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A CNDO-MO Calculation of VCl_4

C. A. L. Becker

Department of Chemistry, The University of Texas, Austin, Texas 78712

J. P. Dahl

Department of Chemistry, The University of Copenhagen, Universitetsparken 5,
Copenhagen Ø, Denmark

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The electronic structure of the tetrahedral molecule VCl_4 is investigated within the CNDO-MO approximations. The metal and ligand valence orbitals, $3d$, $4s$, $4p$; and $3s$, $3p$; respectively, have been systematically varied in an attempt to minimize the total energy; "optimum" V $4s(\zeta_4 = 1.10)$ and $4p(d^3p^2)$ orbitals have been established, but V $3d(d^n)$ and $Cl(-\delta)$ valence orbitals are only seen to favor lower energy for expanded orbitals. Since determining the one-electron molecular orbital level which is occupied by the vanadium lone electron is a major aspect of this investigation, all calculations have been performed in triplicate: calculations assuming the unpaired electron occupies the $3a_1$, $2e$, and $4t_2$ molecular orbital (ground state electronic configurations $^2A_1$, ^2E, and $^2T_2$, respectively). The Hartree-Fock equations have been solved by Roothaan's SCF method for open shells, but off-diagonal multipliers between filled and partly filled molecular orbitals of the same symmetry have been neglected. As a qualitative estimate of the error introduced by this simplification, the pertinent overlap integrals between the eigenfunctions from calculations for the three possible configurations, $^2A_1$, ^2E, and $^2T_2$, are investigated as functions of the component $3d(d^n)$ and $Cl(-\delta)$ valence orbitals. The overlap integrals from the relevant $^2A_1$ and $^2T_2$ calculations are reasonably small, but the neglect of off-diagonal multipliers in calculations on the ^2E state is found to be a poor approximation. An ordering of the non-filled molecular orbitals in VCl_4 of $4t_2 < 3a_1 < 2e < 5t_2$ seems most consistent with the numerous calculations. This suggested ground state electronic configuration of $^2T_2$ introduces new aspects to the consideration of a (dynamic) Jahn-Teller effect in VCl_4. Experimental data pertinent to the electronic structure of VCl_4 has been briefly summarized, but unfortunately it is inadequate to confirm or deny the present calculations.

Die Elektronenstruktur von VCl_4 wird mittels des CNDO-Verfahrens untersucht, wobei die Metallorbitale mit $n = 3$ und 4 systematisch variiert wurden. Optimale Werte für V-$4s$ und V-$4p$ werden angegeben, jedoch V-$3d$ und $Cl(-\delta)$ ergeben tiefere Energien nur für räumlich ausgedehnte Orbitale. Da die Zustandsfunktion des ungepaarten Elektrons besonders interessierte, wurde für drei verschiedene Fälle gerechnet: $3a_1$, $2e$ und $4t_2$-Symmetrie. Im Rahmen des Roothaan'schen Verfahrens für offene Schalen wurden nicht-Diagonal-Faktoren zwischen ganz und teilweise besetzten MO's gleicher Symmetrie vernachlässigt und der dadurch verursachte Fehler an Hand der Überlappungsintegrale abgeschätzt, wobei lediglich der ^2E-Zustand schlecht abschneidet. Als Reihenfolge für die nicht doppelt besetzten Orbitale scheint sich $4t_2$, $3a_1$, $2e$, $5t_2$ zu ergeben, was interessante Fragen bezüglich des Jahn-Teller-Effektes (Symmetrie $^2T_2$) aufwirft. Die experimentellen Daten gestatten leider keine eindeutige Bestätigung der Ergebnisse.

Etude de la structure électronique de la molécule tétraédrique VCl_4 dans le cadre d'approximations CNDO–MO. Les orbitales $3d$, $4s$ et $4p$ du métal et les orbitales $3s$ et $3p$ du ligand ont été systématiquement variées afin d'essayer de minimiser l'énergie totale; on a trouvé des orbitales «optimales» V $4s$ $(\zeta_4 = 1{,}10)$ et V $4p$ (d^3p^2) mais les orbitales de valence V $3d$ (d^n) et Cl $(-\delta)$ ne font que favoriser une plus basse énergie orbitale. Comme la détermination de l'orbitale moléculaire occupée par l'électron célibataire du vanadium est un des aspects principaux de cette étude, tous les calculs ont été effectués en trois versions, en supposant successivement que l'électron célibataire occupe les orbitales moléculaires $3a_1$, $2e$ et $4t_2$ (configurations électroniques $^2A_1$, ^2E et $^2T_2$ respectivement). Les équations de Hartree-Fock ont été résolues par la méthode SCF de Roothan pour couches ouvertes, mais les multiplicateurs non diagonaux entre orbitales moléculaires occupées et partiellement occupées de même symétrie ont été négligés. Afin d'estimer qualitativement l'erreur ainsi introduite, on a étudié en fonction de la composition en orbitales $3d$ (d^n) et Cl ($-\delta$) le recouvrement entre les fonctions propres calculées pour les trois configurations $^2A_1$, $2E$ et $^2T_2$. Les intégrales de recouvrement pour les calculs relatifs à $^2A_1$ et $^2T_2$ sont raisonnablement faibles, mais l'erreur introduite est importante pour les calculs sur ^2E. L'ordre le plus cohérent des orbitales moléculaires incomplètes de V Cl$_4$ est: $4t_2 < 3a_1 < 2e < 5t_2$. Cette configuration suggérée pour l'état $^2T_2$ introduit de nouveaux aspects dans l'effet dynamique Jahn-Teller de VCl$_4$. Les expérimentales relatives à la structure électronique de VCl$_4$ ont été brièvement résumées, mais elles ne sont pas en measure de confirmer ou d'infirmer nos calculs.

1. Introduction

Extensive CNDO-type molecular orbital calculations on the tetrahedral molecule TiCl$_4$ [1, 2] have suggested an ordering of the unoccupied (virtual) one-electron MO levels and of the electric dipole allowed one-electron transition energies that differ drastically from the order suggested from ligand theory extrapolated to the Ti (IV) case. Considerable variation of the valence orbitals even fails to indicate any substantial stabilization of the $2e$ molecular level (i.e. $3d[e]$) with respect to the $4t_2$ ($3d[t_2]$) or $3a_1$ ($4s[a_1]$) levels in this (formally) d° case.

The purpose of this present work is to investigate the (formally) d^1 tetrahedral molecule VCl$_4$ – which should be in some analogy to the TiCl$_4$ molecule – within the same CNDO approximations and specifically observing the behavior of these same higher energy one-electron MO levels, one of which must now be partially occupied, in order to see if the ligand field picture is re-established for the V(IV) case. In particular it will be most important to attempt to determine the ground state configuration of VCl$_4$, now that the familiar configuration expected from simple ligand field theory, $[(1t_2)^6\,(1a_1)^2\,(2t_2)^6\,(2a_1)^2\,(1e)^4\,(3t_2)^6\,(t_1)^6]\,(2e)^1$; i.e., a ^2E ground state, seems to be questioned in light of the results for TiCl$_4$.

In a closed shell molecule like TiCl$_4$ all molecular orbitals satisfy the same Hartree-Fock equation [3], but a complication arises in going to VCl$_4$, which is an open shell system. Orbitals from the partly filled shell must now be treated differently from the closed shell orbitals [4], and Lagrangian off-diagonal multipliers occur between the two shells, for orbitals of like symmetry. The role of these multipliers is to ensure orthogonality between the two kinds of orbitals. In the present work the off-diagonal multipliers have been neglected, and we have in this respect followed Croto and Santry [5] who found, in studying smaller molecules, that orbitals from different shells remained "almost orthogonal" after the neglect of the multipliers. Also [5], "the level of approximation of the present theory does not warrant the extra computational difficulties which would follow from the inclusion of these off-diagonal terms". We must, however, be aware that a new approximation has been introduced, in addition to the approximations already present in our CNDO method [6, 7].

