

# Chemical Effects on Inner Shells Studied by Photo-Electron Spectrometry\*

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Fluorine 2s orbitals with ionization energies  $I$  about 40 eV still show perceptible inter-ligand chemical effects (in molecules with short  $F-F$  distances) in agreement with the mutual overlap integral. Other inner shells show only a chemical shift (amounting to 5 or more eV) and adjacent  $I$  values when the groundstate has positive  $S$ .

The relativistic separation of the two  $I$  of  $4f$  is measured in 88 compounds of the elements from tantalum to uranium. The behaviour of the rare earths and hafnium is also discussed as well as the large width of  $4d$  due to short half-life of the ionized state before a  $4f$  electron fills the vacancy. The quantum-mechanical aspects of slowly auto-ionizing states are studied.

In Molekülen mit besonders benachbarten Fluoratomen verursachen die Fluor-2s-Orbitale trotz ihrer Energie von ca. 40 eV entsprechend ihren Überlappungen beachtliche chemische Wechselwirkungen. Die Wechselwirkung anderer Orbitale innerer Schalen liefert dagegen nur eine chemische Verschiebung um größenordnungsmäßig 5 eV und eine Aufspaltung der Ionisierungsenergien im Falle eines positiven  $S$ -Wertes im Grundzustand.

Die Spin-Bahn-Aufspaltung der beiden  $4f$ -Ionisierungsenergien in 88 Verbindungen der Elemente Ta bis U wurde gemessen und diskutiert. Auf die große Linienbreite der  $4d$ -Ionisierung wird eingegangen.

Les orbitales 2s de fluor avec l'énergie d'ionisation  $I$  autour de 40 eV montrent d'effets chimiques quand les ligandes ont la distance mutuelle courte, et ils sont proportionnels aux intégrales de recouvrement. Les autres couches intérieures montrent seulement un déplacement chimique (de l'ordre de grandeur 5 eV) et des valeurs multiples de  $I$  quand l'état fondamental a  $S$  positif. La séparation d'origine relativiste des deux  $I$  de la couche  $4f$  est mesurée dans 88 composés des éléments entre le tantale et l'uranium. Le comportement des terres rares et de l'hafnium est discuté ainsi que la grande largeur du signal  $4d$ , où l'état ionisé a une durée très faible parce que la position vacante rapidement est reprise par un électron  $4f$ . On étudie les états sujet à l'auto-ionisation lente de point de vue de mécanique ondulatoire.

## 1. Direct Chemical Bonding between Inner Shells

When the atomic spectroscopists classify energy levels of monatomic systems using electron configurations, the orbitals forming the configurations have a far more objective existence than one would accept from the argument that the anti-symmetrized Slater determinant of a closed-shell system is invariant by a unitary transformation of the orbitals, forming new linear combinations. The weak point of this argument is that the total wave-function  $\Psi$  is not exactly an anti-symmetrized Slater determinant (because of correlation effects) and a closer analysis [1] shows that the individual orbitals (which would be the diagonalized

\* Dedicated to the memory of Prof. K. H. Hansen.

eigen-functions of the effective one-electron operator, if such a concept was sharply defined) are those orbitals which are the most appropriate for describing the manifold consisting of the groundstate and the low-lying excited levels, and which form what is called the preponderant electron configuration.

It is not excluded that the preponderant electron configuration may present vacancies in penultimate orbitals (e. g.  $1s^2 2s 2p^6 4f$  of a neon atom) and frequently, they correspond to auto-ionizing states like the levels belonging to the configuration  $[\text{Ar}] 3d4d$  of the calcium atom at higher energy than  $[\text{Ar}] 4s$  of  $\text{Ca}^+$ . It has been realized since the time of Moseley that the X-absorption spectra, and in particular the X-emission lines, are narrow and indicate a quite individual behaviour of the inner shells. There is no intrinsic difference between ultra-violet and X-ray spectra at this point; thus the gaseous potassium atom have excited levels belonging to the configuration  $[\text{Ne}] 3s^2 3p^5 4s^2$  at energies about four times higher than needed to form the groundstate of  $\text{K}^+$ . According to a proposal by Mulliken, we denote such vacancies by the exponent  $(-1)$ , such as  $(3p)^{-1}$ .

