A STUDY OF THE ROTATIONAL SPECTRA OF SOME OF
THE TRI-HYDRIDES OF THE FIFTH GROUP OF
ELEMENTS OF THE PERIODIC TABLE

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree Doctor of Philosophy in the
Graduate School of The Ohio State
University

By
The Ohio State University
1953

Approved by:

[Signature]
DEDICATION

This work is dedicated to my wife, whose patience, perseverance, and help have made it possible.
ACKNOWLEDGEMENTS

It gives me great pleasure to acknowledge the help and cooperation that I received from many persons during the course of this investigation.

I would like especially to express my appreciation to Dr. Robert A. Oetjen, who served as my advisor, for his continual interest, helpful comments, and guidance. I am very grateful to Dr. H. H. Nielsen for the help he gave in the analysis of the near infrared data, and to Dr. E. E. Bell for his aid in interpreting the far infrared spectra. I am indebted to Dr. H. H. Sisler and Dr. A. B. Garrett of the Chemistry Department for their suggestions as to preparation of the samples. I would like especially to thank Mr. Carl McWhirt whose staff constructed several unusual cells for this investigation. I am appreciative of the help of my friends, R. L. Brown, P. W. Davis, and E. D. Palik, for their ever present aid. Acknowledgment is made to the Wright Air Development Center for assistance in making the far infrared spectrograph available for obtaining these data. The investigation was supported in part from funds granted to The Ohio State University by the Research Foundation for aid in fundamental research.
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INTRODUCTION

The tri-hydrides of the fifth group of elements of the periodic table have the geometric form of a regular pyramid in which the hydrogen atoms are at the corners of an equilateral triangle and the nitrogen, phosphorus, arsenic, antimony, or bismuth* atom is at the apex of the pyramid. These molecules are thus of the $XY_3$ model and represent the simplest nonlinear, nonplanar, symmetric rotator molecules. The far infrared spectrum of the members of this group have been reported for only ammonia and phosphine, the only mention of the latter being the four lines obtained by Wright and Randall in 1933 (1)**; however, ammonia has been extensively studied and in its usual form $NH_3$ will not be a subject in this paper though use is made of the result of these studies.

The study of the near infrared spectra of this family of molecules is usually complicated by a mixing of the fundamental rotation-vibration bands which makes a satisfactory analysis very difficult.

Randall (2) has pointed out that, aid to, or a check on, the analysis of the near infrared spectra of these

* Bismuthine is not chemically stable.

** Numbers in parenthesis refer to the bibliography.
molecules is available in their pure rotational spectra which appear in the far infrared. For each molecule this spectrum is quite simple. It consists of a series of quite widely separated and nearly evenly spaced lines. As part of the rotational spectra of these molecules occur within the range of the far infrared spectrograph (3) available on The Ohio State University campus, a study was undertaken of the rotation spectrum of phosphine, deuterated phosphine, arsine, deuterated arsine, and deuterated ammonia. Attempts were made to obtain a spectrum of stibine but they were not successful.
HISTORY

The first far infrared spectrum of a molecule of this group was obtained by Badger and Cartwright (4) in 1929 when they observed six rotational lines of ammonia in the region between 79 and 177 K*. This was the first reported polyatomic far infrared rotation spectrum. Subsequent study of the far infrared ammonia spectrum was carried on by Wright and Randall (1) at The University of Michigan where three of the ammonia lines, earlier reported by Badger and Cartwright, and four phosphine lines were observed in 1933. The ammonia lines show doubling due to inversion. No later spectrum of phosphine has been reported.

In 1935, Barnes (5), working at Princeton, reported ten pure rotation lines of ammonia, four previously unreported, and six lines of heavy ammonia, ND₃. These were observed less highly resolved than the earlier spectra of NH₃ reported by Wright and Randall, but are the only reported rotation spectra of ND₃. Foley and Randall (6),

* 1 Kayser (K) is equivalent to 1 cm⁻¹. This is in accord with the recent action of The Joint Commission for Spectroscopy, Subcommittee e (Notation for Atomic Spectra) J.O.S.A. 43, 422 (1953).
using the second far infrared spectrograph built at The University of Michigan (7), studied the fine structure of five of the ammonia lines in 1940. Three of these lines had been reported earlier and two additions were made. In 1951, McCubbin at Johns Hopkins University using a grating spectrograph employing focal isolation, reported four lines of the ammonia spectra, three previously unreported, between 19 and 81 K. The Ohio State University far infrared spectrograph was used by Hansler (9) to obtain data for eight ammonia rotational absorptions in 1952. This instrument, only slightly modified, was used for this study. As a result of all investigations, 15 different NH₃ rotational lines have been observed and six ND₃ rotational lines have been reported.

It was Barker (10) who was the first to note experimentally the doubling of infrared bands of NH₃. This phenomenon was later studied by Dennison and Hardy (11) and explained theoretically more rigorously by Dennison and Uhlenbeck (12). Slawsky and Dennison (13), using the near infrared data on ND₃ of Migeotte and Barker (14), obtained the potential constant of ammonia and gave a theoretical discussion of the effect of centrifugal distortion of the XY₃ molecules. Extensive use will be made of this paper, for by using it, it is possible to predict the far infrared spectra of the other members of the
family.

The ammonia molecule was chosen as one of the five typical molecules to be treated fully by Dennison in his discussion of "The Infrared Spectra of Polyatomic Molecules" in 1940 (15). The potential functions of Manning (16) which Dennison used in this treatment are not convertible for use with the other members of the family of molecules without more information of multiple and difference bands than is at present available, so a different approach to the analysis of the parallel bands is necessary. Nielsen has developed a different method which is now being published and which is used here.

The near infrared spectrum of deuterated ammonia was investigated by Migeotte and Barker (14) in 1936. Burgess (17) examined the spectrum of ND₃ in 1948 and Berlad (18) re-examined the ND₃ spectrum in 1950.

The first near infrared spectrum of phosphine was obtained by Robertson and Fox in 1928 (19). They used a prism instrument. Fung and Barker (20) in 1934 repeated this work and observed the spectrum of phosphine under the higher resolution of a grating spectrograph. The Raman spectrum of PH₃ was obtained by Yost and Anderson (21) in 1934, and de Hemptinne and Delfosse (22) observed the Raman spectrum of PD₃ in 1936. Lee and Wu (23) in 1939 obtained the near infrared spectrum of heavy phosphine and
used the theoretical work of Howard (24) to determine the normal frequencies. Sutherland, Lee, and Wu (25) calculated the dimensions of the molecules. They obtained a value of $\psi = 62^\circ 30'$ where $\psi$ is the angle between a P-H bond and the altitude of the pyramid. Loomis and Strandberg (26) have studied the microwave lines of PH$_3$D and arrived at an $\psi$ of 57°. McConaghy and Nielsen (27) analyzed the spectrum of phosphine in 1948 and Ward (28) recorded the spectrum of PD$_3$ in 1951.

The near infrared spectrum of arsine has been investigated by Robertson and Fox (19), Barker (10), Dehnison and Hardy (11), Lee and Wu (23), McConaghy and Nielsen (27) (29), and Nielsen (30). The molecular constants listed here are based upon the observed data reported by McConaghy and Nielsen (29) in 1949. Some of the constants of the molecule as determined from this work have been somewhat changed in the process of reworking these basic data. The more recent values of the physical constants of Dumond and Cohen (31) have been used. Loomis and Strandberg (26) have obtained microwave data on one of the partially deuterated arsines (AsH$_2$D) and have arrived at a value for the angle between the As–H bond and the altitude of the pyramid of 56° 9'.

Stibine is the last chemically stable member of the tri-hydrides of the fifth group of elements of the
periodic table. It has been investigated by D. C. Smith (32) in the near infrared in 1951 using a prism spectro-graph, by W. H. Haynie (33) in 1951, and by Loomis and Strandberg (26) (SbHgD) in the microwave absorption in 1951.

Early studies of the rotation-vibration energy of the pyramidal $\text{XY}_3$ model were made by Dennison in 1926 (34), by Lechner (35) in 1932, and by Rosenthal in 1935 (36) using various potential functions. Wilson (37), and Howard and Wilson (38) considered the pyramidal model from its symmetry properties -- group theory point group $C_{3v}$. Teller and Tisza (39), Teller (40), and Johnston and Dennison (41) considered some of the effects of Coriolis interactions. Slawsky and Dennison (13) discussed the effects of centrifugal stretching in 1941. A complete treatment of the rotation-vibration problem was published by Shaffer (42). Nielsen (43) in 1945 discussed the Coriolis interaction of the $\text{XY}_3$ molecules and found the general form of the energy matrix and later (44) showed how this might be used in the analysis of the parallel bands.

In Summary: The near infrared experimental data of this family of molecules is good and quite complete; however the derived geometries of the molecules as obtained from the near infrared and the microwave data differ a

---

A more complete bibliography of the study of these molecules is given by F. Halverson, Rev. Mod. Phys. 19, 87 (1947).
Table I shows the number of far infrared lines of this family of molecules previously reported and those added by this investigation.

**TABLE I**

**ROTATION LINES OF THIS FAMILY OF MOLECULES**

<table>
<thead>
<tr>
<th>Number of Lines</th>
<th>Number of Lines</th>
<th>Previously Reported</th>
<th>Reported, Here</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>15</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>ND₃</td>
<td>6</td>
<td>14 (8 additional ones)</td>
<td></td>
</tr>
<tr>
<td>PH₃</td>
<td>4</td>
<td>18 (14 additional ones)</td>
<td></td>
</tr>
<tr>
<td>PF₃</td>
<td>9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>AsH₃</td>
<td>0</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>AsD₃</td>
<td>0</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>SbH₃</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>SbD₃</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
MOLECULAR CONSTANTS AND PREDICTED ROTATIONAL SPECTRA

The tri-hydrides of the fifth group of elements of the periodic table have rotational spectra because they possess a permanent dipole moment. The rotational spectrum of each of these is produced by the molecule rotating about an axis perpendicular to the symmetry axis and the spacing in the rotational spectrum can be predicted from the near infrared data.

