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MICROWAVE SPECTRUM OF PHOSPHINE, ARSINE AND STIBINE

C. C. LOOMIS
M. W. P. STRANDBERG

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RESEARCH LABORATORY OF ELECTRONICS
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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C. C. Loomis
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Abstract

The microwave spectrum of the mono-deuterated phosphine (PH_2D), arsine (AsH_2D), and stibine (SbH_2D) has been measured. Although a supposedly pure sample of stibine was prepared, phosphine and arsine proved to be major impurities. They were separated from the sample; the microwave spectrometer was used to monitor the distillation process. The quadrupole fine structure associated with the absorption transitions for AsH_2D is used to illustrate the special assumptions which may be made with these molecules having an axis of charge symmetry. These assumptions allow one to rotate the coordinate system from the charge-symmetry axes to the inertial axes without thereby adding unknown cross derivatives to the descriptions of the dyadic ∇E_{zz} . Interpretation of the spectrum of SbH_2D is more complicated. It is not found possible to fit the theory to the observed lines without making use of the second-order perturbations due to a nearby level of different symmetry but of the same J . This perturbation involves the cross derivatives which had previously been assumed to be zero. With the assumption of cross derivatives approximately one percent of the diagonal terms, the theory fitted experiment within the experimental error.

In order to measure the electric dipole moment of arsine and stibine a slight extension is made to the theory of asymmetric tops in a uniform electric field.

The ground-state inversion splitting is determined to be less than 0.5 Mc/sec for all three molecules.

MICROWAVE SPECTRUM OF PHOSPHINE, ARSINE AND STIBINE

Introduction

The essential problem, the solution of which forms the topic of this report, is that of verifying the spins assigned to the two stable antimony isotopes and of determining the ratio of their quadrupole moments. Antimony forms one of a small group of stable elements (Hg, Xe, Rb, Ir, Sb) (Ref. 1) in which the addition of two neutrons changes the spin by one unit. All of the spin assignments to these nuclei have been made by means of measurement of hyperfine structure of optical spectra. None has as yet been verified by microwave spectroscopy, where the resolution available is sufficient to fix the spin of the nucleus without a doubt. Antimony is of interest because of the recent revival of the shell model for nuclei. On the basis of this model those nuclei which come just after or just before the closing of a shell should have easily predictable electric and mechanical moments. Since antimony falls in the periodic table just after the closing of a proton shell at 50, a precise determination of its properties is of interest to the theories of shell structure (2,3, 4, 5).

The nuclear information which one obtains from measurements using the techniques of microwave spectroscopy is contained in the fine structure associated with the absorption lines caused by the transition of a molecule from one rotational state to another. Before the nuclear information can be interpreted, the structure of the molecule must be determined. Consequently any investigation of nuclear properties carries with it, as a by-product, the determination of the structure of the molecule used. The only known simple molecule containing antimony and possessing the necessary properties of volatility and a permanent electric dipole moment is stibine. Before the advent of microwave spectroscopy with its discovery of the prevalence of s-p hybridization, Stevenson (3) predicted the structure of the molecules phosphine, arsine, and stibine, using vibrational data, and published covalent radii for the first two and extrapolated to the structure of stibine. He assumed that the stability of the s orbitals in the heavy atom would be such as to make the bonds almost pure p and therefore the bond angle (the angle formed by any two hydrogens and the heavy atom) would be 90 degrees. He allowed himself a fair amount of latitude, quoting ± 1 degrees and $\pm .02$ A. It was not felt, however, that the angle, in particular, could be predicted that accurately. The physical properties (7) of this chemical group of molecules, fortunately, have been precisely determined, and in particular the fact has been established that both stibine and arsine are quite unstable at room temperature, disintegrating into hydrogen gas and the metal. The investigation was begun therefore, with the following data:

Heavy atom	μ (debye units)	Bp	Mp	r (A)	θ	I	Q(10^{-24} cm ²)
P**	.55	-87.4°	-132.5°	1.42 ± 0.02	93° ± 1°	1/2	-
As	.15	-58.5°	-111.7°	1.53 ± 0.02	90° ± 1°	3/2	0.3
Sb ¹²¹	.5*	-17.0°	-88.5°	1.73 ± 0.02	90° ± 1°	5/2	-0.3 ± 0.2
Sb ¹²³	.5*	-17.0°	-88.5°	1.73 ± 0.02	90° ± 1°	7/2	-1.2 ± 0.2

* Estimates.

** For phosphine (PH₃), from infra-red spectroscopy,

$$I_2 = I_3 = 6.22 \times 10^{-40} \text{ gm-cm}^2 \text{ (Ref. 8).}$$

Perhaps the simplest transition on which to measure the fine structure due to nuclear quadrupole interaction is the $J = 0 \rightarrow 1$ in a symmetric top. In the case of stibine, however, this theoretical simplicity is not obtained without experimental complexity. The $J = 0 \rightarrow 1$ transition of SbD_3 , indeed, comes in the region around 85,000 Mc/sec or roughly three times the frequencies produced by the highest frequency reflex klystrons in general use at the end of the war. Techniques for employing the third harmonics of 11-mm klystrons, however, had been developed by Robert Kyhl while at this laboratory. It was first proposed to search for the $J = 0 \rightarrow 1$ transition of SbD_3 by using these techniques. However the available sensitivity ($\alpha \sim 10^{-6}$) was such that, even with a pure sample of SbD_3 in the absorption cell, the lines would not have been seen if the dipole moment was a factor of two or more smaller than the hoped-for value of 0.5 debye units.

With these facts in mind calculations were begun on the variation of transition frequency with structure of the isotopic species SbD_2H and SbH_2D . These molecules fall in the class known as asymmetric tops for which Cross, Hainer and King (9) have tabulated the energy levels as a function of J , the two symmetry indices K_{-1} and K_{+1} , and κ , the asymmetry parameter. If one assumes that the bond angle is the same in all four isotopic species, and that the bond distance is not changed by substituting a deuterium for a hydrogen, then great simplification occurs in the calculation of κ . If the coordinate system is set up as in Fig. 1, the molecular dipole moment is along the z' axis, and one is interested in c-type transitions for small ϕ' and a-type for large ϕ' . Since there is no component of the dipole moment along the b axis, b-type transitions have zero intensity.

