

## Theoretical Calculation of the Electronic Structure and the Optical Spectrum of $\text{CrF}_6^{2-}$

S. GUTIÉRREZ ORELLANA AND L. PUEYO

*Departamento de Química Física, Facultad de Química, Universidad de Oviedo, Oviedo, Spain*

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The electronic structure of the  $\text{CrF}_6^{2-}$  cluster has been analyzed by solving the Hartree-Fock equations on several electronic states, at five values of  $R$ , the metal-ligand distance in the  $a_{1g}$  vibration. The methodology of J. W. RICHARDSON, T. F. SOULES, D. M. VAUGHN, AND R. R. POWELL (*Phys. Rev. B* **4**, 1721 (1971)) has been used. The computed  $R_e$  is in close agreement with the observed value in alkali hexafluorochromates(IV). The nuclear potentials of the  $d^2$  triplets are almost parallel to the ground state potential, giving rise to a weak  $R$ -dependence of the spin-allowed transitions and a negligible contribution of the  $a_{1g}$  progression to the vibrational structure of the broad bands. The absorption spectrum has been discussed in terms of the results of different SCF calculations. A new assignment is proposed that avoids most of the earlier difficulties of the spectral interpretation. The best calculated spectrum agrees with the one observed in  $\text{Rb}_2\text{CrF}_6$  within 1.5 kK. © 1984 Academic Press, Inc.

### I. Introduction

The absorption spectrum of the  $\text{CrF}_6^{2-}$  cluster in  $\text{Rb}_2\text{CrF}_6$  has been reported by Allen and El-Sharkawy (1). At 77°K the broad bands do not show vibrational structure. This is a rather interesting feature, since such fine structure appears in other quadrivalent hexafluorocomplexes:  $\text{NiF}_6^{2-}$  (2),  $\text{MnF}_6^{2-}$  (3),  $\text{CoF}_6^{2-}$  (4). This negative evidence has been related to the low value of the nephelauxetic ratio in  $\text{CrF}_6^{2-}$  (1). Another problem in this spectrum is the assignment of the second spin-allowed transition, only tentatively made by Allen and El-Sharkawy, because it is superimposed upon a more intense ligand-to-metal charge transfer. Moreover, the third spin-allowed transition has not been assigned and the relative positions of the lowest excited states

$^1T_{2g}$ ,  $^1E_g$  (which are degenerate at first-order) remain unknown (1). These and other features of this spectrum have been analyzed in this work in the framework of the open-shell Hartree-Fock methodology developed by Richardson *et al.* (5). Since Allen and El-Sharkawy gave only the spectrum of  $\text{Rb}_2\text{CrF}_6$  and reported that the spectra of the K, Rb, and Cs hexafluorochromates(IV) are very similar (1), we have limited our study to the calculation of the  $\text{CrF}_6^{2-}$  unit *in vacuo*. We have solved the SCF equations at different values of the metal-ligand distance on several electronic states, including the ground state. At this level of approximation, our prediction on the equilibrium conformation along the  $a_{1g}$  vibration,  $R_e = 1.69 \text{ \AA}$ , is in very good agreement with the value reported by Bode and Voss (6) for the alkali hexafluoro-

chromates(IV), 1.72 Å. Other interesting result of our calculation is the almost negligible horizontal displacement of the excited states along the  $a_{1g}$  coordinate. This result gives rise to theoretical transition energies only weakly dependent on  $R$  (the spin-allowed ones) or practically  $R$ -independent (the spin-forbidden). For that reason, the particular choice of  $R$  in the vertical calculation of the spectrum seems to be a relatively unimportant question in this case. Of course, there is the problem of explaining the different values of  $R_e$  in different alkaline-earth hexafluorochromates(IV) (7), but this theoretical work cannot be done without extensive calculations of the respective cluster–lattice interactions (8, 9), and it is beyond the limits of this paper.

We have analyzed the spectrum of  $\text{Rb}_2\text{CrF}_6$  at different levels of approximation, including configuration interaction limited to the  $d^2$  configuration. At each level we compare our SCF results with the crystal-field analysis that can be done within the simplest, three-parameter theory. From these comparisons we illustrate how the SCF results, although approximate, give important information which could not be deduced at all from the semi-empirical approach. In this way we have proposed an assignment (different from that in Ref. (1)) which is compatible with a simple crystal-field analysis, resolves the relative positions of the lowest singlets and gives a reasonable description of the complete  $d$ – $d$  spectrum within 1.5 kK. Furthermore, our study includes the SCF prediction on the  $R$ -dependence of all the  $d$ – $d$  transitions. The spectral parameters and their  $R$ -dependence have also been computed. Finally, the lack of vibrational structure in the absorption spectrum is understood as a consequence of the very small values of the horizontal displacements of the excited states.

