

QUADRUPOLE INTERACTION AND ISOMERIC SHIFTS OF THE 23.8-keV GAMMA
TRANSITION IN Sn^{119} IN ORGANIC TIN COMPOUNDS

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Submitted to JETP editor May 18, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) **43**, 1242-1247 (October, 1962)

Resonance absorption spectra have been measured for the 23.8 keV γ transition in Sn^{119} in organic compounds of tin: $(\text{C}_4\text{H}_9)_2\text{SnX}_2$ (where X is a halogen atom), $(\text{C}_4\text{H}_9)_2\text{SnO}$, $(\text{C}_4\text{H}_9)_2\text{SnS}$, $(\text{C}_4\text{H}_9)_2\text{SnSO}_4$, and $(\text{C}_4\text{H}_9)_2\text{SnSO}_3$, and also in the compounds $(\text{C}_4\text{H}_9)_4\text{Sn}$, SnCl_4 , and SnBr_4 . The values of the quadrupole interaction constant for the 23.8 keV excited state in Sn^{119} and the isomeric shifts of the 23.8 keV γ transition in these compounds were determined (relative to the transition energy in tin dioxide). It was shown that for compounds of the type $(\text{C}_4\text{H}_9)_2\text{SnX}_2$ and SnX_4 these quantities vary regularly with changing electronegativity of the atom X. The electric field gradient at the tin nucleus was found to be influenced by double bonds in the molecule and also by atoms with high electronegativity that are not directly bonded to the tin atom. A possible qualitative interpretation of the observed regularities is discussed.

THE first investigations^[1,2] of the Mössbauer spectra of resonance absorption of 23.8-keV γ quanta by Sn^{119} nuclei in organic tin compounds showed that such measurements can give extremely valuable information concerning the change in the distribution of electronic charge in the molecule as a function of the structure and the special features of its chemical bonds. Measurements of resonance absorption spectra permit one to determine two quantities characterizing the interaction of the nucleus with the electric field of the electrons in the molecule: the isomeric shift of the γ transition energy and the quadrupole interaction constant. The magnitude of the isomeric shift (which we shall denote by δ) is given in first approximation by the formula

$$\delta = E_I - E_{II} = C (R_e^2 - R_0^2) (\psi_I^2(0) - \psi_{II}^2(0)),$$

where C is a constant, R_e and R_0 are the effective radii of the charge distribution in the excited and ground states, $\psi_I(0)$ and $\psi_{II}(0)$ are the wave functions of the electrons in the region of the nucleus in two chemical compounds, E_I and E_{II} are the energies of the transition in these two compounds. Since $R_e > R_0$ for Sn^{119} ,^[3,4] a positive value of δ corresponds to the case of $\psi_I^2(0) > \psi_{II}^2(0)$. The spins of the ground and excited states of Sn^{119} are $1/2$ and $3/2$, respectively, so the quadrupole interaction is different from zero only for the excited state.

The quadrupole interaction is characterized by the quantity eqQ (the quadrupole coupling), where e is the electron charge, q is the electric field gradient at the nucleus, and Q is the quadrupole moment of the nucleus. Experimentally one measures the difference between the energies of the sub-levels with magnetic quantum numbers $\pm 1/2$ and $\pm 3/2$, which is equal to $1/2 eqQ$. We shall denote this difference (the quadrupole splitting) by the symbol Δ .

It is of particular interest to study the influence on the isomeric shift and on the value of the electric field gradient of a replacement of one of a group of atoms in the molecule by another, if these groups form some series, for example according to electronegativity. Use of the Mössbauer effect enables one to obtain information which could not be gotten by other methods (for example, nuclear quadrupole resonance cannot be applied to the present case).

In the present work, we studied the resonance absorption spectra for organic compounds of tin of the type $(\text{C}_4\text{H}_9)_2\text{SnX}_n$ (where X is an element or some group of atoms, and n is 1 or 2), and also for some compounds of the type SnX_4 .

