

SINDO THEORY OF TRANSITION METAL COMPOUNDS. II. PHOTOELECTRON AND UV SPECTRA OF $TiCl_4$ AND VCl_4 *

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A scaled INDO semi-empirical method, called SINDO, has been applied to $TiCl_4$ and VCl_4 to test the method and possibly to reinterpret the photoelectron and UV spectra of these molecules in the gaseous state. The method involves one adjustable parameter for each molecule. Two versions of the method are discussed, SINDO/1 and SINDO/2. In the latter version integrals depend on charge and configuration of atoms. The ground state and excited states have been discussed in terms of the Longuet-Higgins and Pople SCF theory, with the energy corrected to account for a proper interelectronic repulsion and a proper total spin. Both versions yield acceptable results. However, similarly as in the case of free atoms and ions, results obtained with SINDO/2 are better.

1. Introduction

In Part I [1] a new semi-empirical INDO-type treatment has been suggested suitable for transition metal compounds. It has been called SINDO, from Scaled INDO. In SINDO/1, the Condon-Shortley parameters F^0 and F^2 are empirical parameters of atomic origin. All other Condon-Shortley parameters are calculated theoretically with approximate Hartree-Fock atomic orbitals and scaled afterwards by the ratio of appropriate empirical and theoretical values of F^2 . Ohno's formula is used for two-center repulsion integrals and Mulliken's one for resonance integrals. In SINDO/2 additional scaling of integrals is performed as a function of charge and configuration of the appropriate atoms. It is

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assumed in this stage that all relative changes in integrals are reproduced to a sufficient accuracy by integrals over Slater-type orbitals with the exponents varied in accordance with the Burns rules. Details of the method and a review of the subject has been given in Part I. It has been shown there that SINDO/1, and particularly SINDO/2, form a sound basis for the theory of transition elements. In the present study we are going to show that SINDO is also useful in the case of molecules.

In the study presented, the Longuet-Higgins and Pople form of SCF equations for closed and open shell systems was used [2], separately for all ground and excited states. The purpose was to optimize the orbitals for all states independently. The total energy was then calculated exactly within the framework of SINDO, with the total wave function being always an eigenfunction of S^2 (square of the total spin) and always of proper symmetry (basis of an irreducible representation).

2. Spectral properties of $TiCl_4$

The electronic structure of $TiCl_4$ has been the subject of many papers. Apart from a pure electrostatic model like that of Jørgensen [3], simplified MO picture like that of Dijkgraaf [4], SCCO MO calculations published by Basch, Viste and Gray [5] several more sophisticated studies appeared related to CNDO [6]-[9], INDO [10] or the $X\alpha$ method [11].

A first (non-empirical) CNDO-type calculation was performed by Dahl and Johansen in 1968 [6]. Considering virtual SCF orbitals the authors claimed a reversion of the approximately d -type levels, $4t_2 < 2e$, in contrast to the prediction of the crystal field theory (CFT). The calculated difference was 8.4 eV, large enough to believe that only drastic changes could reverse the order again. Additional variation of atomic orbitals was performed by Becker and Dahl in 1969, with no change, however, in this conclusion [7]. The method was applied also to interpret the UV spectrum [8]. Numerical agreement with experiment was poor, but the assignment of bands was believed to be adequate.

A qualitatively different result was obtained by Fenske and Radtke [12]. In the case of their virtual orbitals $2e < 4t_2$, in agreement with CFT.

Evaluation of ionization potentials through the use of the Koopmans theorem was performed by Choplin and Kaufman with the modified GTO-CNDO/2 technique [9], by Truax, Gere and Ziegler with a non-empirical INDO technique [10] and by Parameswaran and Ellis with the familiar $X\alpha$ method [11]. The experimental photoelectron spectrum and a tentative assignment of bands were given by Cox, Evans, Hammett and Orchard [13]. The assignment of bands differed from one work to the other and the numerical agreement with experiment was not always satisfactory.

For all these reasons we found it interesting to reconsider the electronic properties of $TiCl_4$, basing on the SINDO theory. To avoid arbitrariness just a single empirical parameter was left, β_{AB}^0 in formula (13) of Part I [1], common here for all types of interactions within the molecule. Atomic orbitals and atomic parameters were exactly the same as those discussed in Part I. The experimental value of the bond length was assumed, $R_{Ti-Cl} = 2.17 \text{ \AA}$.

