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Non-Empirical INDO–MO Calculations on Some Vanadium(IV) Halides

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ODIN, a non-empirical INDO–MO scheme, has been used to determine the ground state electronic configurations for the tetrahedral molecules, VCl_4 and VBr_4. A ^2E ground state was obtained for both molecules. The Photoelectron spectrum and the electronic spectrum have been calculated for VCl_4, and a satisfactory correlation with the corresponding experimental data was made. Also, ODIN was employed to evaluate electronic transition energies and the photoelectron spectrum of VBr_4.

Key words: Vanadium(IV) halides – Photoelectron spectra – Electronic spectra

1. Introduction

Ligand field theory predicts a ^2E ground electronic state for the d^1 tetrahedral complexes VCl_4 and VBr_4 (T_d, point group) where the single d electron occupies a molecular orbital transforming with e symmetry [1]. A number of molecular orbital calculations have been carried out on VCl_4 including those of Fenske and Radtke [2], the CNDO–MO calculations of Becker and Dahl [3] and the unrestricted Hartree-Fock CNDO method of Copeland and Ballhausen [4]. Fenske *et al.* found a ^2E state for VCl_4 consistent with the ligand field theory description. On the other hand, Becker and Dahl found a $^2T_2$ ground state while Copeland and Ballhausen calculated a $^2A_1$ state to be most stable. The recent $X\alpha$ calculation of Parameswaran and Ellis [5] has confirmed the ^2E ground electronic state predicted by ligand field theory and the calculation of Fenske and Radtke [2]. This raised the serious question as to the applicability of the CNDO method [6, 7], and it has been suggested [5] that this technique is not useful for investigating transition metal compounds.

In a previous paper [8], we have reported ODIN [8, 9] calculations on the titanium halides, $TiCl_4$, $TiBr_4$, and TiI_4, for which the theoretical and experimental photoelectron spectra are in good agreement, and the bonding in these molecules is in accord with the traditional description of ligand field theory. Also, our calculations on $TiCl_4$ compared favourably with those of Ellis *et al.* [5]. In view of this success, we have calculated the ground state electronic configuration, the electronic transition energies and photoelectron spectra for VCl_4 and VBr_4 using the same method. This is the first reported calculation for VBr_4. We believe that our results clearly indicate the applicability of our non-empirical INDO method to the investigation of transition metal compounds.

In Section 2, we describe briefly some of the methods used in the calculation of these properties, such as the open shell scheme and the applicability of Koopmans' theorem. Our results are discussed in Section 3 and our conclusions on bonding in these tetrahedral halides in Section 4.

2. Method

The ODIN method has already been described [8, 9], so we shall not discuss it further here.

2.1. The Open Shell Method

The open shell method which is used in the program is the orthogonality constrained basis set expansion (OCBSE) method of Hunt *et al.* [10]. Rather than making use of the coupling operator approach for the solution of the SCF equations [11, 12], the OCBSE method constrains the basis set expansion for an orbital so that its orthogonality to all the remaining occupied orbitals is maintained. This scheme avoids the explicit use of Lagrangian multpliers to maintain orthogonality of the molecular orbitals. For the vanadium halides, an initial run for the VX_4^+ ion was carried out. The molecular orbitals for the closed shell ion were then used as starting vectors for the VX_4 system. The molecular orbitals for the open shell molecule are then varied in such a way as to maintain the orthogonality of a given orbital to all remaining occupied molecular orbitals.

2.2. The Calculations

We have assumed regular tetrahedral structures for VCl_4 and VBr_4 with a V–Cl distance of 2.14 Å [13] and a V–Br distance of 2.30 Å [13]. The ^2E states as deduced from ligand field theory is predicted to be Jahn-Teller unstable, and a static distortion is expected to lift the orbital degeneracy. However, evidence for such a static distortion is meager. Johannesen *et al.* [14] have found a very small static distortion using EPR measurements, whereas other methods find none except at low temperatures [15]. There is some indication of dynamic Jahn-Teller coupling from the optical spectra as seen from the band splitting at 9000 cm^{-1} predicted for the $e \rightarrow t_2$ $d-d$ transition [16]. In view of the paucity of clear evidence we have adopted the regular tetrahedral structure for VCl_4 and VBr_4.

The basis set which we have used for the vanadium halides is given in Table 1. This basis set was effective in giving quantitative results for the titanium halides [8]. The functions, $3s'$, $3p'$ and $3d'$, are called polarization functions, and they give our basis set its flexibility. The $3s'$ and $3p'$ replace the $4s$ and $4p$ functions which were used by Fenske and Radtke [2], Becker and Dahl [3], and Copeland and Ballhausen [4] in their basis sets.

