

## Comparison of electronic structure of group IVA tetrahalides using MS-X $\alpha$ calculations

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**Abstract.** The charge transfer spectral properties of group IVA tetrahalides (where M = Ti, Zr or Hf and X = F, Cl, Br or I) have been calculated using the MS-X $\alpha$  method and compared with experimental values. The order of ligand-to-metal charge transfer energies corresponds to the one-electron oxidation potential of  $X \rightarrow X + e^-$  (F $^-$ /F, Cl $^-$ /Cl, Br $^-$ /Br and I $^-$ /I). The dependence of the ligand-to-metal charge transfer energies on the optical electronegativity of the ligand has been demonstrated. The nature of bonding of the group IVA tetrahalides has been analysed using the MS-X $\alpha$  method.

**Keywords.** MS-X $\alpha$  calculation; charge transfer energies; group IVA tetrahalides.

### 1. Introduction

Electronic structures of transition metal complexes in general and of tetrahalides of group IV A elements, viz. Ti, Zr, or Hf, in particular, have been the subject of many experimental and theoretical investigations. Since the MX $_4$  compounds where M = Ti, Zr or Hf, and X = F, Cl, Br or I are  $d^0$  systems, the role of the 3d, 4d, 5d and 6s orbitals of Hf are of interest (Hillier and Kendrick 1976; Egdell and Orchard 1978; Tossell 1979; Lohr *et al* 1980; Pyykko *et al* 1981; Tse 1981; Veal *et al* 1988; Subramanian *et al* 1991, 1993a; Subramanian and Ramasami 1995). The sensitivity of the ligand-to-metal charge transfer (LMCT) energy gap to the relativistic corrections has been studied. It has been shown that the HOMO–LUMO gap in thioitungstate is not sensitive to the relativistic effect (El Issa *et al* 1991; Subramanian *et al* 1993b). The LMCT gaps are also related to the redox behaviour of the title molecules. The oxidizing character of the molecules decrease in the order Ti, Zr and Hf, while the LMCT transitions exhibit blue-shift in the isoelectronic oxidation state (Lever 1984). The optical electronegativity of the ligand can be expected to influence the observed charge transfer gaps for many metal ions (Lever 1984).

In this investigation, the charge transfer energies of the title molecules have been calculated using Spin Restricted Transition State (SRTS) theory. The effect of relaxation has been assessed using the values calculated from the total energies of ground and excited states. The influence of relativistic effects on LMCT has been studied in the case of title molecules and a quantitative relationship between the electronic transition energies and optical electronegativity has been attempted.

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## 2. Computational details

The multiple scattering- $X\alpha$  (MS- $X\alpha$ ) method originally described by Slater and Johnson has been employed here (Johnson 1973; Slater 1974; Case 1982). The bond lengths of the molecular systems have been obtained from experimental studies (Wilkinson *et al* 1987). The angular basis set  $l = 3, 4$  and  $5$ , were used for Ti, Zr and Hf respectively. For F, Cl, Br and I,  $l = 2, 3, 4$  and  $5$  were used. The  $l$  value on the outersphere was taken to be  $6$ . The Schwarz  $\alpha$  values (Schwarz 1972) and Norman sphere radii method (Norman 1976) have been employed in the calculation. The following orbitals of the halides and metal atoms, F( $1s$ ), Cl( $1s-2p$ ), Br( $1s-3d$ ), I( $1s-4d$ ), Ti( $1s-3s$ ), Zr( $1s-4s$ ) and Hf( $1s-4d$ ) were treated as core orbitals. The standard MS- $X\alpha$  package developed by Cook and Case (1982) was used in the calculation. The eigenvalues were allowed to converge up to a level of  $0.1 \times 10^{-4}$  with a threshold value of  $1 \times 10^{-6}$ . In general, a value of  $0.88$  was used as the Norman reduction factor to achieve a better virial ratio.

## 3. Results and discussion

The bonding orbitals of  $TiX_4$  and  $ZrX_4$  are  $1e$ ,  $2a_1$  and  $3t_2$  and the same orbitals for  $HfX_4$  are  $1e$ ,  $3a_1$  and  $4t_2$ . The orbital compositions of various bonding, anti-bonding molecular orbitals for  $MX_4$  where  $M = Ti, Zr$  or  $Hf$  and  $X = F, Cl, Br$  or  $I$  are given in table 1. It can be observed that  $t_2$  orbitals have larger contributions from the metals as compared to  $a_1$  orbitals. The percentage of halogen contribution to the  $t_2$ ,  $a_1$  and  $1e$  molecular orbitals decreases from F to I. On the other hand, the metal contribution increases from  $TiF_4$  to  $TiI_4$ . Similar observations can be made in the cases of  $ZrX_4$  and  $HfX_4$ . The anti-bonding orbitals  $2e$  are formed by the  $d$ -orbitals of the metal atoms and have higher metal contributions when compared to that in the  $1e$  MO. The

**Table 1.** Metal-ligand compositions of the valence orbitals of the  $MX_4$  systems ( $M = Ti, Zr$  or  $Hf$  and  $X = F, Cl, Br$  or  $I$ ).

