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Mössbauer studies of trimethyl and triphenyl tin chloride adsorbed on grafoil

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Mössbauer studies of trimethyl and triphenyl tin chloride adsorbed on grafoil

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Trimethyl tin chloride $[(\text{CH}_3)_3\text{SnCl}]$ and triphenyl tin chloride $[(\text{C}_6\text{H}_5)_3\text{SnCl}]$ adsorbed on grafoil were studied by the Mössbauer resonance in ^{119}Sn . The temperature dependence of the Mössbauer fraction and the anisotropy ratio of the quadrupole transitions in $(\text{CH}_3)_3\text{SnCl}$ measured at two different angles supplied information on the structure of the substrate and on the anisotropy of the recoilless fraction. The relative orientation of $(\text{C}_6\text{H}_5)_3\text{SnCl}$ adsorbed on grafoil was found to be with the Sn-Cl axis perpendicular to the exposed basal planes of grafoil, contrary to $(\text{CH}_3)_3\text{SnCl}$, where the molecules have their symmetry axes parallel to the grafoil plane.

I. INTRODUCTION

The dynamics of physically adsorbed atoms and molecules has been the subject of considerable interest. It has been investigated by various experimental techniques, such as specific heat measurements, neutron scattering, EXAFS (extended x-ray absorption fine structure), NMR (nuclear magnetic resonance) and Mössbauer spectroscopy.¹⁻⁵ These techniques made possible the observation of two-dimensional phase transitions, surface arrangements and mobility. The Mössbauer effect has been useful in studying phase transitions, the orientation of adsorbed molecules relative to the substrate, and the adsorption forces.

In this work we present results on the study of the dynamics of $(\text{CH}_3)_3\text{SnCl}$ molecules adsorbed on grafoil and on the orientation of $(\text{C}_6\text{H}_5)_3\text{SnCl}$ molecules adsorbed on the same substrate.

II. EXPERIMENTAL

Grafoil (a special form of expanded graphite) has been used extensively for heat capacity studies of adsorbed atoms¹ and more recently as a substrate in neutron scattering, EXAFS, and other experiments. Neutron scattering studies⁶ provided a characterization of grafoil as consisting of microcrystals of graphite of size $\sim 200 \text{ \AA}$ with the basal plane exposed and distributed with a preferred orientation. The distribution of the microcrystals was found to be as follows: one half oriented along the surface of the macroscopic sheet with a Gaussian spread of full width at half-maximum FWHM = 30° and the other half isotropically distributed. Grafoil has an adsorption area of approximately $20 \text{ m}^2/\text{g}$. Isotherms of N_2 and Kr adsorbed on grafoil indicate a homogeneous substrate.¹

In a previous work⁷ Mössbauer studies on $(\text{CH}_3)_3\text{SnCl}$ molecules adsorbed on grafoil at several submonolayer coverages supplied information about the orientation of the adsorbed molecules relative to the substrate.

In this work we have employed samples with a coverage of approximately one monolayer of $(\text{CH}_3)_3\text{SnCl}$ and $(\text{C}_6\text{H}_5)_3\text{SnCl}$. The molecular area was evaluated from known bond lengths and atomic radii. For $(\text{CH}_3)_3\text{SnCl}$

a molecular area of 40 \AA^2 was assumed. This agrees quite well with the recently measured molecular area of $(\text{CH}_3)_4\text{Sn}$ of 45 \AA^2 . Similarly to $(\text{C}_6\text{H}_5)_3\text{SnCl}$, an area of about 50 \AA^2 was assigned. For $(\text{CH}_3)_3\text{SnCl}$ two absorber configurations have been prepared: one with the γ radiation transmitted perpendicular to the grafoil surface of the substrate and one with the γ rays parallel to the surface. For $(\text{C}_6\text{H}_5)_3\text{SnCl}$ the radiation was perpendicular to the substrate. The experiments with these absorbers were performed in a variable temperature cryostat in the temperature range from 4.2 to 200 K. A standard BaSnO_3 source, held at liquid helium temperature, was used.

