that assignment in the relative positions of the ${}^3A_{1g}$, ${}^3A_{2g}$. We would like to discuss briefly this slight difference since it has significant consequences in an empirical analysis of the cluster spectrum.

Inspection of the d^4 electrostatic matrices (7) shows that the relative positions of these two triplets can be reversed by small changes in the Racah parameters B and C . Thus, both Oelkrug's assignment, $E({}^3A_{1g}) < E({}^3A_{2g})$, and the opposite one should be considered in an empirical investigation of the best electrostatic parameters. We found

that both assignments are equally suitable for reproducing the observed transition energies, although they give rise, obviously, to different sets of optimum parameters. This can be seen in Fig. 1, where we present the rms deviation produced by the best set of parameters obtained by linearized fitting of the electrostatic matrices to the experimental spectrum (4). The deviation is plotted against the C/B ratio; curve I corresponds to Oelkrug's assignment and curve II to the opposite one. The last assignment is somewhat better, according to the criterium of the minimum rms deviation. It is satisfactory to see that this assignment coincides, also, with the ordering of triplets predicted by our best SCF MO calculation.

The electrostatic parameters corresponding to the minima in curves I and II of Fig. 1 are collected in Table VIII. The change (I \rightarrow II) in band assignment raises B by 11% and lowers C by 4%, reducing the C/B ratio by 13%. It is interesting to note that the C/B ratio in calculation II is closer to the free-ion value (3.72) predicted with the approximate HF basis of Richardson *et al.* (22).

The most significant conclusion gained from Table VIII concerns the nephelauxetic effect. If we evaluate it through the ratio $B(\text{cluster})/B(\text{free ion})$ we have 0.95 and 1.05 by using assignments I and II, respectively. The ratio $C(\text{cluster})/C(\text{free ion})$ gives 1.04 and 1.00, respectively. In obtaining these ratios we used the free-ion parameters calculated without spin-orbit and Racah-Trees interactions ($B = 826$, $C = 3165 \text{ cm}^{-1}$), i.e., the cluster and free-ion parameters are calculated with the same degree of refinement. On the other hand, use of the best free-ion values ($B = 848$, $C = 3046 \text{ cm}^{-1}$) does not make any significant change in the ratios. Thus, we can conclude that no matter what amount of electron delocalization may occur in the formation of the $\text{Cr}^{2+}\text{-F}^-$ bond in CrF_6^{4-} , we are unable

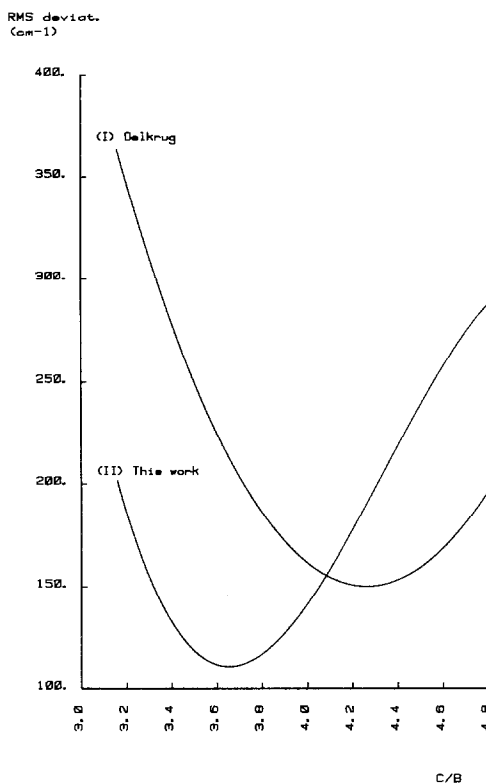


FIG. 1. The rms deviation, δ in cm^{-1} , of two systematic linearizations of the observed spectrum of KCrF_3 , as a function of the parameters ratio C/B . Curve I assumes Oelkrug's assignment, i.e., $E(^3A_{1g}) < E(^3A_{2g})$. Curve II assumes the opposite locations of these triplets, as proposed in this work.

