Combination of the x-ray chemical shift method and the Mössbauer effect technique for the study of the electron valence structure of nontransition elements

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The shifts of the K_{α_1} and K_{β_1} emission x-ray lines of iodine in various compounds relative to crystalline iodine are measured by the crystal diffraction method. A method is proposed for the simultaneous analysis of the experimental data on the x-ray shift and the isomeric shift in the Mössbauer effect is proposed on the basis of self-consistent Dirac–Slater atomic calculations. The analysis is performed for all the investigated compounds. The populations of the $5s$, $5p$ and $5d$ orbitals of iodine are obtained in the effective free ion approximation. The influence of the self-consistent calculation parameters on the results of the analysis is discussed. It is shown that excited iodine $5d$ orbitals take part in the high-valence oxygen compounds of iodine.

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INTRODUCTION

The isomeric shift in the Mössbauer effect, just as the chemical shift of x-ray lines, is determined by the change in the population of the outer electron shells of the atom. The different sensitivity of these parameters to the population of orbitals with different symmetries (s, p, d, or f) makes it possible to combine conveniently the Mössbauer effect with the x-ray chemical shift method in the investigation of the electronic valence structure. The present paper is devoted to a comparison and to a joint analysis of the results of an investigation of iodine compounds by these methods.

The investigation of iodine compounds can be subdivided into two classes: compounds of iodine with oxygen, and of iodine with chlorine. In high-valence compounds of iodine with oxygen, one can expect an appreciable participation of the $5d$ orbitals of iodine in the valence structure (e.g., in accordance with the $2p_\pi \to 5d_\pi$ scheme). The question of the participation of the excited d orbitals in the bond is a serious problem of the chemistry of nontransition elements and has been under discussion for a long time,[1] but is far from resolved. The main arguments against such a participation are the high $np \to nd$ excitation energy and the radial diffuseness of the distribution of the density of the excited d electrons. Quantitative experimental data on the population of the $5d$ orbitals of iodine would cast light on this problem. We have attempted to do so by comparing the results of two aforementioned methods.

From the literature we know only of attempts at such a comparison. These, however, concern transition elements, the analysis being based on empirical and approximate (the Fermi-Segre formula) relations[2] or else the comparison is purely qualitative in character.[3] In the present paper the results of both methods are interpreted on the basis of a single self-consistent Dirac-Slater calculation. A large number of different electron configurations of the iodine ions have been calculated[4] for two different values of the coefficient of the Slater exchange term ($C=1$ and $C=\frac{2}{3}$). The shifts of the x-ray lines of these ions relative to the $5s^2p^5$ configuration of the neutral atom of iodine have been calculated as well as the densities of the electrons at the nucleus.

The gist of the proposed combined analysis of the data of the two methods was reported by us earlier.[5] In the present paper, the values of the experimental x-ray chemical shifts and the orbital populations obtained from them have been made more precise by repeated measurements and by improving the experimental data reduction procedure.

EXPERIMENT AND ANALYSIS RESULTS

The chemical shifts of the K-series x-ray emission lines were measured with a two-meter Cauchois crystal-diffraction focusing spectrometer by a procedure described in detail by Sumbaev.[6] The characteristic x-rays were excited by exposing the samples to the white spectrum of a high-power x-ray tube. It turned out that some of the investigated compounds are not resistant to radiation, and in these cases the samples were replaced in the measurement process as much as thirty times. The absence of radiolysis could be monitored by the absence of a shift of the x-ray line between successive measurement runs on a given sample.

Table I gives the experimental values of the shifts of the K_{α_1} and K_{β_1} lines of iodine for the investigated compounds relative to elemental iodine. The calculated values of the shifts of the K_{α_1} lines for the configurations with different $5s$ and $5p$ populations are shown in Fig. 1. The calculations of the shifts of the K_{β_1} line are presented analogously. It is seen from the figure that a definite value of the shift corresponds to a certain admissible set of electronic configurations. The plot of this set of configurations with the populations of the $5s$ and $5p$ states of iodine as coordinates is almost a straight line, which we shall call the configuration trajectory.

The isomeric shift in the Mössbauer effect is propor-

TABLE I. Experimental values of the shifts of the K_{α_1} and the K_{β_1} lines of iodine relative to elemental iodine.

Compound	x-ray chemical shifts, meV		Compound	x-ray shemical shifts, meV	
	K_{α_1}	K_{β_1}		K_{α_1}	K_{β_1}
I_2	0	0	$KICl_2$	5±5	41±11
$Na_3H_2IO_6$	378±3	545±4	$KICl_4$	96±8	176±11
KIO_4	318±3	425±4	*Ph*ICl_2	47±7	–
KIO_3	238±3	360±4	ICl_6	92±12	–
PhIO_2	164±5	231±12	ICl*py*	25±4	–
*Ph*IO	76±4	93±9	ICl*bipy*	24±4	–

Note. *Ph*–phenyl, *py*–pyridine, *bipy*–2, 2′-bipyridyl.

