Relativistic MS-Xα Calculations for some Thallium(I) Compounds

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Abstract

Ionization energies for TlF, TlCl, TlBr, TlI, Tl_2O, Tl_2S, and $TlNO_3$ have been obtained using relativistic overlapping spheres multiple-scattering Xα transition state calculations. The results are compared with other theoretical and experimental ionization energies. It was found that the present results are in agreement with the experimental ionization energies. However, the results of these calculations and other recent calculations strongly suggest that the assignment of the origin of the bands in the photoelectron spectra of thallium(I) compounds has been erroneous. A uniform interpretation for the monovalent compounds of group IIIA and divalent compounds of group IVA is proposed.

Introduction

The valence levels of thallium(I) compounds have been the subject of several theoretical studies as both solids and free molecules. The results of these studies have differed on the assignment of the Tl 6s level, whether its major contribution is to the most labile level [1–4] or to a level at higher binding energy [5–9]. In this paper, we report the results of relativistic MS-Xα calculations on TlF, TlCl, TlBr, TlI, Tl_2O, Tl_2S, and $TlNO_3$. With the aid of these calculations and by careful examination of experimental data, we have been able to suggest an uniform interpretation for the monovalent compounds of group IIIA and divalent compounds of group IVA.

Multiple-scattering Xα Calculations

The multiple-scattering Xα program employed in this study is a modified version of the program originally written by Smith and Johnson [10]. The program incorporates the 'Latter' tail option [11] and was modified by Yih to include the relativistic correction of Koelling and Harmon [12] as proposed by Wood and Boring [13].

Relativistic MS-Xα calculations using the overlapping-spheres approach of Bloor and Sherrod [14] were performed for TlF, TlCl, TlBr, TlI, Tl_2O, Tl_2S, and $TlNO_3$. The effects of spin–orbit coupling were omitted as this aspect of the thallium(I) halides has been adequately explained previously [1]. The theoretical values obtained for the π levels in these calculations may be viewed as weighted averages of the actual $\pi_{3/2}$ and $\pi_{1/2}$ levels. The basis set included spherical harmonics up to $l_{max} = 4$ for the outer and Tl spheres and up to $l_{max} = 3$ for all other spheres. In all the calculations, the outer sphere was chosen to be tangential to the outermost peripheral atomic sphere. The atomic radii were chosen to encompass $Z - n$ units of integrated charge density as calculated for the neutral atom using a Herman–Skillman program where Z is the atomic number of the enclosed nucleus and n the magnitude of the ionic charge. The value of α was taken as a constant for a given molecule and was chosen to be a weighted average obtained from the approximate atomic values [15] and is given by

$$\alpha = \Sigma Z_i \alpha_i / \Sigma Z_i$$

where Z_i is the atomic number for each atom and α_i the approximate atomic value. Core electrons were not frozen during the self-consistency procedure. Ionization energies were calculated using Slater's half-electron transition state formalism [16]. The convergence criteria for the eigenvalues were $\epsilon \leqslant 6 \times 10^{-3}$ for the ground state calculations and $\epsilon \leqslant 1 \times 10^{-3}$ for the transition state calculations.

Experimental bond lengths were employed for the halides and the nitrate [17, 18]. For Tl_2O and Tl_2S, bond distances and angles were estimated as Tl–O, 2.044 Å; Tl–O–Tl, 101°; Tl–S, 2.343 Å; and Tl–S–Tl, 92°.

The results of the calculations are summarized in Tables I–VII. The theoretical ionization energies are compared to experimental values as determined by photoelectron spectroscopy. In addition, the calculated percentage contributions of each atomic orbital rounded to the nearest tenth are listed for each molecular orbital. Atomic orbitals with contributions of less than 1% are not listed, so that the percentage contributions may not sum to 100%.

TABLE I. Molecular Orbital Energies and Constituencies for TlF

MO	Ionization energy (eV)		AO % composition
	Theor.	Exp.[a]	
$17\sigma^+$	10.0	10.8	Tl6s(30.8), 6p(6.7), 5d(3.7), F2p(57.6)
9π	12.9	11.9	Tl5d(1.3), F2p(97.7)
$16\sigma^+$	13.5	14.4	Tl6s(52.2), 6p(1.5), 5d(2.0), F2p(43.3)
$15\sigma^+$	21.3		Tl5d(94.2), F2s(1.1), 2p(3.5)
4δ	21.4		Tl5d(100.0)
8π	21.4		Tl5d(99.5)
$14\sigma^+$	31.8		Tl5d(1.4), F2s(97.2)

[a]Values from ref. 19.