Appendix I is devoted to giving a rather complete discussion with references as to how the rotational spectra can be determined from the near infrared. Reference should be made to it in order to fill in the details omitted in the brief remarks that follow.

The rotational spectrum of a member of this family would consist of a series of equally spaced lines, provided the molecule were perfectly rigid, and the spacing of these lines would be determined by the moment of inertia about an axis perpendicular to the symmetry axis. However, the bonds of the molecule are not rigid but deform as the molecule vibrates and rotates and because of this, the simple picture of equally spaced lines is changed somewhat by a convergence of the lines at higher frequencies due to distortion of the molecule.
There is a series of energy levels belonging to the total angular momentum of the molecule. \( J \) is the quantum number associated with this total angular momentum. In addition, the shape of the rotation lines and thus the center of the lines is partially dependent on the component of angular momentum which is directed along the symmetry axis of the molecule. \( K \) is the quantum number associated with this component as \( J \) is with the total angular momentum.

The energy levels of the non-rigid symmetric top molecule in the notation of Herzberg (45) are as follows:

\[
\epsilon(J\tilde{K}l) = BJ(J+l) + (A-B)K^2 - DJ(J^2(J+1)^2 - D_{JJK}(J(J+1)K^2 - D_{K}K^2)
\]

where the \( D_J, D_{JK}, \) and \( D_K \) are relatively small compared to the \( A \) and \( B \). The \( A \) and \( B \) are the rotational constants of the molecule.

\[
A = \frac{h}{4\pi c I_A}
\]

\[
B = \frac{h}{4\pi c I_B}
\]

in which \( h \) is Planck's constant, \( c \) is the velocity of light, \( I_A \) is the moment of inertia about the molecular symmetry axis, and \( I_B \) is the moment of inertia about an axis perpendicular to the symmetry axis. \( D_J, D_{JK}, \) and \( D_K \) are the centrifugal distortion constants of the molecule. They are functions of the atomic mass, the force constants, and the size and shape of the molecule.

The selection rules for the rotational spectrum of
symmetric tops have been determined by Dennison (46). They are $\Delta J = \pm 1$, and $\Delta K = 0$.

The frequencies of the transitions to be observed in Herzberg's notation are given by the difference of the energy levels found using the selection rules above. Thus

$$F(J+1, K) - F(J, K) = \nu = 2B(J+1) - 4D_J(J+1)^3 - 2D_K(J+1)k^2$$

where $\delta$ is the quantum number of the lower state. Although this formula differs in form, it is essentially equivalent to the one obtained from the work of Slawsky and Dennison (13) where $J$ is the quantum number of the upper state. The formula of Slawsky and Dennison,

$$\nu = \frac{A^2}{J^2B} \left[ 2J + \gamma (P_2 - P_2)J - 4P_2J^3 + 4(P_2 - P_2-2P_2)k^2J \right]$$

was used to predict the rotational spectra because the constants appearing in it were more easily obtainable. The quantities involved in this equation are given in Appendix I.

In order to predict the rotational spectrum of each member of the family of molecules, it is necessary to know the geometry and the potential constants of the molecule. The geometries of the molecules can be determined from both near infrared and microwave data. The potential constants have been determined from the near infrared data.

* In the case of inversion doubling, there is an additional selection rule $\alpha \rightarrow \beta$ where $\alpha$ and $\beta$ refer to the symmetry of the wave function of the molecular state.
A discussion of the determination of these data appears in Appendix I.

The constants of the molecules used in this work are given in Tables II, III, IV, and V. These constants have been determined from the near infrared spectra. The data for ammonia were obtained mainly from Dennison [15] with some parts from Sheng, Barker and Dennison [47], Migotte and Barker [14], and Berlad [18]. The phosphine, arsine, and stibine tables are based upon the heights of the pyramids, \( h \), and \( \alpha \) and \( \beta \) angle, as given by Nielsen. These two quantities fix the geometry of the molecules. The distance \( r \) and the angle between \( r \) and \( h \) is \( \beta \). The moments of inertia \( I_a \) and \( I_b \), and the reciprocals of inertia, \( B \), and \( A \), are determined by the geometry of the molecule. The frequencies of the band centers, \( \omega \), and the line spacing \( a(l-\psi)R \) and \( [((l-\psi)R-B) \) are the experimental work of McConaghy [27] and Ward [28] for phosphine; McConaghy [27] for arsine; and Haynie [33] for stibine. From these data, the normal frequencies \( \omega \) and the six potential constants \( a, b, c, \alpha, \beta, \gamma \) have been determined and are listed for each of the molecules.

The predicted rotational spectra of these molecules appear in Table VI.

* A personal communication.
### TABLE II

**AMMONIA**

\[ h = 0.377 \, \text{Å}, \quad r = 1.014 \, \text{Å} \]

\[ \theta = 107^\circ.3', \quad \phi = 68^\circ.12' \]

<table>
<thead>
<tr>
<th></th>
<th>( \text{NH}_3 )</th>
<th>( \text{ND}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_A )</td>
<td>( 4.482 \times 10^{-40} , \text{gm cm}^2 )</td>
<td>( 8.698 \times 10^{-40} , \text{gm cm}^2 )</td>
</tr>
<tr>
<td>( t_B )</td>
<td>( 2.814 \times 10^{-40} , \text{gm cm}^2 )</td>
<td>( 5.447 \times 10^{-40} , \text{gm cm}^2 )</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>3335.9-337.5 K*</td>
<td>2419. K (2421.0 K)**</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>3414*</td>
<td>2555. (2558.8)**</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>931.58-968.08*</td>
<td>747.3 (745.90-749.24)**</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>1627.5*</td>
<td>1191. (1191.2)**</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>3639. K*</td>
<td>2521. K</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>3622*</td>
<td>2670.</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>1051.</td>
<td>806.6</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>1895.4</td>
<td>1221.6</td>
</tr>
<tr>
<td>( a )</td>
<td>( 5.171 \times 10^5 , \text{dyne/cm} )</td>
<td></td>
</tr>
<tr>
<td>( b )</td>
<td>( 6.811 \times 10^5 , \text{dyne/cm} )</td>
<td></td>
</tr>
<tr>
<td>( c )</td>
<td>( 3.078 \times 10^5 , \text{dyne/cm} )</td>
<td></td>
</tr>
<tr>
<td>( d )</td>
<td>( 10.494 \times 10^5 , \text{dyne/cm} )</td>
<td></td>
</tr>
<tr>
<td>( f )</td>
<td>( 4.028 \times 10^5 , \text{dyne/cm} )</td>
<td></td>
</tr>
<tr>
<td>( g )</td>
<td>( 4.168 \times 10^5 , \text{dyne/cm} )</td>
<td></td>
</tr>
</tbody>
</table>

---

* As given by Herzberg (45).

** Quantities in parenthesis are the values of Berlad (18).

---
### TABLE III

**PHOSPHINE**

\[ \alpha = 93^\circ.50! \]

<table>
<thead>
<tr>
<th></th>
<th>( \text{PH}_3 )</th>
<th>( \text{PD}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu )</td>
<td>2322.9 K</td>
<td>1682.75 K</td>
</tr>
<tr>
<td>( \nu )</td>
<td>2328.0</td>
<td>1688.6</td>
</tr>
<tr>
<td>( \nu )</td>
<td>989.5-992.5</td>
<td>727.5</td>
</tr>
<tr>
<td>( \nu )</td>
<td>1121.0</td>
<td>804.7</td>
</tr>
</tbody>
</table>

\( 2(\nu - \nu) \) 11.16 K

**Quantities Derived From The Above**

<table>
<thead>
<tr>
<th></th>
<th>( \alpha = 57^\circ.31' )</th>
<th>( \lambda = 1.425 \text{A}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_B )</td>
<td>( 6.284 \times 10^{-40} \text{ gm cm}^2 )</td>
<td>( 12.123 \times 10^{-40} \text{ gm cm}^2 )</td>
</tr>
<tr>
<td>( I_A )</td>
<td>( 7.228 \times 10^{-40} \text{ gm cm}^2 )</td>
<td>( 14.446 \times 10^{-40} \text{ gm cm}^2 )</td>
</tr>
<tr>
<td>( B_e )</td>
<td>4.453 K</td>
<td>2.308 K</td>
</tr>
<tr>
<td>( A_e )</td>
<td>3.871</td>
<td>1.937</td>
</tr>
<tr>
<td>( 2440.2 \text{ K} )</td>
<td>1744.3 K</td>
<td>1730.1</td>
</tr>
<tr>
<td>( 2406.9 \text{ K} )</td>
<td>1012.8</td>
<td>759.4</td>
</tr>
<tr>
<td>( 1148.9 \text{ K} )</td>
<td>3.524 \times 10^5 \text{ dyns/cm}</td>
<td>2.854 \times 10^5 \text{ dyns/cm}</td>
</tr>
<tr>
<td>( 2.578 \times 10^5 \text{ dyns/cm} )</td>
<td>3.863 \times 10^5 \text{ dyns/cm}</td>
<td></td>
</tr>
<tr>
<td>( 1.761 \times 10^5 \text{ dyns/cm} )</td>
<td>1.560 \times 10^5 \text{ dyns/cm}</td>
<td></td>
</tr>
</tbody>
</table>
\[
\begin{array}{ll}
T & 1.06 \times 10^5 \\
1.789 & 1.06 \\
2.668 & 1.06 \\
3.591 & 1.06 \\
2.329 & 1.06 \\
\end{array}
\]

