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Ab Initio Calculations on $KNiF_3$: Ligand-Field Effects

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Restricted Hartree-Fock molecular-orbital calculations have been carried out for various states of the cluster NiF_6^{4-} "*in vacuo*" and in a surrounding of several sets of point charges representing the perovskite lattice $KNiF_3$. All electrons were included. A "double-ζ" basis set of contracted Gaussian orbitals has been used. The calculations were performed with the computer program IBMOL IV. The Hartree-Fock approximation gives a reasonable description of the covalency effects and the spectral properties of $KNiF_3$. The calculated hyperfine-field parameters f_s and f_σ and the $10Dq$ value are about 10–25% smaller than the experimental values. Similar deviations were found for the spectral transition energies. It is argued that magnitude and sign of the crystal field splitting in this compound can be understood in terms of the well-known ionic electrostatic model provided the Born repulsion is properly taken into account.

I. INTRODUCTION

In recent years $KNiF_3$ has served as a test case for studying covalency effects in transition-metal salts. Various theoretical studies have been carried out, the results of which include predictions of the electron-spin densities at the fluorine nuclei, the cubic-crystal-field-splitting parameter, and the reduction of the Racah parameters in the crystal with respect to the free-ion values. These previous studies can be subdivided into three groups: crystal field calculations, first-order approaches to the calculation of covalency effects, and many-electron self-consistent-field (SCF) calculations.

Crystal field theory,[1] when treated as a semi-empirical theory with the crystal-field-splitting parameter $10Dq$ as an adjustable parameter, has been highly successful in fitting experimental data. As a fundamental theory for the behavior of transition-metal ions in crystalline fields, however, crystal field theory fails in predicting the experimental $10Dq$ value. The inadequacy of the crystal field theory has extensively been discussed in the literature[2] and will not be repeated here.

The second group of calculations[3–8] may be characterized by the fact that although the theoretical framework is exact, the working expressions that are finally used are highly simplified. We classify these calculations therefore as first-order approaches. For a review of this type of calculation we refer to an article of Owen and Thornley.[9] The calculations are all applied to a cluster consisting of a Ni^{2+} ion, surrounded by six F^- ions, assuming that the potential of the remainder of the crystal in the region of the cluster is sufficiently constant to justify this approach. Furthermore, they have in common that only the $3d$ electrons on the Ni^{2+} ion and the $2s$ and $2p$ electrons on the F^- ions are considered explicitly. Although this second group of calculations clearly points to the relative importance of covalency in ionic crystals, they suffer from making severe approximations, such as the use of an "ionic" Hamiltonian, the employment of a basis set of unperturbed free-ion wave functions, the neglect or approximation of many multicenter integrals, the neglect of higher-order terms in the overlap and covalency parameters, and the limitation introduced by using an effective core potential instead of the core electrons explicitly.

In the third group of calculations on $KNiF_3$, which we shall discuss in somewhat more detail the NiF_6^{4-} cluster, is treated as a many-electron system and efforts are made to eliminate the deficiencies summarized above as much as possible.

Unrestricted Hartree-Fock (HF) calculations were carried out by Ellis *et al.*[10] on NiF_6^{4-} and on a triatomic cluster $NiFNi^{3+}$. They used a mixed one-center Slater-type-orbital (STO) basis centered on the central site, containing functions to describe the distributions of the central-site electrons as well as functions to simulate the distributions of the electrons on the other sites. A $10Dq$ value was found which is about 45% larger than the experimental value. This value is hardly changed when the remainder of the crystal is taken into account in the point-charge approximation. A rough calculation showed that about 0. 8 units of negative charge has been transferred onto the Ni^{2+} ion, leaving a net charge of + 1. 2. Their calculation of the hyperfine parameters f_s and f_σ directly from the isotropic and anisotropic contributions to the hyperfine field gives much too large values. These computations represent only a very crude approximation to a solution of the HF equations because of the limited character of the basis which is probably inferior to a minimal Slater basis.

Gladney and Veillard[11] have carried out restricted HF molecular-orbital (MO) calculations for the $^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}$, and $^1T_{1g}$ states of NiF_6^{4-} *in vacuo* and in a field of 38 point charges, representing the perovskite lattice. With a rather small basis of 59 contracted-Gaussian-type orbitals (GTO's) they obtained a reasonable value for $10Dq$ almost independent of the field of the remainder of the crystal, but the calculated hyperfine parameters are about three times smaller than the experimental values. They found the open-shell $3d$ functions to be slightly more contracted than the free-ion $3d$ functions, while those of the closed shell are slightly more expanded. A Mulliken population analysis[12] shows that the net charge on the nickel ion is + 1. 9594 and on each fluorine ion – 0. 09932, which indicates only a small amount of electron transfer from the fluorine ions to the metal ion. The experimentally found decrease with respect to the free-ion values of the spectral Racah parameters B and C is not reflected by the parameters obtained from the SCF total energies of the excited states. The authors ascribe the failure to insufficient delocalization of the calculated d orbitals.

Richardson *et al.*[13,14] reported restricted-HF MO calculations on a series of clusters. Their molecular orbitals are linear combinations of atomic STO's which for the metal ions are obtained by fitting to atomic HF orbitals, $4s$ and $4p$ orbitals are included optionally. One- and two-center integrals were calculated exactly, but three-center integrals were obtained using the Mulliken approximation.[15] Four-center integrals were neglected. Including $4s$ and $4p$ orbitals they obtained a $10Dq$ value for $KNiF_3$ which agrees very well with experiment. Without $4s$ and $4p$ orbitals the value is about 10% larger. The hyperfine parameters obtained are fairly good. The calculated reduction of the Racah parameters is about 5%.