In a solid, the lowest ionization energy  $I$  relative to vacuo is given by the threshold energy for Einstein photo-electric emission. By the same token, it is relatively easy to determine the lowest  $I$  of a gaseous molecule from the lower limit of photon energy needed to maintain a current through the gas. The great progress made possible by photo-electron spectroscopy (either done on gaseous samples with 21.2 or 40.8 eV radiation [2] or on the outermost 50 Å of solid samples with 1253.6 or 1486.6 eV radiation [3] coming from a magnesium or aluminium anti-cathode) is that all the  $I$  values for penultimate orbitals and inner shells can be measured up to a higher limit slightly below the energy of the incident photons.

This opens a most valuable opportunity to compare MO calculations with experimentally verifiable quantities and to study regularities by induction from a comparison of many compounds. It is usually argued that the kinetic energy of the emerging photo-electrons is given as the difference between the photon energy (1486.6 eV in our Varian IEE-15 instrument) and the sum of  $I$  and the work function of metallic materials. However, in the case of non-conducting samples, it is more appropriate to use an internal standard of reference, and it has been discussed [4] why the  $I$  value for the carbon  $1s$  orbital in one-sided scotch tape must be close to 290.0 eV. Hence, we define a correction  $C_{st}$  as the difference between 290.0 eV and the  $I^*$  value recorded by the apparatus for the carbon signal at lowest  $I$ . Both in the original instrument in Uppsala and in a home-made instrument in Berkeley [5] magnetic deflection is used, like in the  $\beta$ -ray spectrograph, whereas the commercial instruments generally use electrostatic fields alone.

The photo-electron spectrum of the neon atom [3] shows  $(2p)^{-1}$  at  $I = 21.6$  eV,  $(2s)^{-1}$  at 48.4 and  $(1s)^{-1}$  at 870.2 eV. The isoelectronic molecule methane has three degenerate orbitals with  $(t_2)^{-1}$  at 14 eV,  $(2a_1)^{-1}$  at 24 and  $(1a_1)^{-1}$  at 290.8 eV. The water molecule has lower symmetry and correspondingly five distinct  $I$  values at 12.6, 14.8, 18.6, 32.2 and 539.7 eV. There is no doubt that the highest  $I$  value in  $\text{CH}_4$  and  $\text{H}_2\text{O}$  corresponds essentially to  $1s$  of the carbon or oxygen atom. The chemist may then ask whether a given  $I$  corresponds to  $2s$ . This is the case, energy-wise, for the 24 eV orbital of methane and the 32.2 eV orbital of water. However, it is expected that the electronic density of these MO is partly

delocalized on the hydrogen atoms. In the LCAO approximation, these orbitals are mainly mixtures of H 1s and 2s of the heavier atom.

It has been realized from the study of electron transfer spectra of transition group complexes [6] that the interactions between the filled  $p$  shells of adjacent ligands  $X^-$  in hexahalide complexes  $MX_6^{+z-6}$  are sufficiently strong that the loosest bound MO having many node-planes (four and three) between the ligands are about 1 eV easier to excite than the approximately non-bonding combination. The corresponding effects are stronger [3] in the photo-electron spectrum of  $CF_4$ . Thus, the  $\pi$  orbitals have  $I = 16.3, 17.5$  and  $18.6$  eV and the two sets of  $\sigma$  orbitals  $I = (22.2$  and  $25.1)$  and  $(40.3$  and  $43.8)$  eV. These two sets are, energy-wise, very close to carbon 2s and fluorine 2s, but the former set is probably fluorine 2p to a larger extent. Anyhow, the separations (2.9 and 3.5 eV) between three degenerate  $\sigma$  orbitals of symmetry type  $t_2$  in the point-group  $T_d$  and the stronger bound, totally symmetric  $a_1$  orbital must be due to interactions between the four fluoride ligands. A similar effect is observed [3] in  $SF_6$  having the six  $\sigma$  orbitals formed mainly from F2s distributed at  $(e_g)^{-1}$  39.3,  $(t_{1u})^{-1}$  41.2 and  $(a_{1g})^{-1}$  44.2 eV.

