Mössbauer and x-ray electron investigations of the valence configurations of tin (II) atoms in various compounds

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A combination of γ-resonance and x-ray electron spectroscopy methods is used to determine the effective valence configurations of the tin in the Sn(II) compounds SnO, $SnSO_4$, SnC_2O_4, $SnCl_2{\cdot}2H_2O$ and $SnC_4H_4O_6$. By means of the configurational dependence of the isomeric shift δE on the difference of the binding energy of $3d_{5/2}$ and $4d$ electrons in Sn, calculated for the atoms and ions by the Hatree–Fock–Slater method, it is possible to determine the number of s and p electrons in valence configurations. Calibration of the isomeric-shift scale yields the value $\delta R/R=(1.68\pm0.14)\times10^{-4}$ for the change of the charge radius of the Sn^{119} nucleus in the 23.8-keV γ transition. This value is in satisfactory agreement with the results of a number of other investigations.

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The state of valence electrons of an atom in a compound can be described with the aid of an effective valence configuration. To obtain information on the valence configuration, frequent use is made of data on the electron density and the electric-field gradient at the nucleus of the atom, data obtained, for example, from measurements of the isomeric shifts and the quadrupole interactions by the method of γ-resonance spectroscopy. Unfortunately, however, these experimental results cannot be uniquely interpreted without additional information. The necessary additional information can be obtained, for example, from measurements of the chemical shifts of x-ray lines.[1]

In the present study, to determine the effective valence configurations, we used a combination of the γ-resonance and x-ray-electron spectroscopy methods. We investigated the γ-resonance and x-ray-electron spectra of compounds of Sn(II) for the purpose of determining the valence-electron configurations of the tin in these compounds. To analyze the experimental data we plotted the theoretically calculated values of the isomeric shifts δE against the difference between the binding energies of the $3d_{5/2}$ and $4d$ electrons, $\Delta\varepsilon^{\text{theor}}$, for tin atoms with various configurations of the valence electrons. In Fig. 1, the points through which the interpolation lines are drawn connect the quantities

$$\delta E=5.34\cdot10^2\frac{\delta R}{R}\Delta|\psi(0)|^2\ (\text{mm/sec}\cdot a_0^3)\tag{1}$$

with $\Delta\varepsilon^{\text{theor}}$ for the corresponding valence configurations of tin (a_0 is the Bohr radius). The electron density at zero $|\psi(0)|^2$ and $\Delta\varepsilon^{\text{theor}}$ for different configurations of tin were calculated by Band and Trzhaskovskaya using the Hartree–Fock–Slater method of reconciling the fields of the ions and atoms in the relativistic approximation.[2] The change $\delta R/R$ of the charge radius of the tin atom was assumed by us to be 1.8×10^{-4}, in agreement with published data (see, e.g.,[3]). The number U_p of unbalanced p electrons was determined from the measured values of the quadrupole splitting ΔE by using the relation

$$\Delta E=\frac{U_pe^2Qq_{\text{at}}}{2},\tag{2}$$

where Q is the quadrupole moment of the tin nucleus in the excited state, equal to -0.07 b, and q_{at} is the gradient of the electric field produced at the nucleus of the free atom by one p electron in a state with total angular momentum $j=\frac{3}{2}$, determined by the expression (see, e.g.,[4])

$$eq_{\text{at}}=\frac{2e}{5}\langle r^{-3}\rangle.\tag{3}$$

1. MEASUREMENT RESULTS

The nuclear-gamma-resonance (NGR) and x-ray-electron spectra were plotted for five Sn(II) compounds: SnO, $SnSO_4$, SnC_2O_4, $SnCl_2\cdot2H_2O$, and $SnC_4H_4O_6$. The NGR spectra were obtained with an electrodynamic installation operating in the constant-acceleration mode. The measurements were made at liquid-nitrogen tem-

