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The influence of relativistic effects on electronic energy levels in metal tetraiodides MI_4 (M = Ti, Zr, Hf, Th) [☆]

Jennifer C. Green [*], Russell G. Egdell

Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK

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ABSTRACT

The influences of scalar relativistic effects and spin orbit coupling on electronic energy levels in TiI_4, ZrI_4, HfI_4 and ThI_4 have been explored by density functional theory. Calculated ionization energies are compared with previously published He(I) and He(II) photoelectron spectra of TiI_4, ZrI_4 and HfI_4 and with new experimental data for ThI_4.

1. Introduction

There is a growing realization that relativistic effects have a strong influence on the energetics, bonding and functional properties of compounds of the heavy elements [1,2]. For example it has recently been shown that the unusual quasi-linear stereochemistry found in HgO arises from relativistic stabilization of the valence 6s orbitals of Hg along with indirect destabilization of the Hg 5d levels [3]. The consequent small separation between the 5d and 6s orbitals then allows oxygen mediated mixing between them in the D_{4h} coordination environment: shallow core d level mixing with O 2p levels is much less pronounced in ZnO and CdO where the d levels are deeper in energy and these oxides have respectively regular tetrahedral and octahedral coordination around the metal [4]. Elsewhere Pykko and coworkers have explored the energetics of the lead acid battery using first principles calculations of thermodynamic parameters and conclude that the battery voltage of around 2 V would be very much lower in the absence of relativistic stabilization of the 6s levels of Pb [5]. More recently relativistic stabilization of Pb 6s orbitals has been shown to be very important in determining the optical properties of lead-based perovskite iodides now exciting great interest as absorber materials in a new generation of solar cells [6–8].

Developments in computational techniques have allowed relativistic calculations to be performed on increasingly more complex molecules [9–11] and solids [8]. However it is important to benchmark the approaches now being used against experimental data for simple molecular systems. Here we explore the influence of scalar relativistic effects and spin–orbit coupling on the molecular electronic energy levels in the simple tetraiodides TiI_4, ZrI_4, HfI_4 and ThI_4. The calculated molecular ionization energies are compared with previously published photoelectron spectra of the three transition metal halides [12]. The paper also presents experimental He(I) and He(II) photoelectron spectra of ThI_4. The dominant scalar effect transpires to be stabilization of the molecular a_1 level in HfI_4 and ThI_4, paralleling stabilization of the atomic 6s and 7s orbitals in Hf and Th respectively. Spin–orbit coupling in these molecules involves a complex interplay between spin–orbit coupling based on iodine with an increasingly important contribution from the metal atom as one progresses through the series from TiI_4 to ThI_4.

2. Experimental

ThI_4 was prepared by direct combination of the elements. A weighed lump of the metal (ca. 2 g) was placed in a quartz tube (~1.5 cm OD) and a constriction was worked into the upper end of the tube. The tube was dried under dynamic vacuum and a stoichiometric quantity of iodine was then sublimed from another vessel onto the cooled (liquid N_2) metal. The tube was then sealed at the constriction. Reaction was initiated by radio-frequency induced heating and was sustained until the thorium had completely reacted with the iodine. Analysis: % I calc. 68.6, found 68.3.

PE spectra were measured on a Perkin-Elmer PS 16/18 spectrometer, modified for He(II) measurements by the inclusion of a

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[☆] We dedicate this paper to Professor Mike Mingos, an esteemed colleague and friend.

[*] Corresponding author. Tel.: +44 01865 272600.
E-mail address: jennifer.green@chem.ox.ac.uk (J.C. Green).

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Table 1
Calculated and experimental interatomic distances (Å) for MI_4.

M	Method	Ti	Zr	Hf	Th
M–I	Exp	2.546 [21]	2.660 [21]	2.662 [21]	2.91 [22]
	NR	2.58	2.73	2.72	3
	ZORA	2.57	2.71	2.69	2.95
	SO	2.57	2.71	2.69	2.95
I–I	ZORA/SO	4.19	4.43	4.39	4.82

Table 2
Kohn–Sham orbital energies (eV) for MI_4 without and with the inclusion of scalar relativistic effects.

MI_4	TiI_4		ZrI_4		Hf I_4		ThI_4	
	NR	ZORA	NR	ZORA	NR	ZORA	NR	ZORA
$1t_1$	−6.88	−6.79	−7.03	−6.97	−7.05	−6.95	−7.29	−7.14
$3t_2$	−7.73	−7.63	−7.67	−7.61	−7.69	−7.65	−7.23	−7.28
1e	−7.94	−7.84	−7.89	−7.92	−8.03	−7.92	−7.67	−7.69
$2t_2$	−8.28	−8.21	−8.38	−8.34	−8.41	−8.34	−7.96	−8.06
$2a_1$	−9.01	−9.01	−8.81	−8.93	−8.89	−9.41	−8.00	−8.57

hollow cathode discharge lamp and high current power supply (Helectros Developments). The discharge lamp heats the sample, which was contained in a quartz tube. An adequate vapour pressure for measurement of spectra was obtained with a sample temperature of 500 °C.

Samples were introduced into the spectrometer under an argon filled dry bag. Spectra were calibrated using He(Iα), He(Iβ) and He(IIα) excited signals of admixed inert gases and N_2. Band areas were corrected to allow for variation in analyzer transmission function with electron kinetic energy.

