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Ab Initio Calculations of the Ground, Excited, and Ionic States of Titanium and Vanadium Tetrachlorides

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Ab initio restricted Hartree–Fock calculations of the ground states of $TiCl_4$, VCl_4, and VCl_4^+ are described. The excited states of these molecules are calculated by means of configuration interaction calculations and are used to interpret the absorption spectra of $TiCl_4$ and VCl_4 and the photoelectron spectrum of VCl_4. The photoelectron spectrum of $TiCl_4$ is discussed with the aid of Koopmans' theorem. These calculations lead to a generally satisfactory interpretation of the spectroscopic data.

The d^0 and d^1 systems, $TiCl_4$ and VCl_4, are among the simplest and most fundamental transition metal complexes. For these reasons they have been extensively studied both theoretically and experimentally. The He(I) photoelectron spectra[1,2] and uv absorption spectra of these molecules have been reported[3,4] and have been discussed with the aid of CNDO[5] and other[6] approximate molecular orbital (MO) methods and by the use of the Hartree–Fock–Slater (HFS) model.[7] In this paper we report ab initio calculations of the ground, excited, and ionic states of these molecules to discuss their mode of bonding, and to interpret the spectroscopic data related to the electronic structure of these molecules.

Computation Details

The ground states of the two molecules were calculated by the restricted Hartree Fock (RHF) method using a basis of Gaussian type functions (GTF). The core atomic orbitals and metal 4s and chlorine 3s orbitals were represented by a single Slater type orbital (STO) with best atom exponents,[8] expanded in three GTF's.[9] The metal 3d and chlorine 3p orbitals were a double-ζ basis of STO's,[10] expanded in three and two GTF's, respectively. Metal 4p STO's of exponent unity were used, expanded in three GTF's.

Excited states were calculated by the configuration interaction method, using as basis MO's those obtained from the RHF calculations on the $^1A_1$ and ^2E ground states of $TiCl_4$ and VCl_4 respectively. The expansions included singly excited configurations only, 192 for $TiCl_4$, involving the filled MO's ($8a_1 - 2t_1$) and the first 16 virtual MO's, and for VCl_4 single excitations from the $2t_1$ and 2e MO's to the (2e – 4e) MO's.

Valence-shell ionization potentials (IP) of the closed-shell molecule $TiCl_4$ were computed using Koopmans' theorem. Although we have found that such an approximation is inaccurate for many transition metal complexes,[11] due to the different relaxation energies associated with ionization from metal and from ligand MO's, we expect that such an approximation will not be seriously in error for the d^0 system, $TiCl_4$. The calculation of the ionization potentials of the open-shell molecule VCl_4 is rather more complicated due to the possibility of forming both singlet and triplet states of VCl_4^+ from the same orbital configuration. We adopt the procedure of performing an RHF calculation on the $^1A_1$ ground state of VCl_4^+ obtained by the removal of the unpaired d electron and performing a configuration interaction calculation on this molecule, which is now isoelectronic with $TiCl_4$, in the same way as described for the latter molecule.

All calculations were performed using the ATMOL system of programs on the CDC 7600 computer of the University of Manchester Regional Computing Center.

We now describe the results of the calculations we have performed on these two molecules.

Computational Results

Table I. Calculated Ground State of $TiCl_4$

		Atomic composition, %				
		Titanium orbital			Chlorine orbital	
Orbital	Energy, au	3d	4s	4p	3s	3p
4e	0.8580					97
$10a_1$	0.5378	88				8
$11t_2$	0.1952	3		91	4	
$9a_1$	0.1406		93		6	
$10t_2$	−0.0320	72		4		23
3e	−0.0476	85				15
$2t_1$	−0.4924					98
$9t_2$	−0.5371			4		93
2e	−0.5586	16				83
$8t_2$	−0.5678	21			3	74
$8a_1$	−0.5787	9			5	85

Orbital populations		Atomic Charge	
Ti	Cl	Ti	Cl
3d 2.34 4s 0.08 4p 0.51	3s 1.89 3p 5.50	1.00+	0.25−