The resulting interpretation of the first three bands of the UV absorption spectrum and the optimal choice of β_{AB}^0 follow directly from Fig. 1. Dotted horizontal lines represent the experimental maxima found by Becker, Ballhausen and Trabjerg [8]. Dotted vertical lines refer to the optimal values of β_{AB}^0 , in accordance with a least square fit.

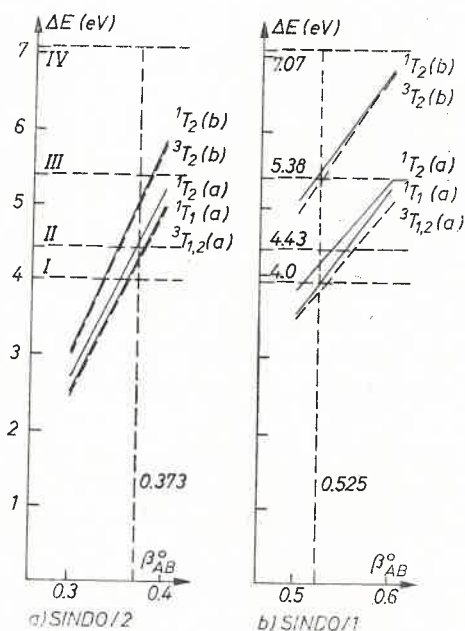


Fig. 1. Theoretical analysis of the UV spectrum of gaseous TiCl_4

The following conclusions can be drawn from Fig. 1.

(i) The calculated transition energies depend sharply on β_{AB}^0 . A least square fit to all three bands yields $\beta_{AB}^0 = 0.373$ in the case of SINDO/2 and $\beta_{AB}^0 = 0.525$ in the case of SINDO/1.

(ii) Comparing the results of SINDO/1 and SINDO/2 one finds a slightly better fit to experiment in the case of SINDO/1. Maximum deviation amounts to 0.15 eV and 0.30 eV accordingly.

(iii) Singlet and triplet excited states are strongly overlapping; for this reason triplet states might be difficult to observe.

(iv) Numerical agreement with experiment is now qualitatively better than that of the CNDO treatment of Becker et al. [8] (Table I).

(v) The assignment of the bands is now different (Table I). According to the present calculations the first two bands result from the same orbital excitation, $1t_1 \rightarrow 2e$. In all the former treatments the transition energy was estimated from the difference of orbital energies of occupied and virtual orbitals. Only the average energy of 1T_1 and 1T_2 could be thus estimated in this way. Our calculation, being more sophisticated, seems to be more reliable at least in this respect.

TABLE I

Electronic absorption spectrum of gaseous TiCl_4 (in eV)

Assignment	SINDO/1 ^a	SINDO/2 ^b	Experiment [8]	CNDO [8]
$(1t_1 \rightarrow 2e) \ ^3T_2$	3.88	4.24	—	—
$\ ^3T_1$	3.90	4.26	—	—
$\ ^1T_1$	3.99	4.28	ca 4.0	$t_1 \rightarrow 3a_1$ (1.39)
$\ ^1T_2$	4.28	4.51	4.43	$3t_2 \rightarrow 3a_1$ (2.49)
$(1t_1 \rightarrow 4t_2) \ ^3T_2$	5.37	5.04	—	—
$\ ^1T_2$	5.52	5.07	5.38	$t_1 \rightarrow 4t_2$ (4.39)

^a for $\beta_{AB}^0 = 0.525$; ^b for $\beta_{AB}^0 = 0.373$.

(vi) SCF energies of $(1t_1 \rightarrow 2e) \ ^1T_{1,2}$ terms are lower than that of the $(1t_1 \rightarrow 4t_2) \ ^1T_2$ state. Hence the splitting of the approximately d -type levels, $2e$ and $4t_2$, is here qualitatively the same as that following from CFT, being correct to the order of 1 eV. Thus the conclusion on the order of d -type levels, drawn by Dahl and Johansen [6], Becker and Dahl [7], is not confirmed.