TABLE II. Molecular Orbital Energies and Constituencies for TlCl

MO	Ionization Energy (eV)		AO % composition
	Theor.	Exp.[a]	
$19\sigma^+$	9.0	9.9	Tl6s(15.1), 6p(7.7), 5d(1.9), Cl3p(74.7)
10π	10.3	10.3	Cl3p(98.6)
$18\sigma^+$	13.1	13.9	Tl6s(71.3), Cl3s(2.1), 3p(24.5), 3d(1.0)
$17\sigma^+$	20.7		Tl5d(86.6), Cl3s(11.0), 3p(1.5)
4δ	22.2		Tl5d(100.0)
9π	22.2		Tl5d(99.6)
$16\sigma^+$	22.6		Tl5d(11.7), Cl3s(86.2)

[a]Values from ref. 5.

TABLE III. Molecular Orbital Energies and Constituencies for TlBr

MO	Ionization energy (eV)		AO % composition
	Theor.	Exp.[a]	
$22\sigma^+$	8.8	9.5	Tl6s(13.4), 6p(7.5), 5d(1.6), Br4p(77.1)
12π	9.9	9.9	Br4p(98.7)
$21\sigma^+$	13.1	13.7	Tl6s(77.7), Br4s(1.7), 4p(19.1)
$20\sigma^+$	20.9		Tl5d(91.1), Br4s(7.5)
5δ	22.3		Tl5d(100.0)
11π	22.3		Tl5d(99.8)
$19\sigma^+$	22.6		Tl5d(8.1), Br4s(94.1)

[a]Values from ref. 5.

Separate transition state calculations were performed for each MO except those marked with an asterisk for Tl_2O and Tl_2S. For Tl_2O (Table V) and Tl_2S (Table VI), the values so marked were taken from the shifted energies obtained from the transition state calculations for the $12a_2$ and $13a_2$ levels, respectively.

Discussion

The results of the calculations as summarized in Tables I–VII agree with the experimentally estab-

lished band ordering and energy assignments. For Tl_2O, the theoretical ionization energies are not in particularly good agreement with the experimental values [7]. This is probably the result of the particular molecular geometry chosen for the calculations. The present results differ from the previously assigned band origins [1, 19, 20]. In particular, the present calculations show a reversal in the constituencies of the two outermost σ levels for the thallium(I) halides and the corresponding MOs for other thallium(I) compounds.

TABLE IV. Molecular Orbital Energies and Constituencies for TlI

MO	Ionization Energy (eV)		AO % composition
	Theor.	Exp.[a]	
$25\sigma^+$	8.2	8.7	Tl6s(9.6), 6p(7.7), 5d(1.1), I5p(81.3)
14π	9.0	8.9 / 9.7	I5p(98.8)
$24\sigma^+$	13.1	13.1 / 13.5	Tl6s(81.9), I5s(2.6), 5p(13.8), 5d(1.1)
$23\sigma^+$	19.2		Tl5d(15.9), I5s(82.8)
6δ	22.6		Tl5d(100.0)
13π	22.6		Tl5d(99.8)
$22\sigma^+$	22.6		Tl5d(83.6), I5s(14.7)

[a]Values from ref. 5.

TABLE V. Molecular Orbital Energies and Constituencies for Tl_2O

MO	Ionization energy (theoretical) (eV)	AO % composition
$28b_2$	8.3	Tl6s(2 × 12.1), 6p(2 × 8.1), 5d(2 × 1.7), O2p(55.2)
$30a_1$	8.7	Tl6s(2 × 6.8), 6p(2 × 6.7), 5d(2 × 2.7), O2p(65.6)
$14b_1$	10.1	Tl6p(2 × 1.8), 5d(2 × 1.4), O2p(92.8)
$27b_2$	12.3	Tl6s(2 × 30.8), 5d(2 × 2.3), O2p(31.3)
$29a_1$	12.8	Tl6s(2 × 33.5), O2s(4.6), 2p(24.5)
$28a_1$	19.5[a]	Tl5d(2 × 44.8), O2s(7.2), 2p(2.0)
$26b_2$	19.7	Tl5d(2 × 49.8)
$13a_2$	19.9	Tl5d(2 × 50.0)
$25b_2$	19.9	Tl5d(2 × 49.9)
$12a_2$	20.0	Tl5d(2 × 50.0)
$13b_1$	20.0[a]	Tl5d(2 × 49.9)
$27a_1$	20.0[a]	Tl5d(2 × 49.8)
$12b_1$	20.2[a]	Tl5d(2 × 49.6)
$26a_1$	20.3[a]	Tl5d(2 × 49.2)
$24b_2$	20.3[a]	Tl5d(2 × 47.5)
$25a_1$	26.2	Tl6s(2 × 1.6), 6p(2 × 1.4), 5d(2 × 5.6), O2s(81.5)

[a]See text.

