THEORETICAL STUDY ON THE GROUND AND EXCITED STATES OF CHROMYL FLUORIDE (CrO$_2$F$_2$)

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RESUM

S'investiga l'estructura electrònica del CrO$_2$F$_2$ fent ús de la teoria del funcional de la densitat i d'un procediment matemàtic proposat per Ziegler i col.laboradors (el mètode de la suma). Per al cas de l'estat fonamental s'analitza la naturalesa dels orbitals frontera i es troba que hi ha una bona correlació amb la dels orbitals de l'espècie isoelectrònica CrO$_4^{2-}$. L'estat excitat singlet de més baixa energia, $^1B_2$, prové de la promoció electrònica $5b_2 \rightarrow 9a_1$. Les energies de transició calculades s'empren per assignar les principals bandes de l'espectre electrònic d'absorció enregistrat en fase gas.

RESUMEN

Se investiga la estructura electrónica del CrO$_2$F$_2$ mediante la teoría del funcional de la densidad, junto con un procedimiento matemático propuesto por Ziegler y colaboradores (el método de la suma). En el caso del estado fundamental se analiza la naturaleza de los orbitales frontera y se encuentra que hay una buena correlación con la de los orbitales de la especie isoelectrónica CrO$_4^{2-}$. El estado excitado singlete de más baja energía, $^1B_2$, proviene de la promoción electrónica $5b_2 \rightarrow 9a_1$. Las energías de transición calculadas se utilizan para asignar las principales bandas del espectro electrónico de absorción registrado en fase gas.

ABSTRACT

The electronic structure of CrO$_2$F$_2$ is investigated by using approximate density functional theory together with a mathematical procedure by Ziegler et al. (the sum method). Insight into the nature of the frontier orbitals is given for the ground state, and a good direct correlation is found with that of the parent isoelectronic CrO$_4^{2-}$ species. The lowest singlet excited state, $^1B_2$, is calculated to arise from the $5b_2 \rightarrow 9a_1$ promotion. The computed transition energies are used to assign the main bands of the gas-phase electronic absorption spectrum.

Keywords: Excited states, density functional theory, sum method, closed-shell transition-metal complexes, chromyl fluoride.

INTRODUCTION

Chromyl fluoride, which is a highly reactive oxidizing agent, is isoelectronic with permanganate (MnO$_4^-$) and chromate (CrO$_4^{2-}$) ions. Since the initial studies of Wolfsberg and Helmholtz (1), the electronic structures of closed-shell transition metal compounds have received extensive theoretical investigation (2-11). However, much of this work has focused on MnO$_4^-$ and CrO$_4^{2-}$ as archetypical complexes, with other systems receiving less attention.

In the case of MnO_4^-, reasonable assignments have been recently given for the spectrum (5), together with the electronic mechanism of the photodissociation reaction of this tetraoxo complex (6) by means of the symmetry adapted cluster (SAC) and SAC-configuration interaction (SAC-CI) approaches (12-13). The electronic structures of the ground and excited states of CrO_4^{2-} have also been studied by many theoretical methods (7-11), since Teltow et al. (14) reported the ultraviolet (UV) absorption spectrum of the ion in 1939.

Recently, the lower excited states of CrO_4^{2-}, CrO_3X^-, and CrO_2X_2 with X = F, Cl have received renewed experimental interest with the observation of their previously elusive lowest lying spin-triplet states (15-18). By contrast, from the theoretical side, perturbation of the electronic structure engendered by changing one or more of the oxygen ligands for a given tetraoxo metal complex has received less study. In particular, only a few theoretical investigations have examined the electronic structures of the relatively low excited states of CrO_2F_2. Jasinski et al. (19) have measured gas phase electronic absorption spectra of CrO_2F_2 and CrO_2Cl_2 in the visible and near UV regions. They explained these spectra using molecular orbital calculations based on the self-consistent field (SCF)-Xα-SW method, and correlated the results with those for the isoelectronic species MnO_4^- and CrO_4^{2-}. Later, Miller et al. (10) studied the lower excited states of CrO_4^{2-}, CrO_3X^-, and CrO_2X_2 (X = F, Cl), using the same method, in order to compare the electronic structure of the members of the series.