\text{dye/cm}

\[
\begin{array}{ll}
\text{7.16} & 1.07 \\
6.96 & 1.07 \\
7.082 & 1.07 \\
7.928 & 1.07 \\
8.499 & 1.07 \\
9.74 & 1.07 \\
\end{array}
\]

\text{g/cm}

\[
\begin{array}{ll}
\text{4.1} & 10^{-4} \\
9.02 \pm 0.2 & 10^{-4} \\
9.06^* & 10^{-4} \\
2.127 & 10^{-4} \\
2.746.1 & 10^{-4} \\
\end{array}
\]

Quantitative data from the above

\[
\begin{array}{ll}
(1-5)^{0.16x} \\
1000.0 & 0 \\
90.4 \pm 0.9 & 0 \\
66.0 & 0 \\
5.22 & 0 \\
1.628.1 & 0 \\
2.746.1 & 0 \\
\end{array}
\]

and

\[
\begin{array}{ll}
\text{h} & 0.0 \pm 0.0 \\
\text{z} & 310 \pm 24 \\
\end{array}
\]

AVS

AVS

TABLE I

TABLE I
### TABLE V

**STIBINE**

\[ h = 0.830 \text{ Å} \quad \& = 91^\circ 30' \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T )</th>
<th>( u )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SbH}_3 )</td>
<td>1890.9 K</td>
<td>1358.8 K</td>
</tr>
<tr>
<td>( \text{SbD}_3 )</td>
<td>1894.2</td>
<td>1362.9</td>
</tr>
<tr>
<td>( \text{Sb} )</td>
<td>761.5</td>
<td>561.1</td>
</tr>
<tr>
<td>( \text{Sb} )</td>
<td>850.2</td>
<td>592.5</td>
</tr>
</tbody>
</table>

\( [(\text{H}+\text{D})] = 0.04 \text{ K} \)

**Quantities Derived From The Above**

<table>
<thead>
<tr>
<th>( a )</th>
<th>55° 48'</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r )</td>
<td>1.685 \text{ Å}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( L_B )</th>
<th>8.937 x ( 10^{-40} ) \text{ gm cm}^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_A )</td>
<td>9.401 x ( 10^{-40} ) \text{ gm cm}^2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( B_e )</th>
<th>3.131 K</th>
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</thead>
<tbody>
<tr>
<td>( A_e )</td>
<td>2.977</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( p )</th>
<th>1988.9 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p )</td>
<td>1674.5</td>
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<tr>
<td>( q )</td>
<td>975.9</td>
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<tr>
<td>( q )</td>
<td>344.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( a )</th>
<th>1.900 x ( 10^5 ) \text{ dyne/cm}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b )</td>
<td>2.075 x ( 10^5 )</td>
</tr>
<tr>
<td>( c )</td>
<td>2.599 x ( 10^5 )</td>
</tr>
<tr>
<td>( d )</td>
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TABLE VI

PREDICTED ROTATIONAL SPECTRA
To Be Expected Within The Range Of The Spectrograph

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* J'' is the quantum number of the lower state.
THE PREPARATION OF GASES

The gases were prepared in a system made primarily of glass; however, in some instances a steel generator was substituted for the glass one for safety. The system consisted of a generator, drying tube, crude products condenser, and accompanying carrier gas ingress and egress apparatus. (Figure 1)

The glass generator (a) was a water-cooled 750 cc Erlenmeyer flask with gas inlet and outlet tubes on opposite sides, and a fine control burette dropper at the top. The metal generator (Figure 2) was made from a solid piece of steel rod with a cavity cut lengthwise in it, three inches in diameter and four inches deep. A steel ring five and one half inches in diameter and one half inch thick was threaded to and welded on the open end of the hollowed rod to provide room for a vacuum seal. The lid was bolted on and had three openings in it, two for the gas flow and one for making additions to the contents of the generator. The lid was removable and a vacuum seal was obtained by using a gasket. It was planned to make the vacuum seals by means of aluminum gaskets; however, a tight system was not obtained this way so rubber gaskets were used. Liquid was allowed to drop into the generators and the resulting gas.
formed was swept out by a carrier gas to the drying tube.

The drying tube (b) was approximately 30 inches in length. The drying agent was held in position by gravity as it was found that such an inert plug as glass wool was apt to collect sufficient crud to cause serious blocking to the flow of gas. To prevent the same thing from happening at the drying agent surface, only a very coarse agent was used and the inlet or horizontal portion of the tube was partially filled so that a portion of the agent might become completely fused without hindering the flow of gas.

The crude products condenser (b) was a 100 cc ampule, shaped to fit into a liquid nitrogen dewar. The bottom of the inlet tube was lower than that of the outlet tube and the condenser had a stopcock on the inlet, and one on the outlet so that the condenser could be isolated.

The carrier gas was dried and purified by passing it through a drying train of calcium sulfate, concentrated sulfuric acid bubblers, phosphorous pentoxide drying tower and ascarite. It was then admitted to the generator through a T junction and stopcock by means of which it was possible to reverse the flow of gas from the generator while the crude products condenser was shut off. During this time the carrier gas and the gas generated passed out of the system through a neutralizing copper sulfate bubbler to the exhaust. After the carrier gas had passed through the
drying tube and the crude products condenser, it entered a drying tube (d) about 20 inches long, and was bubbled through copper sulfate (e) and to the exhaust.

In order to obtain as pure a product as possible, arrangements were made to fractionally distill the crude products condensate. (Figure 3) This could be done by immersing the crude products condenser, which now became the boiler, in a solution which was slightly warmer than the boiling point of the condensate. The fractions were collected in ampules of a shape similar to that of the crude condenser which were cooled by liquid nitrogen. The third fraction was usually left in the boiler itself.

The entire gas producing system was made with the same size glass joints and the parts could be rearranged more or less at will. A modification found convenient was that made by joining together of the generating and fractionating systems into a continuous train by means of a three-way stopcock between them. The entire system was arranged so that it could be evacuated to assure that the system was tight and to eliminate the water vapor.

Little difficulty was incurred in the production of phosphine \((PH_3)\). A method similar to the one used by Ward (28) and McDonaghie (48) was used. Commercially obtained calcium phosphide was placed in the generator and distilled water was dropped upon it. The chemical reaction is: 
Figure 3

Fractional Distilling System
$\text{Ca}_4\text{P}_2 + 6\text{H}_2\text{O} \rightarrow \text{Ca}_4(\text{OH})_6 + 2\text{PH}_3$ ↑

It is not claimed that the resulting phosphine was chemically pure; but the impurities had no bothersome absorptions in the region of the spectrum investigated.

Phosphine is a colorless gas with an offensive smell similar to rotten fish. It is very poisonous. Its physical characteristics are: melting point, $-133.5$ °C; boiling point, $-87.4$ °C; density, $1.529$ g/l; and molecular weight, $54.043$ g/mol. Dry nitrogen was used as the inert carrier and dry ice and acetone were used to fractionally distill the phosphine. The normal yield was good. According to Mellor (49) this reaction should give a yield of about 87 percent.

Some difficulty was incurred in the production of arsine ($\text{AsH}_3$). The method finally used was that described by Pearson (50). A mixture of ten grams arsenuous oxide, $\text{As}_2\text{O}_3$, per 150 cc of dilute hydrochloric acid (0.2 normal) was dropped on magnesium turnings. The mixture formed a weak solution of arsenuous acid and the excess hydrochloric acid reacted with the magnesium turnings producing a nascent hydrogen atmosphere which combined with the arsenuous acid giving off arsine. The chemical reaction is:

$$\text{H}_2\text{AsO}_3 + 3\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}_3\text{As}$$
The main contaminant of the arsine was water vapor, but this was eliminated by the use of sufficient drying agent. HCl was frequently identified in the arsine spectrograms, but it was not a bothersome impurity since its far infrared spectrum is well known. The strength of the HCl in the arsine spectrograms increased with the increase in dropping rate in the generator, but it could be eliminated by fractionally distilling the crude condensate. The generating system was designed to fill cells of less than a fifth the volume of the cell finally used. As a result of the small volume generated, the entire sample was used in order to obtain a relatively high cell pressure from a reaction which was always quite low in its yield.

Arsine is a colorless, smelly, and extremely poisonous gas. Its physical characteristics are: melting point, -113.5 °C; boiling point, -55.0 °C; density, 3.484 g/l; and molecular weight, 77.93 g/mol. Dry nitrogen was used as the inert carrier gas and a salt-water ice bath was used to fractionally distill the arsine. The yield was generally not good.

Considerable difficulty was incurred while attempting to prepare stibine, SbH₃. A method essentially the same as that used by Smith (32) was used. Freshly boiled hydrochloric acid, approximately 0.2 normal, was dropped on an alloy of zinc and antimony (80% Zn—20% Sb). The
reaction was similar to that by which arsine was produced but the yields appeared to be even less. Little or no success was had in attempting to enrich the yield by fractional distillation. This characteristic of stibine had been noted earlier (33) and after considerable time of attempting an enrichment process of the normal, the practice was discontinued.

