

CHEMICAL SHIFTS OF THE K_{α_1} LINES AND THE VALENCE STRUCTURE OF TRANSITION METALS OF THE FIFTH AND SIXTH PERIOD

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Measurements of the differences ΔE of the energies K_{α_1} lines in metals and in saturated oxides of transition elements of the fifth and sixth period (Sr–Mo, Ba–W) are used to verify further the previously obtained^[1] relation (1'') between ΔE , the degree of ionicity i , and the factor $\sum m_l C_l$ describing the valence structure of the metal. Analysis of the data of the fifth period confirms the additivity of the effect in the valence structure m and yields experimental values of the constants $C_{5sp} = +80 \pm 12$ meV and $C_{4d} = -120 \pm 4$ meV—the values of the shifts of the K_{α_1} lines when a 5sp or 4d electron respectively is completely removed. The valence structures (7) are in satisfactory agreement with the experimental data. Starting from the experimental values of ΔE and the constants C_{sp} and C_d obtained from the analysis of the data of the fifth period, an attempt is made to determine the valence structure of the transition metals of the sixth period. The resulting good agreement of the calculated and experimental values of ΔE yields the valence structures (8).

INTRODUCTION

IN our previous paper^[1] devoted to a study of the chemical shift of inner (K and L) levels of heavy atoms ($34 \lesssim Z \lesssim 74$) it was assumed that the experimentally measurable energy difference of the K_{α_1} lines of a given element in compounds A and B can be written in the form

$$E_A - E_B = \Delta E_{AB} = \sum_l \Delta m_l C_l \tag{1}$$

Here Δm_l is the change in the number of valence electrons (outside the core) with a given value of the orbital quantum number l in the atom of the investigated element on going from compound A to B

$$\Delta m_l = m_l^B - m_l^A,$$

C_l is a constant equal to the shift of the K_{α_1} line for the complete removal of one l -type valence electron.¹⁾ If in one of the compared compounds, for example A, the distribution of the electrons outside the core over the l states (the structure of the covalent bond) is known, then relation (1) makes it possible to obtain information about the valence structure of this element in compound B. The simplest special case of a compound with a known structure is an ionic one with a one-hundred percent ionicity of the bond in which the investigated atom has no valence electrons. In this case $m_l^A = 0$ and relation (1) is of the form

$$\Delta E_{AB} = \sum_l m_l^B C_l \tag{1'}$$

i.e., it describes directly the unknown valence of compound B.

Another example is the case when the distribution of the valence electrons of the investigated atom over the

sublevels l in compounds A and B is unknown, but there are reasons for assuming that it remains unchanged and the compounds differ only in the degree of ionicity of the bond i:

$$m_l^A = m_l(1 - i_A), \quad m_l^B = m_l(1 - i_B).$$

Here

$$\Delta E_{AB} = (i_A - i_B) \sum_l m_l C_l, \quad \sum_l m_l = m, \tag{1''}$$

where m is the total number of valence electrons (the valence of the atom). The system (1'') describes the unknown valence structure of the compounds A and B²⁾.

Let us consider the properties of the coefficients C_l . The most important property of C_l which affects the very presence of the chemical shift of the inner levels in heavy elements is the weak dependence of C_l on the atomic number Z of the element, or, in other words, its weak dependence on the principal quantum number of the valence electron. This property was indicated qualitatively by our first estimates which stimulated the beginnings of the experimental search of the effect for the inner levels of heavy atoms. Utilizing Hartree-Fock functions and the relation

$$\Delta E_K = P \Delta E_{Z, Z-1}, \quad P = \int_0^\infty R_{1s}^2(r_1) \left[\int_0^{r_1} R_{ns}^2(r) dr \right] dr_1 \tag{2}$$

($\Delta E_{Z, Z-1}$ is the difference between the energies of the K level for the elements with Z and $Z - 1$, and R_{1s} and R_{ns} are the radial wave functions of the K electron and the removed valence electron respectively), we obtained for the shifts of the K level the following calculated values:

Mo ($Z = 42$), one 5s electron is removed, $\Delta E_K = +70$ MeV;
 W ($Z = 74$), one 6s electron is removed, $\Delta E_K = +50$ MeV;
 Hg ($Z = 80$), one 6s electron is removed, $\Delta E_K = +50$ MeV.