In Section II we give the main details of the SCF calculation. The cluster geometry

TABLE I  
STO ORBITAL EXPONENTS (IN PARENTHESES) AND  
AO EXPANSION COEFFICIENTS FOR  $\text{Cr}^{4+}$  AND  $\text{F}^-$   
IONS<sup>a</sup>

AO	STO		
	1s(23.29)	2s(8.9)	3s(4.06)
1s <sub>M</sub>	1.0		
2s <sub>M</sub>	-0.36240564	1.06364368	
3s <sub>M</sub>	0.14156036	-0.47925202	1.09703726
	2p(9.70)	3p(3.74)	
2p <sub>M</sub>	1.0		
3p <sub>M</sub>	-0.30745939	1.04619852	
	3d <sub>0</sub> (2.40)	3d <sub>1</sub> (4.95)	
	{3d <sub>0</sub> (2.20)}		
3d <sub>M</sub>	0.53658679	0.56818601	
	{0.58216579}	{0.54596792}	
3d <sub>I</sub>		1.0	
Fluoride basis	1s <sub>F</sub> (8.7)	2s <sub>F</sub> (2.425)	
1s <sub>F</sub>	1.0		
2s <sub>F</sub>	-0.21754530	1.02338944	
	2p <sub>F</sub> (2.425)		
2p <sub>F</sub>	1.0		

Note. 3d<sub>0</sub> orbital exponent and 3d<sub>M</sub> coefficients for  $\text{Cr}^{3+}$  appear in braces.

<sup>a</sup> Ref. (10).

is discussed in Section III and the last two Sections are dedicated to the spectral calculation at the theoretical equilibrium geometry and the  $R$ -dependence of the spectrum, respectively.

## II. SCF–MO Calculations on $\text{CrF}_6^{2-}$

We follow in this work the Hartree–Fock methodology described by Richardson and collaborators (5) and we use the same multicenter Slater-type basis (10) and numerical procedures which gave good results for similar systems (11–13). The STO exponents and the AO coefficients are presented in Table I. Note that the difference between the  $\text{Cr}^{4+}$  and  $\text{Cr}^{3+}$  basis lies only in the outer 3d STO. Independent SCF calculations at five values of the metal–fluoride distance  $R$ , ranging from 3.05 (1.61 Å) to 3.59 a.u. (1.90 Å), were performed on the cluster ground state,  $t_{2g}^2 e_g^{-3} T_{1g}$ , and the  $t_{2g} e_g^{-3} T_{av}$ . The latter state is defined in terms of

TABLE II  
OPEN-SHELL RESOLUTION ENERGIES OF  $\text{Cr}^{4+}$  AND  
CEC COEFFICIENTS

Electronic transition <sup>a</sup>	Observed kK <sup>b</sup>	Calculated kK <sup>c</sup>	CEC kK <sup>d</sup>		
${}^3F \rightarrow {}^1D = 5B + 2C$	12.529	15.879	-3.350		
$\rightarrow {}^3P = 15B$	15.200	18.990	-3.790		
$\rightarrow {}^1G = 12B + 2C$	21.361	24.741	-3.380		
$\rightarrow {}^1S = 22B + 7C$	50.488	61.272	-10.784		
$B^c = 1.266 \text{ kK}$ $C^c = 4.775 \text{ kK}$					
$\langle iSL   t_{2g}^x e_g^y - js\Gamma \rangle$	coefficients ( $x + y = 2$ )				
${}^3T_{1g}$	$t_{2g}^2$	$t_{2g}e_g$	${}^1T_{2g}$	$t_{2g}^2$	$t_{2g}e_g$
${}^3P$	$(1/5)^{1/2}$	$(4/5)^{1/2}$	${}^1D$	$-(3/7)^{1/2}$	$(4/7)^{1/2}$
${}^3F$	$(4/5)^{1/2}$	$-(1/5)^{1/2}$	${}^1G$	$(4/7)^{1/2}$	$(3/7)^{1/2}$
${}^1E_g$	$t_{2g}^2$	$e_g^2$	${}^1A_{1g}$	$t_{2g}^2$	$e_g^2$
${}^1D$	$(3/7)^{1/2}$	$(4/7)^{1/2}$	${}^1S$	$(3/5)^{1/2}$	$(2/5)^{1/2}$
${}^1G$	$(4/7)^{1/2}$	$-(3/7)^{1/2}$	${}^1G$	$(2/5)^{1/2}$	$-(3/5)^{1/2}$

<sup>a</sup> Formulas taken from Ref. (20), p. 86.

<sup>b</sup> Ref. (24).

<sup>c</sup> Computed with the basis of  $\text{Cr}^{4+}$  in Table I, Ref. (10).

<sup>d</sup>  $\text{CEC}(iSL) = \Delta E(\text{obs}) - \Delta E(\text{calc})$ .

its energy  $E({}^3T_{av}) = [E(t_{2g}e_g-{}^3T_{1g}) + E(t_{2g}e_g-{}^3T_{2g})]/2$ . The MO solutions of the ground state calculations were used for the theoretical determination of the cluster geometry. On the other hand, the spectral calculations were done with the solutions of the  ${}^3T_{av}$ . We worked within the core-valence partition called SPDD (11), in which the valence shell is formed by the  $3s$ ,  $3p$ ,  $3d_M$ , and  $3d_I$  orbitals of the metal ion and the  $2s$  and  $2p$  of the six fluoride ions. The  $3d_M$  is the regular  $2-\zeta$   $3d$  metal function (10) and  $3d_I$  its inner STO.

