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—Review—

EVALUATION OF THE EFFECTIVE CHARGES OF ATOMS FROM COMBINATION OF THE X-RAY $K_{\alpha 1}$ CHEMICAL SHIFTS AND THE ISOMER SHIFTS OF THE NMR SPECTRA

By

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Abstract

The chemical shifts of $K_{\alpha 1}$ and $K_{\beta 1}$ X-ray emission lines for a number of elements (I, Sn, Cd, Te, Ru...) have been obtained with a 2 m bent-quartz-crystal spectrometer. An application of the "free ion" model for evaluation of the effective charges from the X-ray chemical shifts has been described and shown that for intranion elements with ns and np valence electrons the parameters of the theoretical equations describing dependence of the chemical shift on the number of removed electrons for $K_{\alpha 1}$ and $K_{\beta 1}$ lines are interdependent in HF approximation. The partial effective charges for 5s and 5p electrons of iodine and tin and for 5s and 4d electrons of ruthenium in their compounds were evaluated by combining X-ray $K_{\alpha 1}$ chemical shifts with the isomer shifts of NMR spectra. Additionally, the ligands of the hexacoordinated compounds of Ru were arranged into series according to their donor-acceptor abilities. The effective charges of atoms in about 90 compounds of considered elements are given in Tables.

Introduction

The X-ray emission spectra arising from transitions between the deepest inner electron levels ($1s \rightarrow 2p \dots$) provide a reliable information about the redistribution of the electron densities between atoms in solids and molecules. As is well known, the chemical shifts (δ_X) of the X-ray emis-

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sion lines of K series may be applied to evaluate the effective charges of atoms¹⁻⁶). We shall describe now a variant of analysis in which for this purpose the experimental data of the shifts δ_x and the isomer shifts of NFR spectra* (δ_r) have been used together with the theoretical data. It is convenient to define a partial contribution of nl valence electron Q_{nl} to the effective charge of atom as follows:

$$\sum_{(nl)} Q_{nl} = Q, \quad (1)$$

where Q -the total effective charge and in the sum (nl) runs over all valence shells involved in the chemical bond.

The idea of dividing Q into Q_{nl} is well known and several methods have been already proposed⁴⁻⁶). In this paper we report a new version of the analysis with a basic use of the theory given by KARAZIJA⁷).

Theory

For the sake of chemical applications it is convenient to express the expected chemical shift of X-ray emission line according to ref. 7) as follows:

$$\begin{aligned} \Delta E_{n'l' \rightarrow n''l''}(\overline{n_1 l_1^{m_1}}, \overline{n_2 l_2^{m_2}}) = & m_1 C_{n_1 l_1} + m_2 C_{n_2 l_2} + \\ & m_1(m_1-1) \Delta_{n_1 l_1} + m_2(m_2-1) \Delta_{n_2 l_2} + m_1 m_2 \Delta_{n_1 l_1, n_2 l_2}. \end{aligned} \quad (2)$$

Here ΔE represents the energy change of $(n'l' \rightarrow n''l'')$ X-ray emission line due to the removal of m_1 and m_2 electrons from $n_1 l_1$ and $n_2 l_2$ valence subshells, respectively. C_{nl} is the shift caused by the removal of a single nl electron from atom with the chosen reference electron configuration, Δ_{nl} and $\Delta_{n_1 l_1, n_2 l_2}$ - some electrostatic corrections defined in ref. 7). As has been shown in ref. 7), C_{nl} may be estimated from the solution of HARTREE-FOCK equations for two configurations with vacancies in the inner shells, involved into the X-ray transition:

$$C_{nl} = \varepsilon_{nl}(\overline{n'l'}) - \varepsilon_{nl}(\overline{n''l''}), \quad (3)$$

where ε_{nl} - the binding energy of nl electron.

In Fig. 1 we compared the experimental and the theoretical X-ray chemical shifts for the most typical cases. Here the experimental data are plotted versus the formal valency of atom (W) and the theoretical shifts calculated according to (2) as a function of a number of the removed electrons (m). One can always find a similarity between them, though in the experiment the results are expressed with respect to molecule or metal,

*) NFR spectra: nuclear γ -ray spectra.

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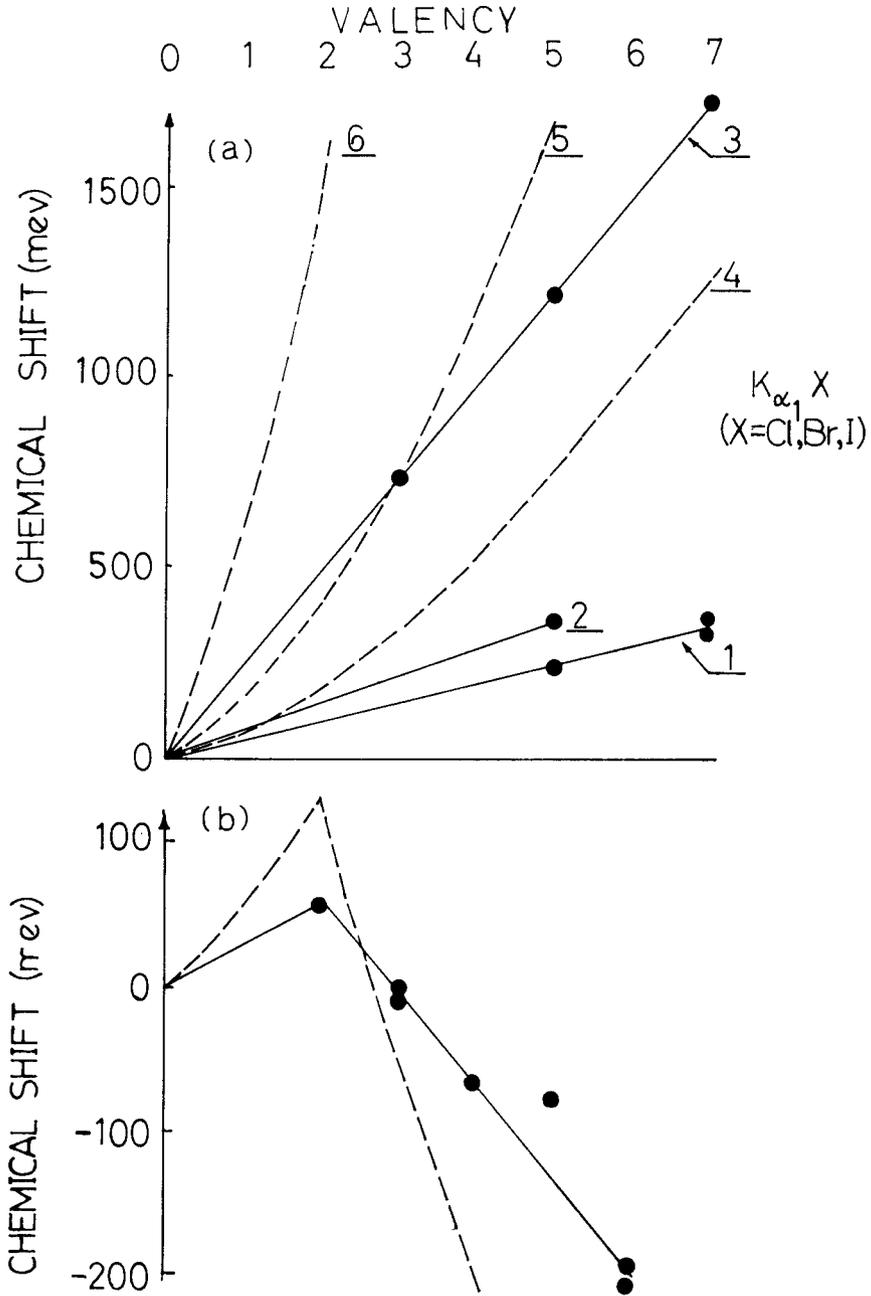


Fig. 1.

