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A CNDO-MO Calculation of $TiCl_4$

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The electronic structure of the tetrahedral molecule $TiCl_4$ is investigated within the CNDO-MO approximations. The metal and ligand valence orbitals have been extensively varied, and the dependency of the ordering of molecular orbital levels and of the calculated energies for the expected electric dipole allowed one-electron transitions with respect to these component atomic orbitals has been investigated.

Die Elektronenstruktur des tetraedrischen $TiCl_4$-Moleküls wird im Rahmen des CNDO-MO-Verfahrens untersucht. Dabei werden Metall- und Ligandenorbitale stark variiert und die Abhängigkeit der Reihenfolge des MOs sowie die der Energie der Dipol-erlaubten Einelektronenübergänge davon verfolgt.

La structure électronique de la molécule tétraédrique $TiCl_4$ est étudiée dans le cadre des approximations CNDO MO. Les orbitales de valence du métal et du ligand ont été largement variées et l'on a étudiée l'effet de ces variations sur l'ordre des niveaux des orbitales moléculaires et sur les énergies calculées des transitions monoélectroniques permises.

1. Introduction

The CNDO-MO scheme has been suggested as a semi-quantitative method for investigating transition metal complexes. The electronic structure of the tetrahedral permanganate ion [1, 2], as well as the analogous chromate and vanadate ions [3], has been satisfactorily explained within the approximations of this theory. Preliminary calculations on the $TiCl_4$ molecule [3] indicated an ordering of unoccupied MO levels in an inverted order to that expected from simple crystal field theory, but as the atomic wavefunctions used were those analogous to the optimal orbitals for MnO_4^- and no attempt had been made to optimize these component atomic orbitals specifically for $TiCl_4$, these results were not considered conclusive.

It is the purpose of this present work to re-investigate the $TiCl_4$ system within the CNDO approximations then, systematically varying the atomic orbitals used in constructing the valence LCAO-MO wavefunctions in an attempt to minimize the total energy. Previous work [2] has clearly established the need for this optimization procedure, and it is to be hoped that additional information regarding the forms of atomic wavefunctions in molecule formation can be obtained in this way.

The $TiCl_4$ molecule has been taken as regularly tetrahedral with a Ti-Cl bond length of 2.170 Å [4].

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2. Atomic Orbitals

The component atomic orbitals used in constructing the LCAO-type molecular orbitals of the present CNDO treatment were taken from, or extrapolated from, the available tables of radial wavefunctions computed with minimal basis sets of normalized Slater-type functions [5, 6, 7] the "double-zeta" forms being used for the Ti 3*d* orbitals. The titanium "core orbitals" — i.e., 1*s*, 2*s*, 2*p*, 3*s*, and 3*p* — were taken from Richardson *et al.* [6], and the Ti 3*d* orbitals from that work, plus extrapolated configurations for expanded wavefunctions, are listed in Table 1, using the notation of Ref. [2].

Table 1. *Titanium 3d orbitals*

d^n	n_j	ζ_j	C_j	d^n	n_j	ζ_j	C_j
$3d(d^1)$	3	4.55	0.4956	$3d(d^5)$	3	4.55	0.4028
	3	2.00	0.6335		3	1.20	0.8258
$3d(d^2)$	3	4.55	0.4623	$3d(d^6)$	3	4.55	0.3804
	3	1.80	0.6910		3	1.00	0.8665
$3d(d^3)$	3	4.55	0.4391	$3d(d^7)$	3	4.55	0.3456
	3	1.60	0.7397		3	0.80	0.9065
$3d(d^4)$	3	4.55	0.4206	$3d(d^8)$	3	4.55	0.2817
	3	1.40	0.7839		3	0.60	0.9461

Table 2. *Titanium 4s orbitals*

$d^n s^m$	n_j	ζ_j	C_j	$d^n s^m$	n_j	ζ_j	C_j
$4s(d^3s^2)$	1	21.40	-0.003665	$4s(d^2s^2)$	1	21.40	-0.022317
	2	8.05	0.012659		2	8.05	0.077510
	3	3.64	-0.031109		3	3.64	-0.198530
	4	0.64	1.000405		4	1.20	1.016369
$4s(d^3s^1)$	1	21.40	-0.011756	$4s(d^2s^1)$	1	21.40	-0.029524
	2	8.05	0.040715		2	8.05	0.102736
	3	3.64	-0.102073		3	3.64	-0.266950
	4	0.94	1.004350		4	1.35	1.029420
$4s(\zeta_4)$	1	21.40	-0.016686	$4s(d^1s^2)$	1	21.40	-0.038408
	2	8.05	0.057866		2	8.05	0.133972
	3	3.64	-0.146559		3	3.64	-0.354525
	4	1.07	1.008951		4	1.52	1.051371
$4s(\zeta_4)$	1	21.40	-0.019639	$4s(d^1s^1)$	1	21.40	-0.045037
	2	8.05	0.068160		2	8.05	0.157388
	3	3.64	-0.173657		3	3.64	-0.422457
	4	1.14	1.012546		4	1.64	1.072253

