Core level binding energies for the elements Hf to Bi (Z=72-83)

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LETTER TO THE EDITOR

Core level binding energies for the elements Hf to Bi ($Z = 72$–83)

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Abstract. The binding energies of all core levels in the N and O shells for the elements Hf to Bi have been measured by means of electron spectroscopy. The binding energies obtained are compared to previously reported values.

High-accuracy measurements of the binding energies of most of the core levels in the 5d transition metals cannot be found in the literature. We have therefore recorded all core levels in the elements from $Z = 72$ to 83 accessible with Al Kα radiation. Special care has been taken to obtain clean sample surfaces and a reliable calibration procedure.

Spectra were recorded with a Hewlett–Packard 5950A ESCA spectrometer using monochromatised Al Kα radiation. Some modifications in the standard HP instrumentation have been made: for instance, the power supply which defines the starting point of the energy scan has been replaced by a Systron Donner Model M106A power supply, which has a much higher accuracy. The samples were cleaned *in situ* using a micro-mill with a rotating diamond edge. In this way we were able to obtain an oxide-free surface in all samples except for Hf and Ta. In Ta, however, only a very weak oxide signal was detected (see figure 1). For the calibration a thick layer of gold was evaporated on the sample surface and the given binding energy values are referred to the Au $4f_{7/2}$ level (84.00 eV).

The obtained binding energies (taken as the peak maxima) together with available literature data are given in table 1. The 4f core electron spectra are shown in figure 1. The data for Re, Os and Tl have been published elsewhere (Berndtsson *et al* 1979, Mårtensson *et al* 1980). The values for Hg are taken from Svensson *et al* (1976). However, except for the 4f and 5d levels, the calibration of the solid state values in that work might be somewhat uncertain. More accurate binding energies can be anticipated if one combines energy differences from the vapour phase (Svensson *et al* 1976) with the measured $4f_{7/2}$ solid phase value. We have, however, chosen to include only the directly measured values in table 1.

The Hf 4s level is not included in the table since it was disturbed by the O 1s signal from the oxide layer. The 5s and 5p levels in some of the elements are obscured by the characteristic energy loss peaks of the 4f levels and could not be detected with high accuracy. Figure 2 shows the 4f and 5p core electron spectra. The $4f_{7/2}$ levels are used as the zero point of the binding energy scale. The positions of the 5p levels then form a curve, smoothly varying with the atomic number. We can see that the $5p_{3/2}$ and $5p_{1/2}$ levels cross the 4f levels at Re and Ir respectively. From the systematic behaviour of the 5p binding

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Table 1. Binding energies in eV for the elements Hf to Bi from this work and from the literature. The binding energies from this work are calibrated against the Au $4f_{7/2}$ level (84.00 eV).

