Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR V. I. GOLDANSKII, G. M. GORODINSKII,

1962

SovietRxiv

Abstract

Full Text

Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR V. I. GOLDANSKII, G. M. GORODINSKII,
S. V. KARYAGIN, L. A. KORYTKO, L. M. KRIZHANSKII, E. F. MAKAROV,
I. P. SUZDALEV, V. V. KHRAPOV

STUDY OF THE MÖSSBAUER EFFECT IN TIN COMPOUNDS

The influence of the structure of electron shells on the energy of recoil-free nuclear gamma transitions opens up a number of interesting possibilities for chemistry. An illustration of such possibilities is provided by the investigations described here of the Mössbauer effect in compounds of tetravalent tin, in which the results of our work ([1,2]) have received further development and interpretation. The experiments were carried out on an apparatus of the Institute of Chemical Physics of the Academy of Sciences of the USSR, which ensures (by combining two motions—fast and slow) uniform motion of the absorber relative to the source at velocities from zero to ~ 15 mm/sec (in steps of 0.07 mm/sec) and from ~ 15 to ~ 30 mm/sec (in steps of 0.14 mm/sec). In this case, with the aid of an EPP-09 self-recorder, continuous monitoring of the velocity of motion is carried out. Several measurements were also performed on the apparatus of the V. G. Khlopin Radium Institute, on which the velocity of motion of the absorber varied with time according to a sinusoidal law. The sources of 23.8-keV γ-quanta (Sn^{119m}) were β-Sn and $\mathrm{SnO_2}$ (the chemical shift of which relative to β-Sn is -2.7 mm/sec). In the first series of experiments, the spectra of "symmetric" compounds of tetravalent tin ($\mathrm{SnCl_4, SnBr_4, SnJ_4, Sn(C_6H_5)_4}$, and $\mathrm{SnO_2}$) were investigated; in these compounds, four identical atoms are located next to tin (in the case of $\mathrm{SnO_2}$, each Sn atom is bonded to four O atoms, and each O atom to two Sn atoms). In all cases singlet Mössbauer spectra were observed. The values of the chemical shifts δ of the lines of different absorbers relative to β-Sn, expressed in mm/sec (1 mm/sec $= 7.9 \cdot 10^{-8}$ eV), are given in Fig. 1 as a function of the electronegativity of the atoms neighboring tin ([3]). It is evident that the energy of the gamma transition decreases linearly with increasing electronegativity X in $\mathrm{SnX_4}$, with strengthening of the ionic character of the Sn–X bonds of tetravalent tin. The magnitude of the chemical shift for the γ-transition in Sn^{119} nuclei is determined by the following general relation (for example, ([4])):

$$\delta = 1.6 \cdot 10^{-29} \left[|\psi_s(0)|^2_{\text{abs}} - |\psi_s(0)|^2_{\text{src}} \right] \frac{\Delta R}{R} \text{ eV}, \tag{1}$$

Fig. 1

Figure 1: Fig. 1

$|\psi_s(0)|^2$ is the density of S-electrons in the region of the Sn^{119} nucleus; $\Delta R = R_{\mathrm{v}} - R_{\mathrm{o}}$ is the difference between the radii of this nucleus in the excited (R_{v}) and ground (R_{o}) states.

For subsequent estimates of $|\psi_s(0)|^2$, we shall use data on the degree of ionicity of the Sn—Hal bonds, obtained by the method of nuclear quadrupole resonance (^{5}), as well as in studies of refraction and dielectric permittivity (^{6}). Comparing these data with the values of δ (see Fig. 1) and extrapolating to a completely ionic bond, we obtain that for such a bond $\delta_{\mathrm{ion}} = -(5.6 \pm 0.5)$ mm/sec $= -(4.4 \pm 0.4) \cdot 10^{-7}$ eV. On the other hand, the difference in the values of $|\psi_s(0)|^2$ for fully ionized Sn^{4+} (completely filled $n = 1, 2, 3$, and 4 *spd*-shells) and β-Sn (in which 5 sp^3-electrons are fully represented) can be calculated from the Fermi—Segrè formula (^{7}).

The difference $(|\psi_s(0)|^2_{\mathrm{abs}} - |\psi_{ns}(0)|^2_{\mathrm{src}})$ for a β-Sn source and an Sn^{4+} absorber is $1.5 \cdot 10^{26}$ cm^{-3} (4). Comparing this value with (1) and with the data of Fig. 1, we obtain

$$\frac{\Delta R}{R}(Sn^{119}) = +(1.9 \pm 0.2) \cdot 10^{-4}.$$

Using the results obtained here, one can subsequently determine directly $|\psi_{5s}(0)|^2_{\mathrm{abs}}$ from the quantities δ (eV)—the chemical shifts relative to β-Sn.