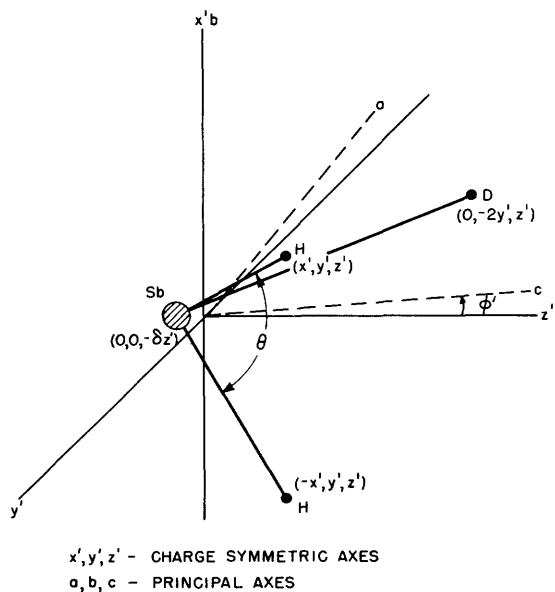


Fig. 1. Molecule-fixed coordinate systems.

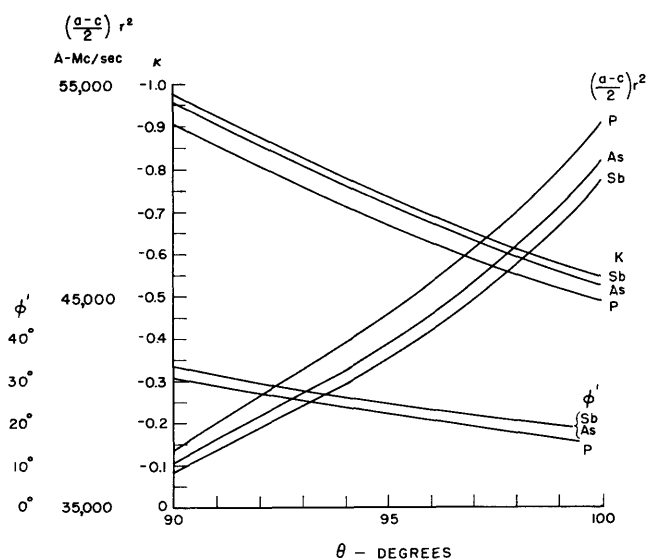


Fig. 2. Molecular parameters vs. bond angle, SbH_2D .

If the energy of the asymmetric top is expressed as

$$E_{J\tau} = \frac{a+c}{2} J(J+1) + \frac{a-c}{2} E_{\tau}^J(\kappa)$$

$$a = \frac{\hbar^2}{2I_a} \quad b = \frac{\hbar^2}{2I_b} \quad c = \frac{\hbar^2}{2I_c} \quad \tau = K_{-1} - K_{+1}$$

and $\Delta J = 0$ transitions are considered, then

$$h\nu = \frac{a-c}{2} \left[E_{\tau}^J(\kappa) - E_{\tau'}^J(\kappa) \right]$$

The quantities $(a-c)/2$ and κ can be obtained as a function of θ from a graph such as that in Fig. 2. Consequently the transition frequencies may also be plotted as a function of θ . With θ varying only from 90 to 100 degrees possible transitions in the species SbD_2H varied in frequencies from 0 to the order of 100,000 Mc, with κ going over almost the whole gamut of values. With SbH_2D , it was quite different, and the frequencies of the first few transitions for the lowest few J values have been plotted in Fig. 3 as a function of θ .

It can be seen that near 90 degrees SbH_2D is an almost symmetric top but one with a dipole moment perpendicular to the symmetry axis. It may also be noted, that while SbH_2D is an asymmetric top as determined by its mechanical moments, it is still charge-symmetric about the z' axis.

Since arsine and phosphine, from stability considerations, were likely impurities, the microwave spectra of AsH_2D and PH_2D were calculated and are shown in Figs. 4 and 5.

Experimental Data

PH_2D . The sample (see Appendix 1), though supposedly pure stibine, yielded phosphine for a first fraction as indicated by the spectrometer. The $3_{03} + 3_{13}$ line was found and identified by means of the Stark effect. The lack of any fine structure (± 2000 Mc/sec) indicated no quadrupole interaction and a single isotope. Since the transition frequency is such a rapid function of θ , the bond angle may be expressed in the following fashion

$$\theta = 93.5^\circ - 0.2^\circ \Delta r$$

Δr = deviation of bond length from 1.419A in 0.01A unit.

This determination of θ suffices to determine κ and $(a-c)/2$ so that the dipole moment may be calculated from the Stark effect as 0.55 debye unit. Furthermore, if this value for the dipole moment is used, the estimated line intensity checks the estimated value.

Following Stevenson's (6) original argument that s orbital stability increased with Z , the region of search for arsine and stibine transitions was thus materially reduced.

AsH_2D . By using the spectroscope to monitor the fractionation, the phosphine was removed from the sample. The next fraction then yielded absorptions due to arsine,

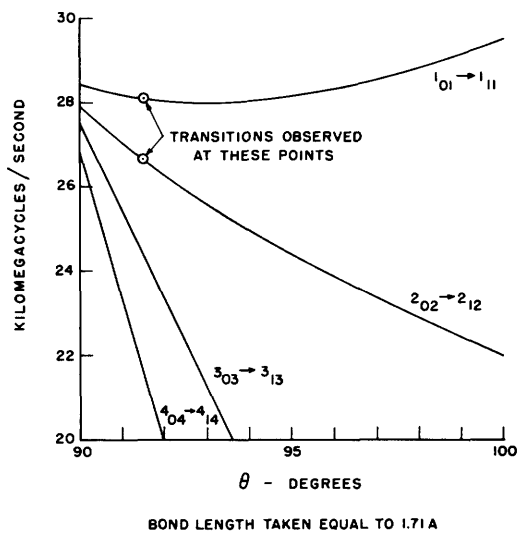


Fig. 3. Transition frequency vs. bond angle, SbH_2D .

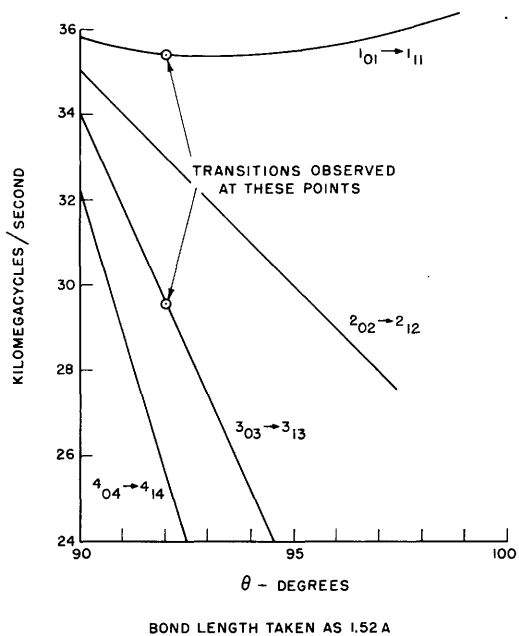


Fig. 4. Transition frequency vs. bond angle, AsH_2D .