If either the $2e$ or $4t_2$ one-electron MO level is postulated as the lowest-lying non-filled electronic level, resulting in a ^2E or $^2T_2$ ground state, respectively, we know of course from the theory of Jahn and Teller [8] that a lowering of this symmetry should occur. Experimental [9–12] and theoretical [13–15] investigations of VCl_4, however, seem to suggest no evidence for a static Jahn-Teller effect in the vapor and solution phases at least, so at best only a dynamic Jahn-Teller effect can be at this time postulated operative. A dynamic Jahn-Teller effect, as described by Ballhausen [29, p. 196], corresponds to the situation in which the splitting of a potential surface is of the same order of magnitude as the zero point energy associated with the normal mode responsible for the splitting, so that a direct coupling between the electronic and vibrational motions effectively takes place. For the static Jahn-Teller effect, however, the splitting is sufficiently large compared to the vibrational energy that the lowest energy state of the system may be drastically removed from regular symmetry. The static Jahn-Teller effect can often then be observed in crystalline environment, where a particular one of the usually several distorted configurations may be favored statistically. For these present calculations, therefore, the VCl_4 molecule has been taken as regularly tetrahedral with a V-Cl bond length of 2.138 Å [12].

The atomic orbitals used as valence orbitals in constructing the LCAO-MO wavefunctions have been extensively and systematically varied – as before and as shown necessary in other CNDO-MO calculations [1, 7] – in an effort to minimize the total energy and thereby allow selection of the optimum valence orbitals. In general this treatment of the VCl_4 molecule follows closely the procedures used for $TiCl_4$ [1], for which this work provides the logical completion.

2. Selection of the Optimum Valence Orbitals

The atomic orbitals used to construct the LCAO-molecular orbitals have been taken as minimal basis sets of normalized Slater-type orbitals (STO's). The vanadium core orbitals (i.e., 1*s*, 2*s*, 2*p*, 3*s*, 3*p*) and 3*d* and 4*p* valence orbitals were taken directly from tabulations by Richardson *et al.* [16, 17], and the vanadium 4*s* valence orbitals (Table 1) were straightforwardly calculated from the zeta values

Table 1. *Vanadium* 4*s orbitals*

$d^n s^m$	n_j	ζ_j	C_j	$d^n s^m$	n_j	ζ_j	C_j
$4s(d^4s^2)$	1	22.395	−0.00310	$4s(d^3s^2)$	1	22.395	−0.02188
	2	8.475	0.01065		2	8.475	0.07548
	3	3.850	−0.02589		3	3.850	−0.19137
	4	0.640	1.00028		4	1.250	1.01517
$4s(\zeta_4)$	1	22.395	−0.00621	$4s(d^3s^1)$	1	22.395	−0.02919
	2	8.475	0.02133		2	8.475	0.10090
	3	3.850	−0.05232		3	3.850	−0.25953
	4	0.795	1.00114		4	1.410	1.02774
$4s(d^4s^1)$	1	22.395	−0.01053	$4s(d^2s^2)$	1	22.395	−0.03869
	2	8.475	0.03621		2	8.475	0.13408
	3	3.850	−0.08972		3	3.850	−0.35154
	4	0.950	1.00335		4	1.600	1.05037
$4s(\zeta_4)$	1	22.395	−0.01576	$4s(d^2s^1)$	1	22.395	−0.04666
	2	8.475	0.05429		2	8.475	0.16208
	3	3.850	−0.13599		3	3.850	−0.43222
	4	1.100	1.00769		4	1.750	1.07529

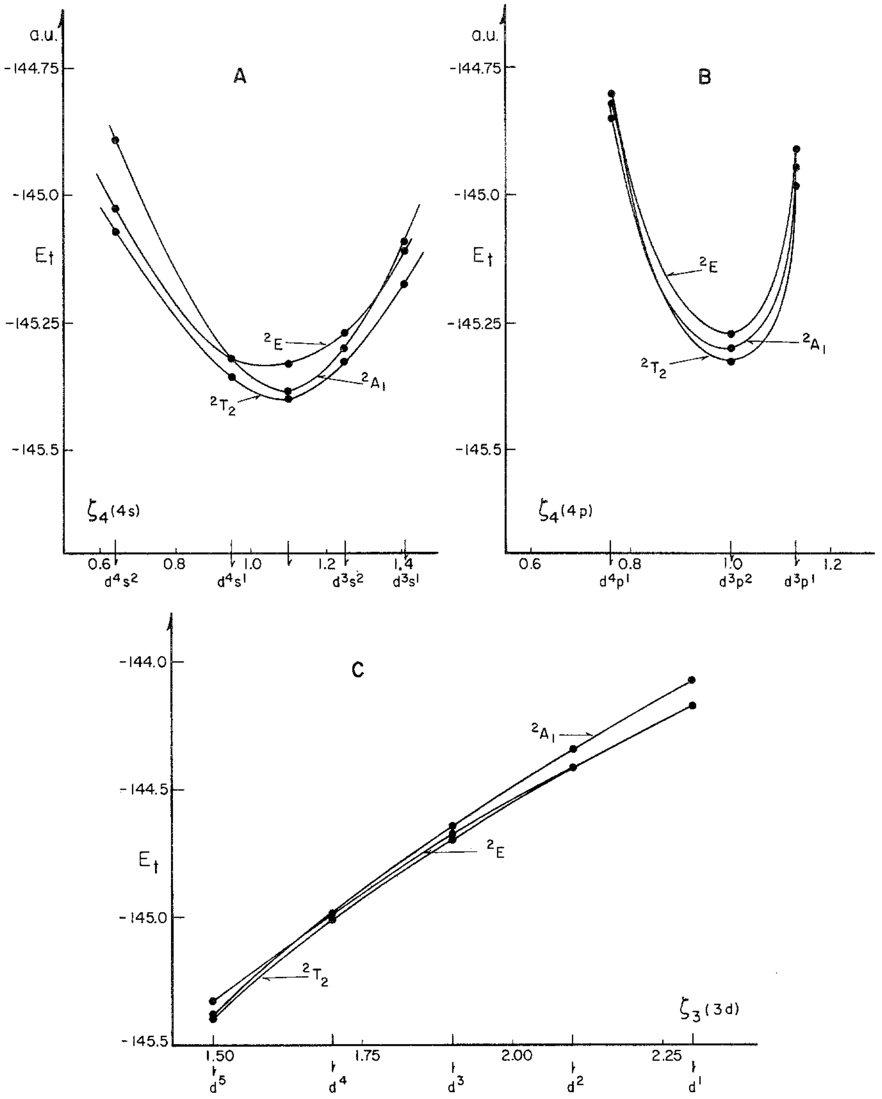

Fig. 1. Attempted minimization of the total energy with respect to the atomic valence orbitals: A, Variation of the $4s(\mathrm{V})$ orbitals with respect to $3d(d^5)$, Cl(-0.5), and $4p(d^3p^2)$ valence orbitals; B, Variation of the $4p(\mathrm{V})$ orbitals with respect to $3d(d^5)$, Cl(-0.5), and $4s(d^3s^2)$ valence orbitals; C, Variation of the $3d(\mathrm{V})$ orbitals with respect to Cl (-0.5), $4s(\zeta_4 = 1.10)$, and $4p(d^3p^2)$ valence orbitals; each variation being performed for the situation in which the unpaired electron is assumed to be in the $3a_1$ $(^2A_1)$, $2e$ (^2E), or $4t_2$ $(^2T_2)$ one-electron molecular orbital

therein according to previously illustrated method [1]. The chlorine core and valence orbitals have been constructed from orbital exponents according to Clementi and Raimondi [18], and are tabulated elsewhere [1].