Normally, the chemist would not expect significant chemical bonding to take place with orbitals having  $I$  above 20 eV; it must be remembered that a quite strong single bond with the dissociation energy 115 kcal/mole represents only 5 eV to be distributed among two bonding electrons. What is worse in this respect is that these interactions between equivalent ligands correspond to all the anti-bonding and bonding MO being simultaneously filled what is the standard explanation for the strong repulsion between noble gas atoms brought to a shorter distance than the Van der Waals contact. The photo-electron spectra have demonstrated the presence of a "Underground chemistry" of deep-lying MO, and there is little doubt that the dissociation energy of  $SF_6$  is decreased at least 4 eV by the inter-ligand repulsion of the fluorine 2s orbitals.

A direct homo-atomic bond occurs in ethane, and actually, two  $I$  values separated by 3.5 eV have replaced the 24 eV value for methane [3]. Again, this is very impressive when comparing with the dissociation energy of the central C-C bond. However, this is probably a rather extreme case of strong interactions between equivalent atoms at a short distance. Thus, we have studied solid GaS having a direct Ga-Ga bond, and found no convincing evidence for a similar effect in the broad signals in the valence region. We found only one Ga 3d signal at  $I^* = 22.9$  eV and corrected  $I = 27.9$  eV to be compared with  $I = 22.7$  eV for metallic gallium, 27.6 eV for  $Ga_2(SO_4)_3$ , 18  $H_2O$ , 27.6 eV for  $(NH_4)_3 GaF_6$  and 28.7 eV for  $Ga_2O_3$ . This variation is a normal chemical shift  $dI$  and is also found for deeper shells, such as  $I$  for  $2p_{3/2}$  at 1125.2, 1120.6, 1124.9, 1125.0 and 1125.7 eV for the five samples. Also salts of  $BF_4^-$ ,  $SiF_6^{2-}$  show much weaker effects [7] of inter-ligand repulsion than the isoelectronic neutral molecules  $CF_4$  and  $SF_6$ .

From a theoretical point of view, one expects a proportionality between the energetic separation and the overlap integral  $S_{XX}$  in the homonuclear case [8] whereas the second-order perturbation in the case of weak heteronuclear bonding rather is proportional to the square  $S_{MX}^2$ . For our purposes, it is sufficient to consider the model expression for  $S_{XX}$  between two hydrogenic 1s orbitals with the Slater coefficient  $\mu$

$$S_{XX} = \left( 1 + \mu R + \frac{1}{3} \mu^2 R^2 \right) \exp(-\mu R) \quad (1)$$

In the case of two adjacent fluorine ligands at a distance 5 bohr units, the approximate value  $\mu = 1.2$  produces the overlap integral 0.047. Obviously, the overlap attenuates strongly with distance. Two fluorine atoms in trans-position in  $\text{SF}_6$  are known to have  $R = 6$  bohr and hence  $S_{XX} = 0.019$  whereas the actual F-F distance in  $\text{CF}_4$  is only 4 bohr and  $S_{XX} = 0.111$ .

In the homonuclear case [8], the proportionality factor in the energetic effects is related to the kinetic energy operator and should be approximately  $\mu^2$  hartree for large  $R$ . Hence, the order of magnitude expected is 4.4 eV for  $R = 4$  bohr, 1.8 eV for  $R = 5$  and 0.4 eV for  $R = 6$  bohr in agreement with the observations. On the other hand, the inner shells have vanishing energetic effects. Thus, for  $R = 4$  bohr, the fluorine 1s shells with  $\mu = 8$  produce the overlap integral  $5 \cdot 10^{-12}$  and even when multiplied with 64 hartree, the energy separations expected are only  $10^{-8}$  eV. It may be noted that Eq. (1) is  $10^{-3}$  for  $\mu R = 10.9$ ,  $10^{-4}$  for  $\mu R = 13.5$  and  $10^{-5}$  for  $\mu R = 16.2$ .