¹⁾The idea of introducing variants of the expressions analogous to (1), (1'), and (1'') in the analysis of the structure of the chemical shift of the x-ray lines in light elements was previously formulated and used by Shuvaev [2] and Nefedov [3] (see also the review article [4]).

²⁾It is precisely this particular case, realized because of the use in the compound of analog elements as partners of the investigated atom, which was studied in [1].

Table I. Chemical shifts of the K_{α_1} lines in the transition metals of the fifth and sixth period and the proposed valence structures

Compounds	$\Delta E_{\text{exp}} = E_{\text{OX}} - E_{\text{met}}$ meV		$\frac{\Delta E'_{\text{exp}}}{i} = \frac{\Delta E_{\text{exp}}}{i}$	Proposed valence structures	Calculated value of $\Delta E'$	$\frac{\Delta E'_{\text{exp}}}{-\Delta E'_{\text{calc}}}$	p'
Fifth period							
SrO — Sr	-30 ± 4	0,93	-32 ± 4	$= 1\bar{C}_{5sp} + 1C_{4d}$	-40	+8	1
Y ₂ O ₃ — Y	-146 ± 10	0,87	-168 ± 12	$= 1\bar{C}_{5sp} + 2C_{4d}$	-160	-8	1
ZrO ₂ — Zr	-229 ± 15	0,82	-279 ± 19	$= 1\bar{C}_{5sp} + 3C_{4d}$	-280	+1	1
Nb ₂ O ₅ — Nb	-260 ± 5	0,63	-413 ± 9	$= 1\bar{C}_{5sp} + 4C_{4d}$	-400	-13	1
MoO ₃ — Mo	-199 ± 5	0,39	-510 ± 13	$= 1\bar{C}_{5sp} + 5C_{4d}$	-520	+10	1
		$\bar{C}_{5sp} = +80 \pm 12$ meV		$C_{4d} = -120 \pm 4$ meV			
Sixth period							
BaO — Ba	$+142 \pm 20$	0,94	$+151 \pm 22$	$= 2\bar{C}_{6sp}$	+142	+9	1
La ₂ O ₃ — La	-144 ± 20	0,87	-166 ± 23	$= 1\bar{C}_{6sp} + 2C_{5d}$	-145	-21	1
Lu ₂ O ₃ — Lu	$+3 \pm 20$	0,85	$+3 \pm 24$	$= 2\bar{C}_{6sp} + 1C_{5d}$	+34	-31	1
HfO ₂ — Hf	-6 ± 30 *	0,82	-7 ± 35	$= 2\bar{C}_{6sp} + 2C_{5d}$	-74	+67	0.5
Ta ₂ O ₅ — Ta	-113 ± 30	0,63	-179 ± 50	$= 2\bar{C}_{6sp} + 3C_{5d}$	-182	+3	0.25
WO ₃ — W	-110 ± 33	0,39	-282 ± 87	$= 2\bar{C}_{6sp} + 4C_{5d}$	-290	+8	0.13
		$C_{6sp} = +71 \pm 12$ meV		$C_{5d} = -108 \pm 13$ meV			

*In Hf the effect turned out to depend strongly on the (impurity) composition, and varied for different samples from ~ 0 to $\sim +200$ meV. The cited value was obtained with the purest of our samples (hafnium "iodide" with ~ 0.5 percent zirconium).

Quantitatively the fact that C_l is independent of the principal quantum number is confirmed by the results of the previously described^[1] experiment on the chemical shift of K_{α_1} Sn and K_{α_2} Se in the β Sn—SnSe—Se system. Assuming a model according to which the bond in SnSe is due to the 2p electrons of the tin which are partly "pulled over" to the selenium, and making use of (1''), we find³⁾

$$\begin{aligned} \Delta E_{\beta\text{Sn-SnSe}} &= 2C_{5p}i_{\text{SnSe}} = 42 \pm 5 \text{ meV}, \\ \Delta E_{\text{Se-SnSe}} &= -2C_{4p}i_{\text{SnSe}} = -40 \pm 5 \text{ meV}, \\ C_{5p}/C_{4p} &= 1.05 \pm 0.17. \end{aligned} \quad (3)$$