Molecule	$t_2$		$a_1$		$e$		$t_1^a$ X	$2e^b$ M	$5t_2^b$ M
	M	X	M	X	M	X			
$TiF_4$	20%3d	19%2p	9%4s	22%2p	10%3d	19%2p	23%2p	82%3d	70%3d
$TiCl_4$	29%3d	17%3p	15%4s	21%3p	14%3d	18%3p	22%3p	76%3d	62%3d
$TiBr_4$	26%3d	16%4d	16%4s	19%4p	14%3d	17%4p	22%4p	75%3d	55%3d
$TiI_4$	28%3d	15%5p	18%4s	18%5p	16%3d	17%5p	21%5p	72%3d	
$ZrF_4$	17%4d	19%2p	8%5s	21%2p	8%4d	20%2p	23%2p	74%4d	49%4d
$ZrCl_4$	23%4d	16%3p	15%5s	19%3p	12%4d	19%3p	22%3p	71%4d	55%4d
$ZrBr_4$	25%4d	16%4p	18%5s	18%4p	13%4d	18%4p	22%4p	70%4d	56%4d
$ZrI_4$	29%4d	11%5p	23%5s	16%5p	42%4d	11%5p	21%5p	42%4d	39%4d
$HfF_4$	16%5d	20%2p	10%6s	21%2p	6%5d	20%2p	22%2p	70%5d	25%5d
$HfCl_4$	20%5d	18%3p	16%6s	19%3p	19%5d	18%3p	22%3p	65%5d	51%5d
$HfBr_4$	22%5d	17%4p	20%6s	19%4p	10%5d	18%4p	21%4p	65%5d	51%5d
$HfI_4$	24%5d	16%5p	23%6s	17%5p	12%5d	17%5p	21%5p	67%5d	50%5d

<sup>a</sup>Halogen centred orbitals

<sup>b</sup>Metal centred virtual orbitals

non-bonding MO,  $1t_1$  arises from the  $p$ -orbital of the ligand. Hence the  $3d$ ,  $4d$ ,  $5d$ ,  $5s$  and  $6s$  orbitals of metal atoms take part in bonding.

The energy levels of various MO in  $TiX_4$  systems (where  $X = F, Cl, Br$  and  $I$ ) have been estimated from the MS- $X\alpha$  calculations and the MO diagram for  $TiX_4$  molecules is presented in figure 1. The HOMO-LUMO in the title molecules are  $1t_1$  and  $2e$  respectively. It is observed from figure 1 that the energies of both HOMO and LUMO are not significantly influenced by relativistic effects. The MO energies of  $ZrX_4$  and  $HfX_4$  are presented in figures 2 and 3. The HOMO in the case of  $HfCl_4$  is  $2t_1$ . Unlike in the case of  $TiX_4$  molecules, the energies of LUMO follow the order  $ZrF_4 > ZrBr_4 > ZrCl_4 > ZrI_4$  and  $HfF_4 > HfBr_4 > HfCl_4 > HfI_4$  for  $ZrX_4$  and  $HfX_4$  respectively. On the other hand, the HOMO energies follow the general order  $MF_4 < MCl_4 < MBr_4 < MI_4$ . It can be seen from the MO energy diagrams that the

