



Microwave Spectrum and Barrier to Internal Rotation of Methyl Stannane

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FIG. 1. First derivative ESR spectra of uv irradiated H₂O₂. (a) and (b) Polycrystalline material, sample tube axis making angles θ to the magnetic field direction. These two spectra show DPPH markers superimposed on the trace. (c) Glass material, spectrum independent of angle θ . All spectra recorded at 9.35 kMc/sec.

cross section. After irradiation the tube section was mounted in the spectrometer cavity so that ESR spectra could be recorded with the tube axis making various angles (θ) to the magnetic field. As angle θ was altered, marked changes in the ESR spectra were recorded and two typical spectra are shown in Figs. 1 (a) and (b). The g values for the derivative peaks 1 and 2 were independent of θ with $g_1 = 1.999$, $g_2 = 2.017$. The g value for peak 3 showed a large variation with θ approximately described by $g^2 = g_{||}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$, where $g_{11} = g_2$ and $g_{\perp} = 2.042$. This result shows that crystallization does not take place so that the crystallites are randomly orientated but that there is a preferred orientation for the crystallites with an appreciable number of crystallites lying at this orientation. The unit cell of H_2O_2 is tetragonal⁴ and the preferred orientation can be explained if the 001 plane of the crystallites makes one particular angle to the tube axis. Measurements to be discussed in the next paragraph determine this angle to be 90°. The process of crystallite alignment takes place on the crystallization boundary as it moves along the tube axis.

It is also possible to examine preferred orientation relative to the tube wall. The test rests on the short penetration of uv into H_2O_2 — H_2O so that, if the irradiation is perpendicular to the tube axis, a thin section of solution is selected lying on one side of the tube cross section. Spectra were recorded for the tube rotated about its axis, with $\theta=90^\circ$. The spectra were always similar to Fig. 1 (b) and the g values of the peaks remained constant. However, as the angle about the axis was altered, the height of peak 2 varied, the spectrum shape repeating every 90° of rotation. This result can be explained if the 001 crystallite plane lies perpendicular to the tube axis and one particular *mno* plane lies parallel to the tube wall. The irradiated H_2O_2 — H_2O sample then shows the fourfold symmetry of the tetragonal crystallites. Bolz *et al.*⁵ have reported x-ray diffraction studies on 90–95% w/w H_2O_2 — H_2O crystallized by warming the vapor deposited glass. They found⁶ that the 210 plane was orientated parallel to the depositing surface.

In the above discussion it has been assumed that the radicals take up the same positions in H₂O₂ lattice as the H₂O₂ molecules. Other measurements² have shown that the radical has uniaxial symmetry with $g_{11}=2.039$, $g_{\perp}=2.0055$. The spectra of Figs. 1 (a) and (b) can be explained if the axis of symmetry lies along the O—O bond direction of the H₂O₂ molecules. Consideration of the unit cell⁴ shows that for $\theta=0^{\circ}$ all the radicals then make the same angle (69°15′) to the magnetic field and the spectrum should be a single line as found. For $\theta=90^{\circ}$ the radicals can take up angles to the magnetic field between 20°45′ and 90°.

Measurements were also made on a 76% w/w solution which froze to form a glass.³ ESR spectra similar to Fig. 1 (c) were always obtained and the peak g values were independent of orientation with $g_1=2.000$, $g_2=2.015$, $g_3=2.037$. No preferred orientation to the tube axis was found but there was preferred orientation to the tube wall, as shown by a variation in the difference in height between peaks 2 and 3. The spectra were repeated every 180° and therefore it can be concluded that the hydrogen bond helices are preferentially aligned parallel to the tube wall.