Fig. 1. 1—our data, 2—data of (4) (1 and 2—Mössbauer effect—δ); 3—data of (5); 4—data of (6) (3 and 4—other methods—bond ionicity); 5—position of the two lines for SnF_4 (4) (the point is plotted at the center of the doublet)

In the next series of our experiments the spectra of a number of organotin compounds Ph_3SnHal were studied, where $Ph = C_6H_5$ (phenyl), and Hal $= F, Cl, Br, J$. In all these cases the spectra consisted of two lines, one of which was situated to the right and the other to the left of the singlet line of both $SnPh_4$ and $Sn\mathrm{Hal}_4$. The center of the Ph_3SnHal spectrum (which in the case of quadrupole splitting may be regarded as a chemical shift) is displaced along the halogen series in the same direction as the singlet line of $Sn\mathrm{Hal}_4$, but much more weakly.

Of special interest among the above-listed organotin compounds (as also in those previously investigated by us (^{1,2})) is the strong doublet splitting of the Mössbauer spectra, observed in the series of "symmetric" compounds only for SnF_4 (4) (see Fig. 1). Without reproducing here the exact form of the spectra, we shall confine ourselves to a schematic graph (Fig. 2), in which the positions of each of the lines of the doublet spectra of Ph_3SnHal are shown and, for comparison, the positions of the lines of $SnPh_4$ and $Sn\mathrm{Hal}_4$. The difference in the lengths of the two lines in the compounds Ph_3SnHal illustrates the observed asymmetry of the doublet splitting (both the heights and the widths of the two peaks were different). This asymmetry cannot be explained by a random crystalline orientation of the samples along the direction of the γ-quanta (4), since it persisted also upon grinding or dissolving the compounds under study. As magnetic weighing and examination of our samples on an EPR apparatus showed, the observed asymmetry of the peaks could not be explained by the influence of ferromagnetic or paramagnetic impurities. Therefore, before interpreting the data obtained on the basis of ideas about quadrupole splitting, we shall dwell briefly on a possible explanation of the asymmetry of the two peaks in this case. When the axis of the quadrupole crystalline field of a single crystal is oriented at an angle ϑ to the direction of the γ-quanta, the ratio of the resonant-absorption cross sections with formation of the sublevels $\pm 3/2$ and $\pm 1/2$ of the excited nucleus is equal, as can be shown on the basis of (8), to:

$$\frac{\sigma_{13}(\vartheta)}{\sigma_{11}(\vartheta)} = \frac{\sigma(\pm 1/2 \to \pm 3/2)(\vartheta)}{\sigma(\pm 1/2 \to \pm 1/2)(\vartheta)} = \frac{2\sqrt{5}\,\overline{P}_0(\cos\vartheta) + \overline{P}_2(\cos\vartheta)}{2\sqrt{5}\,\overline{P}_0(\cos\vartheta) - \overline{P}_2(\cos\vartheta)}, \tag{2}$$

where $\overline{P}_L(\cos\vartheta)$ is the normalized Legendre polynomial, which upon averaging over angles (equivalent to the use of a polycrystalline sample) gives $\sigma_{13\,\mathrm{poly}}/\sigma_{11\,\mathrm{poly}} = 1$. However, for an anisotropic Mössbauer effect

(9) averaging over angles, necessary for going from single crystals with axial symmetry of the electric field to polycrystals, gives:

$$\frac{\sigma_{13\,\mathrm{full}}}{\sigma_{11\,\mathrm{full}}} = \frac{\displaystyle\int_{-1}^{+1} \left[2\sqrt{5}\,\overline{P}_0(\cos\vartheta) + \overline{P}_2(\cos\vartheta)\right] f(\cos\vartheta)\,d\cos\vartheta}{\displaystyle\int_{-1}^{+1} \left[2\sqrt{5}\,\overline{P}_0(\cos\vartheta) - \overline{P}_2(\cos\vartheta)\right] f(\cos\vartheta)\,d\cos\vartheta}, \tag{3}$$

where the factor determining the intensity of the Mössbauer line is $f(\cos\vartheta) = \sum a_k \overline{P}_k(\cos\vartheta)$; a_k are the expansion coefficients. As a result,

$$\frac{\sigma_{13\,\mathrm{full}}}{\sigma_{11\,\mathrm{full}}} = \frac{2\sqrt{5}\,a_0 + a_2}{2\sqrt{5}\,a_0 - a_2} \neq 1$$

(for $a_2 \neq 0$), and, depending on the ratio of a_0 and a_2 (with $-2\sqrt{5} < a_2/a_0 < 2\sqrt{5}$), either of the peaks of the doublet Mössbauer spectrum may be higher than the other.

Thus, experiments with polycrystals give the ratio a_2/a_0, which can be checked in experiments with single crystals—both from the magnitude of the absolute probability of the Mössbauer effect and from the ratio of the heights of the two peaks at different angles. Thus, it is most natural to assume that in SnF_4 (4), Ph_3SnHal, and other organotin compounds (1,2), quadrupole splitting of the Mössbauer lines is observed, the magnitude of which

