SOVIET PHYSICS JETP VOLUME 22, NUMBER 2 FEBRUARY, 1966

ANALYSIS OF THE VARIATION OF THE Sn^{119} *NUCLEAR CHARGE RADIUS BASED ON ITS MÖSSBAUER SPECTRA*

I. B. BERSUKER, V. I. GOL'DANSKIĬ, and E. F. MAKAROV

Physical Chemistry Institute, Academy of Sciences, U.S.S.R.; Chemistry Institute, Academy of Sciences, Moldavian S.S.R.

Submitted to JETP editor March 24, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 699-706 (August, 1965)

It has been assumed previously that the nuclear charge radius of Sn^{119} in the excited state at 23.8 keV is greater than in the ground state ($\Delta R/R > 0$). This conclusion, obtained from chemical shifts of Mössbauer lines in the compounds of tin, was based on a very crude picture of the structure of the electron shells in these compounds and their interaction with the nucleus. The present analysis gives a general formula for the dependence of the chemical shift on the parameters of the molecular orbits and the orbits of the inner shells; for tetrahalogenides of tin these estimates lead to the conclusion that $\Delta R/R < 0$. These results are important for the interpretation of many experimental data from Mössbauer spectroscopy of tin compounds.

1. INTRODUCTION

THE percentage change in charge radius $\Delta R/R$ of the nucleus when it is excited is an important characteristic of its contact interaction with the electron shell. The determination of this quantity involves familiar difficulties. Some possibilities for determining it come from Mössbauer spectra, from the dependence of the chemical shift of the center of gravity of the spectrum on the change in electron density at the nucleus, in which $\Delta R/R$ enters explicitly:

$$\delta = \mathrm{const}\cdot\frac{\Delta R}{R}\{|\Psi'(0)|^2 - |\Psi(0)|^2\}. \qquad (1)$$

Here $|\Psi(0)|^2$ and $|\Psi'(0)|^2$ are the total electron densities at the nucleus in the γ ray source and absorber, respectively.

For the Sn^{119} nucleus (where const = 1.97 $\times 10^{-22}$ (mm/sec)cm^3) Shpinel', Bryukhanov, and Delyagin[1] first used formula (1) to determine the sign of $\Delta R/R$ from measurements of the chemical shift δ in the absorption spectrum of 23.8 keV γ quanta, and concluded that $\Delta R/R > 0$. Boyle, Bunbury, and Edwards[2] gave a more detailed treatment of this question and estimated the absolute value of the ratio: $\Delta R/R = +1.1 \times 10^{-4}$.

These results are based on a quite crude approximation to the values of $|\Psi(0)|^2$, for which the following basic assumptions were used: 1) only the contribution of the outer 5s electrons is important for the electron density at the nucleus; 2) this contribution is determined only by the number of 5s electrons, which was taken to be zero for the so-called "ionic" compounds of tetravalent tin (for example, SnF_4) and equal to 2 for the similar compounds of divalent tin (SnCl_2); 3) the contribution of each 5s electron can be determined from the Fermi-Segre formula.[3,4]

The value of the ratio $\Delta R/R$ (and even its sign) obtained on these assumptions is certainly subject to doubt in view of the inconsistency of the first two assumptions. In fact, direct observations of nuclear quadrupole resonance spectra in halogens have shown quite convincingly (cf., for example,[5]) that the fraction of the electronic charge that is pulled over to the I, Br and Cl in compounds of the type SnX_4 (the so-called ionic character of the Sn-X bond, cf. below) does not exceed 0.3—0.4. From this there arises the necessity for a more exact determination of the fractions of the electron shells for the 5s-electrons contributing directly to $|\Psi(0)|^2$ and of the 5p-electrons which, by screening the s-electrons, reduce this contribution.[1)]

In the present report we give a more complete treatment of the distribution of the electron shells in compounds of tin and its influence on the electron density at the nucleus. We get a general formula for the dependence of the chemical shift δ

[1)] The direct contribution of the p-electrons (in the $p_{1/2}$ state) to $|\Psi(0)|^2$ does not exceed 4.5% in the case of tin and will not be considered further.