III. THEORETICAL ASPECTS

A Mössbauer effect experiment on molecules adsorbed on an oriented substrate like grafoil involves several parameters that influence the temperature and angular dependence of the shape of the spectrum. These parameters will be briefly discussed.

1. *f* factor

When dealing with a molecule adsorbed on a surface it is reasonable to assume that the recoilless fraction is anisotropic, i. e., that the mean square displacements in the surface (x, y) and in the z direction (z perpendicular to the surface) are different. For a substrate like grafoil, one can assume $f_x = f_y$ (isotropic mean square displacement in the basal plane). Then the mean square displacement as probed by a gamma ray entering at an angle θ with the normal on the surface is:

$$\langle u^2 \rangle = \langle z^2 \rangle \cos^2 \theta + \langle x^2 \rangle \sin^2 \theta \quad (1)$$

Here x represents any direction in the xy plane and the recoilless fraction is then given by:

$$f(\theta) = \exp(-k^2 \langle u^2 \rangle) \quad (2)$$

2. Quadrupole interaction

If a quadrupole interaction exists in the adsorbed molecule at the site of the Mössbauer atom, the spectrum will be split into several lines. The line intensities will depend both on the relative orientation of the incom-

ing radiation and the electric field gradient and on the anisotropy of the mean square displacement.

It should be possible in principle to learn from an experiment on grafoil the degree of alignment of the substrate, the relative orientation between the molecule and the substrate and the degree of anisotropy of the mean square displacement. We will assume that all molecules have their symmetry axes parallel to the basal plane of the microcrystals, according to the previous work,⁷ with a negligible spread in orientation. This assumption appears to be justified by the experimental results.

There will be some polarization of the γ radiation in the parallel geometry; the effect of this on the ratio I_σ/I_τ , however, is estimated to be negligible since our absorbers are thin (effective thickness $t \approx 1$) and only a small fraction of these molecules contributes to this polarization.

3. Temperature dependence of intensities of the absorption lines

The temperature dependence of the relative intensities of the two lines of the quadrupole split spectrum depends on the difference of the mean square displacements $\langle x^2 \rangle - \langle z^2 \rangle$ and on the degree of orientation of the substrate.

The anisotropy of the mean square displacement and the degree of orientation of the substrate can be derived from measurements performed for several γ ray-substrate angles. To fit the experimental results a calculation was performed in the following way.

(i) The mean square displacement is expressed by Eq. (1), in which θ is the angle between the radiation and the normal to the microcrystal surface.

(ii) The angular dependence of the intensities of the quadrupole split transitions is given by:

$$I_\sigma = 3\left(\frac{2}{3} + \sin^2 \alpha\right) \quad \left(\frac{1}{2} - \frac{1}{2} \text{ transition}\right), \quad (3)$$

$$I_\tau = 3(1 + \cos^2 \alpha) \quad \left(\frac{3}{2} - \frac{1}{2} \text{ transition}\right), \quad (4)$$

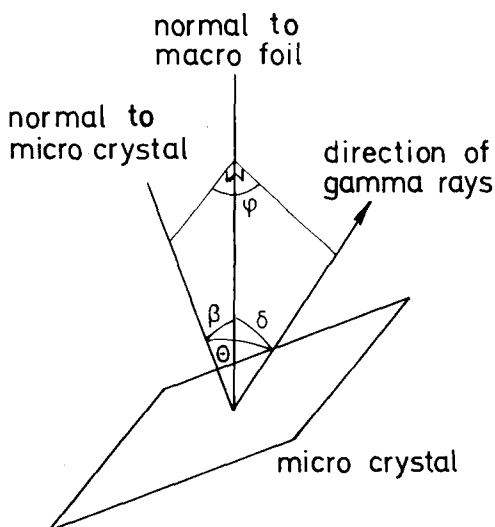


FIG. 1. Definition of angles used in expression (5).

