Valence orbital ionization potentials of $K(2)L(8)M(18)4s^2 4p^6 4d^\alpha 5s^\beta 5p^\gamma$ atoms and ions

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Valence orbital ionization potentials were systematically determined for atoms and ions with the electron configurations $K(2)L(8)M(18)$-$4s^2 4p^6 4d^\alpha 5s^\beta 5p^\gamma$. For the approximation of the dependence of VOIP on the electron configuration and atomic number Anno and Sakai formulae having variables m. n, and Z were used.

Потенциалы ионизации валентных орбиталей были определены для атомов и ионов с электронной конфигурацией $K(2)L(8)M(18)$-$4s^2 4p^6 4d^\alpha 5s^\beta 5p^\gamma$. Для выражения зависимости потенциалов ионизации от электронной конфигурации и атомного числа были использованы формулы Анноа и Сакаиго с переменными m, n, и Z.

Slater's theory of many-electron atoms [1] is based on the Russell—Saunders scheme with a complete neglection of spin-orbital interaction and considers atoms in their average electron configurations. Commonly used methods of quantum chemistry for the calculation of electron structure of molecules are based on the LCAO MO approximation and consider atoms in molecules in the same approximation as the Slater's theory. This theory makes it possible to obtain semiempirical parameters by the analysis of atomic spectra in terms of the Slater's formalism. One of such parameters is the ionization potential of valence electrons (VOIP) defined by the relation

$$VOIP = E_{av}^+ - E_{av} + IP \tag{1}$$

where E_{av} is the average energy of the given electron configuration of atom (ion) with respect to its ground state in the given oxidation state and E_{av}^+ represents

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a similar quantity for the ion obtained by the removal of an electron from the valence orbital of the atom (ion) under consideration. IP is the ionization potential of the atom (ion).

Basch and co-workers [2] evaluated VOIPs for atoms and ions from H up to Kr for different configurations and different oxidation states. The dependence of VOIP on the charge (q) was approximately related by the quadratic equation

$$\text{VOIP} = Aq^2 + Bq + C \tag{2}$$

Anno and *Sakai* [3—5] showed by theoretical analysis that the dependence of VOIP on the electron configuration can be approximated by the function

$$\begin{aligned}
\text{VOIP}(\alpha,\beta,\gamma,Z) = B_1 + B_2\beta + B_3\gamma + B_4\beta^2 + B_5\beta\gamma + B_6\gamma^2 + \\
+ (B_7 + B_8\beta + B_9\gamma + B_{10}\alpha) \cdot \\
\cdot \alpha + (B_{11} + B_{12}\beta + B_{13}\gamma + B_{14}\alpha + B_{15}Z) Z
\end{aligned} \tag{3}$$

where B_k are the constants, which can be determined by the least squares method. This method has been used for the estimation of VOIPs for atoms and ions with electron configurations $K(2)2s^m 2p^n$ [3, 5], $K(2)L(8)3s^2 3p^6 3d^\alpha 4s^\beta 4p^\gamma$ [4, 5], $K(2)L(8)3s^m 3p^n$ [6], and $K(2)L(8)M(18)4s^m 4p^n$ [7], and it was also used in the present work for calculation of VOIPs of atoms and ions of the second transition series with electron configurations $K(2)L(8)M(18)4s^2 4p^6 4d^\alpha 5s^\beta 5p^\gamma$.