Titanium 4*s* valence orbitals are listed in Table 2, where the outer zeta value has been computed according to the relationship,

$$\frac{\zeta_{4s}(d^m s^n)}{\zeta_{4p}(d^m p^n)} = \frac{\zeta_{4s}(d^2 s^2)}{\zeta_{4p}(d^2 p^2)} \tag{1}$$

using the ζ_{4p} values for Ti 4*p* orbitals according to Richardson *et al.* [7], and the 4*s* orbital then constructed by Schmidt orthogonalization of this outer "valence" STO to the three inner, core STO's, which remain unchanged for the different configurations. It was found useful to extrapolate two further outer ζ_{4s} values between the exponents appropriate to the configurations d^3s^1 and d^2s^2, and these orbitals should therefore represent Ti 4*s* orbitals with an expansion intermediate to that of atomic orbitals constructed for a d^3s^1 and d^2s^2 electronic configuration. The Ti 4*p* valence orbitals used are all given by Richardson *et al.* [7] and are not reproduced here.

Table 3. *Chlorine core orbitals*

Orbital	n_j	ζ_j	C_j
1*s*	1	16.5239	1.00000
2*s*	1	16.5239	−0.31117
	2	5.7152	1.047295
2*p*	2	6.4966	1.00000

Table 4. *Chlorine valence orbitals*

Cl(−δ)	n_j	ζ_j	C_j	Cl(−δ)	n_j	ζ_j	C_j
3*s*(0.0)	1	16.5239	0.10167	3*s*(−0.6)	1	16.5239	0.09612
	2	5.7152	−0.38295		2	5.7152	−0.36059
	3	2.3561	1.06482		3	2.2855	1.05767
3*p*(0.0)	2	6.4966	−0.20058	3*p*(−0.6)	2	6.4966	−0.18666
	3	2.0387	1.01992		3	1.9720	1.01727
3*s*(−0.1)	1	16.5239	0.09939	3*s*(−0.7)	1	16.5239	0.09547
	2	5.7152	−0.37374		2	5.7152	−0.35800
	3	2.3272	1.06183		3	2.2772	1.05687
3*p*(−0.1)	2	6.4966	−0.19989	3*p*(−0.7)	2	6.4966	−0.18407
	3	2.0354	1.01978		3	1.9594	1.01680
3*s*(−0.2)	1	16.5239	0.09873	3*s*(−0.8)	1	16.5239	0.09482
	2	5.7152	−0.37111		2	5.7152	−0.35541
	3	2.3189	1.06099		3	2.2689	1.05607
3*p*(−0.2)	2	6.4966	−0.19721	3*p*(−0.8)	2	6.4966	−0.18147
	3	2.0227	1.01926		3	1.9467	1.01633
3*s*(−0.3)	1	16.5239	0.09808	3*s*(−0.9)	1	16.5239	0.09417
	2	5.7152	−0.36849		2	5.7152	−0.35279
	3	2.3106	1.06015		3	2.2605	1.05527
3*p*(−0.3)	2	6.4966	−0.19457	3*p*(−0.9)	2	6.4966	−0.17889
	3	2.0101	1.01875		3	1.9340	1.01588
3*s*(−0.4)	1	16.5239	0.09742	3*s*(−1.0)	1	16.5239	0.09352
	2	5.7152	−0.36584		2	5.7152	−0.35022
	3	2.3022	1.05932		3	2.2522	1.05448
3*p*(−0.4)	2	6.4966	−0.19192	3*p*(−1.0)	2	6.4966	−0.17632
	3	1.9974	1.01825		3	1.9213	1.01543
3*s*(−0.5)	1	16.5239	0.09677				
	2	5.7152	−0.36323				
	3	2.2939	1.05850				
3*p*(−0.5)	2	6.4966	−0.18928				
	3	1.9847	1.01776				

The chlorine core orbitals, in Table 3, are Schmidt orthogonalized STO's with zeta values from Clementi and Raimondi [5]. The chlorine valence orbitals, listed in Table 4, were constructed from outer $3s$ and $3p$ zeta values $\zeta = (Z - \sigma)/n$, computed from the appropriate screening constants as given by Clementi and Raimondi [5],

$$\begin{aligned} \sigma(3s) &= 8.4927 + 0.2501(3s - 1 + 3p) + 0.0778(4s) \\ &\quad + 0.3382(3d) + 0.1978(4p)\,, \\ \sigma(3p) &= 9.3345 + 0.3803(3p - 1) + 0.0526(4s) \\ &\quad + 0.3289(3d) + 0.1558(4p)\,. \end{aligned} \tag{2}$$

Again these outer, "valence" lobes have been strictly Schmidt orthogonalized to the core STO's, which are allowed to remain constant through the slight orbital expansion induced by considering a small negative charge $-\delta$ on the chlorine atom.

It is not argued that the best valence orbitals for the free atoms will necessarily be obtained in the above manner. Rather the atomic orbitals chosen can be considered a satisfactory set of functions from which the best orbitals for the LCAO-molecular orbitals are to be selected by a process of optimization.