Recently, Moskowitz *et al.*[16,17] made restricted- and unrestricted-HF calculations on NiF_6^{4-} and $NiFNi^{3+}$. They used a basis set of 74 contracted GTO's. The $10Dq$ value found in the restricted-HF calculation is only a few percent larger than that for the unrestricted-HF calculation and is about 85% of the experimental value. The Mulliken gross charges on Ni^{2+} and F^- are +1. 82 and – 0. 97, respectively, while the total overlap population of a NiF bond is – 0. 01116, which indicates only a very small covalent (anti-) bonding effect and in this sense $KNiF_3$ may be called an almost ionic compound. They found the same contraction and expansion phenomena of the $3d$ orbitals as reported by Gladney and Veillard, and again only a slight reduction of the Racah parameter B from the free-ion value. The parameters f_s and f_σ for NiF_6^{4-} directly calculated from the isotropic and anisotropic hyperfine-field parameters turned out to be slightly larger than those for $NiFNi^{3+}$. In the restricted- as well as in the unrestricted-HF calculation, Moskowitz *et al.* obtain values for the total energy of the ground state of the NiF_6^{4-}, which are 1. 266 a. u. larger than the sum of the total energies, which they calculated for the free ions. Hence in their calculations the binding energy of the NiF_6^{4-} cluster with respect to the free ions has a negative value of – 1. 266 a. u. If the ions in the NiF_6^{4-} cluster are approximated by point charges one finds, however, a binding energy of 0. 532 a. u. Although the binding energy obtained from HF calculations on the cluster and the free ions will be somewhat smaller than this value, one would not expect such a large difference. In fact the binding energy obtained by Gladney and Veillard (0. 368 a. u.) and the results of our own work to be reported in Secs. II–IV agree with this expectation.

The results of these previous attempts to calculate the hyperfine-interaction parameters, the crystal-field-splitting parameter $10Dq$, and the Racah parameters B and C are summarized in Table I. They indicate that the SCF-MO approximation, when an extended basis set is used, is adequate to reach a fair understanding of a number

TABLE I. Hyperfine-interaction parameters (in %), crystal-field-splitting and Racah parameters (in cm^{-1}).

	f_s	f_σ	$10Dq$	B	C
Experiment[2,3]	0. 54	3. 78	7 250	955	4234
Free ion[11]				1030	4850
Crystal field			1 380		
Sugano and Shulman[3]	0. 42	5. 21	6 350		
Freeman and Watson[2]	0. 31	0. 97	2 815		
Offenhartz[7]	0. 37	1. 63	4 040		
Hubbard *et al.*[8]	1. 02	2. 89	5 380		
Ellis *et al.*[10]	8. 24	6. 29	10 500		
Gladney and Veillard[11]	0. 18	1. 26	4 870	1280	4910
Richardson *et al.*[13,14]	0. 45	2. 23	7 126		
Moskowitz *et al.*[17]					
restricted HF	0. 36	4. 80	6 089	1260	
unrestricted HF	0. 44	6. 32	5 976	1310	
Our results: cluster	0. 46	2. 86	5 440	1280	4810
free ion				1310	4890

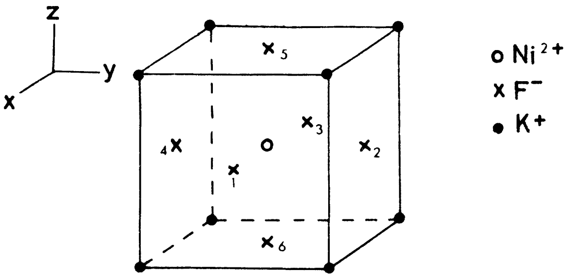

FIG. 1. Crystal structure of KNiF$_3$.

of physical properties of ionic crystals.

From a computational point of view the work to be presented in Secs. II–IV can best be considered as an extension of the work of Gladney and Veillard both with respect to the basis set employed as with regard to investigating the influence of the rest of the crystal on the cluster calculation. In addition, however, we have studied in some detail the various contributions that lead to the finally computed 10Dq value in order to arrive at a reasonably accurate but yet simple interpretation of this quantity in the compound at hand.

II. PROCEDURE

HF SCF MO calculations were performed for the ground state ($^3A_{2g}$), the first-excited state ($^3T_{2g}$), and several other excited states (e.g., $^3T_{1g}$ and $^1T_{1g}$) of the cluster NiF$_6^{4-}$ *in vacuo* and in a surrounding of several sets of point charges in order to study the influence of the remainder of the crystal. All 86 electrons of the cluster were included. The geometry was taken from experiment[18] ($R_{\mathrm{NiF}} = 3.79$ a.u.). The cubic perovskite crystal structure of KNiF$_3$ is illustrated in Fig. 1. The wave functions corresponding to the electronic states may be represented by determinants of holes in incomplete t_{2g} and e_g shells, e.g.,

$$\begin{aligned} &{}^3A_{2g}(e^2),\ \ |\theta\epsilon|,\ \ {}^3T_{1g}(te)z,\ \ |\epsilon\zeta|, \\ &{}^3T_{2g}(te),\ \ |\theta\zeta|,\ \ {}^1T_{1g}(te)z,\ \ (1/\sqrt{2})\,(|\epsilon\bar{\zeta}| - |\bar{\epsilon}\zeta|), \end{aligned} \tag{1}$$

where θ, ϵ are molecular orbitals belonging to the e_g representation and ζ is a MO belonging to the t_{2g} representation. The barred and unbarred orbital symbols in (1) refer to orbitals associated with α and β spin functions, respectively. For the orbitally degenerate states only those components are used that can be expressed in a single determinant over spatial orbitals.[19]

According to the expressions given by Griffith[1] (Table A27) the energy differences can be parametrized as

$$\begin{aligned} &E(^3T_{2g}) - E(^3A_{2g}) = 10Dq\ , \\ &E(^1T_{1g}) - E(^3T_{2g}) = 12B + 2C, \\ &E(^3T_{1g}(te)) - E(^3T_{2g}) = 12B\ . \end{aligned} \tag{2}$$

The calculations were carried out with the program IBMOL IV, developed by Clementi and Davis[20] and Veillard, on an IBM 360/91 computer. This program can handle molecules of general geometry. The one-electron orbitals are expanded in a linear combination of Gaussian-type orbitals which are centered on the atoms in the molecule. For molecular systems such as NiF$_6^{4-}$ optimization of the total GTO basis sets requires too much computer time since adequate bases are too large. Therefore we have optimized basis sets for the ions Ni^{2+} and F$^-$. The optimization procedure and the Gaussian basis set for nickel have been published elsewhere[21] and will not be given here. The basis consists of eight s, four p, and two d functions contracted out of a total of fourteen s-, nine p-, and five d-type GTO's. For the fluorine ion an optimized basis set of ten s- and six p-type GTO's has been contracted to four s- and two p-type basis functions. The orbital exponents and normalized contraction coefficients for F$^-$ are given in Table II. For convenience in Table III the orbital energies and expansion coefficients of the 3d orbital for Ni^{2+} and the 2s and 2p orbitals for F$^-$ are given. Table IV shows the total energies of both ions in comparison with the almost-exact HF values obtained by Clementi.[22] For the NiF$_6^{4-}$ cluster the total basis set contains 92 basis functions. This basis is flexible enough

TABLE II. Orbital exponents and normalized contraction coefficients for F$^-$.

s		p	
exponent	coefficient	exponent	coefficient
18648.5	0.00166	63.1253	0 01506
2790.77	0.01286	14.5012	0.10074
633.258	0.06626	4.38233	0.35376
178.599	0.25787	1.45355	0.67039
57.7896	0.74237		
		0.463237	0.69701
20.4555	0.59068	0.126578	0.40928
7.58796	0.45178		
1.99213	1.00000		
0.749854	0.68226		
0.241845	0.36770		

TABLE III. Some orbital energies (underlined) and coefficients for Ni^{2+} and F$^-$.

