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EFFECT OF γ RADIATION ON THE SHAPE OF MÖSSBAUER RESONANCE ABSORPTION SPECTRA IN TIN-ORGANIC COMPOUNDS

A. Yu. ALEKSANDROV, N. N. DELYAGIN, K. P. MITROFANOV, L. S. POLAK, and V. S. SHPINEL'

Nuclear Physics Institute, Moscow State University, and Petroleum Synthesis Institute, Academy of Sciences, U.S.S.R.

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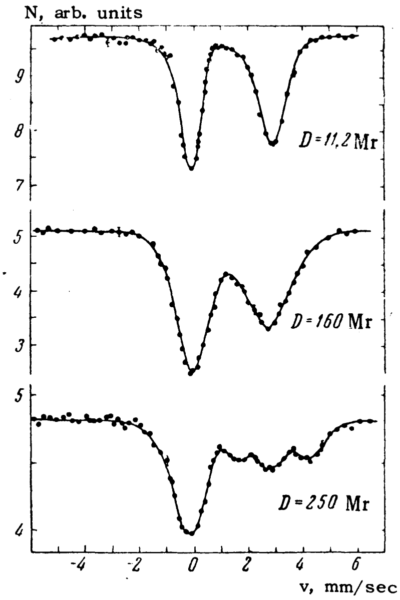
The effect of γ radiation on the shape of Mössbauer spectra from resonance absorption of 23.8-keV γ quanta in tin-organic compounds was studied. The change in the shape of the spectrum for the compound $(C_4H_9)_2SnSO_4$ corresponds to a breakup of the molecule with formation of $SnSO_4$ and possibly $(C_4H_9)_2SnSO_3$ (for irradiation in vacuum). Irradiation of this same compound in the presence of oxygen results in its oxidation to SnO_2 (or some other compound with the same electron configuration around the tin atom). After irradiation of the polymer $[(C_4H_9)_2Sn(OCOCCH_3CH_2)_2]_n$, a broadening of the doublet from quadrupole splitting was observed, which was accompanied by a reduction in the height of one of the components.

THE study of Mössbauer resonance absorption spectra of 23.8-keV γ quanta by Sn^{119} nuclei in tin-organic compounds has shown[1,2] that the shape of the absorption spectrum varies with the valence of the tin atom in the molecule, the structure of the molecule and the nature of the chemical bonds of the tin atom to its nearest neighbors. It was of interest to use this feature of the Mössbauer resonance absorption method for studying the physical and chemical changes which occur in solids and liquids under the action of external radiation (where the solids and liquids can be irradiated at any suitable temperature).

As the first objects for investigation we chose the compound $(C_4H_9)_2SnSO_4$ and the polymer $[(C_4H_9)_2Sn(OCOCCH_3CH_2)_2]_n$. The technique for measuring the resonance absorption spectra was the same as that used earlier.[2] The measurements were made with the source of Sn^{119} in the form of tin dioxide and the sample cooled to liquid nitrogen temperature. The samples were irradiated with Co^{60} γ rays at a temperature of 25—35°C. The radiation doses varied in the range from 4×10^{20} to 3×10^{22} eV/cm^3.

The spectrum of unirradiated $(C_4H_9)_2SnSO_4$ was studied by us previously;[2] it is a doublet (quadrupole splitting of the absorption line), both of whose lines have approximately the same width and intensity. The positions of the absorption maxima correspond to velocities of − 0.6 and +4.2 mm/sec. After irradiation of the sample with a dose of 6×10^{21} eV/cm^3 in vacuum, the shape of the spectrum hardly changed (weak, poorly resolved components appeared in the range 0.6—2.6 mm/sec). For a sample which was given a dose of 3×10^{22} eV/cm^3, a markedly different spectrum shape was observed. The spectrum consisted of an intense, broad line (width 2.1 mm/sec) with the absorption maximum at 4 mm/sec, and a line with its maximum at − 0.3 mm/sec (with an intensity one-third that of the first line). The shapes of both lines differed markedly from Lorentzian, which indicates that the lines are complex. This spectrum shape can be explained by assuming that, as a result of the irradiation, in a considerable fraction of the $(C_4H_9)_2SnSO_4$ molecules there is a rupture of the bonds of the tin atom to the C_4H_9 groups, resulting in formation of $SnSO_4$. In addition, in a relatively small number of cases it seems that there is a detachment of one of the oxygen atoms, giving $(C_4H_9)_2SnSO_3$, which explains the broadening of the line with its maximum of − 0.3 mm/sec. When $(C_4H_9)_2SnSO_4$ is irradiated in the presence of oxygen (dose 3×10^{22} eV/cm^3), no lines characteristic of the irradiated compound were observed in the spectrum; the spectrum consisted of one line at zero velocity, and the intensity of this line decreased very little on heating the sample up to room temperature. Such a spectrum can be interpreted as the result of oxidation by chemically active ozone, which is formed intensively under the action of ionizing γ radiation on the initial compound, which changes to SnO_2 or some other compound with similar electronic surroundings for the tin atom.

