

PHOTOELECTRON AND ABSORPTION SPECTRA OF TiCl_4 AND VCl_4 FROM THE ARCANA METHOD

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ABSTRACT

The ARCANA semiempirical molecular orbital calculations have been used to interpret the photoelectron and absorption spectra of TiCl_4 and VCl_4 . The results are compared with experimental values and previously reported theoretical investigations.

INTRODUCTION

THE photoelectron spectra of TiCl_4 and VCl_4 have been reported^{1,2} and their UV absorption spectra thoroughly studied^{3,4}. Different MO methods have been used to examine the photoelectron and absorption spectra of these systems. Calculations using the CNDO and other approximate MO methods were reported⁴⁻⁸. An *ab initio* restricted Hartree-Fock calculations⁹ and an investigation¹⁰ within the framework of the Hartree-Fock-Slater model have been performed.

In this paper the photoelectron and UV absorption spectra of TiCl_4 and VCl_4 have been interpreted within the framework of the ARCANA¹¹⁻¹⁴ semiempirical MO calculations.

Method of calculations: ARCANA is a FORTRAN IV program written¹¹ for doing semiempirical MO calculations of the extended Huckel type in which effects due to the electrostatic potential of neighbour atoms and charge selfconsistency have been included. In a local coordinate system the atomic orbital basis sets are orthogonalized using the Lowdin¹⁵ orthogonalization and then a transformation to the main coordinate system of the molecule has been performed. If we start in the main coordinate system with the AOs i and j belonging to a set α on atom A and k and l belonging to a set β on atom B , the Hamiltonian matrix elements have been calculated using the following equations¹¹

$$H_{ii} = -h_{ii} - \sum_{B \neq A} Z_B \langle i | 1/r_{iB} | i \rangle + G_{ii}, \quad (1)$$

$$h_{ii} = A_\alpha + B_\alpha Q_A, \quad (2)$$

where A_α is the spectroscopic atomic orbital energy, B_α is the change in orbital energy with change in the net

atomic charge Q_A of atom A , r_{iB} is the distance between the charge distribution on atom A and the nucleus of atom B whose nuclear charge is Z_B and the term G_{ii} has been calculated as follows

$$G_{ii} = \sum_B \sum_{k,l} \left[P_{kk} \langle ii | kk \rangle + P_{kl} \langle ii | kl \rangle \right], \quad (3)$$

where electron repulsion integrals of the form $\langle ii | kl \rangle$ are retained here and P_{kl} are the elements of the electron population matrix.

The off-diagonal elements of the Hamiltonian when the AOs i and k belong to different sets are calculated using the following form¹¹

$$H_{ik} = -0.5 S_{ik} (2 - |S_{ik}|) (h_{ii} + h_{kk}), \quad (4)$$

where S_{ik} is the overlap integral between AOs i and k , and when i and j belong to the same set the following expression¹¹ has been used:

$$H_{ij} = - \sum_B Z_B \langle i | 1/r_{Bj} | j \rangle + \sum_k P_{kk} \langle ij | kk \rangle. \quad (5)$$

Finally the two-centre nuclear attraction and electron repulsion integrals have been calculated using the reciprocal mean radius approximation of Corrington and Cusachs¹², and the final state effects in the photoelectron spectra have been considered in interpreting the results.

The TiCl_4 and VCl_4 molecules have been assumed a regular tetrahedral geometry with Ti-Cl bond distance¹⁶ of 2.185 Å and the V-Cl bond distance of 2.14 Å¹⁷. The parameters used in our calculations are summarized in table 1.

RESULTS AND DISCUSSION

In table 2, the ARCANA calculated one-electron orbital energies of the valence levels of TiCl_4 and VCl_4

Table 1 Parameters used in ARCANA molecular orbital calculations

| Atom | Orbital | (a) A_z (eV) | (b) B_z (eV) | (c) R_z (Å) | (d) ζ |
|------|---------|--------------------|-------------------|------------------|----------------|
| Ti | 3d | 5.53 | 12.04 | 0.5821 | 1.421 |
| | 4s | 6.03 | 4.41 | 1.5875 | 0.770 |
| V | 3d | 6.37 | 13.24 | 0.5292 | 1.57 |
| | 4s | 6.32 | 4.63 | 1.5134 | 0.80 |
| Cl | 3s | 25.27 | 11.51 | 0.6085 | 2.24 |
| | 3p | 14.55 ^d | 9.74 | 0.7197 | 1.36 |

