

# Notes

## Studies on the Electronic Structure of $MCl_4$ ( $M = Ti, Zr, Hf$ ) Type Molecules by the MS- $X\alpha$ Method

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Received January 17, 1992

### Introduction

The multiple-scattering  $X\alpha$  method has been widely used in investigating the electronic structure of transition metal complexes.<sup>2-6</sup> A comparative assessment of scattered-wave calculations in relation to other local density methods has already been made,<sup>7</sup> and there is continued interest in the application of the MS- $X\alpha$  method to transition metal complexes.<sup>2-5</sup> The electronic structure and photoelectron spectra of the tetrahalides of Ti(IV), Zr(IV), and Hf(IV) have attracted interest.<sup>8-14</sup> The experimentally observed values for  $TiCl_4$  differ significantly from the energies predicted previously for charge-transfer energy gaps. A closer agreement of the observed and calculated energies for electronic transitions has been sought here. Further, systematic efforts to predict the optical spectra of  $ZrCl_4$  and  $HfCl_4$  have been limited. A prediction of charge-transfer spectral data for  $ZrCl_4$  and  $HfCl_4$  has now been made in this study.

Spin-restricted (SR) as well as spin-unrestricted (SU) calculations have been performed for the ground and low-lying excited states. Transition-state (TS) and total statistical energy (TE) calculations have been compared. Charge-transfer energy gaps in  $TiCl_4$  have been estimated employing different assumptions in the MS- $X\alpha$  approach. The experimentally observed electronic spectral data for the  $TiCl_4$  system have been compared with the values estimated in this study, and better agreement has been demonstrated.

### Computational Details

The multiple-scattering-wave  $X\alpha$  method originally described by Slater<sup>15,16</sup> and Johnson<sup>17,18</sup> has been employed here. The molecular geometry parameters for  $MCl_4$  ( $M = Ti, Zr, Hf$ ) were taken from the

published structural data.<sup>19</sup> The assigned point group of the molecule is  $T_d$ . The 1s to 2p of Ti, 1s to 3d of Zr, 1s to 4d of Hf, and 1s to 2p of Cl were treated as core levels. The partial waves  $l = 2, 3, 3,$  and  $4$  were used for Cl, Ti, Zr, and Hf, respectively. The Norman sphere method was used to select the sphere radii,<sup>20</sup> and the  $\alpha$  values were taken from Schwarz's atomic calculations.<sup>21</sup> The quasi-relativistic (QR) Hamiltonian used in this study is the same as that reported earlier.<sup>22,23</sup> A standard computer package for MS- $X\alpha$  calculations developed by Cook and Case was implemented on an IBM PC/AT.<sup>24</sup> The relativistic corrections of the charge-transfer energies have been made using the QR approach.

### Results and Discussion

**Electronic Structure of  $TiCl_4$ .** The atomic (metal-ligand) compositions as well as the energies of various (valence) molecular orbitals (MOs) in the system  $TiCl_4$ , estimated using both NR and QR models, are presented in Table I. It is evident that 3p of Cl splits into  $a_1, t_1,$  and  $t_2$  levels whereas Ti valence orbitals split into  $a_1(s), t_2(d), e(d),$  and  $t_2(p)$ . The inclusion of relativistic terms renders the eigenvalues for the orbitals  $1a_1, 2a_1, 1t_2,$  and  $2t_2$  more negative.

The calculated and experimentally observed values of charge-transfer energies for the  $TiCl_4$  system are listed in Table II. The values calculated earlier by ab initio methods as well as MS- $X\alpha$  techniques<sup>12,13</sup> have also been included Table II for comparison. It has been demonstrated that the values calculated in this work are in closer agreement with the experimentally observed values. The data listed in Table II also show that charge-transfer energies of the Ti(IV) system are not sensitive to the inclusion of relativistic effects in the MS- $X\alpha$  approach. Pyykkö and co-workers have also made a similar observation for a related system.<sup>2</sup> In general, the values calculated from the TE method are higher than those from the TS approach. Similar observations have been made by Case et al. in the case of  $CrO_4^{2-}$  and related systems.<sup>5</sup> It is likely that the predictions by the TE and the TS methods differ because of the difference in the magnitude of relaxation of orbitals included in the two types of calculations. Gopinathan has reported that the Slater TS method does not include complete relaxation of electrons. This is believed to originate from the assumptions of the half-charge concept in the Slater TS approach.<sup>25</sup> Whereas TS calculations yielded an underestimate of charge-transfer energies for the  $TiCl_4$  system, values obtained from the TE assumptions were in better agreement with the observed data (Table II). Although SU calculations are generally preferred over SR methods, the SU approach employed in this study provides lower estimates of (than observed) charge-transfer energies for the  $TiCl_4$  system. The differences in the charge-transfer energies predicted by SR and SU calculations may be influenced by the nature of the Slater's exchange potential, which is not orbital dependent. In the case of chromates, a previous study using the same potential function as that used in this study has shown that the experimental values are in closer agreement with the SU rather than the SR calculations.<sup>5</sup> However, in the case of  $TiCl_4$ , experimentally observed data are in better agreement with the