Stibine is a colorless gas, thought to have an offensive odor. It is poisonous. Its physical characteristics are: melting point, -88°C; boiling point, -17°C; density, 5.3 g/l; and molecular weight, 124.28 g/mol. Dry nitrogen was used as the carrier gas. The Marsh test was used and showed that stibine was actually being produced. This test consisted essentially of the depositing of an antimony mirror from the colorless gas. The preparation of stibine is very sensitive to the acid concentration as too large a normality results in the acid reducing the gas before it leaves the generator. The usual yield of stibine was very poor. Mellor (51) indicates a yield of perhaps ten percent should be expected. A spectrum of stibine was never observed.

Deuterated ammonia; 125 ml., was purchased from the Texas Research Foundation, Renner, Texas. The vendor claimed 99 percent purity. Deuterated ammonia was also prepared by treating magnesium nitride with deuterium
oxide. The magnesium nitride used had been prepared by A. L. Berlad (18) some years earlier.

The best deuterated phosphine samples were produced in a manner similar to that used in making regular phosphine. Deuterium oxide, 99.5 percent pure — obtained from the Stuart Oxygen Co., San Francisco, California — was dropped on commercial calcium phosphide. Additional precautions were taken to thoroughly dry the generating system by prolonged evaluation and repeated flamings; however, these additional measures were not sufficient to result in the production of pure PD₃. Instead, the gas samples were mixtures of PD₃, PD₂H, PDH₂, and PH₃. The purest PD₃ was made from the freshest calcium phosphide. The calcium phosphide was kept in a clean, freshly filled, desiccator once the factory seal was broken, but despite this, the relative strength of the PD₃ to PH₃ spectrum decreased with the "age" of the phosphide used.

A second method was used to prepare heavy phosphine but with no better results. In this method, sodium phosphide was formed in the metal generator by heating red phosphorous and dry metallic sodium (10:1) in a helium atmosphere. Heavy water was then slowly dropped on the sodium phosphide forming phosphine gas. The resulting gas was again a mixture of all four phosphines and indicated even a smaller percentage of PD₃ than that prepared
by the first method. The source of the unwanted hydrogen was probably either the red phosphorous, though a new sealed can of this was used, or the products of decomposition of the rubber gasket material due to the prolonged high temperatures needed to form the sodium phosphide from the red phosphorous.

Helium was used as the inert carrier gas in each method and no attempt was made to purify the crude product condensate.

The deuterated arsine was prepared by the method of Saunders (52). Metallic sodium and arsenic were combined in an iron reactor and the resulting sodium arsenide was hydrolyzed. The chemical reaction is

\[ \text{NaAs} + 3\text{H}_2\text{O} \rightarrow 3\text{NaOD} + \text{As}_2\text{O}_3 \]

An excess of arsenic of ten to one was put in the generator in a helium atmosphere and heated. After the combination had occurred, heavy water was dropped upon the sodium arsenide to produce deuterated arsine. Due to the small amount of gas evolved, no attempt was made to fractionate the resulting crude product. Helium was used as the inert carrier gas.
THE SPECTROGRAPH

The spectrograph used for obtaining these data was the one built at The Ohio State University (3). Its construction was sponsored by the Air Research and Development Command through a contract with The Ohio State University Research Foundation.

The source is a strip of platinum, 0.3 x 4 x 0.0005 inches painted with water glass. It is electrically heated to approximately 1300 °K.

The dispersing device of the spectrograph is an echelle grating, seven by nine inches, ruled with 180 lines per inch. The grating has a blaze angle of about 20 degrees, so that first order 100 K radiation is diffracted at the blaze angle.

The detector is a Golay pneumatic cell with a circular aperture and receiver 3/16 inch in diameter. The detector used for obtaining most of the data has a quartz window 0.5 mm thick. This quartz window determines the high frequency limit of the instrument which is about 250 K. The signal from the detector is amplified and presented to a Brown recorder. This system is responsive only to the radiation which is chopped. A ten cps compensated potassium bromide chopper is used to interrupt the longwave
radiation at this frequency without interfering with the shortwave radiation. Compensation of reflection losses at the surfaces of the KBr is accomplished with the positioning of toothpicks in the open spaces of the chopper.

The isolation of a spectral region is accomplished by a combination of several filtering components. A 360 line per inch filter grating is used for examining radiation of frequencies less than 140 K. A reststrahlen plate of KRS-5 is used in addition to the filter grating between 90 and 50 K. For frequencies higher than 140 K, a NaCl reststrahlen plate and no filter grating is used.

A turpentine-soot-on-polyethylene filter is used over the detector window to reduce the amount of shortwave radiation falling upon the detector. A filter of this type at this place is a great aid in the adjustment of the Go-\-lay detector.

The spectrograph and source and filter section are each evacuable. The two units are joined by means of a syphon bellows connection. The vacuum seals are accomplished with "O-rings". A vacuum of 100-200 microns Hg is sufficient to remove all traces of atmospheric water vapor absorption from the spectrum.

Spectral slit widths of between 0.6 and 1.0 K were used for this study.
ABSORPTION CELLS

Four absorption cells were made for the spectograph. The need for a cell different than those previously used with the instrument arose because of the relatively weak dipole moments of the molecules to be investigated, and the largeness of the J value of lines to be studied. Thus, plans were made to obtain as long an absorption path as possible.

The physical limitations of the spectograph housing, without modification, prohibited the use of a conventional cell of long optical path length. Attempts to design a multiple reflection cell to fit within vacuum tanks of the instrument were more or less fruitless because of the limited space available.

The first cell (Figure 4) was one modeled after the wave guides used in the microwave region and the channels used in the near infrared. It consisted of a rectangular brass channel slightly larger than the maximum slit, 2' x 15/32 inches in cross sectional area, and had a path length of about 35 inches. The cell was placed in a converging beam just in front of the entrance slit where the beam is directed downward at an angle of about eight degrees. Except for the four 45 degree corners, the rays
were reflected from the walls of the channel at near grazing incidence. The physical length of the cell was determined by the more or less arbitrary requirements that a central ray of the beam be reflected from the bottom and top of the channel once and then that it enter the slit at the middle directed downward at an angle of about eight degrees. The efficiency of the brass channel for 200 K radiation was less than ten percent. It was at first thought that this low efficiency for the cell was due to the reflectivity of brass, however a test of a single reflection, near normal incidence, showed that brass, copper, and aluminum plates had about the same reflectivity, 85 to 90 percent for long wavelength radiation. By replacing the four 45 degree brass reflecting surfaces with aluminum mirrors, the efficiency of the cell was doubled. In replacing all the brass surfaces with aluminum mirrors, the efficiency of the cell, as measured with a light meter was found to be about 32 percent, a value deemed too small by the author to be usable. The low efficiency of the channel was attributed to the scattering of the beam, the large number of reflections, and for the aluminum cell the imperfections of the edges.

The second cell was made of conventional design except that the glass tube was cut on an angle so that the entire beam would pass through the cell and yet the volume of gas
required to fill, it could be held reasonably small. It was very difficult to make this cell vacuum tight and after breaking several glass sections it was decided that beveling of the glass tubing was a poor mechanical design.

The third absorption cell was made of stainless steel. The cell was made in the shape of the radiation beam as it converges toward the entrance slit and of the maximum length, eight and one fourth inches, that would fit within the vacuum housing of the spectrograph. The cell windows were polyethylene and these were sealed in place by "O-rings" and brass face plates.

The fourth cell was of the same style as the third type cell but larger. (Figure 5) By enlarging the openings in the cover for the source and filter unit and the spectrograph unit, a longer cell could be placed with one end in one unit and the other end in the other unit, part of the cell being in the sylphon bellows connection between the covers. This cell which is 18 inches long is made of stainless steel in the shape of the beam. In placing the cell in the beam, the cell is put within the source and filter unit, and the small end of the cell is then pulled through the bellows into the spectrograph and brought close to the entrance slit. When the cell is in position it is impossible to replace the filter grating with the usual mirror. In order to take care of this, an
additional mirror was made which could be set in front of the grating. The additional mirror changes the path from the source to the slit a negligible amount and the image can be centered on the slit with visible light. In removing the mirror, the grating, which would be more difficult to adjust, is left undisturbed in its regular position. The 18 inch cell was used in obtaining the data on phosphine, arsine, deuterated ammonia, deuterated phosphine, and deuterated arsine.
EXPERIMENTAL RESULTS

Phosphine

Spectrograms of PH₃ were obtained at pressures ranging from 15 to 60 cm of Hg. The phosphine lines showed no trace of inversion doubling. Figure 6 shows a section of one of the phosphine records. The one shown was made using the diamond-windowed Golay detector made available for our use by Elia's Burstein of the Naval Research Laboratories, Washington, D. C.* The signal-to-noise ratio of this detector was better by nearly a factor of two than that of the quartz-windowed detector which was used in recording most of the data.

A plot of one of the complete phosphine records is shown in Figure 7. No attempt was made to measure absolute intensities. The decrease in absorption indicated around 100 K was caused by changing filters which differed considerably in efficiencies. In the vicinity of 100 K there is a transition region for the spectrograph which may be recorded with either a filter grating or a reststrahlen and filter grating combination. The

* The author wishes to express his thanks to Elia's Burstein of the Naval Research Laboratories, Washington, D. C. for suggesting the use of a diamond window and for making the detector available.
Figure 7

PHOSPHINE

55 cm Hg Pressure

45 cm Path Length

Wave Numbers (K)

Absoption
The efficiency of the reatstrahlen introduced is, of the order of 40 percent, and because of this the slit width is usually changed considerably with a resultant change in the recorded line shape.

The frequencies of the observed rotational lines of phosphine in the lowest vibrational state are given in Table VII along with values of calculated frequencies obtained from the rotational constants derived from these rotational data. An indication of how well the derived quantities fit the observed data is shown by the difference between the calculated and observed frequencies.