TABLE II. Populations of outer orbitals of iodine, effective charges of iodine and of ligands.

Chemical compound	Iodine level populations			Z_{eff} of iodine atom	Z_{eff} of ligand
	5*s*	5*p*	5*d*		
$Na_3H_2IO_6$	1.40±0.01	2.15±0.02	0.70±0.06	+2.75±0.06	−1.30±0.01
KIO_4	1.55±0.01	2.55±0.02	1.10±0.10	+1.80±0.10	−0.93±0.02
KIO_3	1.75±0.02	2.60±0.02	0.45±0.07	+2.20±0.10	−1.07±0.03
PhIO_2	1.85±0.05	3.25±0.08	0.65±0.31	+1.25±0.32	⩾−0.62±0.16
*Ph*IO	1.95±0.04	4.15±0.15	0.70±0.5	+0.20±0.53	⩾−0.20±0.53
$KICl_4$	1.92±0.02	3.40±0.10	0	+1.68±0.10	−0.67±0.03
$KJCl_2$	1.98±0.03	4.65±0.18	0	+0.37±0.18	−0.68±0.09
PhICl_2*	1.94±0.02	4.05±0.10	0	+1.01±0.10	⩾−0.50±0.10
I_2Cl_6*	1.95±0.03	3.45±0.10	0	+1.60±0.10	−0.53±0.10
ICl *py* *	1.98±0.02	4.35±0.13	0	+0.67±0.13	−0.67±0.13
2ICl *bipy* *	1.98±0.02	4.35±0.13	0	+0.67±0.13	−0.67±0.13

*It was assumed that the 5*d* orbitals are not populated.

tional to the change of the electron density at the nucleus and to the change of the charge radius of the nucleus on going to the isomeric state. The later quantity for the Mössbauer isomers ^{129}I and ^{127}I is unfortunately not known with sufficient accuracy. Therefore for the calibration of the isomeric shift it was assumed that I^0 (in I_2) and I^- have electron valence configurations $5s^2p^5$ and $5s^2p^6$, respectively. Knowing the calculated values of the electron density at the nucleus for different configurations of the iodine atom (including the reference configurations), it is easy, just as for the x-ray chemical shifts, to set definite isomeric shifts in correspondence with admissible sets of electron valence configurations (Fig. 2). For all the investigated compounds we used the published values of the isomeric shifts, [7–9] and where possible we used the more accurate values of the shifts of ^{129}I.

Thus, we have obtained configuration trajectories satisfying the values of the x-ray chemical shifts of the K_{α_1} and K_{β_1} lines and of the isomeric shift. If the description of the atom in a molecular system by means of an effective free ion is admissible, then the different experimental methods should yield identical values of the level populations of such an ion, i.e., the configuration trajectories should have a common point. Indeed, from Fig. 3 it is seen[1)] that in the case of low valence states of iodine in compounds with chlorine all three trajectories intersect at one point whose coordinates are the populations of the 5*s* and 5*p* orbitals of the iodine in these compounds. In the case of oxygen compounds of iodine, on the other hand, it was impossible to attribute the experimental shifts only to changes of the 5*s* and 5*p* populations, and the population of the 5*d* orbital was included in the analysis.

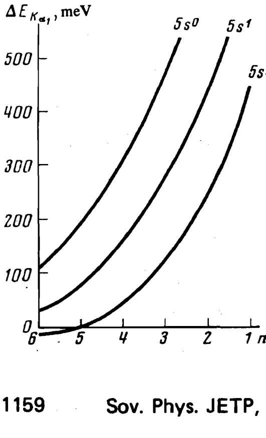

FIG. 1. Calculated values of the shifts of the K_{α_1} line for the configurations of the iodine ion with different 5*s* and 5*p* populations relative to elemental iodine (Dirac-Slater, complete exchange), *n*—number of 5*p* electrons.

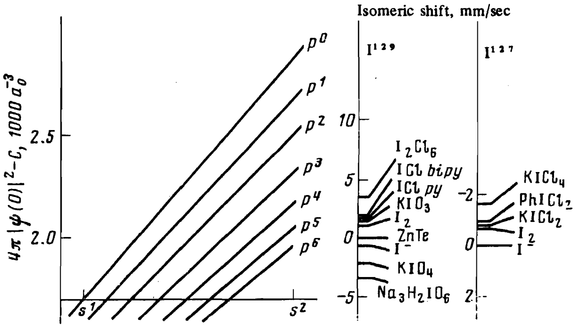

FIG. 2. Calculated plot: electron density at the nucleus–electron configuration–isomeric shift (Dirac-Slater, complete exchange), $C=4\pi|\psi(0)|^2$ for $I^{+1}5s^05p^6$.