Variation of the total energy with respect to valence atomic orbitals is shown in Fig. 1 and Table 2. The notation $^2A_1$, ^2E, or $^2T_2$ indicates that in the specified

Table 2. *Total energy values for the assumed ground states* $^2T_2$, ^2E, *and* $^2A_1$ *of the* VCl_4 *molecule, as dependent upon variation of the* V(3d) *and* Cl($-\delta$) *valence orbitals, with constant* 4s($\zeta_4 = 1.10$) *and* 4p(d^3p^2) *orbitals. Values listed in atomic units*

		Cl(0.0)	Cl(−0.5)	Cl(−1.0)
$3d(d^5)$	$^2T_2$	−145.0882	−145.3996	−145.6595
	^2E	−145.0268	−145.3282	−145.6378
	$^2A_1$	−145.0430	−145.3838	−145.6701
$3d(d^4)$	$^2T_2$		−145.0179	
	^2E		−144.9909	
	$^2A_1$		−144.9861	
$3d(d^3)$	$^2T_2$	−144.3607	−144.6925	−144.9716
	^2E	−144.3318	−144.6775	−144.9688
	$^2A_1$	−144.2815	−144.6430	−144.9491
$3d(d^2)$	$^2T_2$		−144.4157	
	^2E		−144.4123	
	$^2A_1$		−144.3441	
$3d(d^1)$	$^2T_2$	−143.8344	−144.1735	−144.4595
	^2E	−143.8320	−144.1793	−144.4717
	$^2A_1$	−143.7077	−144.0771	−144.3905

calculation the unpaired electron has been assumed to be in the $3a_1$, $2e$, or $4t_2$ one-electron molecular orbital, respectively. It is evident from Fig. 1A and 1B that the V 4s and 4p valence orbitals can be optimized at approximately the same zeta value for assumed $^2A_1$, ^2E, and $^2T_2$ ground states and that these optimum outer zeta values are at ($\zeta_{4p} = 1.0$) or near ($\zeta_{4s} = 1.1$) the values for the "free atom" configuration, $d^3(s,p)^2$. Optimization of the V(3d) orbitals is not achieved over the orbital range $3d(d^5) - 3d(d^1)$ (Fig. 1C), but expanded V 3d orbitals are seen to favor lower total energy. Variation of the Cl($-\delta$) 3s and 3p orbitals also fails to result in conclusive optimization and only shows gradual decrease in total energy for expanded Cl valence orbitals. As in the $TiCl_4$ calculations [1] we have thus successfully optimized the 4s and 4p valence orbitals but must continue to vary the 3d and Cl orbitals in following considerations.

While Fig. 1C shows how energetically close and therefore "competitive" are the three potential ground states, $^2T_2$, ^2E, and $^2A_1$; Table 2 indicates $^2T_2$ as the ground state for most of the $3d(d^n)$ and Cl($-\delta$) valence orbitals investigated. The $^2A_1$ configuration is lowest in energy for the one instance of the most expanded 3d and Cl(3s, 3p) orbitals (i.e., $3d[d^5]$ and Cl[-1.0]), but is seen to be very dependent on the valence orbitals selected. The ^2E configuration is likewise seen to offer the lowest total energy for a limited range of the valence orbitals – in this case, for the contracted V(3d) orbitals, $3d(d^1)$, which are strongly disfavored over the more expanded V(3d) orbitals, $3d(d^5) - 3d(d^3)$, on the basis of total energy considerations. The $^2T_2$ configuration is seen to yield the lowest total energy for all other valence-orbital combinations investigated; and surely the variation of the $3d(d^n)$ and Cl($-\delta$) orbitals has been sufficiently broad to at least include, if not establish, the "best" atomic valence orbitals to be used in constructing the LCAO-molecular orbitals.

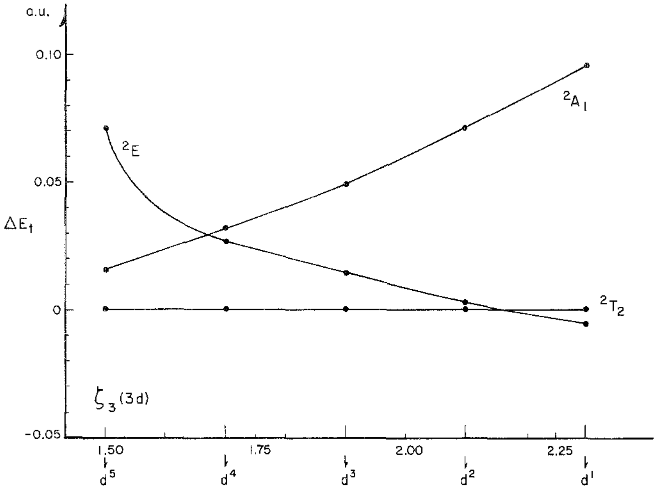

Fig. 2. The energy differences (total valence energy) for the assumed ground states ${}^2T_2$, ${}^2E$, and ${}^2A_1$, relative to the ${}^2T_2$ state, expressed as functions of the $3d$ valence orbitals for constant $4s(\zeta_4 = 1.10)$, $4p(d^3p^2)$, and Cl(-0.5) valence orbitals

Since neither the $3d(d^n)$ nor the Cl$(-\delta)$ valence orbitals have been optimized, however, chemical intuition as well as numerical values must direct our selection of the most reasonable valence orbitals. While the most expanded V($3d$) and Cl$(-\delta)$ orbitals indeed favor lowest total energy, valence orbitals somewhat more similar to those of the free atoms seem more appropriate in molecular orbital formation. In this context the orbital functions for the neutral V and Cl atoms, $3d(d^3)$ (i.e., from the electronic configuration for a free V atom, [Ar] $4s^2 3d^3$) and Cl(0.0), respectively, would be most appropriate. A small concession to the apparently stabilizing effect of valence orbital expansion, however, might suggest the Cl(-0.5) and $3d(d^3) - 3d(d^4)$ orbitals. Even if a partial ionic nature were assumed for the covalent VCl_4 molecule, it would not seem very reasonable to go much beyond the Cl(-0.5) and $3d(d^3)$ orbitals. (Since the $3d$ functions calculated for a $3d^{n-2}4s^2$ configuration are very closely the same as those in the $3d^{n-2}$ configuration [16], the V $3d(d^3)$ orbitals are satisfactory for the $V^0 - V^{2+}$ ions. The $3d(d^2)$ and $3d(d^1)$ functions would of course be required for the V^{3+} and V^{4+} ionized states, respectively, but these seem rather unrealistic for VCl_4). Thus if we are willing to assume as a "reasonable" range for the V($3d$) and Cl$(-\delta)$ valence orbitals $3d(d^4) - 3d(d^3)$, or even $3d(d^5) - 3d(d^2)$, and Cl(0.0) – Cl(-0.5), ${}^2T_2$ is clearly the ground state configuration.

In Fig. 2 the energy differences for the assumed ground states ${}^2T_2$, ${}^2E$, and $2A_1$, relative to the ${}^2T_2$ state, have been expressed as functions of the $3d$(V) valence orbitals. It is seen that throughout most of this range of $3d$-orbital variation, then, the ${}^2T_2$ configuration should be considered as the ground state, but that the relative energies of the ${}^2E$ and ${}^2A_1$ states are very sensitive to the choice of $3d$ orbitals. Assuming neglect of any Jahn-Teller effect, and assuming of course that appropriate $4s$, $4p$, and Cl$(-\delta)$ valence orbitals have been selected, the energy differences from this diagram should be the theoretical values for the "*d-d* type" electronic transitions in VCl_4. Both the energy and the assignment of these *d-d* bands are of course very dependent upon the choice of $3d(V)$ orbitals.

3. Behavior of the One-Electron MO Levels

The behavior of the one-electron MO energies with respect to variation in both the $V(3d)$ and $Cl(-\delta)$ valence orbitals is investigated in Fig. 3. The V $4s$ and $4p$ orbitals have been held constant at $4s(\zeta_4 = 1.10)$ and $4p(d^3p^2)$ for this series of calculations, but the $Cl(-\delta)$ orbitals have been varied over the range Cl(0.0), Cl(−0.5), Cl(−1.0); and the $3d$ orbitals have been taken as $3d(d^5)$ [A], $3d(d^3)$ [B], and $3d(d^1)$ [C]. Graphs of the one-electron MO levels with respect to the V $3d(d^n)$ orbitals: d^5, d^4, d^3, d^2, d^1; for constant Cl(−0.5), $4s(\zeta_4 = 1.10)$, and $4p(d^3p^2)$ valence orbitals show a very regular (although not necessarily linear) behavior, so it is quite reasonable to use only $3d(d^5)$, $3d(d^3)$, and $3d(d^1)$ in describing the variation of V $3d$ valence orbitals. Again separate calculations have been performed for the $^2A_1$, ^2E, $^2T_2$ states.