on the parameters of the molecular orbitals in these compounds. Estimates of these parameters for tetrahalogenides of tin permit the conclusion that $\Delta R/R < 0$, contrary to the result found by Shpinel' et al[1] and Boyle et al.[2] The suggestion that the sign of $\Delta R/R$ is negative was first made by two of us.[6] The negative sign of this ratio for Sn^{119} (and a value $\Delta\langle R^2\rangle/\langle R^2\rangle \leq 2.6 \times 10^{-4}$) was subsequently found by Belyakov[7] on the basis of a calculation, in the approximation of the theory of finite Fermi systems, of the change in the charge distribution of the Sn^{119} nucleus when it is raised to the excited state.

2. BASIC FORMULAS

We consider a molecular complex, consisting of a tin atom and ligands (atoms, molecules, ions, radicals) of the first coordination sphere, and assume that its outer one-electron states can be described by some set of molecular orbitals of the type

$$\Psi_k = N_k\{\psi_k + \lambda_k\chi_k\}, \tag{2}$$

$$N_k^2 = [1 + \lambda_k^2 + 2\lambda_k S_k]^{-1}, \tag{3}$$

$$S_k = \int \psi_k\chi_k d\tau, \tag{4}$$

where ψ_k is a linear combination of atomic functions φ_i for the tin atom:

$$\psi_k = \sum_i a_{ki}\varphi_i, \tag{5}$$

χ_k is the corresponding linear combination of ligand wave functions, and S_k is the overlap integral.

The total electron density at the origin, which appears in formula (1) for the chemical shift can be written approximately as

$$|\Psi(0)|^2 = \sum_k \varepsilon_k N_k^2 a_{ks}^2 |\varphi_{5s}(0)|^2 + \sum_{n=1}^{4} 2|\varphi_{ns}(0)|^2. \tag{6}$$

It is assumed that in the one-electron approximation only s-electrons contribute to the electron density at the origin, where only the 5s-orbit of tin contributes to the formation of the molecular orbitals (2) (where it is obvious that (6) is independent of symmetrization of the one-electron states). The constant ϵ_k characterizes the occupation of the corresponding molecular orbitals and can take on the values 2,1,0, while the second sum in (6) gives the contributions of the inner filled orbits of tin.

Having determined the values of $|\Psi'(0)|^2$ and $|\Psi(0)|^2$ from (6), substituting them in (1) we find

$$\delta = A\left\{\frac{|\varphi_{5s}'(0)|^2}{|\varphi_{5s}(0)|^2}\sum_k \varepsilon_k' a_{ks}'^2 N_k'^2 - \sum_j \varepsilon_j a_{js}^2 N_j^2 + \beta\right\},$$

$$A = 1.97\cdot 10^{-22}\frac{\Delta R}{R}|\varphi_{5s}(0)|^2\ [(\mathrm{mm/sec})\mathrm{cm}^3] \tag{7}$$

The quantity β characterizes the relative contribution of the changes in the inner shells to the electron density at the nucleus when we change from source to absorber:

$$\beta = (|\varphi_{5s}(0)|^2)^{-1}\sum_{n=1}^{4} 2[|\varphi_{ns}'(0)|^2 - |\varphi_{ns}(0)|^2]. \tag{8}$$

We note that when we take account of the difference between $|\varphi'_{ns}(0)|^2$ and $|\varphi_{ns}(0)|^2$ in these formulas, we are including not only the renormalization of the wave functions of the valence electrons as a result of formation of molecular orbitals, but also the redistribution of the electron density in the atomic states as a result of changing from one compound to another.