3d	2s	2p
$\underline{-1.42519}$	$\underline{-1.07000}$	$\underline{-0.18118}$
0.47967	−0.07609	0.57096
0.70478	−0.27975	0.60085
	0.20185	
	0.89304	

TABLE IV. Total energies of free ions.

	Ni^{2+}	F^-
Our results	−1505.8875	−99.44732
Clementi[20]	−1506.0286	−99.45936

to study the expansion and contraction phenomena of the orbitals of the cluster with respect to those of the free ions. To investigate the influence of the 4*s* orbital on Ni^{2+}, we did the SCF calculations with and without inclusion of the two 4*s* basis functions.

The effect of the crystal field of the remainder of the crystal on $10Dq$ was studied by performing SCF calculations for the ground and first-excited state of the NiF_6^{4-} cluster, surrounded by (i) a set of + 1 point charges at the eight nearest-neighbor potassium sites, and (ii) a set of +1, +2, and − 1 point charges at the sites of the eight potassium, six nickel, and 24 fluorine ions, respectively, which are nearest to the center of the cluster.

For the MO's of the NiF_6^{4-} cluster, including the 4*s* orbital, we have carried out a Mulliken population analysis[12] for the ground and first-excited state. A program written by Veillard was used for this purpose. In Sec. III we will tabulate for each symmetry species the total net and gross atomic population $n_\lambda(A)$ and $\hat{n}_\lambda(A)$ with $A =$ Ni or F, and the total overlap populations $n_\lambda(AB)$, with AB = NiF, AB = Fnn for nearest-neighboring F^- ions, and AB = Fnnn for next-nearest-neighboring F^- ions in the NiF_6^{4-} cluster.

III. RESULTS

The SCF orbital energies and orbital coefficients of the valence orbitals in symmetry species that contain open shells, e_g for the ground state and $t_{2g}\zeta$ for the first-excited state of the cluster, are given in Table V. All orbitals are fully occupied except those marked with an asterisk which are half-filled. In Table VI all orbital energies for the ground state are listed together with those for the free ions. To facilitate comparison we have included a column in which the electrostatic effects of the cluster considered as a set of point charges are added to the free-ion energies. To obtain some insight into the amount of admixture of the free-ion functions in the molecular orbitals of the cluster we have given in Table VII a percentage composition of the molecular orbitals based on Mulliken's population analysis. Table VIII presents total energies of the ground and some excited states for various cases, discussed in Sec. IV. The total net atomic, overlap, and gross atomic populations for closed and open shells in each symmetry species are given in Table IX for the ground state and in Table X for the first-excited state.

TABLE V. Orbital energies and coefficients for NiF_6^{4-} of species containing open shells.

		$^3A_{2g}$			$^3T_{2g}$	
	$2e_g$	$3e_g$	$4e_g$*		$1t_{2g}\zeta$	$2t_{2g}\zeta$ *
ϵ	−0.71206	0.16139	0.09106	ϵ	0.15729	0.06137
s_F	−0.07623	0.00013	0.00657	$p\pi_F$	0.55687	−0.06397
	−0.28009	0.00132	0.02398		0.56314	−0.05472
	0.20019	−0.00799	−0.01487	d_{Ni}	0.01818	0.47878
	0.89850	0.02247	−0.09518		0.03535	0.70586
$p\sigma_F$	0.01102	0.56849	−0.11415			
	0.01404	0.63074	−0.15771			
d_{Ni}	0.00769	0.04226	0.48575			
	0.01626	0.08198	0.70569			

IV. DISCUSSION

In this section we will concentrate on various interesting aspects that appear from the results given in Sec. III. In Sec. IV A the molecular orbitals, the orbital energies, and the results of population analysis will be discussed. In Sec. IV B we calculate the covalency parameters γ_i and λ_i, defined for the antibonding and bonding e_g and t_{2g} orbitals of the form

$$\Psi^a = N_a(\Phi - \sum_i \lambda_i \chi_i) \, , \qquad \Psi^b_i = N_b(\chi_i - \lambda_i\Phi + \sum_{j\neq i} \lambda_{ij}\chi_j) \; (i = s, \, \sigma, \text{ or } \pi) \, , \tag{3}$$

TABLE VI. Orbital energies for Ni^{2+}, F^-, and the $^3A_{2g}$ state of NiF_6^{4-} (a.u.).

	Ref. a	Ref. b		Ref. c
$1s_{Ni}$	−306.367	−304.784	$1a_{1g}$	−304.798
$2s_{Ni}$	−38.6165	−37.0334	$2a_{1g}$	−37.0520
$2p_{Ni}$	−33.6755	−32.0924	$1t_{1u}$	−32.1102
$1s_F$	−25.8243	−25.4738	$3a_{1g}$	−25.4538
			$1e_g$	−25.4537
			$2t_{1u}$	−25.4537
$3s_{Ni}$	−5.6001	−4.0170	$4a_{1g}$	−4.0506
$3p_{Ni}$	−3.9997	−2.4166	$3t_{1u}$	−2.4519
$2s_F$	−1.0700	−0.7195	$5a_{1g}$	−0.7263
			$4t_{1u}$	−0.7151
			$2e_g$	−0.7121
			$4e_g$*	0.0911
			$1t_{2g}$	0.1047
			$6a_{1g}$	0.1153
$3d_{Ni}$	−1.4252	0.1579	$5t_{1u}$	0.1478
$2p_F$	−0.1812	0.1693	$3e_g$	0.1614
			$1t_{2u}$	0.1879
			$6t_{1u}$	0.1900
			$2t_{2g}$	0.1955
			$1t_{1g}$	0.2045

[a] Free-ion energies.

[b] Free-ion energies $+6/R = 1.5831$ for Ni^{2+}, $+1/2R + 2\sqrt{2}/R - 2/R = 0.3505$ for F^-.

