Valence orbital ionization potentials of $K(2)L(8)M(18)N(32)5s^25p^65d^\alpha 6s^\beta 6p^\gamma$ atoms and ions

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Valence orbital ionization potentials (VOIP) were systematically determined for atoms and ions with the electron configurations $K(2)L(8)M(18)N(32)5s^25p^65d^\alpha 6s^\beta 6p^\gamma$. The modified Anno and Sakai's relations were used for the approximation of VOIP dependence on the electron configuration and atomic number.

Потенциалы ионизации валентных орбиталей были определены для атомов и ионов с электронной конфигурацией $K(2)L(8)M(18)N(32)5s^25p^65d^\alpha 6s^\beta 6p^\gamma$. Модифицированные отношения Анноа и Сакаиго были использованы для выражения зависимости потенциалов ионизации от электронной конфигурации и атомного числа.

Approximative expressions for calculation of valence orbital ionization potentials (VOIP) of $K(2)L(8)M(18)4s^24p^64d^\alpha 5s^\beta 5p^\gamma$ atoms and ions were determined in previous paper [1]. In the present paper there are proposed analogous relations for calculations of VOIPs of atoms and ions with electron configurations $K(2)L(8)M(18)N(32)5s^25p^65d^\alpha 6s^\beta 6p^\gamma$. The aim of this work is to complete the consistent parametrization of VOIPs for atoms (ions) with atomic numbers 1—83 [1—8], which may be used in semiempirical methods of quantum chemistry.

Proposed approximative expressions of VOIPs are based on the *Anno* and *Sakai*'s relations [6—8]. The spectral values $VOIP^{spect}$ were obtained analogously as in the previous works [1—8] from all accessible spectral data [9]. Due to insufficient number of spectral terms it was necessary to modify the Anno and Sakai formula in the following manner

$$\mathrm{VOIP}_d^{\mathrm{approx}}(\alpha,\beta,\gamma,Z) = B_1 + B_2\beta + B_3\gamma + B_4\beta^2 + B_5\beta\gamma + B_6\alpha + B_7\alpha\beta + B_8\alpha\gamma + B_9\alpha^2 + B_{10}Z + B_{11}Z\beta + B_{12}Z\gamma + B_{13}Z\alpha + B_{14}Z^2 \quad (1)$$

$$\mathrm{VOIP}_s^{\mathrm{approx}}(\alpha,\beta,\gamma,Z) = B_1 + B_2\beta + B_3\gamma + B_4\beta\gamma + B_5\gamma^2 + B_6\alpha + B_7\alpha\beta + B_8\alpha\gamma + B_9\alpha^2 + B_{10}Z + B_{11}Z\beta + B_{12}Z\gamma + B_{13}Z\alpha + B_{14}Z^2 \quad (2)$$

$$\mathrm{VOIP}_p^{\mathrm{approx}}(\alpha,\beta,\gamma,Z) = B_1 + B_2\beta + B_3\gamma(1+\gamma) + B_4\beta^2 + B_5\beta\gamma + B_6\alpha + B_7\alpha\beta + B_8\alpha\gamma + B_9\alpha^2 + B_{10}Z + B_{11}Z\beta + B_{12}Z\gamma + B_{13}Z\alpha + B_{14}Z^2 \quad (3)$$

Table 1

Numerical values of coefficients B_k (eV)

	5*d*	6*s*	6*p*
B_1	6.441921×10^3	7.093896×10^3	4.559662×10^3
B_2	1.501010×10^2	9.274197×10	7.428676×10
B_3	2.606368×10^2	1.310971×10^2	1.304961
B_4	2.124405	5.647646×10^{-1}	1.837709×10^{-1}
B_5	6.115840	3.464748×10^{-1}	9.194617×10^{-2}
B_6	-1.267332×10^2	1.475768×10^2	2.622208×10
B_7	−1.323361	6.028628×10^{-1}	-1.496946×10^{-1}
B_8	6.376120×10^{-2}	1.125305	9.197450
B_9	−3.071848	7.084220×10^{-1}	-4.531814×10^{-1}
B_{10}	-1.593061×10^2	-2.042383×10^2	-1.240668×10^2
B_{11}	−1.887207	−1.333604	-9.983419×10^{-1}
B_{12}	−3.424445	−1.857951	−1.284346
B_{13}	2.265421	−2.118391	−4.188494
B_{14}	9.533385×10^{-1}	1.471862	8.599515×10^{-1}