Results

Energies of individual spectral terms (E_i) were calculated as a weighted average values of the J-structure spectral levels (E_i^J)

$$E_i = \frac{\sum_J (2J + 1) E_i^J}{\sum_J (2J + 1)} \tag{4}$$

Average values of energy of individual electron configurations E_{av} were obtained as a weighted average of energy of individual atomic terms of the given electron configuration

$$E_{av} = \frac{\sum_i (2L_i + 1)(2S_i + 1) E_i}{\sum_i (2L_i + 1)(2S_i + 1)} \tag{5}$$

The required values of ionization potentials were taken from *Moore*'s tables [8]. On the basis of these data the spectral values VOIP^{spect} were calculated (see Table 3)

Table 1

Numerical values of coefficients B_k [eV]

	4d	5s	5p
B_1	2.82136×10^3	-2.90401×10^2	2.09810×10^3
B_2	9.37670×10^1	-8.03137	8.19072×10^1
B_3	1.06927×10^2	9.39417×10^{-1}	-3.36228
B_4	7.37058×10^{-1}	0.00000	5.92631×10^{-1}
B_5	5.21984×10^{-1}	9.67585×10^{-3}	1.88244
B_6	3.24864×10^{-1}	-7.58950	1.07172×10^2
B_7	1.37794×10^2	-1.74974×10^{-1}	2.06424
B_8	2.22539	-1.69943×10^{-3}	7.75502×10^{-1}
B_9	2.46094	-1.27453×10^{-1}	1.29568
B_{10}	1.63284	7.04542	-1.16114×10^2
B_{11}	-1.60570×10^2	2.52366×10^{-2}	-2.32134
B_{12}	-2.68650	-2.13563×10^{-1}	2.01849×10^{-1}
B_{13}	-2.98164	-4.56440×10^{-4}	-2.97653
B_{14}	-3.91864	2.87732×10^{-2}	1.60701
B_{15}	2.28499	0.00000	0.00000

Table 2

Statistical characteristics of the approxima-

ted functions

Interval[a] %	4d	5s	5p
0.0- 1.0	13	5	6
1.0- 2.0	4	5	2
2.0- 3.0	10	3	3
3.0- 4.0	7	6	2
4.0- 6.0	14	8	6
6.0- 8.0	10	7	4
8.0-10.0	9	7	4
10.0	13	16	18
Number of experimental points	80	57	45
Degree of freedom	65	44	31
Standard deviation eV	1.676	1.179	1.550

Table 2 (Continued)

	4d	5s	5p
Correlation coefficient	0.991	0.977	0.981

a) Distribution in various error ranges.

Table 3

Numerical values of $VOIP_{4d}$ [eV]

Atom	β	γ	α	q	$VOIP_{4d}^{spect}$	$VOIP_{4d}^{approx}$	Relative deviation %
Y	2	0	1	0	6.467	6.601	- 2.08
	1	0	2	0	4.853	5.263	- 8.43
	1	1	1	0	7.661	7.122	7.03
	0	1	2	0	5.808	6.971	-20.03
	0	0	3	0	4.179	4.213	- 0.37
	0	2	1	0	8.723	8.723	0.00
	1	0	1	1	13.120	13.171	- 0.39
	0	0	2	1	10.989	11.081	- 0.84
	0	1	1	1	14.011	14.644	- 4.52
	0	0	1	2	20.455	21.215	- 3.72
Zr	2	0	2	0	8.519	7.652	10.18
	1	0	3	0	6.137	6.122	0.24
	1	1	2	0	9.403	8.114	13.71
	0	0	4	0	5.514	4.880	11.49
	0	1	3	0	7.189	7.771	- 8.09
	1	0	2	1	15.738	14.683	6.70
	0	0	3	1	13.380	12.402	7.31
	2	0	1	1	16.509	17.254	- 4.51
	0	1	2	1	17.247	16.097	6.67
	0	0	2	2	24.236	23.189	4.32
	1	0	1	2	27.037	26.511	1.95
	0	1	1	2	27.459	27.689	- 0.84
	0	0	1	3	33.893	37.241	- 9.88
Nb	1	0	4	0	7.235	6.980	3.53
	1	1	3	0	9.795	9.104	7.06
	0	0	5	0	4.609	5.546	-20.83
	0	1	4	0	8.252	8.569	- 3.84
	0	0	4	1	12.443	13.720	-10.27

Table 3 (Continued)