In constructing Fig. 3 we have two sets of one-electron wavefunctions from which to choose in selecting the proper one-electron MO levels for the empty orbitals: the eigenfunctions of the closed-shell Hartree-Fock operator, $\boldsymbol{F}_c$, which are orthogonal to all the filled orbitals but not necessarily orthogonal to a partially-filled MO of the same symmetry; or the eigenfunctions of the open-shell Hartree-Fock operator, $\boldsymbol{F}_0$, which are necessarily orthogonal to only the partially-filled MO. Neither set has any direct physical significance, however, as only the occupied orbitals determine the properties of the ground state. The filled orbitals are of course taken as eigenfunctions of $\boldsymbol{F}_c$, and the one partially-filled orbital in each calculation, as an eigenfunction of $\boldsymbol{F}_0$; the empty orbitals have been taken from the set of eigenfunctions for $\boldsymbol{F}_c$, so that they can be used in constructing excited states, as they are already orthogonal to the other orbitals (except $5t_2$ to $4t_2$ in the $^2T_2$ calculation). There is thus no reason to expect that $2e$, $4t_2$, and $3a_1$ should be in the same order from the $^2T_2$, ^2E and $^2A_1$ calculations, since each of these calculations puts specific emphasis on just one of these orbitals. All that we could expect would be that ^2E and $^2T_2$ give comparable $\varepsilon(3a_1)$, ^2E and $^2A_1$ give comparable $\varepsilon(4t_2)$, and $^2T_2$ and $2A_1$ give comparable $\varepsilon(2e)$. This is certainly satisfied in Fig. 3, even though the partially-filled orbital of a specific ground state calculation is always the lowest non-filled level. Determination of the true ground state symmetry can, therefore, only be done by means of total energy values – as discussed in the preceding section – and not by orbital energy sequences.

Several interesting conclusions and several problems can be immediately seen from the series of MO level energy diagrams in Fig. 3. Except for the obvious confusion of the higher energy occupied levels of the assumed ^2E configuration for the contracted $3d(d^1)$ orbitals (for which the program will automatically re-name $1e$, $2e$), the order of the filled one-electron MO levels: $1t_2 \leqq 1a_1 < 2t_2 < 2a_1 < 3t_2 \simeq 1e < t_1$, and even the energies of the filled one-electron MO levels are relatively constant over this drastic variation of $3d(d^n)$ and $Cl(-\delta)$ valence orbitals

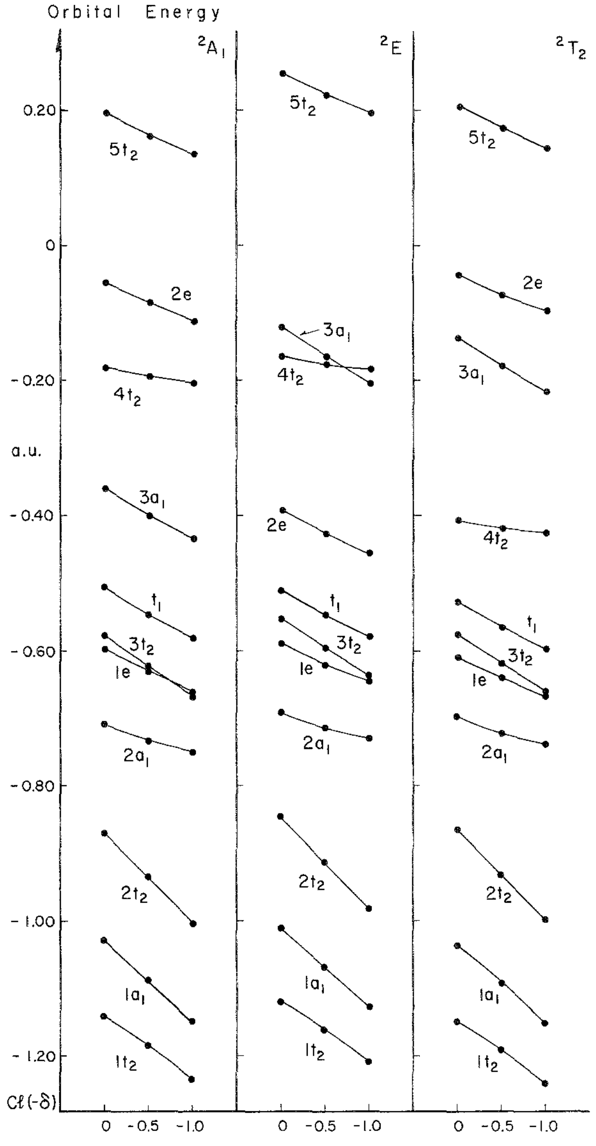

Fig. 3A

Fig. 3A–C. The dependence of the one-electron MO energies for assumed $^2A_1$, ^2E, and $^2T_2$ configuration, respectively, upon the V(3*d*) and Cl($-\delta$) valence orbitals: A, Variation of the one-electron MO levels with respect to Cl($-\delta$) valence orbitals for $3d(d^5)$, $4s(\zeta_4 = 1.10)$, and $4p(d^3p^2)$ valence orbitals; B, Variation of the one-electron MO levels with respect to Cl($-\delta$) valence orbitals for $3d(d^3)$, $4s(\zeta_4 = 1.10)$, and $4p(d^3p^2)$ valence orbitals; C, Variation of the one-electron MO levels with respect to Cl($-\delta$) valence orbitals for $3d(d^1)$, $4s(\zeta_4 = 1.10)$, and $4p(d^3p^2)$ valence orbitals

for the $^2A_1$, ^2E, and $^2T_2$ states and between the assumed configurations themselves. Expanding the Cl valence orbitals (i.e., Cl[0.0]→Cl[−1.0]) tends to lower the energy of all the one-electron MO levels, but the $3a_1$ level seems to be more readily stabilized than the other non-filled levels. Although expanding the $3d(d^n)$

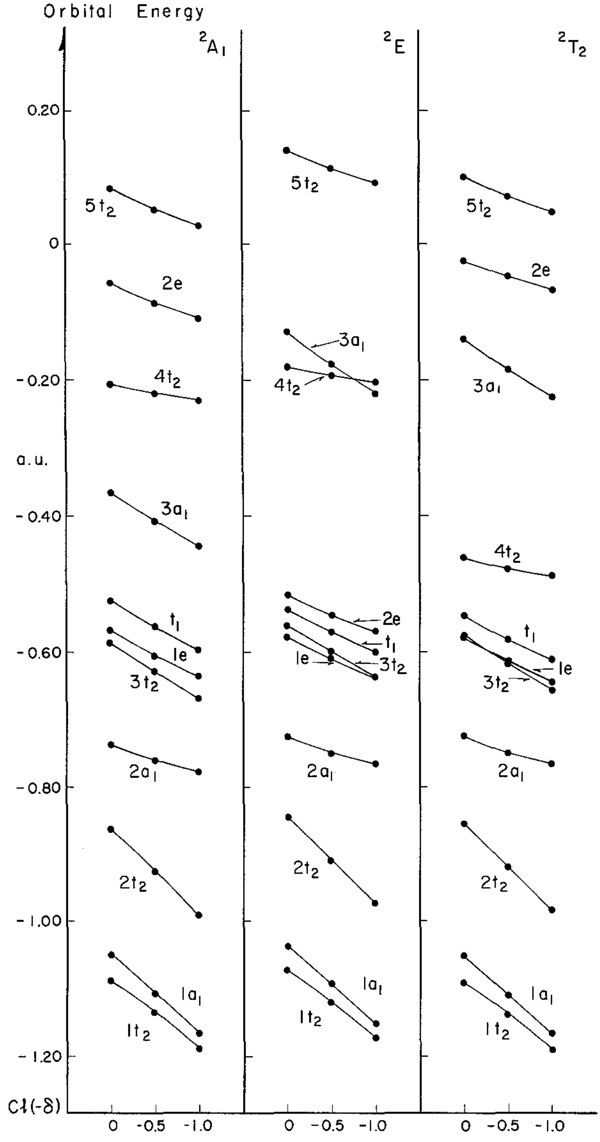

Fig. 3B

valence orbitals (i.e., $3d[d^1] \rightarrow 3d[d^5]$) also results in lower total (valence) energy, any general behavior of the filled one-electron MO levels is less pronounced. Actually, there is relatively little change in the filled MO levels for variation of the $3d$ orbitals except in the case of the upper levels of the assumed ^2E configuration.