[c] Cluster energies (see Table VII for orbital composition).

TABLE VII. Percentage composition of the MO's for NiF_6^{4-}.

MO			($^3A_{2g}$ and $^3T_{2g}$)	
		nickel	ligands	
a_{1g}	1	100.00 $1s$		
	2	100.01 $2s$	−0.01 p	
	3	0.01 s	99.99 $1s$	
	4	99.99 $3s$	0.01 $2p$	
	5	−0.18 s	99.85 $2s$,	0.33 $2p$
	6	0.81 s	98.88 $2p$,	0.31 $2s$
e_g	1		100.00 $1s$	
	2	0.21 $3d$	99.85 $2s$,	−0.06 $2p$
	3	2.42 $3d$	97.64 $2p$,	−0.06 s
	4	97.70 $3d$	2.15 $2p$,	0.15 $2s$
t_{2g}	1	62.51 $3d$	37.49 $2p$	
	2	37.44 $3d$	62.56 $2p$	
t_{1u}	1	100.00 $2p$		
	2		100.00 $1s$	
	3	99.92 $3p$	0.06 p,	0.02 s
	4	0.03 p	99.92 $2s$,	0.05 $2p$
	5	0.09 p	99.81 $2p$	0.10 $2s$
	6	0.01 p	100.07 $2p$,	−0.08 s
t_{1g}	1		100.00 $2p$	
t_{2u}	1		100.00 $2p$	
$e_g\epsilon$	1		100.00 $1s$	
	2	0.51 $3d$	99.54 $2s$,	−0.05 $2p$
	3	62.79 $3d$	36.84 $2p$,	0.37 $2s$
	4	36.94 $3d$	63.01 $2p$	0.05 $2s$
$t_{2g}\zeta$	1	0.50 $3d$	99.50 $2p$	
	2	99.48 $3d$	0.52 $2p$	

where N_a and N_b are normalized constants, Φ stands for a nickel $3d$ orbital, and χ_i for an appropriate symmetry-adapted linear combination of fluorine $2s$ or $2p$ orbitals. We also obtain values for the hyperfine parameters f_s and f_σ. In Sec. IV C an analysis of the crystal-field-splitting parameter $10Dq$ is presented and the influence of the rest of the crystal is investigated. The Racah parameters for the cluster are evaluated in Sec. IV D including a discussion of the absence of an appreciable reduction of these parameters with respect to the free-ion values in the HF approximation. Finally, Sec. IV E contains some concluding remarks.

A. Molecular Orbitals, Orbital Energies, and Populations

The core orbitals of the cluster are almost the same as the core orbitals of the free Ni^{2+} and F^- ions. In the ground state the four e_g orbitals are almost pure nickel $3d$ orbitals, only slightly mixed with fluorine $2s$ and $2p$ orbitals, while the t_{2g} orbitals form bonding and antibonding combinations of the nickel $3d$ orbitals and the fluorine $2p$ orbitals. This formation of a pair of bonding and antibonding orbitals is characteristic for the closed-shell $3d$ orbitals. However, from Table VII we see that the sum of the percentage composition of these bonding-antibonding pairs is almost 100% $3d$ and 100%$2p$, which means that such pairs do not lead to any significant charge transfer.

From the total populations given in the Tables IX and X we see that only the closed shells in the symmetry subspecies, which also have an open shell, lead to positive total overlap populations and total gross atomic populations which indicate an appreciable charge transfer from the ligands to the nickel. About half of this charge transfer is compensated by a back donation of charge by the open shells. Table IX shows that the weakly bonding closed-shell orbitals that form a σ bond between the nickel and one of the ligands, i.e., $e_g\vartheta$ and $e_g\epsilon$, transfer 0.105 units of negative charge from the ligands to the nickel ion, while the corresponding open shells donate back 0.046 units of negative charge. Watson and Freeman[5] have remarked that the charge transfer of the bonding orbitals is fully compensated by the charge transfer of the antibonding partners and that the total charge transfer only results from that of the unpaired bonding orbitals. This is a rather obvious result in a minimum basis-set calculation and it is remarkable that it is also nearly true in our calculation. From comparison of Tables IX and X we see for the ground state, with two closed-shell

TABLE VIII. Energies for NiF_6^{4-} with and without point charges (in a.u.). bfs are basis functions; pch(1) and pch(2) are sets of point charges defined in Sec. IV C 2; T. E. is total energy, including the electrostatic contributions of the point charges.

case		$^3A_{2g}$	$^3T_{2g}$	$^3T_{1g}te$	$^1T_{1g}$
NiF_6^{4-} without $4s$ bfs	T. E.	−2102.9122	−2102.8875	−2102.8172	−2102.7734
NiF_6^{4-} with $4s$ bfs					
ionic orthogonal vectors	T. E.	−2102.8769	−2102.8591		
SCF	T. E.	−2102.9146	−2102.8898	−2102.8196	−2102.7757
NiF_6^{4-} +pch(1)					
cluster vectors	T. E.	−2104.5120	−2104.4857		
SCF	T. E.	−2104.5168	−2104.4904	−2104.4205	−2104.3768
NiF_6^{4-} +pch(2)	T. E.				
cluster vectors	T. E.	−2111.6497	−2111.6255		
SCF	T. E.	−2111.6559	−2111.6316		

TABLE IX. Total net, overlap, and gross atomic populations for NiF_6^{4-} ($^3A_{2g}$). *c* and *o* are closed- and open-shell orbitals, respectively.

		$n_\lambda(\mathrm{Ni})$	$n_\lambda(\mathrm{F})$	$n_\lambda(\mathrm{NiF})$	$n_\lambda(\mathrm{Fnn})$	$n_\lambda(\mathrm{Fnnn})$	$\hat{n}_\lambda(\mathrm{Ni})$	$\hat{n}_\lambda(\mathrm{F})$
$\sum a_{1g}$		6.0494	5.6811	−0.0734	0.3186	0.0244	6.0127	5.9873
$\sum e_g$	*c*	0.0469	12.2286	0.1163	−0.4596	0.0678	0.1051	11.8949
	o	2.0220	0.1295	−0.1395	−0.0179	0.0024	1.9540	0.0460
$\sum t_{2g}$		6.0133	5.5459	−0.0332	0.4849	−0.0109	5.9967	6.0033
$\sum t_{1u}$		12.0330	24.0501	−0.0607	0.0634	−0.0861	12.0027	23.9973
$\sum t_{1g}$			6.6275		0.6135	−0.0139		6.0000
$\sum t_{2u}$			6.2221		−0.2349	0.0128		6.0000
all	*c*	24.1426	60.3553	−0.0510	−0.4411	−0.0059	24.1172	59.8828
total		26.1646	60.4848	−0.1869	−0.4590	−0.0035	26.0712	59.9288

weakly σ-bonding orbitals and two open-shell weakly σ-antibonding orbitals, that the resulting charge transfer from the ligands to the nickel ion is somewhat (~ 0.02) larger than for the first-excited state. The latter has one σ and one π weak-bonding-antibonding pair. Hence in the excitation from the ground state to the first-excited state 0.02 units of negative charge are donated back to the ligands. These results are almost independent of the rather arbitrary construction of the gross atomic populations from the net atomic and overlap populations,[12] since the overlap populations for the closed and open shells considered almost cancel.

