The Chemical Energy Shift of K X-rays

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Abstract. The chemical energy shift of K X-rays is investigated by means of free ion configurations. The influence of the l-quantum number of the valence electron on $\delta K\alpha$ and $\delta K\beta$ is discussed. A method based on free ion calculations is given for the determination of the ionicity and for the change in total electron density $\delta|\psi(0)|^2$ between two chemical compounds.

I. Basic Formulae

To determine the mechanism of the $K\alpha$ and $K\beta$ energy shifts due to different chemical environments we start from the electron potential given by $V_{HF} = V_C + S_e$ where V_C denotes the Coulomb potential of the nucleus and S_e the screening potential due to the surrounding electrons. The screening potential is given by

$$S_e(\vec{r}) = \int \frac{\rho(\vec{r}')\, d^3 r'}{|\vec{r} - \vec{r}'|} \tag{1}$$

where $\rho(\vec{r})$ is the total electronic charge density. The valence electrons involved in a chemical bond give rise to a change $\delta\rho(\vec{r})$ in the total electron density. Therefore, the change of the screening potential is given by

$$\delta S_e(\vec{r}) = \int \frac{\delta\rho(\vec{r}')\, d^3 r'}{|\vec{r} - \vec{r}'|} \tag{2}$$

The energy shift of the K, L and M electrons is then obtained by first-order perturbation theory

$$\Delta E = \int \frac{\delta\rho(\vec{r}')\, \rho(\vec{r})}{|\vec{r} - \vec{r}'|}\, d^3 r'\, d^3 r \tag{3}$$

which is indeed a good approximation in our case.

The change in binding energy ΔE is in the order of magnitude of 10 eV by removal of one valence electron. Assuming that $\delta\rho(\vec{r})$ has spherical symmetry, we obtain from (3) the energy shift in the simple form

$$\Delta E = I_1^{NP} + I_2^{P} \tag{4}$$

where I_1^{NP} is a 'no penetration term' given by

$$I_1^{NP} = \int\limits_0^\infty dr_1 f_1(r_1) \int\limits_0^\infty dr_2 \frac{f_2(r_2)}{r_2} \tag{4'}$$

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and where I_2^P denotes the two 'penetration' integrals

$$I_2^P = \int_0^\infty dr_1 \frac{f_1(r_1)}{r_1} \int_0^{r_1} dr_2 f_2(r_2) - \int_0^\infty dr_1 f_1(r_1) \int_0^{r_1} dr_2 \frac{f_2(r_2)}{r_2} \tag{4''}$$

The function $f_1(r_1)$ is the radial K, L or M electron density and $f_2(r_2)$ is the change of the total radial density due to a change in the valence states' occupations, i.e. $f_2(r_2) = 4\pi r_2^2 \delta\rho(r_2)$. The first term I_1^{NP} is independent of the shell considered K, L or M, so that it does not contribute to the observed shifts $\delta K\alpha$ and $\delta K\beta$. The values of the penetration integrals for different electron configurations account thus for the whole effect.

II. Qualitative Discussion

For a qualitative outline of the problem we use the formula

$$\Delta E_{K,L} = \int_0^\infty \delta S_e(r) f_{K,L}(r)\, dr$$

with

$$\delta S_e(r) = \frac{1}{r} \int_0^r f_2(r')\, dr' + \int_r^\infty \frac{f_2(r')}{r'} dr' \tag{5}$$

which is equivalent to relation (4). First of all, we want to discuss the change $\delta\rho(0)$ of the electron density due to the removal of one valence electron with orbital angular momentum l. The total density $\rho(0)$ taken at the nucleus decreases when s valence electrons are removed since they give a significant contribution to $\rho(0)$ in the vicinity of the nucleus. On the other hand the removal of p, d and f electrons increases the total density by reducing the screening. Hartree–Fock calculations for free ions, e.g. for ^{119}Sn [1], have shown that the screening effect of p valence electrons is very small, however. The change in total electron density due to the removal of d and especially f valence electrons is considerable. Some examples are given in Figure 1 where $\delta\rho(r)$ is shown as a function of the radial distance r for the different type of valence electrons in Praseodymium. Relation (5) shows then that $\delta S_e(r)$ decreases monotonically with r for s electrons and also for p electrons, apart from a slight increase in the nuclear vicinity. For d and f valence electrons, however, one obtains a distinct increase of $\delta S_e(r)$ with radial distance r. Qualitative considerations thus yield for the $\delta K\alpha$ and $\delta K\beta$ chemical shifts strong dependence on the orbital angular momentum of the different valence electrons involved in the chemical bond.