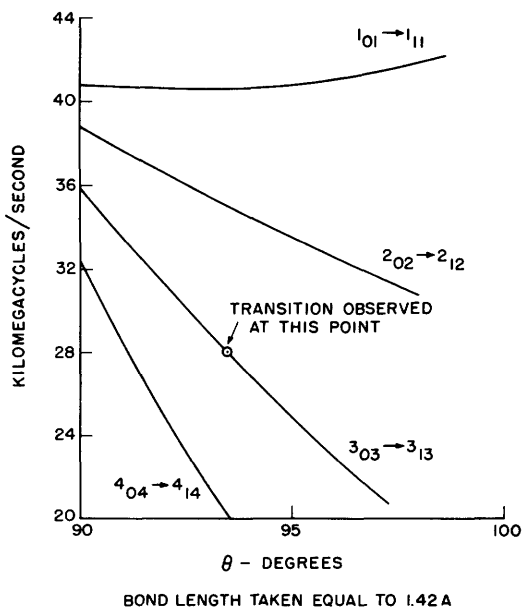


Fig. 5. Transition frequency vs. bond angle, PH_2D .

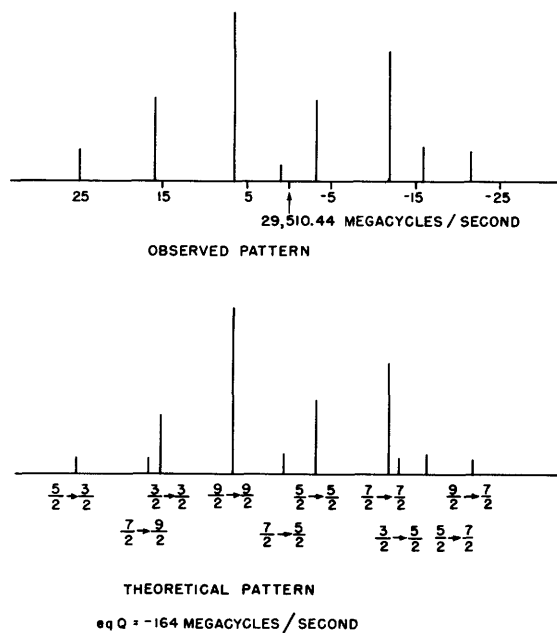


Fig. 6. $3_{03} \rightarrow 3_{13}$ transition of AsH_2D .

AsH₂D. The observed pattern for the $3_{03} \rightarrow 3_{13}$ arsine transition is shown in Fig. 6. This absorption shows nuclear electric quadrupole structure, but, of course, no isotope structure.

The theory of quadrupole coupling in asymmetric tops has been worked out by Knight and Feld (10) and also by Bragg (11). These authors show that while the magnitude of the splitting of each level is a function of the diagonal terms of the dyadic ∇E_{zz} expressed in the coordinates appropriate to the principal axes of the top, and F, the vector sum of I and J. For $J \leq 3$ the notation of Bragg's second article (12) is convenient since the reduced energy matrix may be diagonalized as an explicit function of κ . The theory will be illustrated for $J = 1$ where it is particularly simple. In the usual notation:

$$W_{\text{quad}} = eQ \langle V_{zz} \rangle T(F)$$

$$\langle V_{zz} \rangle = \frac{1}{J(J+1)} \left\{ V_{aa} \left[J(J+1) + E(\kappa) - (\kappa+1) \frac{\partial E(\kappa)}{\partial \kappa} \right] + 2V_{bb} \frac{\partial E(\kappa)}{\partial \kappa} \right. \\ \left. + V_{cc} \left[J(J+1) - E(\kappa) + (\kappa-1) \frac{\partial E(\kappa)}{\partial \kappa} \right] \right\}$$

$$E(\kappa)_{101} = \kappa - 1 \quad E(\kappa)_{111} = 0$$

$$T(F) = \frac{\frac{3}{4} C(C+1) - J(J+1)I(I+1)}{2(2J-1)(2J+3)I(2I-1)}$$

$$C = F(F+1) - J(J+1) - I(I+1) \quad Q = \langle 3z^2 - r^2 \rangle_{\text{nucleus}}$$

substituting:

$$\langle V_{zz} \rangle_{101} = (V_{bb} + V_{cc}) \quad \langle V_{zz} \rangle_{111} = (V_{aa} + V_{cc})$$

and using Laplace's equation,

$$\langle V_{zz} \rangle_{101} = -V_{aa} \quad \langle V_{zz} \rangle_{111} = -V_{bb}$$

In general the coefficients of the V_{aa} , V_{bb} , V_{cc} , are functions of κ and do not come out integers. The values which are appropriate for the $3_{03} \rightarrow 3_{13}$ transition in arsine are

$$\langle V_{zz} \rangle_{303} = \left[.003 V_{aa} + .916 V_{bb} + 1.087 V_{cc} \right]$$

$$\langle V_{zz} \rangle_{313} = \left[.167 V_{aa} + .466 V_{bb} + 1.427 V_{cc} \right]$$

Here $\kappa = -0.8625$; θ is 92.02° .

θ has been fixed here by the fact that the structure of arsine was precisely determined by using the $1_{01} \rightarrow 1_{11}$ transition frequency.