Originally, the Tl 6s orbital was believed to comprise the majority of the outermost level in thallium-(I) compounds based on experimental and theoretical considerations [1]. Evans and Orchard [21] first reported experimental evidence that this assignment might be erroneous and suggested that the interpretation of the photoelectron (PE) spectra of the thallium(I) halides be reassigned. However, subsequent investigations on thallium(I) compounds continued to find evidence for assignment of the outermost valence level as the Tl 6s level [19, 20, 22, 23]. These assignments were supported by the results of semi-empirical and *ab initio* calculations [1–4]. Recent results of SW-Xα [5], DV-Xα [6], and relativistic DVM-Xα [7] for TlCl are at variance with the originally proposed assignments [1]. In addition, Ruscic *et al.* [7] report the results of relativistic calculations for Tl_2O. The results of all these calcula-

tions are in agreement with those reported in Tables II and V and are consistent with the band origins reported for the other thallium(I) compounds in this study.

In addition to the results of the various calculations, experimental evidence supports the contention of Evans and Orchard [21] that the interpretation of the PE spectra of thallium(I) compounds should be changed. Comparison of the spectra of the thallium(I) compounds [5, 19, 20] with the spectra of the corresponding alkali metal compounds [24–27] shows that one additional peak occurs in the spectra of the thallium(I) compounds. This additional peak is relatively weak by comparison to the other peaks in the spectra as noted by Evans and Orchard. Ruscic *et al.* [7] note that MOs receiving major contributions from the Tl 6s level are expected to have relatively low cross-sections for He(I) photons

TABLE VI. Molecular Orbital Energies and Constituencies for Tl_2S

MO	Ionization energy (theoretical) (eV)	AO % composition
$29b_2$	7.8	Tl6s(2 × 9.2), 6p(2 × 8.7), 5d(2 × 1.4), S3p(60.6)
$32a_1$	7.8	Tl6s(2 × 6.6), 6p(2 × 8.1), 5d(2 × 2.0), S3p(65.3)
$15b_1$	9.1	Tl6p(2 × 1.1), 5d(2 × 1.1), S3p(93.2)
$31a_1$	12.2	Tl6s(2 × 32.9), S3s(9.5), 3p(22.7)
$28b_2$	12.5	Tl6s(2 × 35.7), 5d(2 × 1.3), S3p(23.0), 3d(1.2)
$30a_1$	18.1	Tl6s(2 × 1.9), 5d(2 × 29.4), S3s(35.6)
$27b_2$	19.8[a]	Tl5d(2 × 50.0)
$13a_2$	19.9	Tl5d(2 × 50.0)
$14b_1$	19.9[a]	Tl5d(2 × 49.7)
$12a_2$	19.9[a]	Tl5d(2 × 49.9)
$26b_2$	19.9	Tl5d(2 × 49.9)
$13b_1$	20.0[a]	Tl5d(2 × 50.0)
$29a_1$	20.0[a]	Tl5d(2 × 49.6)
$28a_1$	20.1[a]	Tl5d(2 × 50.0)
$25b_2$	20.2[a]	Tl5d(2 × 47.7), S3p(3.1)
$27a_1$	21.1	Tl6s(2 × 1.5), 5d(2 × 22.4), S3s(47.9), 2p(1.9)

[a]See text.