Titanium Tetrachloride. In Table I we show the calculated ground state of $TiCl_4$. As expected, the higher filled MO's are mainly chlorine 3p in character, although the 2e and $8t_2$ show significant metal 3d character. Such covalency results in a considerable deviation from the simple "d^0" description of this complex, with a formal metal charge of only 1.0+. The ordering of the valence orbitals $(8a_1)^2(8t_2)^6(2e)^4(9t_2)^6(2t_1)^6$ corresponds to that proposed by Green et al.[2] in a discussion of their photoelecton spectrum of this molecule. The ionization potentials calculated by Koopmans' theorem are in good agreement with the measured values. Thus, the first ionization potential at 11.78 eV corresponds to ionization from the $2t_1$ MO (calculated IP = 13.4 eV), and the second ionization potential at 12.78 eV to ionization from the $9t_2$ MO (calculated IP = 14.6 eV). We assign the third peak in the photoelectron spectrum, at 13.23 eV to ionization from the closely spaced pair of MO's 2e, $8t_2$ (calculated IP = 15.2, 15.5 eV), in agreement with the conclusions of Green et al.[2] but in contrast to the results of the HFS calculation.[7] The final peak at 13.97 eV is correlated with ionization from the $8a_1$ MO (calculated IP = 15.7 eV). It is of note that although the calculated ionization potentials are rather too high, as is usually found by the use of Koopmans' theorem, the separation of the bands in the photoelectron spectrum is extremely well reproduced by these calculations.

The absorption spectrum of $TiCl_4$ measured by Becker et al.[3] shows a very weak shoulder at 4.0 eV, two well-resolved bands at 4.4 and 5.4 eV, a broad band covering the energy range 6–8 eV, and two final bands at 9.4 and 10.0 eV. In Table II we show the results of our configuration interaction calculation of the excited singlet states of $TiCl_4$, listing the lowest $^1T_1$ state together with the dipole-allowed $^1T_2$ states. The first $^1T_1$ and $^1T_2$ states arise from the same orbital transition, involving the highest filled ($2t_1$, Cl 3p) and first

Table II. Calculated Excited States of $TiCl_4$

Symmetry	Transition energy, eV	Predominant orbital transition	Symmetry	Transition energy, eV	Predominant orbital transition
$^1T_1$	5.9	$2t_1 \rightarrow 3e$	$^1T_2$	7.8	$9t_2 \rightarrow 10t_2$
$^1T_2$	6.2	$2t_1 \rightarrow 3e$	$^1T_2$	8.3	$8a_1 \rightarrow 10t_2$
$^1T_2$	6.7	$2t_1 \rightarrow 10t_2$	$^1T_2$	9.9	$8a_1 \rightarrow 10t_2$
$^1T_2$	7.1	$9t_2 \rightarrow 3e$	$^1T_2$	12.3	$9t_2 \rightarrow 9a_1$
$^1T_2$	7.5	$2e \rightarrow 10t_2$	$^1T_2$	13.0	$8t_2 \rightarrow 9a_1$

virtual MO (3e, Ti 3d) (Table I). The predominant configuration in the second $^1T_2$ state also involves the highest filled MO ($2t_1$), but the virtual MO involved is now the $10t_2$ (Ti 3d) rather than the 3e. We correlate the first very weak band and the first two strong bands in the absorption spectrum with transitions to these three states. The next six $^1T_2$ states which we calculate, covering the energy range 6.7–9.9 eV, we correlate with the broad band observed at 6–8 eV. These $^1T_2$ states are again charge transfer in nature and consist mainly of configurations involving excitations from the $9t_2$, 2e, and $8a_1$ Cl 3p MO's to the metal 3e and $10t_2$ MO's. We now calculate a definite gap (2.4 eV) between this group of states and the two $^1T_2$ states at 12.3 and 13.0 eV which we correlate with the final two bands in the spectrum at 9.4 and 10.0 eV. These involve mainly transitions from the Cl 3p, $9t_2$, and $8t_2$ MO's to the $9a_1$ (Ti 4s) MO. All of the transition energies that we calculate are 2–3 eV higher than the experimental values, as expected in view of the limited configuration interaction calculation we have peformed. However, the calculated separation of the states is in quite good agreement with the experimental observations.