Several studies similar to those mentioned above have shown that electron correlation effects are quite important even for qualitative assignments of the excitation spectra. Jitsuhiro et al. (20) pointed out that whereas SAC-CI method (13) was useful for studying the excited states of metal complexes, most of the previous theoretical results were unreliable, since they had not included a sufficient amount of electron correlation. This makes conventional single-determinant Hartree-Fock (HF) theory a relatively poor approximation. In contrast, techniques based on density functional theory (DFT) (21) appear to be as good as correlated HF treatments (especially for molecular geometries and vibrational frequencies), and at a significantly reduced computational cost. However, as far as excitation energies are concerned, the latter method has to be taken with some care because in principle its formalism has been developed only for ground state properties. For excited states, there is no foundation equivalent to the Eckart's theorem. This notwithstanding, in many situations, excitations of a given system are required, and it is an important question to what extent these can be obtained within the framework of approximate DFT.

In recent years, several methods for calculating excited state properties have appeared, ranging from those that are rigorously justified within the DFT formalism to ones where the justification is essentially empirical. Among the former it is worth mentioning the work of Ziegler et al. (22,23), together with a formulation of Kryachko et al. (24) based on mathematical foundations.

Prompted by the first results reported using the aforementioned methods, in this paper we shall investigate the excited states of CrO_2F_2 by means of DFT. The electronic spectrum reported for CrO_4^{2-} will be taken as reference. Theoretical assignments for CrO_2F_2 will be compared to experimental values (19).

METHODOLOGICAL ASPECTS

According to the first Hohenberg-Kohn theorem (25), the exact ground-state one-electron density $\rho_o(r)$ for a system of N interacting electrons is in a one-to-one correspondence with the external potential $\upsilon(r)$. This implies that if by some means $\rho_o(r)$ is known, then the Hamiltonian for this system may be determined. Moreover, as pointed out by Kryachko et al. (24), by solving Schrödinger's equation, not only the ground-state energy E_o and the ground-state wave function Ψ_o but also all other eigenvalues and eigenfunctions for the excited states may be obtained. In this general sense, therefore, the energies of the excited states may be regarded as functions of ρ_o.

Despite this, practical applications require some care. Hence, the only input required to calculate the energy of the lowest-lying state within approximate DFT is the total density and the spin density, but the particular form for the exchange energy has a number of features which makes it difficult to evaluate space and spin multiplets in an unambiguous way. Insight into such problems was provided by Ziegler et al. (22) who showed that DFT calculations can be performed only when states are represented by a single determinant. Exchange energies for multiplets represented by linear combinations of determinants must be evaluated indirectly by Slater's sum rules.

In general, the energy $E(D_i)$ of each possible single determinant D_i in a given configuration can be represented as a weighted sum of multiplet energies H_j

$$E(D_i) = \sum_j C_{ij} H_j$$

(1)

The idea of the sum method is to replace $E(D_i)$ in Eq. (1) by the corresponding statistical energy $E(\rho_i)$ and in this way obtain a set of equations

$$E(\rho_i) = \sum_j C_{ij} H_j$$

(2)

from which one can find the multiplet energies H_j, provided that the number of determinants with different energies, $E(\rho_i)$, equals the number of multiplets.

There are situations where the latter condition is not met. In such cases, not all multiplets can be calculated. An example is the first excited configuration of benzene, which gives rise to six states but for which there are only four determinants of different energy. By contrast, satisfactory agreement between calculated and experimental multiplet energies has been obtained for CrO_4^{2-} and small organic molecules (22,23).