The shifts of the K_{α_1} lines are determined by the shifts of the K and L_{III} levels and can change sign depending on which of these levels undergoes a larger shift when the valence electron is removed. The shifts of the levels depend in turn on the degree of overlap of their wave functions with the wave function of the removed electron [see, for instance, relation (2)], i.e., on the symmetry of the latter which is determined by the orbital quantum number l . A strong dependence of C_l on the value of the l of the removed electron (including even a change of sign) should therefore be expected. This is the meaning of the notation in the expression for ΔE in the form of relation (1). In our case the available theoretical estimates of the shift of the K and L levels on removing the valence electrons in light elements^[2-6] allowed us to assume that the coefficients C_s and C_p are positive, whereas C_d is negative. Experimental estimates of $C_{s'l}$ were obtained by us in processing data on the K_{α_1} shifts in di- and tetravalent tin compounds.^[1] We found that

$$\bar{C}_{5sp} = +77 \pm 8 \text{ meV}, \quad (4)$$

or within the framework of a more specific model of the chemical bond in these compounds:

$$C_{5s} \approx +95 \text{ meV}, \quad C_{5p} \approx +80 \text{ meV}. \quad (4')$$

The negative sign of the effect in Mo—MoO₃ and W—WO₃^[7] served at the same time as the experimental confirmation of the negative sign of $C_{4(5)d}$ ^[1].

Obviously, it is precisely the expected difference in the values of C_l which raises hopes that by measuring the chemical shifts one can differentiate between various valence configurations, i.e., hopes for a practical application of relations (1)–(1'') in the investigation of the structure of the chemical bond.

The purpose of this work was further experimental verification of relations (1)–(1''), the determination of the coefficients C_l , and an attempt to apply the effect of the chemical shift of the inner levels in heavy elements together with the obtained relations in a determination of valence structures.

THE EXPERIMENT AND THE RESULTS

The transition elements of the fifth and sixth period of the periodic table, Sr—Mo and Ba—W, were chosen as the objects of the investigation. We measured the energy differences of the K_{α_1} in the metals and in their highest oxides. The experimental method was the same as in all our recent work devoted to the chemical shift.^[1,7,8]

The experimental results are presented in Table I (column 2); the errors are external mean-square errors calculated from the deviations of the results of the individual series from the mean. Table II lists the degrees of ionicity i of the bond in the corresponding oxides. They are calculated from Pauling's expression^[9]:

$$i = 1 - \frac{m}{n} e^{-0.25(\Delta x)^2}, \quad (5)$$

where m is the valence, n —the coordination number, Δx —the metal-oxide electronegativity difference; the electronegativities are taken from the tables.^[10,11]

Figure 1 (solid curve) and Table I (column 4) show the dependence of $\Delta E/i$ [see relation (1'')] on the valence m for the elements of the fifth period. The ionicities of

³⁾The degrees of ionicity of β Sn and Se are taken to be zero.

Table II. Calculation of the degree of ionicity of the bond in oxides

No.	Column	m	n	ΔE [10, 11]	$i = \frac{1-m}{n} e^{-0.25(\Delta E)^2}$	N ₅ n/n	Column	m	n	ΔE [10, 11]	$i = \frac{1-m}{n} e^{-0.25(\Delta E)^2}$
1	SrO	2	6	2.5	0.93	7	HfO ₂	4	8	—	(0.82)*
2	BaO	2	6	2.6	0.94	8	Nb ₂ O ₅	5	6**	1.8	0.63
3	Y ₂ O ₃	3	6	2.3	0.87	9	Ta ₂ O ₅	5	6**	—	(0.63)
4	La ₂ O ₃	3	6	2.3	0.87	10	MoO ₃	6	6	1.4	0.39
5	Lu ₂ O ₃	3	6	2.2	0.85	11	WO ₃	6	6	—	(0.39)
6	ZrO ₂	4	8	2.0	0.82	12	SnO ₂	4	6	1.6	0.65

*For a number of oxides of elements of the sixth period ionicities have been assumed that are equal to the values of the analog elements of the fifth period. In the Table these values are given in parentheses.

**The structures have not been reliably established; the coordination numbers assumed are somewhat provisional.

the metals (i_B) are taken to be zero. The values $\Delta E_{exp}/i$ fit very well a straight line of the form

$$\Delta E/i = C_+ + (m - 1)C_- \quad (6)$$

where C_+ is a positive and C_- a negative constant.