The dependence of ionization energies on β_{AB}^0 is shown in Fig. 2. Dotted horizontal lines correspond to the experimental values found by Cox et al. [13]. Dotted vertical lines correspond to β_{AB}^0 's which had been found to be optimal in the case of the UV

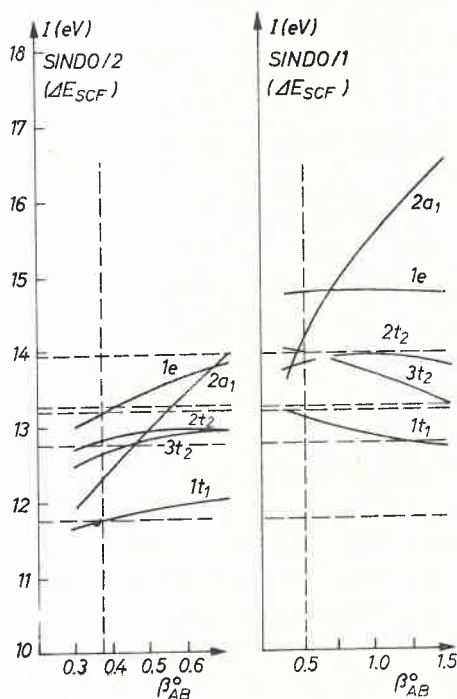


Fig. 2. Theoretical analysis of the photoelectron spectrum of gaseous TiCl_4

spectrum. Interpolated ionization energies are compared with experiment and with other theoretical results in Table II. From Fig. 2 and Table II the following conclusions can be drawn:

TABLE II
Photoelectron spectrum of gaseous TiCl_4 (in eV)

Experiment [13]	CNDO2-GTO [9]	Non-emp. INDO [10]	$X\alpha$ [11]	SINDO/1	SINDO/2
11.78	($1t_1$) 14.39	(t_1) 13.69	($2t_1$) 12.2	($1t_1$) 13.13	($1t_1$) 11.75
12.79	($3t_2$) 15.32	(t_2) 15.89	($9t_2$) 12.7	($2t_2$) 13.87	($2t_2$) 12.35
13.23	($2t_2$) 15.86	(e) 17.00	($2e$) 13.0	($3t_2$) 14.00	($3t_2$) 12.65
		(a_1) 17.03		($2a_1$) 14.07	($2t_2$) 12.83
13.97	($1e$) 16.54	(t_2) 19.42	($8t_2$) 13.8	($1e$) 14.78	($1e$) 13.22
	($2a_1$) 16.82		($8a_1$) 14.1		

(i) Definitely the best numerical agreement with experiment is obtained in the case of SINDO/2 (with no additional fitting of the parameters) and in the case of $X\alpha$ [11] (with fitted α , $\alpha = 0.85$). On the other hand, the agreement in the case of GTO-CNDO/2 [9] and non-empirical INDO [10] is relatively poor.

(ii) In contrast to SINDO/2 the assignment of the photo-electron bands is not unique in the case of SINDO/1.

(iii) Assignment of the lowest band is the same in all treatments (ionization from $1t_1$). Assignment of the other bands, however, varies from case to case. According to our SINDO/2-type calculations the second band corresponds to the ionization from $2a_1$, the third one (asymmetric and broad) to a superposition of ionizations from $2t_2$ and $3t_2$, the fourth one to the ionization from $1e$.

(iv) In contrast to the other authors we did not try to estimate ionization energies from the Koopmans theorem. Ionization energies estimated from this theorem show in our calculations, a much larger spread, similar to that found by the other authors. Also the ordering of occupied orbital levels ($1a_1 < 1t_2 < 2a_1 < 2t_2 < 1e < 3t_2 < 1t_1$) does not follow exactly the order found by independent SCF calculations for each state.

(v) Ionizing $1t_1$, $3t_2$, $2a_1$ or $1e$ electron one obtains a total wave function of a different symmetry in each of these four cases. No essential problem appears then when performing SCF-type calculations. Explanation, however, requires the calculation of the ionization energy from the $2t_2$ level, lower than that of $3t_2$. A fixed electronic configuration has been enforced in this calculation, $(1a_1)^2 (1t_2)^6 (2a_1)^2 (2t_2)^5 (1e)^4 (3t_2)^6 (1t_1)^6$. It was tested that the final wave function was practically orthogonal to the SCF wave function of the lower state of the same symmetry, corresponding to $(1a_1)^2 (1t_2)^6 (2a_1)^2 (2t_2)^6 (1e)^4 (3t_2)^5 (1t_1)^6$. Basically the same procedure is currently used in the transition state version of the $X\alpha$ method.