Systematic variation of the $4s$ valence orbital from $4s(d^4s^2)$ to $4s(d^3s^1)$ for constant $3d(d^5)$, Cl(-0.5), and $4p(d^3p^2)$, and of the $4p$ valence orbital from $4p(d^4p^1)$ to $4p(d^3p^1)$ for constant $3d(d^5)$, Cl(-0.5), and $4s(d^3s^2)$ (not pictured) shows that the VCl_4 one-electron MO levels are rather sensitive to the choice of $4s$ and $4p$ orbitals. The ordering of the filled MO levels according to energy, as

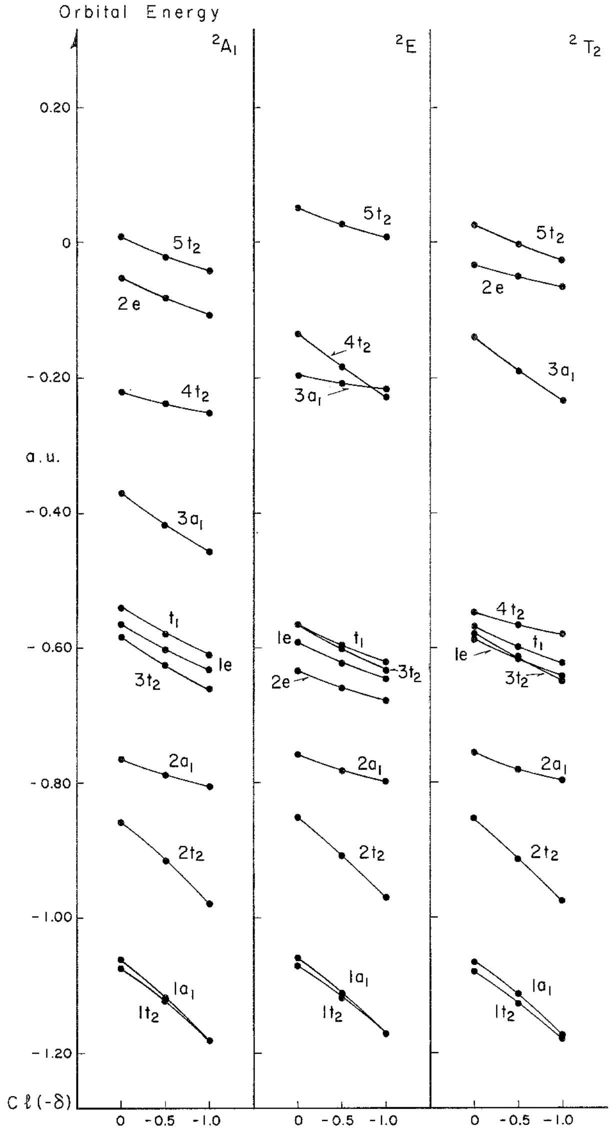

Fig. 3C

has been listed previously, is clearly established, however, for the optimum 4*s* and 4*p* orbitals and their immediately neighboring configurations in all instances and remains unambiguous over the total range of 4*s* and 4*p* variation for all levels except $2a_1$ for greatly expanded 4*s* orbitals ($4s[d^4s^2]$). The one-electron MO levels are more or less uniformly de-stabilized by contraction of the 4*s* orbitals (i.e., $4s[d^4s^2] \rightarrow 4s[d^3s^1]$), except for the $2a_1$ and $3a_1$ levels which are de-stabilized for 4*s* orbitals more contracted than $4s(\zeta_4 = 1.10)$ but are also de-stabilized for 4*s* orbitals less contracted than this optimum valence orbital, so that $2a_1$ crosses $1e$ and $3t_2$ for $4s(d^4s^2)$ (but not for $4s[d^4s^1]$). The one-electron MO levels are all de-stabilized quite sharply for contracted $4p$ orbitals, except the $2t_2$ and $4t_2$ levels. These levels show a distinct energy minimum at $4p(d^3p^2)$ and are de-stabilized for both $4p(d^4p^1)$ and $4p(d^3p^1)$.

4. On the Neglect of Off-Diagonal Multipliers

At this stage it would be useful if we could even qualitatively assess the degree of error introduced through the neglect of the off-diagonal multipliers. In the method of calculation used here, the filled (closed-shell) molecular orbitals, ϕ_c (in Roothaan's notation [4]), have been calculated as eigenfunctions of a Hartree-Fock equation of the type

$$F_c\phi_\kappa = \sum_l \phi_l\theta_{l\kappa} + \sum_n \phi_n\theta_{n\kappa}$$

(in the sense of equation (25) of Roothaan, not (31) [4]), while the partially-filled (open-shell) molecular orbitals, ϕ_0, have been calculated with a different Hartree-Fock operator

$$F_0\phi_m = \sum_l \phi_l\theta_{lm} + \sum_n \phi_n\theta_{nm}\,.$$

The customary selection of basis functions suffices to diagonalize the Lagrangian multipliers within the sets of closed-shell and open-shell orbitals; i.e., $\theta_{l\kappa}$ and θ_{nm}, respectively, but does not remove the off-diagonal multipliers $\theta_{n\kappa}$ and θ_{lm} between closed- and open-shell orbitals of the same symmetry. Thus, our treatment would be mathematically correct only if $\theta_{n\kappa}$, θ_{lm} were negligibly small.

The different Hartree-Fock operators give rise to two sets of eigenfunctions, each containing wavefunctions for the closed- and open-shell orbitals, but the filled molecular orbitals are selected from the eigenfunctions of the closed-shell Hartree-Fock operator and the partially-filled levels come from the open-shell Hartree-Fock operator. While the two sets of eigenfunctions are internally orthonormal, the closed-shell orbitals selected from one set will not necessarily be orthogonal to the open-shell orbitals of the same symmetry taken from the other set, as they would be if the connecting off-diagonal multipliers had not been neglected. In fact, this non-orthogonality between the partially-filled molecular orbitals and filled molecular orbitals of the same symmetry should be at least a qualitative measure of the validity, or the lack of validity, of neglecting the off-diagonal multipliers.

In Tables 3 and 4 the overlap integrals between the partially-filled molecular orbitals $3a_1$, $2e$, $4t_2$ and the corresponding filled molecular orbitals of the same symmetry, $2a_1$, $1a_1$; $1e$; $3t_2$, $2t_2$, $1t_2$; respectively, have been calculated for a number of different sets of component atomic orbitals. Table 3 shows the variation of these overlap integrals with the $3d(d^n)$ orbitals and constant $4s(\zeta_4 = 1.10)$, $4p(d^3p^2)$, and Cl(-0.5) valence orbitals, calculated for the assumed electronic configurations $^2A_1$, ^2E, and $^2T_2$. It is of course only the overlap integrals between orbitals containing electrons that are of energetic importance, and we see that these integrals are quite small for the $^2A_1$ calculations and reasonably small for the $^2T_2$ calculations (except when very contracted d-orbitals are used). The pertinent $\langle 2e|1e\rangle$ integrals, however, are surprisingly large with all $3d(d^n)$ valence orbitals for the ^2E calculations.

Table 3. *Overlap integrals between open-shell and closed-shell orbitals of the same symmetry, according to variation of the* $3d(d^n)$ *valence orbitals, with* $4s(\zeta_4 = 1.10)$ *and* $4p(d^3p^2)$, *as calculated for the* $^2A_1$, ^2E, *and* $^2T_2$ *configurations*

		$3d(d^5)$	$3d(d^4)$	$3d(d^3)$	$3d(d^2)$	$3d(d^1)$
$^2A_1$	$\langle 3a_1 \| 2a_1 \rangle$	−0.0066	−0.0076	−0.0084	−0.0089	−0.0093
	$\langle 3a_1 \| 1a_1 \rangle$	0.0016	0.0019	0.0021	0.0022	0.0024
^2E	$\langle 2e \| 1e \rangle$	−0.1490	−0.2025	−0.2554	−0.3155	−0.3784
$^2T_2$	$\langle 4t_2 \| 3t_2 \rangle$	−0.0243	−0.0508	−0.0967	−0.1665	−0.2456
	$\langle 4t_2 \| 2t_2 \rangle$	−0.0174	−0.0277	−0.0422	−0.0593	−0.0725
	$\langle 4t_2 \| 1t_2 \rangle$	−0.0122	−0.0169	−0.0222	−0.0270	−0.0288

Table 4. *Overlap integrals between open-shell and closed-shell orbitals of the same symmetry, according to variation of the* $\mathrm{Cl}(-\delta)$ *valence orbitals, with* $4s(\zeta_4 = 1.10)$ *and* $4p(d^3p^2)$, *as calculated for the* $^2A_1$, ^2E, *and* $^2T_2$ *configurations*

		Cl(0.0)	Cl(−0.5)	Cl(−1.0)
$^2A_1$	$\langle 3a_1 \| 2a_1 \rangle$	−0.0104	−0.0084	−0.0052
	$\langle 3a_1 \| 1a_1 \rangle$	0.0020	0.0021	0.0014
^2E	$\langle 2e \| 1e \rangle$	−0.2593	−0.2554	−0.2518
$^2T_2$	$\langle 4t_2 \| 3t_2 \rangle$	−0.0999	−0.0967	−0.0963
	$\langle 4t_2 \| 2t_2 \rangle$	−0.0436	−0.0422	−0.0404
	$\langle 4t_2 \| 1t_2 \rangle$	−0.0237	−0.0222	−0.0202

In general, then, the $3a_1$ orbital seems to show minimal interaction with the $2a_1$ and $1a_1$ orbitals (as reflected in consistently small overlap integrals) for all $3d(d^n)$ variations. The other overlap integrals regularly increase in absolute value as the $3d(d^n)$ orbitals are contracted from $3d(d^5)$ to $3d(d^1)$, the overlap for $\langle 2e|1e\rangle$ and $\langle 4t_2|3t_2\rangle$ becoming quite large. Table 4 shows that the overlap integrals are relatively insensitive to changes in the $\mathrm{Cl}(-\delta)$ valence orbitals, the sets of values for the three chlorine orbitals all being within the same orders of magnitudes and not showing particularly strong trends.