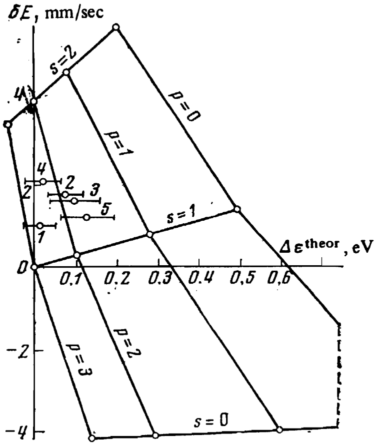

FIG. 1. Configurational dependence of the isomeric shift δE on the change in the difference $\Delta\varepsilon^{\text{theor}}$ between the binding energies of the $3d_{5/2}$ and $4d$ electrons, for the tin atom ($\Delta\varepsilon$ for α-Sn was assumed to be zero): 1—SnO; 2—$SnCl_2\cdot2H_2O$; 3—SnC_2O_4; 4—$SnSO_4$; 5—$SnC_4H_4O_6$.

TABLE I.

Compound	δE, mm/sec	ΔE, mm/sec	$\varepsilon^{\exp}_{3d_{5/2}}$, eV	$\Delta\varepsilon^{\exp}$, eV	U_p	x	z
SnO	0.72±0,05	1,29±0.05	485,7±0.1	460,83±0.04	0.69±0.10	0.82±0.07	0,40
$SnCl_2\cdot 2H_2O$	1.68±0,05	1,31±0.05	486.8±0.1	460.90±0.04	0.70±0.10	0.63±0.07	0,45
SnC_2O_4	1.65±0,05	1 49±0,05	486.7±0.1	460,88±0.06	0,80±0.10	0,66±0 07	0,43
$SnSO_4$	2,00±0,05	0,95±0,05	486.6±0.1	460 89±0.04	0,51±0.10	0.47±0,07	0,28
$SnC_4H_4O_6$	1,18±0,02[9]	1.97±0,02[9]	486.8±0.1	460.92±0.06	1,05±0.10	0.76±0.07	0,60
β-Sn	0,0	0.0	485.72±0,08[8]	460.80±0,06	—	—	—

perature. The results are presented in the second (δE) and third (ΔE) columns of Table I. The x-ray-electron spectra were plotted with a Hewlett-Packard electrostatic spectrometer HP-5950A. The measurements of the spectra of the lines $3d_{5/2}$(Sn) and $4d$(Sn) were performed in a single cycle. As a result of computer reduction of the spectral lines $3d_{5/2}$(Sn) and $4d$(Sn) for different Sn(II) compounds, we obtained the experimental values of $\varepsilon^{\exp}_{3d_{5/2}}$ and $\Delta\varepsilon^{\exp}$ listed in the fourth and fifth columns of the table. Figure 2 shows typical spectra of the $3d$ and $4d$ lines of tin in Sn(II) compounds. It should be noted that the energy value obtained by us for the $3d_{5/2}$(Sn) line in SnO is smaller by 0.7 eV than the value given by Morgan and van Vazer.[5]

The x-ray-electron spectrometer produces stable and reproducible spectra in the range $(\pm 0.03 \pm 0.015 \cdot \Delta T)$ eV for 8 hr, where ΔT is the change of the room temperature during the measurement time in °C. When the calibration is against a sample with known binding energy, the energy calibration accuracy is in the range $(0.003B + 0.01)$ eV, where B is the width of the scanning band (10, 20, or 50 eV). The accuracy in the determination of the second order chemical shifts, which were used by us to determine the effective valence configurations, is much higher because of their relative character, and this estimate is shown in the table.

The energy position of the line was determined with a computer connected to the x-ray-electron spectrometer. The accuracy with which the energy position of a single line was determined is sufficiently high and introduces no additional errors. The doublet line $Sn4d_{3/2,5/2}$ (Fig. 2) actually does not reveal a doublet structure, and was therefore treated here as a single line. The reference line was the 284.3 eV C 1s carbon line of oil vapor adsorbed by the sample surface.