In the Wolfsberg-Helmholz model, the energetic effect in the homonuclear case is approximately  $(K - 1) H_X S_{XX}$  producing the same type of result as above. This is less true for the heteronuclear case where the average energy entering in the non-diagonal element is strongly influenced by the orbital having the highest  $I$ . But since this model agrees with the considerations of the kinetic energy operator in the bond region [8] in assuming energetic effects proportional to the square of the overlap integral, observable consequences disappear for much smaller values of  $\mu R$ .

## 2. Ionization Energies of 4f in Compounds of Heavy Elements

The probability of ionizing an orbital with small  $I$  using photons of 1486.6 eV energy is usually rather low. However, as discussed in the specific case of gold [4] this restriction does not apply to the 4f shell. Table 1 gives the  $I$  values (obtained from  $I^* + C_{st}$ ) of  $4f_{5/2}$  and  $4f_{7/2}$  of compounds of elements having the atomic

Table 1. The two ionisation energies  $I$  of the 4f shell corrected with  $C_{st}$  defined in the text to apply relative to vacuo. All values in eV

	$C_{st}$	$4f_{5/2}$	$4f_{7/2}$	Diff.	
Hf:	$\text{K}_2\text{HfF}_6$	5.0	(27.5)	26.0	1.5
	$\text{Yb}_2\text{Hf}_2\text{O}_1$	4.7	26.1	24.4	1.7
	$\text{Hf}(\text{C}_6\text{H}_5\text{CHOHCO}_2)_4$	5.0	24.9	23.2	1.7
Ta:	$\text{K}_2\text{TaF}_7$	4.5	37.5	35.7	1.8
	$\text{Ta}_2\text{O}_5$	4.9	35.1	33.3	1.8
W:	$\text{Na}_2\text{WO}_4$	5.6	44.7	42.9	1.8
	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	4.0	42.95	41.1	1.85
	$\text{Cs}_2\text{WS}_4$	5.2	42.7	40.9	1.8
Re:	$\text{CsReO}_4$	4.7	56.5	54.3	2.2
	$\text{TiReO}_4$	5.1	56.1	53.9	2.2
	$\text{AgReO}_4$	4.7	(55.5)	53.4	2.1
	$\text{KReO}_4$	3.7	55.1	52.9	2.2
	$\text{As}(\text{C}_6\text{H}_5)_4[\text{ReO}_4]$	3.9	53.0	50.6	2.4
	$\text{K}_2\text{ReCl}_6$	3.7	51.5	49.15	2.35
	$\text{N}(\text{CH}_3)_4[\text{ReS}_4]$	4.4	(50.8)	48.2	—

Table 1 (continued)

