

Millimeter Wave Spectra of SbH_3 and SbD_3 †

ALBERT W. JACHE, GILBERT S. BLEVINS, AND WALTER GORDY
Department of Physics, Duke University, Durham, North Carolina

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The $J=0 \rightarrow 1$ rotational transitions of normal and deuterated stibine have been measured in the shorter millimeter wave region. The B_0 values obtained are, in Mc/sec: 88 031.9 for $\text{Sb}^{121}\text{H}_3$, 88 015.5 for $\text{Sb}^{123}\text{H}_3$, 44 693.3 for $\text{Sb}^{121}\text{D}_3$, and 44 677.1 for $\text{Sb}^{123}\text{D}_3$. The observed Sb nuclear quadrupole couplings, eQq , differ for the normal and deuterated forms of stibine and are, in Mc/sec: for Sb^{121} , 458.7 ± 0.8 in SbH_3 , and 465.4 ± 0.8 in SbD_3 ; for Sb^{123} , 586.0 ± 0.8 in SbH_3 , and 592.8 ± 0.8 in SbD_3 . These couplings lead to the ratio $Q^{123}/Q^{121} = 1.275 \pm 0.003$. The Sb nuclear quadrupole moments are estimated to be: $Q^{121} = -0.8 \times 10^{-24}$ cm², $Q^{123} = -1.0 \times 10^{-24}$ cm². Significant Sb nuclear magnetic coupling was observed for the normal stibine. In SbH_3 the magnetic coupling constant is found to be 0.33 Mc/sec for Sb^{121} and 0.18 Mc/sec for Sb^{123} . The ratio of these, $C^{121}/C^{123} = 1.84$, is in good agreement with the known ratio of the nuclear g factors, $g^{121}/g^{123} = 1.8465$. Slightly different values of the interatomic distances were observed for the normal and deuterated forms. In SbH_3 the Sb-H distance is 1.707 Å and the H-Sb-H angle $91^\circ 18'$. In SbD_3 the Sb-D distance is 1.702 Å and the D-Sb-D angle $90^\circ 56'$.

INTRODUCTION

BOTH SbH_3 and SbD_3 have been previously investigated in the near infrared region,¹ and the asymmetric species SbH_2D has been studied in the microwave region.² Because of their small moments of inertia the symmetric-top forms SbH_3 and SbD_3 could not be investigated with microwave methods until the recent development of the shorter millimeter region.³ Precise microwave measurements have now been made on the symmetric-top forms. Both nuclear and molecular information has been obtained to supplement that known from the other studies. The results are reported here.

EXPERIMENTAL METHOD

The methods of generating and detecting the millimeter wave energy are those described by King and Gordy.³ The deuterated stibines were observed with the third harmonic of the driving klystron, whereas the normal stibines were observed with the seventh harmonic. The frequencies were measured at the fundamental of the klystron with the usual secondary frequency standard⁴ monitored by Station WWV. Because of the small dipole moment of stibine, 0.11 debye units, its rotational lines are weak, $\alpha_{\text{peak}} \approx 10^{-6}$ cm⁻¹. They could not be readily detected with the video spectrometer, but were easily measured with the automatic recording techniques⁴ employing a phase-lock-in detector with repeller modulation of the klystron at the lock-in frequency.

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¹ W. H. Haynie and H. H. Nielsen, *J. Chem. Phys.* **21**, 1839 (1953); R. C. Smith, *J. Chem. Phys.* **19**, 384 (1951).

² C. C. Loomis and M. W. P. Strandberg, *Phys. Rev.* **81**, 798 (1951).

³ W. C. King and W. Gordy, *Phys. Rev.* **90**, 319 (1953); **93**, 407 (1954).

⁴ Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953).