In the calculations on the cluster geometry we have considered the SCF energies, the frozen-orbital energies deduced from the solution of the excited state, and the energies obtained when configuration interaction (CI) limited to the  $d^2$  configuration is included. In the spectral calculation we have studied the 11 multiplets coming from the  $d^2$  configuration under the octahedral field. Spectral results will be given at our theoretical equilibrium configuration al-

though the variation of the transition energies and the spectral parameters with  $R$  will also be discussed. The multiplets have been analyzed at three different levels of approximation: first-order, CI limited to the  $d^2$  configuration, and CI + CEC. CEC is the empirical correlation energy correction introduced by Pueyo and Richardson (14). First-order and CI calculations require the multielectron MO wave functions and the electron repulsion matrix elements for the  $d^2$  case. All this information has been given by Richardson *et al.* (5). In the CEC calculations the metal-ion CEC and the appropriate  $\langle iSL | t_{2g}^x e_g^y - js\Gamma \rangle$  coefficients ( $x + y = 2$ ) are needed. These coupling coefficients have been calculated as in Ref. (14) and are collected in Table II with the  $\text{Cr}^{4+}$  CEC computed with the present basis.

### III. Equilibrium Geometry of the $t_{2g}^2-{}^3T_{1g}$ and $t_{2g}e_g-{}^3T_{av}$

In Table III we present the electronic energy of the ground state computed in three

TABLE III  
ELECTRONIC ENERGY (a.u.) OF THE GROUND AND  
THE  $t_{2g}e_g-{}^3T_{2g}$  STATES OF  $\text{CrF}_6^{2-}$  AS FUNCTION OF  
 $R(\text{Cr-F})$

	$R$ (a.u.)				
	3.05	3.15	3.26	3.425	3.59
A. $\text{Cr}^{4+}$ basis					
$E(\text{SCF})$	-4.65863	-4.69721	-4.69506	-4.63325	-4.52991
$E(\downarrow)^a$	-4.65724	-4.69560	-4.69308	-4.63025	-4.52469
$E(\text{CI})^b$	-4.66270	-4.70129	-4.69918	-4.63745	-4.53416
$E_R^c$ (kK)	0.31	0.35	0.43	0.66	1.15
B. $\text{Cr}^{3+}$ basis					
$E(\text{SCF})$	-4.72139	-4.76033	-4.75931	-4.70035	-4.60064
$E(\downarrow)^a$	-4.71997	-4.75871	-4.75739	-4.69767	-4.59642
$E(\text{CI})^b$	-4.72550	-4.76432	-4.76324	-4.70425	-4.60447
$E_R^c$ (kK)	0.31	0.36	0.42	0.59	0.93
C. Energy of the $t_{2g}e_g-{}^3T_{2g}$					
$\text{Cr}^{4+}$ basis	-4.56645	-4.60610	-4.60701	-4.55081	-4.45236
$\text{Cr}^{3+}$ basis	-4.64679	-4.68261	-4.68140	-4.62466	-4.52747

Note. The origin has been taken at  $E(\infty)$ , the energy of the separate ions.

<sup>a</sup> Computed with the SCF solution of the excited state.

<sup>b</sup> Lowest eigenvalue of the  $d^2-{}^3T_{1g}$  matrix.

<sup>c</sup> Relaxation energy  $E_R = E(\downarrow) - E(\text{SCF})$ .

different ways. First, we see that the SCF solution of this state gives a nuclear potential with a minimum at 3.20 a.u. (1.69 Å). The totally symmetric vibration frequency  $\bar{\nu}(a_{1g})$  turns out to be 0.736 kK according to these calculations. It is remarkable that the SCF calculations performed with the  $\text{Cr}^{3+}$  basis give an electronic energy 0.06 a.u. lower than the  $\text{Cr}^{4+}$ -basis energy. This result clearly shows that in a LCAO molecular calculation the approximate Hartree-Fock atomic orbitals are not necessarily the most efficient basis functions, from a variational point of view. In the system studied in this work both basis give essentially the same geometric information since the nuclear potentials are parallel. In the  $\text{Cr}^{3+}$ -basis calculation we find  $R_e = 3.20$  a.u. and  $\bar{\nu}(a_{1g}) = 0.729$  kK.

With the SCF solutions of the ground state we can compute and diagonalize the  $2 \times 2$   ${}^3T_{1g}$  matrix of the  $d^2$  configuration. This limited CI lowers the diagonal energy by about 1 kK (0.004 a.u.). The effect is rather uniform in the range of  $R$  studied here and again we find  $R_e = 3.20$  a.u. from the CI nuclear potential.

We have estimated the ground state energy with the solution of the excited  $t_{2g}e_g-{}^3T_{av}$  because we will compute the spectroscopic transitions with these MO's and want to know the amount of reorganization energy associated with the change in configuration. These frozen-orbital energies,  $E(\downarrow)$  are collected in Table III. The relaxation energy is an increasing function of  $R$ , as in  $\text{CrF}_6^{3-}$  (13), and its value at  $R_e$  is smaller than 0.40 kK. This figure tells that we are in fairly well conditions to proceed with the spectral calculation from the  ${}^3T_{av}$ . Furthermore, the relaxation energy in the equilibrium region is the same in both bases.