TABLE VII. Molecular Orbital Energies and Constituencies for $TlNO_3$

MO	Ionization energy (eV) Theor.	Exp.[a]	AO % composition
$14b_2$	11.7	9.9	O_a2p(27.8), O_b2p(2 × 34.7)
$26a_1$	11.8	9.9	Tl6s(39.8), 6p(2.4), 5d(1.1), N3d(1.1), O_a2p(3.3), O_b2p(2 × 25.4)
$11b_1$	12.8	10.8	N3d(1.8), O_a2p(64.7), O_b(2 × 16.5)
$5a_2$	12.8	11.1	N3d(1.6), O_b2p(2 × 49.0)
$13b_2$	13.3	11.4	N3d(3.8), O_a2p(62.7), O_b2p(2 × 16.5)
$25a_1$	14.4	14.2	Tl6s(54.6), N3d(1.6), O_a2p(3.0), O_b2p(2 × 19.2)
$10b_1$	18.4	16.7	N2p(58.7), O_a2p(12.7), O_b(2 × 13.2)
$12b_2$	19.6		Tl6p(7.9), N2p(23.7), O_a2p(2.2), O_b2s(2 × 9.6), 2p(2 × 22.4)
$24a_1$	19.8		N2p(24.7), O_a2s(16.5), 2p(33.0), O_b2s(2 × 2.9), 2p(2 × 9.0)
$23a_1$	21.4		Tl5d(15.0), N2s(16.4), O_a2s(13.4), 2p(6.9), O_b2s(2 × 13.3), 2p(2 × 10.0)
$22a_1$	23.7		Tl5d(99.8)
$4a_2$	23.7		Tl5d(100.0)
$9b_1$	23.7		Tl5d(99.8)
$11b_2$	23.7		Tl5d(94.3), N2p(1.7), O_b2p(2 × 1.6)
$21a_1$	23.7		Tl5d(88.6), O_b2s(2 × 2.2)
$10b_2$	32.6		N2s(2.3), 2p(26.5), O_b2s(2 × 31.1), 2p(2 × 3.5)
$20a_1$	33.1		N2p(28.3), 3d(1.8), O_a2s(40.8), 2p(5.3), O_b2s(2 × 9.6), 2p(2 × 1.3)
$19a_1$	38.6		N2s(48.0), 3d(1.1), O_a2s(11.2), 2p(3.5), O_b2s(2 × 12.6), 2p(2 × 3.9)

[a]Values from ref. 20.

and therefore, should result in a weak band in the PE spectrum. Bancroft and Bristow [5] comment that the two outermost σ levels in the thallium(I) halides comprise a bonding–antibonding pair of MOs. The sharpness of the outermost peak in the PE spectra is consistent with ionization from an antibonding orbital.

By analogy to the alkali metal and hydrogen halides [24, 27, 28], the halide π levels are expected to be more labile than the halide σ level. However, the peak areas in the PE spectra do not support this expectation if the Tl 6s level is assigned as the penultimate σ level as originally noted by Berkowitz [1]. This apparent anomaly is easily understood based on qualitative considerations. The bonding in the thallium(I) halides is predominantly ionic [29]. Therefore, the molecular orbital states for TlX may be considered to arise from the ionic levels of the free ions, Tl^+ and Cl^-, based on a simple electrostatic model. The relative energies may be approximated as the ionization energy for the thallium(I) ion [30] and as the electron affinities for the halide ions [31]. For TlCl, the 6s level of the thallium(I) ion lies at approximately 20.4 eV and the 3p levels of the chloride ion at approximately 4.0 eV. Bringing these two oppositely charged ions together will cause these levels to shift, the Tl^+ 6s level and the Cl^- 3p levels will approach each other. The amount that the levels are shifted will be approximately equal and in the 6–8 eV range [24]. Under the influence of the positively charged ion, the Cl^- 3p levels will no longer be equivalent. Instead, the level that lies along the bonding axis will be perturbed more than the two 3p levels perpendicular to the axis and should be shifted to slightly higher energy. Thus, the ordering and approximate ionization energies for TlCl are expected to be Cl 3pπ at 11.0 eV, Cl 3pσ at 11.5 eV, and Tl 6sσ at 13.4 eV. The two σ levels are fairly close in energy, so that configuration interaction might be expected to occur. Through this interaction, some mixing between the two levels will occur and they will repel each other, the predominantly Tl 6sσ level shifting to higher energy and the Cl 3pσ level shifting to lower energy and to the opposite side of the Cl 3pπ level. Similar expectations are applicable to the other halides, and to other thallium(I) compounds if the anion is considered as a point charge. Hence, the observed ordering of the PE spectra, the theoretical ordering of the MOs given in Tables I–VII, and the ordering proposed in other theoretical studies [5–7] are consistent with a simple electrostatic model that includes configuration interaction.

Based on the preceding considerations, it is suggested that the vapor phase PE spectra of thallium(I) halides be interpreted to reflect that major contribution of the Tl 6s level is to the penultimate σ level with the outermost σ level receiving its major contribution from the halide valence p level. In general,

the vapor phase PE spectra of thallium(I) compounds should be reassigned to reflect that the MO(s) receiving the greatest contribution from the Tl 6s level(s) lie(s) below valence p levels of the anion and correspond(s) to the weak peak(s) in the spectra between 12 and 15 eV. This reassignment is consistent with the prevailing interpretation of the PE spectra of solid thallium(I) compounds [32–37].