2.3. Ionization Potentials

Hunt *et al.* [10] claim that the orbital energies obtained by the OCBSE method are approximations to the ionization potentials. In Table 2, we compare the values

Table 1. The basis set used in the vanadium halide calculation

Metal		Ligand	
Function	Exponent[a,b]	Function	Exponent[b]
$3s$	3.9031		Cl
$3s'$	2.0	$3s$	2.3561
$3p$	3.5950	$3p$	2.0387
$3p'$	2.0		Br
$3d$	2.9943	$3s$	2.6382
$3d'$	2.0	$3p$	2.2570

[a] The $3s'$, $3p'$, and $3d'$ functions are discussed in the text.

[b] The remaning basis functions have Clementi-Raimondi exponents [17].

Table 2. Comparison of ionization potentials (in eV) obtained by Koopmans' theorem and the open shell method

Molecular orbital	Open shell calculation	Koopmans' theorem
$2e$	8.55	7.99
$1t_1$	12.37	12.32
$4t_2$	12.74	12.68
$1e$	13.13	12.87
$3a_1$	17.54	16.94
$3t_2$	17.10	17.68

obtained from ^2E ground state calculations by the application of Koopmans' theorem [18] and the values obtained by taking the difference in energy between the ^2E state of VCl_4 and the appropriate singlet ground state of the VCl_4^+ ion. There is good agreement between the two methods for the higher occupied molecular orbitals, however, for the lower energy occupied orbitals, there are discrepancies. For the calculation of the photoelectron spectra, we use the open shell method only for the ionization potentials.

2.4. Transition Energies

The evaluation of transition energies for the vanadium halides was carried out using the method of Huzinaga and Arnau [19]. The transition energy of the n electron system is assumed to be the difference between the virtual orbital energies of the $n-1$ electron problem, $\varepsilon_v^{(n-1)}$, and the occupied orbital energies of the n electron system

$$\Delta E = \varepsilon_v^{(n-1)} - \varepsilon_0^{(n)} .$$

For example, the virtual orbital energies of the VCl_4^+ ion are treated as approximations to the virtual orbital energies of VCl_4. The $\varepsilon_0^{(n)}$ values are the energies of the orbitals initially occupied by the electron undergoing a transition.

3. Results and Discussion

3.1. Vanadium Tetrachloride

Our calculations are consistent with the assignment of the ground electronic state of VCl_4 as ^2E. We also found that this state was insensitive to variations in the exponents of the metal polarization functions. The ground state electron configuration is $(1a_1)^2\ (t_2)^6\ (2a_1)^2\ (3t_2)^6\ (3a_1)^2\ (1e)^4\ (4t_2)^6\ (1t_1)^6\ (2e)^1$. Both the ground state and the ordering of the molecular orbitals are compatible with the results of Fenske *et al.* [2], Ellis *et al.* [5] and the ligand field theory description. The ground state predicted by the CNDO method of Becker and Dahl [3] was $^2T_2$ which arises from the unpaired electron occupying a t_2 orbital. However, Copeland, and Ballhausen [4] have found that the unpaired electron occupies an a_1 orbital of primarily ligand character giving rise to a $^2A_1$ ground state. The difference between our INDO calculations and the CNDO results of Dahl *et al.* [3] and Ballhausen *et al.* [4] may arise, in part, from their choice of valence orbital basis set, but primarily, we believe it to be the result of the various approximations invoked by their CNDO method[1].

The molecular orbitals are described in Table 3. Not surprisingly, the $1a_1$ and $1t_2$ orbitals are primarily vanadium $3s$ and $3p$ functions respectively. The $2t_2$ and $2a_1$ orbitals are mainly ligand orbitals with only a small contribution from the metal polarization functions. As in the case for the titanium halides [8], the energies of the $3t_2$ and $3a_1$ molecular orbitals of VCl_4 are sensitive to the polarization function exponents because of the ~20% contribution of the metal functions to the molecular orbital. The $1e$ and $4t_2$ orbitals are essentially ligand

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[1] It can be shown numerically that because of certain assumptions made by Dahl and Ballhausen [7] that the electron-electron repulsion terms are underestimated in the diagonal matrix elements of the Fock operator for the $4s$ and $4p$ basis functions. This is tantamount to increasing the electronegativity of the $4s$ and $4p$ orbitals which would account for the high $4s$ and $4p$ populations in all calculations on tetrahedral complexes done by the CNDO method of Dahl and Ballhausen [7].