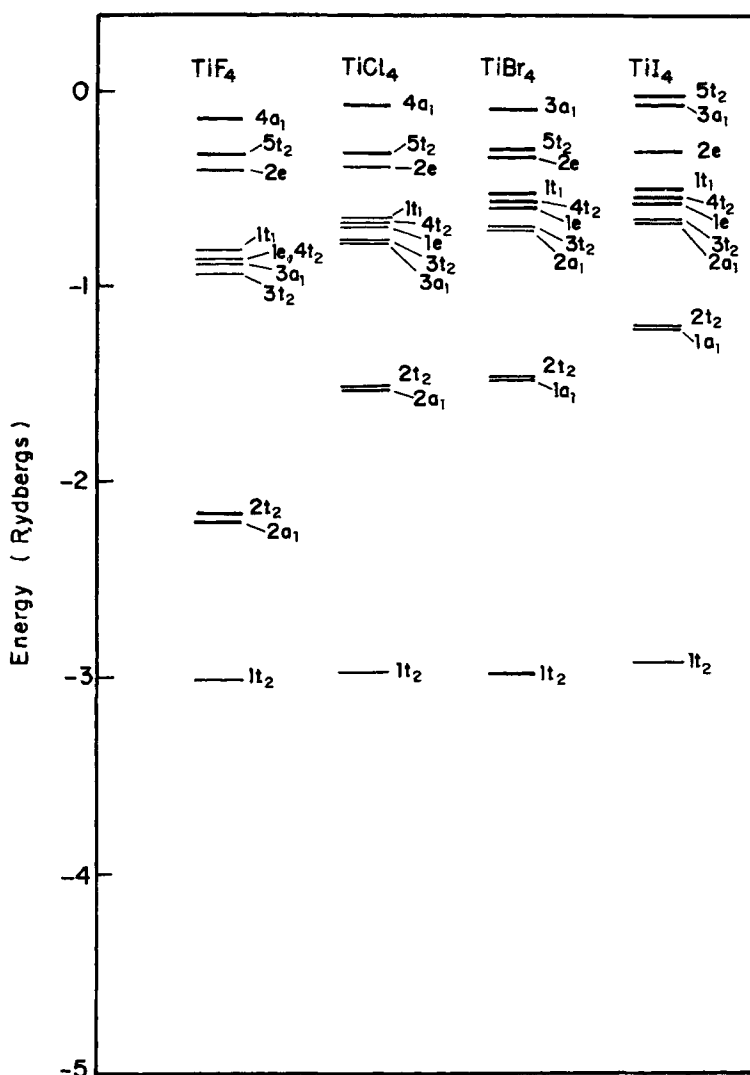


Figure 1. Molecular orbital energies of  $TiX_4$  ( $X = F, Cl, Br$  or  $I$ ).

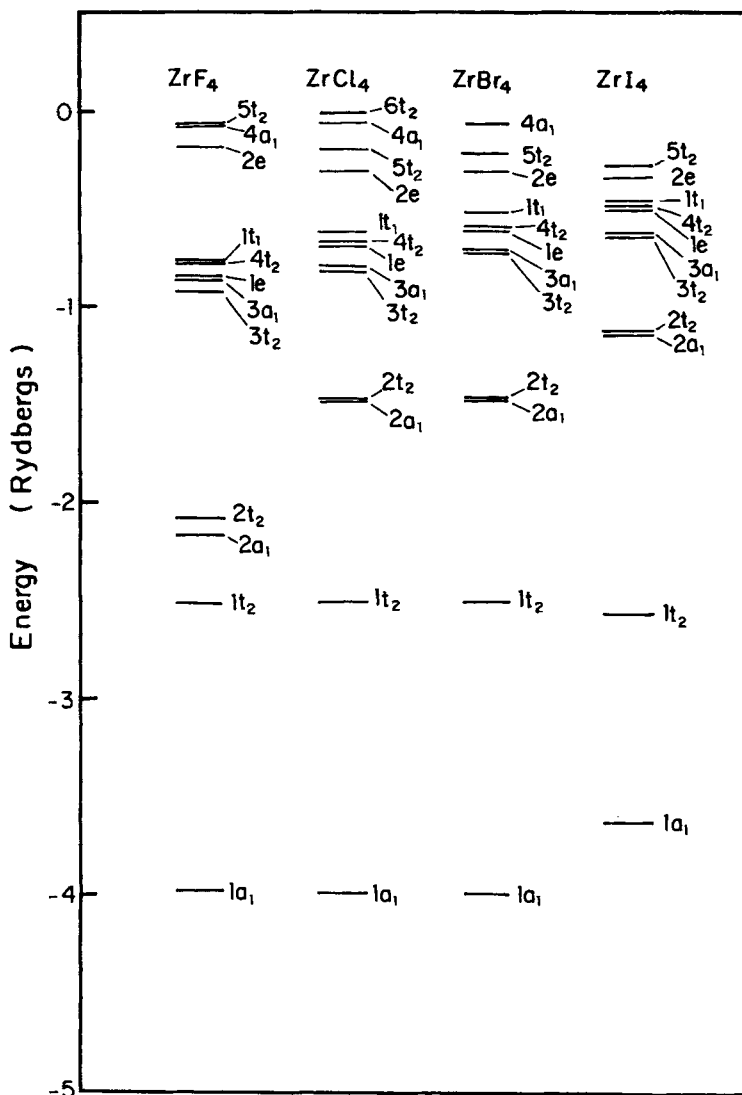


Figure 2. Molecular orbital energies of  $ZrX_4$  ( $X = F, Cl, Br$  or  $I$ ).

