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Abstract

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Investigation of Organotin Compounds by the Method of Mössbauer Resonance Absorption of γ-Quanta

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As is known, the form of the spectrum of Mössbauer resonance absorption of γ-quanta is very sensitive to the distribution of the electron-charge density in a molecule. A change in the electron density in the region of the nucleus whose resonant excitation is being studied leads to a change in the magnitude of the isomeric chemical shift δ (the position of the "center of gravity" of the absorption line); deviation of the electron density from spherical symmetry causes quadrupole splitting of the line. In the present work we have investigated the absorption spectra of γ-quanta with energy 23.8 keV by Sn^{119} nuclei in various organotin compounds. The measurement procedure was described by us earlier$\hat{}$(1). Measurements were made with an Sn^{119} source in the form of tin dioxide, while cooling the absorbers to the temperature of liquid nitrogen. The dependence of the magnitude of resonant absorption of γ-quanta on the velocity imparted to the absorber relative to the source was measured (the spectrum of resonant absorption). In all, 22 organotin compounds were studied. The results of the measurements (the magnitudes of the isomeric shifts δ and the magnitudes of quadrupole splitting Δ) are given in Table 1. Typical spectra of resonant absorption are shown in Fig. 1.

Table 1

Magnitudes of the isomeric shifts δ of the energy of the 23.8 keV γ-transition in the Sn^{119} nucleus and magnitudes of quadrupole splitting Δ. The isomeric shift was measured relative to the energy of the γ-transition in the compound SnO_2. Conversion to energy units (eV) can be made by multiplying the values in the table by 7.94. In this case δ and Δ will be expressed in 10^{-8} eV.

Compound	δ, mm/sec	Δ, mm/sec
Sn $(C_2H_5)_4$	1.33$±0.08|0||Sn(C{6}H{5})1.24$$±0.10|0||Sn(C{4}H{9})_{4}$	

Already in the study of inorganic tin compounds, a sharp dependence of the magnitude of the isomeric chemical shift on the valence state of the tin atom

in the molecule was established^(2), the magnitude of the shift (measured relative to the position of the absorption line in the compound SnO_2) increasing appreciably with an increase in the density of electron charge at the tin nucleus.

A number of interesting regularities was found in the study of organotin compounds^(1,3). One of the results of our previous

work (1) was the establishment, for compounds of the type SnX_4 (X is a halogen atom), of a linear dependence of the quantity δ on the electronegativity of the atom X. In the present work absorption spectra were measured for compounds of the type SnR_4, where R denotes the groups of atoms C_2H_5, C_6H_5, C_4H_9, C_3H_7, and CH_2CH_2CN (see Table 1). The absorption spectrum for each of these compounds consists of a single (unsplit) line (see Fig. 1a), which is characteristic of a symmetric (tetrahedral) electronic environment of the tin atom in the molecule. It is significant that the magnitudes of the measured shifts for the compounds under consideration proved, within the limits of experimental error, to be identical (about 1.3 mm/sec); this permits the conclusion that such a shift characterizes the electron density at the tin nucleus created by the four Sn–C bonds, whereas the other atoms (C, H, and N), not directly bonded to the tin atom, do not exert any appreciable influence on this electron density. It is interesting to note that the obtained value of the shift for SnR_4 compounds agrees well with the dependence of δ on the electronegativity of atom X in SnX_4 compounds ([1]), if for SnR_4 compounds one uses the value of the electronegativity of the carbon atom given in the literature.

The decisive influence of the nearest neighbors of the tin atom on the form of the Mössbauer spectrum (see also ([3])) can be shown using as an example compounds of the type $(C_4H_9)_2Sn(C\ H_2\ _1COO)_2$ (see Table 1).

For all these compounds very close values are observed for the magnitudes of the measured shifts ($\delta = 1.45 \pm 0.10$ mm/sec) and for the quadrupole splitting ($\Delta = 3.45 \pm 0.20$ mm/sec); thus, a change in the number of C and H atoms does not substantially affect the distribution of electronic charge in the Sn–O bond. However, it seemed very probable that, unlike C and H atoms, atoms which, although not directly bonded to the tin atom, possess high electronegativity would nevertheless exert a noticeable influence on the form of the resonance absorption spectrum.