Going back to the results of Table V, we note that the orbital energies of the valence orbitals are positive. This indicates that the NiF_6^{4-} cluster *in vacuo* will be unstable with respect to ionization. An SCF calculation on the cluster NiF_6^{3-} shows indeed a lowering in energy of 0.2585 a.u. with negative orbital energies. In the crystal, however, the orbital energies will become negative, since the potential energy of an electron at the nickel and fluorine sites obtained from the Madelung potential at these sites, excluding the contributions of the cluster ions themselves, is −0.7666 and −0.7763 a.u.[3] We note further that the open-shell 3*d* orbitals have a lower orbital energy than the closed-shell fluorine 2*p* orbitals which might be thought to be inconsistent with a simple aufbau scheme of energy-ordered one-electron orbitals. This situation is similar, however, to the one in the free-transition-metal atoms with regard to 3*d* and 4*s* orbital energies and orbital occupation.[23]

B. Covalency and Hyperfine Parameters

To compare our results with those of the second group of calculations discussed in Sec. I we shall write the molecular orbitals in terms of the covalency parameters γ_i and λ_i. We have seen that only those molecular orbitals lead to appreciable charge transfer that appear in symmetry blocks containing open-shell molecular orbitals. Therefore, in discussing covalency effects, we shall confine our attention to the molecular orbitals of species e_g and t_{2g}. For the ground state and the first-excited state these molecular orbitals can be written according to Eq. (3):

$$(4e_g)=N_{e,3d}\left[d(3d)-\lambda_\sigma p\sigma(3d)-\lambda_s s(3d)\right],$$

TABLE X. Total net, overlap, and gross atomic populations for NiF_6^{4-} ($^3T_{2g}$). *c* and *o* are closed- and open-shell orbitals, respectively.

		$n_\lambda(\mathrm{Ni})$	$n_\lambda(\mathrm{F})$	$n_\lambda(\mathrm{NiF})$	$n_\lambda(\mathrm{Fnn})$	$n_\lambda(\mathrm{Fnnn})$	$\hat{n}_\lambda(\mathrm{Ni})$	$\hat{n}_\lambda(\mathrm{F})$
$\sum a_{1g}$		6.0490	5.6795	−0.0699	0.3171	0.0244	6.0140	5.9860
$\sum e_g\theta$	*c*	0.0234	6.1138	0.0579	−0.2291	0.0339	0.0524	5.9476
	o	1.0110	0.0647	−0.0680	−0.0090	0.0012	0.9770	0.0230
$\sum e_g\epsilon$		2.0439	6.2445	−0.0784	−0.2461	0.0361	2.0047	5.9953
$\sum t_{2g}\zeta$	*c*	0.0042	1.8267	0.0118	0.1610	−0.0036	0.0101	1.9899
	o	1.0006	0.0103	−0.0116	0.0008	0.0000	0.9948	0.0052
$\sum t_{2g}\xi,\eta$		4.0089	3.6961	−0.0222	0.3245	−0.0073	3.9979	4.0021
$\sum t_{1u}$		12.0329	24.0497	−0.0605	0.0640	−0.0860	12.0026	23.9974
$\sum t_{1g}$			6.6294		−0.6154	−0.0140		6.0000
$\sum t_{2u}$			6.2225		−0.2353	0.0128		6.0000
all	*c*	24.1623	60.4621	−0.1613	−0.4594	−0.0037	24.0817	59.9183
total		26.1739	60.5371	−0.2409	−0.4676	−0.0025	26.0535	59.9465

TABLE XI. Atomic-orbital coefficients.

$d(3d)$	$d(2p)$	$d(2s)$	$d(3d')$	$d(2p')$
0.48311	0.3974	0.3732	0.47864	0.3968
0.70185	0.7710	0.7891	0.70565	0.7715
$p(3d, \mathrm{F})$	$p(2p, \mathrm{F})$	$p(2s, \mathrm{F})$	$p(3d' \mathrm{F})$	$p(2p', \mathrm{F})$
0.4897	0.55528	0.5140	0.6309	0.58269
0.6766	0.61608	0.6549	0.5397	0.58925
$s(3d, \mathrm{F})$	$s(2p, \mathrm{F})$	$s(2s, \mathrm{F})$		
−0.0644	0.0075	−0.07592		
−0.2350	0.0757	−0.27895		
0.1457	−0.4583	0.19937		
0.9328	1.2887	0.89484		

Norms $n_a(i)$

$a(i)$	$p\sigma(3d)$	$p\sigma(2p)$	$p\sigma(2s)$	$s(3d)$	$s(2p)$	$s(2s)$	$p\pi(3d')$	$p\pi(2p')$
	1.0502	1.0423	1.0472	1.0055	1.0100	0.0051	0.9650	0.9595

$$
\begin{aligned}
(3e_g) &= N_{e,2p}[p\sigma(2p) + \gamma_\sigma d(2p) + \gamma_{\sigma s} s(2p)] , \\
(2e_g) &= N_{e,2s}[s(2s) + \gamma_s d(2s) + \gamma_{s\sigma} p\sigma(2s)]
\end{aligned}
\tag{5}
$$

and

$$
\begin{aligned}
(2t_{2g}\zeta) &= N_{t,3d}[d(3d') - \lambda_\pi p\pi(3d')] , \\
(1t_{2g}\zeta) &= N_{t,2p}[p\pi(2p') + \gamma_\pi d(2p')] ,
\end{aligned}
\tag{6}
$$

where the orbitals $p\sigma$, $p\pi$, and s are appropriate symmetry-adapted normalized linear combinations of the fluorine $2p$ and $2s$ orbitals. For example,