	4s	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	5s	$5p_{1/2}$	$5p_{3/2}$	$4f_{5/2}$	$4f_{7/2}$	$5d_{3/2}$	$5d_{5/2}$
^{72}Hf		438.2 (6)[a,b]	380.7 (5)[a,b]	222.0 (4)[a,b]	211.5 (4)[a,b]	64.2 (8)[a,b]		29.9 (4)[a,b]	15.91 (20)[a,b]	14.23 (20)[a,b]		
	538[c]	437[c]	380[c]	224[c]	214[c]	65[c]	38[c]	31[c]	19[c]	18[c]		
^{73}Ta	563.4 (8)[a,b]	463.4 (5)[a,b]	400.9 (3)[a,b]	237.9 (3)[a,b]	226.4 (3)[a,b]	69.7 (8)[a,b]		32.7 (4)[a,b]	23.53 (15)[a,b]	21.61 (15)[a,b]		
	563 (1)[d]	462.3 (8)[d]	402.0 (8)[d]	238.6 (5)[e]	227.1 (5)[e]	68.6 (8)[d]	42.4 (8)[d]	33.9 (8)[d]	24.8 (2)[e]	23.0 (1)[e]		
							42.1 (5)[f]	31.4 (5)[f]				
^{74}W	594.3 (8)[a]	490.8 (5)[a]	423.7 (3)[a]	256.0 (3)[a]	243.5 (3)[a]	75.5 (8)[a]	[47 (1)][s]	37.2 (4)[a]	33.48 (10)[a]	31.32 (10)[a]		
	592 (1)[d]	489 (1)[d]	422 (1)[d]	255.2 (5)[e]	242.9 (5)[e]	74 (1)[d]	44 (1)[d]	33 (1)[d]	33.6 (2)[e]	31.5 (2)[e]		
							46.5 (5)[f]	34.7 (5)[f]				
^{75}Re	625.4 (8)[g]	518.7 (5)[g]	446.8 (3)[g]	273.9 (3)[g]	260.5 (3)[g]	83 (1)[g]	[51 (1)][s]	[40 (1)][s]	42.88 (10)[g]	40.46 (10)[g]		
	625.0 (8)[d]	517.9 (8)[d]	444.4 (8)[d]	273.7 (5)[e]	260.2 (5)[e]	82.8 (8)[d]	45.6 (7)[d]	34.6 (6)[d]	42.9 (2)[e]	40.5 (2)[e]		
							50.4 (5)[f]					
^{76}Os	658.2 (8)[g]	549.1 (5)[g]	470.7 (3)[g]	293.1 (3)[g]	278.5 (3)[g]		[57 (1)][s]	44.5 (3)[g]	53.43 (10)[g]	50.70 (10)[g]		
	655[c]	547[c]	469[c]	290[c]	273[c]	84[c]	58[c]	46[c]	52[c]	50[c]		
^{77}Ir	691.1 (8)[a]	577.8 (5)[a]	494.8 (3)[a]	311.9 (3)[a]	296.3 (3)[a]		[61 (1)][s]	48.0 (3)[a]	63.76 (10)[a]	60.75 (10)[a]		
	690.6 (8)[d]	577.6 (8)[d]	494.8 (6)[d]	311.5 (5)[e]	295.8 (5)[e]	95.2 (8)[d]	63.0 (8)[d]	50.5 (8)[d]	63.6 (2)[e]	60.7 (2)[e]		
^{78}Pt	725.7 (8)[a]	609.2 (5)[a]	519.5 (3)[a]	331.5 (3)[a]	314.6 (3)[a]		[67 (1)][s]	51.7 (3)[a]	74.40 (10)[a]	71.07 (10)[a]		
	725 (1)[d]	608.4 (8)[d]	519.9 (8)[d]	331.6 (5)[e]	314.8 (5)[e]	101.7 (8)[d]	65.3 (8)[d]	51.0 (8)[d]	74.5 (1)[e]	71.2 (1)[e]		
					314.5 (1)[h]			51.7 (2)[j]	74.4 (3)[i]	71.1 (3)[i]		
									74.41 (5)[j]	71.1 (1)[h]		
										71.07 (5)[j]		
^{79}Au	762.3 (8)[a]	642.9 (5)[a]	546.4 (3)[a]	353.3 (3)[a]	335.2 (3)[a]		74.2 (4)[a]	57.2 (3)[a]	87.67 (10)[a]	84.00		
	759 (1)[d]	643.5 (3)[i]	546.5 (3)[i]	353.0 (8)[d]	335.1 (1)[h]	107.2 (8)[d]	71.2 (8)[d]	58 (1)[d]	87.6 (1)[e]	84.0 (1)[e]		
									87.7 (3)[i]	84.0 (1)[h]		
									87.74 (2)[k]	84.0 (3)[i]		
										84.07 (2)[k]		
^{80}Hg	803[l]	681[l]	576.9[l]	378.5[l]	359.3[l]		84[l]	65[l]	104.0 (3)	99.9 (3)[l]	9.8 (2)[l]	7.8 (2)[l]
	800 (2)[d]	677 (2)[d]	571 (2)[d]	378 (2)[d]	360 (2)[d]	120 (2)[d]	81 (2)[d]	65 (1)[d]	103.9 (3)[e]	99.8 (3)[e]	9.5 (1)[m]	7.7 (1)[m]

