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CNDO Investigations of the Electronic Structures of $TiCl_4$ and $TiCl_6^{2-}$

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The electronic structures of $TiCl_4$ and $TiCl_6^{2-}$ are investigated on the basis of CNDO procedure. Average energies of electronic configurations of atoms are used to evaluate local core hamiltonian $U_{\mu\mu}$ and the Slater exponents which reproduce one-center repulsion integrals $\gamma_{\mu\nu}$ assuming that they arise from spherically symmetric charge distributions of the valence atomic orbitals. Quite good agreement has been obtained in the interpretation of the experimental data as the photoelectron spectrum of $TiCl_4$ and the optical spectra of the examined systems.

Introduction

Molecular orbital calculations according to the semi-quantitative CNDO method are at present largely employed to discuss the electronic structure of molecules. Pople and coworkers[1] have given appropriate parameters to compute wavefunctions for molecules containing the elements H to Cl and obtained good outcome in reproducing some observables connected with the ground state. Del Bene and Jaffè[2] however pointed out that a substitution of semi-empirical coulomb integrals, similar to those of Pople–Pariser–Parr, and of new resonance integrals in the CNDO method is necessary in order to obtain significant results about the electronic spectrum of organic molecules.

Dahl and Johansen[3] applied to transition metal compounds a CNDO procedure in which all the coulomb integrals were evaluated theoretically considering the atomic orbitals to be angular independent and no empirical parameter was introduced. In spite of such nearly rigorous approach the results have received some criticisms.[4]

Other authors[5] emphasized that the valence orbitals cannot be treated according to a complete neglect of differential overlap method and that invariance to local axes rotation and hybridisation must be sacrificed in dealing with transition metal compounds.

Method of Calculation

The use of CNDO approximations in the Roothaan LCAO SCF equations is well understood and described in various papers.[6] Applications of the same criteria on the free atoms make necessary to consider only average energies of configurations E_{av} and therefore different configurations belonging to the same oxidation state of atom differ in energy for the $U_{\mu\mu}$ quantities. Such state of affairs can be partially accepted dealing with the lighter elements even if the value of $\gamma_{\mu\mu}$, calculated on the basis of Slater exponent rule, is greater than the experimental, thus preventing the applicability of CNDO to electronic spectra interpretation.[2]

In the present approach E_{av}'s are evaluated for configurations of three adiacent oxidation states making use of data of ref. 7. The atomic orbitals of the valence set (3d, 4s and 4p for titanium, 3s and 3p for chlorine) are assumed to be s-like in their angular dependence. The E_{av}'s are thus fitted to obtain the $U_{\mu\mu}$ and the Slater exponents ζ_μ associated with the valence set orbitals in such a way that they reproduce the experimental quantities according to the expression:[7]

$$E_{av} = C + \sum_{\mu} n_\mu U_{\mu\mu} + {}^1/_2 \sum_{\mu \neq \nu} n_\mu n_\nu \gamma_{\mu\nu} + {}^1/_2 \sum_{\mu} n_\mu (n_\mu - 1)\gamma_{\mu\mu} \quad (1)$$

The constant C appearing in the expression has the same meaning of the quantity named "ateng" in Pople and Beveridge[6] computer program, provided that it is chosen to fit the electronic ground state of neutral atom; moreover, as outlined,[7] such constant makes the expression (1) able to reproduce E_{av}'s of three adiacent oxidation states.

Titanium ζ' are evaluated considering average energies of the electronic configurations of all the transition metals from Ti to Cu for the oxidation states 0, +1 and +2 by imposing a linear trend all along the sequence. Because of the lack of some $d^{n-2}s^2$ and $d^{n-2}p^2$ configurations in the atomic spectra, ζ' for 4s and 4p are assumed to reproduce the g_{ss} and g_{pp} of ref. 8. One-center quantities for Ti and Cl, evaluated for –1,0 and +1 oxidation states, are summarized in Table I.

Coulomb repulsion integrals matrix elements are thus evaluated theoretically on assuming a spherical charge distribution of the valence set orbitals. For that concerns the core matrix elements $H_{\mu\nu}$, commonly referred to as resonance integrals, they are taken according to the formula $H_{\mu\nu} = {}^1/_2(\beta_\mu + \beta_\nu)S_{\mu\nu}$ where

TABLE I. One-center quantities for titanium and chlorine (U and β in eV).

	U_{ss}	U_{pp}	U_{dd}	β_s	β_p	β_d	ζ_s	ζ_p	ζ_d
Ti	−28.72	−23.29	−36.51	−6.07	−3.35	−5.58	1.15	1.00	1.65
Cl	−102.87	−80.50		−25.26	−14.22		2.34	1.48	

$S_{\mu\nu}$ is the overlap integral and β's are assumed to have the values of the ionization energies as shown in Table I.

$TiCl_4$ is considered to have a regular tetrahedral geometry while $TiCl_6^{2-}$ octahedral with bond distances of 2.17 Å[9] and 2.35 Å[10] respectively. Overlap integrals are evaluated using the radial functions given by Richardson *et al.*[11] for titanium (3d: d^3, 4s: d^2s^2, 4p: d^3p) and by Clementi[12] for chlorine.