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while the theoretical calculations were performed with free atom (ion) provided, that at any stage of ionization was removed the least bound nl electron. This is particularly obvious for the transition metals as far, as their valence electrons (s, d and f) considerably differ in their screening abilities and contribution from them into resulting chemical shift may be of opposite signs. This was clearly observed in $K_{\alpha 1}$ line of Cr, Mo, Ru and in $L_{\alpha 1}$, $L_{\beta 2}$, $L_{\gamma 1}$ lines of U⁹). The conformity of the characteristic features of $\delta_{(W)}^{\text{exper}}$ and $\delta_{(m)}^{\text{Theor}}$, (that is, a sign of the effect, position of a break of the curve, decrease or increase of the shift) provides a way to distinguish different nl electrons participating in the chemical bonding. Besides it becomes possible to bridge the gap between the theory and the experiment by introducing into the theoretical equation (2) parameter of delocalization q_{nl} and assuming that just only the valence electrons of an atom are being involved in the chemical bonding. In other words, hereafter we are neglecting the higher-laying virtual nl electron levels.

On returning to (2) and using the definition (1) we may now assume the following equations to be valid:

$$\begin{aligned} \delta_X^{\text{exper}} = & C_{ns} Q_{ns} + C_{(n-1)d} Q_{(n-1)d} + Q_{ns}(Q_{ns}-1) A_{ns} + \\ & + Q_{(n-1)d}(Q_{(n-1)d}-1) A_{(n-1)d} + Q_{ns} \cdot Q_{(n-1)d} A_{ns,(n-1)d} \dots \end{aligned} \quad (4)$$

(for the transition elements, neglecting participation of the virtual (np) electrons in bonding), and

$$\begin{aligned} \delta_X^{\text{exper}} = & C_{ns} Q_{ns} + C_{np} Q_{np} + Q_{ns}(Q_{ns}-1) A_{ns} + Q_{np}(Q_{np}-1) A_{np} + \\ & + Q_{ns} Q_{np} A_{ns,np} \end{aligned} \quad (5)$$

(for intranition elements, neglecting participation of the virtual (nd) electrons in bonding).

Our first step consisted of application of eqs. (4) and (5) to evaluate the effective charges of atoms in compounds assuming that the total number

Fig. 1. Comparison of the experimental chemical shifts of $K_{\alpha 1}$ line with the theoretical (HF) shifts. The experimental data are given with respect to molecule X_2 ($X=I, Br, Cl$) or to metal (in case of Mo). The theoretical values were obtained as described in ref. 7).

a) Intranition elements: 1, 2 and 3 solid lines are drawn through the experimental values (filled circles) of the chemical shifts of $K_{\alpha 1}$ lines of I, Br, Cl, respectively, expressed as a function of valence state of X; 4, 5 and 6-broken curves correspond to the theoretical shifts of $K_{\alpha 1}$ line of I, Br, Cl, respectively, plotted versus a number of removed electrons (m).

b) Transition element-Mo. The solid line is drawn through the points (filled circles) corresponding to the shifts of $K_{\alpha 1}$ Mo line in the compounds containing Mo in different valence state from Mo II ($MoCl_2$) through Mo VI-(NH_4)₂MoO₄, MoO₃; the broken line represents the results obtained theoretically⁷) for the successive removal of the least bound in atom (ion) nl electrons, provided that the initial electron conjugation of Mo is $5s^2 4d^4$.

of electrons of atom participating in the chemical bonding were equal to its degree of oxidation. This meant, for instance, that in case of IO_3^- only five valence 5p electrons of iodine were taken into account ("pure 5p bonding"), for IO_4^- —seven electrons (two 5s and five 5p) *etc.* Besides to a first approximation for all electrons participating in the chemical bonding the equal quantities of q have been ascribed:

$$\bar{q}_{nl,n'l'} = \frac{Q_{nl}}{m_{nl}} \approx \frac{Q_{n'l'}}{m_{n'l'}} \quad (6)$$

it can be easily shown, that (6) enables to solve eqs. (4) and (5), giving \bar{q}

TABLE 1. Comparison of the effective charges with existing data

Compound	Q (our data)	Q (other sources)
ClO_3^-	1.30 ± 0.1	$1.72^{13)}; 1.02^{14)}$
BrO_3^-	1.70 ± 0.1	
IO_3^-	2.25 ± 0.1	
ClO_4^-	1.96 ± 0.06	$2.27^{13)}; 2.10^{14)}$
IO_4^-	2.95 ± 0.1	
SO_3^{2-}	1.54 ± 0.04	$1.96^{13)}; 0.93^{14)}; 1.5^{15)}; 1.75^{16)}$
SO_4^{2-}	1.78 ± 0.01	$2.34^{13)}; 1.79^{14)}; 1.6^{15)}; 2.05^{16)}$

TABLE 2. Experimental $K_{\alpha 1}$ and $K_{\beta 1}$ X-ray shifts and the effective charges Q

(The shifts are given in meV, towards X_2 , $X = \text{Cl, Br, I}$)

Compound	$\delta_{K\alpha 1}$	$Q(K_{\alpha 2})$	$\delta_{K\beta 1}$	$Q(K_{\beta 1})$	\bar{Q}
KI	-47 ± 4	~ -1	—	—	—
KIO_3	234 ± 15	2.25 ± 0.10	—	—	—
LiIO_3	—	—	457 ± 18	2.06 ± 0.06	2.10 ± 0.15
RbIO_3	—	—	404 ± 23	1.86 ± 0.1	—
$\text{Na}_3\text{H}_2\text{IO}_6$	383 ± 13	3.34 ± 0.04	641 ± 18	2.70 ± 0.06	3.0 ± 0.3
NaIO_4	317 ± 10	2.95 ± 0.06	—	—	—
KIO_4	—	—	533 ± 20	2.49 ± 0.07	2.72 ± 0.23
H_5IO_6	361 ± 14	3.21 ± 0.1	—	—	—
NH_4Br	-55 ± 20	~ -1	—	—	—
KBrO_3	356 ± 30	1.7 ± 0.1	—	—	—
NaCl	-220 ± 70	~ -1	—	—	—
NaClO_2	220 ± 70	0.42 ± 0.1	320	0.11	0.26 ± 0.15
NaClO_3	870 ± 70	1.30 ± 0.1	1410	0.46	0.88 ± 0.42
NaClO_4	1380 ± 70	1.96 ± 0.06	3207	0.84	1.33 ± 0.49

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and then the effective charge of atom Q :

$$\bar{Q} = W \cdot \bar{q} \quad (7)$$

Now we shall briefly compare the results obtained for some light elements with existing data (Table 1) and then pass over to our further steps in analyzing of the experimental data. The evaluated quantities of Q turned out to be quite realistic and satisfactorily agree with those obtained by means of earlier established methods. The effective charges of halogens in XO_3^- and XO_4^- increase gradually with Z according to predictions of the electronegativity's concept. Table 2 presents our estimates of Q 's from the X-ray chemical shifts of two emission lines ($K_{\alpha 1}$ and $K_{\beta 1}$) to illustrate their consistency. In deriving the Q data collected in Table 2 we utilized both our¹⁰⁾ and existing (for Cl¹¹⁾) experimental values of $K_{\alpha 1}$ and $K_{\beta 1}$ X-ray chemical shifts.

It may be concluded, that at the present stage the chemical shifts of the most intensive $K_{\alpha 1}$ and $K_{\beta 1}$ lines may be interpreted in terms of SCF HF theory for isolated atoms (ions) with an accuracy $\sim \pm 10\%$ in the range of $Z \sim 50$ and $\sim \pm 25\%$ in the range $Z \sim 20$, according to ratio $\frac{\sigma Q}{Q}$. It is worth while at this stage to examine to which extend the experimental and theoretical shifts remain to be comparable if the upper electron level involved into the X-ray transition rises. Some shifts for $K_{\alpha 1}$, $K_{\beta 1}$ and $K_{\beta 2,4}$ lines of iodine are given in Fig. 2 for I(VII), I(V) (experimental) and I^{+7} , I^{+5} (HF theory). Instead of successive growth of δ_{χ} in the series $K_{\alpha 1}-K_{\beta 1}-K_{\beta 2,4}$ predicted by HF theory we observe a break of the curve at the point corresponding to $K_{\beta 1}$ line and the experimental shift falls down up to its level in $K_{\alpha 1}$ line. The example of the kind is typical for all intranion elements indicating, that at present only $K_{\alpha 1}(K_{\alpha 2})$ and $K_{\beta 1}(K_{\beta 3})$ lines may be considered as reliable sources for getting information about the chemical bond in terms of the modern HF theory. In addition we should note, that according to our observations for transition metals (Mo, Ru) this is true only with $K_{\alpha 1}(K_{\alpha 2})$ lines, because here the experiment and the theory diverge remarkably already in $K_{\beta 1}$ line.