	$C_{st}$	$4f_{5/2}$	$4f_{7/2}$	Diff.	
Os:	$K_2OsO_2(OH)_4$	4.8	63.2	60.7	2.5
	$Cs_2OsCl_6$	4.8	62.4	59.8	2.6
	$Cs_2OsBr_6$	3.8	61.8	59.1	2.7
	$K_2OsCl_6$	3.8	61.6	58.9	2.7
	$Tl_2OsBr_6$	6.0	60.7	57.9	2.8
	$Ni_2[Os(CN)_6]$	5.2	60.6	57.9	2.7
Ir:	$Cs_2IrCl_6$	5.7	73.4	70.7	2.7
	$[Ir(NH_3)_5Cl]Cl_2$	4.4	71.5	68.65	2.85
	$[N(CH_3)_4]_2IrCl_6$	4.4	71.3	68.5	2.8
	$[N(C_4H_9)_4]_3IrCl_6$	4.4	69.8	67.1	2.7
Pt:	$Ir[S_2P(OC_3H_7)_2]_3$	4.5	69.8	66.85	2.95
	$K_2PtBr_6$	5.0	84.6	81.3	3.3
	$(NH_4)_2PtCl_6$	3.3	84.15	80.9	3.25
	$K_2Pt(SeCN)_6$	4.8	83.9	80.6	3.3
	$K_2Pt(SCN)_6$	4.8	83.1	80.0	3.1
	$[Nien_2] [Pt(CN)_4]$	4.0	82.3	79.2	3.1
	$K_2PtCl_4$	4.0	82.2	79.0	3.2
Au:	Pt	5.7	80.1	76.8	3.3
	$KAuCl_4$	3.2	97.4	93.85	3.55
	$KAu(CN)_2$	4.5	94.85	91.15	3.7
	$AuSCH_2CO_2H$	3.9	94.45	90.8	3.65
Hg:	Au	5.4	92.2	88.85	3.65
	$HgO$	5.5	112.6	108.55	4.05
	$K_2HgI_4$	4.6	111.85	107.8	4.05
	$K_2Hg(SCN)_4$	5.0	110.85	106.75	4.1
	$Hg(SCN)_4Co$	4.7	110.6	106.55	4.05
Tl:	TLF	5.2	131.6	127.2	4.4
	$TlReO_4$	5.1	131.45	127.0	4.45
	$TlIO_3$	5.1	131.4	126.95	4.45
	$Tl_2SO_4$	5.2	131.25	126.8	4.45
	$TlWO_4$	4.8	130.9	126.45	4.45
	$Tl_2MoO_4$	4.8	130.4	125.95	4.45
	$Tl_2CO_3$	4.7	130.35	125.9	4.45
	$Tl_2CrO_4$	4.5	129.95	125.55	4.4
	$TlBr$	4.6	129.9	125.45	4.45
	$TlB(C_6H_5)_4$	5.0	129.55	125.1	4.45
	$TlI$	4.85	129.4	125.05	4.35
	$Tl_2WS_4$	4.5	129.3	124.85	4.45
	$[Co(NH_3)_6]TlCl_6$	3.7	129.0	124.6	4.4
	$Tl_2OsBr_6$	0.0	128.75	124.4	4.35
	$TlBr$	3.1	128.75	124.3	4.45
	$Tl_2O_3$	4.4	127.35	123.0	4.35
	Pb:	$Pb(NO_3)_2$	5.3	152.1	147.2
$PbI_2$		5.1	151.7	146.75	4.95
$PbSO_4$		4.5	150.95	146.1	4.85
$PbCl_2$		4.6	151.0	146.1	4.9
$PbBr_2$		4.9	150.85	145.95	4.9
$PbF_2$		4.75	150.75	145.9	4.85
$PbS$		4.15	149.85	145.0	4.85
$PbCO_3$		3.2	149.8	145.0	4.8
$PbSO_4$		3.3	149.75	144.9	4.85
$PbO$		3.3	149.0	144.15	4.85
$PbCrO_4$		3.3	148.6	143.75	4.85

Table (continued)

	$C_{st}$	$4f_{5/2}$	$4f_{7/2}$	Diff.	
	Pb [S <sub>2</sub> P(OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	4.8	148.2	143.3	4.9
	PbO <sub>2</sub>	4.4	147.2	142.4	4.8
Bi:	Bi <sub>2</sub> O <sub>3</sub>	4.7	172.2	166.85	5.35
	NaBiO <sub>3</sub>	4.55	171.8	166.5	5.3
	BiI <sub>3</sub>	5.0	171.8	166.5	5.3
	CsBiI <sub>4</sub>	5.0	171.6	166.3	5.3
	BiOI	5.05	171.4	166.1	5.3
	[Co(NH <sub>3</sub> ) <sub>6</sub> ] BiCl <sub>6</sub>	3.6	170.2	164.2	5.3
Th:	ThF <sub>4</sub>	4.9	354.75	345.4	9.35
	Th <sub>0.95</sub> U <sub>0.05</sub> O <sub>2</sub>	6.4	352.35	343.0	9.35
	ThO <sub>2</sub>	4.6	352.0	342.65	9.35
	Th <sub>0.6</sub> Ce <sub>0.2</sub> U <sub>0.2</sub> O <sub>2</sub>	5.9	351.4	342.1	9.3
	Th <sub>0.9</sub> Pr <sub>0.1</sub> O <sub>2</sub>	5.5	351.1	341.8	9.3
	Th <sub>0.5</sub> Eu <sub>0.5</sub> O <sub>1.75</sub>	5.8	351.1	341.75	9.35
U:	Cu(UO <sub>2</sub> ) <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub>	4.6	400.9	390.0	10.9
	RbUO <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>	4.8	400.6	389.7	10.9
	K <sub>2</sub> UF <sub>6</sub>	4.9	400.4	389.5	10.9
	Th <sub>0.95</sub> U <sub>0.05</sub> O <sub>2</sub>	5.0	400.1	389.2	10.9
	Th <sub>0.6</sub> Ce <sub>0.2</sub> U <sub>0.2</sub> O <sub>2</sub>	5.9	400.05	382.15	10.9
	(NH <sub>4</sub> ) <sub>2</sub> U <sub>2</sub> O <sub>7</sub>	4.7	399.9	389.05	10.85
	Ce <sub>0.5</sub> U <sub>0.5</sub> O <sub>2</sub>	6.1	399.5	388.8	10.7
	UO <sub>2</sub>	3.6	398.1	387.3	10.8
	U <sub>3</sub> O <sub>8</sub>	4.1	398.0	387.2	10.8
	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> H] <sub>2</sub> UCl <sub>6</sub>	4.64	396.6	386.0	10.6