DESCRIPTION OF EXPERIMENT

The measurements of resonance absorption spectra were made on two different equipments:

Compound	δ , mm/sec	Δ , mm/sec	Compound	δ , mm/sec	Δ , mm/sec
SnBr ₄	1.1 ± 0.1	0	(C ₄ H ₉) ₂ SnI ₂	1.8 ± 0.15	2.9 ± 0.15
SnCl ₄	0.78 ± 0.07	0	(C ₄ H ₉) ₂ SnO	0.95 ± 0.1	2.2 ± 0.2
Sn(C ₄ H ₉) ₄	1.3 ± 0.1	0	(C ₄ H ₉) ₂ SnS	0.9 ± 0.2	1.9 ± 0.2
(C ₄ H ₉) ₂ SnF ₂	1.45 ± 0.15	3.9 ± 0.2	(C ₄ H ₉) ₂ SnSO ₄	1.8 ± 0.15	4.8 ± 0.15
(C ₄ H ₉) ₂ SnCl ₂	1.6 ± 0.2	3.25 ± 0.15	(C ₄ H ₉) ₂ SnSO ₃	1.3 ± 0.2	4.0 ± 0.2
(C ₄ H ₉) ₂ SnBr ₂	1.7 ± 0.15	3.15 ± 0.5			

one with a variable velocity of the absorber, changing linearly with time,^[5] and an apparatus which gave the absorber a constant velocity relative to the source. For most materials the spectra were measured by both methods. The constant velocity apparatus could give higher accuracy in determining the positions of lines in the spectra: use of this apparatus together with a resonant counter,^[6] having a selective sensitivity for the 23.8-keV γ quanta which are emitted without recoil, enabled us to increase the magnitude of the resonance absorption effect considerably (by approximately a factor of four relative to the effect observed using a scintillation counter). The source of γ quanta was the compound SnO₂ containing the Sn^{119m} isomer. The source thickness was 5 mg/cm².

In all measurements the source was held at room temperature and the absorber at liquid nitrogen temperature. Absorbers of materials which are solids at room temperature were prepared by pressing in a mixture with beryllium oxide; absorbers of liquid materials were prepared by filling a flat thin-walled Plexiglas container with liquid. Most of the compounds studied were specially synthesized for these measurements. Chemical analyses showed that the absorbers contained no impurities which could significantly affect the shape of the resonance absorption spectrum. The absorber thicknesses for different compounds varied from 30 to 100 mg/cm².

The values of the isomeric shifts δ of the 23.8-keV γ transition relative to the transition energy in SnO₂ and the value of the quadrupole splittings Δ are shown in the table. The values can be converted to energy units by multiplying by 7.94— δ and Δ are then expressed in 10⁻⁸ eV.

RESULTS OF MEASUREMENTS AND DISCUSSION

In the present work we studied compounds of tetravalent tin of the type SnX₄, in which the tin atom has symmetric (tetrahedral) surroundings of atoms (or groups of atoms) X, and compounds of the type (C₄H₉)₂SnX_n (n = 1 or 2) where the atoms (or groups of atoms) are halogens, oxygen, sulfur and the acid radicals SO₄ and SO₃.

The values found for the isomeric shift δ and the quadrupole splitting Δ are given in the table. The resonance absorption spectra for compounds of the type (C₄H₉)₂SnX_n are shown in Figs. 1 and 2.¹⁾

The magnitude of the isomeric shift is determined entirely by the electrons in the region of the nucleus and, as mentioned above, in the present case an increase in the isomeric shift (i.e., an increase in energy of the γ transition) corre-

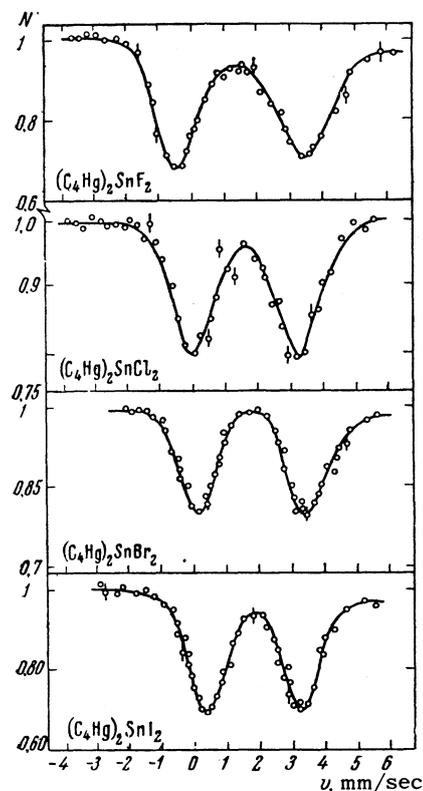


FIG. 1. Resonance absorption spectra for compounds of the type (C₄H₉)₂SnX₂ (where X is a halogen atom). The abscissa gives the absorber velocity (a positive velocity corresponding to motion of the absorber toward the source). The ordinate is the counting rate in arbitrary units; the spectra were obtained on a constant velocity apparatus using a resonant detector.