Let us verify now whether a problem of dividing Q into Q_{nl} may be directly reduced to solution of the system of eqs. (4) for a set of different X-ray lines ($K_{\alpha 1}$ and $K_{\beta 1}$, first of all). It would be a way reminding of the earlier proposed in ref. 5). To make it clear, we first examined the theoretical shifts in pair $I^{+7}-I^0$, calculated in a way described in ref. 7): $\delta_{K_{\alpha 1}} = 1253.2$ meV, $\delta_{K_{\beta 1}} = 2508.3$ meV. A number of the removed electrons in this case was known, $Q_{5s} = 2$, $Q_{5p} = 7$. If the equations of the type (5) for $K_{\alpha 1}$

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and $K_{\beta 1}$ were compatible with each other then they would constitute a system which could be solved to reproduce initial values of Q_{nr} . A solution of the system might be carried out graphically to give coordinates of an intersection point of two correlation functions easily derived from (5):

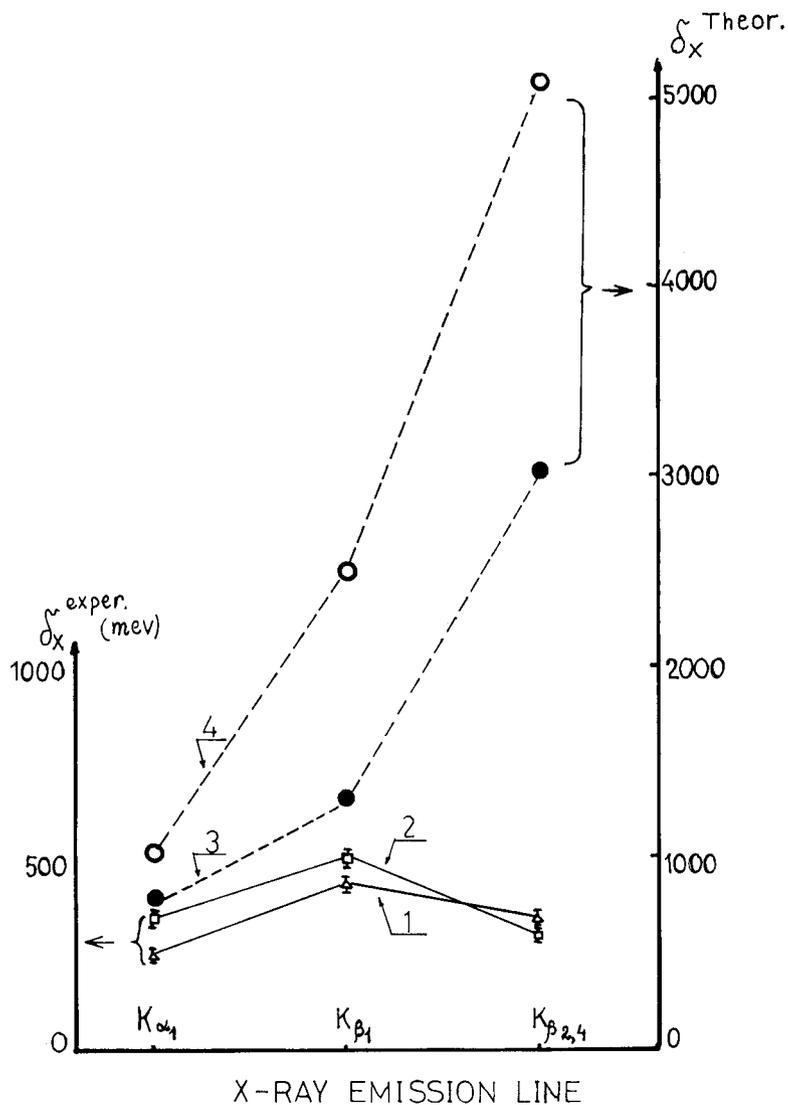


Fig. 2. Comparison of the experimental and theoretical (HF) shifts for $K_{\alpha 1}$, $K_{\beta 1}$ and $K_{\beta 2,4}$ lines of iodine. The solid lines correspond to the experiment for KIO_3 (1) and KIO_4 (2), the broken lines-HF theory for I^{+5} (3) and I^{+7} (4).

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$Q_{5s} = f_1(Q_{5p})$ and $Q_{5s} = f_2(Q_{5p})$ with $Q_{5s} \in /0, 2/$ and $Q_{5p} \in /0, 5/$. The resulting graphs (Fig. 3 a) shows a coincidence of both curves revealing the existence

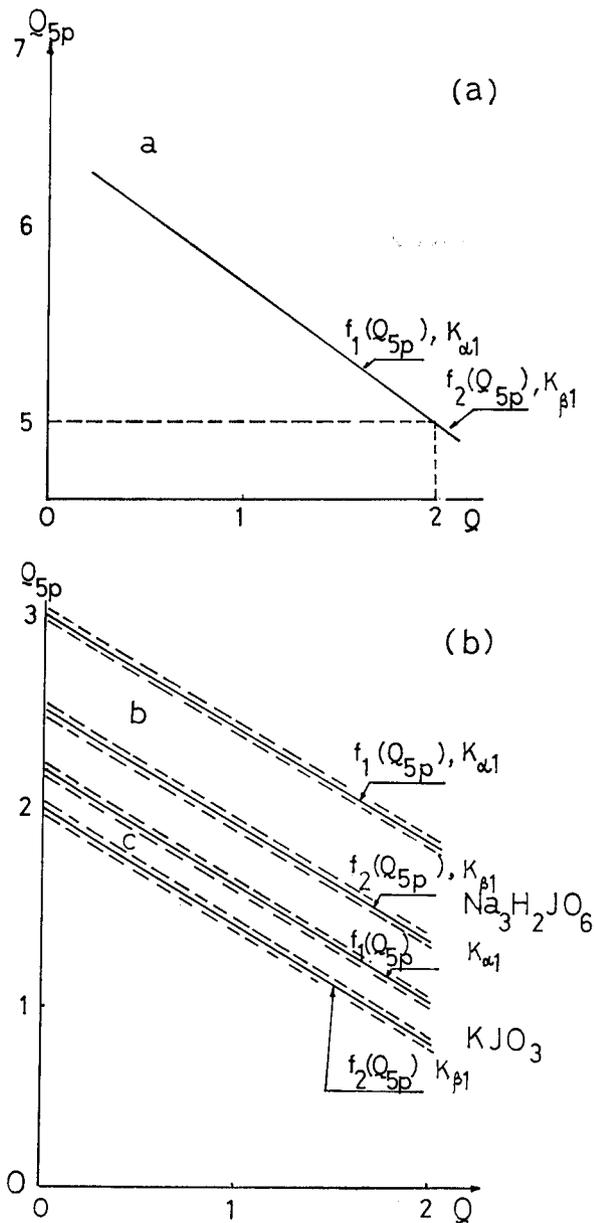


Fig. 3. Illustration of the correlation function $f_1(Q_{5p})$ and $f_2(Q_{5p})$ obtained from eq. (5) for $K_{\alpha 1}$ and $K_{\beta 1}$ lines, respectively, by using approximation (6).

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Line (λ)	C_{5s}	C_{5p}	$A_{5s,5s}$	$A_{5p,5p}$	$A_{5s,5p}$	$R = \frac{\text{parameter } K_{\alpha 1}}{\text{parameter } \lambda}$
$K_{\alpha 1,2}$	58	80	14.6	19.4	32.0	1
$K_{\beta 1,3}$	113.6	156.1	30.3	39.7	64.6	0.48-0.51
$K_{\beta 2,4}$	306.6	305.8	70.1	78.4	134.6	0.19-0.25
$K_{\beta 5}$	95.5	135.4	26.2	34.2	55.6	0.56-0.61
$L_{\alpha 1}$	37.1	55.5	11.7	14.8	24.2	1.25-1.56

of infinite number of solutions. It means that according to HF theory the shifts in $K_{\alpha 1}$ and $K_{\beta 1}$ lines are interdependent with an accuracy at least not worse than achieved by now in the experiment. All the coefficients of the eq. (4) for $K_{\alpha 1,2}$ and $K_{\beta 1,3}$ lines: C_{nl} and A_{nl} are in pairs connected with each other by factor ~ 0.5 (Table 3). As a result $K_{\alpha 1}$ and $K_{\beta 1}$ lines may not be considered as independent sources of information. When we extended a number of X-ray lines and examined some other intensive ones for ^{53}I ($K_{\beta 2,4}$, $K_{\beta 5}$ and $L_{\alpha 1}$) the results remained similar (see Table 3).