to estimate such an amount by simply using the optimum values of B, C calculated from the cluster and the Cr^{2+} spectra. Moreover, B and C would give different estimates for such nephelauxetic effects. The importance of a correct selection of empirical parameters is, of course, recognized when using crystal-field theory. But even if great care is exercised in the selection, it is usually difficult to obtain reliable information about the metal-ligand bonding from the electrostatic parameters. This idea has been pointed out recently by Witzke (17) and we have observed that this is true in CrF_6^{4-} .

TABLE VIII
RESULTS OF TWO DIFFERENT LINEARIZATIONS OF
THE d^4 ELECTROSTATIC MATRICES TO THE
OBSERVED SPECTRUM OF $KCrF_6$ AT 78 K

Transition	Observed	I	II
$t^3e^{1.5}E_g \rightarrow$			
a^3E_g	16,840	17,084	17,013
b^3T_{1g}	17,900	17,783	17,625
a^3T_{2g}	18,600	18,694	18,600
${}^3A_{1g}(I), a^3A_{2g}(II)$	20,100	20,183	20,355
$a^3A_{2g}(I), {}^3A_{1g}(II)$	20,600	20,321	20,455
rms deviation		156	118
B		782	867
C		3,296	3,177
C/B		4.21	3.66

Note. Calculation I has been done assuming $E({}^3A_{1g}) < E({}^3A_{2g})$ as in Ref. 4. Calculation II corresponds to the opposite assignment, as predicted by our CI + CEC calculation (Table VI). All numbers in cm^{-1} .

C. Electron Delocalization in CrF_6^{4-}

From our MO wavefunction we will discuss different ways of analyzing the electronic charge distribution in the antibonding t_{2g} and e_g MOs. These MOs are mainly metal orbitals and belong to the open shells of the system. We will use results of our SCF calculation on the ground state $t_{2g}^3e_g^{-5}E_g$. First, we can obtain the electronic charge on the metal by means of the population analysis. Let us call $\alpha(tt)$ and $\alpha(ee)$ the results of this analysis for the t_{2g} and e_g antibonding MO's, respectively. These α 's change when R_{ML} changes and they are collected in the first two rows of Table IX.

Next, we can define three sets of Racah parameters, depending upon whether only t_{2g} MOs, only e_g MOs, or both, are involved in the repulsion integrals. Their definitions are in terms of the ten independent repulsion integrals (9). Let us call them $B(tt)$, $B(ee)$, and $B(et)$. If B is the free-ion value of the second Racah parameter calculated with the basis set used in this work (22), we can obtain theoretical values of $\beta_{55} = \beta(tt) = B(tt)/B$ and $\beta_{35} = \beta(et) = B(et)/B$. Values

of these β 's also appear in Table IX, as functions of R_{ML} .

We can now explore the concepts of central field covalency, CFC, and symmetry-restricted covalency, SRC, proposed by Jørgensen (12). He assumes a one-electron MO

$$\psi_{MO} = a\phi_{3d}(\lambda r) + b\phi_L,$$

where a, b are mixing coefficients, ϕ_L is a symmetry-adapted ligand group orbital, and $\phi_{3d}(\lambda r)$ is a metal $3d$ wavefunction scaled by a factor λ . Jørgensen suggests that the integrals B and C are mainly determined by ϕ_{3d} . In the ionic limit we will find

$$B(tt) = a_t^4 \lambda B,$$

$$B(ee) = a_e^4 \lambda B,$$

$$B(et) = a_e^2 a_t^2 \lambda B,$$

and, therefore, $B(ee)/B(et) = a_e^2/a_t^2$, $B(et)/B(tt) = a_e^2/a_t^2$, and, finally,

$$\beta_{35}/\beta_{55} = \beta_{33}/\beta_{35} = a_e^2/a_t^2.$$

We can check this result by computing the factor a_e^2/a_t^2 , independently, from our wave-