$$
p\sigma(i) = n_{p\sigma}(i) \textstyle\sum_{\mathrm{F}} t'_{\mathrm{F}} p(i, \mathrm{F}) , \tag{7}
$$

where $n_{p\sigma}(i)$ are the norms and t'_{F} the normalization coefficients if one supposes that the fluorine orbitals on different centers do not overlap. The orbitals $d(i)$, $p\sigma(i)$, $p\pi(i)$, and $s(i)$ are generally different for each molecular orbital i. The coefficients of the atomic orbitals $d(i)$, $p(i, \mathrm{F})$, and $s(i, \mathrm{F})$ and the norms $n_a(i)$, defined in Eq. (7), are given in Table XI. By comparing the coefficients of the atomic orbitals of Table XI with those of the free-ion atomic orbitals of Table III one can see that for the σ-antibonding and -bonding MO's of Eq. (5) all atomic orbitals extend over a larger region of space than the free-ion orbitals, except the $d(3d)$ orbital. For the π MO's of Eq. (6), the d orbitals are more expanded and the $p\pi$ orbitals more contracted than the free-ion orbitals. The suggestion of Marshall and Stuart[24] that the observed lowering of the spin-orbit parameters in transition-metal complexes (~ 30%) is caused by an expansion of the $d(3d)$ orbital with respect to the free-ion orbital does not, therefore, seem to hold for KNiF$_3$.

TABLE XII. Normalization constants N_a.

a	$e, 3d$	$e, 2p$	$e, 2s$	$t, 3d$	$t, 2p$
	1.0055	0.9823	0.9990	1.0003	0.9960

Covalency parameters and overlap integrals

	our results			SS[a]		WF[b]		HRH[c]
i	λ_i	γ_i	S_i	γ_i	S_i	γ_i	S_i	γ_i
s	0.1009	0.0206	0.0711	0.031	0.0814	0.017	0.0798	0.076
σ	0.2207	0.1082	0.1094	0.285	0.1107	0.066	0.1050	0.215
π	0.1050	0.0460	0.0602	0.173	0.0765	0.032	0.0708	0.132
$s\sigma$		0.0205	−0.0488					
σs		0.0176	−0.0488					

[a] Sugano and Shulman, Ref. 3.

[b] Watson and Freeman, Ref. 5.

[c] Hubbard, Rimmer, and Hopgood, Ref. 8.

The normalization constants, the covalency parameters, and the overlap integrals, calculated for the free-ion orbitals, are given in Table XII together with the values obtained by Sugano and Shulman,[3] Watson and Freeman,[5] and Hubbard, Rimmer, and Hopgood.[8] Since the orbitals $p\sigma(3d)$ and $s(3d)$ are different from the free-ion orbitals we prefer to calculate the parameters f_s and f_σ directly from the isotropic and anisotropic hyperfine-field parameters A_s and A_σ for which we refer to the work of Ellis *et al.*[10] and Moskowitz *et al.*[17] The calculated values for the parameters A_s and A_σ and the corresponding parameters A_{2s} and A_{2p} calculated for the free F$^-$ ion are given in Table XIII together with the experimental values.[25] From Table XIII calculated values of 0.46% and 2.86% are obtained for f_s and f_σ, respectively. We conclude that the $2s$ contribution in the open-shell orbitals is in fair agreement with experiment[25] (0.54%), while the $2p\sigma$ contribution is less satisfactorily reproduced (experiment 3.78%).

C. Crystal-Field-Splitting Parameter 10*Dq*

1. Results and Interpretation

For the various cases given in Table VIII the contributions to the crystal-field-splitting parameter are summarized in Table XIV. We see that the inclusion of $4s$ orbitals has only a very small effect on the calculated $10Dq$ value. The quantity $10Dq$ is defined here as the difference in energy between the states ${}^3A_{2g}$ and ${}^3T_{2g}$. The difficulties encountered when one tries to relate this quantity to the $10Dq$ parameter of the semiempirical ligand-field theory, e.g., in terms of orbital energy differences, have been discussed by Dahl and Ballhausen[26] and especially by Richardson *et al.*[14] These problems do not exclude, however, a qualitatively simple and quantitatively reasonably correct interpretation of the calculated ${}^3A_{2g} - {}^3T_{2g}$ energy difference. To this end we consider the finally computed value as being obtained in the following five consecutive steps:

(a) Ni^{2+} surrounded by six negative point charges (the classical point-charge model); (b) inclusion of the direct Coulombic effect of replacing the

TABLE XIII. Hyperfine-field parameters (in 10^{-4} cm^{-1}).

	A_{2s}	A_{2p}	A_s	A_σ
Calc.	14946	421.7	34.482	6.034
Expt.[2]			33.9	8.10

TABLE XIV. Crystal field splitting $10Dq$ (in cm^{-1}). bfs are basis functions; pch(1) and pch(2) are sets of point charges defined in Sec. IV C 2; K. E. is kinetic energy; N. A. E. is nuclear-attraction energy; E. R. E. is electron-repulsion energy.

NiF_6^{4-} without 4s bfs				5420
NiF_6^{4-} with 4s bfs				
SCF	contributions:	K.E.	25 330	
		N.A.E.	−9130	
		E.R.E.	−10 760	
				5440
NiF_6^{4-} + pch(1)				
cluster vectors				5770
SCF	contributions:	K.E.	26 030	
		N.A.E.	−1320	
		E.R.E.	−18 920	
				5790
NiF_6^{4-} + pch(2)				
cluster vectors				5310
SCF	contributions:	K.E.	24 930	
		N.A.E.	−13 670	
		E.R.E.	−5930	
				5330
Ni^{2+} + 6 point charges (crystal field approximation)				1380
experiment				7250

point charges by extended F^- ions (Kleiner's correction); (c) inclusion of the two-electron metal-ligand-exchange interactions associated with (b); (d) orthogonalization of the ionic wave functions to achieve proper normalization of the $^3A_{2g}$ and $^3T_{2g}$ starting wave functions and computation of the corresponding energy expectation values ("overlap" contribution); (e) the final SCF result ("covalent" contribution). Rounded-off contributions to $10Dq$ up to and including each step are listed in Table XV. It appears that by far the largest contribution stems from the orthogonalization or, put in another way, from the Pauli repulsion exerted on the metal d electrons by the closed electron shells of the ligands. It is worth mentioning that this contribution is dominated by the increase in electronic kinetic energy as might have been expected. The implication is that for $KNiF_3$ the classical ionic model still provides a good physical basis to explain the major part of the crystal field splitting. The emphasis should, however, not be laid on the electrostatic-Madelung term of the model but on the Born-repulsion term instead. For systems with closed-shell ions it is known that the Born repulsion is a short-range effect which is closely connected with the interpenetration of the electron shells of different ions, i.e., with the orthogonalization effects described above. In the case of open d or f shells the situation will be the same in first approximation, i.e., there will be a spherically symmetric-average repulsion term for the open shell as a whole. In the next approximation, according to our results, allowance must be made for slightly different repulsive terms for the various octahedral substates that arise from each atomic state. The qualitative features of this repulsive effect can be inferred from the spatial properties of the d orbitals much in the same way as is done in the conventional electrostatic picture.