All calculations reported in the present paper were carried out by using the DFT-based package ADF, developed by Baerends et al. (26). The numerical integration scheme employed was that of te Velde and Baerends (27). A triple-ζ STO basis set was used for the $3s$, $3p$, $3d$ and $4s$ orbitals of chromium. For fluorine ($2s$, $2p$), and oxygen ($2s$, $2p$), double-ζ basis sets augmented by an extra polarization function were employed. Electrons in lower shells were treated within the frozen

core approximation. A set of auxiliary s, p, d, f, and g STO functions, centered on all nuclei, was introduced for the sake of fitting the one-electron molecular density and Coulomb potential accurately in each SCF cycle. All calculations were performed including gradient corrections to the local density approximation part of the density functional: Becke's nonlocal correction for exchange (28), and Perdew's nonlocal correction for correlation (29). Singlet excitaton energies for electronic spectra were evaluated according to the sum method described above (22,23).

RESULTS AND DISCUSSION

Chromyl fluoride has an approximately tetrahedral configuration. Therefore, some similarity between the results of the present calculation and those for tetrahedral molecules such as CrO_4^{2-} and MnO_4^- might be expected. However, it is not easy to correspond the MOs and the excited states of these molecules. The decrease in symmetry causes considerable mixing of the orbitals and excited states.

I. Ground state

Figure 1 displays the energy level diagram for the higher filled and lower unfilled orbitals in the ground states of CrO_4^{2-} (T_d), CrO_3F (C_{3v}), and CrO_2F_2 (C_{2v}). The correlation between T_d and C_{2v} symmetry in these systems indicates that the lowering of the symmetry should produce singly degenerate excited states of symmetries A_1, A_2, B_1, and B_2 for an orbital electron transfer which is equivalent to the parent $t \rightarrow e$ transition in tetrahedral symmetry. Orbitals below the dashed line are filled in the ground state. The lowest energy excitation corresponds to $t_1 \rightarrow e$ in CrO_4^{2-}, $a_2 \rightarrow e$ in CrO_3F, and $b_2 \rightarrow a_1$ in CrO_2F_2. Their experimental values are 3.3 eV (3), 2.8 eV (30), and 2.6 eV (19), respectively.

Figure 1 Fig. 1, Torrent et al., Sci. Gerund.

The calculated DFT orbital energies and the orbital nature of CrO_2F_2 in the ground state are shown in Table 1. Orbitals below the dashed line are filled in the ground state. The many-electron ground state for this closed-shell system is $^1A_1$. As far as the numbering of the orbitals is concerned, notice that orbitals have been labeled without taking into account core orbitals. Consequently, our $5b_2$ orbital corresponds to the orbital usually labeled $7b_2$ in the literature (10). All other labels for the remaining orbitals are also shifted.

The six highest occupied valence MOs are bonding MOs between Cr, O, and F atoms which involve primarily Cr(3d), O(2p), and F(2p) orbitals. The three highest MOs, $5b_2$, $2a_2$, and $5b_1$, roughly correlate to the threefold degenerate t_1 orbitals in the T_d symmetry, and the remaining three MOs, $8a_1$, $4b_2$, and $4b_1$, correspond to the t_2 orbitals (Figure 1).