Table 1.—*continued.*

	4s	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	5s	$5p_{1/2}$	$5p_{3/2}$	$4f_{5/2}$	$4f_{7/2}$	$5d_{3/2}$	$5d_{5/2}$
^{81}Tl	846.4 (8)[o]	720.0 (8)[o]	609.7 (5)[o]	405.8 (3)[o]	385.0 (3)[o]		94.6 (4)[o]	73.4 (4)[o]	122.17 (10)[o]	117.73 (10)[o]	14.72 (10)[o]	12.47 (10)[o]
	846 (2)[d]	721 (2)[d]	609 (2)[d]	407 (2)[d]	386 (2)[d]	136 (1)[d]	100 (1)[d]	73 (1)[d]	123 (1)[d]	119 (1)[d]	14.53 (7)[p]	12.30 (7)[p]
											15.64 (10)[q]	13.43 (10)[q]
82Pb	892 (1)[a]	761.9 (8)[a]	643.5 (5)[a]	434.1 (3)[a]	412.0 (3)[a]		106.6 (7)[a]	83.3 (5)[a]	141.64 (10)[a]	136.78 (10)[a]	20.59 (10)[a]	17.96 (10)[a]
	893 (1)[d]	763 (1)[d]	644 (1)[d]	434.2 (5)[e]	412.0 (5)[e]	147 (1)[d]	104 (1)[d]	82 (1)[d]	141.2 (3)[e]	136.4 (3)[e]	20.32 (7)[p]	17.70 (7)[p]
											20.18 (10)[q]	17.52 (10)[q]
83Bi	939 (1)[a]	805.4 (8)[a]	678.8 (5)[a]	464.0 (3)[a]	440.1 (3)[a]		119.1 (8)[a]	92.8 (6)[a]	162.16 (10)[a]	156.85 (10)[a]	26.86 (10)[a]	23.84 (10)[a]
	939 (1)[d]	805.8 (8)[d]	679.4 (8)[d]	464.2 (5)[e]	440.5 (5)[e]	159.3 (7)[d]	116.8 (7)[d]	93.1 (7)[d]	162.2 (3)[e]	159.3 (3)[e]	26.94 (7)[p]	23.90 (7)[p]
				463.7 (2)[j]	440.3 (2)[j]				162.21 (5)[j]	156.88 (5)[j]	26.9[r]	23.8[r]
											27.4 (1)[q]	24.3 (1)[q]
											26.97 (5)[j]	23.86 (5)[j]

[a] This work.
[b] Partly oxidised sample.
[c] Siegbahn *et al* (1967).
[d] Obtained by combining the photoemission binding energies with energy differences from Bearden and Burr (1967).
[e] Kowalczyk (1976).
[f] From characteristic electron energy loss measurements (Hartley 1969).
[g] Berndtsson *et al* (1979).
[h] Schön (1972–3).
[i] S Hüfner: private communication in Cardona and Ley (1978).
[j] van Attekum and Trooster (1979).
[k] Asami (1976).
[l] Svensson *et al* (1976) calibrated against the Hg valence band edge.
[m] Kowalczyk *et al* (1972).
[o] Mårtensson *et al* (1980).
[p] Ley *et al* (1972).
[q] Poole *et al* (1973).
[r] Hurych and Benbow (1977).
[s] Obtained from the systematic behaviour of the 5p binding energies in the neighbouring elements (see figure 2 and text).

energy values it is possible also to get a relatively good estimation of the positions of the 5p levels for the elements in which these levels interfere with the 4f spectrum. The binding energies determined in this way are given in square brackets in table 1.