To estimate the ratio $|\varphi'_{5s}(0)|^2/|\varphi_{5s}(0)|^2$ we can use the Fermi-Segre formula.[3,4] Remembering that the effective quantum number n_{eff} that appears in the formula is a slowly varying function of the effective charge Z, we can immediately write:

$$|\varphi_{5s}'(0)|^2 / |\varphi_{5s}(0)|^2 \approx Z'^2/Z^2, \tag{9}$$

where Z' and Z are the effective charges for the tin atom in the absorber and source, respectively. Their values are determined both by the charge of the atomic core Z_0 and by the screening effect of the other valence electrons, which depends on the parameters of the corresponding molecular orbitals. Denoting the screening parameter of a 5s-electron by other 5s-electrons or the 5p-electron by α (since they are electrons in the same shell, they screen approximately equally), we can write

$$Z' = Z_0 - \alpha\left(\sum_k \varepsilon_k' N_k'^2 - 1\right),$$

$$Z = Z_0 - \alpha\left(\sum_j \varepsilon_j N_j^2 - 1\right),$$

$$Z'/Z = 1 + b\left(\sum_j \varepsilon_j N_j^2 - \sum_k \varepsilon_k' N_k'^2\right), \tag{10}$$

where we have introduced the source parameter

$$b = \alpha\Big/\left[Z_0 - \alpha\left(\sum_j \varepsilon_j N_j^2 - 1\right)\right]. \tag{11}$$

We can get an estimate of the relative change of $|\varphi_{ns}(0)|^2$ for the inner electrons from (8) by using the results of Crawford and Schawlow,[8] which they obtained from an estimate of the influence of the screening of inner electrons by outer electrons on the value of the isotope shift. Assuming that the main contribution to the screening comes from 5s-electrons, we have

$$\beta = \sum_n 2 \frac{|\varphi_{ns}(0)|^2}{|\varphi_{5s}(0)|^2} \frac{2}{Z_{ns}} f_{ns}, \tag{12}$$

$$f_{ns} = \sum_j \varepsilon_j N_j^2 a_{js}^2 \int_0^\infty P_{ns}^2(r_1)\,dr_1 \int_0^{r_1} P_{5s}^2(r)\,dr - $$

$$- \sum_k \varepsilon_k' N_k'^2 a_{ks}'^2 \int_0^\infty P_{ns}'^2(r_1)\,dr_1 \int_0^{r_1} P_{5s}'^2(r)\,dr, \tag{13}$$

where $P_{ns}(r) = rR_{ns}(r)$, $R_{ns}(r)$ is the radial part of the wave function.

The difference between the functions P_{5s}' and P_{5s} in (13) becomes less and less important as the region of integration increases, and can thus be of importance only for deep-lying ns-states. But for them the term f_{ns} and its contribution to β are very small (cf.[8]). Thus we can neglect this difference in estimating β. Then we have

$$\beta = \beta_0 \Big(\sum_j \varepsilon_j N_j^2 a_{js}^2 - \sum_k \varepsilon_k' N_k'^2 a_{ks}'^2 \Big), \tag{14}$$

$$\beta_0 = \sum_n 2 \frac{|\varphi_{ns}(0)|^2}{|\varphi_{5s}(0)|^2} \frac{2}{Z_{ns}} \int_0^\infty P_{ns}^2(r_1)\,dr_1 \int_0^{r_1} P_{5s}^2(r)\,dr. \tag{15}$$

A similar correction term can also be written for the screening effect of the outer p-electrons.

Substituting (9), (10), and (14) in (7), we get the general formula for the chemical shift of the Mössbauer spectrum of the Sn^{119} nucleus in the absorber compound relative to the source compound, expressed in terms of the molecular orbital parameters for the two compounds:

$$\delta = A \Big\{ \Big(\Big[1 + b \Big(\sum_j \varepsilon_j N_j^2 - \sum_k \varepsilon_k' N_k'^2 \Big) \Big]^2 - \beta_0 \Big)$$

$$\times \sum_k \varepsilon_k' a_{ks}'^2 N_k'^2 - (1 - \beta_0) \sum_j \varepsilon_j a_{js}^2 N_j^2 \Big\}. \tag{16}$$