The HOMO, $5b_2$, is mainly a nonbonding lone-pair orbital localized on the O atoms. The same applies for $2b_2$, and $4a_1$ MOs. The $4b_1$, $2b_1$ and $3a_1$ MOs can be considered nonbonding lone-pair orbitals localized on the F atoms. Mülliken population analysis shows that the net total charge distribution is about -0.594 for O atoms, and -0.509 for F atoms. The net charge of the Cr atom is +2.205. Although
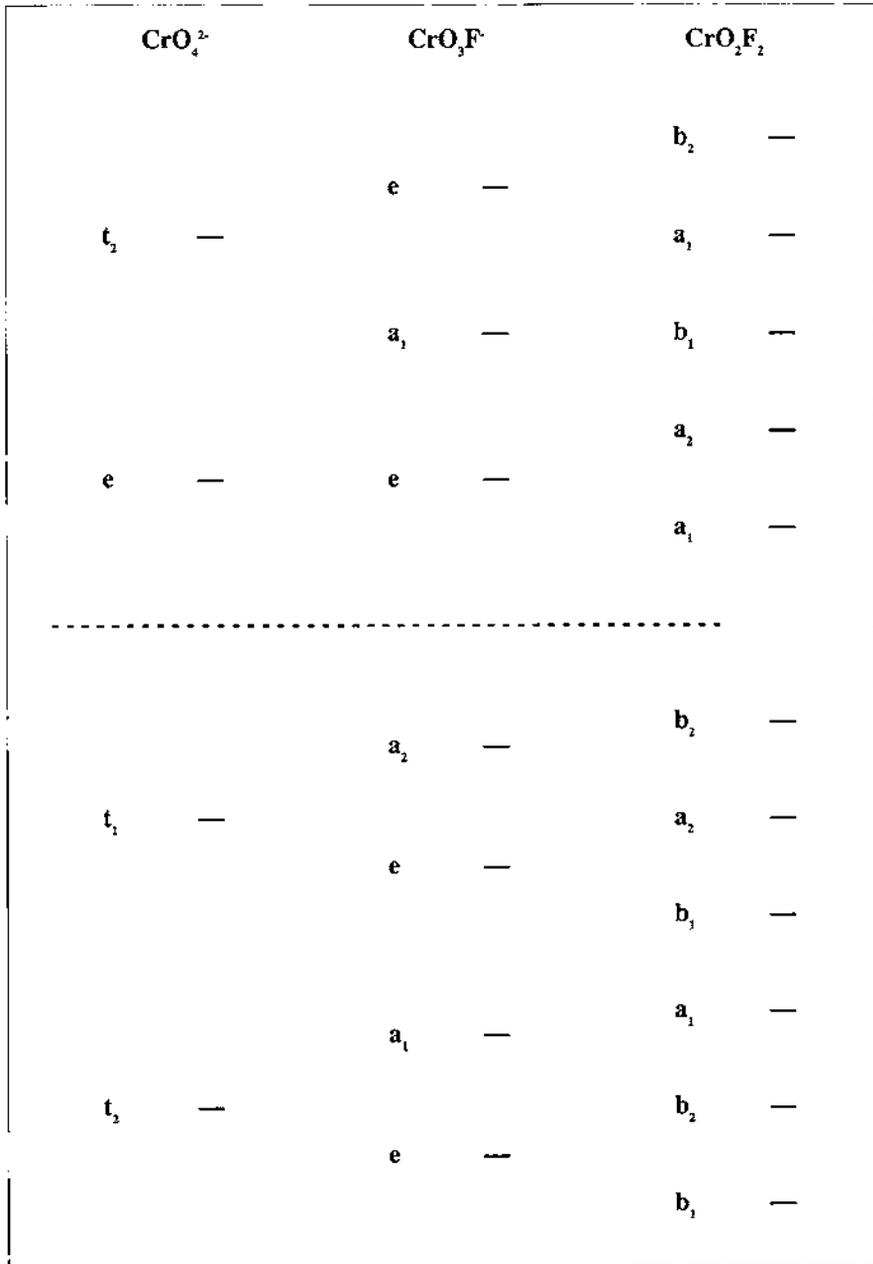
Figure 1. *Energy level diagram for the higher occupied and lower unoccupied orbitals in the ground states of CrO_4^{2-} (T_d), CrO_3X^- (C_{3v}) and CrO_2X_2 (C_{2v}).*

the formal charge of Cr in CrO_2F_2 is +6, the Cr-O and Cr-F bonds have large covalent character due to the back donation of electrons from O and F, respectively, to Cr through the nonbonding MOs.