¹⁾We note that for the compound (C₄H₉)₂SnF₂ the lines in the absorption spectrum differ noticeably in intensity and width (similarly to the case of (C₄H₉)₂SnCl₂ which was previously noted^[2]). The reason for this difference has not yet been established.

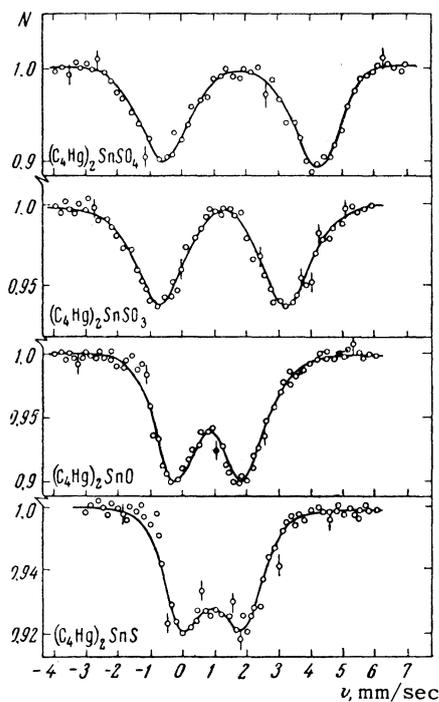


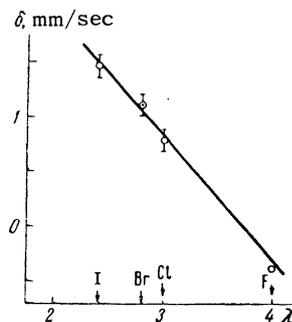
FIG. 2. Resonance absorption spectra for compounds $(C_4H_9)_2SnO$, $(C_4H_9)_2SnS$, $(C_4H_9)_2SnSO_4$ and $(C_4H_9)_2SnSO_3$. The spectra were obtained with the variable velocity apparatus.

sponds to an increase in the value of $\psi^2(0)$.

Obviously the change in the value of $\psi^2(0)$ will depend primarily on the distribution of the density of valence electrons between the tin atom and the atoms which are combined with it. Then if the electron distribution is not spherically symmetric, there may be a nonzero gradient of the electric field at the tin atom. It is apparently not possible to assign to each atom of the periodic table (or to a group of atoms) a fixed quantitative characteristic which would determine the distribution of electron density between neighboring atoms (or groups of atoms) in the molecule, probably because this distribution must depend on the nature of the bonds and on various collective effects. Nevertheless, within a series of molecules of similar structure one such characteristic which can be used is the electronegativity^[7] of the atoms. A qualitative correlation between electronegativity and the values of δ and Δ for certain inorganic compounds was pointed out earlier.^[8]

The connection between the value of δ and the electronegativity of atoms combined with tin shows itself clearly in the values of the isomeric shifts for compounds SnX_4 , where X is a halogen atom (Fig. 3). We see that the dependence of δ on electronegativity χ is quite accurately linear. A similar dependence may also be seen for the values of δ and Δ in the compounds $(C_4H_9)_2SnX_2$, but in these

FIG. 3. Dependence of isomeric shift δ for compounds of type SnX_4 (where X is a halogen atom) on electronegativity of atom X. Data for SnF_4 taken from [4], those for SnI_4 from [8].



cases the range of variation of δ and Δ is comparatively small so that the dependence cannot be established as reliably as for the case shown in Fig. 3. It is of interest to try to find a correlation between the experimentally determined quantities (i.e., δ and Δ) without invoking the concept of electronegativity. For the reason given above, the only correlation which can be considered to be reliable is that between the value of Δ for compounds of the type $(C_4H_9)_2SnX_2$ and the value of δ for compounds of the type SnX_4 (where we compare the values of Δ and δ for molecules containing the same atom X). In this case also the relation was linear. It is interesting to note that from this fact it follows directly that there is a linear relation between the value of the electric field gradient at the tin nucleus in compounds $(C_4H_9)_2SnX_2$ and the value of δ in the corresponding compounds SnX_4 .