The results obtained with the polymer sample are shown in the figure (the abscissa is the absorber velocity, the ordinate is the counting rate). The upper part of the figure shows the spectrum of the polymer obtained by radiation polymerization with a dose of 11.2 Mr, which corresponds to complete polymerization of the initial monomer. The shape of the spectrum is typical for compounds of this type. The line with its maximum at − 0.15 mm/sec has a width at half maximum of $\Gamma = 0.9$ mm/sec, which corresponds to the unbroadened line of the absorption spectrum (for measurements with the source in the form of tin dioxide). The line with its maximum at 2.85 mm/sec has a noticeably lower intensity and a width of 1.2 mm/sec. As the dose is raised one observes a regular increase in line width, the line at 2.85 mm/sec broadening more rapidly than the one at − 0.15 mm/sec; correspondingly there is a relative reduction in the height of the line at 2.85 mm/sec. The middle part of the figure shows the absorption spectrum obtained for the polymer after a dose of 160 Mr. As in the upper part of the figure, the areas under the two lines are the same (within the accuracy of the measurements). When the dose was increased to 250 Mr, there was a splitting of the line at 2.85 mm/sec into several poorly resolved components (cf. the lower part of the figure). The line at − 0.15 mm/sec scarcely changed its shape, although its width increased to 1.5 mm/sec.



A noticeable asymmetry of the resonance absorption spectra (difference in heights and widths of the two components in the case of quadrupole splitting of the absorption spectrum) was observed earlier[1,2] for various tin-organic compounds. Such an asymmetry can be explained by assuming that there is a magnetic field in the molecule, whose interaction with the Sn^{119} atom is much weaker than the energy of quadrupole interaction. For certain angles between the electric field gradient and the direction of the magnetic field, one will observe a different broadening of the quadrupole splitting components (thus, at 90° the component corresponding to a transition from the $m = \pm 3/2$ sublevel of the excited state will be broadened much less than the component corresponding to a transition from the $m = \pm 1/2$ sublevel). On such an interpretation, our data would indicate an increase in the strength of the magnetic field with increasing radiation dose. However, the available experimental data do not permit any unique conclusion concerning the nature of the observed asymmetry of the absorption spectra. In particular, the absorption spectrum found for the polymer after a dose of 250 Mr, in which a splitting of one of the spectrum components was seen, does not fit the assumption of the existence of an internal magnetic field in the polymer. But at such a large dose of radiation, other factors apparently begin to affect the shape of the absorption spectrum (e.g., destruction, "knitting" of the polymer, etc). It is of interest to extend this type of investigation using different methods of physicochemical analysis, both from the point of view of studying resonance absorption spectra and from the point of view of use of the Mössbauer effect as a technique for studying chemical processes occurring under the influence of radiation and other factors which induce reactions.

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[1] Bryukhanov, Gol'danskiĭ, Delyagin, Korytko, Makarov, Suzdalev, and Shpinel', JETP **43**, 448 (1962), Soviet Phys. JETP **16**, 321 (1963).

[2] Aleksandrov, Delyagin, Mitrofanov, Polak, and Shpinel', JETP **43**, 1242 (1962), Soviet Phys. JETP **16**, 879 (1963).

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