The original interpretation of the PE spectra of the thallium(I) halides [1] was employed as the basis for the interpretation of the PE spectra of the vapors of the indium(I) [38] and lead(II) [39] halides. It has been proposed that this interpretation should be extended to the other monovalent compounds of group IIIA [38]. However, in view of the preceding reassignment of the PE spectra of the thallium(I) compounds, further consideration of the spectra of the group IIIA monovalent and group IVA divalent compounds is in order. Employing a qualitative discussion based on a simple electrostatic model as outlined above for thallium(I) compounds, the valence s level of the group IIIA and IVA metals is expected to contribute predominantly to the MO(s) that lie(s) below the valence p levels of the anion(s) [40].

Further examination of the literature for studies pertaining to lead(II) compounds reveals mixed interpretations as was encountered for the thallium(I) compounds. Banna *et al.* [41] report the vapor phase PE spectra of the lead dihalides and interpret them to show the Pb 6s level contributing predominantly to the outermost MO. Evans and Orchard [21] report spectra for the lead(II) halides that exhibit an additional weak peak not previously recorded. This peak lies below the halide p levels and Evans and Orchard suggest that this is the Pb 6s level. Calculations on the group IVA dihalides show the outermost MO to be comprised of 30–45% metal s character with remainder of the metal valence s level contributing to a MO below the valence p levels of the halide [2, 42–44]. PE and theoretical studies on the solid lead(II) compounds have predominantly been interpreted as placing the Pb 6s level below the valence p levels of the anion [34, 45–53].

Additional PE studies of the group IIIA monovalent compounds have been reported for all the suboxides. Dyke *et al.* [54] report a vapor phase PE study of Al_2O along with a DV-Xα calculation. In addition to Tl_2O, Ruscic *et al.* [7] studied the PE spectra of Ga_2O and In_2O and report the results of relativistic DVMXα calculations for all the group IIIA monovalent suboxides. The spectra of all these compounds exhibit at least one weak peak below 12.5 eV that can be attributed to the valence s level of the metal. The accompanying calculations suggest that one oxygen p level mixes extensively with a metal s level. Thus, the assignment of an additional MO that is predominantly metal s in character is not possible.

Finally, it is informative to examine studies on indium(I), thallium(I), and lead(II) dihalides that employed He(II) photons. Egdell and Orchard [55] studied the indium and thallium monohalides with both He(I) and He(II) photons. For the indium(I) halides, they report quantitative intensity alterations for the two sets of spectra. The alterations in the two σ levels suggest that there is extensive mixing of the indium 5s level with the valence p level of the halide. However, the intensity alterations suggest that the majority of the indium 5s level contributes to the penultimate σ level [56]. The same observations can be made for the intensity alterations for the two sets of thallium(I) halide spectra. In this case, the observed intensity alterations suggest that the Tl 6s level predominantly contributes to the penultimate σ. Potts and Lyus [57] report the He(II) spectra of the lead(II) halides which when compared to the He(I) spectra [21] lead to the same conclusion as for the thallium(I) halides, the Pb 6s level predominantly contributes to a MO that lies below the valence p levels of the halide.

Conclusions

The PE spectra of thallium(I) compounds should be reassigned to reflect that the Tl 6s level contributes predominantly to a MO that lies below the valence p levels of the anion. The Tl 6s level will mix slightly with the corresponding anion p level of proper symmetry and will contribute to a minor extent to the most labile molecular orbital. This conclusion is supported by the weak intensity of the peak found in the 12.5—14.5 eV range in all the PE spectra [56], the results of the relativistic calculations presented in this paper, previous calculations on TlCl [5—7] and Tl$_2$O [7], and by the intensity alterations observed between He(I) and He(II) PE spectra for the thallium(I) halides [55].

A similar reassignment for lead(II) compounds appears to be supported by the weak peak in the 14—17 eV range of the PE spectra [21] and the intensity alterations between He(I) and He(II) PE spectra [57]. For other group IIIA monovalent and group IVA divalent compounds, more extensive mixing of the valence s level of the metal with a corresponding valence p level of the anion occurs such that the metal s level contributes extensively to the most labile MO and a MO that lies below the anion p levels. However, the major contribution of the metal s level is expected to occur in the MO that lies below the anion p levels.

Acknowledgement

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