From these calculations of overlap integrals – which should bear some direct correlation to the error introduced by neglect of the off-diagonal multipliers – we have reason to question the reliability of all the molecular orbital calculations for the ^2E configuration and some of the calculations for the $^2T_2$ configuration, especially for greatly contracted $3d(d^n)$ orbitals. Although the open- and closed-shell orbitals of the same symmetry are also non-orthogonal in the calculations for the $^2A_1$ configuration, these overlap integrals are consistently small for all variation of the component $3d(d^n)$ orbitals, approaching a maximum absolute value of 0.03, and *may* therefore indicate that the error in neglecting the off-diagonal multipliers is relatively small in these calculations. Only a complete open-shell treatment would of course establish this fact. In the absence of a calculation of this type, however, we are forced to tentatively accept the $^2A_1$ calculations, then, and the $^2T_2$ calculations which are in close agreement with the $^2A_1$.

Unfortunately, many of the more recent semi-quantitative molecular orbital calculations on transition metal complexes with open-shell electronic configurations (e.g., [19–21]) have been performed assuming an approximation of the closed-shell treatment. Perhaps one should tend to view these procedures a bit cautiously.

5. Ordering of Non-Filled Molecular Orbitals

At this point it may be interesting to at least speculate as to the ordering of the non-filled molecular orbitals in VCl_4. While there is probably insufficient data to draw definite conclusions, several observations can be made. A ${}^2T_2$ ground state has already been tentatively assigned on the basis of total energy considerations, so we should not be concerned with the partially-filled MO level in each calculation. The ${}^2A_1$ calculations, which are of course the "best" mathematically, suggest an ordering of *empty* one-electron molecular orbitals (if ${}^2A_1$ were the ground state, in an excited configuration, say): $4t_2 < 2e < 5t_2$. The ${}^2T_2$ calculations, which we have tentatively accepted, then, as the ground state calculation for VCl_4, suggest an ordering of empty MO's: $3a_1 < 2e < 5t_2$. The ${}^2E$ calculations, which we have cause to question, suggest that *empty* $4t_2$ and $3a_1$ levels are close in energy, well below $5t_2$. Conclusions regarding empty molecular orbitals cannot necessarily by applied to partially-filled orbitals, however, and we should not use any of this data to argue ground states. Thus, while the total energy calculations suggested an ordering of electronic configurations $2T_2 < {}^2E < {}^2A_1$ for all but the most expanded $3d(d^n)$ and $Cl(-\delta)$ valence orbitals (and very contracted valence orbitals), an ordering of the one-electron molecular orbital levels of $4t_2 < 3a_1 < 2e < 5t_2$ seems more consistent with our calculations.

The postulated ground state (tetrahedral) electronic configuration for VCl_4 as ${}^2T_2$ is in disagreement with all previous molecular orbital calculations for VCl_4 (e.g., [13, 14, 21–24]) except the first [25], and is of course in disagreement with interpretations based on crystal field theory (e.g., [26–31]). It is interesting to note that the ordering, $4t_2 < 3a_1 < 2e < 5t_2$, was the one first predicted for tetrahedral molecules in the original Wolfsberg-Helmholz semi-empirical molecular orbital calculation [25], and that this ordering was then inverted to achieve harmony with crystal field theory in the next following [22] and all subsequent [23, 24] Wolfsberg-Helmholz type MO calculations on tetrahedral molecules. This agreement, however, is probably strictly fortuitous. There is of course a possibility that upon correcting the ${}^2E$ calculations by inclusion of the off-diagonal multipliers the total energy for the ${}^2E$ calculation will become optimized. This possibility cannot be denied on the basis of this work. When and if this is established, however, this present work will have served its purpose, nevertheless, by prompting a new investigation of a problem once thought solved.

6. Eigenvector Coefficients

The eigenvector coefficients calculated for the molecular orbitals of VCl_4 using the $3d(d^3)$, $4s(\zeta_4 = 1.10)$, $4p(d^3p^2)$, and $Cl(-0.5)$ valence orbitals and assuming a ${}^2T_2$, ${}^2A_1$, and ${}^2E$ configuration are shown in Tables 5–7, respectively. As

Table 5. *The molecular orbitals for* VCl_4 *using* $3d(d^3)$, $4s(\zeta_4 = 1.10)$, $4p(d^3p^2)$, *and* Cl(−0.5) *valence orbitals, as calculated for the* $^2T_2$ *electronic configuration*

MO level	Eigenvector								
a_1		4s(V)			$3\sigma_s$(Cl)			$3\sigma_p$(Cl)	
t_2	4p(V)			3d(V)	$3\sigma_p$(Cl)	$3\sigma_s$(Cl)			$3\pi_p$(Cl)
e			3d(V)				$3\pi_p$(Cl)		
t_1					$3\pi_p$(Cl)				
$1t_2$	−0.1838			0.2445	0.0323	0.9509			−0.0333
$1a_1$		−0.2973			0.9504			−0.0914	
$2t_2$	0.7095			0.2888	0.4571	0.0630			0.4475
$2a_1$		0.8094			0.3016			0.5038	
$1e$			0.2807				0.9598		
$3t_2$	−0.1040			0.3998	0.5906	−0.1665			−0.6729
t_1					1.0000				
$4t_2$	−0.5591			0.5586	−0.0827	−0.2529			0.5519
$3a_1$		−0.5064			−0.0758			0.8590	
$2e$			0.9598				−0.2807		
$5t_2$	−0.3085			−0.6443	0.6580	0.0914			0.2198

Table 6. *The molecular orbitals for* VCl_4 *using* $3d(d^3)$, $4s(\zeta = 1.10)$, $4p(d^3p^2)$, *and* Cl(−0.5) *valence orbitals, as calculated for the* $^2A_1$ *electronic configuration*

MO level	Eigenvector								
a_1		4s(V)			$3\sigma_s$(Cl)			$3\sigma_p$(Cl)	
t_2	4p(V)			3d(V)	$3\sigma_p$(Cl)	$3\sigma_s$(Cl)			$3\pi_p$(Cl)
e			3d(V)				$3\pi_p$(Cl)		
t_1					$3\pi_p$(Cl)				
$1t_2$	−0.1863			0.2480	0.0236	0.9500			−0.0282
$1a_1$		−0.3138			0.9230			−0.1108	
$2t_2$	0.6963			0.3069	0.4976	0.0563			0.4126
$2a_1$		0.7963			0.3249			0.5102	
$1e$			0.3370				0.9415		
$3t_2$	−0.1908			0.4022	0.5831	−0.1764			−0.6563
t_1					1.0000				
$3a_1$		−0.5245			−0.0727			0.8483	
$4t_2$	−0.5938			0.4911	0.0635	−0.2287			0.5915
$2e$			0.9415				−0.3370		
$5t_2$	−0.3024			−0.6643	0.6386		0.1047		0.2200

can be seen, the eigenvectors are quite similar for these three calculations. While the optimum orbitals have not been established for all component atomic orbitals, there are some reasons to view this selection of valence orbitals as one of the most reasonable. The 4*s* and 4*p* orbitals are the "optimized" atomic orbitals; i.e., the component atomic orbitals which minimize the total (valence) energy; they are also very close to the "free atom" values for vanadium. Expanded chlorine valence orbitals are shown to favor minimum total energy, so Cl(−0.5) 3*s* and 3*p* orbitals