In our calculations, we do not use such expanded orbitals as atomic $4s$ and $4p$ orbitals for reasons given in [9]. As a result, inclusion of higher order terms in S are unnecessary.

Table 3. Composition of the molecular orbitals of VCl_4

Orbital	Main component(s)[a]
$1a_1$	Metal $3s$, 98.4%
$1t_2$	Metal $3p$, 98.7%
$2t_2$	Ligand $3s$, 83.1%; some metal $3p'$, $3d$, and $3d'$ contribution
$2a_1$	Ligand $3s$, 89.3%; metal $3s'$, 7.8%
$3t_2$	Ligand $3s$ and $3p$, 70.9%; some metal $3p'$, $3d$, and $3d'$ contribution
$3a_1$	Ligand $3s$ and $3p$, 76.3%; metal $3s'$, 23.0%
$1e$	Ligand $3p$, 92.3%; some metal $3d$ contribution
$4t_2$	Ligand $3p$, 97.9%
$1t_1$	Ligand $3p$, 100.0%
$2e$	Metal $3d$, 92.6%
$5t_2$	Metal $3p'$ and $3d$, 84.5%

[a] The percentages give the contribution of the major components in the molecular orbital. They are obtained by summing the squares of the coefficients of the appropriate metal or ligand basis functions.

Table 4. Comparison of the experimental and calculated photoelectron spectra obtained by various methods for VCl_4 (all ionization potentials in eV)

PE[a]	This work	Experiment[b]	Level[c]
7.4	8.55	9.41	$2e$
12.0	12.37	11.75	$1t_1$
12.6	12.74	12.88	$4t_2$
12.8	13.13	13.54	$1e$
13.7	17.10	15.56	$3t_2$
14.1	17.53		$3a_1$

[a] Ellis *et al.* Ref. [5] (for $\alpha = 0.85$).

[b] Cox *et al.* Ref. [20].

[c] The numbering of the symmetry orbitals results from the choice of basis set and the number of electrons included in the calculation, and may differ from author to author.

orbitals and for this reason are insensitive to variations in metal function exponents. Since there are no functions in the metal basis set which transform with t_1 symmetry, the $1t_1$ orbitals are nonbonding ligand $3p$ orbitals. Of special interest are the $2e$ and $5t_2$ molecular orbitals. They correspond to the e and t_2 orbitals of ligand field theory. Our calculation shows that the $2e$ orbital has 92.6% $3d$ function character while the $5t_2$ is a mixture of $3d$ functions (80.5%) with some $3p'$ character (4.0%). The agreement between the qualitative features of ligand field theory predictions and our results is gratifying.

A comparison of the calculated and the experimental photoelectron spectrum is made in Table 4. The spectrum calculated by Parameswaran and Ellis [5] has also been included. The experimental spectrum measured by Cox *et al.* [20] is complicated by the fact that a number of multiplets are possible upon ionization. For example, ionization of a t_1 or a t_2 electron would create $(t_1)^5\ (e)^1$ or $(t_2)^5\ (e)^1$ configurations which give rise ${}^{3,1}T_1 + {}^{3,1}T_2$ states. Similarly, the configuration $(1e)^3\ (2e)^1$ results in ${}^{3,1}A_1 + {}^{3,1}A_2 + {}^{3,1}E$ states, and the $(3a_1)^1\ (2e)^1$ results in ${}^{3,1}E$ states. In spite of the large number of peaks present in the spectrum, we can tentatively assign the signal at 9.41 eV to the ionization of the $2e$ electron. The line at 11.75 eV may arise from the ionization of an electron from the ligand non-bonding $1t_1$ orbitals. The peak at 12.88 eV, we associate with the ionization of a $4t_2$ electron, and the signal at 13.54 eV we attribute to the ionization of a $1e$ electron. The above assignment is also in agreement with the calculated spectrum of Parameswaran and Ellis [5]. The remaining peak cannot be assigned using our calculations.

Using the method of Huzinaga and Arnau [19] which was briefly described in Section 2, we have calculated the electronic absorption spectrum for VCl_4. Since the $2e$ and $5t_2$ orbitals consist mainly of vanadium $3d$ functions, the first transition, $2e \rightarrow 5t_2$, corresponds to the "$d-d$" transition of ligand field theory with $10\,Dq = 1.71$ eV. The remaining transitions are charge transfer bands since they originate from molecular orbitals of largely ligand character and the final orbitals, $2e$ or $5t_2$, have mainly metal function character. Alderdice [21] has reservations on the assignment of the 3.71 eV bands. He suggests that they may arise from $VOCl_3$ which may have contaminated the VCl_4 sample. The transition