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Microwave Spectrum and Barrier to Internal Rotation of Methyl Stannane*,†

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WE have re-examined the microwave spectrum of methyl stannane, CH₃SnH₃, first investigated by Lide,¹ in an effort to determine the barrier to internal

	118 _{8n} obs calc		116 _{8n} obs	117 _{Su} obs	119 _{8n} obs	120 _{8n} obs	122 _{8n} obs	124 _{8n} obs
OA OE	800.31		820.87	810.73	790.49	780.72	761.24	742.56
1E	775.97	775.90	796.43	786.22	765.89	756.27	736.90	
1A	778.92	778.84	799.38	789.11	768.87	759.20	740.01	721.1
2A	757.87	757.70	778.22	767.81	747.81	737.98		
2E	759.66	759.77						
3E	755.22	754.12				735.34		
3.4	749.70	749.49	769.94			729.81		

TABLE I. Torsional assignment of observed 0-1 frequencies (13 000 Mc should be added to each entry).

rotation. Greater spectrographic sensitivity and a pure sample have allowed us to observe a number of torsional satellites and two additional tin isotopes not observed in the first work.

The compound was prepared by first reducing SnCl₄ with LiAlH₄ in diglyme [bis-(2 methoxyethyl) ether] to give SnH₄, which in turn was reacted with sodium in liquid ammonia and methyl iodide, as previously described,² to yield methyl stannane. The use of diglyme instead of ethyl ether avoided the difficulty of separating the stannane from the ether solution.

Thirty-one lines, observed in the frequency region 13 720-13 820 Mc, were assigned to torsional levels of the J=0-1 transition for seven tin isotopes using the formula developed by Kivelson³ for the coupling of internal and over-all rotation of symmetric tops (see Table I). The observed frequency of the 0-1 transition for various torsional states is given by the following expression:

 $\frac{1}{2}\nu = B_v + F_v \langle m \mid 1 - \cos 3\theta \mid m \rangle + G_v \langle m \mid \Pi_z^2 \mid m \rangle,$

 B_v , F_v , and G_v are independent of the torsional quantum number (denoted by m), and of the rotational quantum numbers. Π_z is the internal angular momentum operator and θ the angle of internal rotation. The matrix elements $\langle m \mid \Pi_{s}^{2} \mid m \rangle$ and $\langle m \mid 1 - \cos 3\theta \mid m \rangle$ are readily obtainable from tables⁴ for different torsional states as a function of the reduced barrier parameter $s(=4V_3/9F)$, $F = (1/I_{\text{SnH}_2} + 1/I_{\text{CH}_2})h/8\pi^2$. The parameters which gave the best fit to the above formula were, for ¹¹⁸Sn, $B_v = 6906.35$ Mc, $G_v = -0.3521$ Mc, $F_v = -17.492$ Mc, and $s = 13.33 \pm 0.33$.

Calculated values for isotopes other than ¹¹⁸Sn are easily obtained from the usual substitution formulas, since to a very good approximation only B_{v} is affected by isotopic substitution of tin. Using as structural \angle HSnH = 109°28', \angle HCH = 108°25', parameters: d(Sn-H) = 1.700 A, d(C-H) = 1.083 A, and the above value for s, we obtained $V_3 = 650 \pm 30$ cal/mole $(227 \pm 10 \text{ cm}^{-1}).$

Quantitative intensity measurements could not be made because of limited sample stability and interference from Stark effects of neighboring lines. However, qualitative measurements agreed with expected statistical weights, $g_{iA}/g_{iE}=2^{5}$ for the satellites and with isotope ratios calculated from tables of natural abundances. Only one 2E line was observed due to the presence of stronger satellites.

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Preparation and Optical Transmission of Cadmium Fluoride Crystals

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THE preparation and optical transmission of CdF_2 **L** have been reported previously.^{1,2} Between 700 m μ and 8μ the transmittance was constant but then decreased due to restrahlen absorption. Below 700 m μ , the transmittance was found to decrease gradually in both cases. The absorption in the visible was sufficient to give the crystals a yellow color. Rubenstein² took the fundamental absorption edge to be at 265 m μ . Haendler¹ prepared CdF_2 crystals which had higher transmission in the visible and ultraviolet, but his measurements seemed to indicate the presence of an absorption band peaking at 220 m μ and no estimate of the absorption edge was given. Our measurements on CdF₂ crystals of greater purity are in substantial agreement with the previous data in the infrared but differ in the visible and ultraviolet.