At this point one could plot a number of patterns using different scales until some of the lines were identified, at which point the scales for the individual levels could be determined by taking differences. It is also possible, by using the charge symmetry of the molecule, to make a very good first guess. If we express the dyadic ∇E_{zz} in the $x'y'z'$ coordinate system of the charge symmetric axes and then transform to the inertial axes, we get the following expressions:

$$\begin{aligned} V_{aa} &= V_{y'y'} \cos^2 \phi' + 2V_{y'z'} \sin \phi' \cos \phi' + V_{z'z'} \sin^2 \phi' \\ V_{bb} &= V_{x'x'} \\ V_{cc} &= V_{y'y'} \sin^2 \phi' - 2V_{y'z'} \sin \phi' \cos \phi' + V_{z'z'} \cos^2 \phi' \end{aligned}$$

In the charge symmetric coordinates the following relations among the elements of ∇E_{zz} obtain:

$$\begin{aligned} V_{x'y'} &= V_{y'z'} = V_{z'x'} = 0 \\ V_{x'x'} &= V_{y'y'} = -\frac{1}{2} V_{z'z'} \end{aligned}$$

Reducing the equations for V_{aa} , V_{bb} , and V_{cc} , to equations in terms of $V_{z'z'}$ and ϕ' gives

$$\begin{aligned} V_{aa} &= -\frac{1}{2}(1 - 3 \sin^2 \phi') V_{z'z'} \\ V_{bb} &= -\frac{1}{2} V_{z'z'} \\ V_{cc} &= -\frac{1}{2}(1 - 3 \cos^2 \phi') V_{z'z'} \end{aligned}$$

When these values of V_{aa} , V_{bb} , and V_{cc} , with ϕ' determined from the graph in Fig. 2, were substituted in expression for the splitting of the 3_{03} and the 3_{13} levels given above, the pattern which is shown in Fig. 6 resulted. When the center of gravity of the unresolved lines is used, the observed lines fit the theory to within the experimental error of ± 0.2 Mc/sec where $eQV_{z'z'} = -164$ Mc/sec.

As stated above, the $1_{01} \rightarrow 1_{11}$ transition was found and measured and the same transformation of the dyadic ∇E_{zz} applied here. If the angle, as fixed by the undeviated $3_{03} \rightarrow 3_{13}$ line and the undeviated $1_{01} \rightarrow 1_{11}$ line, is used as it was used to fix the pattern of the $3_{03} \rightarrow 3_{13}$ transition, there is a slight discrepancy between the measured and experimental values for the $1_{01} \rightarrow 1_{11}$ transition. This discrepancy can be eliminated by contracting slightly the amount by which the 1_{01} state is split. The source of this perturbation is not known, but at least two causes are possible. First it may be due to the effect of rotation-vibration interaction which has not been determined. The second is that the cross-derivatives in the charge symmetric coordinate system may not

be identically zero. At the angle of rotation $\phi' = 29.2^\circ$, which turns out to be the case in arsine, V_{aa} and consequently the splitting of the lower level are approaching 0, being approximately $1/8$ of $V_{z'z'}$. As a result a small cross-derivative has a proportionately larger effect than would be the case in the $3_{03} \rightarrow 3_{13}$ transition where V_{aa} plays a small part. From the results to be described in the case of stibine, this latter cause seems perhaps to be preferred. One can express this adjustment in either of two ways. ϕ' can be changed from 29.2° to 30.0° with perhaps a change in the effective value of θ from 92.02° to 91.6° . On the other hand if ϕ' is left unchanged at the value determined by the transition frequencies, $eQV_{y'z'}$ turns out to be 4.7 Mc/sec.

Finally, with the identification of the lines in the $3_{03} \rightarrow 3_{13}$ transition of arsine, the Stark splitting of one component in an applied electric field may be measured and the dipole moment computed. The $9/2 \rightarrow 9/2$ transition, which is also the most intense, was selected and the data

$$\begin{array}{cc} \Delta \nu & E \\ 2.38 \text{ Mc/sec} & 10.5 \text{ esu/cm} \end{array}$$

gives a dipole moment of $.22 \pm .02$ debye unit, as compared with the value of 0.18 measured by the Debye method (13). In order to reduce the data to a dipole moment the theory of Golden and Wilson (14) was used, with $J = 3$ and $m_j = 3$. The justification for this is given in Appendix 3.

SbH_2D . Final fractionation of the sample was performed by making use of the arsine $3_{03} \rightarrow 3_{13}$ absorption as a monitor. The residue then indicated stibine on a silver nitrate test, since the arsine had been removed as indicated by the spectroscope.

Two groups of absorption lines were found, one just above the K-band region and one at the frequency predicted for the $1_{01} \rightarrow 1_{11}$ transition. The lines at the position of the

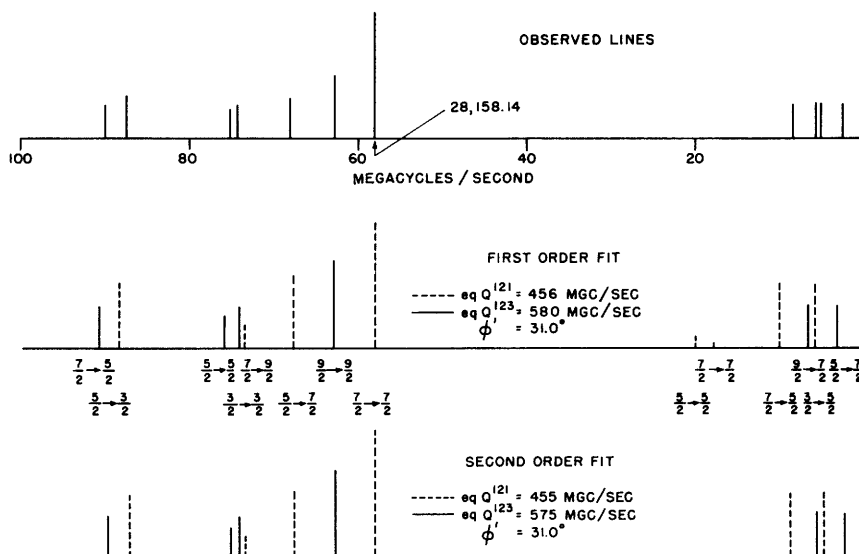


Fig. 7. $1_{01} \rightarrow 1_{11}$ transition of SbH_2D .

$1_{01} \rightarrow 1_{11}$ transition are shown in Fig. 7. Since the $1_{01} \rightarrow 1_{11}$ transition does not determine the bond angle, it is not possible from a measurement of the position of this transition alone to plot the predicted quadrupole pattern. Furthermore, as can be seen from a reference to the graphs in Fig. 3, the other transitions fall rather close together if the bond angle is close to 90 degrees. Consequently a careful search was undertaken toward higher frequencies in order to make sure that there were no other observable lines. None were found within a region of 1,500 Mc/sec above and none were found between 28,150 Mc/sec, the position of the next group of lines found below the $1_{01} \rightarrow 1_{11}$. Assuming that no lines have been missed, these two groups are the $J = 1$ and $J = 2$ transitions respectively, and they fix both the bond angle and the bond length.