number  $Z$  above 72. Already in the rare earths, the  $4f$  signals are quite perceptible. We find  $I = 15.6$  eV for Gd<sub>2</sub>O<sub>3</sub>, broad structures between 17 and 13 eV in Dy<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub> and Tm<sub>2</sub>O<sub>3</sub>,  $I = 13.6$  eV in Yb<sub>2</sub>O<sub>3</sub>, 13.7 eV in Yb<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, 14.6 eV in both Yb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 8 H<sub>2</sub>O and YbAsO<sub>4</sub>, 15.0 eV in Yb<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>, 15.1 eV in Yb<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> and 16.7 eV in YbF<sub>3</sub>, all having a weaker signal at 4 eV higher  $I$ ; and an unresolved (but broadened) signal at 16.0 eV in Lu<sub>2</sub>O<sub>3</sub>. As will be discussed later with Dr. Christiane Bonnelle and Dr. R. C. Karnatak, these structures are in agreement with the general theory of  $f^q$  configurations [1] assuming the parameters  $D = 0.8$  eV and  $(E - A) = 0.5$  eV. Hedén, Löfgren and Hagström [9] have reported  $I^*$  relative to the Fermi level of Lanthanide metals, e.g.  $I^* = 7.8$  eV for Gd which is said [10] to have the work function 3.2 eV. The difference in  $I$ -values from 15.6 eV for Gd<sub>2</sub>O<sub>3</sub> to 11.0 eV for Gd is a quite normal chemical shift  $dI$  from the oxide to a metal.

It is well-known from absorption spectra in the near infra-red [11] that the difference ( $7\zeta_{4f}/2$ ) between  $4f_{7/2}$  and  $4f_{5/2}$  is 1.3 eV in all ytterbium (III) compounds. HfO<sub>2</sub> shows an unresolved signal at  $I = 25.0$  eV. As discussed later with Dr. Lucette Balsenc, metallic hafnium shows  $I = 23.7$  eV which may conceivably be due to a superficial suboxide of the type Hf<sub>3</sub>O. As seen from Table 1, the compounds starting with tantalum show two distinct  $4f$  signals, and the chemical shifts  $dI$  between the compounds of the same element achieve values up to 5 eV. Professor Carl Nordling and Dr. Jan Hedman were so kind as

to supply  $I^*$  values for the oxide-free metals relative to the Fermi level:

Os	53.6	and	50.8	
Ir	64.0	and	61.0	
Pt	74.4	and	71.0	(2)
Au	87.5	and	83.8	

The  $5d$  structures of these metals have been studied [12] and it is probable that  $I$  is some 4–5 eV larger than the  $I^*$  values of Eq. (2). Among the compounds in Table 1, the salts of  $WS_4^{-2}$  and  $ReS_4^-$  are later going to be discussed with Professor A. Müller and Dr. E. Diemann, the salts of  $Os(CN)_6^{-4}$  and  $Pt(CN)_4^{-2}$  together with Professor A. Ludi, and the salts of  $TiCl_6^{-3}$  and  $BiCl_6^{-3}$  were kindly provided by Dr. Peter Day.