3. Search for Best Atomic Orbitals

The variation of the molecular energy with respect to the component atomic orbitals is shown in Fig. 1, in which the total energy has been plotted against a linear scale of the outer zeta values for the titanium $4p$, $3d$, and $4s$ orbitals, respectively. In Fig. 1*A* we see, within the scale of the graphing technique used, that the energy is minimized for a Ti $4p$ orbital corresponding to the atomic configuration of d^2p^2 when d^2s^2-configurational $4s$ orbital is used, and that the optimum $4p$ orbital remains very close to $4p(d^2p^2)$ when the $4s(d^3s^1)$ and $4s(d^2s^1)$ orbitals are also used, the Ti $3d$ and Cl $3s$ and $3p$ orbitals being held constant at $3d(d^4)$ and Cl(0), respectively. In Fig. 1*C* the $4s$ orbital has been varied with respect to the $4p(d^2p^2)$, $4p(d^2p^1)$, and $4p(d^3p^1)$ orbitals (clearly the optimum $4p$ and the closest neighboring expanded and contracted $4p$ orbitals), and $3d(d^4)$ and Cl(0) orbitals again constant. The optimum Ti $4s$ orbital is seen to be located between the configurations d^3s^1 and d^2s^2, so it was taken as the $4s$ orbital apparently optimum for the $4p(d^2p^2)$ orbital, and has an outer zeta value (ζ_4) of 1.14 and is therefore quite similar to the $4s(d^2s^2)$ orbital. Similar $4s$ and $4p$ variations with the $3d(d^2)$ orbital and spot checks with other $3d(d^n)$ and Cl$(-\delta)$ orbitals also seem to indicate that these optimum $4s$ and $4p$ orbitals are rather "stable" with respect to variation of Ti $3d$ and Cl $3s$, $3p$ valence orbitals.

Attempted optimization of the Ti $3d$ orbitals, however, as indicated in Fig. 1*B*, is not straightforward. Here the total molecular energy, for constant $4s(\zeta_4 = 1.14)$, $4p(d^2p^2)$, and Cl(0) orbitals, is treated as a function of the $3d$ second zeta value. The existing apparent energy minimum occurs only at zeta values corresponding to greatly expanded $3d$ orbitals, however; so much expanded in fact that they are no longer acceptable from a chemical point of view. Thus at this stage we only recognize that a somewhat expanded titanium $3d$ orbital leads to a more favorable energy, but we are forced to be guided by chemical intuition in selecting the most reasonable orbital. In the work that follows the $3d(d^4)$ orbital has been assumed when necessary to specify a particular $3d$ orbital, but whenever possible the $3d$ orbitals have been allowed to vary.

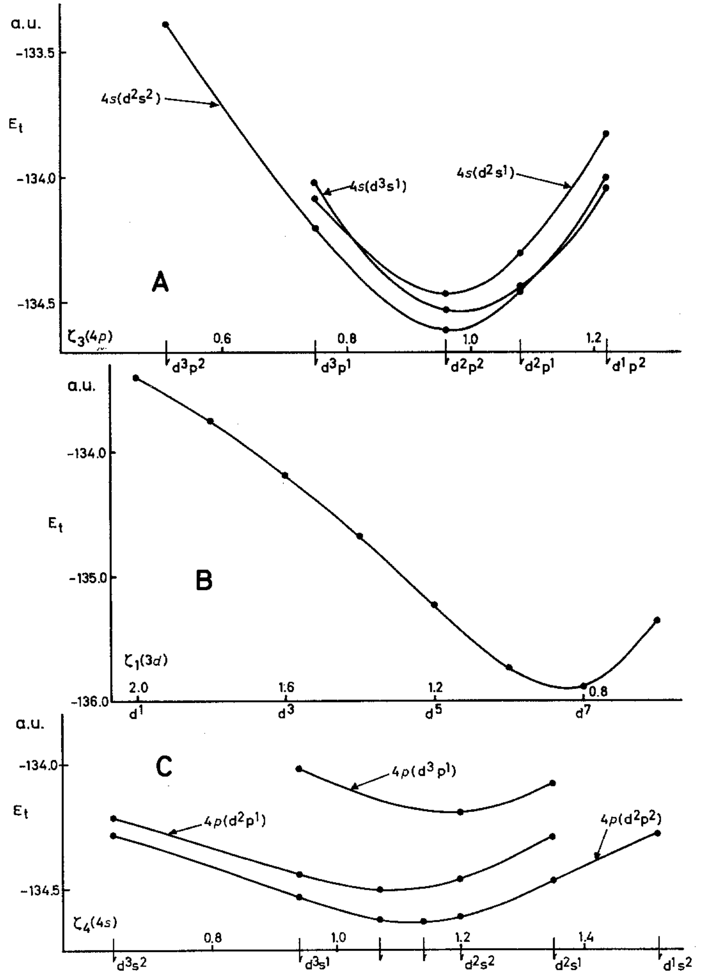

Fig. 1. Minimization of the total energy with respect to the component atomic orbitals: 1*A* Optimization of the $4p$(Ti) orbitals with respect to $3d(d^4)$, Cl(0) and $4s(d^3s^1)$, $4s(d^2s^2)$, $4s(d^2s^1)$ valence orbitals; 1*B* optimization of the $3d$(Ti) orbitals with respect to $4s(\zeta_4 = 1.14)$, $4p(d^2p^2)$, and Cl(0) valence orbitals; 1*C* optimization of the $4s$(Ti) orbitals with respect to $3d(d^4)$, Cl(0) and $4p(d^3p^1)$, $4p(d^2p^2)$, $4p(d^2p^1)$ valence orbitals