The SbH_3 was prepared by reacting a Zn-Sb alloy with phosphoric acid. The alloy was prepared by heating a mixture of Zn_3Sb until fusion occurred. Sb was in slight excess of that needed to give a mixture corresponding to Zn_3Sb . The SbD_3 was prepared in a similar fashion using a completely deuterated phosphoric acid prepared from P_2O_5 and D_2O . In both of these preparations a large amount of a gas (presumably H_2 or D_2) not condensable in liquid air was formed. All reactions were carried out in a previously evacuated system. Fluorinated stop-cock grease was employed with the SbD_3 to prevent exchange of D with H.

EXPERIMENTAL RESULTS

Figure 1 shows a recorder tracing of the $J=0 \rightarrow 1$ transition of SbH_3 . There are six component lines, three for each Sb isotope. The relative spacing and intensities are not faithfully reproduced by the recorder, primarily because of the nonuniform rate of sweep of the klystron.

Table I gives the observed frequencies and the calculated relative intensities. No effort was made to

TABLE I. Observed frequencies with calculated relative intensities.

Molecule	Transition $J=0 \rightarrow 1$ $F \rightarrow F$	Observed frequency in Mc/sec	Relative intensity (theoretical)
$\text{Sb}^{121}\text{H}_3$	$5/2 \rightarrow 5/2$	$176\ 142.92 \pm 0.5$	75
	$5/2 \rightarrow 7/2$	$176\ 047.74$	100
	$5/2 \rightarrow 3/2$	$176\ 004.64$	50
$\text{Sb}^{123}\text{H}_3$	$7/2 \rightarrow 7/2$	$176\ 120.60 \pm 0.5$	80
	$7/2 \rightarrow 9/2$	$176\ 008.39$	100
	$7/2 \rightarrow 5/2$	$175\ 973.49$	60
$\text{Sb}^{121}\text{D}_3$	$5/2 \rightarrow 5/2$	$89\ 462.46 \pm 0.3$	75
	$5/2 \rightarrow 7/2$	$89\ 365.05$	100
	$5/2 \rightarrow 3/2$	$89\ 322.65$	50
$\text{Sb}^{123}\text{D}_3$	$7/2 \rightarrow 7/2$	$89\ 440.38 \pm 0.3$	80
	$7/2 \rightarrow 9/2$	$89\ 326.39$	100
	$7/2 \rightarrow 5/2$	$89\ 291.93$	60

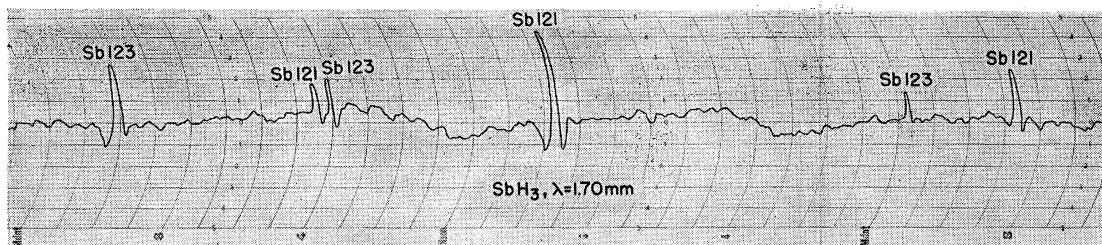


FIG. 1. Recorder tracing of the $J=0 \rightarrow 1$ transitions of $\text{Sb}^{121}\text{H}_3$ and $\text{Sb}^{123}\text{H}_3$ in the region of 176 kMc/sec.

measure the line intensities to an accuracy beyond that needed for identification of the different components.

The frequency of the $J=0 \rightarrow 1$ transition of a symmetric-top molecule in the ground vibrational state, if nuclear interaction is neglected, is

$$\nu_0 = 2B_0 - 4D_J, \quad (1)$$

where $B_0 = h/8\pi^2 I_b$ and I_b is the moment of inertia about any axis perpendicular to the symmetry axis, and D_J is a small stretching constant. Since only one transition was observed in the present work, D_J could not be obtained. From a comparison with arsine (see the following paper) it is estimated to be of the order of 1.5 Mc/sec for SbH_3 and 0.4 Mc/sec for SbD_3 . It, therefore, can be neglected entirely in the structural determinations.