(vi) Note that occupation of orbitals of the lowest possible orbital energy must not necessarily lead to the lowest total energy! A good example is just the crossing of the

total SCF energies in Fig. 2 in the case of ionizations from $2t_2$ and $3t_2$ levels, found in the case of SINDO/1. One is usually not quite aware of such a possibility. Consequences of this effect might be important not only in a semi-empirical theory.

3. Spectral properties of VCl_4

The electronic structure of VCl_4 has been studied by several methods, both experimental and theoretical. Restricting the discussion to more advanced theoretical models, we would like to point out some difficulties raised with regard to the ground state of this molecule.

According to CFT it is a d^1 case, with 2E being the ground state. The same result was obtained in the parameter-free MO calculation by Fenske and Radtke [12], and in the $X\alpha$ -type calculation by Parameswaran and Ellis [11]. Becker and Dahl [14], on the other

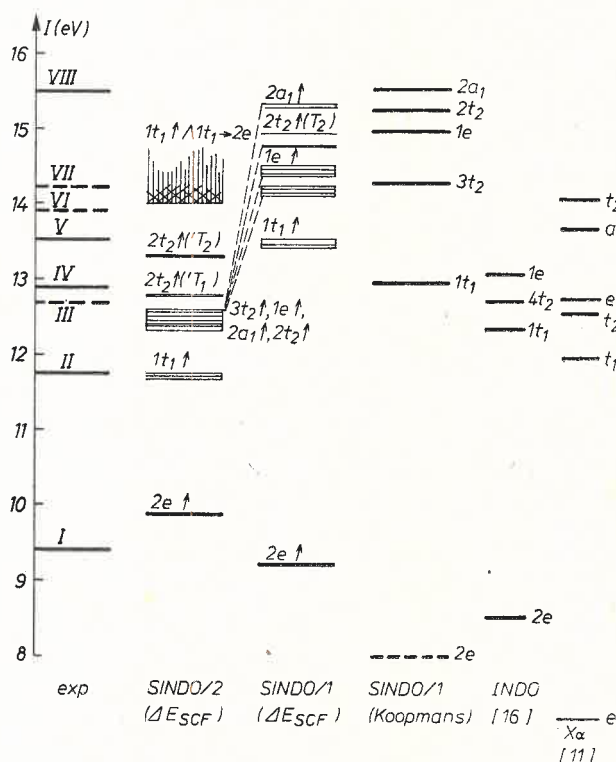


Fig. 3. Theoretical analysis of the photoelectron spectrum of gaseous VCl_4 and a comparison with results obtained by other authors

hand, basing on the non-empirical CNDO method and neglecting off-diagonal Lagrangian multipliers found the 2T_2 term to be that of ground state, with the $4t_2(d)$ level lying thus lower than that of $2e(d)$. To still a different conclusion came Copeland and Ballhausen [15].

TABLE III

Photoelectron spectrum of VCl_4 (in eV)