Atom	β	γ	α	q	VOIP$_{4d}^{spect}$	VOIP$_{4d}^{approx}$	Relative deviation %
Nb	1	0	3	1	15.350	16.194	- 5.50
	0	1	3	1	16.659	17.548	- 5.34
	0	0	3	2	28.495	25.160	11.70
	1	0	2	2	31.206	28.674	8.11
	0	1	2	2	32.115	29.793	7.23
	0	0	2	3	37.908	39.866	- 5.16
	1	0	1	3	42.159	45.303	- 7.46
Mo	1	0	5	0	7.977	7.836	1.77
	0	0	6	0	5.985	6.210	- 3.77
	0	1	5	0	9.717	9.365	3.61
	1	0	4	1	16.353	17.703	- 8.26
	0	1	4	1	17.548	18.997	- 8.26
	1	0	3	2	30.735	30.836	- 0.33
	0	1	3	2	31.722	31.895	- 0.55
	0	0	3	3	46.827	42.469	9.26
	1	0	2	3	49.965	47.235	5.46
	0	1	2	3	50.995	48.058	5.76
Tc	1	0	6	0	8.272	8.690	- 5.05
Ru	1	0	7	0	9.476	9.543	- 0.70
	2	0	6	0	9.135	11.841	-29.62
	0	0	8	0	6.905	7.534	- 9.10
	1	1	6	0	12.389	12.064	2.63
	0	1	7	0	10.912	10.954	- 0.38
	0	0	7	1	15.301	17.667	-15.46
	1	0	6	1	17.183	20.716	-20.56
	0	1	6	1	18.406	21.891	-18.94
Rh	1	0	8	0	10.297	10.314	- 0.94
	0	0	9	0	7.792	8.193	- 5.15
	0	1	8	0	11.947	11.745	- 1.69
	0	0	8	1	19.440	18.979	2.37
	1	0	7	1	23.991	22.220	7.38
	0	1	7	1	25.095	23.336	7.01

Table 3 (Continued)

Atom	β	γ	α	q	VOIP$_{4d}^{spect}$	VOIP$_{4d}^{approx}$	Relative deviation %
Pd	0	0	10	0	8.549	8.851	- 3.53
	1	0	9	0	11.664	11.244	3.60
	0	1	9	0	13.263	12.535	5.49
	0	0	9	1	20.308	20.290	0.09
	1	0	8	1	24.206	23.723	2.00
	0	1	8	1	25.410	24.779	2.48
Ag	1	0	10	0	12.833	12.092	5.78
	0	1	10	0	14.571	13.324	8.56
	0	0	10	1	21.766	21.599	0.76
	1	0	9	1	25.645	25.224	1.64
	0	1	9	1	26.839	26.220	2.30
Cd	2	0	10	0	17.927	16.003	10.73
	1	1	10	0	13.144	15.988	-21.64
	1	0	10	1	27.377	26.723	2.39
	0	1	10	1	28.899	27.660	4.29
	2	0	9	1	31.624	30.829	2.51
	0	0	10	2	37.830	38.917	- 2.87
	1	0	9	2	41.962	43.774	- 4.32
	0	1	9	2	43.397	44.475	- 2.49

Table 4

Numerical values of VOIP$_{5s}$ [eV]

Atom	β	γ	α	q	VOIP$_{5s}^{spect}$	VOIP$_{5s}^{approx}$	Relative deviation %
Y	2	0	1	0	6.673	5.956	10.75
	2	1	0	0	8.752	7.610	13.05
	1	0	2	0	6.104	5.013	17.87
	1	1	1	0	7.670	6.736	12.18
	1	2	0	0	10.027	10.085	- 0.58
	2	0	0	1	13.326	14.040	- 5.36
	1	0	1	1	12.239	13.196	- 7.91
	1	1	0	1	14.020	14.629	- 4.34
	1	0	0	2	19.574	21.087	- 7.73

310

Table 4 (Continued)