The five lowest unoccupied orbitals are antibonding MOs between Cr and ligands. They have negative orbital energies. The two lowest MOs, $3a_2$ and $9a_1$, correlate to the twofold degenerate e orbitals in the T_d symmetry. The remaining three MOs, $6b_2$, $10a_1$, and $6b_1$, correspond to the t_2 orbitals. The $9a_1$ (LUMO) and $6b_1$ MOs are antibonding between Cr and O and between Cr and F, whereas the other MOs, $6b_2$, $10a_1$, and $3a_2$, are mainly antibonding between Cr and O only.

Orbital	Energy	Cr charge	O charge	F charge
$6b_2$	-0.1459	0.5517	0.3144	0.0422
$10a_1$	-0.1672	0.5841	0.3282	0.0877
$6b_1$	-0.1985	0.6302	0.1802	0.1896
$3a_2$	-0.2256	0.5832	0.3566	0.0601
$9a_1$	-0.2379	0.6377	0.2196	0.1426
$5b_2$	-0.3353	0.0075	0.9576	0.0350
$2a_2$	-0.3741	0.0875	0.4420	0.4705
$5b_1$	-0.3749	0.0561	0.6539	0.2901
$8a_1$	-0.3926	0.0776	0.7193	0.2033
$4b_2$	-0.4077	0.0614	0.2985	0.6398
$4b_1$	-0.4198	0.0315	0.1185	0.8501
$7a_1$	-0.4292	0.1644	0.4990	0.3364
$6a_1$	-0.4600	0.3090	0.1786	0.5123
$1a_2$	-0.4611	0.3242	0.2066	0.4692
$3b_2$	-0.4613	0.3426	0.3747	0.2827
$5a_1$	-0.4824	0.2432	0.0544	0.7023
$3b_1$	-0.4885	0.2840	0.0442	0.6720
$2b_2$	-0.9107	0.0179	0.9821	0.0000
$4a_1$	-0.9206	0.0000	1.0000	0.0000
$2b_1$	-1.1112	0.0000	0.0000	1.0000
$3a_1$	-1.1157	0.0000	0.0000	1.0000
$1b_1$	-1.9169	0.9880	0.0016	0.0103
$2a_1$	-1.9186	0.9849	0.0096	0.0055
$1b_2$	-1.9189	0.9813	0.0181	0.0006
$1a_1$	-2.9313	0.9857	0.0098	0.0045
(CORE)				

Table 1. Energies (in a.u.) and distributions of electronic charge for the ground-state orbitals of CrO_2F_2.

In order to evaluate the effects of symmetry reduction on the nature of frontier orbitals, it is worth comparing the distributions of electronic charge computed for CrO_2F_2 (Table 1) to those previously reported for CrO_4^{2-} (10) (Table 2). As seen from Table 2, the highest occupied level $1t_1$ consists essentially of just O partial waves (2p), and has only slight Cr character. Hence, it represents an O lone-pair level. The highest filled orbitals derived from the correlation $1t_1$ $(T_d) \rightarrow 5b_2 + 2a_2 + 5b_1$ (C_{2v}) have also slight Cr character (Table 1). Among them, the $5b_2$ has the greatest O amplitude and the least halogen amplitude, so that the highest occupied orbital is still mainly an O lone-pair level. The halogen character increases in $2a_2$.

Orbital	Energy	Cr charge	O charge
$7a_1$	-0.0588	0.003	0.008
$7t_2$	-0.0928	0.527	0.082
$2e$	-0.2487	0.631	0.066
$1t_1$	-0.4893	0.007	0.208
$6t_2$	-0.5601	0.038	0.184
$6a_1$	-0.6017	0.116	0.198
$1e$	-0.6727	0.290	0.132
$5t_2$	-0.7218	0.390	0.142
$4t_2$	-1.6047	0.071	0.219
$5a_1$	-1.6316	0.052	0.218
$3t_2$	-3.6196	0.958	0.011
$4a_1$	-5.6128	0.978	0.006
$2t_2$	-37.4661		(1s)
$3a_1$	-37.4661		(1s)
$1t_2$	-41.6367	(2p)	
$2a_1$	-48.8028	(2s)	
$1a_1$	-428.9378	(1s)	

Table 2. Energies (in Ry) and distributions of electronic charge[a] for the ground-state orbitals of CrO_4^{2-}.