Table 7. *The molecular orbitals for* VCl_4 *using* $3d(d^3)$, $4s(\zeta_4=1.10)$, $4p(d^3p^2)$, *and* Cl(−0.5) *valence orbitals, as calculated for the* ^2E *electronic configuration*

MO level	Eigenvector								
a_1		$4s$(V)			$3\sigma_s$(Cl)			$3\sigma_p$(Cl)	
t_2	$4p$(V)			$3d$(V)	$3\sigma_p$(Cl)	$3\sigma_s$(Cl)			$3\pi_p$(Cl)
e			$3d$(V)				$3\pi_p$(Cl)		
t_1					$3\pi_p$(Cl)				
$1t_2$	−0.1942			0.2246	0.0289	0.9538			−0.0363
$1a_1$		−0.3081			0.9473			−0.0872	
$2t_2$	0.7242			0.2569	0.4443	0.0907			0.4517
$2a_1$		0.8108			0.3095			0.4968	
$1e$			0.3007				0.9537		
$3t_2$	0.0547			−0.3482	−0.6172	0.1381			0.6897
t_1					1.0000				
$2e$			0.8453				−0.5343		
$4t_2$	−0.6126			0.4896	0.2172	−0.2262			0.5355
$3a_1$		−0.4976			−0.0823			0.8635	
$5t_2$	0.2442			0.7229	−0.6113	−0.1088			−0.1796

were assumed, although Cl(−1.0) could also have been used. The V $3d$ orbitals were also seen to lower total energy as they were expanded from $3d(d^1)$ to $3d(d^5)$, so the choice of the free atom value, $3d(d^3)$ (i.e., V: (Ar[$4s^2 3d^3$), is a compromise between optimum orbitals ($3d[d^5]$) and formal oxidation state ($3d[d^1]$). Although the energy of the MO levels may be rather strongly affected by choice of component atomic orbitals, the eigenvector coefficients show regular slowly-varying trends with changes in $3d(d^n)$ and Cl$(-\delta)$ valence orbitals, so the same general picture would emerge from most of the CNDO-MO calculations performed on the VCl_4 molecule in this work.

The eigenvector coefficients for VCl_4 are very analogous to those for $TiCl_4$ [1], in that they show strong participation of the V $4s$ and $4p$ orbitals in bonding molecular orbitals (i.e., the $2a_1$ and $2t_2$, $4t_2$ orbitals, respectively) and that, as a rather direct consequence, the virtual orbitals $3a_1$ and $5t_2$ have major ligand and $3d$ contributions. The VCl_4 calculation shows slightly less $4p$ contribution and more $3d$ contribution in the $4t_2$ molecular orbital and slightly more $4p$ contribution and less $3d$ contribution in the $5t_2$, however, and less $4s$ participation in $2a_1$ and more $4s$ participation in $3a_1$ than in the $TiCl_4$ calculations [1]. These eigenvector coefficients for VCl_4 are still, nevertheless, quite unlike the results from semi-empirical molecular orbital calculations [24, 32].

7. Experimental Data on VCl_4

Much experimental data has been amassed on the VCl_4 molecule in recent years; this section briefly tries to summarize that information which may be of interest to understanding the electronic structure. Magnetic susceptibility measurements of VCl_4, both as the pure liquid and in solution, have been recorded under various temperatures and conditions [10, 30, 33–35]; the effective magnetic moments, $\mu_{\text{eff}} = 1.72$ B.M. [34], 1.66 – 1.63 B.M. [33], 1.671 B.M. [10], 1.612 B.M. [30], 1.69, 1.71 B.M. [36], are of course indicative of a single unpaired electron, and are slightly lower than a spin-only value (1.732 B.M.). The magnetic measurements have been interpreted in terms of the conventional ^2E ground state configuration for VCl_4 [30, 36, 37], but magnetic data of this nature is by no means diagnostic for a unique ground state: the data fits a ^2E ground state, but other situations could give rise to similar information.

Of the numerous spectral investigations of VCl_4 in the gaseous or condensed phase, it seems that the more recent [28, 30, 31, 38–40] are in fair agreement that the visible and quartz UV spectrum consists of three moderately strong *d-d* type bands around 9000 cm^{-1} and two or more absorption bands of greater intensity in the higher energy region. The lower energy bands have been placed at 6600 ($\varepsilon = 70$), 7850 (135), and 9250 cm^{-1} (145) for gaseous VCl_4 [28], and at 6600 ($\varepsilon = 65$), 7880 (124), and 9010 cm^{-1} (130) for VCl_4 in CCl_4 solution [30]. Intense absorption bands of a charge-transfer nature have been reported at 24.2, 24.8, 25.0 kK ($\varepsilon = 3500$, 1000, 2800) and 33.2, 33.9, 34.1 kK ($\varepsilon = 6500$, 2400, 4500) [31, 39, 40, respectively]. Contamination of the VCl_4 by $VOCl_2$ (non-volatile) and $VOCl_3$ has been a major problem [28, 40], so the additional bands reported at 29.95 kK ($\varepsilon = 3950$) [40] and 40.0, 40.8 kK ($\varepsilon = 5550$) [39, 40] are attributed to $VOCl_3$ [40, 41]. A shoulder peak has also been reported [39] at 45.5 kK ($\varepsilon = 5000$) on a very intense ($\varepsilon > 12{,}000$) band above 50 kK.

The theoretical CNDO-MO calculations on VCl_4 are in reasonable agreement with this experimental spectral data. Three *d-d* type electronic transitions cannot of course be predicted from these MO energy diagrams without assuming a splitting of at least one degenerate energy level, presumably via some sort of dynamic Jahn-Teller effect, but these calculations introduce the additional possibility of a transition to the $3a_1$ level as well as between the $4t_2$ and $2e$ levels, thereby not requiring a three-fold splitting of the $4t_2$ level as has been suggested [30]. Presumably an electronic transition between $4t_2$ (or a component level originating from $4t_2$) and $3a_1$ would be Laporte-forbidden as an electric dipole transition, quite analogous to the *d-d* bands and therefore may be expected to be of comparable intensity. (The possibility of the $3a_1$ level being the lowest-energy, non-filled MO – which would remove the necessity of any Jahn-Teller effect in the ground state – has not been totally excluded by these calculations, incidentally, only suggested less likely than the $^2T_2$ ground state).

The observed energies of 6600, 7850, and 9250 cm^{-1} [28], or in atomic units: 0.030, 0.036, and 0.042 a.u., respectively, are within the order of magnitude anticipated from Fig. 2. This diagram has been constructed from the total energies calculated for the $^2T_2$, $^2A_1$, and ^2E configurations as functions of the component $3d(d^n)$ orbitals, however, and therefore has limited reliability for the expanded *d*-orbitals (i.e. $3d[d^5]$), and even less for contracted *d*-orbitals. It should, however, indicate rough values of the expected transition energies for expanded *d*-orbitals. Unfortunately, these present calculations are of insufficient accuracy to really justify further numerical interpretation at this time. Attempted interpretation of the charge-transfer spectra; i.e., the higher-energy, greater-intensity bands, would likewise be rather useless now, since the ground state configuration has not been unambiguously established. The electronic spectra, therefore, neither confirm nor deny these molecular orbital calculations.

Much effort has been expended in trying to establish a Jahn-Teller distortion in the VCl_4 molecule. Electron diffraction studies on VCl_4 [9, 11, 12] have invariably suggested a regular tetrahedral structure, but one [12] has also observed an abnormally large mean square amplitude of the Cl–Cl distance, which has been attributed to vibronic interactions indicative of a dynamic Jahn-Teller effect. The infrared and Raman spectra of VCl_4 have been observed for gaseous, liquid, thin-film, CCl_4-solution, $TiCl_4$-solution, and flow-method gaseous phase [10, 12, 28, 42], and the results interpreted to suggest both absence [10] and presence [28] of a Jahn-Teller effect. Possible contamination of the VCl_4 by $VOCl_3$ has again been a major difficulty. Perhaps the strongest statement that can be made at the present time is that the IR and Raman spectra of VCl_4 are consistent with an interpretation including vibronic effects [12] and that while a Jahn-Teller effect has not been unambiguously established for VCl_4, it has also not been proved absent [42].