The electronic energy of the  $10 Dq$  state,  $t_{2g}e_g-{}^3T_{2g}$ , is also presented in Table III. This energy has been computed from the SCF solution of the intraconfigurational

${}^3T_{av}$  with a very small relaxation energy. The nuclear potential of this excited state is really parallel to the ground state potential. The horizontal displacement with respect to the ground state minimum,  $\delta = R_e({}^3T_{2g}) - R_e({}^3T_{1g})$ , turns out to be 0.006 a.u. in the  $\text{Cr}^{4+}$  basis and  $-0.001$  a.u. in the  $\text{Cr}^{3+}$  basis. These very small values of  $\delta$  will have consequences in the  $R$ -dependence of  $10 Dq$  (15). Also, they constitute an interesting explanation for the lack of vibrational structure in the absorption spectrum of  $\text{Rb}_2\text{CrF}_6$  (1) (see below).

As far as we know, there is no experimental information on  $\bar{\nu}(a_{1g})$ . Our computed  $\bar{\nu}(a_{1g})$  has the order of magnitude of those in  $\text{CrF}_6^{3-}$  (13) and  $\text{CrF}_6^{4-}$  (16). On the other hand, our  $R_e$  agrees well with the 1.72 Å reported by Bode and Voss for the alkali hexafluorochromates(IV) (6). Siebert and Hoppe (7) gave values from 1.79 to 1.90 Å for the  $M(\text{II})\text{CrF}_6$  compounds, deduced from the analysis of powder diagrams. These differences can surely be analyzed in terms of a careful representation of the corresponding cluster-lattice interaction but, as we state in the Introduction, we have not attempted it in this work.

#### IV. The Optical Spectrum of $\text{CrF}_6^{2-}$

The low-temperature, diffuse reflectance spectrum of  $\text{Rb}_2\text{CrF}_6$  measured by Allen and El-Sharkawy (1) shows two very weak features at 11.4 and 14.8 kK, a clearly resolved broad band at 20.2 kK and a very broad band at 29.6 kK. The second broad band has two prominent shoulders on its high-energy side at about 32 and 37 kK, respectively, and a further one, rather slight, on the other side, at about 27.5 kK (1). The assignment of Allen and El-Sharkawy was  ${}^3T_{1g} \rightarrow {}^1T_{2g}$ ,  ${}^1E_g$  at 11.4,  ${}^3T_{1g} \rightarrow {}^3T_{2g}$  at 20.2, and  $\pi \rightarrow t_{2g}$  charge transfer excitations at 29.6 and 37 kK. The weak peak at 14.8 kK was interpreted as due to analytically insig-

TABLE IV  
CRYSTAL-FIELD AND SCF MO FIRST-ORDER DESCRIPTIONS OF THE SPECTRUM OF Rb<sub>2</sub>CrF<sub>6</sub>

Electronic transition <sup>a</sup>	CF(1st assignment) <sup>b</sup> ( $B = 0.61, C = 3.88, \Delta = 22.0$ )	CF(2nd assignment) <sup>c</sup> ( $B = 0.88, C = 3.08, \Delta = 22.8$ )	SCF-MO
$t_{2g}^2-3T_{1g} \rightarrow$			
${}^3T_{2g} = \Delta - 3B$	20.2	20.2	19.3
${}^3T_{1g} = \Delta + 9B$	27.5	30.7	31.1
${}^3A_{2g} = 2\Delta - 3B$	42.2	43.0	41.5
${}^1T_{1g} = \Delta + 9B + 2C$	35.3	36.9	38.1
$a^1T_{2g} = 6B + 2C$	11.4	11.4	12.9
$b^1T_{2g} = \Delta + 5B + 2C$	32.8	33.4	33.7
$a^1E_g = 6B + 2C$	11.4	11.4	12.9
$b^1E_g = 2\Delta + 5B + 2C$	54.8	56.2	56.7
$a^1A_{1g} = 15B + 5C$	28.6	28.5	32.2
$b^1A_{1g} = 2\Delta + 13B + 4C$	67.5	69.3	72.1

Note. Numbers in kK.

<sup>a</sup> Strong-field energies taken from Ref. (20), p. 410.

<sup>b</sup> Crystal-field calculation with  $B$  and  $C$  obtained from the assignment  ${}^3T_{1g} \rightarrow {}^3T_{1g} = 27.5$  kK.

<sup>c</sup> Calculation from the assignment  ${}^3T_{1g} \rightarrow {}^3T_{1g} = 30.7$  kK.

nificant amounts of CrF<sub>6</sub><sup>3-</sup> ( ${}^4A_{2g} \rightarrow {}^4T_{2g}$ ), the shoulder at 27.5 kK was tentatively associated with the  ${}^3T_{1g} \rightarrow {}^3T_{1g}$  transition and the feature at 32 kK remained unassigned. From this assignment Allen and El-Sharkawy reported  $\Delta = 21.7$  kK,  $B = 0.68 \pm 0.08$  kK and a nephelauxetic ratio  $\beta = 0.67 \pm 0.07$ . Let us see now the results of our crystal-field and SCF-MO calculations.