2. DETERMINATION OF EFFECTIVE VALENCE CONFIGURATIONS OF TIN IN Sn(II) COMPOUNDS

The experimental points for the investigated Sn(II) compounds are superimposed on the configuration plots of δE against $\Delta\varepsilon^{\text{theor}}$ (Fig. 1). It is seen from Fig. 1 that the experimental error in the measurement of the binding energy does not make it possible to determine exactly the number of p electrons in the valence configuration in the valence configuration of the tin in these compounds. For the p electrons we can indicate only the limits within which the actual number of p electrons lies in the valence configuration. As to the s electrons, their number is determined with great accuracy, for in this case the accuracy depends on the accuracy with which the isomeric shift is measured (if we disregard the errors of $\delta R/R$), which is very high. Thus, with the aid of the configuration dependence of δE on $\Delta\varepsilon^{\text{theor}}$, we obtained the following values for the valence configuration of tin in the investigated compounds:

$$\begin{gathered} \mathrm{SnO}\ s^{1,18\pm0,07}\ p^{3\div2,3}, \\ \mathrm{SnCl_2\cdot 2H_2O}\ s^{1,37\pm0,07}\ p^{2,4\div1,7}, \\ \mathrm{SnC_2O_4}\ s^{1,34\pm0.07}\ p^{2,3\div1,5}, \\ \mathrm{SnSO_4}\ s^{1,53\pm0,07}\ p^{3\div2}, \\ \mathrm{SnC_4H_4O_6}\ s^{1,24\pm0,07}\ p^{2,3\div1,3}. \end{gathered} \tag{4}$$

In the sixth column of the table are given the values of U_p obtained from (2) from the measured values of ΔE. For $\langle r^{-3}\rangle$ we have assumed the value $10.87a_0^{-3}$, which corresponds to the configuration $5s^1 5p^1_{1/2}p^2_{3/2}$ (for the other possible valence configurations this value varies within a range of 10%). The seventh column lists the values of x determined from the valence configuration $5s^{2-x}$ obtained for the s electrons and given in (4). It is seen that the values of x and U_p are almost equal. One can therefore conclude that a number x of s electrons goes over into the p state, thus unbalancing the populations of the states $p_{3/2}$ with different values of j_s. In the case of a partially ionic (or polar bond, when a fraction of the electron charge (z) is drawn away from the electron atom, the valance configuration takes the form $5s^{2-x}5p^{2+x-z}$.

The values of the charge z were obtained by a procedure proposed by Shirley and co-workers.[6] The idea of the method is that the experimentally measured binding-energy difference of the electrons $\delta\varepsilon_{nlj} = \varepsilon_{nlj}(A, X) - \varepsilon_{nlj}(A, Y)$, where n, l, and j are the quantum numbers and X and Y are different compounds containing the atom A, can be expressed as a function of the charge z by means of the relation

$$\delta\varepsilon_{nlj} = \delta\varepsilon^{\text{ion}}_{nlj}(z) + 0.75\delta\varepsilon_M(+1) + \delta\varepsilon_{\text{rel}}. \tag{5}$$

In this relation, $\delta\varepsilon^{\text{ion}}_{nlj}$ is the difference between the theoretically calculated binding energies for the ions and can be expressed as a function of the charge z. In the case of tin we obtain on the basis of the data of the table in[2] $\delta\varepsilon^{\text{ion}}_{3d_{5/2}}(z) = 0.35z^2 + 9.92z - 1.90$. The difference $\delta\varepsilon_M(+1)$ between the Madelung energies can be represented as a function of the charge if it is assumed that the crystal consists of opposite charges $z < 1$. The calculation of the Madelung potential reduces to a calculation of lattice sums of the type $\Sigma 1/r_{ij}$, which we have carried out with a computer by Ewald's method.[7] The influence of the surface on the value of the Madelung correction was taken into account by introducing the coefficient 0.75 (see[6]). The relaxation energy of the electron cloud around the positive hold $\delta\varepsilon_{\text{rel}}$ was esti-