From Table XIV one sees that also in the final SCF value for $10Dq$ the main sign-determining contribution is the difference in electronic kinetic energy between the $^3A_{2g}$ and $^3T_{2g}$ states. In Table XVI $10Dq$ is analyzed further in terms of one-center and multicenter contributions to the three energy components. Richardson *et al.*[14] have analyzed their computed $10Dq$ value in the same way as we have done above. They obtain similar results except for the final "covalency" step for which they find a substantially higher contribution than we do and which leads to a very good agreement with the experimental value. In their work, however, three-center integrals containing the product of two basis functions on different fluoride ions have been neglected. The numbers in Table XVI show that this kind of three-center contribution to $10Dq$ is not negligible and will in fact lower the computed value.

2. Influence of Cluster Surroundings

According to Table XIV, surrounding the cluster by eight positive point charges at the potassium sites [case pch(1) in Table XIV] causes $10Dq$ to increase. Adding two layers of point charges of appropriate sign on the nickel and fluorine sites nearest to the cluster [case pch(2) in Table XIV] causes $10Dq$ to decrease again. The numbers show that the point-charge effect on $10Dq$ when calculated with the unchanged cluster orbitals is very close to the final SCF result. The influence of nine successive layers of point charges has therefore been investigated by calculating for each layer the corresponding change in the one-electron energies of the $^3T_{2g}$ and $^3A_{2g}$ states on the basis of the unchanged cluster orbitals. The results are summarized in Table XVII and Fig. 2. They show that after inclusion of the first two layers the cluster value of $10Dq$ tends to be slowly restored. After the ninth layer the result is about 90 cm^{-1} (1.7%) lower than that of the cluster. It is difficult to assess the sig-

TABLE XV. Contributions to $10Dq$.

	$10Dq$ (cm^{-1})	% of SCF value
Point charges	1400	25
"Kleiner"	50–100[a]	1–2
Two-electron exchange	−1000[a]	−20
Orthogonalization	4000	75
SCF	5500	100
Experiment	7250	

[a] Numbers are estimated.

TABLE XVI. One- and multicenter contributions to kinetic (K.E.), nuclear-attraction (N.A.E.), electronic-repulsion (E.R.E.), and total-energy differences between the $^3T_{2g}$ and $^3A_{2g}$ states of the NiF_6^{4-} cluster.

	One-center		Two-center		Three-center			Four-center	total
	Ni	6F	6NiF	15FF	12FNiF (nn)	3FNiF (nnn)	20FFF		
K.E.	0.077	0.059	−0.020	0.000					0.116
N.A.	−0.365	−0.386	0.458	−0.385	0.517	0.064	0.055		−0.042
E.R.E.	0.271	0.311	−0.378	0.444	−0.561	−0.075	−0.065	0.004	−0.049
sum	0.017	−0.016	0.060	0.059	−0.044	−0.011	−0.010	0.004	0.025

nificance of this small difference, however, because the effect of approximating the ions by point charges is unknown. Probably this effect will not be negligible for the ions in the first layer.

D. Racah Parameters

In the simplest theoretical description of the $t_{2g}^x e_g^y$ $(x+y=8)$ states of the NiF_6^{4-} cluster one assumes one set of core orbitals and one $3d$ radial function common to all states. In addition it is assumed that the influence of the ligands can be taken into account by an external potential of appropriate symmetry. With these assumptions the energy of each state can be expressed linearly in terms of two-electron integrals A, B, and C as in the free-ion case and a one-electron quantity $10Dq$ which is determined by the $3d$ radial function and the external potential. Energy differences will depend only on $10Dq$, B, and C. A more refined treatment involves the use of t_{2g} and e_g orbitals that are unrelated to each other but which are still the same for all states. The various energies can now be described by nine two-electron integrals (ten if configuration interaction is included) and the one-electron quantity $10Dq$.[1,14]

TABLE XVII. Contribution of some layers of point charges to $10Dq$ (in cm^{-1}). n is number of point charges in a layer.

Layer		Coordinates[a]	n	$\Delta(10Dq)$	$10Dq$
	NiF_6^{4-}				5443
1	K^+	$(\pm R, \pm R, \pm R)$	8	325	5768
2	Ni^{2+}	$(\pm 2R, 0, 0)$	6	−527	5241
3	F^-	$(\pm 2R, \pm R, 0)$	24	91	5332
4	Ni^{2+}	$(\pm 2R, \pm 2R, 0)$	12	40	5372
5	F^-	$(\pm 2R, \pm 2R, \pm R)$	24		
	F^-	$(\pm 3R, 0, 0)$	6	−17	5355
6	K^+	$(\pm 3R, \pm R, \pm R)$	24	−22	5333
7	Ni^{2+}	$(\pm 2R, \pm 2R, \pm 2R)$	8	21	5354
8	F^-	$(\pm 3R, \pm 2R, 0)$	24	2	5356
9	Ni^{2+}	$(\pm 4R, 0, 0)$	6	18	5374

[a] The Ni^{2+} site is taken as the origin in the unit cell of Fig. 1 and R is the nearest-neighbor Ni-F distance.

Finally, individual all-electron SCF calculations can be made for each state. In this case none of the assumptions given applies anymore but one can still try to fit the calculated energies to linear expressions which are formally similar to those derived for the simplest theoretical treatment. For the free ions such a fitting procedure seems to work quite well.[27,28] Now, however, the quantities B and C, and in the case of the cluster also $10Dq$, are just parameters consisting of one-electron as well as two-electron contributions and they have no simple interpretation anymore. The parameters B and C may be called theoretical Racah parameters. The similar parametrization of observed free-ion or cluster states is of course well known. The resulting experimental parameters must again consist of one-electron as well as two-electron contributions on account of the virial theorem. Moreover, they incorporate the effects of electron correlation or configuration interaction. These are important effects that cause in the case of free Ni^{2+} the B parameter to be about 30% smaller than its theoretical counterpart (Table I and Ref. 27).