Figure 4 shows the calculated dependence of the x-ray chemical shift and of the electron density at the nucleus on the 5*d* population. Introducing the calculated shift corrections for the change in the 5*d* population, we can obtain new configuration trajectories. It is shown in Fig. 5 how the inclusion of the 5*d* orbital makes it possible to obtain a single self-consistent configuration. The results of this analysis for all the investigated compounds are given in Table II. As a check, the obtained reconciled non-integer configurations were calculated by the Dirac-Slater method, and the agreement between

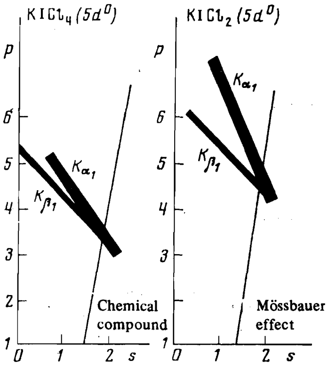

FIG. 3. Configuration trajectories for iodine chlorides.

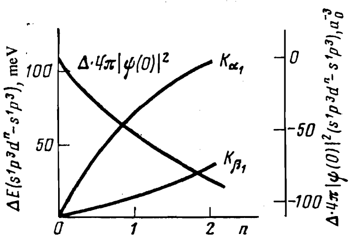

FIG. 4. Calculated dependence of the *x*-ray shifts and of the electron density at the nucleus on the 5*d* population of iodine (Dirac-Slater, complete exchange). *n* is the number of 5*d* electrons.

the calculated shifts and the experimental values provided evidence of the correctness of the graphic analysis.

DISCUSSION OF RESULTS

The electronic configurations of iodine, obtained by us for iodine chlorides, show that only the 5p population changes when bonds are produced in these compounds. The existing insignificant non-congruence of the trajectory intersection points (Fig. 3) for iodine chlorides cannot be corrected in this manner, as was done for the oxygen compounds, inasmuch as the population of the 5d orbital only increases the disparity between the x-ray chemical shifts and the Mössbauer effect, and the point of intersection of the K_{α_1} and K_{β_1} trajectories shifts even farther away into the unphysical region (s-population > 2). In these cases, the reconciled configuration was chosen such that the self-consistent calculation yields for it the calculated values of the shifts that are as close as possible to experiment.

The cause of the small but systematic difference of the 5s population from 2 in these compounds (Table II) may be the lowering, for example, in the self-consistent calculation, of the value of $\Delta|\psi(0)|^2$ by one removed 5s electron. For $Ph\mathrm{ICl}_2$, $\mathrm{I}_2\mathrm{Cl}_6$, ICl$py$, and 2ICl$bipy$ we measured only the shifts of the K_{α_1} line, because these compounds could not endure radiation and were agressive. However, if it is assumed that 5d level is not populated, then from an analysis of only the x-ray chemical shift of the K_{α_1} line and the isomeric shifts it is seen (see Table II) that in these compounds, too, the bond of the ion is of pure p-character. This result agrees with the conclusions by others.[8-10]

The effective charges at the atoms I and Cl calculated from the electronic configurations (Table II) have reasonably small values and agree with the values obtained from the Mössbauer effect.[8,9] It is curious to note that in order to obtain electronic configurations for these iodine chlorides from the Mössbauer effect use is made of the correlation of the quadrupole-splitting constant and the isomeric shift, and the configurations in Table II were obtained only from the x-ray chemical shift and the isomeric shift. Using the data on the structure of these compounds, the 5p population of Table II and the linear dependence of the quadrupole-splitting constant on the number of "unbalanced" p electrons, which was proposed by Townes and Dailey,[11] we can estimate the value of this constant. Table III lists these estimates. In the case when the natural width of the Mössbauer line is large and the quadrupole-splitting constant cannot be reliably determined, owing the poor resolution, such estimates seem to make sense, despite the large uncertainties, which are connected in this case with the errors in the values of the x-ray chemical shifts.

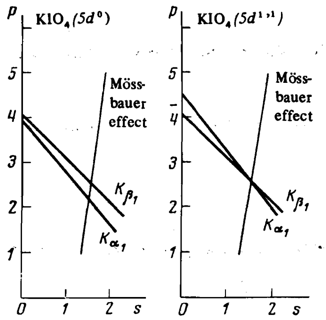

FIG. 5. Configuration trajectories for KIO$_4$.

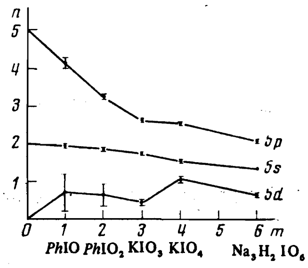

FIG. 6. Dependence of the populations on the number of ligands (m is the number of oxygen atoms bound with the iodine atom, n is the population of the iodine orbitals).