Regardless of the nuclear spin values, the hyperfine structure of a $J=0 \rightarrow 1$ transition consists of only three lines for a single coupling nucleus. The relative level spacing in terms of the nuclear quadrupole coupling constant, eQq , as well as the relative intensities are readily obtained from the numerical tables in the appendix of reference 4.

Because of the large values of B as compared with eQq , the second order terms in the quadrupole coupling are smaller than the experimental error. Nevertheless, it was found that the observed line spacing did not fit, within the experimental error, the spacing calculated with first order quadrupole coupling theory. The nuclear magnetic interaction term,

$$E = \frac{1}{2}A[F(F+1) - J(J+1) - I(I+1)], \quad (2)$$

superimposed upon the quadrupole coupling did account completely for the results. See Table II. The extremely good agreement in the last column is partly fortuitous because there are in each case two adjustable parameters to fit only three observed frequencies.

The magnetic coupling constant A for $\text{Sb}^{121}\text{H}_3$ is large. The fact that it is appreciably larger than that for $\text{Sb}^{121}\text{D}_3$ suggests that the magnetic field which gives rise to the interaction is generated by the molecular rotation. The magnetic coupling constants of $\text{Sb}^{121}\text{H}_3$ and $\text{Sb}^{123}\text{H}_3$ have the ratio 1.84, in good agreement with ratios of the nuclear g factors, $g(\text{Sb}^{121})/g(\text{Sb}^{123}) = 1.8465$. The ratios for the corresponding deuterides do not agree so well with the g -factor ratios because the smaller A 's

for the deuterides could not be measured with as good accuracy.

The Sb nuclear quadrupole couplings, eQq , and magnetic coupling constants for the different isotopic forms are given in Table III. The B_0 values and moments of inertia, I_B , obtained from the ν_0 values ($J=0 \rightarrow 1$ frequencies corrected for nuclear perturbations) are listed in Table IV.

MOLECULAR STRUCTURES

Since only one principal moment of inertia per isotopic species is obtained and since there are two independent molecular parameters, we must employ data from two different isotopic species for calculation of the molecular structure. In so doing, we make the assumption that the effective molecular dimensions are the same for both species. Because the zero-point vibrational energies are only slightly altered by exchange of the two heavy antimony isotopes, the assumption of equivalent dimensions in $\text{Sb}^{121}\text{H}_3$ and $\text{Sb}^{123}\text{H}_3$ or in $\text{Sb}^{121}\text{D}_3$ and $\text{Sb}^{123}\text{D}_3$ is justified. The error in the molecular dimensions caused by our inability to measure accurately the small differences, about 33 Mc/sec, of the $0 \rightarrow 1$ frequencies for the two Sb isotopes is believed to be the limiting factor in the accuracy and is of the order of 0.2 percent. In contrast, the differences in vibrational energies of the normal and deuterated forms of stibine are so great that significant differences in the

TABLE II. Values of nuclear quadrupole coupling of Sb from the three different hyperfine spacings.

Molecules	With magnetic coupling neglected (Mc/sec)	With correction for magnetic coupling (Mc/sec)
$\text{Sb}^{121}\text{H}_3$	460.93	458.74
	453.24	458.72
	478.89	458.69
$\text{Sb}^{121}\text{D}_3$	466.04	465.42
	463.85	465.35
	471.13	465.57
$\text{Sb}^{123}\text{H}_3$	588.44	585.96
	581.85	585.99
	610.75	585.99
$\text{Sb}^{123}\text{D}_3$	593.79	592.77
	591.10	592.80
	602.99	592.78

TABLE III. Observed nuclear couplings.