Without loss of generality, we can simplify this formula by taking as the source of γ quanta tetrahedral gray tin (α-Sn). For it we can assume, in good approximation, that each tin atom is tetrahedrally bonded to the surrounding tin atoms by four hybrid sp^3-orbitals. In this case we easily find:

$$a_{js}^2 = 1/4, \quad \varepsilon_j = 2, \quad \lambda_j = 1, \quad 2N_j^2 = (1+S)^{-1},$$

$$j = 1, 2, 3, 4,$$

and formula (16) becomes

$$\delta = A \Big\{ \Big(\Big[1 + b \Big(\frac{4}{1+S} - \sum_k \varepsilon_k' N_k'^2 \Big) \Big]^2 - \beta_0 \Big)$$

$$\times \sum_k \varepsilon_k' N_k'^2 a_{ks}'^2 - (1 - \beta_0)(1 + S)^{-1} \Big\}, \tag{17}$$

$$b = \alpha / [Z_0 - \alpha(3 - 4S)]. \tag{18}$$

We can in principle calculate δ from this formula if we know the parameters of the molecular orbitals and $\Delta R/R$. Conversely, if δ and $\Delta R/R$ are known we can use them to find the parameters of the molecular orbitals. Later we shall use (17) to estimate the quantity $\Delta R/R$ which enters in A.

Here we mention that, of the three fundamental assumptions that were made earlier in interpreting data on the chemical shift in Mössbauer spectra, only one has been used in formulas (16) and (17)—the possibility of determining $|\varphi_{5s}(0)|^2$ from the Fermi-Segre formula.[3] One may hope that, as a result of the extension of the limits of validity of the latter by Foldy,[4] this assumption is not very restrictive. There remain, of course, all the assumptions associated with the validity of the molecular orbital method.

3. ESTIMATES AND CONCLUSIONS

To determine $\Delta R/R$ from (17) it is necessary to know the parameters of the molecular orbitals of the tin compounds for which δ is measured. We look at the simplest class of such compounds, the tetrahedral molecules of the type SnR_4, where R is a monovalent atom or radical. For them, as for tetrahedral tin, the bond is formed from four hybrid sp^3-orbits: $\epsilon_k' = 2$, $a_{ks}'^2 = 1/4$, $k = 1, 2, 3, 4$, but the Sn–R bond, unlike the Sn–Sn bond, may be polar, so that $\lambda_k' = \lambda \neq 1$. Obviously λ depends on the acceptor nature of R, which in many cases (for example, for the halogenides) can be judged from experimental data obtained with nuclear quadrupole resonance.[5]

We introduce a parameter γ, satisfying the relation

$$2N'^2\lambda^2 = 1 + \gamma. \tag{19}$$

Since $2N'^2\lambda^2$ is equal to the fraction of the electron charge shifted to the ligand in the two-electron bond Sn–R, γ obviously characterizes the change in the charge of R when it forms bonds. We note that in a nonpolar bond, i.e., when $\lambda = 1$, the parameter $\gamma = -S'(1+S')^{-1}$, i.e., is different from zero. It follows that, although γ plays approximately the same role as the so-called ionic character of the bond, it is not identical with it, being smaller by an amount of the order of the overlap integral S′. From Eqs. (3) and (19), neglecting S^2 compared to unity, we find

$$2N'^2 = 1 - \gamma - 2S'\sqrt{1-\gamma^2}. \qquad (20)$$

Taking account of this relation, formula (17) becomes

$$\delta = A\{[1 + 4b(\gamma - S + 2S'\sqrt{1-\gamma^2})]^2 \times (1 - \gamma - 2S'\sqrt{1-\gamma^2}) + \beta_0(\gamma - S + 2S'\sqrt{1-\gamma^2}) - 1 + S\} \qquad (21)$$

for tetrahedral molecules. In this formula A, b, and β_0 are treated as parameters (the overlap integrals S and S′ are easily computed) and if δ is measured for three tetrahedral tin compounds for which the value of γ is known, then the determination of A and consequently of the ratio $\Delta R/R$ involves no difficulties.

As already mentioned, the parameters γ for the tetrahalogenides of tin SnX_4, X = Cl, Br, I, are determined from nuclear quadrupole resonance of the halogens. Unfortunately the values of γ thus obtained depend on other factors, mainly on the possibility of formation of $d_\pi - p_\pi$ bonds Sn–X, the fraction of which is not too well known (cf. [5]). But the behavior of γ through the series of different X, i.e., the differences $\gamma_{Cl} - \gamma_{Br}$, $\gamma_{Br} - \gamma_I$, etc, are almost independent of these other factors.