*A. First-order description.* First of all, we note that from Table II the best free-ion repulsion parameters turn out to be  $B = 1.041$ ,  $C = 3.956$  kK, with  $C/B = 3.80$ . Our theoretical parameters (see Table II) are 22% larger but conserve the  $C/B$  ratio (3.77). Different "best" values could be deduced from the observed spectrum if more terms were considered in the free-ion Hamiltonian. For instance, Stewart (17) obtains  $B = 1.072$ ,  $C = 3.891$  ( $C/B = 3.63$ ),  $\zeta = 0.321$ , and  $\alpha = 0.092$  kK, from the spectrum in Moore's compilation (18), when the spin-orbit and the Racah-Trees (19) interactions are taken into account. Since we neglect here these two refinements we will use  $B = 1.041$ ,  $C = 3.956$  as free-ion values.

In Table IV we collect our first-order results on CrF<sub>6</sub><sup>2-</sup>. The first column contains the first-order strong-field transition energy equations taken from Griffith (20). In the next two columns we present two different crystal-field, CF, calculations and the last column contains our nonempirical SCF results. The first CF calculation follows the assignment of Allen and El-Sharkawy (1). From  ${}^3T_{1g} \rightarrow {}^3T_{2g} = 20.2$  kK and  ${}^3T_{1g} \rightarrow {}^3T_{1g} = 27.5$  kK (1, 21) we find  $\Delta = 22.0$  and  $B = 0.61$  kK. Using this  $B$  in the  ${}^3T_{1g} \rightarrow {}^1T_{2g}$ ,  ${}^1E_g$  (11.4 kK) transition, we have  $C = 3.88$  kK. With these  $\Delta$ ,  $B$ ,  $C$ , and the formulas in the first column we obtain the remaining transitions. This calculation gives  $C/B = 6.36$ , an unusually high value. The observed  $C/B$  ratios for  $d^2$  systems vary in the range 3.5 to 4.5 (22). It is rather difficult to understand such a large separation from the free-ion value. Furthermore, in this calculation a spin-allowed transition is associated with a slight shoulder at 2 kK from the band peak whereas a spin-forbidden transition ( ${}^3T_{1g} \rightarrow b^1T_{2g}$ ) becomes associated with a prominent shoulder at the same distance of the

TABLE V  
CRYSTAL-FIELD CI, SCF-MO-CI, AND SCF-MO-CI + CEC DESCRIPTIONS OF THE SPECTRUM OF  $\text{Rb}_2\text{CrF}_6$

Electronic transition	CF(1st assignment) <sup>a</sup>	CF(2nd assignment) <sup>a</sup>		
	( $B = 0.57, C = 3.86, \Delta = 21.5$ )	( $B = 0.81, C = 3.06, \Delta = 21.8$ )	SCF + CI	SCF + CI + CEC
$t_{2g}^2-{}^3T_{1g} \rightarrow$				
$\rightarrow {}^3T_{2g}$	20.2	20.2	20.2	21.8
$\rightarrow {}^3T_{1g}$	27.5	30.7	31.1	31.2
$\rightarrow {}^3A_{2g}$	41.7	41.9	42.4	43.8
$\rightarrow {}^1T_{1g}$	34.8	36.0	39.1	40.5
$\rightarrow a^1T_{2g}$	11.4	11.4	13.4	11.4
$\rightarrow b^1T_{2g}$	32.7	33.1	35.1	33.2
$\rightarrow a^1E_g$	11.5	11.6	10.6	8.7
$\rightarrow b^1E_g$	54.1	54.7	61.0	59.1
$\rightarrow a^1A_{1g}$	24.7	25.1	29.7	24.7
$\rightarrow b^1A_{1g}$	69.9	70.3	77.2	70.3

Note. Numbers in kK.

<sup>a</sup> Same meaning as in Table IV.

peak, from the other side. Both difficulties are essentially eliminated if the prominent shoulder at 32 kK is associated with the  ${}^3T_{1g} \rightarrow {}^3T_{1g}$  transition. The analysis of the more elaborate results (CI and CI + CEC, see below) suggests the assignment  ${}^3T_{1g} \rightarrow {}^3T_{1g} = 30.7$  kK. With this value we prepared the second CF calculation in Table IV, having  $B = 0.88$  kK,  $C = 3.08$  kK, and  $C/B = 3.51$ . The shoulder at 27.5 could now be associated with the first  ${}^1A_{1g}$ .

The SCF results in Table IV give a good representation of the first band, which is predicted within 1 kK from the observed value. The degenerate singlets  ${}^1T_{2g}, {}^1E_g$  are also computed in good agreement with the experiment. The  ${}^3T_{1g} \rightarrow {}^3T_{1g}$  transition, at 31.1 kK, suggests the alternate assignment just commented. The rms deviation between columns 2 and 4 of Table IV is 2.6 kK. Between columns 3 and 4 it results to be 1.81 kK.