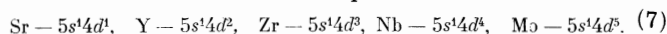
The valence electrons (outside the core) of the elements of the fifth period can, as is well known, be of the 5s, 4d, and 5d levels. Taking into account the properties of C_{sp} and C_d described in the Introduction, it is natural to assume that $C_+ \equiv C_{5s}$ (or C_{5p} , since we probably cannot differentiate between them on account of the closeness of C_s and C_p), and $C_- \equiv C_{4d}$. Relation (6) can now be written in the form

$$\Delta E/i = \bar{C}_{5sp} + (m - 1)C_{4d}. \quad (6')$$

The most important fact that follows from (6) and (6') is the additivity of the effect in m; in other words, the effect of removing n valence electrons is n times larger than the effect due to the removal of one valence electron of the same type l. It is obvious that the additivity in m is the only assumption essential for writing the basic relation in the form (1).

The dashed curve in Fig. 1 has been drawn through the raw experimental values of ΔE uncorrected for the degree of ionicity of the bond. Dividing by i turns this curve into a straight line. This fact can serve as an experimental confirmation of the fact that the employed scale of ionicities is sensible.

The ionicities of the oxides of strontium, yttrium, and zirconium are close to unity, i.e., a situation occurs in which relation (1') should be valid; the monotonic nature of the dependence of Fig. 1 (the straight line) makes it natural to assume that for niobium and molybdenum the conditions are realized for the applicability of relation (1''); as a result of this the effect as a whole is also described by relation (1'). Thus the sum in the right-hand side of (6') yields the distribution over the available levels of the electrons outside the core in the metals, in other words, the valence structure of the transition metals of the fifth period⁴⁾:



Relations (6') can now be considered as an overdetermined system of five equations with two unknowns, \bar{C}_{5sp}

⁴⁾We cannot differentiate between C_s and C_p so that the s in the structures should only be understood as being provisional; in some cases $5p^1 4d^8$ structures will possibly occur.

and C_{4d} . This system is presented in columns 4–5 of Table I. Solution by the least-squares method yields⁵⁾:

$$\bar{C}_{5sp} = +80 \pm 12 \text{ meV}, \quad C_{4d} = -120 \pm 4 \text{ meV}.$$

The value of \bar{C}_{5sp} obtained from the data on the transition elements of the fifth period is in good agreement with that cited above [relation (4)] obtained in^[1] from an analysis of tin compounds. The value of C_{4d} turned out to differ strongly from \bar{C}_{5sp} both in sign and in absolute value, making it possible to differentiate readily in the valence structure sp and d electrons.

If it is assumed that all that has been said above is to be taken literally, i.e., that relations (1)--(1'') are valid, that C_l is strictly independent of the principal quantum number, that integer configurations are realized (there is no configuration mixing), and, finally, that the ionicity scale employed is sufficiently sensible, then one can calculate the variants of the magnitudes of K_{α_1} shifts for any elements, for example for the transition metals of the sixth period. We make use of (1'') and, assuming $\bar{C}_{6sp} = \bar{C}_{5sp}$ and $C_{5d} = C_{4d}$, we calculate $\Delta E' = \Delta E/i$ for all conceivable valence structures of metals of the sixth period. For example, the following structure variants and corresponding values of $\Delta E'$ are possible for lanthanum and lutetium ($m = 3$):

$$d^3, \Delta E' = 3C_{5d} = -360 \text{ meV}, \quad s^1 d^2, \Delta E' = 1\bar{C}_{6sp} + 2C_{5d} = -160 \text{ meV}, \\ s^1 p^1 d^1, \Delta E' = 2\bar{C}_{6sp} + 1C_{5d} = +40 \text{ meV}, \quad s^1 p^2, \Delta E' = 3\bar{C}_{6sp} = +240 \text{ meV}.$$

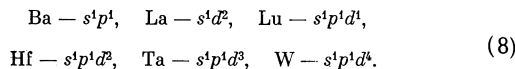
Figure 2 shows a grid of such calculated variants of shifts for $m = 2-6$. Crosses mark the experimental values of $\Delta E'$ for elements of the fifth period used in calculating the constants. The rectangles with error bars mark the experimental values of the K_{α_1} shifts between the metal and the highest oxide for the elements of the sixth period: Ba, La, Lu, Hf, Ta, and W. Good agreement is observed which makes it possible to choose unambiguously the occurring integer variants of the valence structures⁶⁾:

⁵⁾The weights of the equations p' were taken to be equal.