The agreement between the present values and those from other high-precision ESCA

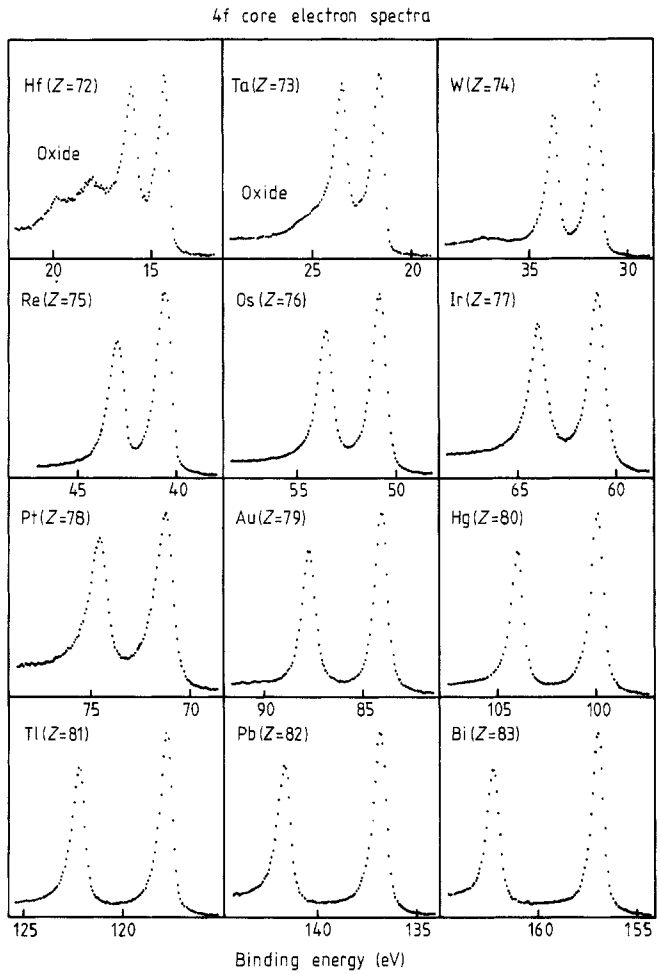

Figure 1. 4f core level spectra for the elements Hf to Bi (Z = 72–83).

measurements is generally good. In a few cases, however, there is a significant difference in the results. One reason for that might be that the quoted binding energy values have been determined from spectra which were not primarily recorded for the sake of obtaining accurate binding energies, and which thus might be insufficiently calibrated.

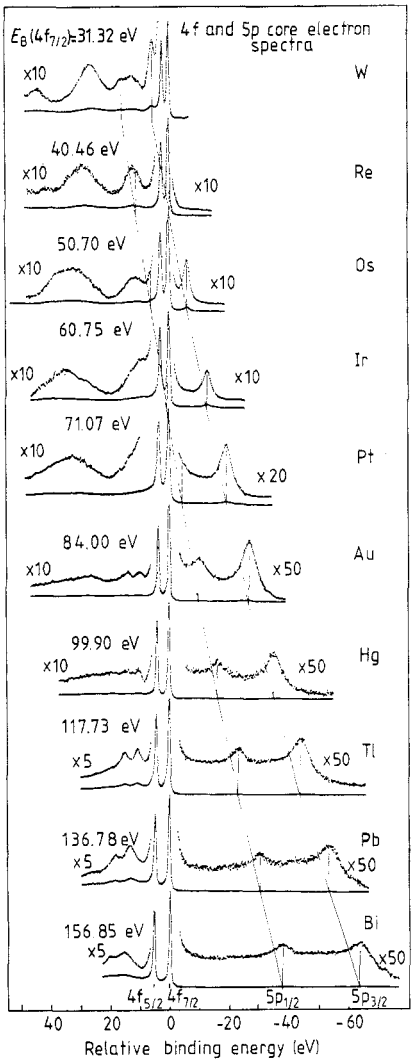

Figure 2. 4f and 5p core electron spectra of the elements W to Bi.

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