*B. CI and CI + CEC descriptions.* In Table V we present the results of these more complete calculations. As in Table IV we give two CF calculations and our SCF-CI and SCF-CI + CEC results. Let us consider, first, the CF results. In both CF calculations we have assigned the peak at 11.4 kK to the  ${}^3T_{1g} \rightarrow {}^1T_{2g}$  transition. This choice

has been adopted in view of the best SCF results (last column in Table V). On the other hand, we have observed that assigning this peak to the  ${}^3T_{1g} \rightarrow {}^1E_g$  transition produces very minor effects on the best values of  $B$  and  $C$ . Again, the first CF calculation follows the original assignment ( $I, 2I$ ). Then,  $B = 0.57$  kK,  $C = 3.86$  kK, and  $C/B = 6.77$ . This  $C/B$  ratio is still more separated from the usual range of values than that obtained in the first-order calculation. The alternate assignment gives  $B = 0.81$  kK,  $C = 3.06$  kK, and  $C/B = 3.78$ . From a pure CF calculation it can be seen that if the  ${}^3T_{2g}$  lies at 20.2 kK and the  $a^1T_{2g}$  at 11.4 kK, the position of  $\bar{\nu}_2 = {}^3T_{1g} \rightarrow {}^3T_{1g}$  determines the  $C/B$  ratio in such a way that the ratio decreases when  $\bar{\nu}_2$  increases. If  $\bar{\nu}_2 \leq 30.0$  kK,  $C/B \geq 4.3$  and if  $\bar{\nu}_2 \geq 31.0$ ,  $C/B \leq 3.6$ . These are the limits of the usual range for the  $C/B$  ratio and they really should constrain the position of the  $b^3T_{1g}$ . Thus, we can say that the simpler CF theory suggests the alternate assignment. On the other hand, the best SCF calculation of  $\bar{\nu}_2$ , 31.2 kK, gives further support to this assignment. We propose the particular choice  $\bar{\nu}_2 = 30.7$  kK because it gives a  $C/B$  ratio very close to the experimental and theoretical free-ion values and it is in very good agree-

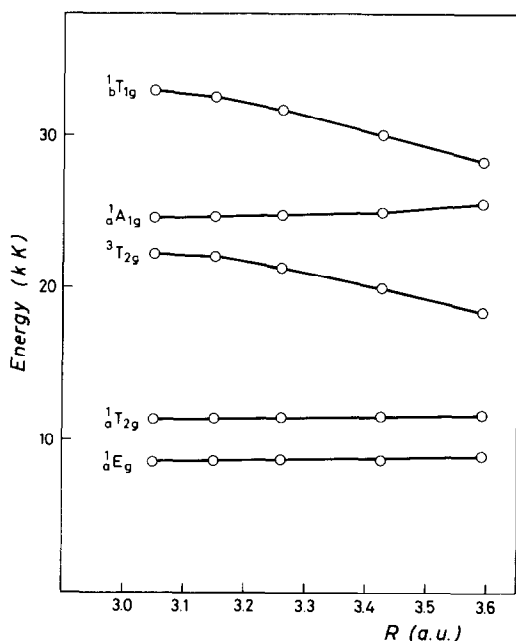


FIG. 1. Variation of the transition energies with the metal-fluoride distance  $R$ , as predicted by the SCF-CI + CEC calculation.

ment with our best SCF calculation. It is clear that any  $30 \leq \bar{\nu}_2 \leq 31$  could be considered. Then, the best CF parameters are those producing the third column in Table V, namely:  $\Delta = 21.8$ ,  $B = 0.81$ ,  $C = 3.06$  kK. They give  $C/B = 3.78$  and  $\beta_B = 0.78$ ,  $\beta_C = 0.77$ . Now we comment on the SCF results. CI rises the values of the first and second spin-allowed transitions, the first one only by 1 kK, because the  $3T_{2g}$  does not suffer CI, but the second one by twice this amount, because it has CI effects in both ground and excited states. The CEC represents a general improvement over the CI image. This empirical correction increases the value of the first band due to the lowering of the ground state (the  $3T_{2g}$  is not affected by the CEC); the theoretical transition deviates now from the experimental value by only 1.6 kK. The CEC reduces the positions of the  $a^1T_{2g}$  and  $a^1E_g$  states because their CEC is larger than that of the

ground state. As already commented, the CEC calculation suggest that the peak at 11.4 kK should be assigned to the  $a^1T_{2g}$ . The prediction of the  $a^1E_g$  at 8.7 kK is not incompatible with the observed spectrum, recorded from 9 to 40 kK (1). It is also interesting to note that the relative position of the lower singlets is the opposite to that obtained without CEC.

The third spin-allowed transition,  $3T_{1g} \rightarrow 3A_{2g}$  is calculated at 43.8 kK, out of the measured spectral range. The positions of the singlets predicted within this range are not incompatible with the observed spectrum. We can conclude that our CI + CEC calculation agrees with the experimental data within 1.5 kK. Moreover, no peak is predicted around 14–15 kK. This result confirms that the weak feature at 14.8 kK is due to the  $CrF_6^{3-}$  (1).