(a) From ref. 20 for the configurations ($d^{n-1}s$) in case of metal 4s and 3d orbitals and ($3s^23p^3$) in case of chlorine 3s and 3p orbitals. (b) Calculated as B (a.u.) = $0.4867/R_z$, ref. 11 (c) From ref. 12 (d) From ref. 21.

are compared with their photoelectron ionization potentials^{1,2}. An MO energy level diagram for both system is shown in figure 1. In the case of TiCl_4 the calculated ordering of the valence orbitals by the ARCANA method leads to the ground state configuration $(8a_1)^2(2e)^4(8t_2)^6(9t_2)^6(2t_1)^6$. This orbital ordering is nearly the same as proposed earlier¹, and *ab initio* and the Hartree-Fock-Slater model calculations^{9,10} except that the $2e$ orbital is calculated to be 0.21 eV lower in energy than the $8t_2$ level indicating that these two levels are closely spaced. The ARCANA calculated orbital energies show that the first ionization potential at 11.78 eV in the analysis of the photoelectron spectra¹ of TiCl_4 , corresponds to ionization from the $2t_1$ orbital. The second ionization potential¹ at 12.78 eV corresponds to an ionization from the $9t_2$ orbital. The third observed peak¹ at 13.23 eV can be assigned to an ionization from the closely spaced $8t_2$ and $2e$ orbitals. Finally, the ionization from the $8a_1$ MO can be correlated with the peak observed at 13.97 eV. These assignments agree with those suggested by Green *et al.*¹. However, the ionization potentials calculated by Koopmans theorem from the ARCANA method are higher than the experimental values¹. Similar higher values have also been obtained from *ab initio* and Hartree-Fock-Slater model calculations^{9,10}. In general, studies with Koopmans' theorem for obtaining ionization potentials have shown^{18,19} an overestimation in Koopmans' theorem values compared with experimental values. This was ascribed^{18,19} to the neglect of electronic relaxations and it has been suggested¹⁸ that the values of Koopmans' theorem might be reduced to allow for the imperfect cancellations of the reorganization energy and correlation energy errors.