Our transition energies calculated by the configuration interaction method are in the same order as the differences in the energies of the filled and virtual MO's which contribute to the predominant configuration of each $^1T_2$ state. Such orbital energy differences are, however, larger by about 6 eV than the calculated transition energies, due to the neglect of some electron repulsion integrals in the expression for the transition energy.[12] Such integrals are expected to be approximately constant for the transitions we consider which are all Cl(3p) → Ti charge transfer in nature and account for the similar assignments of the excited states given by our calculations and by the HFS method,[7] in spite of the latter method using only orbital energy differences to estimate transition energies.

Vanadium Tetrachloride. The ground state of VCl_4 was calculated to be ^2E, the orbital configuration being $(8a_1)^2(8t_2)^6(2e)^4(9t_2)^6(2t_1)^6(3e)^1$. The order of the mainly chlorine 3p MO's is the same as that in $TiCl_4$, the unpaired electron being in the 3e MO which has 85% vanadium 3d character. The order of the virtual orbitals is also the same as that found for $TiCl_4$. The total 3d orbital population in VCl_4 is calculated to be 3.4 e, greater by approximately one electron than that calculated for $TiCl_4$. In view of the close similarity between the electronic structures of these two molecules, we do not present a detailed analysis of the valence MO's of VCl_4.

Three bands are observed in the absorption spectrum of VCl_4, at 1.1, 3.0, and 4.1 eV.[4] In T_d symmetry, transitions from the ^2E ground state to $^2T_1$ and $^2T_2$ excited states are dipole allowed. The first excited state we calculate is $^2T_2$ arising from the $3e$–$10t_2$ (d–d) transition, 1.4 eV above the ground state. As was found for $TiCl_4$, the calculated transition energies to the next charge-transfer states are about 2 eV higher than the experimental value, ^2T states occuring at 5.3, 5.5, 5.6, and 6.0 eV arising from $2t_1$–3e, $10t_2$ charge-transfer transitions. In view of this spread of transition energies, it is not possible to assign definitely the two charge-transfer bands at 3.0 and 4.1 eV.

The photoelectron spectrum of VCl_4 shows a peak at 9.41 eV and seven peaks in the region 11.75–15.26 eV.[1] The first peak clearly corresponds to the ionization of the unpaired 3e electron to give the closed-shell $^1A_1$ ground state of VCl_4^+. Our SCF calculation on this state resulted in a calculated ionization potential of 12.1 eV. As expected this is larger than the experimental value (9.41 eV) due to the inclusion of orbital relaxation effects in the ion and the neglect of correlation energy differences between the ionized and un-ionized molecule. The other peaks in the spectrum, which are closely spaced arise from ionization from the doubly occupied MO's ($8a_1$ – $2t_1$) of chlorine 3p character. Due to the unpaired e electron in VCl_4, a large number of final states of VCl_4^+ are possible: $^{3,1}T_1$ + $^{3,1}T_2$ states from the configuration t^5e^1, together with $^{3,1}A_1$ + $^{3,1}A_2$ + $^{3,1}E(e^3e^1)$ and $^{3,1}E(a_1{}^1e^1)$ states arising from ionization of the e and a_1 filled MO's. Thus, 20 final states of VCl_4^+ are to be assigned on this simple orbital picture. The calculation on the ground state of VCl_4^+ resulted in a 3d population of 3.6 e, very similar to that in the un-ionized molecule showing the large degree of electron reorganization which occurs upon ionization of the 3d (e) electron. When compared to $TiCl_4$, the 2e and $8t_2$ MO's of VCl_4^+ are found to have about 50% greater 3d character, so that there is unlikely to be a detailed correlation between the excited states of these two isoelectronic molecules.