It will be noted in Figure 7 that there are three series of lines. All three series of lines were observed to increase in intensity as the gas pressure within the cell was increased. These lines do not correspond to the spectra of the most probable contaminants, water and arsine. Table VIII lists the position of these two auxiliary series of lines; one of which is nearly twice as intense as the other. Each set of these lines is a consistent series as is shown by a plot of frequency versus J number. Figure 8 shows such a plot of the three series of lines obtained for phosphine.

The origin of the auxiliary series of lines for phosphine is most likely the vibrationally excited phosphine molecules. In Dennison's notation, \( \omega_2 \) (parallel) and \( \omega_3 \)
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TABLE VIII

POSITIONS OF SIDE ABSORPTIONS INgaben FAR INFRARED SPECTRUM OF PH₃
RELATIVE TO MAIN ABSORPTION

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(perpendicular) have values of 1012.8 K and 1145.9 K respectively. These modes have relatively low energies and should be populated in a ratio of 1.8 to 1.0 except that the perpendicular mode, , is doubly degenerate and thus the ratio of the number of molecules in to those in is 1.8 to 2.00. Although this difference is not large, the stronger set of side lines which appear on the low frequency side of the main lines is assigned to molecules in vibrational mode . The weaker set of side lines found on the high frequency side of the main lines is assigned to molecules vibrating in mode .

During the process of obtaining a spectrum of phosphine from one cell of gas, several sources burned out in rapid succession. This was attributed to phosphine leaking from the cell into the evacuated spectrograph and reacting with the hot water-glassed platinum source. As this reaction seemingly occurred while the spectrograph was at a few hundred microns of pressure and as the amount of phosphine lost from the cell was unnoticeable as far as producing a change of pressure within the cell, the amount of phosphine free within the spectrograph was extremely small. It would seem that a heated water-glassed platinum source might be an extremely sensitive detector of the presence of phosphine.
Arsine

A portion of an arsine spectrogram is shown in Figure 9. The record was made with the quartz-windowed Goly detector which was noisier than the diamond-windowed detector.

A complete plot of an arsine spectrum is shown in Figure 10. HCl was used in preparing the gas and it was a common, but not bothersome, contaminant. There were indications of side lines similar to those observed in phosphine in some of the spectrograms of higher cell pressure, but the noise level left their frequencies in doubt. The values of the observed rotational lines of arsine are given in Table IX along with frequencies calculated from the rotational constants derived from this data.

Deuterated Ammonia

The spectrograms of deuterated ammonia did not show inversion doubling. When a spectrum of ND₃ was obtained, at low cell pressures, the lines were single and quite sharp. A plot of a deuterated ammonia spectrum is shown in Figure 11. The gas used to obtain this spectrum was produced locally. NH₃ and D₂O were identified as contaminants. The frequencies of the observed and calculated rotational lines of deuterated ammonia are listed in Table X.
Figure 10

**ARSINE**

60 cm Hg Pressure  45 cm Path Length

![Graph showing absorption peaks for Arsine with wave numbers (K) ranging from 100 to 140 and HCl lines marked at 110 and 120.](image-url)
<table>
<thead>
<tr>
<th>J-value</th>
<th>Frequency</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Upper</td>
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</tr>
<tr>
<td>6:</td>
<td>7</td>
<td>52.33 K</td>
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<td>118.65</td>
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<td>16</td>
<td>17</td>
<td>125.84</td>
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<tr>
<td>17</td>
<td>18</td>
<td>132.98</td>
</tr>
<tr>
<td>18</td>
<td>19</td>
<td>140.27</td>
</tr>
</tbody>
</table>
Figure 11

DEUTERATED AMMONIA

45 cm Path Length 2 cm Hg Pressure

Absorption

Wave Numbers (cm⁻¹)

0 20 40 60 80 100 120 140 160 180 200

0 20 40 60 80 100
<table>
<thead>
<tr>
<th>J-value</th>
<th>Frequency</th>
<th>Difference</th>
</tr>
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<tbody>
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<td>181.98</td>
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<tr>
<td>18</td>
<td>19</td>
<td>191.73</td>
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</table>
Deuterated Phosphine

A plot of a calculated PD₃ spectrum, and a PH₃ spectrum is shown along with two spectra of PD₃ gas samples in Figure 12. It is not difficult to identify the PD₃ lines in the spectrum labeled "Best Sample" by comparing it with the calculated spectrum. However, in the PD₃ spectrum identified as "Poor Sample", it is very difficult to detect the presence of the deuterated phosphine but the PH₃ absorptions are very strong. Table XI gives the values of the PD₃ lines observed and those calculated from the rotational constants derived from the observed data.

In the series of spectrograms made attempting to obtain a pure spectrum, it seemed possible to identify some of the stronger additional lines as being associated with PDH₂ and PD₂H. These are listed in Table XII. The assignment of these lines was made by comparing spectrograms showing strong PD₃ and weak PH₃ absorptions with other spectrograms showing strong PH₃ and weak PD₃ absorptions. The additional strong lines in the spectrograms of the two extremes were not the same. In the samples with strong PH₃ as compared to PD₃, the additional strong lines were assigned to PH₂D. Similarly in the samples with strong PD₃ as compared to PH₃, the additional strong lines were assigned to PHD₂.
DEUTERATED PHOSPHINE

Calculated PO₃ Spectrum

Best Sample

Poor Sample

PH₃ Spectrum

Wave Numbers (K)
TABLE XI

POSITIONS OF MAIN ABSORPTIONS IN FAR INFRARED SPECTRUM OF PD₃

<table>
<thead>
<tr>
<th>J-value</th>
<th>Frequency</th>
<th>Difference</th>
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<tbody>
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<td>Lower</td>
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<tr>
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</table>
TABLE XII

PARTIALLY DEUTERATED PHOSPHINE

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<th>PH₂D</th>
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<td>58.9</td>
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<td>56.1</td>
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Deuterated Arsine

A portion of a spectrogram of AsD₃ is shown in Figure 13. A complete plot of a spectrogram is shown in Figure 14.

The rotational lines observed are listed in Table XIII along with the spectrum calculated from the rotational constants obtained from these data.
Figure 14

DEUTERATED ARSINE

45 cm Path Length, 35 cm Hg Pressure

Wave Numbers (K)
TABLE XIII

POSITIONS OF MAIN ABSORPTIONS IN
PAR INFRARED SPECTRUM OF AsD₃

<table>
<thead>
<tr>
<th>J-value</th>
<th>Frequency</th>
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</thead>
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<td>61.06</td>
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<td>68.64</td>
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<td>72.40</td>
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<td>19 20</td>
<td>76.26</td>
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<td>79.88</td>
</tr>
<tr>
<td>21 22</td>
<td>83.65</td>
<td>83.46</td>
</tr>
<tr>
<td>22 23</td>
<td>87.34</td>
<td>86.98</td>
</tr>
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</table>
ROTATIONAL CONSTANTS

The spectra of symmetric top molecules can be represented by the equation

\[ \nu = 2B(J+1) - \sqrt{D_J (J+1)^2} - 2D_{JK}(J+1)K^2 \]

and the selection rule \( \Delta J = \pm 1 \) and \( \Delta K = 0 \), and from the observed spectra some of the rotational constants have been obtained. The value of the rotational constants \( B \) and \( D_J \) were determined from the observed spectra by ignoring the contribution of the \( D_{JK} \) term and first solving the simultaneous equations in the two unknowns, \( B \) and \( D_J \). A plot was then made of the difference between the positions of the lines as calculated from the derived constants obtained from the simultaneous equations and the observed positions of the lines. The values of the derived constants \( B \) and \( D_J \) were then shifted to minimize the deviation of the position of the observed lines from the calculated spectra obtained from the derived quantities.

A comparison of the rotational constant \( B \) of each member of the family of molecules reported here with those calculated from the geometry of the molecules derived from the microwave data and the near infrared is given in
Table XIV. The microwave data of Loomis and Strandberg \[26\] were used in preparing this table. The near infrared values of Nielsen\[6\] were used for the phosphine and arsine, and the work of Berlad \[18\] was used for deuterated ammonia.

Table XV shows a comparison of the observed centrifugal stretching coefficients with those calculated from the near infrared data. It will be noted that the observed quantities are consistently smaller than the calculated ones. A part of this difference may be accountable for by the fact that a single rotational line is made up of components, one for each value of \(K\), which do not coincide exactly. The term \(4D_J K^2 (J + 1)\) causes a slight shift in the line, as observed, toward higher frequency and thus appears to decrease the convergence of the lines caused by centrifugal stretching. In the Table XV are also the values of \(4D_J K\) as computed by the method of Slawsky and Dennison \[13\] from the near infrared data.