Because of the details of the experimental technique, the distance between the two  $4f$  relativistic sub-shells should be extremely precisely evaluated, and it is interesting to look for possible chemical effects. The average values found for ( $7 \zeta_{4f}/2$ ) are:

W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Th	U	
1.82	2.2	2.66	2.8	3.23	3.6	4.05	4.42	4.87	5.31	9.32	10.83	(3)

Though these values increase with  $Z$ , they do not increase in a fully regular fashion. One effect may be an influence from groundstates with positive  $S$ . Helmer [13] noted that  $2p_{1/2}$  and  $2p_{3/2}$  of chromium (VI) in  $K_2Cr_2O_7$  have the  $I^*$  values 590.8 and 581.6 eV, whereas Cr (III) in  $Cr_2O_3$  has  $I^* = 588.9$  and 579.0 eV. The increase of the separation from 9.2 to 9.9 eV cannot be interpreted exclusively as an increase of ( $3 \zeta_{2p}/2$ ). Actually, the Cr- $3s$  signal of  $Cr_2O_3$  shows two peaks at  $I^* = 81.5$  and 78.2 eV which must be explained by the two excited terms  $^3F$  and  $^5F$  of the electron configuration  $[Ne]3s3p^63d^3$ , separated by effects of interelectronic repulsion. Hence, the situation is rather similar to the behaviour of high-spin nickel (II) complexes (having  $S=1$  in the groundstate) where the  $2p$  region of the photo-electron spectrum shows four signals [4]. The distance between the first and the third peak is 17.7 eV, to be compared with the distance 17.2 eV between the two signals of diamagnetic nickel (II) compounds. The physical origin of these separations is that the probability of ionization is distributed, in a not fully understood fashion, between the 270 states of the ionized configuration containing the two partly filled shells  $2p^5$  and  $3d^8$ . A similar effect of apparently increased relativistic splitting in systems having positive  $S$  in the groundstate seems to occur in  $K_2ReCl_6$  ( $S=3/2$ ) and in  $(P(C_6H_5)_3H)_2UCl_6$  ( $S=1$ ).

It is not excluded that the oxides of uranium are superficially oxidized to U(VI). A large number of mixed oxides [14] of thorium (IV) have been measured, also by Dr. W. G. Proctor in Palo Alto and by Dr. W. Bremser and Mr. F. Linnemann in Darmstadt, all showing the  $4f$  difference very close to 9.32 eV. The chemical shifts of platinum complexes have been measured [15, 16].  $I^*$  for Pt  $4f_{7/2}$  changes from 73.4 eV for  $L_2PtCl_2$  over 71.7 eV for  $PtL_4$  to 71.2 eV for  $L_2Pt(CH_3)_2$  where L is  $P(C_6H_5)_3$ . 5.0 to 5.3 eV have to be added to these values in order to

convert them to our  $I$  scale. The latter example clearly shows that  $dI$  does not indicate the oxidation states Pt(II) and Pt(0) defined [1] on the basis of the preponderant electron configurations  $5d^8$  and  $5d^{10}$  but rather a quantity related to the fractional charge residing on the central atom [8, 17].

This statement is even more clear-cut in the case of  $Tl_2O_3$  having  $I$  distinctly lower than all the 14 thallium(I) compounds in Table 1, and  $PbO_2$  having  $I$  below all the 12 lead (II) compounds. However, a residual effect lingers on the limit of the experimental uncertainty.  $Tl_2O_3$  has the  $4f$  relativistic separation 0.07 eV below the average value for the other thallium compounds. The same is true for  $KAuCl_4$  and  $Cs_2IrCl_6$ . These compounds are particularly oxidizing and it cannot be excluded that the inner  $4f$  shell is slightly modified by the covalent bonding though it is a little surprising that  $\zeta_{4f}$  should be decreased by as much as one percent, more than is the case in erbium(III) and ytterbium(III) compounds [1, 14] with  $I$  eight times smaller.