In the experimental case, analyzing $K_{\alpha 1}$ and $K_{\beta 1}$ shifts in pairs $\text{Na}_3\text{H}_2\text{IO}_6\text{-I}_2$ we again could not find intersect of $f_1(Q_{5p})$ with $f_2(Q_{5p})$. As it is shown in Fig. 3 (b and c) the curves are now parallel with a considerable gap between them. Evidently, the gap is a measure of divergency between HF theory and the experiment relating to the errors ascribed earlier to \bar{Q} values, given in Table 2. Thus, a conclusion is obvious. For intranion elements with ns and np valence electrons (which are rather similar both in their radial distribution in space and in their screening ability) a separation of Q_{nl} can not be based on the analysis of X-ray chemical shifts only. It requires additional sources of information (*e.g.* Mössbauer isomer shifts or ESCA). As to the evaluation of \bar{Q} in the approximation of \bar{q} , it is preferable, that the shifts of $K_{\alpha 1}$ line should be used as the best for comparison with the theory.

As we mentioned above the isomer shifts (IS) of NMR spectra may be chosen in addition to $\delta_{K_{\alpha 1}}$. They also are sensitive to changes in distribution of the valence electrons. The relative role of ns - and np - contributions to IS is basically determined by the screening ability of electrons in a proximity of nucleus and in contrast to $K_{\alpha 1}$ and $K_{\beta 1}$ X-ray lines here ns and np electrons differ considerably.

A number of relations between IS and Q_{nl} have been given for different Mössbauer isomers. If one stays near a fixed reference configuration, *i.e.*

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the charge migration due to the chemical bonding may be considered to be a small perturbation of the initial state, then the linear dependences (8) are assumed to be valid:

$$IS = \delta_r = \sum_{(nl)} I_n Q_{nl} \quad (8)$$

Here I_{nl} is IS due to the removal of nl electron from the atom with the reference configuration ascribed to its neutral initial state ($Q_{nl} = 0$). In addition a useful ratio may be obtained from the relativistic DHF (or DHFS)*) SCF calculations of atoms and ions, if a finite nuclear size is taken into account:

$$R_{n_1 l_1, n_2 l_2} = \frac{I_{n_1 l_1}}{I_{n_2 l_2}} = \frac{\Delta D_{n_1 l_1}(0)}{\Delta D_{n_2 l_2}(0)} \quad (9)$$

where $\Delta D_{nl}(0)$ is a change of the total electron density at the nucleus due to the removal of nl electron from the reference state of atom.

Now a problem consists of estimating one of the unknown quantities I_{nl} . This should be considered in any case separately.

Experiments and Results

In this work the chemical shifts of X-ray K lines have been measured using 2 m crystal bent spectrometer (QUARTZ, 1340, $d = 1.18 \text{ \AA}$, 1 mm) with application of the method proposed by SUMBAEV¹⁷⁾. The load of the primary X-ray tube with a tungsten target was about 150 kV and 10 mA. The fluorescent X-ray emitter for each specimen was in the form of pressed polycrystalline slab. The results of our measurements (δ_x) are collected in Tables together with existing values of the isomer shifts (δ_r).

Partial Effective Charges of Iodine, Tin and Ruthenium in Inorganic Compounds Evaluated from the Chemical Shifts of $K_{\alpha 1}$ X-Ray Line and Isomer Shifts of NTR Spectra

Iodine

The isomer shift data for I are available from the NTR experiments with two isotopes I^{127} (transition $\frac{7^+}{2} \rightarrow \frac{5^+}{2}$; 57.6 keV) and I^{129} (transition

*) DHF: Dirac-Hartree-Fock.

DHFS: Dirac-Hartree-Fock-Slater.

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$\frac{5^+}{2} \rightarrow \frac{7^+}{2}$; 27.7 keV). The isomer shifts have been referred usually to ZnTe source. For consistency in our Tables they will be reported relative to I_2 , as well as the X-ray shift data. It follows from DHFS computations¹³⁾ of the electron density at nuclei of I ($5s^2 5p^5$) and its ions I^+ ($5s^1 5p^5$ and $5s^2 5p^4$) that $R_{5s,5p} \simeq -3.6$. Now assuming, that the isomer shift between KI and I_2 may be understood as arising due to transition from I^- ($5s^2 5p^6$) to I^0 ($5s^2 5p^5$) with the evident change in Q equal to 1 we obtain the following equations:

$$\begin{aligned} \delta_{r_1} \Big|_{(5s^2 5p^5)} &= +2.60 Q_{5s} - 0.72 Q_{5p} \quad (I^{127}, \text{ mm/sec}) \\ \delta_{r_2} \Big|_{(5s^2 5p^5)} &= -4.80 Q_{5s} + 1.36 Q_{5p} \quad (I^{129}, \text{ mm/sec}) \end{aligned} \quad (9)$$

In Table 4 we collected the values of Q_{nl} and Q obtained from combination of the experimental $K_{\alpha 1}$ X-ray and NFR shifts with the theoretical presentations of them in form of eqs. (5) and (9). It may be seen, that our primary Q_x values (see Table 2) have been reproduced in this analysis quite satisfactory, confirming both the initial assumption ($q_s \simeq q_p$) and nearly pure p-bonding of iodine in IO_3^- .

TABLE 4. Chemical shifts of $K_{\alpha 1}$ I (δ_x), isomer shifts of ^{127}I (δ_{r_1}) and ^{129}I (δ_{r_2}). The effective charges of I in compounds.

(δ_x in meV, δ_r in mm/sec)

Compound	$\delta_x(K_{\alpha 1} I)$	$\delta_{r_1}^{127}I$	$\delta_{r_2}^{129}I$	Q_x	Q_{5s}^{x+71}	Q_{5p}^{x+71}	Q_{5s}^{x+72}	Q_{5p}^{x+72}	Q^{x+r}
$Na_3H_2IO_6$	383 ± 13	+1.72	-4.18	3.34	1.26	2.14	1.43	2.00	3.42
KIO_4	317 ± 10	+1.42	-3.01	2.95	1.08	1.92	1.15	1.86	3.00
KIO_3	234 ± 15		+0.73	2.25	—	—	0.39	1.94	2.33
$NaIO_3$	234 ± 15	+0.14	—	2.25	0.56	1.81	—	—	2.37

Tin

In Mössbauer spectroscopy of Sn^{119} the transition $\left(\frac{3^+}{2} \rightarrow \frac{1^+}{2}; 23.8 \text{ keV}\right)$ is used and the isomer shifts are available now for a variety of compounds. As a reference neutral state of tin α Sn and β Sn are accepted. However a little is known about their electron configurations. Now the only way to avoid appearing difficulties consist of presenting them as a mixture of two alternative ones: $5s^1 5p^3$ and $5s^2 5p^2$. To make it clear to which extend such

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TABLE 5. X-ray chemical shifts of $K_{\alpha 1}$ Sn (δ_x), isomer shifts of ^{119}Sn (δ_r) and the effective populations of 5s and 5p subshells of tin in compounds(δ_x and δ_r data are expressed towards β Sn and α Sn, respectively.)