The figure shows experimental curves for the dependence of δ on γ for tetrahalogenides of tin (A—for the case where γ is determined without taking account of $d_\pi - p_\pi$ bonds,[9] and B—with a correction for the formation of such bonds, taken from[5]). From the figure we see that for small γ the experimental dependence of δ on γ is linear. This confirms our result (21). In fact, for small γ, dropping γ^2 compared to unity, we easily find

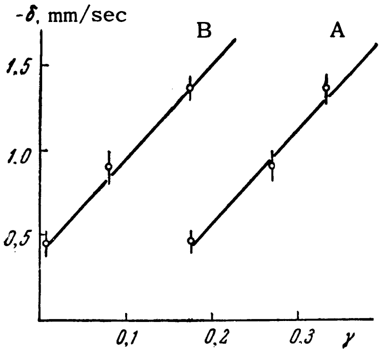
$$\delta = A(8b + \beta_0 - 1)\gamma + A(8b + \beta_0 - 1)(2S' - S). \qquad (22)$$

Comparing this formula with the experimental curve, we easily find from the slope (derivative) at $\gamma = 0$, that

$$A(8b + \beta_0 - 1) = -5.6 \text{ mm/sec} \qquad (23)$$

$$\delta(0) = A(8b + \beta_0 - 1)(2S' - S). \qquad (24)$$

From (23) and (24) we immediately find that $\delta_0 = -5.6(2S' - S)$. This enables us to solve the problem of the absolute values of the "ionicity" γ in these compounds, and by comparing them with values gotten from nuclear quadrupole resonance we can determine the fraction of $d_\pi - p_\pi$ bonds in these compounds. We note that there are no other experimental data for determining this quantity. The consequences of this result will be discussed in another publication.



The ratio $\Delta R/R$ which we want can be determined from Eq. (23) if the parameters b and β_0 are known. Let us try to get an approximate estimate of them. The parameter b essentially depends on the parameter for screening of a 5s-electron by another electron in the same shell, α. We mention that, in a sense which follows from the derivation of the Fermi-Segre formula (cf. [4]), Z_0 denotes the effective charge of the core at large distances. From this it follows that in estimating Z_0 one should take into account as large as possible a fraction of the screening by the other electrons, i.e., as large as possible a value of α. We can therefore assert that $\alpha > \alpha_0 = 0.35$, where α_0 is the Slater value for this parameter, which satisfactorily describes the average screening in the computation of energies and orbits. From formula (18) we see that if we use α_0 in place of α, we reduce the value of the parameter b. Setting S = 0.1 (the usual value; b has only a slight dependence on S), we easily find

$$2b \geqslant 0.25.$$

But if we use the more exact data of Urusov [10] for Z_0 and α, we get $2b \geq 0.5$. In either of these cases, since $\beta_0 > 0$ it follows from (23) that $A < 0$, and thus $\Delta R/R < 0$.

To determine β_0 from (15) we must know the atomic wave functions of the one-electron states, but these are not known for tin. The value of β_0 calculated by Crawford and Schawlow[8] for the mercury ion (Hg^+), is equal to 0.16. Since the 5s-electron in tin screens more strongly than the 6s-electron in mercury, it is natural to take for our β_0 a value larger than 0.16. A rough estimate of β_0 can be gotten by determining the ratio $|\varphi_{ns}(0)|^2/|\varphi_{5s}(0)|^2$ from the Fermi-Segre formula and using for the estimate of the integral in (15) the analogous values calculated for mercury in [8], adjusting them to the case of tin by increasing them in proportion to the ratio $|\varphi_{5s}(0)|^2_{Sn}/|\varphi_{6s}(0)|^2_{Hg}$. We then find $\beta_0 \sim 0.2$. A somewhat larger value of β_0 is gotten from an estimate based on the shifts of K, L, and M x-ray terms, from [11,12].