III. Results

a) Free ion calculations

Various Hartree–Fock–Slater calculations for free ion configurations were performed to get some quantitative results. Since many experimental chemical shifts, especially $\delta K\alpha_1$, are available [2, 3, 4, 5], numerical results are obtained for $\delta K\alpha_{1,2}$ and $\delta K\beta_{1,3}$ by evaluating the penetration integrals of relation (4''). A delta function
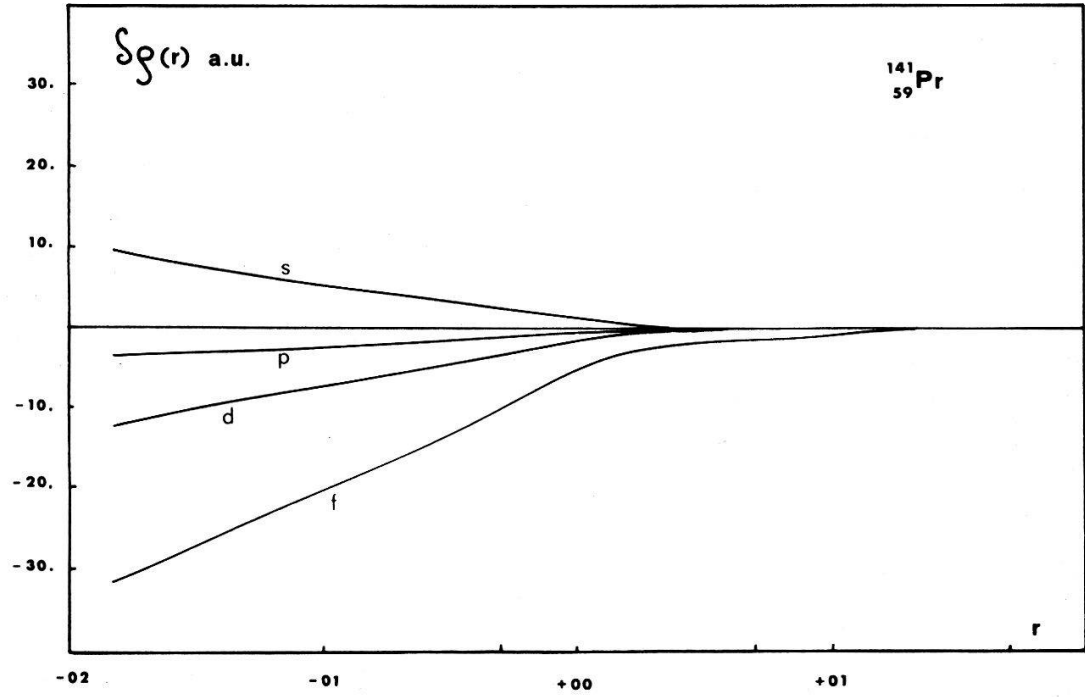
Figure 1

The change in total electron density $\delta\rho(r)$ due to the removal of one s, p, d or f valence electron in Praseodymium is plotted versus the radial distance r. Each curve is labelled by the type of the removed electron, i.e. s, p, d or f. Note that the scale is logarithmic.

approximation for the radial density $f_1(r_1)$ of the K and L shells is found to be valid within a few per cent for the evaluation of $\delta K\alpha_{1,2}$. In Table 1 the ionic $\delta K\alpha_{1,2}$ and $\delta K\beta_{1,3}$ shifts are collected for some elements together with the different configurations assumed. The characteristic l dependence of the chemical shift agrees well with the

Table 1

Calculated ionic K X-ray shifts (all values are given in meV)

The ionic $\delta K\alpha_1$, $\delta K\alpha_2$, $\delta K\beta_1$ and $\delta K\beta_3$ shifts for the given isotopes are collected for their respective different valence configurations

Element	Config.	$\delta K\alpha_1$	$\delta K\alpha_2$	$\delta K\beta_1$	$\delta K\beta_3$
$^{195}_{78}$Pt	$5d^9$–$5d^8$	57.5	52.4	15.7	19.1
	d^9– d^6	222.8	206.3	−29.0	−8.8
	d^9– d^5	322.3	300.9	−110.3	−75.7
$^{57}_{26}$Fe	$3d^7$–$3d^6$	438.4	433.5	−392.1	−367.4
	d^7– d^5	1044.2	1033.0	−1340.6	−1282.5
	d^7– d^4	1800.4	1782.4	−3050.2	−2932.0
	$4s^2$–$4s^1$	−152.4	−152.4	−262.8	−261.0
	s^2– s^0	−416.4	−416.4	−937.1	−917.7
$^{119}_{50}$Sn	$5p^3$–$5p^2$	−24.7	−22.0	−28.0	−27.8
	p^3– p^1	−98.5	−90.0	−114.9	−113.8
	p^3– p^0	−202.0	−185.0	−286.2	−281.9
$^{89}_{40}$Zr	$4d^5$–$4d^4$	102.2			
$^{198}_{79}$Au	$5d^9$–$5d^8$	216.7			