Variation of the total energy with respect to the Cl valence orbitals, for constant $3d(d^4)$, $4s(\zeta_4 = 1.14)$, and $4p(d^2p^2)$ orbitals, is shown in Table 5. The energy is a decreasing (non-linear) function of the postulated charge on the chlorine atom (*i.e.*, $[\mathrm{Ne}]\,3s^2 3p^{5+\delta}$) and has a probable minimum — as suggested from a crudely approximated first derivative. This mathematical minimum would occur at a value of δ considerably greater than 1.0, however, and therefore has no chemical significance. Independent variation of the chlorine $3s(-\delta)$ and $3p(-\delta)$ orbitals likewise does not effect a minimization of the energy but only further indicates that expanded valence orbitals are favored. It appears that while optimum $4s$ and $4p$ orbitals, which satisfy both mathematical and chemical criteria, can be unambiguously assigned in these calculations, the chlorine valence orbitals, like the titanium $3d$ orbitals, must be recognized as somewhat expanded over those of the free atom but cannot be "optimized" in a satisfactory manner. In general, then, it would seem that the LCAO-MO's of this CNDO calculation should be constructed from atomic orbitals differing only a little from those of the free atoms.

Table 5. *Variation of the total energy with respect to the* Cl$(-\delta)$ *valence orbitals for constant* $3d(d^4)$, $4s(\zeta=1.14)$, *and* $4p(d^2p^2)$ *orbitals*

Cl$(-\delta)$	Cl(0.0)	Cl(-0.2)	Cl(-0.4)	Cl(-0.5)	Cl(-0.6)	Cl(-0.8)	Cl(-1.0)
E_t (a.u.)	−134.6781	−134.8053	−134.9333	−134.9983	−135.0508	−135.1620	−135.2587
d-population	2.3501	2.3083	2.2784	2.2627	2.2476	2.2177	2.1888
$-\varepsilon(t_1)$ (eV)	13.7850	14.2492	14.6256	14.8272	15.0167	15.3801	15.7353

As seen also from Table 5 the d-orbital electron population, according to a Mulliken population analysis [8, 1], remains close to the assumed free Ti atom value of 2, throughout this chlorine orbital variation. Indeed, throughout the calculations in which the $3d$ orbitals themselves are varied from $3d(d^1)$ to $3d(d^8)$ the d-population values extend over a rather limited range: 1.3671 (d^1), 1.6658 (d^2), 1.9855 (d^3), 2.3501 (d^4), 2.7638 (d^5), 3.1422 (d^6), 3.1707 (d^7), 2.5374 (d^8). [The anomalously low d-population obtained with the $3d(d^8)$ orbitals is probably a manifestation of the invalidity of symmetrical orthogonalization for very diffuse $3d$ orbitals.] Conversely, maintaining a d-population relatively close to the free atom value of 2 is but another argument in favor of selecting the $3d(d^4)$ orbital as optimum. A variation of the d-population with respect to the Ti $4s$ or $4p$ orbitals becomes somewhat more difficult to interpret and is less meaningful data, but the d-population can be shown to decrease rather systematically from 2.6267 (d^3p^2) to 1.9813 (d^1p^2) for variation of the $4p$ orbitals with respect to constant $3d(d^4)$, $4s(\zeta_4=1.14)$, and Cl(0) orbitals, and to decrease systematically from 2.6379 (d^3s^2), to 2.0704 (d^2s^1) and then increase to 2.2043 (d^1s^2) for variation of the $4s$ orbitals with respect to constant $3d(d^4)$, $4p(d^2p^2)$, and Cl(0) orbitals.

4. Molecular Orbital Levels

An ordering of the one-electron molecular orbital energy levels for $TiCl_4$ is given in Fig. 2, in which the $3d$-orbitals have been varied from $3d(d^1)$ to $3d(d^8)$. Our attention is immediately drawn to two facts: the surprisingly little variation of the energy levels with respect to each other and the order of the unfilled (virtual) orbitals, $5t_2 > 2e > 4t_2 > 3a_1$, which remains unchanged throughout the variation. Indeed, the $1e$ level seems to be very stabilized by expanded $3d$ orbitals and drops below the $2a_1$ level for $3d$ orbitals that are more expanded than $3d(d^5)$, while the $3t_2$ level seems to be less stabilized by expanded $3d$ orbitals than are most of the other MO levels and crosses the t_1 (ligand non-bonding MO) for $3d$ orbitals appropriate to d^7 and d^8 configurations; but in general the order: $1t_2 \ll 1a_1 \ll 2t_2 < 2a_1 < 1e < 3t_2$, $t_1 \ll 3a_1 < 4t_2 \ll 2e < 5t_2$ is maintained fairly consistently for the drastic variation of the $3d$ orbitals, and especially so for the orbitals which can be intuitively felt "reasonable" for $TiCl_4 - 3d(d^1)$ to $3d(d^5)$. Even if we took less confidence in the CNDO calculations and interpreted them to suggest an MO level ordering of $1t_2 < 1a_1 < 2t_2 < 2a_1$, $1e$, $3t_2$, $t_1 < 3a_1$, $4t_2 < 2e < 5t_2$ — which is consistent with widely separated and closely neighboring MO levels — we would still be forced to recognize not only the inversion of the $4t_2$ and $2e$ levels with respect to that extrapolated from simple crystal field theory (for these are the levels which correspond to the Ti $3d$ orbitals) but also the great stabilization of the $3a_1$ level (corresponding roughly to the $4s$ orbital in crystal field theory) with respect to the $2e$ level if not also the $4t_2$.