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**Table I.** Molecular Orbital Energies and Charge Distributions of  $\text{TiCl}_4$  (NR and QR Calculations (in Rydbergs))

orbital	energy (NR)	atomic compn		orbital	energy (QR)	atomic compn	
		Ti	Cl			Ti	Cl
1a <sub>1</sub>	-4.6631	98% 3s		1a <sub>1</sub>	-4.7500	98% 3s	
1t <sub>2</sub>	-2.9978	96% 3p		1t <sub>2</sub>	-3.0160	98% 3p	
2a <sub>1</sub>	-1.5540		23% 3s	2a <sub>1</sub>	-1.5717	3s	23% 3s
2t <sub>2</sub>	-1.5371		23% 3s	2t <sub>2</sub>	-1.5544	3p	23% 3s
3t <sub>2</sub>	-0.7696	29% 3d	17% 3p	3a <sub>1</sub>	-0.7709	16% 4s	20% 3p
3a <sub>1</sub>	-0.7663	15% 4s	21% 3p	3t <sub>2</sub>	-0.7694	29% 3d	17% 3p
1e	-0.7067	14% 3d	18% 3p	1e	-0.7060	14% 3d	18% 3p
4t <sub>2</sub>	-0.6773		20% 3p	4t <sub>2</sub>	-0.6772		20% 3p
1t <sub>1</sub>	-0.6350		22% 3p	1t <sub>1</sub>	-0.6346		21% 3p
2e	-0.3893	76% 3d		2e	-0.3860	76% 3d	
5t <sub>2</sub>	-0.3180	62% 3d		5t <sub>2</sub>	-0.3154	62% 3d	

**Table II.** Charge-Transfer Energies for  $\text{TiCl}_4$  (eV)

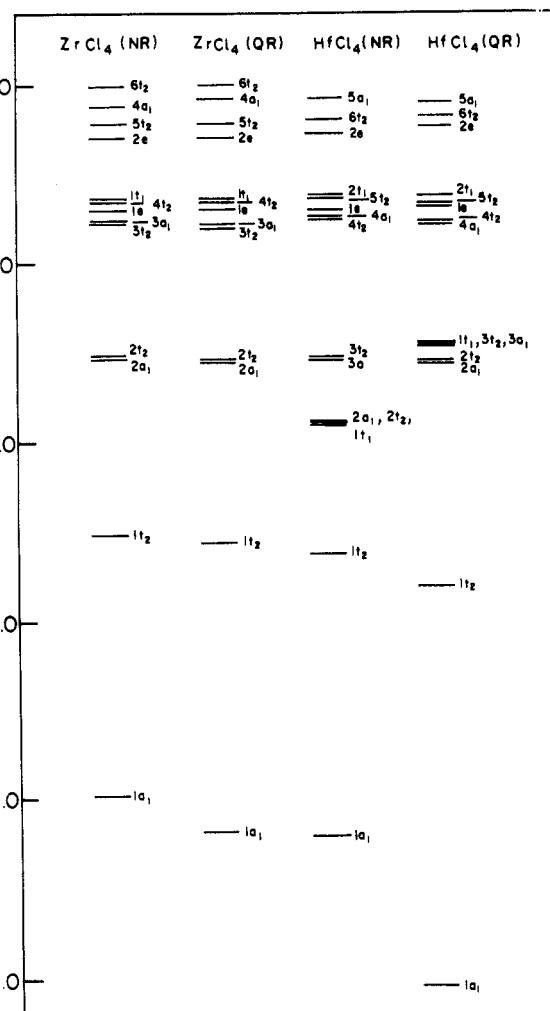
method		transition		
		1t <sub>1</sub> → 2e	4t <sub>2</sub> → 2e	1t <sub>1</sub> → 5t <sub>2</sub>
SR-TS	NR	3.92	4.46	4.72
	QR	3.96	4.51	4.75
SR-TE	NR	4.37	4.93	5.08
	QR	4.42	4.98	5.12
SU-TS	NR	3.62	4.18	4.50
	QR	3.67	4.24	4.54
SU-TS	NR	3.62	4.17	4.50
	QR	3.67	4.22	4.46
SU-TE	NR	4.09	4.66	4.87
	QR	4.14	4.72	4.92
SU-TE	NR	4.08	4.63	4.82
	QR	4.12	4.67	4.87
ab initio <sup>a</sup>		5.90	7.10	6.70
$\chi\alpha^b$		3.80	4.20	4.90
exptl values <sup>b</sup>		4.40		5.40

<sup>a</sup> From ref 12. <sup>b</sup> From ref 13.

SR values. The relative sensitivities of SU and SR calculations to factors like radius of the central metal ion and other atoms, on the one hand, and different allowances for exchange correlation, self-interaction correction, and correlation in the two methods, on the other, may well be some of the probable reasons for the observed trends in the  $\text{TiCl}_4$  and  $\text{CrO}_4^{2-}$  systems.