Table 5. Electronic transition energies (in eV) for VCl_4

Transition	This work	*PE*[a]	Experiment[b]
$2e \to 5t_2$	1.71	0.6	1.12
$1t_1 \to 2e$	4.72	4.6	3.10
$4t_2 \to 2e$	5.07	—	3.71 ($VOCl_3$?)
$1e \to 2e$[c]	5.26	—	—
$1t_1 \to 5t_2$	6.05	5.2	4.32
$4t_2 \to 5t_2$	6.40	—	5.05 ($VOCl_3$?)
$1e \to 5t_2$	6.60	—	—

[a] Ellis *et al.* Ref. [5] ($\alpha = 0.85$).
[b] Alderdice, Ref. [21].
[c] Dipole forbidden.

Table 6. Photoelectron spectrum for VBr_4

Level	Calculated ionization potential (eV)
$2e$	8.30
$1t_1$	10.29
$4t_2$	10.70
$1e$	11.14
$3t_2$	15.35
$3a_1$	16.06

energies as calculated by Parameswaran and Ellis [5] have been included in Table 5, and, apart from the 10 Dq value, there is good agreement between both ODIN and $X\alpha$ methods with experiment.

3.2. Vanadium Tetrabromide

The success which we have had with VCl_4 and the titanium halides allows us to predict with some confidence the ground state, the photoelectron spectrum and transition energies for VBr_4.

The ground electronic state of VBr_4 has ^2E symmetry which is analogous to our VCl_4 results and consistent with the expectations of ligand field theory. The ground state electron configuration has some differences from VCl_4 in the order of the molecular orbitals: $(1a_1)^2\,(1t_2)^6\,(2t_2)^6\,(2a_1)^2\,(3a_1)^2\,(3t_2)^6\,(4t_2)^6\,(1e)^4\,(1t_1)^2\,(2e)^1$. The change in the order of the $4t_2$ and $1e$ levels is deceptive since these levels are nearly degenerate.

The composition of the VBr_4 molecular orbitals are very similar to their counterparts for VCl_4. The $2e$ orbital is mainly vanadium $3d$ in character (89.9 %) while the $5t_2$ orbital has 85.6 % $3d$ and $3p'$ character. The $1t_1$, $4t_2$, and $1e$ molecular orbitals are primarily ligand orbitals as in VCl_4.

The calculated photoelectron spectrum for VBr_4 is given in Table 6. The experimental spectrum has not to our knowledge been measured. The electronic spectrum has also been determined (Table 7). It is interesting to note that 10 Dq for VCl_4 is calculated to be greater than 10 Dq for VBr_4 which is consistent with the spectrochemical series [1].

Table 7. Predicted electronic transition energies for VBr_4

Transition	Calculated energy (eV)
$2e \rightarrow 5t_2$	1.21
$1t_1 \rightarrow 2e$	4.04
$4t_2 \rightarrow 2e$	4.59
$(1e \rightarrow 2e)^a$	4.58
$1t_1 \rightarrow 5t_2$	5.26
$4t_2 \rightarrow 5t_2$	5.80
$1e \rightarrow 5t_2$	5.80

[a] Dipole forbidden.

4. Conclusion

The ODIN method is capable of giving results for VCl_4 in good agreement with the traditional picture of ligand field theory as well as other molecular orbital schemes [2, 5].

The ground state of VCl_4 was found to be ^2E with the valence electron configuration: $(1a_1)^2\,(1t_2)^6\,(2t_2)^6\,(2a_1)^2\,(3t_2)^6\,(3a_1)^2\,(1e)^4\,(4t_2)^6\,(1t_1)^6\,(2e)^1$. The unpaired electron occupies an orbital of largely vanadium $3d$ character which transforms with e symmetry. The first unoccupied orbital has t_2 symmetry and the vanadium $3d$ functions are the main contributors to this orbital also. The calculated photoelectron spectrum for VCl_4 is in reasonable agreement with experiment and with the $X\alpha$ method of Ellis *et al.* [5]. Similarly, the theoretical electronic spectrum is in accord with experiment and the transitions can be interpreted in terms of the usual picture of $d-d$ transitions or charge transfer bands.

These results inspired us to perform calculations on VBr_4. We found a ^2E ground electronic state for this molecule with the valence electron configuration: $(1a_1)^2\,(2t_2)^6\,(2t_2)^6\,(2a_1)^2\,(3a_1)^2\,(3t_1)^6\,(4t_2)^6\,(1e)^4\,(1t_1)^6\,(2e)^1$. The bonding description for VBr_4 is quite analogous to that for VCl_4. The photoelectron spectra and the electronic spectra have been calculated.

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