P. E. Spectrum ^a		SINDO/2 (for $\beta_{AB}^0 = 0.3$)		SINDO/1 (for $\beta_{AB}^0 = 0.6$)	
Band	Value (intensity)	I_{calc}	Probable assignment	I_{calc}	Probable assignment
I	9.41(w)	9.9 ^b	$2e\uparrow: {}^1A_1$	9.2 ^c	$2e\uparrow: {}^1A_1$
II	11.75(s)	11.7— 11.8	$1t_1\uparrow: {}^1T_1(11.8); {}^3T_1(11.7);$ ${}^3T_2(11.7)$	13.4— 13.5	$1t_1\uparrow: {}^1T_1(13.5); {}^3T_1(13.5);$ ${}^3T_2(13.4)$
III	(12.68) ^d	12.3—	$1t_1\uparrow: {}^1T_2(12.3)$	14.1—	$1t_1\uparrow: {}^1T_2(14.1)$
IV	12.88(s)	12.8	$3t_2\uparrow: {}^1T_1(12.4); {}^3T_2(12.4);$ ${}^3T_1(12.5); {}^1T_2(12.6)$ $1e\uparrow: {}^{1,3}A_1(12.4); {}^3E(12.5);$ ${}^3A_2(12.6); {}^1E(12.8);$ $2a_1\uparrow: {}^1A_1(12.6); {}^3A_1(12.5)$ $2t_2\uparrow: {}^3T_2(12.6); {}^{1,3}T_1(12.8)$	14.6	$3t_2\uparrow: {}^1T_1(14.2); {}^3T_2(14.2);$ ${}^3T_1(14.1); {}^1T_2(14.4)$ $1e\uparrow: {}^3A_1(14.5); {}^3E(14.6);$ $2t_2\uparrow: {}^3T_2(14.4); {}^1T_1(14.5);$ ${}^3T_1(14.4)$
V	13.54(ms)	13.3	$2t_2\uparrow: {}^1T_2(\text{ca } 13.3)$	14.7— 14.9	$2t_2\uparrow: {}^1T_2(14.7)$ $1e\uparrow: {}^{1,3}A_2(14.8); {}^1E(14.9)$
VI	(13.9)(m) (14.2)(m)	$\geq 14.0^e$	$(1t_1\uparrow \wedge 1t_1 \rightarrow 2e)^5T_1, {}^3T_2,$ ${}^2T_1, {}^3E, {}^3A_2, 2^1A_1, {}^1A_2,$ ${}^3E, {}^1T_1, {}^3T_2$	15.3	$2a_1\uparrow: {}^{1,3}A_1(15.3)$

^a after Ref. [13]; ^b 9.4 eV for $\beta_{AB}^0 = 0.33$; ^c 9.4 eV for $\beta_{AB}^0 = 0.58$; ^d values in brackets are estimated from Fig. 1 of Ref. [13]; ^e 14.0 refers to 5T_1 . Average energy of the configuration of the ionized state is higher by ca 5 eV.

They carried out unrestricted CNDO-type calculations for possible open shell ground states, followed by a spin-projection to insure a relatively pure doublet state. In accordance with their calculations 2A_1 should be the ground state. This raised the question as to the applicability of the CNDO method to complex compounds [11]. However, it has been shown by Truax, Geer and Ziegler [16] that in the case of their non-empirical scheme the 2E ground state is also obtained and that the order of orbital levels resembles that found by Parameswaran and Ellis.

The photoelectron spectrum of gaseous VCl_4 was originally discussed by Truax et al. [16] and Parameswaran et al. [11], based on the Koopmans theorem. According to our SINDO-type calculations, ionization from the $2e$ level depends strongly on β_{AB}^0 . Carrying out several sets of calculations with the step $\Delta\beta_{AB}^0 = 0.1$ it was found that best results are obtained around $\beta_{AB}^0 = 0.3$ in the case of SINDO/2 and 0.6 in the case of SINDO/1. Results of these approximately optimal calculations are reproduced in detail in Table III and compared with experiment and other results in a condensed way in Fig. 3.

(i) The overall numerical agreement with experiment is again the best in the case of SINDO/2. SINDO/1 yields results of a numerical agreement with experiment comparable to that of Parameswaran and Ellis.

(ii) In our SINDO-type calculations a single empirical parameter was introduced, β_{AB}^0 , to reproduce the molecular properties. We recall that also in the case of appropriate $X\alpha$ -type calculations a single empirical parameter was introduced, α , in order to obtain an overall good agreement with experiment ($\alpha = 0.85$) [11].

(iii) The assignment which follows from the SINDO/2 method is substantially different from that suggested in the other works. The reason seems to lie in the use of the Koopmans theorem by the other authors. It is shown in Fig. 3 that, for example in the case of SINDO/1, the Koopmans theorem leads again to an ordering of ionizations quite similar to that found in non-empirical INDO [16] and $X\alpha$ [11] methods.

