Valence orbital ionization potentials of $K(2)L(8)M(18)4s^24p^64d^{10}5s^m5p^n$ atoms and ions

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Valence orbital ionization potentials were systematically determined for atoms and ions with the electron configurations $K(2)L(8)M(18)4s^24p^64d^{10}5s^m5p^n$. 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.

Систематически были определены потенциалы ионизации валентных орбиталей для атомов и ионов с электронной конфигурацией $K(2)L(8)M(18)4s^24p^64d^{10}5s^m5p^n$. Для приближения зависимостей потенциалов ионизации от электронной конфигурации и атомного числа были использованы отношения Анно и Сакаи с переменными m, n и Z.

Valence orbital ionization potentials (VOIP) are important parameters of semiempirical methods of quantum chemistry. VOIPs are defined as

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

where E_{av} is the average energy of the given electron configuration of atom (ion) with respect to its ground state and E^{+}_{av} is a similar quantity for the ion formed by the removal of one valence electron from the atom (ion) under consideration. IP is the ionization potential of the atom (ion) in its ground state.

Results obtained from atomic spectroscopy show a significant dependence of VOIP on the electron configuration of atoms. *Basch, Viste,* and *Gray* [1] approximated this dependence by the formula

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

where q is the atomic charge and A, B, C are the empirical parameters dependent on the electron configuration of atom under consideration. Determination of these constants is often impossible on account of insufficient number of experimental data.

Anno and *Sakai* [2—4] suggested by theoretical analysis more suitable expression which includes atoms of the whole given row of periodic system, which considerably reduces the number of necessary experimental data.

Table 1

Numerical values of B_k's (eV)

	5*s*	5*p*
B_1	1.7883452×10^{3}	1.6843991×10^{3}
B_2	4.0740181×10^{1}	5.6825000×10^{1}
B_3	5.2761313×10^{1}	4.5230628×10^{1}
B_4	—	1.2907470×10^{-1}
B_5	6.5133050×10^{-1}	6.0782110×10^{-1}
B_6	1.8057100×10^{-1}	$-1.4585400 \times 10^{-2}$
B_7	-8.4321990×10^{1}	-7.9003597×10^{1}
B_8	-1.0260300	-1.3300989
B_9	-1.2507210	-1.0602620
B_{10}	9.9160600×10^{-1}	9.2206600×10^{-1}

Table 2

Statistical characteristics of the approximated functions

Interval[a] %	5*s*	5*p*
0.0— 1.0	12	9
1.0— 2.0	7	7
2.0— 3.0	4	5
3.0— 4.0	2	3
4.0— 6.0	4	3
6.0— 8.0	0	5
8.0—10.0	3	4
>10.0	1	3
Number of experimental points	33	39
Degree of freedom	24	29
Standard deviation (eV)	1.500	1.563
Correlation coefficient	0.99698	0.99521

a) Distribution of data in various error ranges.

Table 3

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

Z	m	n	q	Spectral	Approximative	Relative deviation %
47	1	0	0	7.574	8.185	− 8.06
48	2	0	0	8.991	8.530	5.13
48	1	0	1	10.408	10.598	− 1.81
48	0	1	1	16.904	17.039	− 0.80
49	2	1	0	11.703	11.301	3.44
49	1	2	0	13.151	12.854	2.26
49	2	0	1	18.860	18.342	2.75
49	1	1	1	20.207	20.185	0.11
49	1	0	2	28.030	27.877	0.55
50	2	2	0	13.157	13.915	− 5.76
50	2	1	1	22.077	21.845	1.05
50	1	2	1	24.181	23.173	4.17
50	2	0	2	30.490	30.137	1.16
50	1	1	2	31.852	31.755	0.30
50	1	0	3	40.720	40.698	0.05
51	2	3	0	17.207	16.371	4.85
51	2	2	1	24.941	25.181	− 1.00
51	2	1	2	29.320	34.372	−17.23
51	1	2	2	35.470	35.476	− 0.02
51	2	0	3	44.100	43.915	0.42
51	1	1	3	45.500	45.308	0.42
51	1	0	4	56.000	55.502	0.89
52	2	4	0	17.281	18.671	− 8.04
52	2	3	1	29.043	28.381	2.28
52	2	2	2	42.671	39.451	9.89
52	2	1	3	48.337	48.883	− 1.13
52	1	2	3	48.101	49.762	− 3.45
52	2	0	4	60.000	59.676	0.54
52	1	1	4	61.449	60.845	0.98
52	1	0	5	72.000	72.289	− 0.40
53	2	5	0	20.439	20.814	− 1.83
54	2	6	0	23.393	22.799	2.54
54	2	5	1	33.871	34.288	− 1.23