Fig. 1. Resonance absorption spectra for organotin compounds: **a** – $Sn(CH_2CH_2CN)_4$; –$(C_4H_9)_3SnBr$; –$FSn(CH_2CH_2 \cdot CN)_3$; –$(C_2H_5)_3SnOH$. Along the abscissa axis–the velocity of the absorber in mm/sec; along the ordinate axis–the counting rate in arbitrary units. δ –isomeric chemical shift; Δ –quadrupole splitting.

This assumption was tested by us by comparing the spectrum for the compound $(C_4H_9)_2Sn(CH_3COO)_2$ with the spectra for compounds differing from it by the replacement of one or three hydrogen atoms by chlorine atoms (see Table 1). The presence of a chlorine atom (or atoms) not directly bonded to the tin atom leads to a redistribution of electronic charge in the molecule (the so-called induction

Fig. 1. Resonance absorption spectra for organotin compounds: a – $Sn(CH_2CH_2CN)_4$; –$(C_4H_9)_3SnBr$; –$FSn(CH_2CH_2CN)_3$; –$(C_2H_5)_3SnOH$. Along the abscissa axis–the velocity of the absorber in mm/sec; along the ordinate axis–the counting rate in arbitrary units. δ –isomeric chemical shift; Δ –quadrupole splitting.

Figure 1: Fig. 1. Resonance absorption spectra for organotin compounds: a –$Sn(CH_2CH_2CN)_4$; –$(C_4H_9)_3SnBr$; –$FSn(CH_2CH_2CN)_3$; –$(C_2H_5)_3SnOH$. Along the abscissa axis–the velocity of the absorber in mm/sec; along the ordinate axis–the counting rate in arbitrary units. δ –isomeric chemical shift; Δ –quadrupole splitting.

effect). The increase in the quadrupole interaction constant indicates an increase in the deformation of the distribution of electron density (relative to the tin nucleus). The magnitudes of the chemical isomeric shifts and the quadrupole splitting obtained for a number of other organotin compounds investigated are given in Table 1.

If the doublet splitting of the absorption spectrum is due only to the nuclear quadrupole interaction, the two components of the doublet should have identical widths and heights. However, for a number of organo-

In organotin compounds a doublet splitting is observed, the components of which differ noticeably in the maximum magnitude of absorption at the maximum and in the width of the absorption line (see Fig. 1 and). Such an asymmetry of the absorption spectrum (relative to its "center of gravity") was first discovered ([3]) for the compound $(C_6H_5)_2SnCl_2$, and then ([1,4]) also for other organotin compounds (as well as for some iron compounds ([5])). In all cases observed by us, with such an asymmetry the line of smaller height has a greater width, so that the line areas are equal within the accuracy of the measurements (equality of line areas must necessarily occur in the case of quadrupole interaction if polycrystalline absorbers are used). To explain such an asymmetry of the spectrum, it may be assumed that, in addition to the nuclear quadrupole interaction, there exists in the molecule another interaction, sensitive to the value of the magnetic quantum number of the nuclear sublevel. Such an interaction may be a magnetic interaction, if it is assumed that an internal magnetic field exists in the molecule (the energy of interaction of this field with the Sn^{119} nucleus is, of course, substantially less than the energy of the quadrupole interaction). Thus, for example, if the angle between the axis of the electric-field gradient and the direction of the magnetic field is close to 90°, the component of the quadrupole splitting corresponding to the nuclear transition from the sublevel $m = \pm 3/2$ will be split much less than the component corresponding to the transition from the sublevel $m = \pm 1/2$, which causes asymmetry in the observed absorption spectrum. Depending on the sign of the electric-field gradient, either the sublevel $m = \pm 3/2$ or, conversely, the sublevel with $m = \pm 1/2$ will have the greater energy. This may explain the different character of the asymmetry ob-

served, for example, for the compounds $FSn(CH_2CH_2CN)_3$ and $(C_2H_5)_3SnOH$ (Fig. 1 ,).

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