It is important that the transitions found at 26,700 Mc/sec be assigned to the correct J value since they fix the bond angle and therefore the expected quadrupole pattern for the $J = 1$ level. Because of the complexity of the $J = 2$ quadrupole pattern (there will be 13 lines due to each isotope, completely interlaced, since the isotope shift is of the order of 5 percent of the quadrupole splitting), it would be tedious to measure the frequency of each line and to make a careful estimate of its relative intensity. This is particularly true since from a qualitative observation of the Stark splitting on each line it could be seen that these Stark components required a stronger field to split out than do those at $J = 1$. The use of a strong field tends to vitiate the gains in line intensity made thereby because in the spectrometer as presently designed the electric forces set up mechanical vibrations in the sample cell which modulate the r-f energy in just the same fashion as the absorption lines. Weaker Stark fields make useless the relative intensity estimates. Some other means had to be used to identify these lines.

One cannot assume that merely by searching over the region between these lines one would be certain to see the $J = 2$ transitions, (let us for the moment assume that the lines at 26,700 Mc/sec really are the $J = 3$) because it is possible for the particular transition to have zero Stark effect. The level shifts in a normal second-order Stark perturbation come from the mixing of the two states between which a transition is made in zero field, and, as in such mixing, there is a repulsion of each level by the other. The Stark frequency is thus higher than that of the line in zero field. If there is another energy level nearby to one of the levels involved in the zero-field transition, it also will be mixed in, in proportion to the dipole moment associated with a transition to that level, and will tend to push the affected level away from it. It could, therefore, just cancel or if close enough, completely override the normal Stark effect. If there is no Stark effect, the spectrometer which depends on the Stark effect to modulate the intensity of the main line would detect no absorption. That such a situation could obtain in stibine can be seen from the fact that the level just above the upper of the two levels involved in the transitions desired is approximately 40 times closer to its lower neighbor than the state from which the transition is made.

In order to make sure that no lines have been missed due to the disappearance of the Stark effect, the lines found at 26,780 Mc/sec were tentatively assigned to $J = 3$, and the

Stark effect for $J = 3$ and $J = 2$ computed and compared. Assigning the lines to $J = 3$ fixes the bond angle at 90.2 degrees, ϕ' at 33.6 degrees, and κ as -0.9677. Using these values, one finds that the Stark effect for $J = 3$ and $J = 2$ should be nearly equal but of opposite sign, with that for $J = 2$ going toward lower frequency and that of $J = 3$ going toward higher frequency. Although the Stark effect on the lines found at 26,780 Mc/sec goes toward higher frequency, the fact that the Stark effect on the $J = 2$ lines is of the same magnitude makes certain that they would not have been missed in the search previously described. With the lines at 26,780 Mc/sec assigned to $J = 2$, the structure of the stibine molecule is fixed at the following values:

Bond angle	91.5°
Bond length	1.712 Å
ϕ'	31.0°
κ	-0.9530

Computing the Stark effect for the $J = 2$ lines from these data gives Stark components going toward higher frequency, but a factor of ten less than that observed for the $J = 1$ lines. This agrees with the qualitative observations reported above.

Having fixed the structure of the molecule as listed above, the expected quadrupole patterns for the two isotopes may be calculated by using the theory and transformations outlined in the section under arsine (AsH_2D). When this is done the result is as shown in Fig. 7. It can be seen that the fit is good enough to identify all but one pair of the observed lines both as to isotope and as to F numbers. These patterns are computed for the expected spins of $5/2$ and $7/2$ for Sb^{121} and Sb^{123} respectively; the fit is sufficiently good to verify these spin assignments. It can be seen, however, that the ratio of the quadrupole moments is more nearly 1 and does not lie in the region of 4 as predicted from the previously published data (15).

It was not found possible to fit the observed pattern within even a generous error merely by adjusting the magnitude of eQ and the relative scales of the upper and lower states, as had been done in arsine. It became apparent from an examination of the pattern (by taking differences to determine level spacings) that the trouble was in the 1_{11} level and that an F dependent perturbation was necessary. Because the 1_{10} level is separated 677 Mc from the 1_{11} term compared to the transition frequency of 28,000 Mc/sec it was immediately suspected. Bragg (11) has included at the end of his article a section on the higher order terms in quadrupole coupling. The matrix element for a perturbation from a level of the same J but of a different symmetry is

$$(J_T F | H | J_T' F) = eQ \frac{2J + 3}{J} (J_T J | \nabla E_{ZZ} | J_T' J) T(F) \quad .$$

In the case of $J = 1$, the splitting of each of the three levels is determined by a different diagonal member of ∇E_{ZZ} expressed in the inertial axes of the molecule. In particular the splitting of the 1_{11} is proportional to V_{bb} and the splitting of the 1_{10} is proportional to V_{cc} . The interaction between them is the average, as calculated by the

usual methods (10), is

$$\left\langle 2a_{bz} a_{cz} \right\rangle V_{bc} = \frac{3}{10} V_{bc} \quad .$$

If the cross derivatives are expressed in terms of the charge symmetric coordinates, they are

$$\begin{aligned} V_{bc} &= V_{x'z'} \cos \phi' - V_{x'y'} \sin \phi' \\ V_{ab} &= V_{x'y'} \cos \phi' - V_{x'z'} \sin \phi' \\ V_{ac} &= (V_{y'y'} - V_{z'z'}) \sin \phi' \cos \phi' + V_{y'z'} (\sin^2 \phi' - \cos^2 \phi') \\ &\simeq -\frac{3}{2} V_{z'z'} \sin \phi' \cos \phi' \quad . \end{aligned}$$

In originally making the transformation of $\nabla E_{z'z'}$, the cross derivatives in the charge symmetric system had been assumed to be zero, under the same assumption V_{bc} and V_{ab} would also be zero. V_{ac} , on the other hand, would be quite as large as the diagonal terms. Fortunately it involves an interaction between the two states which are farthest apart and when calculated turns out to shift the levels by 0.1 Mc or less, which is within the present experimental error.

In order to explain the observed distortion of the 1_{11} level, V_{bc} must be assumed non-zero. This assumption is not quite as arbitrary as might first appear because there are two isotopes in identical molecules and therefore any alterations made in the pattern of one must also appear in the other. The quadrupole interaction energy of the 1_{11} level is now expressed as

$$W_{1_{11}}(\text{quad}) = -e V_{bb} Q T(F) - \frac{\left[\frac{3}{2} e V_{bc} Q T(F) \right]^2}{W_{1_{10}}^{(0)} - W_{1_{11}}^{(0)}} \quad .$$

The changes in the 1_{11} level which are necessary to bring the observed lines into agreement with theory are computed separately for each isotope, their ratio must be as the ratio of the Q^2 's, which can be determined to better than one percent from first-order theory. When this is done the following results are obtained:

$$\begin{aligned} \left[\frac{Q^{123}}{Q^{121}} \right]^2 &= 1.60 \pm 0.01 & eQ^{123} V_{bc} &= 7.0 \pm 0.5 \text{ Mc/sec} \\ \left[\frac{eQ^{123} V_{bc}}{eQ^{121} V_{bc}} \right]^2 &= 1.4 \pm 0.2 & eQ^{121} V_{bc} &= 5.8 \pm 0.4 \text{ Mc/sec} \quad . \end{aligned}$$

It can be seen that while the errors are large the assumption of finite cross derivatives is not disqualified. The resulting pattern is shown in Fig. 7.