## V. R-Dependence of the Transition Energies and Spectral Parameters

All the results described above have been obtained at our theoretical equilibrium distance. It is convenient to show how this prediction could vary by changes in  $R$ , not only because of this dependence but also to have an indication of the sensitivity of the vertical calculation with respect to the parameter  $R$ .

In Fig. 1 we show the evolution of the transition energies with  $R$ , up to 40 kK, predicted by the SCF-CI + CEC calculation. We note that in spite of the CI effects, the lower singlets are practically independent of  $R$ , as if they were pure metallic states. The lowest  $1A_{1g}$  is fairly independent of  $R$  although it shows a slightly larger variation than the  $1T_{2g}$ ,  $1E_g$ , due to the somewhat larger off-diagonal element in the  $1A_{1g}$  matrix (20) and a more effective contamination with  $\Delta$ . The positions of these three singlets presented in Section IV is, therefore, quite independent of the particular election of  $R$ . The triplets show a reduction

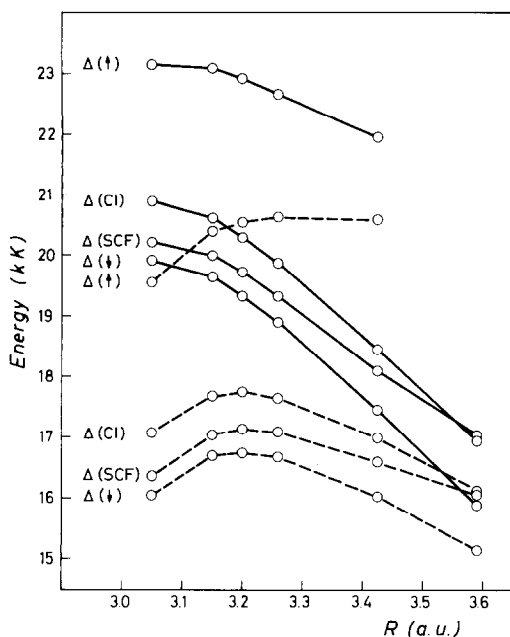


FIG. 2. Different representations of the quantity  $\Delta = 10 Dq$  and their variations with  $R$ . Solid lines:  $\text{Cr}^{4+}$  basis. Broken lines:  $\text{Cr}^{3+}$  basis.

when  $R$  increases (about  $12 \text{ kK} \cdot \text{\AA}^{-1}$ ) less intense than expected. Their respective nuclear potentials are quite parallel to that of the ground state and show rather small horizontal displacements. This calculated behavior of the excited nuclear potentials should be the reason for the relatively small variation of the triplet-triplet transitions with  $R$  (15). For the same reason, the  $a_{1g}$  vibrational states of the excited triplets should give negligible contribution to the (unseen, Ref. (1)) vibrational structure of the absorption broad bands.

It is interesting to relate the  $R$ -dependence of the electronic transitions to that of the spectral parameters. Such dependence has been discussed recently for the orbital splitting parameter  $\Delta$  (15). In  $\text{CrF}_6^{2-}$  we will associate  $\Delta$  with the difference  $E(^3T_{2g}) - E(a^3T_{1g})$ , where  $E$  is the total electronic energy. In the present methodology  $\Delta$  contains both one-electron and two-electron contributions (5) and its value varies with

the method of calculation. We have computed  $\Delta$  in a variety of ways to show the importance of different contributions to it. First, we have  $\Delta(\text{SCF})$ , the value obtained as difference in total energies of independent SCF calculations on the ground and the  $t_{2g}e_g^{-3}T_{2g}$  states. Then we compute  $\Delta(\uparrow)$ , using the frozen-orbital approximation, with the MO solutions of the ground state. Analogously,  $\Delta(\downarrow)$  is computed from the solution of the excited state. Finally, we have  $\Delta(\text{CI})$ , deduced from the CI eigenvalue of the  $^3T_{1g}$  matrix. The  $\Delta(\text{CI} + \text{CEC})$  coincides with the position of the  $^3T_{2g}$  state in Fig. 1 and will not be discussed further. In order to see the influence of the basis set on different properties of the cluster we have obtained these numbers with the regular  $\text{Cr}^{4+}$  basis and also with  $\text{Cr}^{3+}$  basis. All this information is depicted in Fig. 2.