TABLE I. Parameters derived from Mössbauer spectra of the 23.8 keV transition in ^{119}Sn with a $(\text{CH}_3)_3\text{SnCl}$ on grafoil absorber; grafoil surface perpendicular to γ direction. Source at 4.2 K.

T_A (K)	Area 1 (10^{-2} mm/s)	Area 2	$\frac{\text{Area 1}}{\text{Area 2}}$	Isomer shift (mm/s)	Splitting (mm/s)
4.2	6.9(2)	8.3(2)	1.22(5)	1.42(1)	3.43(1)
15	5.08(6)	6.76(7)	1.33(2)	1.42(1)	3.45(1)
30	3.66(19)	4.70(20)	1.28(9)	1.41(1)	3.45(3)
40	1.68(4)	2.36(5)	1.41(5)	1.42(1)	3.43(1)
50	1.66(12)	2.42(14)	1.46(14)	1.43(2)	3.46(4)
70	0.97(9)	1.43(10)	1.48(17)	1.44(2)	3.37(4)
81	0.69(4)	0.97(4)	1.41(10)	1.40(1)	3.41(2)
Source at ~ 80 K					
81	0.68(4)	0.88(4)	1.30(10)	1.43(1)	3.41(3)
90	0.47(3)	0.69(3)	1.46(11)	1.40(1)	3.31(3)
100	0.34(3)	0.52(3)	1.53(15)	1.39(2)	3.40(4)
112	0.24(2)	0.37(3)	1.53(18)	1.40(2)	3.39(4)
120	0.25(3)	0.36(3)	1.40(18)	1.43(3)	3.39(6)

where α is the angle between the electric field gradient and the γ ray. Further we assume:

(iii) The grafoil consists of a fraction p of microcrystals oriented along the macroscopic surface with a (Gaussian) spread Γ_s half-width at half-maximum (HWHM) and a fraction $(1-p)$ with random orientation.

(iv) The molecules have their symmetry axis parallel to the basal plane. The relative intensity of the σ transition for an angle δ between the direction of observation and the normal to the macroscopic foil (see Fig. 1) is then given by:

$$I_\sigma(\delta) = \int_0^{2\pi} d\phi \int_0^{\pi/2} d\beta \sin\beta G(\beta, \Gamma_s, p) \exp[-k^2(\langle z^2 \rangle - \langle x^2 \rangle)] \\ \times \cos^2\theta(\beta, \phi, \delta) \left[\frac{7}{3} + \cos^2\theta(\beta, \phi, \delta) \right] \exp(-k^2\langle x^2 \rangle), \quad (5)$$

where

$$G(\beta, \Gamma_s, p) = (1-p) + pk \exp[-(\beta/\Gamma_s)^2 \ln 2] \quad (6)$$

with k a normalization constant, and

$$\cos\theta(\beta, \phi, \delta) = \cos\beta \cos\delta + \sin\beta \cos\phi \sin\delta. \quad (7)$$

The corresponding expression for I_τ is obtained by replacing $(\frac{7}{3} + \cos^2\theta)$ in the above expression by $(3 - \cos^2\theta)$. These expressions are derived by considering first a set of microcrystals with their c axes parallel but with random orientation of the other axes and after this a distribution of such sets.

The integrals were computer calculated using the Monte Carlo method. In this program the (small) effect of the finite detector solid angle was also taken into account.

In Fig. 3 the results are shown for $\Gamma_s = 15^\circ$, $p = 0.3, 0.4, 0.5$, and 0.6 and $\langle x^2 \rangle - \langle z^2 \rangle$ from 0 to $20 \times 10^{-3} \text{ \AA}^2$ in each case. Figure 4 is similar except for $\Gamma_s = 20^\circ$.

IV. RESULTS AND DISCUSSION

1. $(\text{CH}_3)_3\text{SnCl}$

Some results of the measurements performed on $(\text{CH}_3)_3\text{SnCl}$ are presented in Tables I and II. The earlier

TABLE II. Parameters derived from Mössbauer spectra of the 23.8 keV transition in ^{119}Sn with a $(\text{CH}_3)_3\text{SnCl}$ on grafoil absorber; grafoil surface parallel to γ direction. Source at 4.2 K.