Atom	β	γ	α	q	VOIP$_{5s}^{spect}$	VOIP$_{5s}^{approx}$	Relative deviation %
Zr 2	0	2	0		7.302	6.984	4.35
1	0	3	0		6.630	5.936	10.47
1	1	2	0		8.193	7.698	6.04
2	1	1	0		7.477	8.678	-16.06
1	0	2	1		13.873	14.356	- 3.48
2	0	1	1		14.521	15.324	- 5.53
1	1	1	1		16.038	15.865	1.08
1	0	1	2		22.371	22.521	- 0.67
2	0	0	2		25.048	23.409	6.54
1	0	0	3		29.227	30.431	- 4.12
Nb 1	0	4	0		7.007	6.660	4.94
2	0	3	0		7.649	7.814	- 2.16
1	1	3	0		8.246	8.463	- 2.64
1	0	3	1		12.215	15.336	-25.55
1	1	2	1		15.110	16.885	6.32
1	0	2	2		25.359	23.756	6.32
1	0	1	3		32.062	31.922	0.44
Mo 1	0	5	0		6.977	7.187	- 3.01
2	0	4	0		8.147	8.446	- 3.67
1	1	4	0		9.892	9.030	- 8.72
1	0	3	1		23.176	24.793	- 6.98
1	0	2	2		39.268	33.214	15.42
Tc 2	0	5	0		9.762	8.880	9.03
1	0	6	0		11.964	7.515	37.19
Ru 1	0	7	0		7.461	7.645	- 2.45
2	0	6	0		8.355	9.115	- 9.10
1	1	6	0		11.185	9.567	14.46
2	0	5	1		16.403	18.477	-12.64
1	0	6	1		13.286	17.086	-28.60
1	1	5	1		17.202	18.756	- 9.03
Rh 1	0	8	0		7.254	7.576	- 4.43
2	0	7	0		8.840	9.152	- 3.53
1	0	7	1		15.397	17.273	- 5.34
Pd 1	0	9	0		7.429	7.309	1.62
2	0	8	0		9.352	8.991	3.86
1	1	8	0		10.366	9.312	9.90

Table 4 (Continued)

Atom	β	γ	α	q	VOIP$_{5s}^{spect}$	VOIP$_{5s}^{approx}$	Relative deviation %
Pd 1	0	8	1		16.073	17.261	- 7.39
Ag 1	0	10	0		7.574	6.844	9.63
2	0	9	0		8.807	8.632	1.99
1	1	9	0		10.254	8.887	13.32
1	0	9	1		16.506	17.052	- 3.30
Cd 2	0	10	0		8.991	8.074	10.20
1	1	10	0		4.450	8.264	-85.73
1	0	10	1		16.904	16.644	1.54
2	0	9	1		18.441	18.457	- 0.09
1	1	9	1		20.205	18.474	8.57
1	0	9	2		27.357	26.852	1.85
2	0	8	2		28.779	28.585	0.68

Table 5

Numerical values of VOIP$_{5p}$ [eV]

Atom	β	γ	α	q	VOIP$_{5p}^{spect}$	VOIP$_{5p}^{approx}$	Relative deviation %
Y 2	1	0	0		5.143	4.139	19.53
1	1	1	0		4.258	4.326	- 1.60
0	1	2	0		3.647	4.161	-14.11
1	2	0	0		5.809	5.809	0.00
0	2	1	0		4.514	4.010	11.15
1	1	0	1		9.717	9.103	6.31
0	1	1	1		8.827	8.412	4.71
0	2	0	1		9.802	10.076	- 2.80
0	1	0	2		15.271	15.253	0.11
Zr 1	1	2	0		4.550	4.907	- 7.83
0	2	2	0		5.602	5.826	- 3.98
0	1	3	0		4.040	4.614	-14.21
2	1	1	0		3.843	4.847	-26.14
0	1	2	1		10.230	9.249	9.59
1	1	1	1		10.886	10.069	7.50
0	1	1	2		17.219	16.476	4.31
0	1	0	3		23.653	26.294	-11.17
Nb 1	1	3	0		4.435	5.340	-20.38
0	1	4	0		4.214	4.919	-16.72