qualitative discussion of Chapter II. As expected, $\delta K\alpha_{1,2}$ and $\delta K\beta_{1,3}$ are always negative if only s and p electrons are involved in the bond formation, i.e. $\delta\rho(r)$ is mainly positive for all values of r yielding thus a greater energy shift for the K shell than for the L and M shells. However, one must be somewhat more careful for d valence electrons. The chemical shift of the L shell is always greater than the shift for the K shell, yielding $\delta K\alpha_{1,2} > 0$ whereas the shift $\delta K\beta_{1,3}$ becomes negative in this case. This is due to the fact that $\delta\rho(r)$, mainly negative for d electrons especially for inner shells, becomes positive when $\rho_{3p_{\frac{1}{2}}}(r)$ and $\rho_{3p_{\frac{3}{2}}}(r)$ reach their respective maximum. The energy shifts $\delta K\beta_1$ and $\delta K\beta_3$ are negative for different ionic configurations in this case as they are for s and p valence electrons. This special behaviour of $\delta K\beta_{1,3}$ for d electrons can be seen in Table 1 for ^{195} Pt. Especially for a small change of the ionic configuration, e.g. $5d^96s^0$ to $5d^86s^0$, $\delta K\beta_{1,3}$ becomes small but positive. Stronger changes of the ionicity degree, e.g. $5d^96s^0$ to $5d^56s^0$ involve a much stronger change of $\delta\rho(r)$ so that $\delta K\beta_{1,3}$ changes sign.

b) Connection of δKx with the change in electron density at the nucleus $\delta|\psi(0)|^2$

In the following we characterize valence shells in a chemical bond by their occupation probabilities $P_{n\kappa}$. One can see from the numerical values of Table 1 that the ionic shifts are approximately linear functions of the occupation probability of a given shell $(n\kappa)$. The error introduced by such a linear dependence is at most of some $\pm 10\%$. Therefore, we can write

$$\delta Kx = \sum_{n\kappa} \delta P_{n\kappa} \cdot \delta Kx_{n\kappa}^{\text{theor.}} \tag{6}$$

where $\delta K_{n\kappa}^{\text{theor.}}$ is the free ionic shift calculated in the Hartree–Fock–Slater scheme. The measured energy shift is given by δKx with $x = \alpha_{1,2}, \beta_{1,3}$ and the difference of occupation probabilities of the states $(n\kappa)$ in the two chemical compounds by $\delta P_{n\kappa}$. In the sum $(n\kappa)$ runs over all valence shells involved in the chemical bond. Two terms are expected to be important in practice. The same approximate linear behaviour as found for the X-ray shifts can also be observed for the change in total electron density at the nucleus $\delta|\psi(0)|^2$, i.e.

$$\delta|\psi(0)|^2 = \sum_{n\kappa} \delta P_{n\kappa} \cdot \delta|\psi(0)|^2_{\text{th. }(n\kappa)}. \tag{7}$$

On the right-hand side of this equation we have to insert the change in occupation probability $\delta P_{n\kappa}$ extracted from relation (6) and the calculated changes of electron densities for the assumed ionic configurations. Note that the values of $\delta P_{n\kappa}$ are usually much smaller than unity for practical cases. Therefore, the linearity assumption is justified.

c) Connection of X-ray shifts with Mössbauer isomer shifts

Recently, Boehm et al. [4] reported extensive measurements of X-ray shifts in tri- and tetravalent Praseodymium compounds. We assume that the K X-ray shifts and the changes in electron densities $\delta|\psi(0)|^2$ are due to a change in the $4f$ electrons. This is consistent with the data in Table 2 where the $K\alpha_{1,2}$ and $K\beta_{1,2,3}$ energy shifts for various configurations are collected. Under this assumption relations (6) and (7) reduce to one term and we obtain the value $\delta P_{4f} = 0.54$. This leads to a value of $\delta|\psi(0)|^2 = 17$ a.u. This quantity is of some interest because it can be used together with

Table 2

K X-ray shifts for $^{141}_{59}$Pr in meV

The ionic $\delta K\alpha_{1,2}$ and $\delta K\beta_{1,2,3}$ are collected for different ionic Praseodymium configurations. The last entry shows the ionic change in total electron density at the nucleus $\delta|\psi(0)|^2$ for the two valence configurations given in the corresponding row. All $\delta|\psi(0)|^2$ are given in atomic units. (1 a.u. = $0.675 \cdot 10^{25}$ cm^{-3})