Having fixed the identity of all the lines in the pattern associated with $J = 1$ transition,

the dipole moment of the stibine molecule was determined by making measurements on the $7/2 \rightarrow 7/2$ line of Sb^{121} . The following data:

$\Delta\nu$	E
4.49 Mc/sec	9.79 esu/cm

gives a dipole moment of 0.116 ± 0.003 debye unit. Again, as in arsine, the theory of Golden and Wilson (14) was applied with $J = 1$ and $m_J = 1$; the outermost component only was measured. Had this been a normal second-order Stark effect the splitting at the field quoted above would have been of the order of 0.5 Mc/sec. The nearness of the 1_{10} level increases the accuracy with which the dipole moment can be determined, from ± 20 percent to the quoted ± 3 percent.

Discussion

Molecular Structure. The structure parameters determined in the investigation just described are those numbers which, when fitted into the rigid rotor approximation, give the observed frequencies. Since, at the most, only two groups of lines are measured for each molecule, the system is determined, and the accuracy of the determination is apparently limited only by the measurement of the frequencies. Although the accuracy of frequency measurement is of the order of 1 part in 10^6 , the assignment of such accuracy to the structure parameters would be meaningless outside of the particular transition on which they were measured. While not evaluated in this investigation, several known effects may be pointed out which limit the accuracy of the structure determination.

Because these molecules are so light, rotationally speaking, the energy associated with even a low value of angular momentum is high. Consequently the distortion of the molecule by the rotational motion can be expected to be large. From observations made on such molecules as HDS^{32} the effect can be estimated to be of the order of 10 Mc/sec at $J = 1$, thus reducing the meaningfulness to 1 part in 10^3 . No account, furthermore, has been taken of the zero-point vibrations and in particular of the effect of the one deuterium on the assumption of equal angles and radii. In consideration of the above it was not felt reasonable to quote the structure to more than three significant figures.

	observed		infra-red	estimate (3)	
	r	θ	θ^*	r	θ
Phosphine	1.419* A	93.5°	99.0°	1.42 A	93°
Arsine	1.523 A	92.0°	97.5°	1.53 A	90°
Stibine	1.712 A	91.5°		1.73 A	90°

The absence of any structure due to inversion doubling must also be taken to mean that the ground state inversion vibration frequency in all three molecules is less than the line width, about one half a megacycle (18).

* Infra-red determination of I_b for PH_3 was used to fix r and θ (6).

Dipole Moments. The accuracy of dipole moment determinations by the methods of microwave spectroscopy is ordinarily limited by the precision with which the applied electric field can be measured. In the investigation described above, all the dipole moments were sufficiently small to make the errors quoted those of the frequency measurement.

	debye units	
	observed	previous (13)
phosphine	0.55 \pm 0.01	0.54, 0.56
arsine	0.22 \pm 0.02	0.13, 0.18
stibine	0.116 \pm 0.003	

The previous measurements quoted were all made by Watson (13), with the spread of the readings indicating the accuracy. It may roughly be said that the use of capacity and temperature techniques at present is limited to dipole moments of 0.5 debye unit or greater. Consequently, the disagreement shown above with the previously measured value for arsine is not serious. Watson was unable to measure stibine because of its instability.

Quadrupole Coupling. From the fitting process as applied to the antimony pattern, it can be seen that the value of eQq can be determined to a percent without considering the second-order corrections. The principal reason for the accuracy is that the spread of the pattern is of the order of 100 to 1000 times the error in measuring the frequency. The second-order corrections are, of course, small and nearly symmetrical about the undeviated line. Because the values quoted refer to the charge-symmetry axis of the molecule, the absolute accuracy of an individual determination is only as good as one believes the transformation applied. The ratio of the moments as determined for antimony, however, is independent of this transformation. This ratio, furthermore, is not affected by corrections such as that of approximately 3 percent applied to the ground state of the $J = 1$ transition in arsine.

If the transformations are taken as justified the following values (in Mc/sec) are obtained for the various quadrupole couplings in arsine and stibine:

	$eQV_{z'z'}$	$eQV_{y'y'}$	eQV_{bc}	eQV_{ac}
As ⁷⁵ H ₂ D	- 164	- 4.7	< 10	105
Sb ¹²¹ H ₂ D	455	< 1	\pm 5.8	- 302
Sb ¹²³ H ₂ D	575	< 1	\pm 7.0	- 381

	observed	previous (15)
$\frac{Q_{Sb^{123}}}{Q_{Sb^{121}}} =$	1.263	~ 4

It is to be noted that the sign of eQq changes from arsenic to antimony as expected from the signs of their respective Q 's.

The column headed eQV_{ac} was included as a cautionary measure; these values were not used in the pattern-fitting process. No one, apparently, has considered the possibility that these cross derivatives might be substantial. Consequently, this particular one, which can easily be calculated and is seen to be of the same order of magnitude as that of the diagonal terms, has been displayed. Bragg (11), although mentioning the possibility of their existence, adds that they probably are nearly zero. Bardeen and Townes (17) have applied second-order corrections from levels of different J values to the quadrupole pattern associated with the $J = 3 \rightarrow 4$ transition in ICN in the two cases of $K = 0$ and $K = 1$. In the case of a linear molecule such as ICN, $K = 0$ means the ground vibrational state, while $K = 1$ refers to the bending mode which also produces ℓ -type doubling of the spectral lines. While the theory and the observed lines were in good accord for the ground vibrational state, in the case of $K = 1$ the authors mention small unexplained discrepancies. In calculating the theoretical pattern, the authors take into account the substantial perturbations of the levels whose J values differ by ± 1 and ± 2 and which lie approximately 25,000 Mc away, but apparently they consider the symmetry of the electric field too high for the ℓ doubled levels lying approximately 20 Mc/sec apart to affect each other.