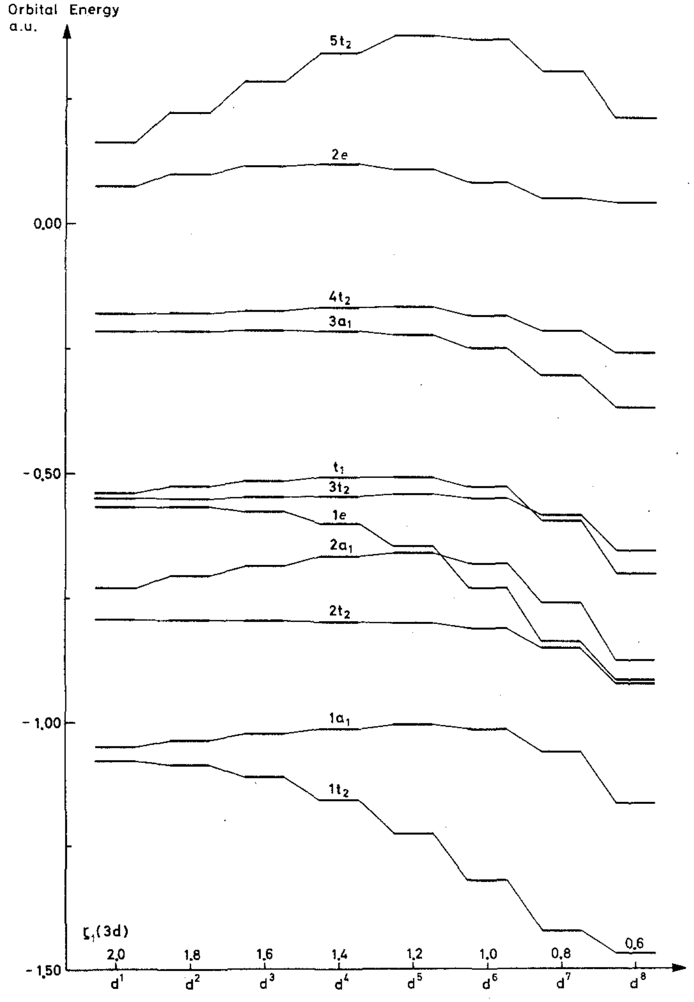

Fig. 2. Variation of the one-electron MO levels with the Ti $3d$ orbitals and constant $4s(\zeta_4 = 1.14)$, $4p(d^2p^2)$ and Cl(0) valence orbitals

The ordering of the MO energy levels with respect to variation of the Ti 4p orbitals is shown in Fig. 3. The same order as observed in Fig. 2; *i.e.*, $1t_2$, $1a_1$, $2t_2$, $2a_1$, $1e$, $3t_2$, t_1, $3a_1$, $4t_2$, $2e$, $5t_2$; is maintained for p-orbitals which are more contracted than the "free-atom" p-orbital, $4p(d^2p^2)$, but for more expanded p-orbitals the $2t_2$ level is seen to displace the $3a_1$ (at $4p(d^3p^1)$) and the $3t_2$, the t_1 (at $4p(d^3p^2)$). In general, the MO levels are seen to have their lowest energies near the zeta value for $4p(d^2p^2)$.

Variation of the MO levels with respect to the Ti 4s orbitals (not pictured) is very analogous to that for the 4p orbitals, with the $3a_1$ level becoming less stable than the $4t_2$ for the $4s(d^3s^2)$ and $4s(d^1s^2)$ orbitals, and the $2a_1$ level crossing and remaining close to both the $1e$ and $3t_2$ levels for these same two, extremely varied 4s orbitals. The same "standard" ordering of MO levels observed for the 3d and 4p orbital variations are maintained, then, for the $4s(d^3s^1)$, $4s(d^2s^2)$, and $4s(d^2s^1)$