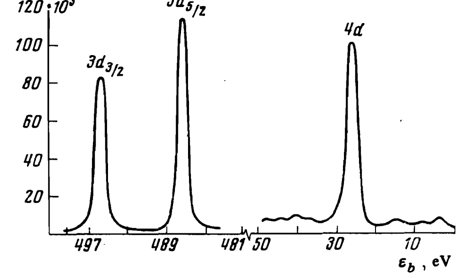

FIG. 2. X-ray-electron spectrum of $3d_{3/2}$, $3d_{5/2}$, and $4d$ lines of Sn in the compund $SnCl_2\cdot 2H_2O$.

mated by use from the formula proposed in[6]. The charge z can thus be obtained substituting the experimental value of the binding-energy difference $\delta\varepsilon^{\text{exp}}_{3d_{5/2}}$ in expression (5). As a result we obtain the following valence configurations of Sn in the compounds:

$$\begin{array}{r}
\mathrm{SnO}\ s^{1,18\pm0,07}\ p^{2,42\pm0,10}\\
\mathrm{SnSO_4}\ s^{1,53\pm0,07}\ p^{2,21\pm0,10}\\
\mathrm{SnC_2O_4}\ s^{1,34\pm0,07}\ p^{2,23\pm0,10}\\
\mathrm{SnCl_2\cdot 2H_2O}\ s^{1,37\pm0,07}\ p^{2,18\pm0,10}\\
\mathrm{SnC_4H_4O_6}\ s^{1,24\pm0,07}\ p^{2,16\pm0,10}
\end{array} \tag{6}$$

The obtained configurations depend significantly on the reliability of the theoretical calculations[2] and on the assumed value of $\delta R/R$. To verify the extent to which the calculations[2] agree with the experimental data, we have independently calibrated the scale of isomeric shifts with the aid of the correlation between the quantities δE and $\delta\varepsilon_{3d_{5/2}}$ for octahedral Sn(IV) compounds of the type $(\mathrm{Et_4N})\mathrm{SnX_6}$ and $(\mathrm{Et_4N})\mathrm{SnX_4Y_2}$ (X and Y are halogens), using the results of[10],

$$\delta E = 1.28 - 1.16\,\delta\varepsilon_{3d_{5/2}}. \tag{7}$$

Assuming that relation (7) is satisfied for the free-tin configuration $5s^2 5p^2$, we obtain from the theoretical value $\delta\varepsilon_{3d_{5/2}} = -1.9$ eV for this configuration $\delta E = 3.88$ mm/sec. We then obtain from the tables of[2] the value $\delta R/R = (1.68 \pm 0.14)\cdot 10^{-4}$, which is in satisfactory agreement with the value 1.8×10^{-4} used by us.

3. DISCUSSION

The effective valence configurations obtained by us for tin Sn(II) compounds and the calibration of the scale of the isomeric shifts are based on relativistic calculations of the wave functions for atoms and ions, carried out by the Hartree–Fock–Slater method. This means that we use an approximation in which the wave function of the valence electron in the compound (the molecular orbital) is represented in the basis of atomic orbitals for which j is a good quantum number. Therefore the number U_p of unbalanced p electrons, determined from (2), is equal to the difference between the populations of the states $j=\frac{3}{2}$, $j_z=\pm\frac{3}{2}$ and $j=\frac{3}{2}$, $j_z=\pm\frac{1}{2}$, since equal populations of states with different j_z result in a zero gradient. Usually in the atomic-orbital method one uses an expansion in the atomic wave functions characterized by the quantum number l, while U_p is expressed in terms of the populations of the P_z, P_x, and P_y orbitals.

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