The configuration interaction calculations on the singlet and triplet states of VCl_4^+ indicate that a simple orbital interpretation of the photoelectron spectrum of VCl_4 is not possible. The states of VCl_4^+ which will be observed in the photoelectron spectrum are those which have large contributions from configurations which differ from the ground state of VCl_4 by the removal of one electron, that is, configurations arising from single excitations from the ground state of VCl_4^+ ($^1A_1$) into the empty 3e MO. We calculate there to be a large degree of interaction among the configurations in our expansion, so that more states than the 20 predicted on a simple orbital picture may be observed. However, these states are grouped together in particular energy ranges so that an interpretation of the observed photoelectron spectrum is possible. Peak II is assigned to a group of six triplet states ($^3T_1$ and $^3T_2$) in the range 3.7–4.2 eV from the ground state of VCl_4^+ composed mainly of configurations resulting from ionization of a $2t_1$ or $8t_2$ electron from VCl_4, together with three similar singlet T states in the range 4.0–4.3 eV. These calculated excitation energies agree well with the experimental separation of peaks I and II of 2.3 eV, when it is recalled that our excitation energies, corresponding to charge-transfer transitions, have been found to be uniformly too high by about 2 eV. There is now a calculated energy gap of 0.4 eV before the next group of three triplet states in the range 4.6–4.8 eV with predominant configurations, $9t_2{}^5 3e^1$ and $8a_1{}^1 3e^1$, and two singlet states at 4.6 and 4.8 eV ($^1T_2$, ^1E) with major configurations $8t_2{}^5 3e^1$ and $2e^3 3e^1$. These states, together with $^1T_1$ ($8t_2{}^5 3e^1$) at 4.4 eV of lower intensity, are correlated with peak IV 3.5 eV from peak I together with the shoulder III. The next group of eight triplet states are in the energy range 5.4–5.8 eV and generally have smaller (~30%) contributions from configurations which differ by one spin orbital from VCl_4. The major configuration in five of these states involves an excitation from the 2e or $9t_2$ MO to the $10t_2$ MO of VCl_4^+ ($^1A_1$) the major configuration in the remaining states having a 3e electron. There is also a group of four singlet states at 5.4 eV, two of which ($^1A_2$, ^1E) involve 2e–3e and $8a_1$–3e excitations, respectively, from the ground state of VCl_4^+ and $^1T_1$ and $^1T_2$ states which involve 2e–$10t_2$ excitations. These states are correlated with peak V at 4.1 eV which, as expected, is weaker than peaks II and III. The shoulders (VI and VII) on the high-energy side of peak V are assigned to the ^3E and ^1E states ($8a_1{}^1 3e^1$) at 6.1 and

6.2 eV, respectively. The assignment of the final very weak peak VIII is rather uncertain, but we do calculate a $^1T_2$ state of VCl_4^+, 9.3 eV from the ground state, with predominant orbital configuration $8a_1{}^1 10t_2{}^1$, having ~20% of configurations which differ from VCl_4 by one spin orbital.

Conclusions

The ab initio calculations we have described here are successful in interpreting the photoelectron and absorption spectrum of $TiCl_4$. The d–d transition in VCl_4 is well described by the limited configuration interaction calculations we have performed, but the charge-transfer states, where more electron reorganization occurs upon excitation, are calculated to be some 2 eV too high, as we also found in the case of $TiCl_4$. Only a tentative interpretation of the photoelectron spectrum of VCl_4 is possible due to the large number of states of VCl_4^+ which are calculated to contribute to the spectrum. It would appear that in this molecule an interpretation of the photoelectron spectrum in terms of a simple orbital picture is not possible.

Registry No. $TiCl_4$, 7550-45-0; VCl_4, 7632-51-1; VCl_4^+, 57842-82-7.

References and Notes

(1) P. A. Cox, S. Evans, A. Hamnett, and A. F. Orchard, *Chem. Phys. Lett.*, **7**, 414 (1970).

(2) J. C. Green, M. L. H. Green, P. J. Joachim, A. F. Orchard, and D. W. Turner, *Philos. Trans. R. Soc. London, Ser. A*, **268**, 111 (1970).

(3) C. A. L. Becker, C. J. Ballhausen, and I. Trabjerg, *Theor. Chim. Acta*, **13**, 355 (1969).

(4) D. S. Alderdice, *J. Mol. Spectrosc.*, **15**, 509 (1965); C. Dijkgraaf, *Spectrochim. Acta*, **21**, 1419 (1965).

(5) J. P. Dahl and J. H. Johansen, *Theor. Chim. Acta*, **11**, 26 (1968); **14**, 26 (1969).

(6) R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, **7**, 479 (1968).

(7) T. Parameswaran and D. E. Ellis *J. Chem. Phys.*, **58**, 2088 (1973).

(8) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

(9) R. F. Stewart, *J. Chem. Phys.*, **52**, 431 (1970).

(10) E. Clementi, *IBM J. Res. Dev.*, **9**, 2 (1965); J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(11) M. F. Guest, I. H. Hillier, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, **29**, 113 (1975).