[a] Contribution of each sphere or region to the normalized electronic charge in each valence orbital. Entries in brackets indicate core orbitals. The orbitals below the dashed line are occupied in the ground state.

Coming back to Table 2, the virtual 2e and $7t_2$ MOs consist predominantly of Cr character (3d) with the $2e < 7t_2$ energy order in agreement with simple crystal field ideas for 3d orbitals in a tetrahedral environment. The five lowest unoccupied orbitals in CrO_2F_2 (Table 1) are also mainly of Cr character. The two lowest MOs follow again from the correlation $e(T_d) \rightarrow a_1 + a_2$ (C_{2v}), the a_1 orbital having larger Cr and halogen character and smaller oxygen O character than the a_2 orbital. The latter trend has been also observed by Miller et al. (10).

II. Excited states

Table 3 summarizes the excitation energies and main configurations of the six lowest vertical transitions in CrO_2F_2. They come from the parent excitation $1t_1 \rightarrow 2e$

in CrO_4^{2-} (T_d), and correspond to the six lowest energy transitions in CrO_2F_2. However, several excitations derived from $6a_1 \rightarrow 2e$ and $1t_1 \rightarrow 7t_2$ are found to be nearby (4.2 - 4.9 eV) as we will discuss later (see below, Table 4). This notwithstanding, these results are in good agreement with earlier studies (10). Both in Tables 3 and 4 we have used the notation adopted by Johnson (2) when referring to orbital electronic transitions in the parent tetrahedral ion.

The lowest value in Table 3 (3.23 eV) lies 0.6 eV above the excitation energy experimentally reported for CrO_2F_2 (19). It has been previously shown (23) that excitation energies computed through approximate DFT often overestimate experimental values. This notwithstanding, other methods yield much less accurate excitation energies. For instance, the lowest singlet excited state for CrO_2F_2, as calculated by the Configuration Interaction Single (CIS) method (31), has been reported to be $^1B_2$ with an excitation energy of 4.5 eV (32). Similar discrepancies using the latter method have been also found for higher excited states of CrO_2F_2. To get better theoretical predictions, either DFT or post-HF methods (such as Complete Active Space SCF) have to be used (32). Therefore, electron correlation effects are very important for adequate descriptions of the excited states of this molecule. This is also true for the excited states of other metal complexes (33-35).

Excitation	DE
$5b_2 \rightarrow 9a_1$	3.23
$5b_2 \rightarrow 3a_2$	3.35
$2a_2 \rightarrow 9a_1$	4.10
$2a_2 \rightarrow 3a_2$	4.89
$5b_1 \rightarrow 9a_1$	4.07
$5b_1 \rightarrow 3a_2$	4.66
Equivalence (T_d): $1t_1 \rightarrow 2e$	

Table 3. Transition energies calculated in eV for the lowest excitations of CrO_2F_2.

From rotational analysis, the lowest singlet excited state of CrO_2F_2 has been experimentally assigned to $^1B_2$ (36-37). According to Table 3, the calculated lowest transition energy comes from the $5b_2 \rightarrow 9a_1$ excitation; therefore, the lowest singlet excited state is predicted to have also a B_2 symmetry, being in good agreement with experimental data.

