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Original Investigations

Valence Orbital Ionization Energies for Second-Row Transition Elements

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Valence Orbital Ionization Energies (VOIEs) are computed from Average Configuration Energies for the elements Sr through to In. VOIEs for a specific configuration are given in the form VOIE $(q) = C_2q^2 + C_1q + C_0$ where q is the atomic excess charge.

Key words: Orbital energy – Transition elements.

1. Introduction

In iterative charge self-consistent semi-empirical molecular orbital calculations, interelectronic repulsion effects are corrected in a first-order way by assigning a value for the Coulomb integral, appropriate to the excess charge and configuration of the atom at which the atomic orbital of interest is centered, thus taking into account, to some extent, the molecular environment. The values of the Coulomb integrals or the Hamiltonian matrix elements are usually taken to be the negative of the Valence Orbital Ionization Energies (VOIEs) [1–3], i.e. the energy needed to remove an electron from an atom in a state in which electrons occupy orbitals with definite space but random spin orientations [4, 5]. It is quite common that in the iterative process to charge self-consistency, a non-integral occupation number of the atomic orbital, from which the molecular orbital is built up, results; VOIEs are computed in such cases based on mixed configurations [6]. Although extensive tabulations of VOIEs as a function of both charge and configuration are found in the literature [4, 6, 8], no such tables are available for second-row transition metals, whose chemistry has become increasingly important. These data should prove useful in quick semi-empirical molecular orbital calculations for molecular

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complexes involving second-row transition metals, where an accurate SCF-MO treatment is not available.

2. Results

We have computed Average Configuration Energies (ACE) as defined by Slater [6, 7] and determined from them VOIEs for the elements Sr through to In. The computational details are given elsewhere [6]. VOIEs for the atomic orbitals of interest were calculated from atomic spectral data [9] considering up to four stages of ionization and the available data were subjected to a least-square fitting across

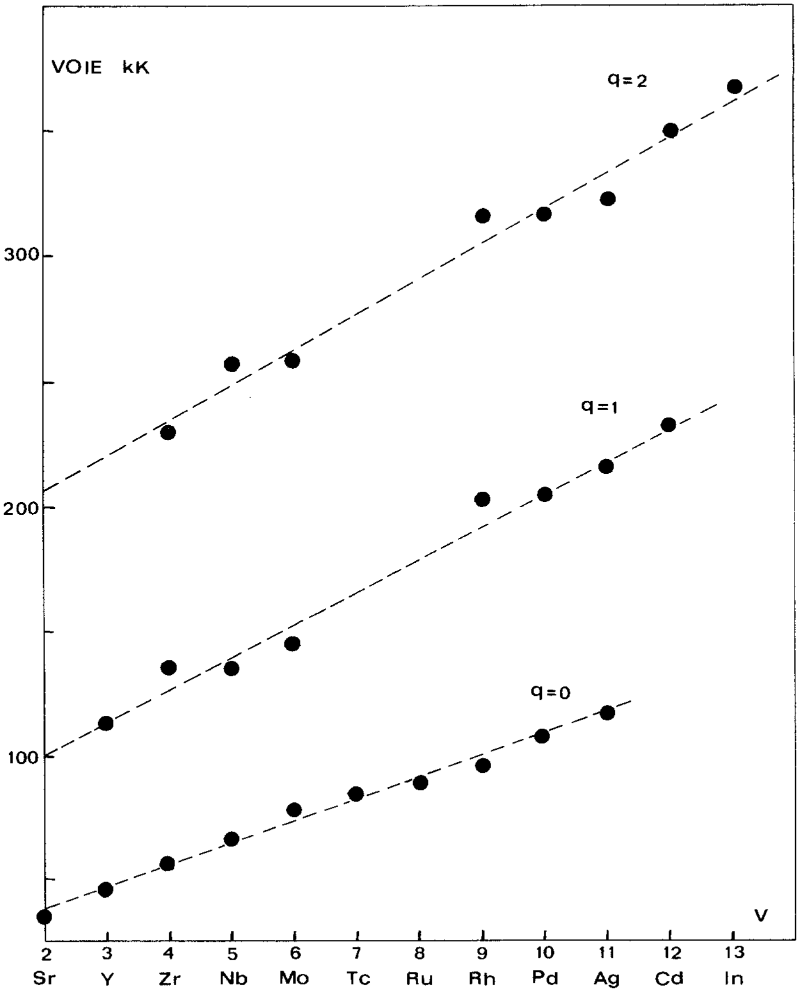

Fig. 1. Valence Orbital Ionization Energies (in kK) for a $4d$ atomic orbital in the configuration ($4d^{v-1}5s^05p^1$) computed from spectral data; v represents valence electrons and q is the atomic excess charge. Dotted lines are the corresponding least-square fittings

the row for a given ($4d^{v-m-n}5s^m5p^n$) configuration and excess charge q. This was done for all values of v, m and n for which data were available. Fig. 1 shows one of these fittings for the particular case of the VOIE for a $4d$ atomic orbital in the configuration ($4d^{v-1}5s^05p^1$), where v represents the valence electrons [2, 4, 6]. Within the uncertainties of the computed ACEs, we found in most of the cases that a linear fitting agreed well with the available points; therefore, a linear dependence of the VOIEs across the row was assumed if the correlation coefficient was higher than 0.95. If this was not the case (as it was for the $5p$ VOIEs in all configurations computed for the neutral atom), then the fitting was quadratic. For some elements, for which there were insufficient data to compute VOIEs, some of the ACEs were estimated based on a previously well established fitting;