T_A (K)	Area 1 (10^{-2} mm/s)	Area 2 (10^{-2} mm/s)	Area 1 Area 2	Isomer shift (mm/s)	Splitting (mm/s)
4.2	8.51(4)	7.99(5)	0.939(7)	1.399(1)	3.408(3)
20	4.47(4)	4.20(5)	0.940(14)	1.399(3)	3.387(6)
30	2.47(2)	2.44(3)	0.988(15)	1.399(3)	3.382(6)
40	1.44(3)	1.49(3)	1.035(30)	1.392(5)	3.359(11)
50	1.005(15)	1.044(16)	1.039(22)	1.388(4)	3.356(8)
60	0.490(20)	0.530(22)	1.08(6)	1.379(11)	3.338(22)
81	0.194(13)	0.208(14)	1.07(10)	1.371(18)	3.336(36)

experiment on $(\text{CH}_3)_3\text{SnCl}$ had shown that in a geometry where the γ radiation is perpendicular to the substrate the intensity of the I_o transition is stronger than that of the I_r transition, indicating that the γ rays make a large average angle with the electric field gradient. In the case where the γ radiation is parallel to the substrate the intensities will then be reversed. This is indeed found in this work.

The temperature dependences of the intensity ratio I_o/I_r for the direction perpendicular and parallel to the foil are given in Fig. 2. A clear trend is observed: the ratio I_o/I_r increases with temperature in both orientations. To explain this one should distinguish between the aligned and the random fraction in the absorber. For the random part the difference of I_o/I_r from unity is a consequence of the Goldanski Karyagin effect. According to this effect lines labeled with different Δm (change in nuclear magnetic quantum number) in the Mössbauer spectrum of a powder or polycrystalline sample consisting of anisotropic material may have intensity ratios deviating from those for a spectrum of a sample of true isotropic material.

In the present case it can easily be understood that for the randomly oriented microcrystals the ratio I_o/I_r is larger than 1 and that it will increase with temperature. This can be seen from the fact that I_o , compared to I_r , is relatively more dependent on $\langle z^2 \rangle$ than on $\langle x^2 \rangle$, as follows from Eqs. (3) and (4) and the fact that the field gradient is in the basal plane.

If $\langle z^2 \rangle = \langle x^2 \rangle$, the ratio I_o/I_r equals 1, but since here

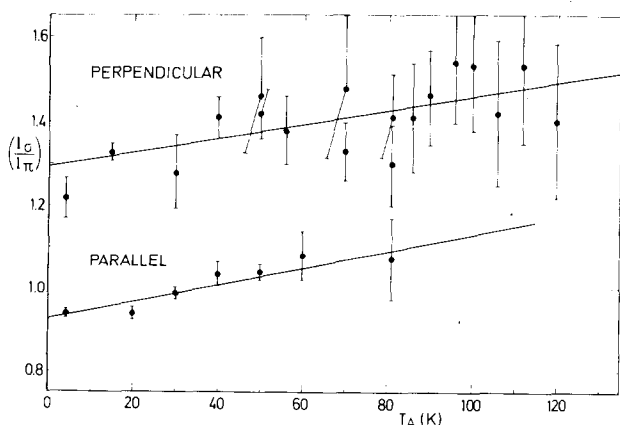


FIG. 2. Experimental values of I_o/I_r fitted with straight lines.