Compound	δ_x (meV)	δ_r mm/sec	Q'_x	Q''_x	Q'''_x	population		Q^{x+r} accepted
						n_{5s}	n_{5p}	
SnF ₂	156 ± 5	1.57	1.92	1.81	2.23	1.81	0.27	1.92
SnCl ₂	137 ± 6	2.14	1.76	1.65	2.07	2.00	0.27	1.73
SnBr ₂	98 ± 7	1.85	1.38	1.28	1.74	1.99	0.65	1.36
SnI ₂	65 ± 7	1.95	1.01	0.93	1.42	2.00	1.01	0.99
SnO	80 ± 6	0.67	1.19	1.10	1.57	1.71	1.10	1.19
β Sn	0	0.55	0	0	0.64	1.90	2.10	0
α Sn	0	0	0	0	0	1.76	2.24	0
SnS	98 ± 9	1.31	1.38	1.28	1.74	1.85	0.78	1.37
SnSe	42 ± 11	1.30	0.72	0.65	1.18	1.97	1.33	0.70
SnTe	66 ± 12	1.23	1.02	0.94	1.43	1.89	1.09	1.02
SnF ₄	(172)	-2.35	2.11	2.08	2.41	0.75	1.10	2.15
SnCl ₄	81 ± 6	-1.25	1.22	1.18	1.61	1.21	1.56	1.23
SnBr ₄	62 ± 9	-0.96	0.99	0.96	1.42	1.32	1.67	1.00
SnI ₄	34 ± 7	-0.65	0.61	0.58	1.10	1.48	1.91	0.61
SnO ₂	172 ± 2	-2.10	2.11	2.08	2.41	0.82	1.04	2.14
SnS ₂	112 ± 6	-0.90	1.55	1.52	1.90	1.24	1.20	1.56
SnSe ₂	76 ± 13	—	1.16	1.13	1.50	—	—	—
(NH ₄) ₂ SnCl ₆	137 ± 4	-1.80	1.80	1.76	2.12	0.95	1.22	1.82
(NH ₄) ₂ SnF ₆	222 ± 6	-2.46	2.51	2.48	2.78	0.65	0.80	2.55

an uncertainty may affect the final effective charges of tin, we evaluated Q_x for a number of compounds of Sn (IV) with two sets of the coefficients C_{nl} and A , computed with the wave functions of the both electron configurations. For this purpose the experimental $K_{\alpha 1}$ shifts were expressed towards β Sn (as given in Table 5). Then for β Sn the alternative configurations were assumed: firstly $-5s^15p^3$, secondly $-5s^25p^2$ and Q_x values were obtained from equation (5), using approximation $q_{5s} \simeq q_{5p}$. According to the configurations, it gave Q'_x and Q''_x which turned out to be rather close to each other (Table 5). In similar manner an estimation of Q'''_x was carried out from the same shifts but expressed towards α Sn with a help of existing quantity¹⁷⁾ $\delta_{K\alpha 1}(\beta \text{ Sn} - \alpha \text{ Sn}) = +37 \pm 10$. In Fig. 4 the isomer shifts for the compound of Sn (IV), expressed towards α Sn are depicted versus evaluated effective charges. The plots are similar and linear regard-

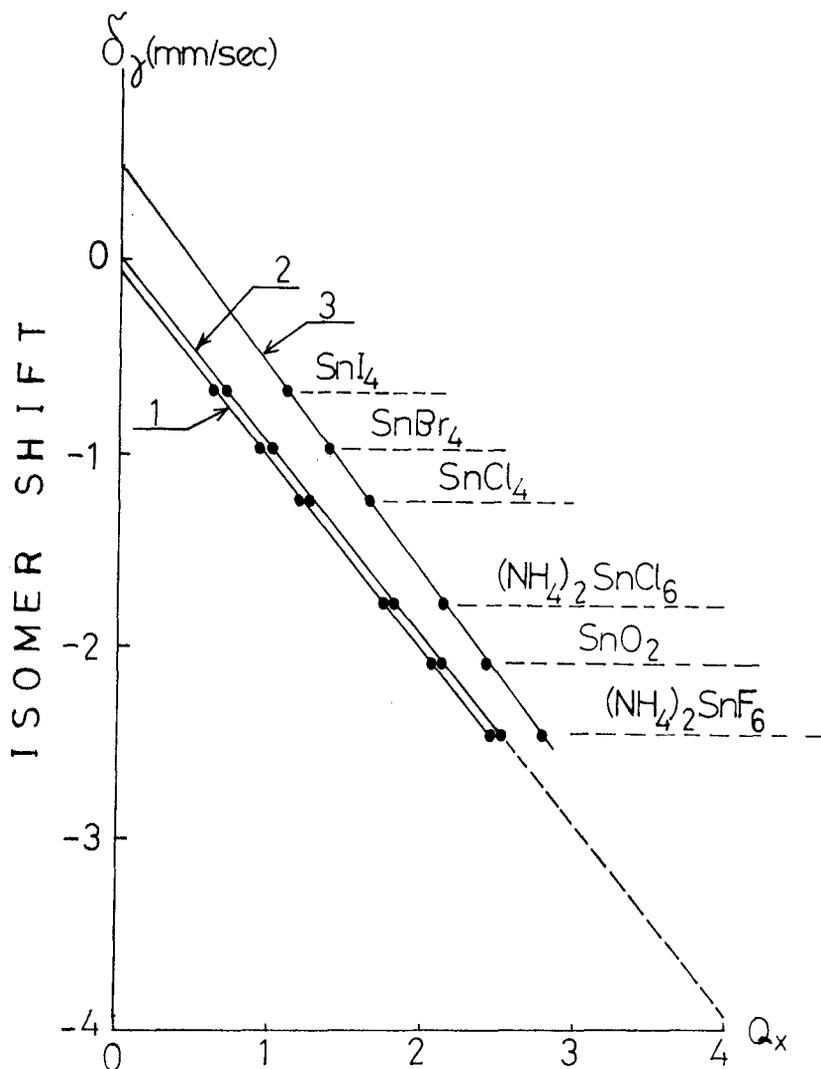


Fig. 4. The isomer shifts of ^{119}Sn for the compounds of Sn IV plotted versus the effective charges Q'_x , Q''_x and Q'''_x given in Table 5.

less of the chosen set of Q_x . The deviations between the three straight lines illustrate uncertainty in the proposed method of interpretation of the observed data. It is worth while to chose for the combined analysis the dependence $\delta_\gamma(\text{Sn IV}-\alpha\text{Sn})$ upon Q'_x as far as it goes from the origin. Evidently, this is equivalent to neglecting of the X-ray $K_{\alpha 1}$ shift between the two modifications of tin. In this case the straight line may be extra-

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polated to purely ionic state of Sn (IV), to give

$$\lim_{Q_x \rightarrow 4} \delta_\gamma(\text{Sn}^{+4} - \text{Sn}) = -3.92 \text{ mm/sec} \quad (10)$$

From the DHFS calculations¹³⁾ for $\text{Sn}^0(5s^15p^3)$, $\text{Sn}^{+1}(5p^3$ and $5s^15p^2)$ follows

$$R_{5s,5p} \Big|_{(5s^15p^3)} \simeq -4.4 \quad (11)$$

If the electron configuration of α Sn were known, (10) and (11) could be used immediately to obtain a calibration scale for the isomer shifts of Sn^{119} . To accept a certain configuration for α Sn, we considered all the possible ones from $5s^15p^3$ (usually ascribed) to $5s^25p^2$ (ascribed to isolated Sn atom in its ground state). According to them we obtain a set of equations calibrating the isomer shift Sn^{119} towards α Sn form

$$\delta_\gamma = -12.3 Q_{5s} + 2.8 Q_{5p} \quad (\alpha \text{ Sn} = 5s^15p^3)$$

up to

$$\delta_\gamma = -2.5 Q_{5s} + 0.58 Q_{5p} \quad (\alpha \text{ Sn} = 5s^25p^2).$$

Note, that the last one is close to the proposed in ref. 18).

As a result, a configuration $5s^{1.76}5p^{2.24}$ for α Sn and equation

$$\delta_\gamma = -3.13 Q_{5s} + 0.57 Q_{5p} \quad (12)$$

were chosen, as far as they led to 5s and 5p populations (n_{5s} and n_{5p} in Table 5) consistent with the idea of "pure 5p-bonding" of tin in SnCl_2 , for which the isomer shift was the most positive. The resulting quantities of n_{5s} and n_{5p} , as well as the total effective charges Q_{r+x} (rather close to Q'_x and Q''_x) were obtained for a number of compounds listed in Table 5 from the combination of (5) and (12), using the coefficients C_{nl} , A for $K_{\alpha 1}$ Sn given in ref. 7) and the experimental data from ref. 12), 17) and 19).