Results and Discussion

Eigenvalues of the m.o. are reported in Table II. First of all the electronic structure of $TiCl_4$ will be discussed. The order of the filled m.o., $2a_1 < 2t_2 \approx 1e < 3t_2 < t_1$ agrees with that found by Parameswaran and Ellis[4] in their calculation within the framework of the Hartree–Fock–Slater model and with the assignment of Green *et al.*[13] or of Cox *et al.*[14] by means of $TiCl_4$ and VCl_4 photoelectron spectra. Recently Diemann and Müller[15] investigations on RuO_4 and OsO_4 with He I photoelectron spectroscopy suggest a reverse order of $2a_1$ and $2t_2$ levels for d^0 transition metal tetroxocompounds. The approaches of Fenske and Radtke,[16] Dahl and Johansen,[3] Choplin and Kaufmann[17] to the electronic structure of $TiCl_4$ accord with the latter assignment thus indicating a similarity between all d^0 tetrahedral metal compounds. Nevertheless oxo-compounds with metal–ligand bond distances contracted relative to halide compounds may not have the same level pattern.

TABLE II. Eigenvalues in eV.

$TiCl_4$		$TiCl_6^{2-}$	
$5t_2$	2.90	$4t_{1u}$	13.42
$3a_1$	2.54	$3a_{1g}$	13.30
$4t_2$	−1.54	$3e_g$	8.84
2e	−1.98	$2t_{2g}$	7.89
t_1	−14.22	$3t_{1u}$	−3.87
$3t_2$	−14.98	t_{1g}	−3.98
1e	−16.15	t_{2u}	−4.81
$2t_2$	−16.16	$2e_g$	−5.47
$2a_1$	−16.73	$2t_{1u}$	−6.54
$1t_2$	−27.15	$1t_{2g}$	−7.11
$1a_1$	−30.20	$2a_{1g}$	−7.63
		$1e_g$	−15.12
		$1t_{1u}$	−17.68
		$1a_{1g}$	−21.74

A comparison of orbital eigenvalues with ionization energies, invoking Koopmans[18] approximation, shows that eigenvalues are lower as expected from the intrinsic defect of CNDO and nevertheless that the spread t_1–$2a_1$(2.5 eV) is in good agreement with the experimental (2.2 eV). The first ionization energy of $TiCl_4$ has also been computed from the total energy of such molecule and that obtained for the $TiCl_4^+$ ion. In the latter case the open-shell calculation has been carried out with different m.o. for α and β electrons and with α exceeding β by one. The value obtained of 13.90 eV do not ameliorate to a great extent the value of 14.22 eV of the t_1 level.

In the examined systems the order of the empty m.o. mainly localized on the titanium 3d a.o. makes the d orbital splittings agree with the crystal field theory. Such a finding is not significant by itself because one electron transition energies are governed not only by eigenvalues but also by a change in the interelectronic integrals. However the calculated electronic spectra have the corrected Δ sign which agrees quite well with the experimental.[19,20] The low-energy transitions involve electron jumps from ligands to mainly d orbitals of the metal while in the paper of Dahl and Johansen[3] and Becker *et al.*[20] the low-laying transition in $TiCl_4$, $t_1 \rightarrow 3a_1$. Because of the smallness of the exchange integrals between m.o. relative to the precision of the method, it is meaningless to assign the orbital symmetry to the one-electron singlet–singlet transitions. Therefore the energies, reported in Table III, have been mediated among all the possible singlet states originated from such excitations.

Table IV summarizes the CNDO and the Mulliken electron population obtained from deorthogonalization of CNDO eigenvectors by the $S^{-1/2}$ matrix. The atom charge on titanium of 2.18 in $TiCl_4$ is comparable

TABLE III. Electronic Transition Energies in eV.

$TiCl_4$		$TiCl_6^{2-}$	
$t_1 \rightarrow 2e$	6.0	$3t_{1u} \rightarrow 2t_{2g}$	5.8
$3t_2 \rightarrow 2e$	6.3	$t_{1g} \rightarrow 2t_{2g}$	6.0
$t_1 \rightarrow 4t_2$	6.5	$2e_g \rightarrow 2t_{2g}$	6.6
$3t_2 \rightarrow 4t_2$	7.2	$t_{2u} \rightarrow 2t_{2g}$	6.8
$2t_2 \rightarrow 2e$	7.6	$t_{1g} \rightarrow 3e_g$	7.0

TABLE IV. Electronic Populations According to CNDO (I) and to Mulliken (II) Population Analysis.

		$TiCl_4$		$TiCl_6^{2-}$	
		I	II	I	II
Ti	4s	0.43	0.21	0.43	0.13
	$4p_x$	0.23	0.08	0.26	0.06
	$3d_{z^2}$	0.21	0.19	0.42	0.36
	$3d_{xy}$	0.37	0.33	0.14	0.12
	q_{Ti}	1.35	2.18	1.53	2.61
Cl	3s	1.77	1.90	1.82	1.93
	3p	5.57	5.65	5.77	5.84

with the ~ 2 charge of Parameswaran and Ellis and it is interesting to note that the addition of two chloride ions to give the esachlorotitanate(IV) reduces the population as also the overlap population of the metal–ligand bond. Such populations of 0.52 and 0.36 electrons, respectively for the tetrahedral and octahedral chlorocomplex, are a factor which contributes to the bond force constant and just we have the decrease of the wavenumber of the ν_1 mode from 388 to 316 cm^{-1} on going from $TiCl_4$ to $TiCl_6^{2-}$.[21,22]

Conclusions

The present application of CNDO scheme to the electronic structures of titanium chlorocomplexes gives results which appear to be sufficiently encouraging to improve such method. For instance it will be necessary to investigate the role of β's and to select those values which reproduce accurate *ab initio* wavefunctions and experimental data.

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