Configuration	$\delta K\alpha_1$	$\delta K\alpha_2$	$\delta K\beta_1$	$\delta K\beta_3$	$\delta K\beta_2$	$\delta|\psi(0)|^2$ a.u.
$4f^26s^1$–$4f^25d^16s^1$	69.5	66.8	11.4	13.5		12.4
$4f^26s^1$–$4f^26s^16p^1$	−26.3	−23	−48.5	−47.2		3.5
$4f^26s^2$–$4f^26s^1$	−27.2	−24.8	−49.4	−48.1		10
$4f^16s^2$–$4f^26s^2$	696.5	631	2034	1993	560	45
$6s^2$ –$4f^16s^2$	675.3	587.1	2666.3	2596.6		50
$4f^1$ –$4f^2$	680	612	2004	1962	$\begin{cases} 495\,p_{1/2} \\ 690\,p_{3/2} \end{cases}$	31
$4f^16s^1$–$4f^1$	−81.5	−76.5	−148	−144	−266	25
$4f^1$ –$4f^15d^1$	76	73.6	−42.2	−36.5	−180	7
$4f^26s^1$–$4f^25d^16s^2$	43.6	42.5	−37.9	−34.6		2.4

measurements of the Mössbauer isomer shift which are quoted by Bent et al. [6]. The change of nuclear charge radius $\delta R/R$ extracted in this manner becomes then $\delta R/R = 2.24 \cdot 10^{-4}$. In deriving a change in electron density of $\delta|\psi(0)|^2 = 17$ a.u. we have assumed that we have no 6s valence electrons as 'spectators'. Since the calculated change in total electron density due to the removal of one 6s electron is $\delta|\psi(0)|^2 = 10$ a.u., however, participation of 6s valence electrons, even to a small extent (+10–20%), in the chemical bond would require a small correction. As pointed out by Boehm [4] molecular orbital calculations should give some more information on the structure of the tri- and tetravalent Praseodymium compounds. Such calculations could then reveal if the fractional charge transfer of the number of 4f electrons is sufficiently reliable. Moreover we should also mention that the value $\delta P_{4f} = 0.46$ obtained by Boehm et al. [4] in a somewhat different way is in very good agreement with ours.

IV. Conclusion

It seems necessary in this last chapter to summarize all the approximations and the conditions under which the K X-rays shifts were calculated. First-order perturbation theory with respect to δS_e, the change in the screening potential, was used. Relativistic Hartree–Fock–Slater bound state wave functions were used for the evaluation of electron densities and it was assumed that the change in total electron density $\delta\rho(r)$ arising from the removal of one valence electron was spherically symmetric. This is certainly a fairly good first approximation. The greatest uncertainty comes in any case from the use of a free ion model for elements in different chemical compounds. It should be emphasized that too much importance should not be attributed to the empirical concept of ionicity however valuable from a chemical point of view, and that the ionicity degree employed to characterize a chemical bond remains somewhat uncertain. More elaborate models such as those based on self-consistent molecular orbital calculations will certainly yield more precise information, but one should not forget that special, sometimes crude approximations must also be accepted in this case. Moreover, possible unknown solid-state effects may play some role and influence the structure of a well-defined chemical compound.

The numerical results of K X-ray shifts well support the obtained fractional change of the number of $4f$ valence electrons $\delta P_{4f} \simeq 0.5$. The important assumption of no contribution from $6s$ electrons for a change from tri- to tetravalent Praseodymium compounds seems at least reasonable from a chemical point of view. It should however be pointed out that *a priori* there is no reason to completely eliminate the $6s$ valence states from the considered chemical bonds since qualitative arguments based on such empirical concepts as ionicity and electronegativity may not be sufficiently accurate for a complete description of the effect. Instead of using first-order perturbation theory it is also possible to get the K X-ray shifts from energy differences of atomic level shifts. The K X-ray shifts calculated in this way and the experimental results given by Boehm et al. [4] for PrF_3–PrO_2 are collected together with our theoretical values in Table 3. It is indeed surprising that such a relatively simple approach to the problem yields such a reasonable agreement with the experiment. Additional measurements of L X-ray shifts would certainly improve the present knowledge of chemical bonds and offer the possibility of clarifying our understanding of this problem.

Table 3

Experimental and theoretical K X-ray shifts in meV for PrF_3–PrO_2

The first and second entries show the experimental and theoretical values of K X-ray shifts in meV as they are reported in ref. [4]. The third entry (theory[2]) shows our calculations based on first-order perturbation theory and also normalized on the $\delta K\alpha_1$ value of the first column

	Exp.	Theory[1]	Theory[2]
$\delta K\alpha_1$	386	(386)	(386)
$\delta K\alpha_2$	322	331	330
$\delta K\beta_1$	1034	977	1080
$\delta K\beta_3$	879	961	1059
$\delta K\beta_2$	423	359	372

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