Ruthenium

Among the transition elements ruthenium manifests extremely high coordination ability, forming complexes nearly with all known ligands. Though they were subjects for a number of studies, including some X-ray spectroscopic^{20,21)} in which a complicated character of bonding was underlined, still a comparative role of 5s and 4d electrons of Ru remained uncertain. Keeping this in view we believed that at present a useful and reliable information of the kind might be derived from a combination of Mössbauer spectroscopy (I.S.) and X-ray spectroscopic data.

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The experimental data are all expressed with respect to ruthenium metal accepted hereafter as a reference neutral state with the electron configuration being $5s^1 4d^7$. This is the first assumption used in the analysis. It may contribute some error in the absolute values of the effective charges, because they are affected by the choice of the initial configuration. But still it is believed to be not very important for the comparative evaluation of the charges with which we are mainly concerned in this part of paper. Secondly, we neglected a participation of the high-laying $5p$ electron states of Ru in chemical bonding, which seemed to be reasonable according to some theoretical and experimental studies^{22,23}. The initial data (δ_X and δ_r) will be used in combination with the theoretical estimates of the chemical shifts, obtained from SCF HF calculations, performed with the program described in ref. 24) and with the theoretical (DHFS) estimates of the total electron density at the nucleus of Ru and its ions, known from ref. 20 and 25).

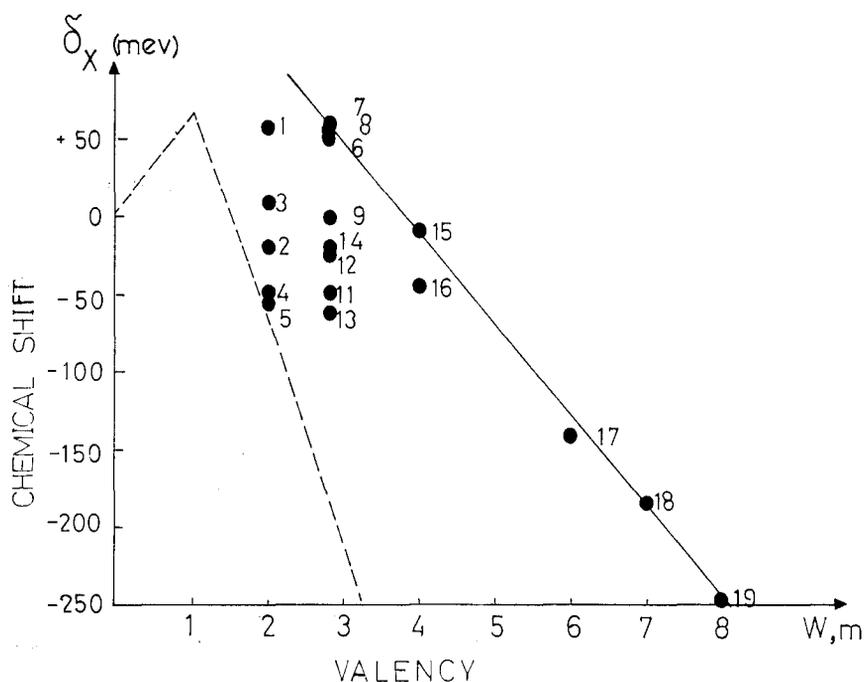


Fig. 5. The chemical shifts of Ru $K_{\alpha 1}$ X-ray line: the filled circles—the experimental data numerated according to position of the compound in Table 6 and plotted versus the valence state of ruthenium. The solid line is drawn through the points corresponding to oxygen-containing compounds, the broken line—through the theoretical values of the shift.

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In Fig. 5 the experimental values of Ru $K_{\alpha 1}$ chemical shifts are plotted towards W which represents the formal oxidation's degree (or valency) of Ru. The broken line corresponds to the theoretically expected shifts caused by the successive removal of the least bound electrons from Ru and its

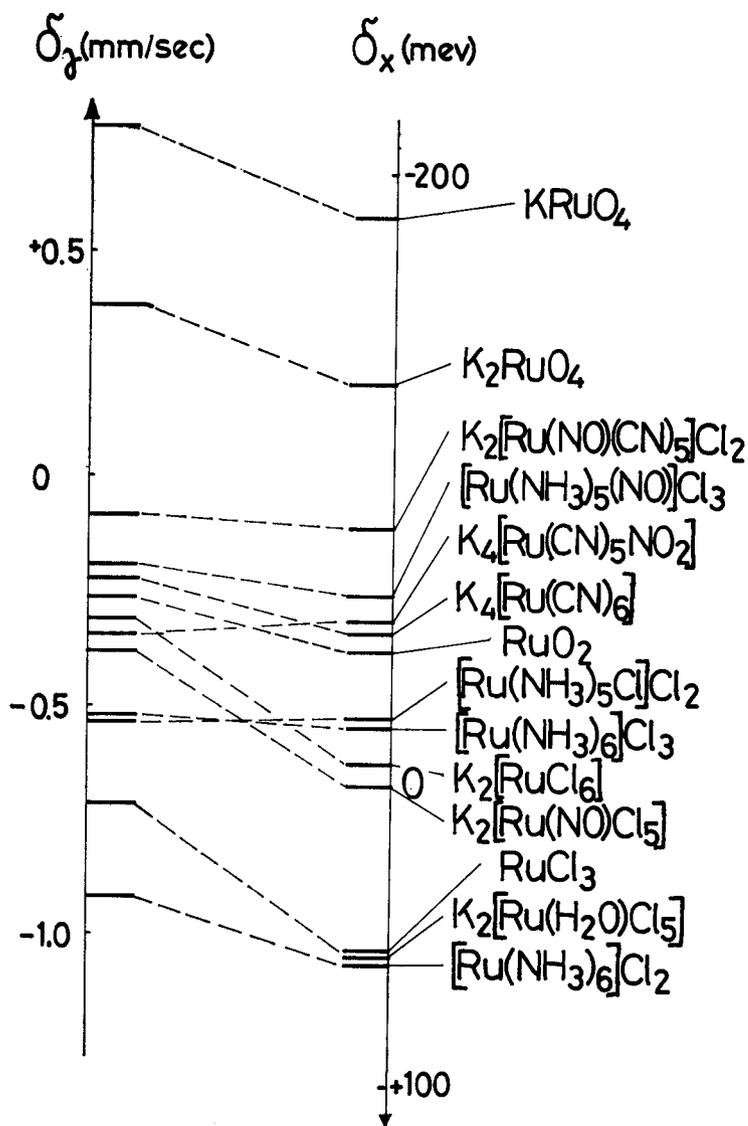


Fig. 6. Illustration of the correlation between the isomer shifts of NMR spectra of ^{99}Ru and the chemical shifts of Ru $K_{\alpha 1}$ line.

ions. They are expressed as a function of a number of the removed electrons m . A considerable overlap of $\delta_{K\alpha 1}$ data may be seen for the compounds containing Ru in different valence states. It certainly reflects a complexity of charge migration associated with the chemical bonding in the listed compounds. A little may be concluded from the graphs like this. But if we now compare our data with the isomer shifts obtained for the same compounds in the laboratory of MOSSBAUER^{25~27)}, we shall see quite a distinct correlation between them (Fig. 6).