(12) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 161 (1951).

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Oxidative Addition of Hydrohalic Acids to Dimolybdenum(II) Species. Reformulation of $Mo_2X_8{}^{3-}$ as $Mo_2X_8H^{3-}$

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Several years ago a series of compounds thought to have the general formula $M^I{}_3Mo_2X_8$ (M^I = K, Rb, Cs; X = Cl, Br) was reported, and the structures of the binuclear anions were described as confacial bioctahedra with one-third of the bridging halogen atoms missing or, alternatively, as pairs of square pyramids sharing a basal edge. We now present evidence that these anions are in fact $Mo_2X_8H^{3-}$ ions with bridging hydrogen atoms and that they result from oxidative addition of HX to intermediates such as $Mo_2X_7(H_2O)^{3-}$. The compounds are diamagnetic. In the case of the chloro species, tritium labeling has demonstrated the presence of the H atoms and the reactions of $Mo_2X_8H^{3-}$ with D^+ or Mo_2X_8D with H^+ generate HD. There is also infrared evidence for the presence of the bridging hydrogen atoms.

Introduction

In 1969 Bennett, Brencic, and Cotton[1] reported that reaction of dimolybdenum tetraacetate with aqueous hydrochloric acid produced, under certain conditions, dinuclear anions which could be precipitated with large alkali cations such as Rb^+ and Cs^+ to give compounds of apparent formula $M^I{}_3Mo_2Cl_8$. An x-ray crystallographic study showed that these were not the desired oxidation products of $Mo_2Cl_8{}^{4-}$ (i.e., species retaining the same $Cl_4MoMoCl_4$ structure); instead, they were species similar in structure to the $Mo_2Cl_9{}^{3-}$ ion, but lacking one bridging Cl^- ion. The $Mo_2Cl_8{}^{3-}$ ion was found at a site of D_{3h} crystallographic symmetry and the occupancy factor for the bridging position was refined to 0.67. It was concluded that the vacancy in one bridging position of each anion was randomly distributed in the crystal as a whole (i.e., that it varied randomly from one unit cell to another). An approximate measurement[1] of the magnetic susceptibility indicated paramagnetism roughly consistent with the existence of one unpaired electron per formula unit, as would be required by the postulated formula. Moreover, the crystal structure analysis excluded the possibility of any other formula, except for the possible presence of one or more hydrogen atoms, a contingency not considered at the time, since the structure and magnetic data appeared perfectly consistent.

More recently, we investigated the analogous bromo compounds[2] and found a structure for $Cs_3Mo_2Br_8$ entirely identical (except for a slight technicality concerning space group symmetry, which is unimportant in the present context) with that of $Rb_3Mo_2Cl_8$. In this case, however, the magnetic susceptibility was not measured until after the structure had been published. It was then found that $Cs_3Mo_2Br_8$ is diamagnetic.[3] The magnetic susceptibility of $Rb_3Mo_2Cl_8$ was then remeasured, using a carefully purified sample. It, too, was found to be diamagnetic.[3]

To reconcile the diamagnetism of these compounds with their structures, only two possibilities appeared to exist: (1) the assumption of strong intermolecular antiferromagnetic interactions, sufficient to put the Néel temperature well above 25 °C; (2) revision of the formulas in the only way consistent with the crystallographic results, namely, by addition of one atom of hydrogen to each formula unit. The first possibility appeared highly improbable and so attention was turned to obtaining direct evidence regarding the latter.

Experimental Section

The cesium salts of $Mo_2Br_8H^{3-}$ and $Mo_2Br_7{}^{3-}$ and the rubidium and cesium salts of $Mo_2Cl_8H^{3-}$ were prepared according to literature methods.[1,2,5] The deuterated compounds were prepared by reaction of DBr or DCl with $Mo_2(CH_3CO_2)_4$ under the same conditions employed in the preparation of the corresponding hydrido compounds but with longer reaction times.

DBr (47% in D_2O) was purchased from Bio-Rad, Richmond, Calif. Concentrated DCl was obtained from the ICN Co., Irvine, Calif. Tritiated water (250 μCi/ml) was purchased from New England Nuclear Corp., Boston, Mass.

Infrared spectra were obtained on Nujol mulls using either polyethylene film or KBr plates. Spectra were calibrated with polystyrene.