---

* A personal communication.
TABLE XIV

ROTATIONAL CONSTANTS $B_{\nu_1 \nu_2 \nu_3 \nu_4}$

<table>
<thead>
<tr>
<th></th>
<th>Near Infrared</th>
<th>Far Infrared</th>
<th>Microwave</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphine</td>
<td>$B_{0000}$</td>
<td>4.453 K</td>
<td>4.454 K</td>
</tr>
<tr>
<td>Phosphine</td>
<td>$B_{0100}$</td>
<td>4.57</td>
<td></td>
</tr>
<tr>
<td>Phosphine</td>
<td>$B_{0001}$</td>
<td>4.30</td>
<td></td>
</tr>
<tr>
<td>Arsine</td>
<td>$B_{0000}$</td>
<td>3.714</td>
<td>3.745</td>
</tr>
<tr>
<td>Deuterated Ammonia</td>
<td>$B_{0000}$</td>
<td>5.109</td>
<td>5.143</td>
</tr>
<tr>
<td>Deuterated Phosphine</td>
<td>$B_{0000}$</td>
<td>2.308</td>
<td>2.316</td>
</tr>
<tr>
<td>Deuterated Arsine</td>
<td>$B_{0000}$</td>
<td>1.891</td>
<td>1.918</td>
</tr>
</tbody>
</table>
TABLE XV

THE CENTRIFUGAL STRETCHING COEFFICIENTS

OF 4D_J AND OF 4D_JK

<table>
<thead>
<tr>
<th></th>
<th>4D_J</th>
<th></th>
<th>4D_JK</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Observed</td>
<td>Calculated</td>
</tr>
<tr>
<td>PH_3</td>
<td>0.000543 K</td>
<td>0.000421 K</td>
<td>0.000577 K</td>
</tr>
<tr>
<td>AsH_3</td>
<td>0.000396</td>
<td>0.000290</td>
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</tr>
<tr>
<td>ND_3</td>
<td>0.000736</td>
<td>0.000540</td>
<td>0.000780</td>
</tr>
<tr>
<td>PD_3</td>
<td>0.000123</td>
<td>0.000095</td>
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</tr>
<tr>
<td>AsB_3</td>
<td>0.000096</td>
<td>0.000070</td>
<td>0.000112</td>
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</table>
SUMMARY

The results of this investigation are as follows:

Phosphine (PH₃)

Fourteen previously unreported rotational lines of phosphine have been added to the four lines reported by Wright and Randall (1).

Arsine (AsH₃)

This is the first reported rotational spectrum of arsine. Fourteen lines are reported.

Deuterated Ammonia (ND₃)

Eight previously unreported rotational lines of deuterated ammonia have been added to the six reported earlier by Barnes (5).

Deuterated Phosphine (PD₃)

This is the first reported rotational spectrum of deuterated phosphine. Eleven lines are reported.

Deuterated Arsine (AsD₃)

This is the first rotational spectrum of deuterated arsine. Ten lines are reported.

The rotational constants for these molecules have been computed and compared with those derived from the near infrared and microwave data.
PROPOSED INVESTIGATIONS

Some extensions to the study of this family of molecules might be made in the following directions:

An investigation of the rotational spectra of these molecules in their higher vibrational states could be made.

A study of the rotational spectra of some of the partially deuterated members of this family of molecules could be made. This investigation would involve some problems of sample preparation and analysis of the spectra.

The rotational spectrum of stibine might be sought if an absorption cell of a few meters path length were available.

The rotational spectrum of each of the molecules reported on Hera might be extended to lower frequencies with the extension of the range of the spectrograph.
APPENDIX I

THEORETICAL WORK EMPLOYED

Appendix I is an outline of the method used to obtain the predicted rotational spectra. References are made to previous work and modifications of them.

The general form of the energy expression of the rotational and vibrational states has been investigated by means of wave mechanics. The energies for a given system are the eigenvalues of the Schroedinger equation:

\[ H \psi = E \psi \]

where \( H \) is the quantum mechanical Hamiltonian of the system and \( \psi \) is a well behaved eigenfunction corresponding to the energy value \( E \).

The quantum mechanical Hamiltonian is an operator related to the total energy of the vibrating-rotating molecule and which depends upon the masses of the atoms, the geometry of the molecule and the forces holding the molecule together. Nielsen (53) has set up the Hamiltonian for the general polyatomic molecule and has separated this complicated expression into parts \( H_0, H_1, \) and \( H_2 \) which contribute to the energy in the zeroth, first, and second orders respectively. He has substituted the Hamiltonian
into the Schrödinger equation and has obtained an expression for the energy term value to the second order of approximation. Shaffer (42) has solved this problem specifically for the pyramid \( \text{XY}_3 \) molecules and has given the energy expression to second order as follows:

\[
\frac{\varepsilon}{\hbar c} = G + F - 2 \mathcal{A} \left( \pm \ell \mathcal{J} \pm \ell \nu \mathcal{S} \right) \mathcal{K},
\]

where \( G \) is the vibrational portion and \( F \) the rotational term;

\[
G_{\text{vib}} = G_0 + \sum \omega \left( v + \frac{d \omega}{d v} \right) + \sum G \left( v + \frac{d \omega}{d v} \right)^2 + \sum G \left( v + \frac{d \omega}{d v} \right) + \sum \left( v + \frac{d \omega}{d v} \right) + \sum \rho_2 \left( \ell^2 - 1 \right) + g_{uv} \left( \ell^2 \right) + g_{uv} \ell \ell \nu \nu.
\]

\[
F_{\text{rot}} = B_v \mathcal{J} \left( \mathcal{J} + 1 \right) + \left( B_r - \mathcal{B}_r \right) \ell^2 + D_k \mathcal{J} \left( \mathcal{J} + 1 \right) \left( \ell^2 + \ell^2 \right) + D_k \mathcal{K} \ell^2
\]

In the vibrational term, \( G \), the quantities \( G_0 \), \( G_{nn} \), \( G_{mn} \), \( G_{22} \), \( G_{24} \), and \( G_{44} \) are complicated functions of the potential constants and the normal frequencies, \( \omega \); \( \mathcal{A} \) is a weight factor which denotes the degree of degeneracy of the \( i \)th normal mode; \( v \) are the vibrational quantum numbers and \( \ell \) and \( \nu \) are additional quantum numbers associated with the two degenerate modes of vibration or internal angular momentum.

In the rotational term, \( J \) is the quantum number.
associated with the total angular momentum of the molecule; $K$ is the quantum number associated with the component of angular momentum directed along the symmetry axis; $D_J$, $D_{JK}$, and $D_K$ are the centrifugal distortion constants which are functions of the atomic mass, the normal frequencies and the force constants of the molecules. $B_v$, $C_v$, and $C_e$ are reciprocals of inertia:

$$\begin{align*}
B_v &= \frac{\hbar}{\gamma \pi c I_{xy}}; & A_e &= \frac{\hbar}{\gamma \pi c I_{yy}}; \\
B_r &= \frac{\hbar}{\gamma \pi c I_{xx}}; & A_r &= \frac{\hbar}{\gamma \pi c I_{yy}}
\end{align*}$$

where the subscripts $v$ and $e$ denote the value of the quantity in the $v$th vibrational state and equilibrium state respectively, and $S_{\kappa}$ are the parameters of the magnitude of the vibrational angular momentum in the degenerate modes $\omega_v$ and $\omega_v$. (Figure 15)

The quantity $\omega \cdot A\{\pm l_{\kappa} S_{\kappa} \pm e_{\kappa} S_{\kappa}\} \kappa$ is the Coriolis interaction term brought about by the internal angular momentum of the $X$ atom as it oscillates as a two dimensional oscillator during the perpendicular vibrations $\omega_v$ and $\omega_v$. Teller (40) has shown that the internal angular momentum caused by this two dimensional oscillator has the magnitude $S_{\kappa}$, where $-l \leq S_{\kappa} \leq l$. The $S_{\kappa}$ are the Teller parameters.

The selection rules are obtained by considering the integrals of the components of the dipole moment, $M_x$;
Figure 15: Normal Modes of Vibration

\[ \omega_1, \omega_2, \omega_3, \omega_4 \]
where the integrals of the eigenfunctions and the component of the dipole are taken over configuration space. The nonvanishing integrations provide the selection rules. The selection rule for vibrational transitions is

\[ \Delta u = 0, \pm 1, \pm 2, \ldots \]

The rotational transitions are controlled by two sets of selection rules depending upon the mode of oscillation. Dennison (46) has obtained these selection rules. They are as follows:

When the dipole moment is oscillating parallel to the symmetry axis i.e. \( \Delta K = 0 \):

\[ \Delta J = \pm 1, \text{ when } K = 0 \]

and \( \Delta J = 0, \pm 1, \text{ when } K = 0 \).

When the dipole moment is oscillating perpendicular to the symmetry axis \( \Delta K = \pm 1, \Delta J = 0, \pm 1 \).

The selection rule for the internal angular momentum has been determined by Teller (40) and is \( \Delta K = \Delta J = \pm 1 \).

In the parallel rotation-vibration band, for each value of \( K \), there is a series of lines for \( \Delta J = 0 \) which is called the Q branch, a series of lines for \( \Delta J = -1 \), called the P branch, and a similar set for \( \Delta J = +1 \) called the R branch. These three branches collectively, for a
particular value of \( K \), are called a sub-band; and that for all values of \( K \) is a complete fundamental parallel band.

If we consider the \( Q \) branch \((\Delta J = 0)\), \( v_1 = 0 \) -- lower state indicated by the double primes -- when

\[
\frac{E''}{\hbar c} = G'' + B'' J(J+1) + (A''-B'')K^2;
\]

and the first excited state, \( v_1 = 1 \) -- upper state indicated by the single primes -- where

\[
\frac{E'}{\hbar c} = G' + B' J'(J'+1) + (C'-B')K^2;
\]

a transition between these states gives an energy difference:

\[
\frac{E'-E''}{\hbar c} = \nu = \nu_o + J''(J''+1)(B'-B'') + \left[ (A'-A'') - (B'-B'') \right] K^2
\]

where \( \nu_o = G'' - G' \). If the quantity \( \left[ (A'-A'') - (B'-B'') \right] K^2 \) is small, the \( Q \) branch of the parallel mode sub-bands will nearly coincide. In the \( R \) and \( P \) branches, \( \Delta J = J' - J'' = \pm 1 \) or \( J' = J'' \pm 1 \), \( K = 0 \), it one considers \( B' = B'' \), the energy difference reduces to

\[
\frac{E'-E''}{\hbar c} = \nu_o + 2B(J+1) \right)
\]

Then the branches will consist of equally spaced lines \( 2B \) apart. Usually, however; \( B'' \) is larger than \( B' \) and this fact causes the \( P \) branch to diverge and the \( R \) branch to converge with increasing \( J \) numbers.