(iv) The photoelectron spectrum of gaseous VCl_4 was measured by Cox et al. [13]. Let us discuss the possible assignment of bands as following from the SINDO/2 theory. Band I is certainly due to the ionization from $2e$. Band II is basically related to the ionization of the $1t_1$ electron, similarly as in the other treatments; terms 1T_1 , 3T_1 and 3T_2 have here almost the same energy. Band IV and the superimposed band III seem

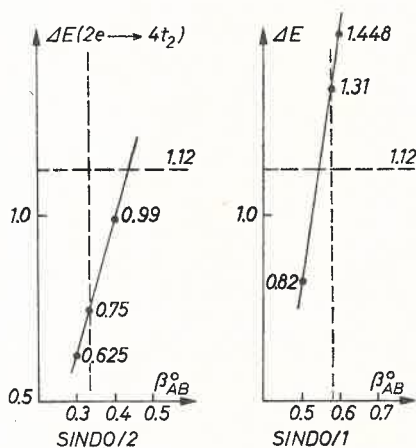


Fig. 4. Dependence of the first transition energy of VCl_4 on β_{AB}^0

to have quite a complex origin. Several molecular terms due to the ionization from $3t_2$, $1e$, $2a_1$ and even $2t_2$ lie quite closely together, being likely responsible for these two bands. Band V might then correspond to ionization from $2t_2$, with 1T_2 as the final state. Bands VI, VII and VIII are in the tail of the spectrum. SINDO/2 bears rather an untypical explanation of these bands. In SINDO/2 all other single ionizations yield ionization energies of the order of 20 eV; however, one can hardly exclude ionization, say from the $1t_1$ level, associated with a simultaneous excitation of a second electron, say from the $1t_1$ state to the low lying $2e$ state. The lowest calculated energy of such a two-electron process is 14.0 eV (to the 5T_1 state). This value is almost identical with the maximum of band VI (13.9 eV). The spread of molecular terms due to

this ionization-excitation process is quite large. A detailed numerical analysis is laborious and rather unjustified in this approximation.

The lowest excitation energy observed in the UV absorption spectrum is equal to 1.12 eV [17]. It corresponds to an approximately $d-d$ type transition. The transition energy calculated by Parameswaran and Ellis [11] was too low (0.6 eV) and that calculated by Truax et al. [16] was too high (1.71 eV). Both these estimations were based on the orbital level scheme. In Fig. 4 we give the dependence of this excitation energy in accordance with SINDO/1 and SINDO/2, based on optimized orbitals separately for the ground state and the excited state, as a function of β_{AB}^0 . The dotted vertical lines correspond to the values of β_{AB}^0 in the case of which a best overall agreement with experimental photoelectron and UV absorption spectra has been obtained: 0.335 in the case of SINDO/2 and 0.578 in the case of SINDO/1. Excitation energies interpolated from Fig. 4 are 0.75 eV and 1.31 eV accordingly.

Certainly a better agreement with experiment could be obtained varying β_{AB}^0 with the type of bonded atoms and the type of orbitals. The results would then show, however, some ambiguity which we have tried to avoid.

4. Comments on the electronic structure of VCl_4 and $TiCl_4$

In Fig. 5 we show the dependence of the net charge of the metal ion as a function of β_{AB}^0 . It is interesting to note that it is almost identical for both atoms, V and Ti. The estimated net charge depends strongly on the model. According to SINDO/2 it lies in the range from 1.8 to 2.0, according to SINDO/1 in the range from 0.4 to 0.6.

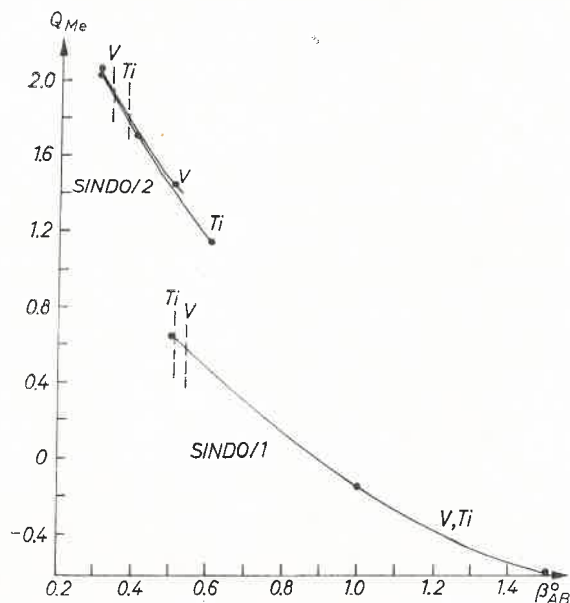


Fig. 5. Dependence of the net charge Q_{Me} of the metal (Ti, V) on β_{AB}^0 . Dotted vertical lines correspond to optimal values of this parameter

