

ASYMMETRY OF THE DOUBLET IN MÖSSBAUER SPECTRA OF SOME ORGANIC COMPOUNDS OF TIN

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Submitted to JETP editor July 3, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 48, 69-71 (January, 1965)

The asymmetry of the doublet in the resonance absorption spectrum of $(C_6H_5)_2SnCl_2$ is considered. The results show that the asymmetry is caused by the presence of certain tin-organic fractions in the compound. Results are presented from studies of this compound in an external magnetic field and from nmr studies.

IN one of the earlier papers from our laboratory on the Mössbauer spectra in organic compounds of tin^[1] it was noted that for $(C_6H_5)_2SnCl_2$ the observed doublet structure has an asymmetric shape. The components of the doublet have different heights and line widths. Later, asymmetric doublet spectra were observed in other tin-organic compounds.^[2] As already pointed out earlier,^[2] the observed shape of the absorption spectrum can occur when there is magnetic interaction in addition to quadrupole interaction.

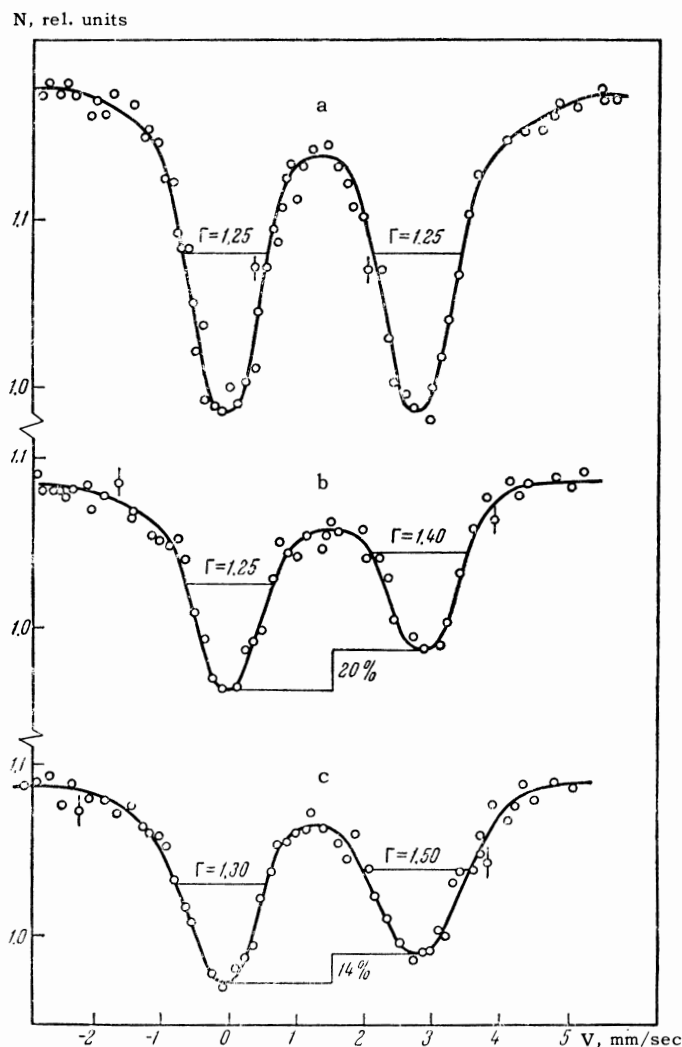
In the papers of Gol'danskiĭ's group^[3] it was asserted that the observed asymmetry is connected with the anisotropy of the Mössbauer effect in the corresponding single crystals, analogous to the case for single crystals of metallic white tin.^[4] The authors^[3] assume that the proposed explanation is supported by their experiments. But there was no basis for such a conclusion since for this one would have to measure the anisotropy of the effect along different crystal axes, and this was not done. Besides, the suggested anisotropy of the Mössbauer effect should cause a difference in intensity of the doublet components, which was actually not observed. Of all the compounds that showed the doublet structure (over 50 were done by us), only $(C_6H_5)_2SnCl_2$, $(C_6H_5)_3SnCl_2$, $(C_2H_5)_3SnOH$ and $FSn(CH_2CH_2CN)_3$ showed the asymmetry.