It is obvious that these estimates do not permit any reliable estimate of the absolute value of $\Delta R/R$. Using the value $|\varphi_{5s}(0)|^2 = 1.56 \times 10^{26}$ cm^{-3} [2] and the values $2b \geq 0.5$, $\beta_0 \geq 0.2$, we find $|\Delta R/R| \leq 1.6 \times 10^{-4}$.

We may hope that the study of other tin compounds on the basis of the general formula (16) or (17) will enable us to get additional data both for the determination of the absolute value of $\Delta R/R$ and the parameters of the electron shells in these compounds. But the estimates of the parameters already found here for the tetrahalogenides (in particular the negative sign of the ratio $\Delta R/R$) must be kept in mind in interpreting data on Mössbauer spectra in tin compounds.

We note that the variation of the ratio $(Z)_{abs.}/Z_{source}$ as a function of the ionicity of the bond (for $\alpha \approx 0.8$) is close to the analogous variation of the ratio $r_{source}/r_{abs.}$, found by Sanderson's method.[13] This permits one to represent the chemical shift as a ratio of ionic radii, as has been done by two of us.[6] As a result we have succeeded in finding some simple relations that explain satisfactorily a whole series of experimental facts. Thus, in a series of tetrahedral tin compounds the quantity $r_{source}/r_{abs.}$ increases continuously with increasing ionicity of the bond. Including this fact in the analysis of chemical shifts leads to the conclusion that the value of $\Delta R/R$ is negative. Continuing this analogy, it is qualitatively easy to see that, for example, with $\Delta R/R < 0$ the chemical shift of white tin (β-Sn) should be positive relative to α-Sn (which is actually the case), since the average atomic radius of the tin in β-Sn is greater than its atomic radius in α-Sn.

A positive sign for the chemical shift can apparently also be obtained for divalent tin compounds, since in the latter, as follows from the work of Rundle and Olson, the covalent radius is considerably greater than the covalent radius in α-Sn. Finally, as was pointed out earlier,[6] on the basis of the atomic radii of tin embedded in different metallic hosts, with a negative value for $\Delta R/R$ one can get good agreement of the calculations of chemical shifts with experiment.

Naturally, for quantitative calculations of the chemical shifts in tin compounds with more complex structures than tetrahedral, it will be necessary to carry out an analysis of formula (17). These questions as well as other consequences of the relations found in this paper will be considered in our next paper.

---

[1] Shpinel', Bryukhanov, and Delyagin, JETP **41**, 1767 (1961), Soviet Phys. JETP **14**, 1256 (1962).

[2] Boyle, Bunbury, and Edwards, Proc. Phys. Soc. (London) **79**, 416 (1962).

[3] E. Fermi and E. Segre, Z. Physik **82**, 729 (1933). S. Goudsmit, Phys. Rev. **43**, 636 (1933).

[4] L. L. Foldy, Phys. Rev. **111**, 1093 (1958).

[5] M. A. Whitehead and H. H. Jaffe, Theor. Chim. Acta **1**, 209 (1963).

[6] V. I. Gol'danskiĭ and E. F. Makarov, Phys. Letters **14**, 111 (1965).

[7] V. A. Belyakov, Phys. Letters, **17** (1965).

[8] M. F. Crawford and A. L. Schawlow, Phys. Rev. **76**, 1310 (1949).

[9] V. I. Gol'danskiĭ et al, DAN SSSR **147**, 127 (1962).

[10] V. S. Urusov, Zhur. Strukt. Khim. **3**, 437 (1962).

[11] O. I. Sumbaev and A. V. Mezentsev, JETP **48**, 445 (1965), Soviet Phys. JETP **21**, 295 (1965).

[12] C. Nordling, Ark. Fysik **15**, 241 (1959).

[13] R. Sanderson, J. Inorg. Nucl. Chem. **7**, 288 (1958).

[14] R. E. Rundle and D. H. Olson, Inorg. Chem. **3**, 596 (1964).

[15] Bryukhanov, Delyagin, and Shpinel', JETP **47**, 80 (1964), Soviet Phys. JETP **20**, 55 (1965).

Translated by M. Hamermesh
90