Table 5 (Continued)

Atom	β	γ	∡	q	VOIP$_{5p}^{spect}$	VOIP$_{5p}^{approx}$	Relative deviation %
Nb	0	1	3	1	8.404	9.940	-18.26
	1	1	2	1	9.991	10.887	- 8.97
	0	1	2	2	20.240	17.551	13.28
	0	1	1	3	26.034	27.755	- 6.61
Mo	0	1	5	0	4.489	5.076	-13.07
	1	1	4	0	5.665	5.625	0.70
	0	1	3	2	17.754	18.479	- 4.09
	0	1	2	3	32.858	29.068	11.54
Tc	1	1	5	0	6.428	5.762	10.35
	0	1	6	0	9.637	5.086	47.23
Ru	0	1	7	0	4.263	4.947	-16.05
	1	1	5	1	11.344	12.456	- 9.80
	0	1	6	1	8.652	11.124	-28.57

Table 5 (Continued)

Atom	β	γ	∡	q	VOIP$_{5p}^{spect}$	VOIP$_{5p}^{approx}$	Relative deviation %
Rh	0	1	8	0	3.920	4.662	-18.91
	0	1	7	1	11.413	11.223	1.67
Pd	0	1	9	0	3.848	4.228	- 9.89
	1	1	8	0	5.155	5.289	- 2.61
	0	1	8	1	10.892	11.175	- 2.59
Ag	0	1	10	0	3.853	3.647	5.35
	1	1	9	0	4.795	4.836	- 0.85
	0	1	9	1	11.048	10.978	0.63
Cd	0	2	10	0	5.335	5.341	- 0.11
	0	1	10	1	11.278	10.635	5.71
	1	1	9	1	13.057	12.479	4.42
	0	1	9	2	20.209	20.942	- 3.63

$$\text{VOIP}_d^{spect}(\alpha,\beta,\gamma,Z) = E_{av}^+(\alpha-1,\beta,\gamma,Z) - E_{av}(\alpha,\beta,\gamma,Z) + \text{IP}(q,Z) \tag{6}$$

$$\text{VOIP}_s^{spect}(\alpha,\beta,\gamma,Z) = E_{av}^+(\alpha,\beta-1,\gamma,Z) - E_{av}(\alpha,\beta,\gamma,Z) + \text{IP}(q,Z) \tag{7}$$

$$\text{VOIP}_p^{spect}(\alpha,\beta,\gamma,Z) = E_{av}^+(\alpha,\beta,\gamma-1,Z) - E_{av}(\alpha,\beta,\gamma,Z) + \text{IP}(q,Z) \tag{8}$$

for atoms and ions of the second transition series. The values of VOIP^{spect} obtained in this way were used for calculation of the constants B_k in eqn (3). For VOIP$_s^{approx}$ and VOIP$_p^{approx}$, due to insufficient number of spectral terms it was necessary to modify the Anno and Sakai formula into the following form

$$\text{VOIP}_a^{approx}(\alpha,\beta,\gamma,Z) = B_1 + B_2\beta + B_3(\gamma+1)\,\gamma + B_4\beta^2 + B_5\beta\gamma + (B_6 + B_7\beta + B_8\gamma + B_9\alpha)\,\alpha +$$
$$+ (B_{10} + B_{11}\beta + B_{12}\gamma + B_{13}\alpha + B_{14}Z)\,Z \tag{9}$$

where $a = 5s$, or $5p$.

The values of coefficients B_k in eqns (3) and (9) calculated by the least squares method are shown in Table 1. Table 2 shows several statistical characteristics and error distribution of the above approximations. VOIPs obtained by the analysis of atomic spectra (VOIP^{spect}) are compared (Table 3) with the values obtained by the method of Anno and Sakai approximation. In Tables 3—5 one can find also 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 theirs application in semiempirical methods of calculation of electronic structures of molecules.

312

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Translated by P. Pelikán