Table 1. Valence Orbital Ionization Energies in the form VOIE $= C_2q^2 + C_1q + C_0$ (kK) (Sr up to Tc)

	Config.	V.O.[a]	$v=2$ Sr	$v=3$ Y	$v=4$ Zr	$v=5$ Nb	$v=6$ Mo	$v=7$ Tc
C_2	d^v	d	17.3	16.4	15.5	14.6	13.7	12.8
C_2	$d^{v-1}s$	d	22.5	20.6	18.6	16.8	14.9	13.0
C_2	$d^{v-1}p$	d	20.7	19.2	17.7	16.1	14.6	13.1
C_2	$d^{v-2}sp$	d	17.3	17.2	17.0	16.8	16.7	16.5
C_2	$d^{v-2}s^2$	d	22.8	20.8	18.8	16.9	14.9	12.9
C_2	$d^{v-1}s$	s	14.2	13.4	12.5	11.7	10.9	10.0
C_2	$d^{v-2}s^2$	s	17.9	16.8	15.7	14.6	13.5	12.4
C_2	$d^{v-2}sp$	s	15.9	15.8	15.8	15.7	15.7	15.6
C_2	$d^{v-1}p$	p	16.9	18.4	17.9	17.1	15.9	14.4
C_2	$d^{v-2}sp$	p	15.4	15.7	16.0	16.3	16.6	16.9
C_1	d^v	d	31.5	37.8	44.1	50.4	56.7	63.0
C_1	$d^{v-1}s$	d	38.2	45.3	52.4	59.4	66.5	73.5
C_1	$d^{v-1}p$	d	41.0	47.1	53.1	59.1	65.1	71.2
C_1	$d^{v-2}sp$	d	44.8	48.4	51.9	55.5	59.0	62.5
C_1	$d^{v-2}s^2$	d	41.7	48.2	54.6	61.0	67.5	73.9
C_1	$d^{v-1}s$	s	31.7	35.2	38.6	42.1	45.5	48.9
C_1	$d^{v-2}s^2$	s	34.6	37.6	40.7	43.8	46.9	49.9
C_1	$d^{v-2}sp$	s	32.4	35.1	37.8	40.5	43.2	45.9
C_1	$d^{v-1}p$	p	20.7	16.2	17.7	20.3	23.9	28.5
C_1	$d^{v-2}sp$	p	25.9	27.7	29.4	31.2	32.9	34.7
C_0	d^v	d	25.2	30.7	36.3	41.8	47.4	53.0
C_0	$d^{v-1}s$	d	30.9	38.7	46.6	54.4	62.2	70.1
C_0	$d^{v-1}p$	d	38.5	47.2	55.8	64.5	73.2	81.9
C_0	$d^{v-2}sp$	d	52.2	61.8	71.4	81.1	90.7	100.3
C_0	$d^{v-2}s^2$	d	42.9	53.3	63.8	74.2	84.6	95.0
C_0	$d^{v-1}s$	s	45.7	47.5	49.3	51.2	53.0	54.9
C_0	$d^{v-2}s^2$	s	52.0	54.5	56.9	59.4	61.9	64.3
C_0	$d^{v-2}sp$	s	60.0	62.9	65.7	68.5	71.3	74.1
C_0	$d^{v-1}p$	p	25.1	30.8	32.6	33.6	33.9	33.7
C_0	$d^{v-2}sp$	p	34.9	35.7	36.6	37.4	38.2	39.1

[a] V.O. stands for Valence Orbital.