3. Computational methods

Density functional calculations were carried out using the Amsterdam Density Functional program suite, ADF 2012.01 [13,14]. TZP basis sets were used with triple-ξ accuracy sets of Slater-type orbitals [15,16], with polarization functions added to all atoms. Relativistic corrections were made using the ZORA (zero-order relativistic approximation) formalism, and the spin–orbit formalism. The BP functional was employed [17–20]. The core electrons were frozen up to 2p for Ti, 3d for Zr and 4p for Hf and I and 4f for Th. The geometries of MI_4 (M = Ti, Zr, Hf, Th) were optimized with a T_d symmetry constraint. Frequency calculations confirmed energy minima. The effect of freezing the core orbitals was tested with single point all electron spin–orbit calculations. Only small differences in orbital energies were found (see ESI). Vertical ionisation energies were calculated by direct unrestricted calculations on the molecular ions in their ground and appropriate excited states, and subtraction of the energy of the neutral molecule. Cartesian coordinates for the optimized structures are given in the electronic Supplementary information.

4. Results and discussion

Density functional calculations were carried out for the four MI_4 molecules (M = Ti, Zr, Hf, Th) at three different levels. The first neglected relativistic effects (NR), the second included scalar relativistic effects (ZORA) and the third included the effect of spin orbit coupling (SO). The geometries of the four MI_4 molecules were optimized at these three levels. The resulting tetrahedral geometries are given in Table 1. Inclusion of relativistic effects reduce the calculated M–I bond length, the effect increasing down the group. Addition of spin–orbit coupling makes little difference to the geometry.

Table 3
Kohn–Sham orbital energies (eV) and Mulliken populations for MI_4.

		$1t_1$	$3t_2$	1e	$2t_2$	$2a_1$
TiI_4	Energy	−6.79	−7.63	−7.84	−8.21	−9.01
	%I 5p	100	84	75	71	81
	%Ti 3d		9	25	19	
	%Ti 4s					15
	%Ti 4p		6		6	
ZrI_4	Energy	−6.97	−7.61	−7.92	−8.34	−8.93
	%I 5p	100	89	74	73	80
	%Zr 4d		4	27	21	
	%Zr 5s					15
	%Zr 5p		8		1	
HfI_4	Energy	−6.95	−7.65	−7.92	−8.34	−9.41
	%I 5p	100	88	75	74	73
	%Hf 5d		5	24	19	
	%Hf 6s					22
	%Hf 6p		7		3	
ThI_4	Energy	−7.14	−7.28	−7.69	−8.06	−8.57
	%I 5p	92	94	80	73	76
	%Th 5f	7			2	3
	%Th 6d			20	20	
	%Th 7s					17
	%Th 7p		4			

5. Electronic structure

With neglect of spin–orbit coupling, the 32 valence electrons of the Group 4 tetrahalides occupy orbitals with the general ordering

$$1t_1 > 3t_2 > 2e > 2t_2 > 2a_1 > 1t_2 > 1a_1$$

The $1a_1$ and $1t_2$ orbitals are predominantly I 5s in character and are not considered in the subsequent discussion as they are not observed in the experimental spectra.

The effect of inclusion of scalar relativistic effects (ZORA) is shown in Table 2.

The most striking effect on the orbital energies is the stabilization of the $2a_1$ level for HfI_4 and ThI_4 on inclusion of the scalar corrections. Kohn–Sham orbital energies, calculated with scalar relativistic corrections but without spin–orbit coupling, and their compositions are given in Table 3 and plotted in Fig. 1a.

In all cases the orbital ordering is the same. The spread of energies is strongly influenced by through space interactions between the I 5p orbitals and is therefore a function of the I–I distance. Thus the $1t_1$ orbital involves out of phase through space antibonding interactions which become less important as the I–I separation increases. It follows that TiI_4 has the highest energy $1t_1$ orbital. Conversely, the $2a_1$ orbital involves in-phase through space interactions and this orbital is at lower energy in TiI_4 than in ZrI_4 and ThI_4. However the $2a_1$ orbital is much more stable in HfI_4 than in ZrI_4, even though the bond lengths are almost identical in the two compounds. The increased stability of the $2a_1$ orbital of HfI_4 mirrors stabilisation of the 6s orbital in Hf as compared to Zr and is influenced by two effects. Hf occurs in the periodic table after the filling of the 4f shell. The 4f orbitals have no radial nodes and are unable to shield the highly penetrating 6s orbitals from the increase in nuclear charge across the lanthanide series. At the same time the 6s orbital in atomic Hf is strongly stabilised by scalar relativistic effects, which become increasingly important with increasing atomic number. Thus the valence s ionisation energies in Ti, Zr and Hf are respectively 6.828 eV, 6.634 eV and 6.825 eV. The $2a_1$ bonding orbitals have a contribution from their respective metal ns orbitals (Table 3) and thus the increase from ZrI_4 to HfI_4 mirrors the increase in the atomic ionisation energy.

The energies of the orbitals tend to rise for all of the orbitals in ThI_4, apart from the $1t_1$ orbital, which is the most stable of the Group IV set. The stability maybe in part a consequence of the