As it has been pointed out in ref. 27) the isomer shift of the recoilless 90 keV γ -rays ^{99}Ru in the majority of the compounds monotonically increases with an increase of the oxidation state (valency) of Ru. The X-ray data show quite a contrasting tendency. This kind of correlation could be expected, if to take into consideration that the removal of 4d electrons, mostly responsible for the observed tendencies, differently affects the total electron density at the nucleus, and in the vicinity of the electrons (1s and 2p)

TABLE 6. Chemical shifts $K_{\alpha 1}$ Ru (δ_x), isomer shifts of ^{99}Ru (δ_r) and the effective charges of Ru in compounds

(with respect to Ru metal: δ_x in meV, δ_r in mm/sec)

N	Compounds	δ_x	δ_r	Q_{5s}	Q_{4d}	Q_{x+r}	Q_x
1	[Ru(NH ₃) ₆]Cl ₂	58 ± 6	-0.92 ± 0.01	0.34	-0.24	0.10 ± 0.08	0.21
2	[Ru(NH ₃) ₅ CO]Cl ₂	-23 ± 9	—	—	—	—	0.67
3	[Ru(dipy) ₃]Cl ₂	10 ± 6	—	—	—	—	0.48
4	K ₄ [Ru(CN) ₆]	-50 ± 7	-0.22 ± 0.01	0.34	0.47	0.81 ± 0.10	0.83
5	K ₄ [Ru(CN) ₅ NO ₂]	-54 ± 8	-0.34 ± 0.02	0.44	0.55	0.99 ± 0.12	0.85
6	RuCl ₃	54 ± 8	-0.71 ± 0.01	0.23	-0.26	-0.03 ± 0.03	0.23
7	K ₂ [Ru(H ₂ O)Br ₅]	59 ± 8	—	—	—	—	0.21
8	K ₂ [Ru(H ₂ O)Cl ₅]	55 ± 8	-0.71 ± 0.02	0.22	-0.26	-0.04 ± 0.08	0.23
9	K ₂ [Ru(NO)Cl ₅]	0 ± 3	-0.36 ± 0.03	0.23	0.10	0.33 ± 0.08	0.54
10	K ₂ [Ru(NO)(CN) ₅]	-84 ± 7	-0.08 ± 0.01	0.39	0.70	1.09 ± 0.10	1.02
11	[Ru(NH ₃) ₄ (NO)Cl]Cl ₂	-50 ± 10	—	—	—	—	0.82
12	[Ru(NH ₃) ₅ Cl]Cl ₂	-22 ± 8	-0.53 ± 0.01	0.44	0.34	0.78 ± 0.13	0.66
13	[Ru(NH ₃) ₅ NO]Cl ₃	-62 ± 7	-0.19 ± 0.01	0.38	0.56	0.94 ± 0.10	0.89
14	[Ru(NH ₃) ₆]Cl ₃	-19 ± 7	-0.49 ± 0.01	0.40	0.38	0.70 ± 0.09	0.65
15	K ₂ RuCl ₆	-7 ± 4	-0.31 ± 0.01	0.24	0.17	0.41 ± 0.08	0.58
16	RuO ₂	-44 ± 9	-0.26 ± 0.01	0.35	0.44	0.79 ± 0.06	(0.79)
17	K ₂ RuO ₄ *)	-132 ± 11	0.38 ± 0.01	0.27	0.91	1.18 ± 0.14	(1.18)
18	K Ru O ₄	-186 ± 16	0.82 ± 0.02	0.16	1.14	1.30 ± 0.19	(1.30)
19	Ru O ₄	-248 ± 10	1.06 ± 0.01	0.22	1.49	1.71 ± 0.13	(1.71)

*) δ_r is given for BaRuO₄.

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involved in $K_{\alpha 1}$ transition. It should lead to the contrasting changes in δ_{γ} and δ_X provided, that the change of the mean square nuclear radius is positive.

In the both sets of the data a considerable spread is observed for the compounds containing Ru in the same oxidation state but bound with different ligands. In this case only systematical study of the complexes similar to each other in coordination and slightly different in composition could serve to clarify the mechanism of the chemical bonding in them. The choice of the compound collected in Table 6 will help us later to derive some useful charge differences which may be ascribed to certain ligands.

Let us pass over to the analysis of the data. Here we shall utilize the definition of the partial effective charges, which keeping in mind the above assumptions may be written as follows :

$$Q = Q_{4d} + Q_{5s} \quad (13)$$

To find out a relative role of 5s and 4d electrons in the chemical bonding of ruthenium, one should be able to separate their contributions into the observed shifts. For the X-ray chemical shifts it may be done using the theory given by KARAZIJA⁷⁾, which enables us to represent $\delta_X^{\text{exper.}}$ as a function of the the partial effective charges :

$$\begin{aligned} \delta_X^{\text{exper.}} = & C_{5s} Q_{5s} + C_{4d} Q_{4d} + Q_{5s}(Q_{5s} - 1) A_{5s} + \\ & + Q_{4d}(Q_{4d} - 1) A_{4d} + Q_{5s} Q_{4d} A_{5s,4d} \dots \end{aligned} \quad (14)$$

The coefficients of eq. (14) are (in meV): $C_{5s} = 68$; $C_{4d} = -175$; $A_{5s} = 16.6$; $A_{4d} = -15.6$ and $A_{5s,4d} = 30.6$. In addition the equation of calibration for the isomer shift of ^{99}Ru may be used in the linear form, provided that deviations of the electron configuration of Ru in its compounds from the reference state are small :

$$\delta_{\gamma} = I_{5s} Q_{5s} + I_{4d} Q_{4d}, \quad (15)$$

where I_{nl} is the isomer shift caused by the removal of nl electron from the reference state of atom. To evaluate the coefficients I_{nl} numerically, we first obtained a useful quantity $R_{5s,4d}$:

$$R_{5s,4d} = \frac{\Delta D_{5s}(0)}{\Delta D_{4d}(0)} \simeq -2^*, \quad (16)$$

*) From ref. 20) and 25) it may be derived that the simultaneous removal of one 5s and two 4d electrons from the initial configuration of Ru (transition $5s^1 4d^7 \rightarrow d^5$) does not affect considerably $D(0)$. It corresponds to (16).

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where $\Delta D_{nl}(0)$ is the change of the total electron density at the nucleus due to removal of nl electron.

Evaluation of $R_{5s,4d}$ was carried out utilizing the results of DHFS computation given in ref. 20) and 25). Then we treated eq. (14) applying

$$q_{5s} \simeq q_{4d} = \bar{q}$$

approximation to have estimates of $\bar{Q} = W\bar{q}$ for a number of the oxygen-containing compounds: RuO_4 (a), KRuO_4 (b) and K_2RuO_4 (c). It yielded the following results:

- a) $W = 8, Q_{5s} = 0.21, Q_{4d} = 1.47, Q = 1.68$;
- b) $W = 7, Q_{5s} = 0.18, Q_{4d} = 1.08, Q = 1.26$;
- c) $W = 6, Q_{5s} = 0.17, Q_{4d} = 0.85, Q = 1.02$.

Now using the isomer shifts (Table 6) and ratio (16) we have

$$I_{4d} = (0.97 \pm 0.10) \text{ mm/sec.}$$

In this approach we made use of the X-ray shifts expressed with respect to ruthenium metal and the coefficients C_{nl} and A computed with the wave functions of ruthenium atom ($5s^1 4d^7$), *i.e.* we applied the assumption which is not obvious, principally speaking. We shall avoid this weak point treating only the shifts between the compounds and assuming that only 4d electrons are responsible for them. In this case contributions to the shifts come from the changes in Q_{4d} and therefore the latters may be expressed, as

$$\Delta \delta_x \simeq C_{4d} A Q_{4d}$$

It leads to $I_{4d} = (1.05 \pm 0.17) \text{ mm/sec.}$ Similarly, from the X-ray and the isomer shifts between $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ with the same ligands in inner coordination sphere, which contain Ru atom in different oxidation states, we have $I_{4d} = 0.98 \text{ mm/sec.}$ The close values of the resulting estimates enable us to propose the following equation for the isomer shifts of ^{99}Ru NMR spectra (in mm/sec):

$$\delta_r^{\text{exper.}} = -(2.0 \pm 0.2) Q_{5s} + (1.0 \pm 0.1) Q_{4d} \quad (17)$$

The results of the combination of eqs. (14) and (17) with the experimental data are collected in the entries 5 to 7 of Table 6.

The effective charges of ruthenium in the compounds vary within comparatively narrow limits with Q_{5s} slightly deviating from its averaged value $Q_{5s} = 0.31 \pm 0.02$ (maximum deviation < 0.15). It means, that for all considered compounds is characteristic nearly the same level of involvement

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of 5s electron in chemical bonding. The maximum effective charge, as could be expected *a priori*, was obtained for $\text{RuO}_4(1.71 e)$. As to the hexacoordinated complexes of Ru(II) and Ru(III), here we observe rather complicated redistributions of the partial charges between 5s and 4d sub-levels with the maximum value (1.1 e) in the case of $\text{K}_2[\text{Ru}(\text{NO})(\text{CN})_5]$. The unexpected strange charges obtained for RuCl_3 and $\text{K}_2[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]$ represent probably the result of the mentioned above uncertainty in the reference state of Ru. It could affect so the final quantities for the compounds in case if a balance of the partial charges (see Q_{5s} and Q_{4d} in Table 6) was close to zero.