Table 2

Statistical characteristics of the approximated functions

Interval [a] %	5*d*	6*s*	6*p*
0.0— 1.0	5	9	9
1.0— 3.0	8	13	8
3.0— 5.0	4	8	6
5.0— 7.0	2	0	5
7.0—10.0	3	5	2
> 10.0	5	6	4
Number of experimental points	27	41	34
Degree of freedom	13	27	20
Correlation coefficient	0.9985	0.9970	0.9980

a) Numbers of points in given error range.

where α, β, γ are the numbers of s, p, d electrons, respectively, and Z is the atomic number.

The values of B_k coefficients in eqns (*1—3*) calculated by the least squares method are given in Table 1. Table 2 shows several statistical characteristics and

Table 3

Numerical values of $VOIP_{5d}$ (eV)

Atom	β	γ	α	q	$VOIP_{5d}^{spect}$	$VOIP_{5d}^{approx}$	Relative deviation %
Hf	2	0	2	0	6.520	6.101	− 6.43
	1	0	3	0	6.147	7.846	27.65
	1	1	2	0	8.472	8.472	0.00
Ta	2	0	3	0	7.684	6.422	− 16.43
	1	0	4	0	7.096	7.499	5.68
	0	0	5	0	11.077	9.330	− 15.77
W	1	0	5	0	7.729	7.446	− 3.64
Re	2	0	5	0	6.902	7.944	15.10
	1	0	6	0	7.073	7.687	8.68
	0	1	6	0	9.129	9.129	0.00
Os	1	0	7	0	7.480	8.222	9.92
Pt	1	0	9	0	10.716	10.173	− 5.06
	0	0	10	0	8.656	8.665	0.10
Au	1	0	10	0	11.854	11.590	− 2.32
Hg	2	0	10	0	15.579	16.895	8.45
	1	1	10	0	18.066	18.066	0.00
	1	0	10	1	24.906	24.631	− 1.12
	2	0	9	1	26.083	23.407	− 10.25
	0	0	10	2	34.878	36.616	4.98
	1	0	9	2	29.400	29.819	1.42
	2	0	8	2	23.315	23.774	1.97
Tl	1	0	10	2	40.234	39.580	− 1.62
Pb	2	1	10	1	37.626	37.626	0.00
	2	0	10	2	45.540	44.924	− 1.35
	1	0	10	3	57.355	56.435	− 1.60
Bi	2	0	10	3	59.644	61.798	3.61
	1	0	10	4	76.038	75.197	− 1.11

q — charge of given atom.

error distribution of the above approximations. VOIPs obtained by the analysis of atomic spectra ($VOIP^{spect}$) and also the values obtained using eqns (*1*—*3*) are given in Tables 3—5 for comparison, together with the relative deviations of $VOIP^{approx}$ from $VOIP^{spect}$ in percentages.

The results show that the approximated values are in a good agreement with the spectral values, which justifies their usage in semiempirical methods of calculation of electron structures of molecules.

Table 4

Numerical values of $VOIP_{os}$ (eV)

Atom	β	γ	α	q	$VOIP_{os}^{spect}$	$VOIP_{os}^{approx}$	Relative deviation %
Hf	2	0	2	0	7.853	7.670	− 2.33
	1	0	3	0	8.190	8.939	9.13
	1	1	2	0	10.226	10.228	0.02
Ta	2	0	3	0	8.410	7.629	− 9.28
	1	0	4	0	9.915	8.928	− 9.95
W	2	0	4	0	7.472	7.713	3.21
	1	0	5	0	8.189	9.040	10.39
Re	2	0	5	0	7.647	7.920	3.57
	1	1	5	0	10.403	10.472	0.67
Os	2	0	6	0	7.886	8.251	4.63
	1	1	6	0	10.918	10.802	− 1.06
Pt	1	0	9	0	8.622	7.228	−16.17
Au	1	0	10	0	9.220	11.461	24.31
	2	0	9	0	10.109	9.988	−12.00
Hg	2	0	10	0	10.430	10.813	3.68
	1	1	10	0	12.001	13.357	11.26
	2	1	9	0	12.006	12.107	0.84
	1	0	10	1	18.751	18.732	− 0.10
	2	0	9	1	19.837	18.043	− 9.04
	1	0	9	2	28.642	26.563	− 7.26
	2	0	8	2	23.155	26.688	15.26
Ti	2	1	10	0	13.130	13.026	− 0.79
	1	2	10	0	15.244	15.173	− 0.46
	2	0	10	1	20.420	19.694	− 3.55
	1	1	10	1	21.929	21.713	− 0.98
	1	0	10	2	29.800	28.946	− 2.86