The room-temperature, gas-phase electronic absorption spectrum of CrO_2F_2 is shown in Figure 2. The spectrum consists of four separate areas of absorption (19), which are referred to as bands I-IV, as follows: i) An intense band with considerable vibrational structure appears in the region from ca. 17000 to 25000 cm^{-1} (2.1 - 3.1 eV); ii) a band with approximately one third the intensity of band I also exhibiting much vibrational structure occurs between ca. 25000 and 32000 cm^{-1} (3.1 - 4.0

eV); iii) an intense band appearing as a shoulder to band IV is located between *ca.* 32000 and 41000 cm⁻¹ (4.0 - 5.1 eV) and displays vibrational structure; and iv) a very intense broad band exists at *ca.* 50500 cm⁻¹ (6.3 eV). A single, irregular vibrational progression has been seen to be superimposed over the low energy side of the latter band.
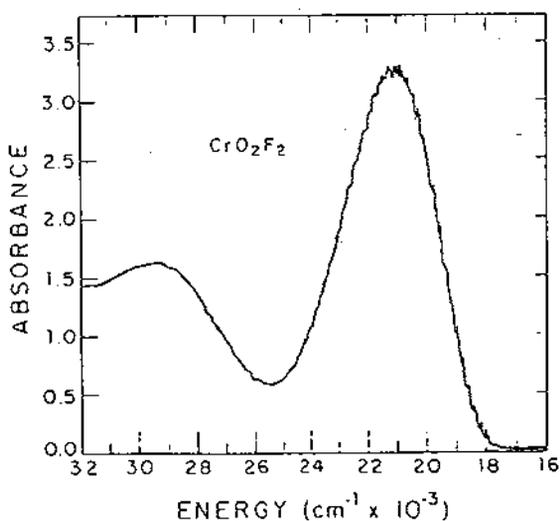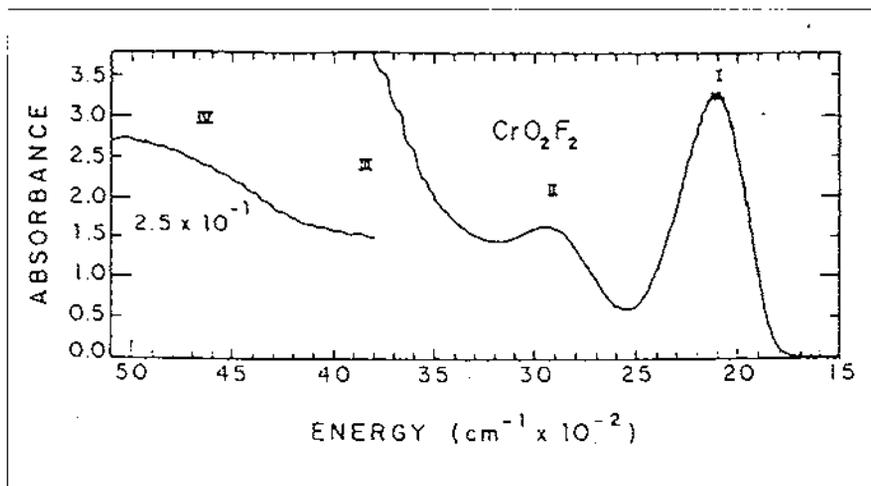
Figure 2. Gas-phase electronic absorption spectrum of CrO_2F_2 in the region 15000 - 50000 cm⁻¹ (above). The region 16000 - 32000 cm⁻¹ has been magnified (below).

Bands I-IV can be assigned using the present calculations, provided that theoretical energies are shifted to lower values according to the aforementioned overestimation. Based on our results, absorption band I can be attributed mainly to the $1t_1 \rightarrow 2e$ transition (Table 3). In particular, the lowest excited states are predicted to come from the two lowest transitions ($5b_2 \rightarrow 9a_1$ and $5b_2 \rightarrow 3a_2$).