### 3. Conclusions

The persistence of inner shells in compounds [18] has been magnificently manifested by photo-electron spectra of solid samples. It seems to be exaggeratedly prudent to emphasize the possible delocalization of phosphorus  $2p$  orbitals [19] with the exception of the rare compounds (such as  $H_2PPH_2$ ) having a homonuclear bond. As a matter of fact, the chemical effects on fluorine  $2s$  orbitals seem to be connected with the unusual short F–F distances (well below twice the ionic radius of  $F^-$ ) in  $CF_4$  and  $SF_6$  and they agree with the expected proportionality with the overlap integral in the homonuclear case. Corresponding heteronuclear effects on inner shells should almost vanish because of the dependence on the (much smaller) square of the overlap integral.

However, one must accept one possible source of chemical effects. The total wave-functions of systems lacking an inner electron cannot be treated variationally. The Hartree-Fock approximation has the additional constraint of a prescribed electron configuration. This is already necessary in the groundstate of certain gaseous anions such as  $H^-$  and  $O^{-2}$  (in contrast to the isoelectronic  $F^-$  and Ne). The latter ion can be stabilized in solid oxides by the Madelung potential but is unstable relative to  $O^-$  and an electron at large distance in the gaseous state, and the Hartree-Fock solution only exists in a confined volume or with the superposed condition of six equivalent electrons. Hence, it is not clear whether unexpected effects from the continuum [8] may not influence the  $I$  values observed. Manne and Åberg [20] demonstrated that the primary peaks correspond to ionized states where the other electrons have contracted their orbitals, adapting to the more negative central field. The positions of the primary peaks may be influenced by polarizability besides the conventional Madelung potential. As also seen from Table 1, iodides and caesium salts have unexpectedly high  $I$  values [4]. The chemical shift  $dI$  seems essentially to be an indicator [8, 17] of the variation of the Hartree potential  $U(x, y, z)$  including the Madelung potential produced by the surrounding atoms, and if this description is appropriate, the large variation of  $dI$  known to have the order of magnitude



5 to 10 eV for most elements does not contribute to the heat of formation of the compound considered, because its contribution cancels when the total energy is evaluated [11].

Another interesting aspect of the auto-ionizing character of our  $(nl)^{-1}$  systems is the half-width of the photo-electron signals corrected for the background. Under our standard conditions of 100 eV analyzer energy, a normal signal has the sum of  $\delta(-)$  and  $\delta(+)$ , the half-widths towards smaller and larger  $I$ , between 1.9 and 2.0 eV. It is considered evidence for the presence of adjacent signals if this sum exceeds 2.2 eV [4]. However,  $\delta(-)$  of the  $4d_{5/2}$  signal of  $\text{Lu}_2\text{O}_3$  at  $I=203.9$  eV is 2.1 eV. In the earlier lanthanides,  $\delta(-)$  is far larger. Thus, 2.0 eV for  $\text{Tm}_2\text{O}_3$  having  $I=184.5$  eV, 3.0 eV for  $\text{Ho}_2\text{O}_3$  having  $I=169.4$  eV, and the  $4d$  signal expands to a broad hill with  $\delta(-)=4.4$  eV in  $\text{Dy}_2\text{O}_3$  and returns to the normal width 1.1 eV at  $I=98.7$  eV in  $\text{BaSO}_4$ . Fadley and Shirley [21] suggest that the anomalous broadening of the  $4d$  signals in Lu(III) is due to a short half-life, transforming rapidly via  $4f \rightarrow 4d$  transitions. In the earlier lanthanides, an additional source of broadening is the interelectronic repulsion separating the many states belonging to the configuration containing the two partly filled shells  $4d^9$  and  $4f^9$ . On the other hand, our  $4f$  signals in elements heavier than hafnium have their normal  $\delta(-)$  close to 1.0 eV.

The possibility of photo-electron spectrometry with the present technique is based on the moderately good monochromacy of the photons corresponding to the width due to Heisenberg's uncertainty principle, combined with the fortunate fact that the radiative half-life of the  $(nl)^{-1}$  systems usually is above  $10^{-14}$  sec with exception of cases such as Lu  $4d$ .

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