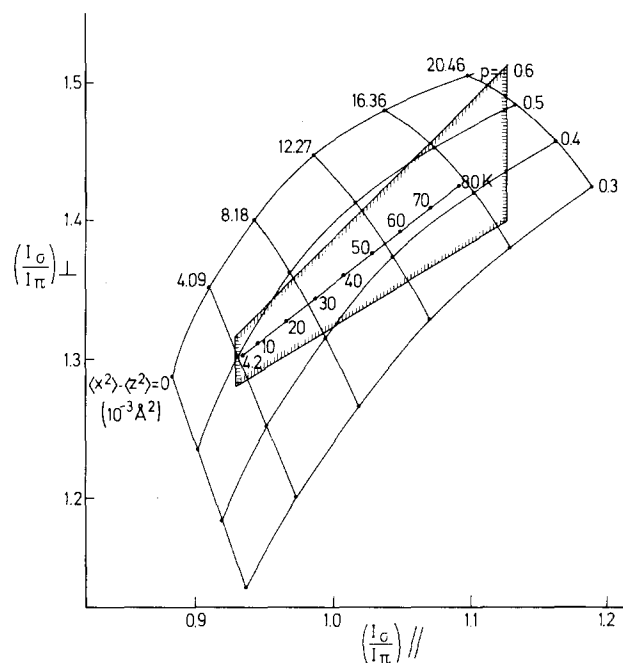


FIG. 3. Calculated intensity ratio I_o/I_r in the perpendicular geometry vs the ratio in parallel geometry for an angular spread of microcrystal planes $\Gamma_s = 15^\circ$ and different values of the oriented fraction of microcrystals p and $\langle x^2 \rangle - \langle z^2 \rangle$. The points labeled with temperatures represent experimental values.

$\langle z^2 \rangle$ is smaller than $\langle x^2 \rangle$ and increases more slowly with temperature, I_o will be larger than I_r and will decrease more slowly with temperature.

In the case of the aligned part the situation will be as follows: Let us assume for the moment that there is no angular spread for the aligned fraction and that all microcrystals are parallel to the macroscopic sheet. In the perpendicular case the amplitude of the Mössbauer effect is determined by $\langle z^2 \rangle$. From this it is clear that I_o/I_r does not depend on temperature. The same holds for the parallel case where the intensities depend only on $\langle x^2 \rangle$. The ratio I_o/I_r for perfectly oriented microcrystals would be $\frac{5}{3}$ for the perpendicular and $\frac{7}{3}$ for the parallel case, independent of temperature. For a spread in alignment, as has been found for the oriented fraction, these ratios become closer to one, but the temperature dependence remains small.

In our case the difference in the ratio I_o/I_r between the perpendicular and parallel geometry indicated clearly an oriented substrate while the temperature dependence of I_o/I_r shows that a spread or random part is present.

To facilitate the quantitative analysis straight lines have been fitted to the experimental data of Fig. 2. From these fits values of I_o/I_r for several temperatures have been taken. They yield the points which are labeled with temperatures in Figs. 3 and 4. The area between the shaded lines forms the region in which the experimental data scatter. In Fig. 3 these experimental data are represented together with the calculations for $\Gamma_s = 15^\circ$; in Fig. 4 together with calculations for $\Gamma_s = 20^\circ$. In these figures $(I_o/I_r)_\perp$ is plotted versus $(I_o/I_r)_\parallel$ while the parameters of the grid are the oriented