**Electronic Structure of  $\text{ZrCl}_4$  and  $\text{HfCl}_4$ .** The energies calculated for various MOs in  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  using the MS-X $\alpha$  method are given in Figure 1. The QR model predicts the stabilization of the inner core electrons of Zr and Hf. Some valence orbitals, 1a<sub>1</sub>, 1t<sub>2</sub>, 2a<sub>1</sub>, and 2t<sub>2</sub> of  $\text{ZrCl}_4$ , are stabilized by the inclusion of relativistic corrections. On the other hand, the valence orbital derived from 4d electrons, viz. 2e, is destabilized. The MOs 2a<sub>1</sub>, 2t<sub>2</sub>, and 1t<sub>1</sub> derived from 4f orbitals in  $\text{HfCl}_4$  are degenerate in the NR calculation. The inclusion of relativistic corrections renders these levels nondegenerate and destabilized by ~24%. The relative destabilization of the 2e orbital derived from 5d of Hf is 12%.

An elaborate MS-X $\alpha$  calculation has been performed in this study on the  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  systems. Atomic compositions are listed in supplementary Tables I and II. The charge-transfer energies estimated in this investigation for the  $\text{ZrCl}_4$  and  $\text{HfCl}_4$

**Figure 1.** Molecular orbital energies for  $\text{ZrCl}_4$  and  $\text{HfCl}_4$ .

systems are listed in Table III. Although the inclusion of relativistic effects leads to the destabilization of the 2e MO by 12% in  $\text{HfCl}_4$ , it does not influence significantly the estimates of

**Table III.** Charge-Transfer Energies for  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  (eV)

method		$\text{ZrCl}_4$ transition energy			$\text{HfCl}_4$ transition energy		
		1t <sub>1</sub> → 2e	4t <sub>2</sub> → 2e	1t <sub>1</sub> → 5t <sub>2</sub>	2t <sub>1</sub> → 2e	5t <sub>2</sub> → 2e	2t <sub>1</sub> → 6t <sub>2</sub>
SR-TS	NR	5.04	5.34	5.89	5.31	5.61	6.17
	QR	5.23	5.54	6.03	5.78	6.15	6.48
SR-TE	NR	6.20	6.51	6.78	5.75	6.07	6.49
	QR	6.39	6.72	6.89	6.23	6.60	6.80
SU-TS <sup>a</sup>	NR	4.84	5.15	5.75	5.12	5.44	6.10
	QR	5.03	5.35	5.87	5.60	5.98	6.36
SU-TE <sup>a</sup>	NR	6.02	6.35	6.64	5.58	6.38	5.90
	QR	6.22	6.19	6.79	6.04	6.68	6.42

<sup>a</sup> Triplet instead of singlet assumptions gave rise to marginal differences in charge-transfer energies ( $\pm 0.05$  eV).

electronic transition energies in the molecule. Pyykkö and co-workers have also reported that, in  $WS_4^{2-}$ , the HOMO-LUMO gap is not sensitive to the relativistic effects. The net charge distribution in various regions of the molecules has now been computed for both ground and excited states of  $MCl_4$  systems. Although, these transitions involve an electron transfer from ligand to metal, no significant buildup of electron density on the metal is predicted by the MS-X $\alpha$  approach. A similar observation has also been made by Case and co-workers in the case of the  $CrO_4^{2-}$  system.<sup>5</sup> Possibly the MS-X $\alpha$  formalism permits delocalization of charges in the excited states of the molecules investigated.

Comparison of the data listed in Table III shows that both NR and QR models predict the ordering of HOMO-LUMO gaps as  $TiCl_4 < ZrCl_4 < HfCl_4$  in TS calculations and  $TiCl_4 < HfCl_4 < ZrCl_4$  in TE methods. This implies that the effect of relaxation of orbitals is more pronounced in the case of Hf(IV) than in the case of Zr(IV). Although SU-TE is more appropriate for the calculation of charge-transfer energies than the SR-TE methods, muffin-tin approximation, errors in exchange-correlation potential, and absence of correlation in the Hamiltonian seem to influence SU calculations in the MS-X $\alpha$  method so that they

provide an underestimate of charge-transfer energy in the case of the  $TiCl_4$  system. Since the total energy calculations give the best fit for the observed spectroscopic data in the case of the  $TiCl_4$  system, the same calculations have been preferred for the prediction of spectroscopic parameters for  $ZrCl_4$  and  $HfCl_4$  systems also. On the basis of the results of this investigation, values of  $6.30 \pm 0.1$  and  $6.13 \pm 0.1$  eV<sup>26</sup> appear appropriate for the HOMO-LUMO gap in the  $ZrCl_4$  and  $HfCl_4$  systems, respectively.

**Acknowledgment.** We thank Prof. M. S. Gopinathan, Indian Institute of Technology, Madras, for stimulating discussions and the Council of Scientific and Industrial Research for a research fellowship for V.S.

**Supplementary Material Available:** Supplementary Tables I and II containing the molecular orbital energies and atomic compositions for  $ZrCl_4$  and  $HfCl_4$  complexes (1 page). Ordering information is given on any current masthead page.

(26) These estimates are based on TE and QR models and represent an average of both SU-TE and SR-TE methods. The differences in the values are not very significant.