$$\Delta = \frac{1}{2} eQ \frac{\partial^2 v}{\partial z^2}$$

(where Q is the quadrupole moment of the isomeric nucleus Sn^{119*}) is determined by the electric-field gradient $q = \partial^2 v/\partial z^2$ in the region of the Sn^{119} nucleus. Estimates of q for axially symmetric tin bonds with coordination number 4 and 6 can be made on the basis of the Townes method (10). For completely covalent bonds of tetravalent tin, both for complete sp^3-hybridization and for nonhybridized s- and three p-bonds, $q = 0$. The absence of a field gradient is also retained for completely covalent and, moreover, hybridized sp^3d^2-bonds. If, however, with complete sp^3-hybridization one of the bonds has a partially ionic character (fraction x), then $q = 6.9 \cdot 10^{18} x$ V/cm^2. Interpreting the data of Fig. 2 in this way and assuming that for Sn^{119*} $Q = 8 \cdot 10^{-26}$ cm^2 (4), we obtain that in the series $\mathrm{Ph_3SnHal}$, $x \simeq 0.55$ (J), 0.7 (Br, Cl), and 1 (F). However, the indicated interpretation is by no means the only possible one, as is clear from the presence of quadrupole splitting for $\mathrm{SnF_4}$ (4), as well as for compounds of the type $\mathrm{R_2SnHal_2}$ and $\mathrm{RSnHal_3}$ (2). Such splitting may be associated with d-orbitals, all the more so since $\mathrm{SnF_4}$ is assigned the structure of a coordination polymer in which each Sn atom is bonded to six fluorine atoms (11). For wholly hybridized sp^3d^2-bonds, the greatest value of q corresponds to the electron configuration

$$\boxed{\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\ |}$$

and in this case $q = 9 \cdot 10^{18}$ V/cm^2, and slightly exceeds the maximum possible value for a pure p_z-electron. The configuration

$$\boxed{\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\ |}$$

when one of the six sp^3d^2-bonds is completely ionic, corresponds to $q = 4.6 \cdot 10^{18}$ V/cm^2. For $Q = 8 \cdot 10^{-26}$ cm^2

Fig. 2.
Diagram labels visible in the figure: β-Sn; $\mathrm{SnO_2}$; +1, 0, −1, −2, −3 mm/sec; $\mathrm{SnPh_4}$; $\mathrm{JSnPh_3}$; $\mathrm{SnJ_4}$; $\mathrm{BrSnPh_3}$; $\mathrm{SnBr_4}$; $\mathrm{ClSnPh_3}$; $\mathrm{SnCl_4}$; $\mathrm{FSnPh_3}$; $\mathrm{SnF_4}$.

experiment gives, for Sn, $F_4 \doteq 3.3 \cdot 10^{18}$ V/cm^2, which may be explained as a consequence of the superposition of completely covalently bound states and two indicated configurations (predominating in $\mathrm{Ph_3SnHal}$, where $q = 3.8$ (J), 4.8 (Br, Cl), 6.9 (F) $\cdot 10^{18}$ V/cm^2). It would be very interesting to carry out direct determinations of the effective charges of the halogen and tin atoms in compounds of the type investigated, in order to choose between all the variants considered for interpreting the quadrupole splitting.

In conclusion we note that, upon irradiation on the linear accelerator of the Institute of Chemical Physics of an equimolecular mixture of $SnPh_4 + SnJ_4$ with electrons of energy 1.6 MeV (dose 200 Mrad), we observed a sharp change in the shape of the Mössbauer spectra, apparently associated with the superposition of spectra of different products of the disproportionation reactions—Ph_iSnJ_{4-i}. This result is encouraging from the point of view of applications of the Mössbauer effect not only to the study of chemical structure, but also to problems of chemical kinetics and radiation chemistry.

The authors are sincerely grateful to Corresponding Member of the Academy of Sciences of the USSR K. A. Kocheshkov and Yu. Kravtsov for providing samples of the compounds studied, to B. I. Rogozev for assistance with the measurements, and to S. I. Vetchinkin and M. E. Dyatkina for participating in the discussion of the results.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
21 VII 1962

REFERENCES

1. V. A. Bryukhanov, V. I. Gol' danskii, N. N. Delyagin, E. F. Makarov, V. S. Shpinel' , ZhETF, **42**, 637 (1962).
2. V. A. Bryukhanov, V. I. Gol' danskii, N. N. Delyagin, L. A. Korytkov, E. F. Makarov, I. P. Suzdalev, V. S. Shpinel' , ZhETF, **43**, 448 (1962).
3. L. Pauling, *The Nature of the Chemical Bond*, 1947; 3rd Amer. ed., 1960.
4. A. J. F. Boyle, D. S. P. Bunbury, C. Edwards, Proc. Phys. Soc., **79**, 416 (1962).
5. A. L. Schawlow, J. Chem. Phys., **22**, 1211 (1954).
6. M. M. Yakshin, V. M. Ezuchevskaya, V. A. Salmenkova, ZhKh, **6**, 2425 (1961).
7. E. Fermi, E. Segre, Zs. Phys., **82**, 729 (1933).
8. A. M. Baldin, V. I. Gol' danskii, I. L. Rozental' , *Kinematics of Nuclear Reactions*, Moscow, 1959.
9. Yu. M. Kagan, DAN, **140**, 794 (1961).
10. C. Townes, A. Schawlow, *Radiospectroscopy*, IL, 1959.

11. I. Khaiduk, Usp. Khimii, **30**, 1124 (1961).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.