HOMO–LUMO energy gaps decrease from tetrafluorides to tetraiodides. The quasi-relativistic MO energies of  $HfI_4$  have been presented in this study although the influence of relativistic effects on all  $MX_4$  systems have been investigated. It can be readily observed that the MO arising from the  $4f$  level namely  $1t_1$ ,  $2a_1$  and  $2t_2$  undergo destabilization in relativistic calculations.

It can be seen from figure 3 that the HOMO–LUMO energy gap in the case of  $HfI_4$  is not strongly influenced by the relativistic effects, supporting the earlier observations in the case of  $5d$  transition elements (El-Issa *et al* 1991; Subramanian *et al* 1993b). The energies calculated in this study for the optical transitions employing Slater's transition state method in the  $TiX_4$  (where  $X = F, Cl, Br$  or  $I$ ) systems investigated have been presented in table 2 and the predicted transition energies for  $ZrX_4$  and  $HfX_4$  are

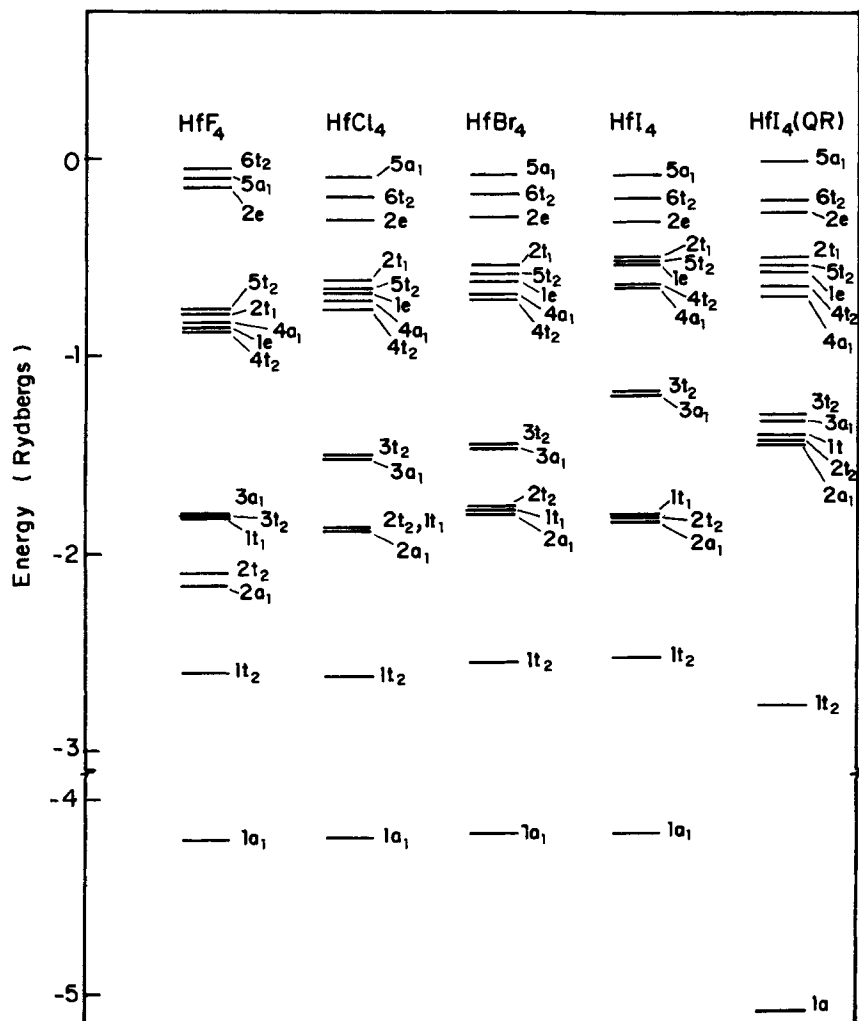


Figure 3. Molecular orbital energies of  $HfI_4$  ( $X = F, Cl, Br$  or  $I$ ).

presented in table 3. It can be seen from the tables that the lowest energy charge transfer transitions are less sensitive to relativistic effects. It may be observed from the data presented in tables 2 and 3 that the total energy calculation (SRTE) of the predicted transition energies are greater than those calculated from the transition state (SRTS) approach. This, in part, may arise from the higher allowances for the relaxation of orbitals in the total energy method compared to Slater's transition state method as explained by Gopinathan (1979).