One can obtain \( B' \) and \( B'' \) from the combination relations:

\[
R(J-1) - P(J+1) = 2B''(2J+1) = \Delta, F''(J)
\]
\[ R(J) - P(J) = 2B'(2J+1) = \Delta_c F''(J) \]
and
\[ R(J) + P(J) = 2 \Theta + 2(B' - B'')J. \]

These relations are obtained by finding the difference or sum as indicated between judiciously chosen lines in the P and R branches. A plot of the indicated sum or difference, for all possible values of \( J' \), against \( (2J'' + 1) \) for the first two or against \( J' \) for the third, has as slopes \( 2B'' \), \( 2B' \), and \( 2(B' - B'') \) respectively. The intercept of the third relation is \( 2 \Theta \).

From an analysis of the parallel bands of a molecule and its deuterated companion, one is able to determine the geometry of the molecule. The moment of inertia perpendicular to the symmetry axis can be found from the reciprocal of inertia. Then it can be shown that for a pyramidal \( XY_3 \) molecule that this moment of inertia is

\[ \bar{I}_{xy} = \frac{3m}{2} h^2 \left[ \frac{1}{2} \hbar \omega \beta + \frac{M}{3m + M} \right], \]

where \( M \) is the mass of the X atom, \( m \) is the mass of the Y atom, \( h \) is height of the pyramid, and \( \beta \) is the angle between the altitude and an X-Y bond. If the assumption is made that the geometry of the deuterated and non-deuterated are the same from the moments of inertia of the two molecules, the unknown \( h \) can be eliminated:

\[ \frac{\bar{I}_{xy}}{I_{xy}} = \frac{m}{M} \left[ \frac{1}{2} \hbar \omega \beta + \frac{M}{3m + M} \right]. \]
where the \( m' \) refers to deuterium as a Y atom.

As this expression is in terms of only one unknown, we may solve for it and have:

\[
\tan^2 \beta = 2 \left\{ \frac{m'B}{m'B'} \left[ \frac{M'}{3m' + M} \right] - \frac{M}{3m' + M} \right\} \left( 1 - \frac{m'B}{m'B'} \right)
\]

With the \( \Delta \) known, substitution of this quantity into

\[
I_{xx} = 3m' \hbar^2 \left[ \tan^2 \beta + \frac{M'}{3m' + M} \right]
\]

enables the height of the molecules to be determined. The X-Y distance, \( r \), is given by

\[
r = \frac{\hbar}{\cos \beta}
\]

and the angle Y-X-Y is found from

\[
\frac{\sqrt{2}}{2} \sin \beta = \sin \frac{\Delta}{2}
\]

The moment of inertia of the molecule about its symmetry axis is obtained from the relation

\[
I_{zz} = 3m' \hbar^2 \tan^2 \beta.
\]

The relations used to determine the geometry of the molecule were originally based on the equilibrium values of the reciprocals of inertia, but in the determination of \( \Delta \beta \), only the ratio of the reciprocals is involved; so the dimensions of the molecule are determined unambiguously.

The perpendicular bands likewise consist of a superposition of sub-bands, one for each value of \( K \). Each sub-band has the appearance of a parallel band, but even if the rotational constants do have the same value in the
upper and lower states, the respective Q branch lines will not fall together unless the value of $2k\left[(1-\xi^2)A - B\right]$ is zero. The splitting of the Q branch thus makes it possible to determine one of Teller's parameters, $\xi$. If the Q branch is not split, a series of lines is found with spacing $2(1-\xi^2)A$, in the $\text{R}_{\text{F}}\text{P}_{\text{R}}$ and $\text{R}_{\text{P}}\text{P}_{\text{P}}$ branches, that is for transitions $\Delta J = +1$, $\Delta K = \pm 1$ and $\Delta J = -1$, $\Delta K = \pm 1$, assuming $B'' = B'$ and $C'' = C'$. One or other of these quantities $[1-\xi A - B]$ or $2(1-\xi^2)A$ is available and may be used to determine two of the Teller parameters and thus the normal frequencies.

Nielsen (53) has shown that to the second order, the only kinds of resonance that need be considered are the Fermi-Dennison type and the Coriolis type. The Fermi-Dennison interaction is between a fundamental frequency $\omega$, and a combination frequency $\omega + \omega_k$, which principally causes a shift of the vibration band centers. The Coriolis interaction occurs between two fundamentals and changes the effective moments of inertia and causes anomalous spacing of the rotational lines. Nielsen (44) has shown that between $\omega$ and $\omega_v$ of PH$_3$ and AsH$_3$ there is a strong Coriolis interaction and Haynie (33) has observed the same in SbH$_3$.

A determination of the normal frequencies and an evaluation of the potential constants of the pyramidal XY$_3$. 
molecules is based upon the separation of the problem into two parts or symmetry classes. There are $3N-5$ normal frequencies to be determined of which two pairs are degenerate. The four degenerate modes constitute one symmetry class, the perpendicular modes. The remaining two normal frequencies are of oscillations along the symmetry axis of the molecule and they are called the parallel frequencies. As there are only four independent fundamental frequencies, there are only six independent potential harmonic force constants.

The symmetry coordinates used in the discussion of the $XY_3$ molecules are those of Dennison (15). For the two parallel frequencies a coordinate $\mathcal{S}$ is used to denote the displacements from the equilibrium positions of the $Y$ atoms in their plane. Each atom approaches the axis of the pyramid by an amount $\mathcal{S}/3$. The second coordinate is $z$ which measures the displacement of the $X$ atom along the symmetry axis away from or relative to the $Y_3$ plane. As these two coordinates are perpendicular to each other, the kinetic energy will be the sum of these kinetic energies:

$$2\overline{T} = \hbar \mathcal{S}^2 + \mu z^2,$$

* The number of independent potential constants is $\frac{1}{2} \sum_{\nu} (\nu + 1)$ if there are no degeneracies and $\frac{1}{2} \sum_{\nu} \nu (\nu + 1)$ with degeneracy where the sum is taken over the various symmetry classes.
where \( \mu = \frac{2mM}{2m+M} \) is the reduced mass. The potential energy function is quadratic in the coordinates;

\[
2V = a \xi^2 + b \zeta^2 + 2ce \zeta^2
\]

with three unknown potential constants \( a, b, \) and \( c. \)

Setting up the secular determinant,

\[
\begin{vmatrix}
\mu \lambda - a & -c \\
-c & m \lambda - b \\
\end{vmatrix}
\]

and, solving for \( \lambda \) which is equal to \( \sqrt{\pi} \) times the normal frequencies \( \omega \), the following relationships are found for the normal frequencies:

\[
\lambda_1 + \lambda_3 = \frac{a}{\mu} + \frac{a}{m}
\]

and

\[
\lambda_1 \lambda_3 = \frac{ab - c^2}{\mu m}
\]

It is at once apparent that to determine the three parallel potential constants it will be necessary to know more than two normal parallel frequencies of a single \( XY_3 \) molecule. However, with the additional information from the same molecule but with deuterium substituted for the hydrogens, the problem is solvable, provided the normal frequencies are known.

In order to determine the normal frequencies, Nielsen has developed a method for the parallel frequencies.
similar to the one Dennison (15) has used for the perpendicular frequencies. If one takes the relation,
\[ \lambda_1 \lambda_2 = \frac{a b - c^2}{m m'} \]
and sets up a ratio of the quantities from the deuterated and non-deuterated molecules; a product relationship,
\[ \left( \frac{\omega_2 \omega_3}{\omega_1 \omega_3} \right)^2 = \frac{m m'}{m m} \]
is obtained, where the primed quantities pertain to the deuterated molecule. In the simplification to this form, the assumption is made that the potential constants of the two molecules are the same. Such an assumption is similar to the earlier one of assuming the geometries of the two molecules to be the same.

Expressing the normal frequencies in terms of the position of the fundamental band centers by means of an anharmonic correction factor, to be determined later, the product relation expressed above can be reduced to an equation of two unknowns. In so doing, the normal frequency may be written as \( \omega_c = \nu_c (1 + \alpha_c) \); and that of the isotopic molecule as \( \nu_c' = \omega_c' (1 - \frac{\omega_c'}{\omega_c} \alpha_c) \), or
\[ \omega_c' = \nu_c' \left( 1 + \frac{\nu_c'}{\omega_c'} \alpha_c \right), \]
which is approximately
\[ \omega_c' = \nu_c' \left( 1 + \frac{\nu_c'}{\nu_c} \alpha_c \right), \]
where in the unknowns are the \( \alpha_c \).

Substituting these in the product relation reduces it to
an equation in two unknowns, namely $\alpha_1$ and $\alpha_3$

$$\frac{\omega_1, \omega_3}{\omega'_1, \omega'_3} = \frac{\nu_1 \nu_3 \left( 1 + \frac{\nu'_1}{\nu'_3} \alpha_1 + \frac{\nu'_3}{\nu'_3} \alpha_3 \right)}{\nu'_1 \nu'_3 \left( 1 + \frac{\nu'_1}{\nu'_3} \alpha_1 + \frac{\nu'_3}{\nu'_3} \alpha_3 \right)} = \left( \frac{m \nu_1}{m \nu_3} \right)^{\frac{1}{2}} \tag{a}$$

where the terms $\alpha_1, \alpha_3$ and $\alpha_1 \frac{\nu'_1}{\nu'_3} \alpha_3$ have been disregarded as being of second order. It is necessary now to find another equation in terms of these unknowns in order to solve for the normal parallel frequencies.