Table 4 (Continued)

Atom	β	γ	α	q	$VOIP_{6s}^{spect}$	$VOIP_{6s}^{approx}$	Relative deviation %
Pb	2	2	10	0	15.956	15.160	− 4.98
	2	1	10	1	22.625	22.992	1.62
	1	2	10	1	24.931	24.615	− 1.27
	2	0	10	2	31.930	31.518	− 1.29
	1	1	10	2	34.351	33.013	− 3.89
	1	0	10	3	42.310	42.103	− 0.49
	2	0	9	3	43.744	42.984	− 1.73
Bi	2	3	10	0	16.899	17.214	1.86
	2	2	10	1	26.866	26.212	− 2.43
	2	1	10	2	34.312	35.902	4.63
	1	2	10	2	36.109	37.000	2.47
	2	0	10	3	45.300	46.286	2.18
	1	1	10	3	48.016	47.256	− 1.58
	1	0	10	4	56.000	58.204	3.93
	2	0	9	4	61.939	59.870	− 2.95

q — charge of given atom.

Table 5

Numerical values of $VOIP_{6p}$ (eV)

Atom	β	α	γ	q	$VOIP_{6p}^{spect}$	$VOIP_{6p}^{approx}$	Relative deviation %
Hf	1	1	2	0	5.426	6.071	−11.88
Ta	1	1	3	0	5.715	6.004	− 5.07
	2	1	2	0	6.028	5.328	+11.60
	0	1	4	0	6.950	6.441	+ 7.32
Re	1	1	5	0	5.907	5.800	+ 1.82
	2	1	4	0	5.188	5.477	− 5.58
Os	1	1	6	0	5.692	5.660	+ 0.54
Au	0	1	10	0	4.273	4.473	− 4.68
	1	1	9	0	5.443	5.099	+ 6.31
Hg	1	1	10	0	4.869	4.864	+ 0.10
	2	1	9	0	6.128	5.428	+11.43
	0	2	9	1	6.036	6.112	− 1.26
	0	1	10	1	11.614	11.665	− 0.44
	1	1	9	1	11.789	11.712	+ 0.65

Table 5 (Continued)

Atom	β	α	γ	q	$VOIP_{6p}^{spect}$	$VOIP_{6p}^{approx}$	Relative deviation %
Tl	2	1	10	0	5.462	5.345	+ 2.14
	1	2	10	0	6.553	6.032	+ 7.96
	1	1	10	1	12.752	12.778	− 0.21
	0	2	10	1	13.239	13.741	− 3.79
	0	1	10	2	20.622	20.578	+ 0.21
Pb	2	2	10	0	6.814	6.043	+ 11.32
	2	1	10	1	13.864	13.981	− 0.84
	1	2	10	1	13.484	14.382	− 6.66
	1	1	10	2	23.169	22.412	+ 3.27
	0	2	10	2	23.404	23.088	+ 1.35
	2	1	9	2	21.779	21.817	− 0.18
	0	1	10	3	31.127	31.210	− 0.27
Bi	2	3	10	0	8.140	8.502	− 4.44
	2	2	10	1	15.596	15.114	+ 3.09
	1	3	10	1	18.108	17.747	+ 1.99
	2	1	10	2	23.842	24.337	− 2.08
	1	2	10	2	23.042	24.451	− 6.12
	1	1	10	3	34.830	33.766	+ 3.05
	0	2	10	3	34.950	34.156	+ 2.27
	0	1	10	4	42.813	43.563	− 1.75

q — charge of given atom.

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