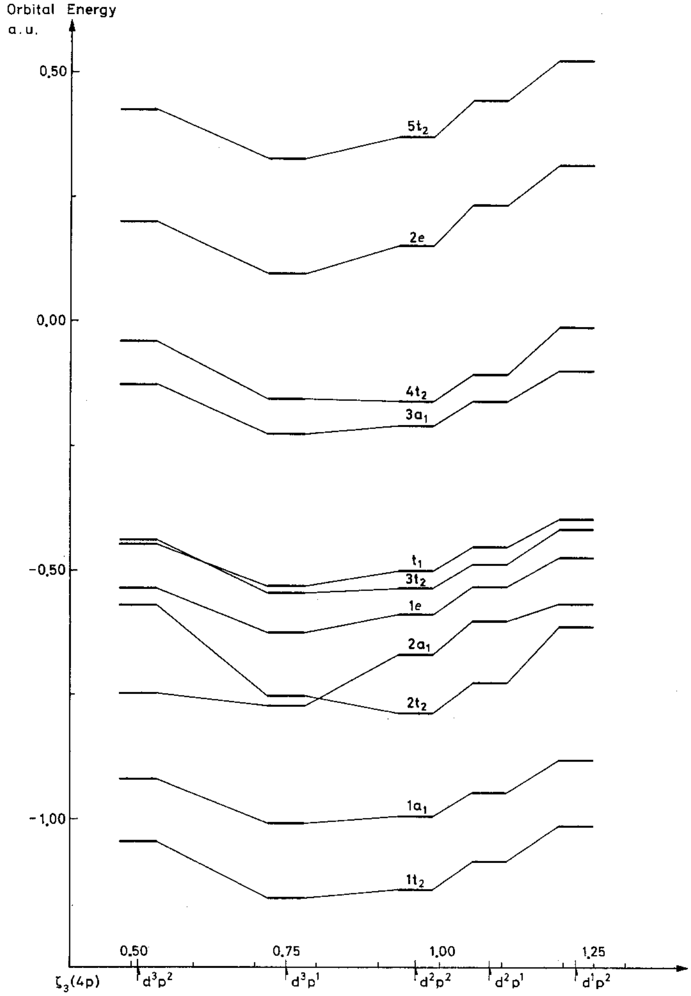

Fig. 3. Variation of the one-electron MO levels with the Ti 4p orbitals and constant $3d(d^4)$, 4s ($\zeta_4 = 1.14$), and Cl(0) valence orbitals

orbitals. A graph of the energies for the one-electron MO levels plotted against $-\delta$, the assumed, small "negative charge" on the chlorine atom (*i.e.*, [Ne] $3s^2 3p^{5+\delta}$), shows a rather insensitive but very linear dependency — that is, the graph may be closely represented by straight lines, many of which are almost parallel and are of small, negative slopes. There will be no crossing of MO energy levels for variation of the Cl$(-\delta)$ valence orbitals within a wide range far exceeding that intuitively "reasonable".

Table 6. *The molecular orbitals for* $TiCl_4$ *using* $3d(d^4)$, $4s(\zeta=1.14)$, $4p(d^2p^2)$, *and* $3Cl(-0.5)$ *valence orbitals*

MO level	Eigenvector								
a_1		4s(Ti)			$3\sigma_s$(Cl)			$3\sigma_p$(Cl)	
t_2	4p(Ti)			3d(Ti)	$3\sigma_p$(Cl)	$3\sigma_s$(Cl)			$3\pi_p$(Cl)
e			3d(Ti)				$3\pi_p$(Cl)		
t_1					$3\pi_p$(Cl)				
$1t_2$	−0.1093			0.3800	0.1374	0.9074			0.0382
$1a_1$		−0.3175			0.9451			−0.0772	
$2t_2$	0.6937			0.2518	0.4482	−0.1105			0.4921
$2a_1$		0.8746			0.3233			0.3614	
$1e$			0.3855				0.9227		
$3t_2$	−0.1386			0.2651	0.6953	−0.2069			−0.6199
t_1					1.0000				
$3a_1$		−0.3665			−0.0473			0.9292	
$4t_2$	−0.6910			0.2569	0.2163	−0.2483			0.5899
$2e$			0.9227				−0.3855		
$5t_2$	0.1001			0.8099	−0.5000	−0.2449			−0.1551

5. Eigenvector Coefficients

The eigenvector coefficients observed for our CNDO-MO calculations on $TiCl_4$ are easily understandable in terms of the energy minimization and are in qualitative agreement with other CNDO-MO calculations (see Ref. [2] and [3]). The coefficients for the MO calculation using the $3d(d^4)$, $4s(\zeta_4=1.14)$, $4p(d^2p^2)$, and 3Cl(−0.5) valence orbitals are shown in Table 6. It is important to note the radical disparity with semiempirical MO calculations. In both the extended Wolfsberg-Helmholz MO calculations (see, *e.g.*, the calculation for MnO_4^- by Viste and Gray [9]) and the recent semiempirical method by Oleari *et al.* [10], the participation of the 4s and 4p orbitals in the molecular orbitals has been restricted almost entirely to the least stabilized virtual orbitals. That is to say, the energetically highest t_2 and a_1 levels ($5t_2$ and $3a_1$ in Ref. [9], $4t_2$ and $2a_1$ in Ref. [10]) are constructed predominantly from the metal 4p and 4s orbitals, respectively, with these metal valence orbitals being little used in the lower, filled molecular orbitals. Certainly the strong participation of the 4p(Ti) orbitals in the $4t_2$ and $2t_2$ levels and less participation in the $5t_2$, and the stronger 4s(Ti) participation in the $2a_1$ level than in the $3a_1$ is unheard of in the semiempirical molecular orbital calculations. The major $3d(t_2)$ participation has thus been relegated to the $5t_2$ level.

Undoubtedly the explicit consideration of the overlap problem through Schmidt orthogonalization of the 4*s*(Ti) and 4*p*(Ti) orbitals to the chlorine valence orbitals has contributed to their strong participation in the bonding molecular orbitals. Thus a major contribution of 4*s* and 4*p* atomic orbital character to the occupied tetrahedral molecular orbitals seems to be an inevitable conclusion of these CNDO-MO calculations.