In Table XVIII are summarized the results of separate SCF calculations for the 10 cluster states together with the linear expressions to which they are fitted and the results of the fitting. Note that parameters A_1, A_2, and A_3 have been introduced whose difference should reflect the conventional crystal field splitting. By definition, $28(A_2-A_1) = 10Dq$ and it is easily checked, that with the listed

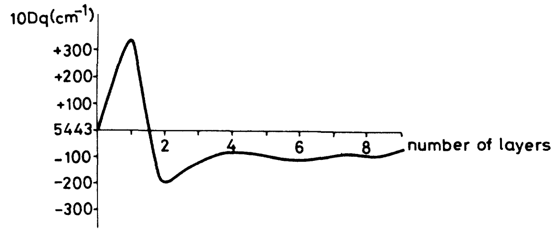

FIG. 2. $10Dq$ plotted against the number of point-charge layers.

TABLE XVIII. Total energies of *d-d* excited states (in a.u.), energy differences, and their one- and two-electron contributions.

State		Expressions	Total energy	Parameter form	Energy differences one-electron part	Energy differences two-electron part	Total	Fit[a]
$t_{2g}^6e_g^2$	$^3A_{2g}$	$28A_1-50B+21C$	-2102.9146					
	^1E_g	$28A_1-42B+23C$	-2102.8265	$8B+2C$	-0.0183	0.1065	0.0881	0.0895
	$^1A_{1g}$	$28A_1-34B+25C$	-2102.7337	$16B+4C$	-0.1049	0.2859	0.1809	0.1790
$t_{2g}^5e_g^3$	$^3T_{2g}$	$28A_2-50B+21C$	-2102.8898					
	$^3T_{1g}$	$28A_2-38B+21C$	-2102.8196	$12B$	0.0216	0.0486	0.0702	(0.0702)
	$^1T_{2g}$	$28A_2-42B+23C$	-2102.8015	$8B+2C$	0.0220	0.0664	0.0883	0.0895
	$^1T_{1g}$	$28A_2-38B+23C$	-2102.7757	$12B+2C$	0.0228	0.0903	0.1141	0.1129
$t_{2g}^4e_g^4$	$^3T_{1g}$	$28A_3-47B+21C$	-2102.8474					
	$^1T_{2g}$	$28A_3-41B+23C$	-2102.7677	$6B+2C$	0.0736	0.0061	0.0797	0.0778
	^1E_g	$28A_3-41B+23C$	-2102.7677	$6B+2C$	0.0745	0.0052	0.0797	0.0778
	$^1A_{1g}$	$28A_3-32B+26C$	-2102.6485	$15B+5C$	0.0266	0.1722	0.1989	0.1945

[a] $B=0.00585$ a.u.; $C=0.02135$ a.u.

value of B, $28(A_3-A_2)=10Dq$ also which is a gratifying result. In fact the results of the fitting procedure are quite satisfactory as a whole and illustrate the relative insensitivity of total energies with respect to small changes in the wave functions in spite of the far greater changes in the one- and two-electron contributions separately. Some striking examples are included in Table XVIII. These conclusions are similar to the ones reached by Richardson *et al.* in their discussion of $10Dq$.[14]

The theoretical B and C values obtained in this way show a reduction of about 2% with respect to the theoretical values found for the free Ni^{2+} ion (Table I). The reduction is significantly less than that of about 10% found for the experimental parameters and it leads to significant differences between the observed[29] and calculated transition energies as can be seen from Table XIX which includes the values calculated by Richardson *et al.*[14] The fact that our SCF results do not reproduce the desired reduction of the Racah parameters may well be inherent to the HF approximation since the results of Gladney and Veillard as well as those of Moskowitz *et al.* are very similar to ours in this respect. This is perhaps not surprising considering the substantial correlation or configuration-interaction effects on the parameters for the free ion. These effects will be at least as substantial in the cluster and they may in fact well be larger because of the presence of new molecular states, in particular charge-transfer states. Such a state of affairs would imply, however, that the prevailing interpretation of the observed parameter reduction as a "cloud-expanding" or "nephel auxetic" effect[30] should be reconsidered.

E. Final Remarks

The restricted SCF-LCAO (linear-combination-of-atomic-orbitals) approximation presented here gives a reasonable but not too precise description of the covalency effects and the spectral properties of $KNiF_3$. The parameters f_s and f_σ and the $10Dq$ value are about 15–25% smaller than the experimental values. Similar deviations were found for the spectral transition energies. At present it is not possible to estimate whether or not exact solution of the HF equations for the cluster will lead to much better agreement. In Sec. IV we have indicated the importance of correlation or configuration-interaction effects with regard to the calculated transition energies with specific reference to the influence of charge-transfer states. It is an interesting question whether the calculated $10Dq$ value can be significantly changed by taking these effects into account; interesting, because it can be shown that Brillouin's theorem[31] holds for the SCF solutions of both the $^3A_{2g}$ and the $^3T_{2g}$ states. Hence, singly excited configurations will not contribute when the configuration-interaction matrix is diagonalized in first order. Doubly excited charge-transfer states have been calculated to yield a small increase in $10Dq$ of about 10 cm^{-1} in the same order of approximations. The role of the charge-transfer states including the singly excited ones may be seriously underestimated, however, since a proper treatment of these states must account for the orbital-relaxation effects that will occur with respect to the SCF orbitals

TABLE XIX. Transition energies.

	α^3T_{1g}	α^1E_g	a^1T_{2g}	b^3T_{1g}
Our results	9500	18000	22720	25990
Richardson *et al.*[14]	12480	18870	25460	28950
Experiment[3]	12530	15440	20920	23810

obtained in the ground-state calculation. If these relaxation effects are large, as may be expected for this kind of excitation, a first-order evaluation of the configuration-interaction matrix will be of little value. These effects are in principle accounted for in the valence-bond approach of Hubbard, Rimmer, and Hopgood[8] where the wave function is given as a linear combination of Slater determinants representing the ionic ground state and various charge-transfer states. The latter states are not necessarily based on the orbitals used to describe the ionic state. The authors obtain a total "covalency" contribution to $10Dq$ of about 3200 cm^{-1}, which might be compared with our SCF covalency contribution of 1550 cm^{-1}. If this comparison is allowed even in a rough fashion it suggests that configuration-interaction contributions to $10Dq$ can be as high as 1000–1500 cm^{-1}.

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