In the compounds $(C_4H_9)_2SnO$ and $(C_4H_9)_2SnS$, the O and S atoms are coupled to the tin atoms by double bonds. From the data in the table we see that the values of the isomeric shifts and quadrupole couplings for these compounds differ significantly from the analogous quantities for compounds of the type $(C_4H_9)_2SnX_2$ considered above. If we formally use the dependence of Δ on the electronegativity of atom X which was considered above, we should expect that the value of Δ for $(C_4H_9)_2SnO$ should be no less than for $(C_4H_9)_2SnCl_2$, and that for $(C_4H_9)_2SnS$ be no less than the value for $(C_4H_9)_2SnI_2$. However it appears that the presence of the double bond causes a marked reduction in the electric field gradient at the tin nucleus. On the other hand, for the compounds $(C_4H_9)_2SnSO_4$ and $(C_4H_9)_2SnSO_3$ one finds large quadrupole couplings. These two compounds differ from those of the series $(C_4H_9)_2SnX_2$ considered above in that, in addition to the two (oxygen) atoms directly bonded to the tin atom, in these compounds there are groups of atoms (O and S) having high electronegativity. These atoms are not bonded directly to the tin atom, but they have a significant effect on the distribution of charge in the molecule as a whole, and this ap-

parently is the cause of the increased electric field gradient at the tin nucleus. This hypothesis is supported by the noticeable difference between the field gradients at the tin nucleus in the compounds $(C_4H_9)_2SnSO_4$ and $(C_4H_9)_2SnSO_3$: removal of one oxygen atom, which is not directly bonded to the tin atom, causes a noticeable reduction in the gradient. The induction effect which is familiar from the theory of the chemical bond, can be regarded as the analog of the phenomenon observed here. The presence of atoms with high electronegativity causes a concentration of the electronic charge in the region of the molecule where these atoms are located, i.e., there is a deformation of the electron cloud of the molecule and we get an electric field gradient at the tin nucleus. Obviously, for compounds of the type $(C_4H_9)_2SnX_2$ the greatest deformation of the electron cloud occurs when the atom X has the highest electronegativity (fluorine). Thus we can explain the dependence of the electric field gradient on the electronegativity of atom X.

As we said above, for compounds of the type SnX_4 the change in the isomeric shift from SnF_4 to SnI_4 (cf. Fig. 3) is easily interpreted in terms of the dependence of the electron density (mainly of s electrons) at the nucleus of the tin atom on the electronegativity of atom X (cf. also [8]). A simple extension of such an interpretation to the compounds of the series $(C_4H_9)_2SnX_2$ encounters some difficulties. Thus if we start by considering the number of atoms with marked electronegativity in the molecule, one might expect that for compounds of the series $(C_4H_9)_2SnX_2$ the isomeric shift would be intermediate between the values for SnX_4 and $Sn(C_4H_9)_4$. However, as we see from the table, the value of δ for the compounds $(C_4H_9)_2SnX_2$ is always much greater than for the compounds SnX_4 and $Sn(C_4H_9)_4$. Thus for compounds of the type $(C_4H_9)_2SnX_2$ the presence in

the molecule of atoms (or groups of atoms) with high electronegativity does not cause a corresponding reduction of the electron density in the region of the nucleus. This fact can be understood if we assume, for example, that in the compounds $(C_4H_9)_2SnX_2$ the bond between the tin atom and the halogen atoms is formed mainly by p electrons, while the s electron part of the wave function is concentrated mainly in the bond of the tin atom to the C_4H_9 groups. In that case the halogen atoms will not have any significant influence on the magnitude of the isomeric shift, and therefore the density of s electrons at the tin nucleus in compounds $(C_4H_9)_2SnX_2$ will be greater than in the compounds SnX_4 or $Sn(C_4H_9)_4$.

The authors thank V. I. Makarov for preparing the series of organic tin compounds.

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Translated by M. Hamermesh
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