The fact that different corrections are applied to the $J = 1$ transitions of arsine and stibine is a discrepancy which needs comment. That the second-order correction, as applied to stibine, is probably too small to be detected in arsine can be seen by taking the following ratios, all derived from the formula for the second-order correction displayed above:

$$\begin{aligned} \text{(Stibine Correction)} \quad & \frac{(eQq)_{As}^2}{(eQq)_{Sb}^2} \frac{\Delta W_{Sb}}{\Delta W_{As}} \frac{T(F)_{As}^2}{T(F)_{Sb}^2} \\ (\sim 2 \text{ Mc/sec}) \quad & \frac{164^2}{575^2} \frac{770}{2670} \frac{0.250^2}{0.143^2} = 0.14 \text{ Mc/sec} \end{aligned}$$

This is smaller than the experimental error of ± 0.2 Mc/sec.

No such ratio can explain away the correction applied to the 1_{01} state in arsine, and one is left with the following rationalization: The existence of the cross derivatives depends on the lack of symmetry of the molecular electric field which is actually surprisingly symmetrical considering the fact that one of the hydrogens in the completely symmetric SbH_3 has been replaced by an atom which is twice as heavy. The increase in bond angle from stibine to arsine with its attendant enhancement of the inertial asymmetry may, therefore, be just sufficient to raise the electric asymmetry to the measureable point.

Quadrupole Moments. Using the ratio of the Q's which has been determined above, the value of the quadrupole moment of one isotope can be determined from the other. Which isotope to select as a standard is a moot question. The quadrupole moments of antimony have been determined from optical spectra by the following roundabout method: Tombouliau and Bacher (19) published data on the hyperfine structure of a transition in SbII which they had observed, but they declined to identify the transition. Murakawa and Suwa (15) remeasured a transition previously identified by Badami and from these measurements deduced the value $-0.3 \pm 0.2 \times 10^{-24} \text{ cm}^2$ for the quadrupole moment of Sb^{121} . By identifying the transition reported by Tombouliau and Bacher, Murakawa and Suwa calculate the quadrupole moment of Sb^{123} to be $-1.2 \pm 0.2 \times 10^{-24} \text{ cm}^2$. The ratio of these two moments is 4 or by taking the maximum error for each it can be reduced to 2, but not to 1.26.

The quadrupole moment of Sb can be calculated by still another method, that suggested by Townes and Dailey (20) in which a value of V_{z^2} for a p electron is calculated from atomic data and the number of contributing p electrons is estimated from the observed structure of the molecule concerned. While no great accuracy is claimed for this method an attempt can be made to improve all the approximations by comparing the results obtained through incorporation of the same nucleus in several different molecules. In the case of antimony this is not possible but by the following roundabout path a similar ruse may be used: Iodine, which has only two more protons than antimony, has been measured in several molecules, and its quadrupole moment has been measured from optical spectra. The contributing structures have been analyzed by Townes and Dailey (19) so that by using the known value of the quadrupole moment one can obtain an estimate of V_{z^2} for iodine. This can then be converted to antimony by multiplying by the ratio of their effective $Z_{\text{eff}}^4 = (Z-4)^4$. This figure is on a per-p electron basis. In order to estimate the effective number of p electrons causing the nonspherical field at the nucleus in such a nearly spherical field as must prevail in stibine, use can be made of the fact that arsenic in AsF_3 has been measured and analyzed by Townes and Dailey (19).

molecule	θ	eqQ	No. of p electrons contributing
AsF_3	100°	- 235 Mc/sec	- 0.4
AsH_2D	92.0°	- 164 Mc/sec	- 0.28

For iodine the average eqQ per p electrons is 2500 Mc/sec. If the quadrupole moment is taken as $0.46 \pm 0.15 \times 10^{-24} \text{ cm}^2$ (Ref. 6) then eq for iodine is $5.4 \times 10^{27} \text{ Mc/sec cm}^2$. The ratio of the effective Z_{eff}^4 is 0.847 giving an eq for antimony of $4.6 \times 10^{27} \text{ Mc/sec cm}^2$. The number of contributing p electrons will certainly not be greater than in arsenic so that, using the value 0.28, one gets a lower limit. An upper limit may be obtained by assuming that the number of contributing p electrons decreases linearly with θ from the value obtained for arsenic, certainly an outside guess since the number has only increased to 0.4 at 100° .

	upper	lower	previous
Sb ¹²³	- 0.62	- 0.45	- 1.2 ± 0.2
Sb ¹²¹	- 0.50	- 0.35	- 0.3 ± 0.2

Units are 10^{-24} cm^2 .

The error in the estimates must be at least of the order of 50 percent but even so the agreement with the optical value for Sb¹²¹ is astonishingly good.

Finally, one might make the comparison suggested by Gordy (7). He has pointed out the empirical fact that the ratio of the magnetic moments of two isotopes is nearly the same as that of their quadrupole moments, and that the sense of the ratio depends upon whether the sign of the quadrupole moments is positive or negative. Fortunately the magnetic moments of the antimony isotopes have recently been measured in two separate places (21, 22) and identical answers were obtained.

$$\frac{Q_{\text{Sb}^{121}}}{Q_{\text{Sb}^{123}}} = \frac{-455}{-575} = 0.791 \qquad \frac{\mu_{\text{Sb}^{123}}}{\mu_{\text{Sb}^{121}}} = 1.3191$$

for negative Q's:

$$\frac{\mu_1}{\mu_2} \frac{Q_2}{Q_1} = 0.791 \times 1.3191$$

$$= 1.043$$

The average of the examples given by Gordy was 1.12. Townes (3) takes issue with this observation but principally with the extension of the idea by Gordy to predict the quadrupole moments of elements of both different Z and N.

The existence of the isotopic species of molecule SbD₂H and AsD₂H might be pointed out again now that the structure of stibine and arsine are known. While the search for the transitions in these molecules analagous to the ones described in this investigation would have been tedious indeed, it is now a relatively simple task. The usefulness of these molecules lies in two places. First of all the apparent structure as determined from the microwave measurements will be interesting to compare with that obtained above. Second, the inertial symmetry of these molecules is sufficiently different to make possible the determination, perhaps, of more of the electric field structure than was possible in this investigation alone.

The spectrometer used for this work has been described previously (23). A table of observed absorptions is appended.

Appendix 1

PREPARATION OF SAMPLE

The stibine was prepared as follows. An alloy of 80 percent magnesium, 20 percent antimony was powdered and placed in a reaction flask which was connected through a trap at dry-ice and acetone temperature (to remove water vapor) to the sample-collecting trap held at liquid nitrogen temperature. The appropriate acid (DCl for SbD_3 or a mixture of DCl and HCl for SbH_2D) was dripped slowly on the powder. The gas generated was swept gently along with dry nitrogen.