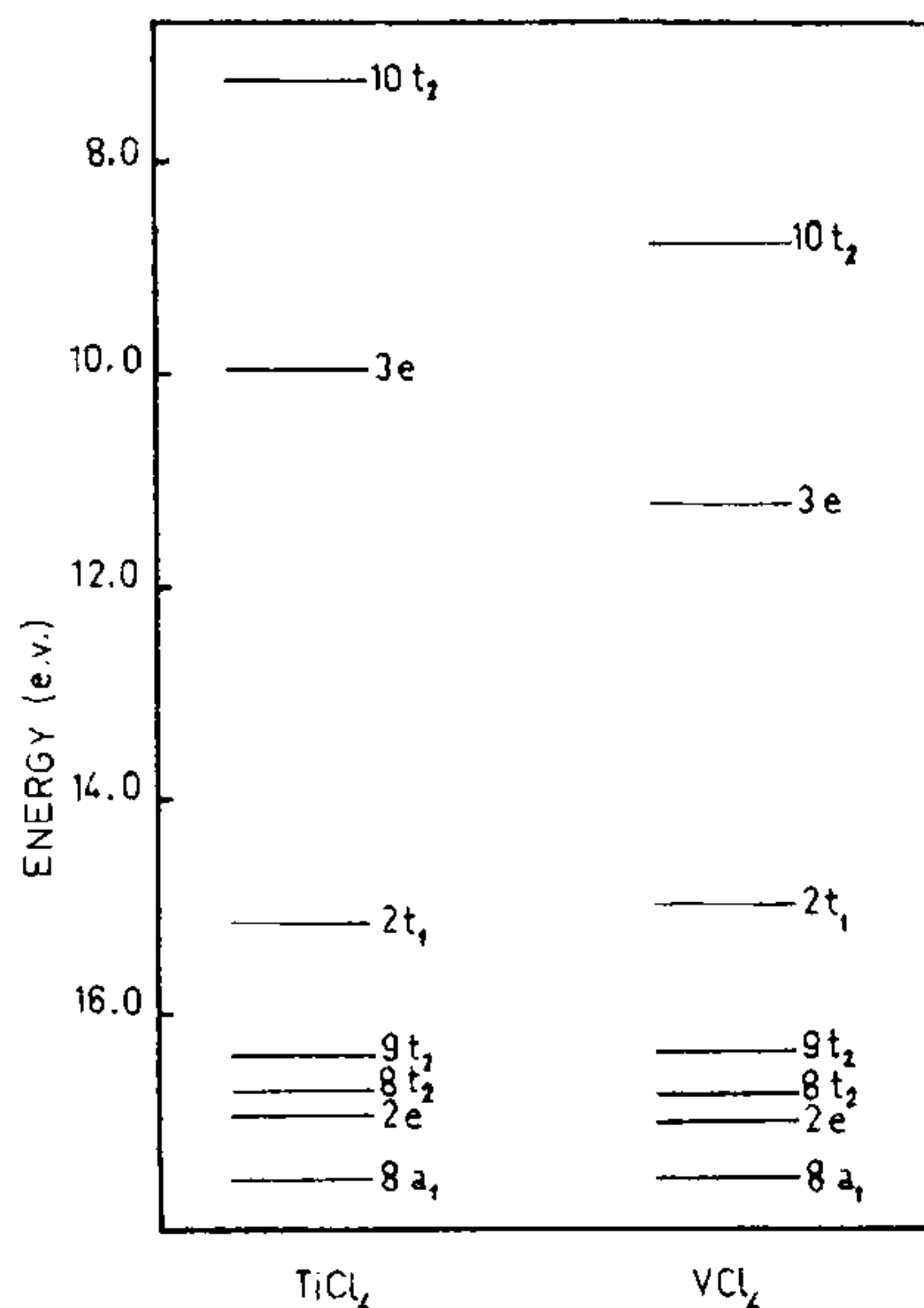


Figure 1. ARCANA MO energy level diagram for TiCl_4 and VCl_4 .

The UV absorption spectrum of TiCl_4 , being a d^0 system with a closed shell ground state, is expected to be dominated by ligand \rightarrow metal charge transfer excitations. The calculated eigenvectors of the $3e$ and $10t_2$ MOs are predominantly Ti 3d in character while those of the $2t_1$, $9t_2$, $8t_2$, $2e$ and $8a_1$ are predominantly

Table 2 ARCANA orbital energies and experimental ionization potentials of TiCl_4 and VCl_4

| Molecule | Orbital | Energy (eV) | Exptl. ^(a) (eV) |
|-----------------|---------|-------------|----------------------------|
| TiCl_4 | $2t_1$ | 15.13 | 11.78 |
| | $9t_2$ | 16.35 | 12.78 |
| | $8t_2$ | 16.71 | 13.23 |
| | $2e$ | 16.92 | — |
| | $8a_1$ | 17.54 | 13.97 |
| VCl_4 | $3e$ | 11.22 | 9.41 |
| | $2t_1$ | 14.96 | 12.88 |
| | $9t_2$ | 16.36 | — |
| | $8t_2$ | 16.73 | 13.54 |
| | $2e$ | 17.01 | — |
| | $8a_1$ | 17.52 | 15.26 |

(a) From ref. 1 for TiCl_4 and ref. 2 for VCl_4 .**Table 3** ARCANA orbital energy differences compared with experimental transition energies for TiCl_4 and VCl_4

| | Transition | Energy (eV) | Exptl. ^(a) (eV) |
|-----------------|--------------------------|-------------|----------------------------|
| TiCl_4 | $2t_1 \rightarrow 3e$ | 5.20 | 4.4 |
| | $2t_1 \rightarrow 10t_2$ | 7.93 | 5.4 |
| | $9t_2 \rightarrow 3e$ | 6.42 | |
| | $9t_2 \rightarrow 10t_2$ | 9.13 | |
| | $8t_2 \rightarrow 3e$ | 6.78 | 7.1 |
| | $8t_2 \rightarrow 10t_2$ | 9.49 | 7.4 |
| | $2e \rightarrow 10t_2$ | 9.70 | |
| | $8a_1 \rightarrow 10t_2$ | 10.32 | |
| VCl_4 | $3e \rightarrow 10t_2$ | 2.47 | 1.12 |
| | $2t_1 \rightarrow 3e$ | 3.74 | 3.05 |
| | $2t_1 \rightarrow 10t_2$ | 6.21 | 4.15 |