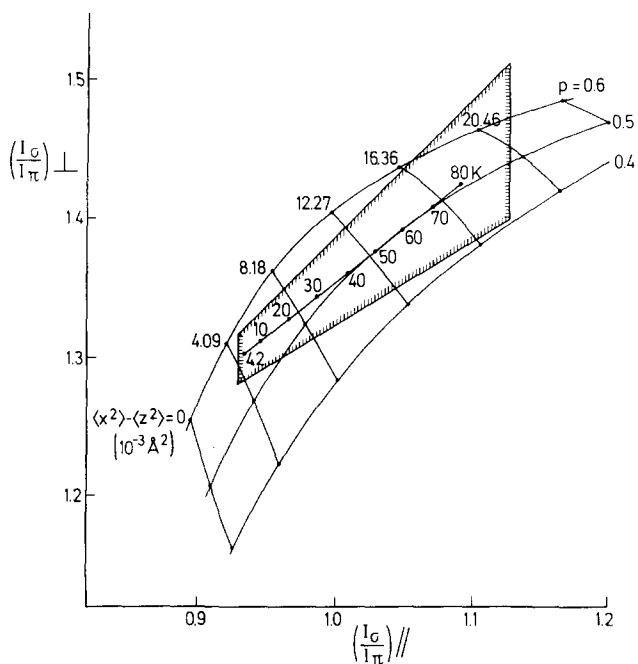


FIG. 4. Intensity ratio I_{\perp}/I_{\parallel} in the perpendicular geometry vs the ratio in parallel geometry for an angular spread of microcrystal planes $\Gamma_s = 20^\circ$ and different values of the oriented fraction of microcrystals p and $\langle x^2 \rangle - \langle z^2 \rangle$. The points labeled with temperatures represent experimental values.

fraction p of microcrystals and the difference in the mean square displacement $\langle x^2 \rangle - \langle z^2 \rangle$.

From our results we could not obtain a unique pair of Γ_s and p , because a decrease in alignment may be compensated to a high degree by an increase in p . Assuming a value of $2\Gamma_s = 30^\circ$ for the FWHM of the Gaussian distribution of the orientation, obtained from the neutron diffraction data of Taub *et al.*⁶ we find an oriented fraction of 0.44, in fair agreement with the neutron data. With their value for the random fraction we obtain $\Gamma_s < 15^\circ$. From this it appears that there is no extra deorientation due to spread in alignment of $(\text{CH}_3)_3\text{SnCl}$ with respect to the basal planes.

The high temperature values for $(I_{\perp}/I_{\parallel})_{\perp}$ are close to the limiting value of 1.67 for perfect alignment. This

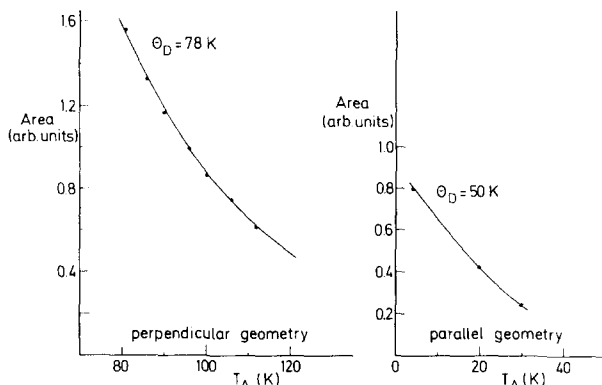


FIG. 5. Temperature dependence of the absorption area (a) perpendicular geometry; (b) parallel geometry.

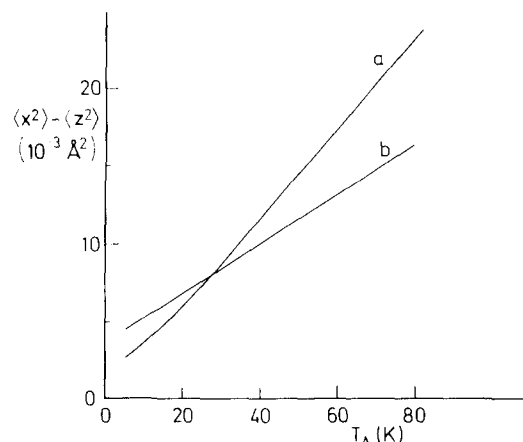


FIG. 6. Temperature dependence of $\langle x^2 \rangle - \langle z^2 \rangle$ (a) straight line through experimental points, (b) assuming a Debye model with Θ_D (perpendicular) 78 K and Θ_D (parallel) 50 K.