As it was already said early, the best correlation between δ_x and δ_r data was obtained for the oxygen-containing compounds (from RuO_2 through RuO_4). The quantities Q_{nz} and Q_{x+r} evaluated for them seemed to be the most reliable and we considered it would be useful to have estimates of the effective charges of Ru in other compounds from the X-ray chemical shifts only. These charges were calculated for all the complexes starting from K_2RuCl_6 , using the quantity $Q_{\text{Ru}(\text{RuO}_2)}=0.79$ (see Table 6) as the initial one and ascribing variations in δ_x data to the differences in 4d electron participation in the chemical bonding easily determined as

$$\Delta Q_{4d} \simeq \frac{\Delta \delta_x}{C_{4d}}$$

The charges obtained in this way were denoted as Q_x and given in the last entry of Table 6. It was worth while to estimate them for a sake of comparison with Q_{x+r} values keeping in view, that in the most cases we have no opportunity of combining X-ray and NMR data being limited with the X-ray chemical shifts only. As may be seen, as a whole, the values of Q_{x+r} and Q_x agree satisfactory, with averaged error $\sim \pm 0.1$. The convergency of the results should be underlined because of a variety of the compounds, different sources of the experimental data and the theoretical computations used in the analysis.

Now we compare the resulting Q values to derive some information related to electron-donor and electron-acceptor properties of the involved ligands. For this purpose we shall additionally assume, that to the first approximation the ligands preserve their charges in the complexes or, in other words, the induction reciprocal effects in the first coordination sphere are negligible. Then, comparing Q_x data (they give more complete picture) for different hexacoordinated complexes, we obtain the following approximate differences between the effective charges of the ligands Q_L :

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$$Q_{\text{NH}_3} - Q_{\text{Cl}} = 0.45$$

$$Q_{\text{NH}_3} - Q_{\text{NO}} = \left. \begin{array}{l} 0.16 \\ 0.25 \end{array} \right\} = 0.20 \pm 0.05$$

$$Q_{\text{NH}_2} - Q_{\text{CO}} = 0.46$$

$$Q_{\text{CN}} - Q_{\text{NO}_2} = 0.02$$

$$Q_{\text{Cl}} - Q_{\text{CN}} = 0.10$$

$$Q_{\text{H}_2\text{O}} - Q_{\text{NO}} = 0.31$$

If we accept now, that the effective charges of chlorine atom in $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ are equal, then we shall have immediately estimates of the absolute charges for two ligands: internal NH_3 and external Cl:

$$Q_{\text{Cl}}^{\text{ext}} = -0.44$$

$$Q_{\text{NH}_3} = 0.11$$

Finally, we are able to arrange all the ligands into series according to their ability to attract the electron density from ruthenium (Table 7).

TABLE 7. Effective charges of ligands in the complexes of ruthenium

L	NO_2	$\text{CN} \approx \text{Cl}^*$	CO	$\text{Cl} \approx \text{Br}$	NO	Cl_{br}	NH_3	dipy	H_2O
Q_{L}	-0.46	-0.44	-0.35	-0.34	-0.09	-0.08	+0.11	+0.13	+0.22

Cl^* , Cl and Cl_{br} are external, internal and bridged Cl-ligands, respectively.

The effective charges of Cd, Te, Si and P in their compounds

In many other cases we can obtain estimates of the effective charges of atom only by using approximation $q_{ns} \approx q_{np}$. As it has been shown earlier, at least for intranition elements it gives acceptable values of Q . They are collected in Tables 8 to 10. For some compounds the effective charges of two elements were evaluated from the X-ray $K_{\alpha 1}$ chemical shifts (see Tables 8~10) and then from the electroneutrality of the compound additional useful quantity of the effective charges of oxygen could be obtained, which turned out to be very close to -1 .

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TABLE 8. The chemical shifts of Cd $K_{\alpha 1}$ X-ray line and the effective charges of Cd in compounds.
(δ_X is given with respect to Cd metal, in meV)

N	Compound	$\delta_{K\alpha 1}$	$Q(\text{Cd})$	Distribution of Charges
1	CdF ₂	172 ± 4	~2	$Q(\text{F}) = -1$
2	CdCl ₂	96 ± 4	0.90	$Q(\text{Cl}) = -0.45$
3	CdBr ₂	77 ± 7	0.67	$Q(\text{Br}) = -0.34$
4	CdI ₂	48 ± 6	0.34	$Q(\text{I}) = -0.17$
5	CdSO ₄	170 ± 5	1.96	$Q(\text{S}) = +1.8$; $Q(\text{O}) = -0.94$
6	Cd(NO ₃) ₂	170 ± 6	1.96	$Q(\text{NO}_3) = -0.98$
7	Cd ₃ (PO ₄) ₂	153 ± 6	1.67	$Q(\text{P}) = +1.42$; $Q(\text{O}) = -0.90$
8	CdCO ₃	152 ± 6	1.66	$Q(\text{CO}_3) = -1.66$
9	CdTeO ₃	150 ± 8	1.62	$Q(\text{Te}) = +1.90$; $Q(\text{O}) = -1.17$
10	CdO	98 ± 5	0.91	$Q(\text{O}) = -0.91$
11	CdSe	82 ± 13	0.75	$Q(\text{Se}) = -0.75$

TABLE 9. The chemical shifts of Te $K_{\alpha 1}$ X-ray line and the effective charges of Te in compounds.
(δ_X given with respect to Te metal, in meV)

N	Compound	$\delta_{K\alpha 1}$	$Q(\text{Te})$	Distribution of Charges
1	TeO ₂	174 ± 6	2.09	$Q(\text{O}) = -1.04$
2	TeO ₃	269 ± 5	2.73	$Q(\text{O}) = -0.91$
3	Te(OH) ₄	172 ± 10	2.06	$Q(\text{OH}) = -0.51$
4	CdTeO ₃	172 ± 15	2.06	$Q(\text{Cd}) = +1.62$; $Q(\text{O}) = -1.23$
5	Fe ₂ (TeO ₃) ₃	150 ± 11	1.86	$Q(\text{Fe}) \approx +2.7$ $Q(\text{O}) = -1.23$
6	K ₂ TeO ₄	316 ± 9	3.04	— —
7	TeI ₂	32 ± 9	0.49	$Q(\text{I}) = -0.24$

TABLE 10. The effective charges of Si and P in compounds

Compounds	X-ray line	$\delta_{K_{\alpha 1,2}}^*$ (meV)	Q
SiC	K $_{\alpha 1,2}$ Si	220	0.54
SiS ₂		500	1.06
SiO ₂		590	1.20
MgSiF ₆		900	1.64
ZrSiO ₄		490	1.04
Mg ₂ SiO ₄		610	1.23
AlP	K $_{\alpha 1,2}$ P	-290	-1.00
Na ₃ PO ₄		790	1.42
Na ₂ HPO ₄		760	1.39
NaH ₂ PO ₄		800	1.43
Na ₄ P ₂ O ₇		790	1.42
PCl ₅		590	1.15
Na ₂ HPO ₃		660	1.15
H ₃ PO ₃		590	1.05
PCl ₃		410	0.80

*) The experimental data are cited from ref. 4).

Conclusion

A number of questions related to interpretation of the chemical shifts of X-ray emission lines has been discussed. The most reliable interpretation at present may be achieved for K $_{\alpha 1}$ line.

Essential limitations of the proposed analysis consisted of ignoring of the high-laying (nl) virtual states of atom of studied elements and application of two different theoretical methods (HF and DHFS). In the future it would be worth while to apply the relativistic method for evaluation of the effects both in X-ray line and in NTR spectra. It might bring interesting results. Though the described approach contains some assumptions and is approximate, nevertheless in all cases considered here it yields quite realistic quantities of the charges of atoms and gives for the compounds of ruthenium a reasonable arrangement of the ligands reminding of the "averaged serie" obtained from the optical spectra and ESCA^{28,29}. Besides it gives numerical values of Q_L and a correct position of the border line between donors and acceptors and therefore may serve as a basis for a comparative study of a larger number of elements and ligands.

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