Nucleus	Electric coupling eQq in Mc/sec	Magnetic coupling A in Mc/sec
Sb ¹²¹ in SbH ₃	458.7±0.8	0.33
Sb ¹²¹ in SbD ₃	465.4±0.8	~0.9
Sb ¹²³ in SbH ₃	586.0±0.8	0.18
Sb ¹²³ in SbD ₃	592.8±0.8	~0.07

effective molecular dimensions of SbH₃ and SbD₃ exist. For this reason we do not combine the normal and deuterated species in the solutions although the wide separations of their rotational frequencies allow a highly accurate evaluation of the differences in their moments of inertia.

Table V gives the molecular dimensions of SbH₃ and SbD₃ as obtained from the two Sb isotopic species of each. Note that in agreement with its smaller zero point vibrational energy, the bond length and bond angle in SbD₃ are smaller than those of SbH₃. A comparably smaller size is found for the deuterated forms of arsine (see next paper) and of phosphine.⁵

In the work of Loomis and Strandberg² on SbH₃D it was necessary to assume the equivalence of the Sb-H

TABLE IV. Rotational constants.

Molecule	$\nu_0(J=0 \rightarrow 1)$ in Mc/sec ^a	B_0 in Mc/sec ^b	I_B in 10 ⁻⁴⁰ g cm ²
Sb ¹²¹ H ₃	176 069.85	88 031.92	9.529 ₆₂
Sb ¹²³ H ₃	176 037.07	88 015.54	9.531 ₄₀
Sb ¹²¹ D ₃	89 388.08	44 693.29	18.77 ₀₄
Sb ¹²³ D ₃	89 355.77	44 677.13	18.77 ₇₂

^a Rotational frequency corrected for nuclear perturbations.

^b Obtained from ν_0 with $D_J=1.5$ Mc/sec for SbH₃ and 0.4 Mc/sec for SbD₃, both estimated from the known stretching constants of arsine.

and Sb-D lengths and H-Sb-H and H-Sb-D angles to obtain a structural evaluation. For this reason their values of the bond angle (91.5°) and bond length (1.712 Å) are not directly comparable with our results. It would seem that the mean values for the hybrid species should lie between the values for SbH₃ and SbD₃ whereas the Loomis-Strandberg values are larger than those we find for SbH₃. The discrepancy is not great, however, and is probably well within the range of errors in the two experiments.

The most surprising feature of the structure is the fact that the bond angle is so nearly a right angle, considering the large nuclear quadrupole coupling which exists. As in AsH₃ (see following paper), the almost normal bond angle implies bonding to the heavier atom

TABLE V. Molecular structures.

Molecule	Bond length	Bond angle
SbH ₃	1.7073±0.0025 Å	91°18'±20'
SbD ₃	1.7021±0.0025 Å	90°56'±20'

⁵ Burrus, Jache, and Gordy, Phys. Rev. **95**, 706 (1954).

through almost pure p orbitals, whereas the nuclear quadrupole coupling in each case indicates a more complex type of bonding with appreciably hybridized orbitals.

NUCLEAR QUADRUPOLE COUPLINGS AND MOMENTS OF Sb¹²¹ AND Sb¹²³

Considerable disagreement exists in the literature on the values of the nuclear quadrupole moments of the antimony isotopes. From hyperfine structure in optical spectra. Murakawa⁶ recently deduced the values $Q^{121} = -(0.52 \pm 0.1) \times 10^{-24}$ cm² and $Q^{123} = -(0.67 \pm 0.1) \times 10^{-24}$ cm², while concurrently Sprague and Tomboulian,⁷ also from optical hyperfine structure, obtained the values $Q^{121} = -1.3 \times 10^{-24}$ cm² and $Q^{123} = -1.7 \times 10^{-24}$ cm². The work of Murakawa is based upon a more completely resolved spectra obtained by concentrated isotopic samples. Both sets of values are outside the range of limits $Q^{121} = (-0.35$ to $-0.50) \times 10^{-24}$ cm² and $Q^{123} = (-0.45$ to $-0.62) \times 10^{-24}$ cm² estimated by Loomis and Strandberg² from their microwave measurements. Although the principle applied by Loomis and Strandberg seems sound to the approximation they expected, their limits are badly off, primarily because the nuclear quadrupole moment of I¹²⁷ and the I¹²⁷ coupling per unbalanced p electron which they employed in the estimation are now known to be incorrect.