means that in the high temperature region the Debye Waller factor obtained from the temperature dependence of the total area is related directly to $\langle z^2 \rangle$. The temperature dependence of the area for the perpendicular case is presented in Fig. 5. The lattice vibration spectra in the perpendicular and in the parallel direction are probably very different. One should probably assume an Einstein model for the perpendicular case and a two-dimensional Debye model in the parallel. It is known that the Mössbauer effect is not very sensitive to the exact shape of the phonon spectrum and usually in the high temperature region the recoilless fraction has an exponential dependence on temperature. To facilitate some comparison between the parallel and perpendicular phonon distribution we shall use for both cases the three-dimensional Debye approximation in the high temperature limit. The Debye temperature which can be fitted to this temperature dependence is $\Theta_D = 78$ K. The low temperature region of the parallel case, on the other hand, contains a large contribution of $\langle x^2 \rangle$. From the temperature dependence of the area of the absorption lines for low temperature we obtain a Debye temperature of 50 K. Though the Debye model is certainly not very well suited for such a system one can compare the order of magnitude of $\langle x^2 \rangle - \langle z^2 \rangle$ for the Debye approximation and the experimental values obtained from Fig. 3 ($p \approx 0.44$ and $\Theta_s = 15^\circ$). This comparison is made in Fig. 6, where we used $\Theta_D = 50$ K for the calculation of $\langle x^2 \rangle$ and $\Theta_D = 78$ K for $\langle z^2 \rangle$. It is seen that a reasonable agreement exists between the results of the Debye fits and the experiments.

2. $(\text{C}_6\text{H}_5)_3\text{SnCl}$

The quadrupole splitting in bulk $(\text{C}_6\text{H}_5)_3\text{SnCl}$ was measured to be 2.46 mm/s.⁸ The large difference of the quadrupole splitting between $(\text{CH}_3)_3\text{SnCl}$ and $(\text{C}_6\text{H}_5)_3\text{SnCl}$ was explained by the chainlike structure of solid $(\text{CH}_3)_3\text{SnCl}$, which produces a five coordinated arrangement around the Sn atom and increases the quadrupole interaction while in $(\text{C}_6\text{H}_5)_3\text{SnCl}$ the Sn atom is four coordinated.⁹ When adsorbed on graphite, $(\text{CH}_3)_3\text{SnCl}$ preserves the same chainlike structure as in bulk.

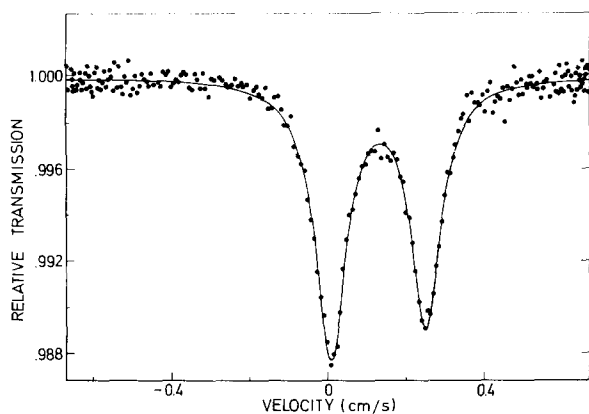


FIG. 7. Mössbauer spectrum of $(C_6H_5)_3SnCl$ at 4.2 K. γ rays perpendicular to the grafoil.

It is interesting to see what orientation single $(C_6H_5)_3SnCl$ molecules have relative to the substrate. Figure 7 presents a Mössbauer spectrum of $(C_6H_5)_3SnCl$ adsorbed on a grafoil absorber with the γ rays transmitted perpendicular to the substrate. The quadrupole splitting of the adsorbed molecules is 2.43 ± 0.01 mm/s and the isomer shift 1.29 ± 0.01 mm/s, very similar to the bulk values. The high intensity line, close to zero velocity, corresponds to the $\frac{3}{2} \rightarrow \frac{1}{2}$ transition (I_r).⁹ From Eqs. (2) and (3) we see that the γ direction must be parallel or at a small angle to the electric field gradient

axis in contrast with the $(CH_3)_3SnCl$ results. The ratio $I_g/I_r = 0.85$ at 4.2 K, decreases to 0.81 at 78 K, showing the same trend of pseudoalignment as for $(CH_3)_3SnCl$. $(C_6H_5)_3SnCl$ is built in a form of a pyramid with the C_6H_5 groups and the Sn atom on the base plane and the Cl atom at the apex. Our result indicates that the Cl-Sn axis is perpendicular to the exposed surface of the grafoil.

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