6. One-Electron Transitions

The electric dipole allowed one-electron transitions from the $^1A_1$ ground state of $TiCl_4$ which are predicted to occur below the first ionization potential (taken as the negative energy of the highest populated MO level, t_1) are shown in Fig. 4

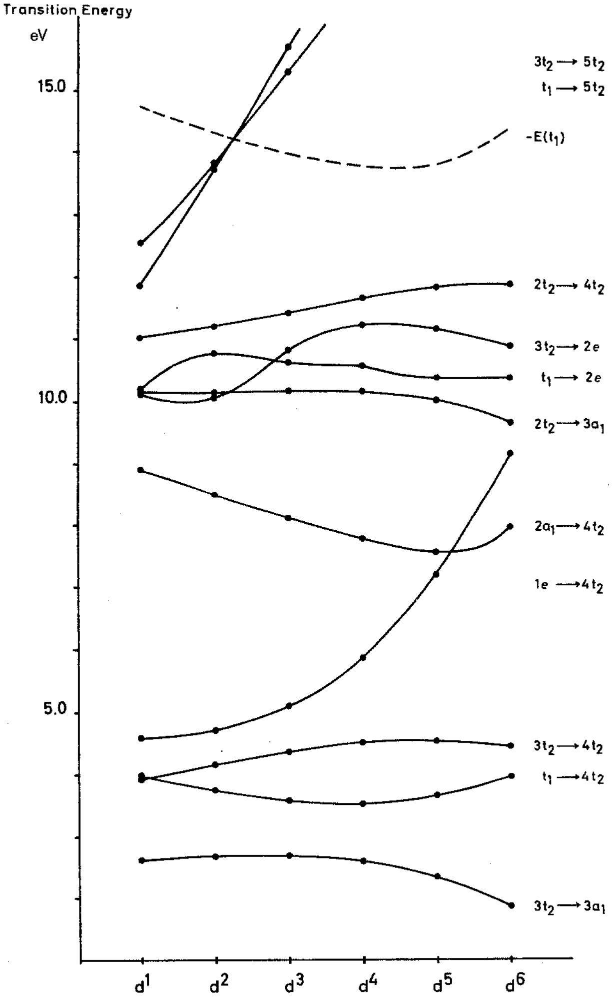

Fig. 4. Dependency of the electric dipole allowed one-electron transitions on the Ti 3*d* orbitals, with $4s(\zeta_4 = 1.14)$, $4p(d^2p^2)$, and Cl(0) other valence orbitals

as functions of the component $3d$(Ti) atomic orbitals. The transition energies have been taken as:

$$\Delta E_{i\to k} = \varepsilon_k - \varepsilon_i - J_{ik} \tag{3}$$

where the exchange and other similar two-electron integrals have been neglected [1, 2]. It is readily seen that a general ordering of the expected one-electron transitions can be reasonably suggested over most of this range of $3d$(Ti) orbital variation: $3t_2 \to 3a_1 < t_1 \to 4t_2 < 3t_2 \to 4t_2 < 1e \to 4t_2 < 2a_1 \to 4t_2 < 2t_2 \to 3a_1, t_1 \to 2e$, $3t_2 \to 2e$, $2t_2 \to 4t_2$. Also of interest is the fact that the lowest energy transition possible, $t_1 \to 3a_1$, not included in this tabulation because it is not an electric dipole allowed transition, remains positive for all the atomic orbital variations performed [*i.e.*, variations of the $3d$, $4s$, $4p$, and Cl$(-\delta)$ valence orbitals].

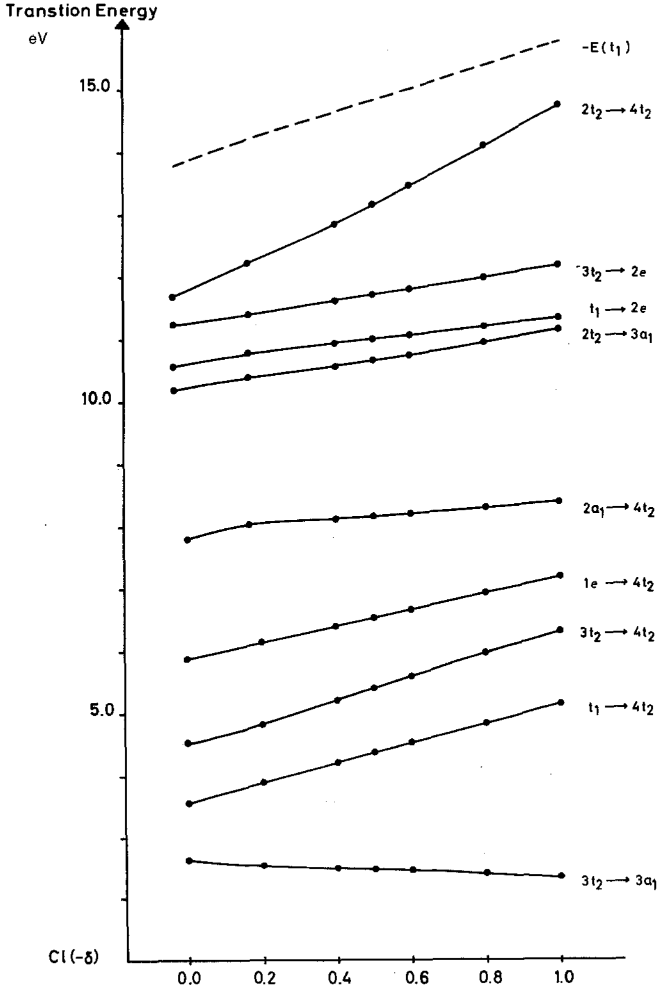

Fig. 5. Dependency of the electric dipole allowed one-electron transitions on the chlorine valence orbitals, with $3d(d^4)$, $4s(\zeta_4 = 1.14)$, and $4p(d^2p^2)$ other valence orbitals