Loomis and Strandberg estimated $q \equiv \partial^2 V / \partial z^2$ per unbalanced p electron in Sb in terms of the q for I by applying a correction for the difference in nuclear change of the two atoms. The q 's should be in the approximate ratios of the fourth powers of their effective nuclear charges,

$$q(\text{Sb})/q(\text{I}) \approx (Z_{\text{Sb}} - 4)^4 / (Z_{\text{I}} - 4)^4 = 0.85. \quad (3)$$

For I, q can now be accurately obtained from the atomic beam results⁸ and is

$$q_{m=0} = 13.8 \times 10^{-12} \frac{eQq \text{ (Mc/sec)}}{Q \text{ (cm}^2\text{)}} \text{ esu.} \quad (4)$$

$$\begin{aligned} q(\text{I})_{m=0} \text{ (per } p \text{ electron)} &= 13.8 \times 10^{-12} \frac{(0.2296)}{0.819 \times 10^{-24}} \\ &= 3.86 \times 10^{16} \text{ esu.} \end{aligned}$$

Hence,

$$q(\text{Sb})_{m=0} \text{ (per } p \text{ electron)} = 3.3 \times 10^{16} \text{ esu.}$$

We now express the nuclear quadrupole moments in terms of the unbalanced p electrons in SbH₃,

$$Q \text{ (cm}^2\text{)} = \frac{13.8 \times 10^{-12} eQq \text{ (Mc/sec)}}{U_{p,q,m=0} \text{ (per } p \text{ electron)}}, \quad (5)$$

⁶ K. Murakawa, Phys. Rev. **93**, 1233 (1954).

⁷ G. Sprague and D. H. Tomboulian, Phys. Rev. **92**, 105 (1953).

⁸ Jaccarino, King, Satten, and Stroke, Phys. Rev. **94**, 1798 (1954).

where U_p represents the fractional number of unbalanced p electrons in SbH₃.

From the measured couplings in SbH₃ and the estimated q one obtains:

$$Q^{121} = 0.192 \times 10^{-24} \text{ cm}^2 / (U_p \text{ in SbH}_3),$$

$$Q^{123} = 0.245 \times 10^{-24} \text{ cm}^2 / (U_p \text{ in SbH}_3),$$

where the sign of U_p is taken to be negative for an excess concentration of p electronic charge along the symmetry axis as in stibine. Now U_p for AsH₃ can be obtained from the known coupling and $Q(\text{As})$; it is -0.27 . Because of the smaller bond angle in SbH₃ over that in AsH₃ and because of the greater ionic character (of the form Sb^-H_3^+) expected for stibine, we are inclined to agree with Loomis and Strandberg that U_p SbH₃ will not be greater in magnitude than that in AsH₃. This assumption yields, with the new values:

$$Q^{121} > |-0.71 \times 10^{-24} \text{ cm}^2|,$$

$$Q^{123} > |-0.91 \times 10^{-24} \text{ cm}^2|.$$

These limits are above the upper error limits of the values given by Murakawa⁶ but are appreciably lower than the values given by Sprague and Tombouliau.⁷ If, as is assumed by Loomis and Strandberg, the unbalanced p electronic charge can at most decrease in proportion to the decrease in the angle toward 90°, then U_p for Sb must be at least one-half the magnitude of that for As. This assumption, with Eq. (5), leads to the upper limits:

$$Q^{121} > |-1.4 \times 10^{-24} \text{ cm}^2|,$$

$$Q^{123} > |-1.8 \times 10^{-24} \text{ cm}^2|.$$

Thus the values -1.3×10^{-24} and -1.7×10^{-24} cm² of Sprague and Tombouliau lie within the maximum and minimum values estimated here and near the upper limits. We are inclined to believe the actual values lie much nearer to the lower than to the upper limits here given, since it does not seem reasonable that a change of only one degree in the bond angle from AsH₃ to SbD₃ would correspond to the large change in bond hybridization required to change U_p by 0.14. A more reasonable assumption is that the approximately equal bond angles in AsH₃ and SbH₃ indicate essentially equivalent bonding orbitals of Sb and As. Certainly there is no close correlation of bond angle with hybridization for these elements where both d and s contributions to the bonding orbitals are possible.

We select the values of Q listed in Table VI as the most probable estimates from present information. These values are somewhat nearer to the lower than to the upper limits estimated above from microwave data. They are the approximate means of the two sets of values obtained from optical hyperfine structure. We have not applied directly the Sternheimer⁹ correction for the polarization of the core because this correction is indirectly applied through the I^{127} moment employed. The sign and order of magnitude of the Sb quadrupole moments are those expected from the correlation with the shell model.¹⁰ Although the absolute values of the Sb quadrupole moments are still only roughly evaluated, accurate values of the ratios Q^{121}/Q^{123} are known with good accuracy. The ratios obtained here are in good agreement with the ratio obtained with pure quadrupole resonance by Dehmelt and Kruger.¹¹

A measurable difference has been found in the coupling constants of normal and completely deuterated

TABLE VI. Nuclear moments.

Nucleus	Spin	Quadrupole moment Q in 10^{-24} cm ²	Ratio $Q(\text{Sb}^{123})/Q(\text{Sb}^{121})$
Sb ¹²¹	5/2	-0.8	1.275 ± 0.003
Sb ¹²³	7/2	-1.0	

stibine (see Table III). A similar difference was found for arsine (see the following paper). In each instance the coupling is larger for the deuterated compound. If one considers the difference in bond angles alone, the opposite variation would be predicted since presumably the s hybridization and hence the coupling would be expected to decrease with decreasing angle. Nevertheless, the s hybridization should be greater the shorter the bond length, and a comparison of bond lengths suggests a larger coupling for the deuterides, as is observed.

We are now attempting, in collaboration with the Oak Ridge National Laboratory, to use the same transitions of stibine observed here to measure the nuclear moments of radioactive Sb¹²⁵.

⁹ R. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951).

¹⁰ W. Gordy, Phys. Rev. **76**, 139 (1949).

¹¹ H. G. Dehmelt and H. Kruger, Z. Physik **130**, 385 (1951).

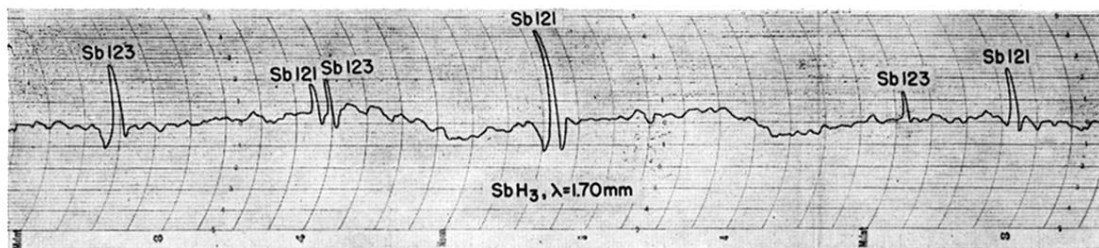


FIG. 1. Recorder tracing of the $J=0 \rightarrow 1$ transitions of $\text{Sb}^{121}\text{H}_3$ and $\text{Sb}^{123}\text{H}_3$ in the region of 176 kMc/sec.