The order of the lowest energy transition ligand-to-metal charge transfer transition viz.  $MF_4 > MCl_4 > MBr_4 > MI_4$ , parallels the one-electron oxidation potential of  $X^- \rightarrow X + e^-$  ( $F^-/F, Cl^-/Cl, Br^-/Br$  and  $I^-/I$ ) couples. The dependence of the LMCT energy calculated for  $MX_4$  systems on the optical electronegativity of the halogen atoms is illustrated in figure 4. It can be seen from the figure that LMCT energies vary linearly with the optical electronegativities of the halogens.

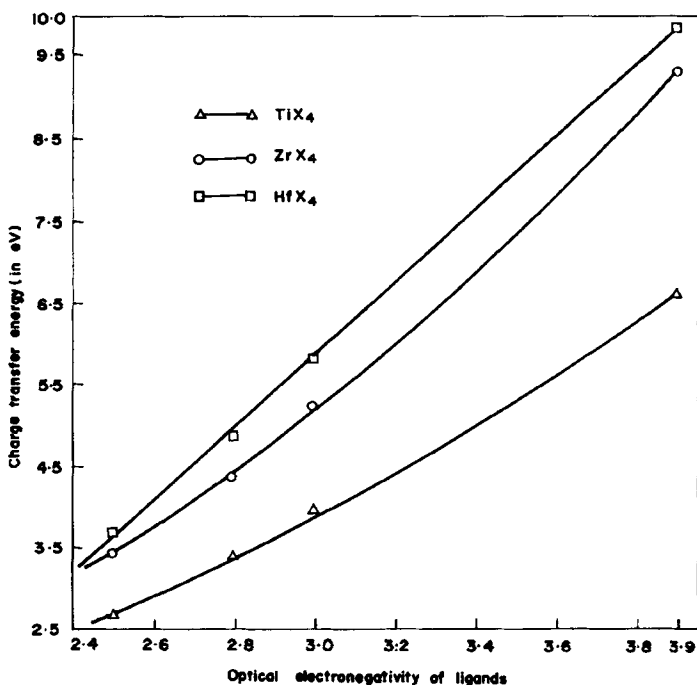
**Table 2.** Calculated electronic transition energies of the  $\text{MX}_4$  systems (where  $\text{M} = \text{Ti}$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}$  or  $\text{I}$ ) (in eV)

Molecule	$1t_1 \rightarrow 2e$			$1t_1 \rightarrow 5t_2$			$4t_2 \rightarrow 2e$		
	TS	TE	Exp <sup>a</sup>	TS	TE	Exp <sup>a</sup>	TS	TE	Exp <sup>a</sup>
$\text{TiF}_4$	6.65	7.03		7.73	8.06		6.90	7.28	
$\text{TiCl}_4$	3.96	4.42	4.40	4.51	4.98	5.40	4.75	5.12	
$\text{TiBr}_4$	3.40	3.79	3.66	4.13	4.45		4.04	4.43	
$\text{TiI}_4$	2.68	3.21	2.43	6.80	6.51		3.37	4.59	3.45

<sup>a</sup>Experimental values from Lever (1984).

**Table 3.** Calculated electronic transition energies of the  $\text{MX}_4$  systems (where  $\text{M} = \text{Zr}$  or  $\text{Hf}$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}$  or  $\text{I}$ ) (in eV).

Molecule	$1t_1 \rightarrow 2e$		$1t_1 \rightarrow 5t_2$		$4t_2 \rightarrow 2e$	
	TS	TE	TS	TE	TS	TE
$\text{ZrF}_4$	9.35	9.98	10.23	10.30	9.34	9.98
$\text{ZrCl}_4$	5.23	6.39	5.54	6.72	6.03	6.89
$\text{ZrBr}_4$	4.36	5.53	5.11	5.18	5.40	5.80
$\text{ZrI}_4$	3.43	4.81	4.05	4.23	3.89	4.66
$\text{HfF}_4$	9.85	10.16	10.25	10.33	9.96	10.27
$\text{HfCl}_4$	5.78	6.23	6.15	6.60	6.48	6.80
$\text{HfBr}_4$	4.83	5.18	5.53	5.80	5.27	5.80
$\text{HfI}_4$	3.70	4.23	4.30	4.66	4.18	4.66



**Figure 4.** Variation of charge transfer energies of the  $\text{MX}_4$  systems with optical electronegativity of the halides.

#### 4. Conclusion

In summary, the nature of bonding and LMCT energies of group IV A halides have been compared using the MS-X $\alpha$  method. The relativistic effect does not influence the HOMO–LUMO gap of the heavy atoms in group IV A halides also. A similar observation has been made by Pyykko and also by our group on  $WS_4^{2-}$  (El-Issa 1991; Subramanian *et al* 1993b).

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