In Table IV the population of atomic orbitals is given for selected molecular states. Let us consider the excitation $2e \rightarrow 4t_2$ in VCl_4 . We see from the table that $\Delta d(e) = -1.16$ and $\Delta d(t_2) = +1.18$; an excited electron pulls another electron with it. The mechanism of this process is simple: in accordance with Table IV there is a charge transfer from $d(e)_V$ to $p_{\pi L}(e)$ and a strong back donation of σ -type electrons from ligands s and p_{σ} type orbitals to $d(t_2)_V$.

TABLE IV

Population of atomic orbitals for selected molecular states (SINDO/2, $\beta_{AB}^0 = 0.3$)

State	s_{Me}	p_{Me}	$d(e)_{Me}$	$d(t_2)_{Me}$	s_{L1}	$p_{\sigma L1}$	$p_{\pi L1}$		p_{nL1}
							(e)	(t_2)	
VCl_4									
ground state	0.325	0.537	1.359	0.734	1.874	1.821	0.910	1.407	1.500
$2e \rightarrow 4t_2$	0.322	0.532	0.203	1.918	1.647	1.782	0.949	1.399	1.500
$2e\uparrow$	0.373	0.598	0.384	1.556	1.637	1.643	0.904	1.361	1.500
TiCl_4									
ground state	0.307	0.463	0.302	0.875	1.878	1.804	0.925	1.406	1.500
$1t_1\uparrow$	0.310	0.479	0.332	0.893	1.879	1.802	0.917	1.398	1.250

Somewhat different pictures are in the case of the ionization from the $2e$ level. Subtraction of the practically d -type electron (in 88%) is followed by a large charge redistribution. The final net charge of vanadium is changed insignificantly. The reason is a strong back donation of σ -type electrons. In result $\Delta d(t_2) = +0.82$.

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REFERENCES

- [1] A. Gołębiewski, R. Nalewajski, M. Witko, *Acta Phys. Pol.* **A51**, 617 (1977).
- [2] H. C. Longuet-Higgins, J. A. Pople, *Proc. Phys. Soc. (London)* **A68**, 591 (1955).
- [3] G. Berthier, *Advan. Quantum Chem.* **8**, 183 (1974).
- [4] C. Dijkgraaf, *Spectrochim. Acta* **21**, 769, 1419 (1965).
- [5] H. Basch, A. Viste, H. B. Gray, *J. Chem. Phys.* **44**, 10 (1966).
- [6] J. P. Dahl, H. Johansen, *Theor. Chim. Acta* **11**, 26 (1968).
- [7] C. A. L. Becker, J. P. Dahl, *Theor. Chim. Acta* **14**, 26 (1969).
- [8] C. A. L. Becker, C. J. Ballhausen, I. Trabjerg, *Theor. Chim. Acta* **13**, 355 (1969).
- [9] F. Choplin, G. Kaufmann, *Theor. Chim. Acta* **25**, 54 (1972).
- [10] D. R. Truax, J. A. Geer, T. Ziegler, *J. Chem. Phys.* **59**, 6662 (1973).
- [11] T. Parameswaran, D. E. Ellis, *J. Chem. Phys.* **58**, 2088 (1973).
- [12] R. F. Fenske, D. D. Radtke, *Inorg. Chem.* **7**, 479 (1968).
- [13] P. A. Cox, S. Evans, A. Hammett, A. F. Orchard, *Chem. Phys. Lett.* **7**, 414 (1970).
- [14] C. A. L. Becker, J. P. Dahl, *Theor. Chim. Acta* **19**, 135 (1970).
- [15] D. A. Copeland, C. J. Ballhausen, *Theor. Chim. Acta* **20**, 317 (1971).
- [16] D. R. Truax, J. A. Geer, T. Ziegler, *Theor. Chim. Acta* **33**, 299 (1974).
- [17] D. S. Alderdice, *J. Mol. Spectrosc.* **15**, 509 (1965).