The assignment for bands II and III is less clear. The second band centered at 3.7 eV is probably composed of the transitions derived from the $6a_1 \rightarrow 2e$, together with the more energetic of the $1t_1 \rightarrow 2e$ transition, and the less energetic of the $1t_1 \rightarrow 7t_2$ (Table 4). The third absorption band centered at 4.6 eV may include all transitions coming from the $6t_2 \rightarrow 2e$, the $6a_1 \rightarrow 7t_2$, and the more energetic from the $1t_1 \rightarrow 7t_2$ block. Finally, band IV consists of most of the transitions from the parent $6t_2 \rightarrow 7t_2$ transition (> 7.0 eV).

Excitation	ΔE	Equivalence (T_d)
$8a_1 \rightarrow 9a_1$	4.69	$6a_1 \rightarrow 2e$
$8a_1 \rightarrow 3a_2$	4.90	
$5b_2 \rightarrow 6b_1$	4.19	$1t_1 \rightarrow 7t_2$
$5b_2 \rightarrow 10a_1$	5.16	
$5b_2 \rightarrow 6b_2$	5.54	
$2a_2 \rightarrow 6b_1$	5.29	
$2a_2 \rightarrow 10a_1$	6.01	
$2a_2 \rightarrow 6b_2$	6.68	
$5b_1 \rightarrow 6b_1$	5.34	
$5b_1 \rightarrow 10a_1$	6.02	
$5b_1 \rightarrow 6b_2$	6.57	
$4b_2 \rightarrow 9a_1$	5.10	$6t_2 \rightarrow 2e$
$4b_2 \rightarrow 3a_2$	5.56	
$4b_1 \rightarrow 9a_1$	6.08	
$4b_1 \rightarrow 3a_2$	6.58	
$7a_1 \rightarrow 9a_1$	5.63	
$7a_1 \rightarrow 3a_2$	5.89	
$8a_1 \rightarrow 6b_1$	5.64	$6a_1 \rightarrow 7t_2$
$8a_1 \rightarrow 10a_1$	6.52	
$8a_1 \rightarrow 6b_2$	7.32	
$4b_2 \rightarrow 6b_1$	6.20	$6t_2 \rightarrow 7t_2$
$4b_2 \rightarrow 10a_1$	7.11	
$4b_2 \rightarrow 6b_2$	7.98	
$4b_1 \rightarrow 6b_1$	7.05	
$4b_1 \rightarrow 10a_1$	8.18	
$4b_1 \rightarrow 6b_2$	8.66	
$7a_1 \rightarrow 6b_1$	6.79	
$7a_1 \rightarrow 10a_1$	7.83	
$7a_1 \rightarrow 6b_2$	8.10	

Table 4. Transition energies calculated in eV for several excitations of CrO_2F_2.

CONCLUSIONS

Approximate DFT has been applied to the calculation of the ground and excited states of CrO_2F_2. The lower excitations are found to be from the ligand nonbonding MOs to the metal-ligand antibonding MOs, and have charge transfer nature. The higher excitations are from the metal-ligand bonding MOs to the metal-ligand antibonding MOs. Excitations in the middle energy range are the combinations of these two types of excitations. As compared with the spectra of tetrahedral complexes, the lower symmetry of CrO_2F_2 causes a considerable mixture of states, which makes its spectrum more complex than those of T_d molecules.

The calculated energies have been used to rationalize the experimentally reported absorption bands of the CrO_2F_2 electronic spectrum. The agreement is judged to be reasonable considering the approximations in the calculations. Hence, a better assignment of the bands might have been possible if theoretical intensities had been available. In order to evaluate such intensities, dipole moment integrals are required (which in their turn come from the exact knowledge of the ground- and excited-state wave functions). This procedure has not been implemented yet in the algorithms employed. However, only in the case of highly asymmetric molecules, this lack of data can make it difficult to elucidate electronic spectra.

The treatment of multiplets within the framework of approximate DFT is still incomplete despite the progress mentioned above (23). Much work remains to be done in this area which is emerging into one of the most challenging fields in approximate DFT.

ACKNOWLEDGMENTS

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