In agreement with the discussion in Ref. (15),  $\Delta(\downarrow)$  always shows the steepest variation with  $R$ . The high value of  $\Delta(\uparrow)$  can be related to the electron-repulsion contribution in CF theory and indeed  $\Delta(\uparrow)$  is comparable with the CF value in Table IV.  $\Delta(\text{CI})$  is larger than  $\Delta(\text{SCF})$  because the ground state is stabilized by CI. All these quantities decrease when  $R$  increases but if a function of the type  $\Delta = CR^{-n}$  is assumed,  $n$  becomes 0.48, 1.09, 1.39, and 1.29 for  $\Delta(\uparrow)$ ,  $\Delta(\text{SCF})$ ,  $\Delta(\downarrow)$ , and  $\Delta(\text{CI})$ , respectively. This particularly small values of  $n$  (about 1.5 in  $\text{CrF}_6^{3-}$ , 3.2 in  $\text{CrF}_6^{4-}$ , 5 in CF theory (15)) are still reduced in the  $\text{Cr}^{3+}$  basis. This basis effect can be due to the very small horizontal displacement of the  $^3T_{2g}$  state with respect to the ground state: 0.006 and  $-0.001$  a.u. in the  $\text{Cr}^{4+}$  and  $\text{Cr}^{3+}$  basis, respectively. The negative value obtained in  $\text{Cr}^{3+}$  explains the near independence of  $\Delta$  with  $R$  in this basis ( $\Delta(\uparrow)$  even increases with  $R$ , see Fig. 2). The  $\text{Cr}^{3+}$  basis implies a reduction in  $\Delta$  of about 3 kK, due to a different variational efficiency of this basis in these two electronic states. Finally, the quoted results indicate an interesting re-



TABLE VI  
BEST ORBITAL SPLITTING ( $\Delta$ ) AND NEPHELAUXETIC  
( $\lambda$ ) PARAMETERS AS FUNCTIONS OF  $R(\text{Cr-F})$

	$R$ (a.u.)				
	3.05	3.15	3.16	3.425	3.59
$\Delta(\text{First-order})$	23.3	22.8	21.8	20.1	18.4
$\Delta(\text{CI})$	23.8	23.3	22.4	20.7	19.2
$\Delta(\text{CI} + \text{CEC})$	24.4	23.9	23.0	21.3	19.7
$\lambda(\text{First-order})$	0.76	0.76	0.76	0.75	0.75
$\lambda(\text{CI})$	0.74	0.74	0.74	0.73	0.71
$\lambda(\text{CI} + \text{CEC})$	0.62	0.62	0.61	0.60	0.60

*Note.* Different SCF solutions have been used to compute these parameters through systematic linearization.

lationship between the ionization state of the central atom and the exponent  $n$ : this number seems to decrease when the ionization increases.

Finally, the  $R$ -dependence of the electron repulsion parameters can be deduced from a systematic linearization of the electrostatic matrices (23) in the form

$$\bar{\nu}_i = \alpha_i \Delta + \beta_i \lambda$$

where  $\bar{\nu}_i$  is the  $i$ th electronic transition,  $\Delta$  the CF orbital splitting parameter,  $\lambda$  the scaling factor of the  $3d$  radial wavefunction,  $R_{3d}(r) \rightarrow R_{3d}(\lambda r)$ , and  $\alpha_i, \beta_i$  numerical coefficients to be found. The  $\lambda$  is a measure of the nephelauxetic effect because one can show (23) that  $B(\text{CrF}_6^{2-}) = \lambda B(\text{Cr}^{4+})$ . Given a known set  $\{\bar{\nu}_i\}$ , we can obtain the  $\Delta, \lambda, \alpha_i, \beta_i$  that best fit the CF matrices to it (23). We use as  $\{\bar{\nu}_i\}$  the theoretical SCF transition energies and then we can perform the linearization with the first-order, the SCF-CI and the SCF-CI + CEC solutions. Results can be seen in Table VI. The evolution of  $\Delta$  with  $R$  is entirely analogous to that shown by the direct SCF calculation. The  $\lambda$  shows a very slight variation with  $R$ , in agreement with the negligible  $R$ -dependence of the singlets in Fig. 1. From Table VI we note a weak effect of CI on  $\lambda$  and a further reduc-

tion induced by the CEC, as it should be. From these values of  $\lambda$  we obtain our theoretical  $B(\text{CrF}_6^{2-}) = \lambda B(\text{Cr}^{4+})$  and  $C(\text{CrF}_6^{2-}) = \lambda C(\text{Cr}^{4+})$ . At first-order  $\lambda = 0.76$  and  $B = 0.96, C = 3.63$  kK. After CI,  $\lambda = 0.74$  and  $B = 0.94, C = 3.53$  kK. These nonempirical parameters are higher than the CF values deduced in Section IV ( $B = 0.88, C = 3.08$  kK at first-order;  $B = 0.81, C = 3.06$  kK after CI) due to the electron correlation error in the SCF wavefunction. After the CEC,  $\lambda = 0.62$  and  $B = 0.79, C = 2.96$  kK. These numbers should be compared with the CF values after CI (the best CF calculation) and, indeed, the agreement is good. Small quantitative differences are due to the fact that in Section IV the parameters have been estimated from three observed transition. Numbers in Table VI, however, are the best fitting parameters deduced from a calculation which includes all the electronic transitions of the  $d^2$  configuration.

Finally, the nephelauxetic effect in the SCF-CI + CEC calculation should be obtained by means of the ratio  $B(\text{SCF})/B(\text{observed, free-ion})$ , in accordance with the meaning of the CEC (14). Then, we have a nephelauxetic ratio of 0.75 in agreement with the CF prediction after CI, i.e., 0.78. This is our best estimate of the nephelauxetic effect. It is somewhat larger than the value reported in Ref. (1),  $0.67 \pm 0.007$ , as a consequence of a new assignment.

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