Of more importance than the calculated transition energies themselves – which in general are not expected to be quantitatively acceptable because of numerous approximations [1, 2] (*e.g.*, neglect of exchange integrals and configuration interactions) – is perhaps a pattern for the electronic absorption spectrum which can be predicted from these calculations. On the basis of Fig. 4 we would expect a rather limited number of electronic transitions occuring below the first ionization potential (a maximum of nine predicted, but the upper four are rather close to this ionization limit and may therefore be experimentally obscured), of which the first four are in the near ultraviolet region separated from each other by roughly an electron volt, the fifth seems to be rather isolated in the spectrum being separated from other transitions by 1.5—2 eV, and the last four expected transitions are at high energies and seem to be closely neighboring. Strong configuration-interactions may tend of course to alter this simple picture drastically.

In Fig. 5 the same one-electron transitions have now been treated as a function of the $3\mathrm{Cl}(-\delta)$ valence orbitals, with assumed $3d(d^4)$, $4s(\zeta_4 = 1.14)$, and $4p(d^2p^2)$ orbitals. This variation appears to be linear (with rather slight deviations), and the ordering of the transition energies predicted from the $3d(d^n)$ variations has been retained. The separations between electric dipole allowed transitions seem to be increased slightly with expanded chlorine valence orbitals.

7. Conclusion

In a CNDO-MO treatment of the $TiCl_4$ molecule it is found possible to optimize the Ti 4*s* and 4*p* orbitals at $4s(\zeta_4 = 1.14)$ and $4p(d^2p^2)$, respectively, but valence orbitals which are slightly expanded over those of the free atoms must be assumed for the Ti 3*d* and Cl 3*s* and 3*p* orbitals. The variations of the one-electron MO levels with changes in the valence atomic orbitals is less than might be expected, and a unique ordering of the MO levels can be suggested over wide ranges of atomic orbitals.

The ordering of the unoccupied level is, however, found to be in an inverted order to that predicted from qualitative ligand field theory (Dijkgraaf [11] and Dijkgraaf and Rosseau [12]) or semiempirical MO calculations (Basch *et al.* [13] and Fenske and Radtke [14]). Such treatments lead to the same molecular orbital level diagram for all tetrahedral complexes of first-row transition metals.

Fenske and Radtke's calculation [14] is of the same complexity as ours, but the two methods are different in many respects. In particular the former authors use maximum overlap criteria for choosing their atomic orbitals, where we use arguments based on the value of the total energy, and the overlap problem is treated quite differently. Also, Fenske and Radtke include a metal 4*d* orbital in the basis set, but this is not balanced by simultaneous introduction of metal 5*s* and 5*p* orbitals, and higher ligand orbitals. It is not really surprising, then, that the two methods predict different orderings of the unoccupied levels. What is very pleasing is, however, that there is quite good quantitative agreement between the two schemes as regards the orbital energies for filled levels. The unoccupied levels do not, of course, contribute to the properties of the ground state, and that is the state under investigation in both calculations.

When the unoccupied levels are used for the construction of excited states, as in Section 6, then the results should only be used in a qualitative manner, as changes in the formalism and the dimension of the basis set may have quite drastic effects. A discussion of the electronic spectrum of $TiCl_4$ on the basis of existing calculations will be presented in the following paper.

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References

1. Dahl, J. P., and C. J. Ballhausen: Advances Quantum Chem. **4**, 170 (1967).
2. —, and H. Johansen: Theoret. chim. Acta (Berl.) **11**, 8 (1968).
3. — — Theoret. chim. Acta (Berl.) **11**, 26 (1968).
4. Morino, Y., and H. Uehara: J. chem. Physics **45**, 4543 (1966).
5. Clementi, E., and D. L. Raimondi: J. chem. Physics **38**, 2686 (1963).
6. Richardson, J. W., W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell: J. chem. Physics **36**, 1057 (1962).
7. — R. R. Powell, and W. C. Nieuwpoort: J. chem. Physics **38**, 796 (1963).
8. Mulliken, R. S.: J. chem. Physics **23**, 1833 (1955).
9. Viste, A., and H. B. Gray: Inorg. Chem. **3**, 1113 (1964).
10. Oleari, L., G. De Michelis, and L. Di Sipio: Molecular Physics **10**, 111 (1966).
11. Dijkgraaf, C.: Spectrochim. Acta (Roma) **21**, 769 (1965).
12. —, and J. P. G. Rousseau: Spectrochim. Acta (Roma) **24**, 1212 (1968).
13. Basch, H., A. Viste, and H. B. Gray: J. chem. Physics **44**, 10 (1966).
14. Fenske, R. F., and D. D. Radtke: Inorg. Chem. **7**, 479 (1968).

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