(a) From ref. 4 for TiCl_4 and ref. 3 for VCl_4 .

ligand $3p$ orbitals. Thus the ligand $3p \rightarrow$ metal $3d$ transitions will dominate the absorption spectra of TiCl_4 . The observed absorption spectrum⁴ of TiCl_4 shows two bands at 4.4 and 5.4 eV. These bands can be correlated with the $2t_1 \rightarrow 3e$ and $2t_1 \rightarrow 10t_2$ excitations whose transition energies calculated as the one-electron orbital energy differences are 5.20 and 7.93 eV respectively. A broad band was also observed⁴ covering the energy range 6–8 eV with maximum at 7.4 eV and a shoulder at 7.1 eV. The charge transfer excitations from the MOs $9t_2$, $8t_2$, $2e$ and $8a_1$ to the $3e$ and $10t_2$ MOs can be correlated with this broad band.

In the case of VCl_4 the ARCANA calculated ordering of the valence orbitals leads to the ground state configuration $(8a_1)^2(2e)^4(8t_2)^6(9t_2)^6(2t_1)^6(3e)^1$. As in TiCl_4 the $2e$ level is calculated to be 0.28 eV lower in

energy than the $8t_2$ level which is also different from the *ab initio* results⁹ and Hartree-Fock-Slater model calculations¹⁰. The calculated ionization potentials by Koopmans' theorem are given in table 2. The observed photoelectron spectrum² of VCl_4 shows¹ many more peaks than that of TiCl_4 . This can be ascribed to the multiplet structure resulting from the ionization of an electron from any of the inner filled levels in this open shell system. Thus, a comparison of the calculated one-electron energies of VCl_4 with experimental values will not be very significant. However, the first observed peak at 9.41 eV can be clearly assigned to the ionization of the unpaired $3e$ electron to give the VCl_4^+ closed shell system. The three peaks observed at 12.88, 13.54 and 15.26 eV have been assigned to ionizations from the $2t_1$, $8t_2$ and $8a_1$ MOs respectively¹⁰. As in TiCl_4 , the imperfect cancellation of the reorganization energy and the correlation energy errors may explain the overestimation in the Koopmans' theorem calculated ionization potentials.

The UV absorption spectrum of VCl_4 shows³ three bands at 1.12, 3.05 and 4.15 eV. The low-lying energy band can be assigned as a $3e \rightarrow 10t_2$ *d-d* transition with a calculated excitation energy of 2.47 eV. The other two bands may be correlated with the two charge transfer transitions $2t_1 \rightarrow 3e$ and $2t_1 \rightarrow 10t_2$ which are predominantly ligand $3p \rightarrow$ metal $3d$ transitions. The calculated one-electron orbital energy differences for these excitations are 3.74 and 6.21 eV respectively. As seen from table 3, the ARCANA calculated transition energies are higher than the experimental values. However, similar results have been obtained⁹ using *ab initio* calculations with limited configuration interaction where the higher values calculated for the charge

transfer states have been ascribed to the high electron reorganization occurring during excitation.

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ANNOUNCEMENT

ALL INDIA SEMINAR ON ANIMAL, PLANT AND MICROBIAL TOXINS

An "All India Seminar on Animal, Plant and Microbial Toxins" will be held during **March 4-6, 1987**, at the Department of Life Sciences, University of Bombay. Major Scientific Sessions and Invited Lectures on important themes shall be arranged. Among the topics to be covered are: 1. Biology/Anatomy; 2. Chemistry/Biochemistry; 3. Physiology/Pharmacology; 4. Structure—function re-

lationship/evolution and 5. Immunological and chemical aspects. The presented papers will be published as proceedings. For details please contact: Dr. Vijay Khole, Convenor, All India Seminar on Animal, Plant and Microbial Toxins, Department of Life Sciences, University of Bombay, Vidyanagari, Santacruz (East), Bombay 400 098.