Table 2. Valence Orbital Ionization Energies in the form VOIE $= C_2q^2 + C_1q + C_0$ (kK) (Ru up to In)

	Config.	V.O.[a]	$v = 8$ Ru	$v = 9$ Rh	$v = 10$ Pd	$v = 11$ Ag	$v = 12$ Cd	$v = 13$ In
C_2	d^v	d	11.9	11.0	10.1	9.2	8.3	7.4
C_2	$d^{v-1}s$	d	11.1	9.2	7.3	5.4	3.5	1.6
C_2	$d^{v-1}p$	d	11.5	10.0	8.5	6.9	5.4	3.9
C_2	$d^{v-2}sp$	d	16.4	16.2	16.0	15.9	15.7	15.5
C_2	$d^{v-2}s^2$	d	10.8	8.9	6.9	4.9	2.9	0.9
C_2	$d^{v-1}s$	s	9.2	8.3	7.5	6.7	5.8	5.0
C_2	$d^{v-2}s^2$	s	11.3	10.2	9.1	8.0	6.9	5.7
C_2	$d^{v-2}sp$	s	15.6	15.5	15.4	15.4	15.3	—
C_2	$d^{v-1}p$	p	12.6	10.5	9.1	7.7	6.8	4.9
C_2	$d^{v-2}sp$	p	17.2	17.5	17.7	18.0	15.9	—
C_1	d^v	d	69.3	75.7	82.0	88.3	94.6	100.9
C_1	$d^{v-1}s$	d	80.6	87.7	94.7	101.8	108.8	115.9
C_1	$d^{v-1}p$	d	77.2	83.2	89.2	95.3	101.3	107.3
C_1	$d^{v-2}sp$	d	66.1	69.6	73.2	76.7	89.3	83.8
C_1	$d^{v-2}s^2$	d	80.3	86.8	93.2	99.7	106.1	112.5
C_1	$d^{v-1}s$	s	52.4	55.8	59.2	62.7	66.1	69.5
C_1	$d^{v-2}s^2$	s	53.0	56.1	59.2	69.2	65.3	68.4
C_1	$d^{v-2}sp$	s	48.5	51.2	54.0	56.6	59.3	—
C_1	$d^{v-1}p$	p	34.1	40.6	44.8	49.1	52.4	57.6
C_1	$d^{v-2}sp$	p	36.4	38.2	39.9	41.7	51.0	—
C_0	d^v	d	58.5	64.4	69.5	75.2	80.8	86.3
C_0	$d^{v-1}s$	d	77.9	85.9	93.6	101.4	109.3	117.1
C_0	$d^{v-1}p$	d	90.5	99.2	107.9	116.6	125.2	133.9
C_0	$d^{v-2}sp$	d	109.9	119.5	129.2	138.8	148.4	158.0
C_0	$d^{v-2}s^2$	d	105.5	115.9	126.3	136.7	147.1	157.5
C_0	$d^{v-1}s$	s	56.7	58.5	60.4	62.2	64.1	65.9
C_0	$d^{v-2}s^2$	s	66.8	69.2	71.7	74.2	76.6	79.1
C_0	$d^{v-2}sp$	s	76.9	79.7	82.5	85.3	88.1	—
C_0	$d^{v-1}p$	p	32.7	31.0	31.0	30.9	30.8	30.7
C_0	$d^{v-2}sp$	p	39.9	40.7	41.6	42.4	38.1	—

[a] V.O. stands for Valence Orbital.

this was done as follows: for Mo, average energies for the configurations $(4d^4 5s^1 5p^1)$, $(4d^3 5s^1 5p^0)$ and $(4d^3 5s^0 5p^1)$ can be computed from spectral data; nevertheless, the energy for the configuration $(4d^3 5s^1 5p^1)$ cannot be determined in this way. A good fitting for the VOIE of a $4d$ atomic orbital is obtained for the configuration $(4d^{v-2} 5s^1 5p^1)$, this allows us to estimate the energy associated with the process of removal of a $4d$ electron in Mo in the $(4d^4 5s^1 5p^1)$ configuration, and thus, to estimate the ACE of $(4d^3 5s^1 5p^1)$. The knowledge of this last value allows us in turn computation of the VOIEs for the $5s$ and $5p$ atomic orbitals in the configuration $(4d^3 5s^1 5p^1)$. The VOIEs estimated with this back-generation of data were included in the fitting if they were not off the available-data fitting curve by more than two standard deviations. The resulting VOIEs were represented then quadratically [4] in the form VOIE $(q) = C_2q^2 + C_1q + C_0$ where q is the net atomic charge. Tables 1 and 2 show the tabulated values of C_0, C_1 and C_2 for VOIEs of 4*d*, 5*s* and 5*p* orbitals for several configurations. There, it is to be understood that successive values of q mean that the configurations differ in the number of *d* electrons [4, 6].

Basch et al. [4] have extensively discussed the accuracy of VOIEs evaluated in this manner. Inaccuracies arising from the factors discussed by these authors are enhanced, to some extent, in the present work for the Russell–Saunders scheme becomes less valid and less spectral data are available. Although the elements Sr, Y, Cd and In do not fall into the transition metals category, VOIEs for these elements were included in the fittings for they correlated well with VOIEs computed for the Zr–Ag series. The quadratic representation of VOIE as a function of q was computed considering only four stages of ionization; therefore, one should proceed with caution in computing VOIEs in this way for values of excess charge q greater than +2 and less than −1, although this is very seldom the case [10].

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