TABLE IX
DIFFERENT THEORETICAL ESTIMATES OF
ELECTRONIC CHARGE DISTRIBUTION IN
ANTIBONDING t_{2g} AND e_g MOs, AS
FUNCTIONS OF R_{ML}

Quantity	R_{ML} (Å)			
	1.72	1.81	1.90	2.11
$\alpha(tt)^a$	0.962	0.970	0.976	0.987
$\alpha(ee)$	0.912	0.917	0.921	0.932
$\alpha(ee)/\alpha(tt)$	0.948	0.945	0.944	0.944
$\beta(tt) = \beta_{55}$	0.881	0.887	0.892	0.903
$\beta(ee) = \beta_{33}$	0.911	0.906	0.899	0.880
$\beta(et) = \beta_{35}$	0.893	0.891	0.890	0.886
β_{33}/β_{35}	1.020	1.017	1.010	0.994
β_{35}/β_{55}	1.014	1.005	0.997	0.981
a_t^2	1.002	0.997	0.995	0.994
a_e^2	1.082	1.045	1.019	0.984
a_e^2/a_t^2	1.080	1.048	1.025	0.989

^a See text for definitions.

function. This ratio of MO coefficients appears in the last row of Table IX.

From this table we can immediately see that Jørgensen's assumption is satisfied in the neighborhood of the equilibrium value of R_{ML} . However, the differences between the β ratios and the coefficients' ratio increase when R_{ML} decreases. This is obvious, since the overlap effects must be more important at smaller values of R_{ML} . We can say that, according to our SCF calculation, the coefficients' ratio could be estimated from the β ratios in the region of interest.

On the other hand, the effects of the metal-ligand overlap integrals are evident when we compare the function $\alpha(ee)/\alpha(tt)$ with a_e^2/a_t^2 , in Table IX. These functions should give the same information if the overlap integrals were negligible. It is clear that it is not so, in this case.

In the zero-overlap approximation we observe that at $R_{\text{ML}} = R_e$, the mixing coefficients are practically equal to one and $\beta_{33} = \beta_{55} = \beta_{35} = 0.90$. These results tell us that within this approximation there is a CFC of about 0.9 and there is no SRC since all the β 's are almost identical.

When the overlap integrals are properly taken into account, as in the results of our population analysis appearing in the first two rows of Table IX, we detect a degree of metal-ligand mixing, in the equilibrium region, different for different symmetries: about 0.98 for t_{2g} and 0.92 for e_g . So, we have SRC. Both t_{2g} and e_g covalencies increase when R_{ML} decreases as is to be expected.

Finally, it is interesting to note that the R_{ML} dependence of β_{33} is opposite to that of β_{55} . The behavior of β_{55} is that which was expected and it follows the evolution of $\alpha(tt)$. On the other hand, β_{33} shows an unexpected increase in covalency when the cluster goes to $R_{\text{ML}} = \infty$. That could be related to a significant CI of our ground state with charge-transfer configurations;

our ground state could go to a more complicated dissociation state than the simple $\text{Cr}^{2+} + 6\text{F}^-$. β_{35} lies between β_{33} and β_{55} and its values are determinant in locating all the triplet states intraconfigurational with the ground state. That explains the entire parallelism between β_{35} and the nephelauxetic ratios deducible from Table VII.

In conclusion, we have found that in CrF_6^{4-} we cannot detect any covalency at all if we limit ourselves to the empirical analysis of optical spectra. Estimates based on the neglect of metal-ligand mixing give rise to a CFC of the correct order of magnitude but fail to reveal the variations of the covalency with the metal-ligand distance and the appreciable SRC. The correct analysis of the mixing coefficients reveals a stronger covalency in the e_g block, possibly due to the more internal character of the $3dt_{2g}$ metal orbitals.

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