Table 4

Numerical values of VOIP_{5p} (eV)

Z	m	n	q	Spectral	Approximative	Relative deviation %
47	0	1	0	3.834	3.458	− 9.82
48	1	1	0	4.731	4.703	0.60
48	0	2	0	5.335	5.284	0.95
48	0	1	1	11.227	10.990	2.11
49	2	1	0	5.602	5.390	3.79
49	1	2	0	6.190	6.591	− 6.47
49	1	1	1	12.759	12.749	0.08
49	0	2	1	13.246	13.601	− 2.68
49	0	1	2	20.582	20.366	1.05
50	2	2	0	6.842	7.340	− 7.28
50	1	3	0	7.442	8.174	− 9.83
50	2	1	1	14.277	13.950	2.29
50	1	2	1	15.762	15.421	2.16
50	1	1	2	22.690	22.640	0.22
50	0	2	2	23.433	23.761	− 1.40
50	0	1	3	31.558	31.587	− 0.09
51	2	3	0	8.436	8.984	− 6.50
51	2	2	1	20.899	16.684	20.17
51	1	3	1	16.171	17.788	−10.00
51	2	1	2	19.865	24.355	−22.61
51	1	2	2	25.278	26.096	− 3.23
51	1	1	3	34.645	34.374	0.78
51	0	2	3	35.308	35.765	− 1.30
51	0	1	4	45.145	44.652	1.09
52	2	0	4	9.791	10.323	− 5.43
52	2	3	1	18.290	19.112	− 4.49
52	1	4	1	21.554	19.849	7.91
52	2	2	2	30.506	27.872	8.61
52	1	3	2	31.918	29.246	8.37
52	2	1	3	37.238	36.604	1.70
52	1	2	3	36.172	38.614	− 6.75
52	1	1	4	48.901	47.953	1.94
52	0	2	4	49.519	49.614	− 0.19
52	0	1	5	59.452	59.561	− 0.18
53	2	5	0	11.556	11.356	1.73
54	2	6	0	12.562	12.084	3.81
54	2	5	1	22.090	23.052	− 4.35
54	1	6	1	23.040	23.054	− 0.06
54	2	4	2	33.141	33.991	− 2.57

For the elements with incompletely occupied s and p shells with electron configurations $s^m p^n$ VOIPs are approximated by the function [2, 4]

$$\mathrm{VOIP}(m, n, Z) = B_1 + B_2 m + B_3 n + B_4 m^2 + B_5 mn + B_6 n^2 + \\ + (B_7 + B_8 m + B_9 n + B_{10} Z) Z \qquad (3)$$

where B_k are empirical constants for the given row of periodic table. By this method were estimated VOIPs for atoms and ions with electron configurations $K(2)2s^m2p^n$ [2, 4], $K(2)L(8)3s^m3p^n$ [5, 6], $K(2)L(8)M(18)4s^m4p^n$ [7], $K(2)L(8)3s^23p^63d^\alpha4s^\beta4p^\gamma$ [3, 4], and $K(2)L(8)M(18)4s^24p^64d^\alpha5s^\beta5p^\gamma$ [8]. In the present paper this method is used for the determination of VOIPs for atoms and ions with electron configurations $K(2)L(8)M(18)4s^24p^64d^{10}5s^m5p^n$

Results

The energies of individual atomic terms were obtained as a weighted average of the J-structure of the given spectroscopic term. These values were used for the determination of the average energies of atoms (ions) in the given electron configuration (E_{av}). The energies of J-levels of atomic terms and the values of IP were extracted from Moore's spectroscopic tables [9]. The obtained spectroscopic values of VOIPs were used for determination of the B_k coefficients (Table 1) by means of the least squares method. In Tables 3 and 4 are listed spectral values of VOIP (spectral) and values obtained from eqn (3) (approximative) with their relative deviation in percentages. Some statistical characteristics of the used approximation are presented in Table 2.

The approximated values are in good correlation with spectral data, and are thus applicable in semiempirical methods of quantum chemistry. The obtained results are useful because they make possible to calculate the electron structure of compounds with chemically interesting atoms as I, Te, Sb, ..., in a consistent parametrization.

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