Electron paramagnetic resonance is not observed for VCl_4 in heptane solution at 90–330° K [43], interpreted as indicative of a degenerate ground state and/or close proximity of an excited state (resulting in very short relaxation times), but the eight hyperfine components for ^{51}V are observed for pure VCl_4 in Kr and Xe matrices [44] and VCl_4 in $TiCl_4$ matrix below 9° K [35]. This esr signal can be interpreted to indicate a static Jahn-Teller distortion of VCl_4 below 9° K [35], but may alternatively be interpreted as simply the result of host-lattice effects, since even the $TiCl_4$ matrix is not regularly tetrahedral [45]. Solid VCl_4 also exhibits an additional electronic absorption band at 17.2 kK not observed in the gaseous phase, which has been interpreted as suggestive of a Jahn-Teller splitting [39].

Various Jahn-Teller calculations have been performed on the VCl_4 molecule [13–15, 27, 28, 35]. The results range from predicting no, or very small, static Jahn-Teller distortion [13–15], to static Jahn-Teller effects [28], to dynamic Jahn-Teller effects at higher temperatures and static Jahn-Teller effect at sufficiently low temperature [27, 35]. All these calculations have of course assumed a ^2E ground state. The results of our CNDO-MO treatment for VCl_4 are also amenable to Jahn-Teller calculations, but now the postulated situation is that of the triply-degenerate $^2T_2$ ground state with possible further complications from the close proximity of the $3a_1$ virtual level. Again these present calculations are of insufficient accuracy to merit additional calculations at this time, but significantly new results may be obtainable from calculations along these lines.

Semiquantitative molecular orbital calculations on VCl_4 by Fenske and Radtke [21] are in fairly good quantitative agreement with our filled-orbital eigenvalues, for most component atomic orbital variations; not only is the same ordering maintained: $1t_2 < 1a_1 < 2t_2 < 2a_1 < 1e \leqq 3t_2 < t_1$, but the individual eigenvalues are also comparable. Closest agreement is achieved with our $3d(d^5)$, Cl(0.0), $4s(\zeta_4 = 1.10)$, and $4p(d^3p^2)$ valence orbitals, but in general the eigenvalues for the ^2E calculation show greater similarity than those for $^2A_1$ or $^2T_2$. The non-filled molecular orbitals, especially the $3a_1$, however, show tremendous disagreement, and as has been suggested previously for $TiCl_4$ [1] this is probably due to the unusual choice of high-energy valence orbitals assumed by Fenske and Radtke [21]. It has been shown very dangerous to perform molecular orbital calculations with unbalanced orbital basis sets [46].

8. Conclusion

It would be superfluous to try to *conclude* just about anything from these semiquantitative molecular orbital calculations on VCl_4. The supposed validity of the CNDO-MO method, however, should prompt us now to *question* some of the conclusions from previous molecular orbital treatments of tetrahedral systems and to possibly realize that their electronic structures may not be a solved problem at all. Aside from the additional complications incurred through the open-shell electron configuration – which can only be resolved by a complete open-shell treatment of the Hartree-Fock equations – these calculations on VCl_4 place its electronic structure about midway between that anticipated from $TiCl_4$ calculations [1]: [Ti(Ar), Cl(Ne)] $(1t_2)^6(1a_1)^2(2t_2)^6(2a_1)^2(1e)^4(3t_2)^6(t_1)^6(3a_1)^1(4t_2)^0(2e)^0(5t_2)^0$, and that predicted from crystal field theory: [Ar] $(2e)^1(4t_2)^0(3a_1)^0(5t_2)^0$. Again the question can be raised: Do we really expect a crystal field-type behavior to extend to VCl_4? Now, of course, it would be very interesting to see what a CNDO-MO treatment (with open-shell procedures) would predict for $CrCl_4$ and/or CrF_4 and MnF_4. Presumably a crystal field-type behavior would eventually be established in going across the first transition metal period.

To say that the "crystal field ordering" of the molecular orbitals for VCl_4 [24, 47]: $(1a_1)^2\,(1t_2)^6\,(1e)^4\,(2t_2)^6\,(2a_1)^2\,(3t_2)^6\,(t_1)^6\,(2e)^{(1)}\,(4t_2)^0\,(5t_2)^0\,(3a_1)^0$, is predicted from the extended Wolfsberg-Helmholz semi-empirical molecular orbital theory may be a question of confusing *results* with presupposed *starting assumptions*. As has been pointed out earlier the original Wolfsberg-Helmholz treatment for tetrahedral systems [25] indicated the ordering of molecular orbitals: [Ar] $(1a_1)^2(1t_2)^6(1e)^4(2t_2)^6(t_1)^6(3t^2)^{(1)}(2a_1)^0(2e)^0(4t_2)^0$; but this ordering was later reversed in subsequent calculations [22, 24, 47]. Indeed Fenske and Sweeney [48] concluded that these results were strongly dependent upon the initial assumptions employed in the semi-emirical method. Even if the extended Wolfsberg-Helmholz method may have been justified now in the MnO_4^- calculations [6, 47], there is still the problem of extrapolation to VCl_4 and all other tetrahedral systems.

Molecular orbital calculations of a "non-Wolfsberg-Helmholz nature" are more in agreement with our results for VCl_4. Semi-empirical calculations by Oleari *et al.* [32] were able to establish an ordering of molecular orbitals: $(1a_1)^2(1e)^4(1t_2)^6(2t_2)^6(t_1)^6(2e)^0(3t_2)^0(2a_1)^0(4t_2)^0$, for MnO_4^- with an effective central metal oxidation state (q_A) of 0.0, but for $q_A = +1.0$, the order became: $(1t_2)^6(1e)^4(1a_1)^2(2t_2)^6(t_1)^6(3t_2)^0(2e)^0(2a_1)^0(4t_2)^0$. For the CrO_4^{2-} calculations the ordering was $(1a_1)^2(1e)^4(1t_2)^6(2t_2)^6(t_1)^6(2e)^0(2a_1)^0(3t_2)^0(4t_2)^0$ for $q_A = 0.0$, while for $q_A = +1.0$ the order of the virtual orbitals became $2a_1 < 2e < 3t_2 < 4t_2$. The approximated oxidation states were $+0.1$ for manganese and $+0.78$ for chromium [32].

The optimum CNDO-MO calculations for MnO_4^- [6, 7] established the order $(1a_1)^2 \simeq (1t_2)^6\,(2t_2)^6\,(2a_1)^2\,(1e)^4 \simeq (3t_2)^6\,(t_1)^6\,(2e)^0\,(4t_2)^0\,(3a_1)^0\,(5t_2)^0$, in agreement with recent Wolfsberg-Helmholz calculations [47]. Under variation of the component atomic orbitals, however, the $1e$ and $2e$ levels are seen to be destabilized for contracted $3d$ orbitals, so for Mn $3d(d^5)$ the virtual molecular orbitals have become $4t_2 < 2e < 3a_1 < 5t_2$ and for Mn $3d(d^3)$ the virtual levels are $4t_2 < 3a_1 < 2e < 5t_2$. Extending the CNDO-MO calculations to the isoelectronic series, MnO_4^-, CrO_4^{2-}, VO_4^{3-} [49], establishes that a unique ordering of the virtual levels is not even maintained throughout these slight variations. For CrO_4^{2-} the energies have become $4t_2 \simeq 2e$ and for VO_4^{3-}, $4t_2 < 3a_1 < 2e < 5t_2$. The component atomic orbitals were not specifically optimized for CrO_4^{2-} and VO_4^{3-} [49], however, but orbitals analogous to those optimum for the MnO_4^- calculation [7] were assumed. In view of the close agreement between the filled molecular orbitals, it is unfortunate that a meaningful comparison of the non-filled molecular orbitals obtained in this work and in the semiquantitative calculations of Fenske and Radtke [21] cannot be made. One can only speculate that if a balanced set of valence orbital basis functions; as e.g., V $3d$, $4s$, $4p$; Cl $3s$, $3p$; had been used in both calculations, perhaps the results would have been much more similar.

Thus it would seem that although this semiquantitative CNDO-MO treatment of VCl_4 may not have solved the problem of the electronic structure for this (formally) d^1 tetrahedral molecule, it has at least re-opened several questions even more fundamental than that of a possible Jahn-Teller distortion. Unfortunately present experimental data seems inadequate to confirm or deny these calculations.

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Dr. J. P. Dahl
Department of Chemistry
The University of Copenhagen
Universitetsparken 5
Copenhagen Ø, Denmark