The present paper describes various experiments carried out to find the cause of the asymmetry of the doublet splitting in a polycrystalline sample of $(C_6H_5)_2SnCl_2$. The measurements were made on a constant velocity apparatus, using a source of Sn^{119} in the form of SnO_2 and Mg_2Sn . The γ quanta were detected by the usual scintillation method using a resonant counter. The spectra obtained when a magnetic field was applied to the absorber showed that the doublet structure is actually due to quadrupole interaction. At our request,

I. F. Shegolev of the Institute for Physical Problems of the USSR Academy of Sciences made nmr measurements on this compound, which showed that there are no regions with unpaired spins in this molecule, and that the asymmetry of the doublet does not have a magnetic origin. In our later investigations it was established that after careful purification and recrystallization of this sample, carried out in the Institute for Organic Compounds of the USSR Academy of Sciences, the resonance absorption spectrum became a symmetric doublet (curve a of the Figure; all the spectra, a, b, and c, were taken with a scintillation counter).

It is known that in the course of obtaining $(C_6H_5)_2SnCl_2$ various tin-organic fractions are formed (in small quantities, of course), such as $(C_6H_5)_3SnCl$, $(C_6H_5)SnCl_3$, $(C_6H_5)_4Sn$, $SnCl_4$. To check our assumption, after obtaining $(C_6H_5)_2SnCl_2$ by the usual method from $Sn(C_6H_5)_4$, a sample of thickness 80 mg/cm² was prepared without prior purification and recrystallization. The spectrum for this sample is shown in the Figure as curve b. We see that the spectrum is an asymmetric doublet with line widths 1.25 and 1.4 mm/sec. The percentage asymmetry of the line (relative to the more intense component) is ~20%, while the areas under the peaks are equal within experimental error. Such a spectrum could be obtained, for example, by superposing the spectrum of $(C_6H_5)_2SnCl_2$ on the spectrum of one of the compounds listed above. But a comparison of the spectra of all these compounds shows that superposing them does not give the observed asymmetry, though we cannot completely exclude an effect of superposing the spectrum of $(C_6H_5)_3SnCl$, because of the errors in the measurements.

Of interest is the fact that all the tin-organic compounds containing halogens, OH, and certain other groups, can be easily hydrated. Taking this



into consideration, we prepared an absorber made from pure $(C_6H_5)_2SnCl_2$ and kept for ~ 120 hr in a desiccator above water. During this time the sample weight actually increased by $\sim 10\%$ above its initial value. The sample thickness was unchanged, ~ 80 mg/cm². The resonance absorption spectrum of this sample is shown as curve c in the Figure. We see that the spectrum is an asymmetric doublet with widths 1.30 and 1.50 mm/sec, while the areas under the lines are also equal within the error of the measurements. The asymmetry of the lines is $\sim 14\%$. After recrystallization of the sample, the spectrum had the initial shape a in the Figure.

Thus we can conclude that the spectrum shown as curve c is formed by the superposition of two spectra: those of $(C_2H_4)_2SnCl_2$ and $(C_6H_5)_2SnCl_2 \cdot nH_2O$. We may therefore propose that an asymmetric doublet will be obtained if the components near zero velocity almost coincide while the other two are shifted somewhat relative to one another. One should then see some shift of the broadened line. A small shift (~ 0.10 mm/sec) was actually observed. One can similarly explain the asymmetry of the

doublet in the case of spectrum b.

We take this opportunity to express our sincere gratitude to I. F. Shegolev for the nmr measurements.

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', DAN SSSR 148, 126 (1962).

³ S. V. Karyagin, DAN SSSR 148, 1102 (1963); V. I. Gol'danskiĭ, Reports of the Working Conference on the Mössbauer Effect, Dubna, 1962, p. 133; Gol'danskiĭ, Karyagin, Gorodinskiĭ, Krizhanskiĭ, Khrapov, Korytko, Makarov and Suzdalev, DAN SSSR 147, 127 (1962); Gol'danskiĭ, Makarov and Khrapov, JETP 44, 752 (1963), Soviet Phys. JETP 17, 508 (1963).

⁴ Alekseevskiĭ, Pham Zuy Hien, Shapiro and Shpinel', JETP 43, 790 (1962), Soviet Phys. JETP 16, 559 (1963).

Translated by M. Hamermesh