The alloy was prepared by placing the powders in a carbon crucible and heating to a bright-red heat in a hydrogen atmosphere. Antimony sublimes before magnesium melts so that this heating must be done quickly.

The pure DCl was prepared by collecting the gas given off of the constant boiling mixture of D_2O and P_2O_5 in excess NaCl.

Appendix 2

TABLE 1

Observed Transition Frequencies in Stibine

		ν (Mc/sec)	α (10^{-7} cm $^{-1}$)
Sb ¹²¹ H ₂ D	5/2 → 3/2	28,187.74	1.28
	3/2 → 3/2	unresolved	0.55
1 ₀₁ → 1 ₁₁	5/2 → 7/2	28,168.04	1.31
	7/2 → 7/2	28,158.14	2.35
	5/2 → 5/2	unobserved	0.16
	7/2 → 5/2	28,108.55	1.31
	3/2 → 5/2	28,105.28	1.28
Sb ¹²³ H ₂ D	7/2 → 5/2	28,190.15	1.05
	5/2 → 5/2	28,175.07	0.57
	7/2 → 9/2	28,174.48	1.05
1 ₀₁ → 1 ₁₁	9/2 → 9/2	28,162.78	1.65
	7/2 → 7/2	unobserved	0.07
	9/2 → 7/2	28,105.80	1.05
	5/2 → 7/2	28,102.66	1.05

2₀₂ → 2₁₂ lines for Sb¹²³H₂D and Sb¹²¹H₂D were observed at 26,780 Mc/sec. α was computed for 100 percent abundance of SbH₂D. In this investigation the values above should be multiplied by 0.4.

Observed Transition Frequency in Arsine

		ν (Mc/sec)	α (10^{-6} cm $^{-1}$)
AsH ₂ D	1/2 → 3/2	35,460.08	1.73
	5/2 → 3/2	35,455.64	1.87
1 ₀₁ → 1 ₁₁	3/2 → 3/2	35,450.51	0.55
	5/2 → 5/2	35,435.19	4.37
	3/2 → 5/2	35,430.10	1.87
	1/2 → 1/2	unobserved	0.35
	3/2 → 1/2	35,413.79	1.73
3 ₀₃ → 3 ₁₃	9/2 → 7/2	29,545.05	1.55
	5/2 → 7/2	29,539.38	2.00
	3/2 → 5/2 } 7/2 → 7/2 }	unresolved	1.48
	5/2 → 5/2	29,535.30	11.31
	5/2 → 5/2	29,526.69	7.65
	7/2 → 5/2	29,522.64	2.00
	9/2 → 9/2	29,516.96	17.00
	3/2 → 3/2 } 7/2 → 9/2 }	29,507.91	5.93
		unresolved	1.55
	5/2 → 3/2	29,498.52	1.48

Observed Transition Frequency in Phosphine

		ν (Mc/sec)	α (10^{-4} cm $^{-1}$)
PH ₂ D	3 ₀₃ → 3 ₁₃	28,157.72	4.44

Appendix 3

STARK EFFECT IN ASYMMETRIC TOPS WITH QUADRUPOLE COUPLING

The general formulation of the problem for diatomic and linear molecules has been given by Fano (24), and the extension to symmetric and asymmetric tops is immediate. The calculation in any particular case, however, is tedious, even in the case of a diatomic molecule. For the purpose of the present investigation, the exact position of all of the Stark components is of little consequence, since the only information wanted is the dipole moment of the molecule. Because the transitions under consideration above are all $\Delta J = 0$ there is one particular Stark component whose position can be calculated with ease by using the published line-strength tables of Cross, Hainer, and King (16). How this comes about can be seen by considering the general Stark problem.

The general problem is that of calculating the matrix elements of the direction cosines of the molecule-fixed dipole moment to the space-fixed electric field axis. The possibility of accidentally degenerate states will be ignored since it did not happen to occur; consequently there will be no first-order Stark effect. The second-order energy shift of the i th state due to the mixing of the i th and the j th states is as follows:

$$W_i^{(2)} = \sum_{i \neq j} \frac{\left| \int \psi_i^* \vec{\mu} \cdot \vec{E}_z \psi_j dV \right|^2}{W_i^{(0)} - W_j^{(0)}} .$$

If
$$\vec{\mu} \cdot \vec{E}_z = \mu E_z \Phi$$

then

$$W_i^{(2)} = \mu^2 E_z^2 \sum_j' \frac{|\langle i | \Phi | j \rangle|^2}{W_i^{(0)} - W_j^{(0)}}$$

and the problem is that of finding a representation in which it is convenient to evaluate the direction cosine elements.

If one of the nuclei in the molecule has a quadrupole moment, it may be coupled to the molecular rotation by the gradient of the molecular electric field at the position of the nucleus. For small coupling energies, $eqQ \ll a, b, c$, (in stibine $eqQ \simeq 10^{-3} a, b, \text{ or } c$) the total angular momentum of the molecule F can be considered as the vector sum of two components I and J , the nuclear spin angular momentum and the molecular rotational angular momentum, respectively. The projection of F on a space-fixed axis will be a good quantum number M_F , but because of the coupling now considered, m_I and m_J need not be good quantum numbers. The Stark components whose positions are desired will be characterized by M_F .

It is convenient to expand the wave function in terms of the zero-order wave functions, i. e. those associated with no quadrupole coupling. If there is no coupling, the wave

equation must be separable and the zero-order functions are of the following form:

$$\psi(J, m_J) \phi(I, m_I) \quad .$$

When F and M_F are the good quantum numbers each state will be described by a sum of terms each of which is compatible with the F and M_F to be described. The number of terms in each series will be determined by the number of ways the state can be constructed. For $F < J + I$ there may be several terms in the series for each F and M_F .

There is one state whose description is limited to one term. This is the state for which $F = J + I$ and also $M_F = I + J$. For this one state it is sufficient to apply existing theory of the Stark effect in asymmetric tops using the J, M_J representation associated with this one state. In the case of $\Delta J = 0$ there is an allowed transition between two states, both of which lend themselves to this simple description. Furthermore, the spectral line associated with this particular transition is the most intense of the pattern. It is on the outermost Stark component of this line, labelled by $F_{\max} \rightarrow F_{\max}$ in the patterns in Figs. 6 and 7, that the measurements to determine the dipole moment of each molecule were made.

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