⁶⁾The triangle marks the experimental point for αSn [1]:

$$\frac{\Delta E_{\text{expt}}}{i} = \frac{204 \pm 11}{0.65} = +314 \pm 17 \text{ meV}$$

In complete agreement with the well known $s^1 p^3$ valence structure of αSn , it coincides with the calculated value of $\Delta E/i = 4\bar{C}_{5sp} = +320 \text{ meV}$.



Using these structures, one can write down an over-determined system of equations in the unknowns C_{6sp} and C_{5d} (see Table I) also for the elements of the sixth period, and calculate their refined values:

$$\bar{C}_{6sp} = 71 \pm 12 \text{ meV}, \quad C_{5d} = -108 \pm 13 \text{ meV}.$$

As was to be expected, the equalities are fulfilled within the error limits.

$$\bar{C}_{6sp} = \bar{C}_{5sp} \text{ and } C_{5d} = C_{4d}.$$

CONCLUSION

The use of the chemical shift of the inner levels in heavy atoms for an investigation of the valence structure has led to unexpectedly simple results. A comparison of these with the complex picture usually obtained by using other approaches, whose semiquantitative interpretation even requires allowance for many factors and resort to more refined models, arouses one's suspicion that the treatment presented is somewhat primitive and that the good agreement with experiment is in some sense accidental. The final answer to this question can only be obtained after an accumulation of examples of practical application of the described method for determining structures and an extensive analysis of the obtained results.

One circumstance which can be the reason for the observed simplicity should however be noted. The internal screening mechanism which causes the shift of the inner levels in heavy atoms apparently possesses the unique property of being weakly attenuated as one penetrates deeper into the atom. The other effects and mechanisms (see, for example,^[3]) whose presence obscures and complicates the picture when using a number of methods which analyze directly the band structure of the atom are attenuated much more rapidly. As the limiting values of the depths of levels beyond which only the internal screening mechanism remains one can take, for example, the limits generally accepted, before the role of the internal screening was realized, as the limits of the existence of the chemical-shift effect^[12]:

$$\begin{aligned} Z > 26 & \text{ for } L_{II-III}\text{-levels,} \\ Z > 29 & \text{ for } M_I\text{-levels,} \\ Z > 32 & \text{ for } M_{II-III}\text{-levels, etc.} \end{aligned} \quad (9)$$

The use of the effect of the chemical shift when conditions (7) are fulfilled, i.e., the use of the chemical shift of precisely the inner levels in sufficiently heavy elements permits one to exclude automatically the influence

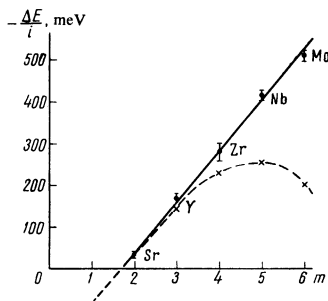


FIG. 1. Dependence of the reduced value (divided by the degree of ionicity i) of the shift of the $K\alpha_1$ line of the metal and the highest oxide on the valence m for a number of transition elements of the fifth period. The dashed curve is drawn through the raw experimental values of the shifts ΔE .

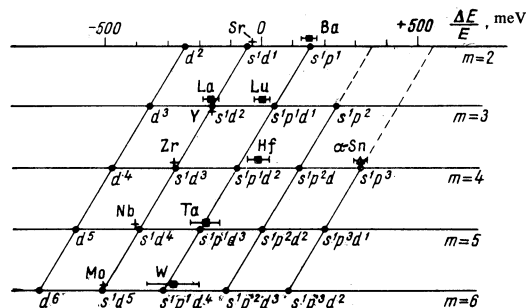


FIG. 2. Determination of the valence structure of the transition metals of the sixth period. The circles at the lattice points with the structure indices are variants of the $K\alpha_1$ shifts calculated in accordance with (1') using the constants \bar{C}_{5sp} and C_{4d} found from the analysis of the experimental values of the shifts for elements of the fifth period (crosses). Rectangles with error bars—experimental values of $\Delta E/i$ for elements of the sixth period. Triangle—experimental value of $\Delta E/i$ for $\alpha\text{-Sn}$.^[1]

of interfering side effects, and the picture takes on an unusual simplicity.

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