In contrast to the iodine chloride, for all the investgated oxygen compounds of iodine the reconciled configurations yield a nonzero population of the 5d orbital (Table II). Unfortunately, it is impossible to make a direct comparison of the populations for there are no published molecular calculations with an expanded atomic basis for these compounds. However, calculations of analogous compounds of elements of group III yield appreciable populations of the d orbitals. Thus, Johanson[12] gives for the 3d orbital of Cl in ClO_4^- a population 0.88, while Dolin and Dyatkina[13] give a value of 1.17. It should be noted that for fluorides of the elements of group III the calculations also give a noticeable population of the 3d orbital,[14] but it would be incorrect to compare the populations obtained by us in iodine-chloride with the fluorides, since in view of the high ionicity and the short lengths, the bond with fluorine should differ noticeably from the bond with other halogens.[15] Our preliminary results of the investigation of xenon fluorides confirms this difference.

Figure 6 shows the change of the populations of the 5s, 5p, and 5d levels (n) as functions of the number of oxygen atoms bound with the iodine (m). It is seen that the populations change in a definite manner, and the 5s and 5p populations decrease with increasing degree of oxidation and with increasing coordination number. It is frequently assumed that the population of the 5d orbital is due to the reverse transport of unshared pairs of electrons from the ligand to the free orbitals of the central atom. If this mechanism operates in this case, then it is precisely the reason why the effective charges of the central atom and of the ligand are small. In all

TABLE III. Comparison of the experimental values of the quadrupole-splitting constant with those calculated in the present paper.

Chemical compound	e^2qQ^{127}, MHz		
	Experiment		Calculation by the equation*
	Mössbauer effect	NQR	
KICl_4	+3094±20 [8]	3059 [17]	+2981±90
KICl_2	−3189±20 [8]	3140 [17]	−3096±300
$\mathrm{I}_2\mathrm{Cl}_6$	+3060±10 [9]	–	+2924±90

*These values were obtained from the equation $e^2q_{\mathrm{mol}}Q^{127} = 2293\ U_p$, where U_p (the number of "unbalanced" p electrons) was determined from the obtained 5p populations.

TABLE IV. Dependence of the populations of the external orbitals of iodine in KIO_4 on the parameters of the self-consistency procedure.

Method*	Level populations		
	$5s$	$5p$	$5d$
$DS, C=1$	1.55	2.55	1.1
$DS, C={}^2/_3$	1.50	2.30	1.1
$DSL, C=1$	1.55	2.50	1.3

**DS*-Dirac-Slater, *DSL*-Dirac-Slater-Letter

cases (except $Na_3H_2IO_6$) the charge at the oxygen is of the order of unity.

The electron valence configuration obtained for $Na_3H_2IO_6$ yields a surprisingly low $5d$ population and leads to high effective charges both at the iodine atom and at the oxygen (Table II). The reason for this anomalous behavior is still unclear, while the values of the x-ray chemical shifts for this compound on the K_{α_1} and K_{β_1} lines were verified by repeated measurements.

The cited errors in the values of the population are purely statistical and are determined by the errors in the shifts. However, in the calculation of the population we used Dirac–Slater calculations, in which the exchange is taken into approximately, statistically.[16] In such approximate calculations one can use different values of the fact C of the exchange term in the expression for the potential energy of the electron. Usually this factor is taken in the range $\frac{2}{3} < C < 1$. We used calculations with complete exchange ($C = 1$). In addition, in calculations with the exchange taken into account by Slater's method, Letter's correction is frequently used to correct the potential at large distances from the nucleus. To understand the extent to which the obtained values of the populations are stable to variation of the parameter C and to the introduction of the Letter correction, we have carried out additional calculations and a complete configuration analysis for KIO_4. It is seen from Table IV that when the parameters of the self-consistent calculation are varied, a noticeable change takes place only in the $5p$ population. This change, however, does not hinder a comparative study of the populations, in series, similar to that shown in Fig. 6, nor does it change the fact that to explain the bonds of the iodine with oxygen in the investigated compounds it is necessary to resort to $5d$ orbitals.

Another source of systematic errors may be the already mentioned deviation of the $5s$ population of iodine chlorides from 2. If the cause of this difference is assumed to be the imperfection of the self-consistent calculation, then the correction would lead to an increase of the $5d$ population and the oxygen compounds of iodine. We note that the uncertainty in the choice of the coefficient C in the calculation of the atomic structure can be eliminated by using a self-consistent Dirac–Fock calculation.

The combination of the method of the chemical shift of x-ray lines and of the Mössbauer effect seems to us quite fruitful for the study of the electronic valence structure of non-transition elements and makes it possible to obtain information that does not follow from each method separately.

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[1)] The widths of the lines in Figs. 3 and 5 equal the standard deviations.

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