Shaffer (42) has shown that the Coriolis coupling factor $\hat{c}$ between normal $\omega_1$ and $\omega_3$ can be expressed as

$$\hat{c} = \gamma \left[ \alpha \left( 1 - \hat{c}^2 \right)^{\frac{1}{2}} + \frac{1}{\sqrt{2}} \beta \right] \hat{c}.$$

Nielsen (44) has subsequently shown that for the pyramidal $XY_3$ molecules $\hat{c}_{12}$ is approximately zero. If one assumes $\hat{c}_{12}$ is identically zero, a second equation in $\alpha_1$ and $\alpha_3$ is obtainable.

In the equation $\alpha^2 \left( 1 - \hat{c} \right) = \frac{1}{2} \beta \hat{c}^2$ the notation has the following meaning:

$\alpha$ and $\beta$ are the roots of the secular equation written as

$$\alpha^2 = \frac{1}{2} \left[ 1 + \left( \frac{a_1 - b_1}{a_2 - b_2} \right)^2 \left[ \frac{\nu_2^2}{\nu_1 m} + \left( \frac{a_1 - b_1}{a_2 - b_2} \right)^2 \right]^{\frac{1}{2}} \right]$$

$$\beta^2 = \frac{1}{2} \left[ 1 - \left( \frac{a_1 - b_1}{a_2 - b_2} \right)^2 \left[ \frac{\nu_2^2}{\nu_1 m} + \left( \frac{a_1 - b_1}{a_2 - b_2} \right)^2 \right]^{\frac{1}{2}} \right]$$

and

$$\hat{c} = \left( 1 - \frac{\nu_2^2}{\nu_1 \nu_3} \right)^{\frac{1}{2}}.$$

Substitution of these quantities into the first relationship and subsequent reduction provides the equation
Using this equation, the frequencies

\[ \omega_1 = \frac{1}{\sqrt{2}} \left\{ \left( \frac{a}{w} - \frac{b}{m} \right) + \left[ \left( \frac{a}{w} - \frac{b}{m} \right)^2 + \frac{4c^2}{w^2m^2} \right] \right\}^{\frac{1}{2}} \]

\[ \omega_3 = \frac{1}{\sqrt{2}} \left\{ \left( \frac{a}{w} + \frac{b}{m} \right) - \left[ \left( \frac{a}{w} + \frac{b}{m} \right)^2 + \frac{4c^2}{w^2m^2} \right] \right\}^{\frac{1}{2}} \]

may be written as,

\[ \omega_1 = \frac{1}{\sqrt{2}} \left\{ \left( \frac{a}{w} - \frac{b}{m} \right) + c \left( \frac{a}{w} - \frac{b}{m} \right) \right\}^{\frac{1}{2}} \]

and \( \omega_3 = \frac{1}{\sqrt{2}} \left\{ \left( \frac{a}{w} - \frac{b}{m} \right) - c \left( \frac{a}{w} - \frac{b}{m} \right) \right\}^{\frac{1}{2}} \)

and squaring these, we obtain:

\[ \omega_1^2 = \frac{1}{2} \left\{ (1+c) \frac{a}{w} + (1-c) \frac{b}{m} \right\} \]

and \( \omega_3^2 = \frac{1}{2} \left\{ (1-c) \frac{a}{w} + (1+c) \frac{b}{m} \right\} \).

Multiplying the \( \omega_1 \) by (1-C) and taking from this \( \omega_3 \) times (1+C), and simplifying produces the equation

\[ (1-C) \omega_1^2 - (1+C) \omega_3^2 = -C \frac{2b}{m} , \]

or

\[ b = \frac{m}{2C} \left\{ (C-1) \omega_1^2 + (C+1) \omega_3^2 \right\} \]
However, it is also apparent that

$$\mu \left( \omega_1^2 + \omega_2^2 \right) - \mu' \left( \omega_1^2 + \omega_3^2 \right) = b \left( \frac{\omega_1}{m} - \frac{\omega_3}{m} \right)$$

and, substituting the value just obtained for the potential constant \(b\), the following equation is arrived at:

$$\mu \left( \omega_1^2 + \omega_2^2 \right) - \mu' \left( \omega_1^2 + \omega_3^2 \right) = \frac{m}{2e} \left[ (\zeta - 1) \omega_1^2 + (\xi' - 1) \omega_3^2 \right] \left( \frac{\omega_1}{m} - \frac{\omega_3}{m} \right)$$

[6]

Now, expressing the normal frequencies in terms of an anharmonic factor and the observed band centers and discarding as of second order the anharmonic factors squared, that is:

$$\omega_1 = \nu_1^2 \left( 1 + 2 \alpha_1 + \alpha_1^2 \right) \simeq \nu_1^2 \left( 1 + 2 \alpha_1 \right)$$

$$\omega_3 = \nu_3^2 \left( 1 + 2 \alpha_3 + \alpha_3^2 \right) \simeq \nu_3^2 \left( 1 + 2 \alpha_3 \right)$$

$$\omega_1' = \nu_1'^2 \left( 1 + 2 \frac{\nu_1'}{\nu_1} \alpha_1 + \frac{\nu_1'^2}{\nu_1^2} \alpha_1^2 \right) \simeq \nu_1'^2 \left( 1 + \frac{2 \nu_1'}{\nu_1} \alpha_1 \right)$$

and

$$\omega_3' = \nu_3'^2 \left( 1 + 2 \frac{\nu_3'}{\nu_3} \alpha_3 + \frac{\nu_3'^2}{\nu_3^2} \alpha_3^2 \right) \simeq \nu_3'^2 \left( 1 + \frac{2 \nu_3'}{\nu_3} \alpha_3 \right)$$

equation [6] reduces to one in terms of only two unknowns, namely \(\alpha_1\) and \(\alpha_3\). Now with equation [9] and equation [6], it is possible to determine \(\alpha_1\) and \(\alpha_3\), and then the normal parallel frequencies. Once the normal frequencies are found, the parallel potential constants \(a\), \(b\), and \(c\) can be evaluated except for the sign of \(c\). Howard (24) has shown that the potential function of ammonia is primarily of the
valence type, so c is assigned a positive sign.

In discussing the perpendicular frequencies, the method of Sutherland, Lee, and Wu (25), and the coordinates of Slawsky and of Dennison (13) are used wherein the displacement of the X atom from a line drawn perpendicular to the Y$_3$ plane and through the center of gravity of the X atom is called $x$. There are two directions possible for a displacement, perpendicular to the symmetry axis so a complementary coordinate $y$ is necessary. A second set of coordinates $\xi$ and $\eta$ denote the two motions of the Y$_3$ atoms in their plane. The kinetic energy for the perpendicular frequencies can then be written as

$$2T = m \kappa (\dot{x}^2 + \dot{y}^2) + m (\dot{\xi}^2 + \dot{\eta}^2),$$

where $\kappa = \frac{uB}{2m\bar{H}}$, and $C$ and $B$ are the reciprocals of inertia. In the potential energy, the coordinates must appear quadratically and equivalently so the potential energy becomes,

$$2V = \alpha (x^2 + y^2) + \beta (\xi^2 + \eta^2) + 2\gamma (x\xi + y\eta).$$

Rewriting the kinetic and potential energies taking into account the dualness of the coordinates:

$$2T = m \kappa \dot{\sigma}^2 + m \dot{\phi}^2,$$

$$2V = \alpha \sigma^2 + \beta \phi^2 + \gamma \sigma \phi,$$

and forming the secular determinant:
one finds that the normal frequencies are then related by
\[ \lambda_1 + \lambda_2 = \frac{\alpha}{m} \lambda + \frac{\beta}{m} \]
and
\[ \lambda_1 \lambda_2 = \frac{\alpha \beta - \gamma^2}{m^2 \lambda \lambda'}. \]

Again it is evident that to determine the potential constants, it is necessary to have data from an isotopic companion molecule of the one being studied, for there are only two independent perpendicular frequencies to determine three independent potential constants.

The ratio formed of \( \lambda_1 \lambda_2 = \frac{\beta - \gamma^2}{m^2 \lambda \lambda'} \) for the plane and isotopic molecules provides the Teller–Redlich relation, \( \left( \frac{\omega_x \omega_x}{\omega_y \omega_y} \right)^2 = \frac{m \cdot k'}{m \cdot k} \)
where \( k = \frac{n_x I_{xx}}{2m I_{xx}} \) and \( k' = \frac{n_x' I_{xx}'}{2m' I_{xx}'} \).

Adjusting the frequencies according to the method of Dennison (15), the following relation is obtained:

\[ \left( \frac{m \cdot k'}{m \cdot k} \right)^2 = \frac{\nu_x \omega_y (1 + \alpha \nu \nu)}{\nu_x' \omega_y' (1 + \alpha \nu \nu')}, \quad [6] \]
when the terms \( \alpha_1 \gamma_1 \) and \( \alpha_2 \gamma_2 \) have been discarded as being terms of second order. This, then, provides one equation \([c]\) in terms of the two unknown anharmonic factors \( \alpha_1 \) and \( \gamma_1 \).

The second equation in terms of these two unknowns \( \alpha_1 \) and \( \gamma_1 \) has been derived by Dennison (15) from the observed spacing of the fine structure of the perpendicular bands. The most prominent feature of a perpendicular band is usually the individual Q branches which are separated one from another by

\[
\alpha = \left[ (1 - \gamma) \alpha - \beta \right].
\]

If the separation of the Q branches is inobservably small, it is often possible to identify lines and their J values. If this is possible, as it is in some cases with \( \omega_\gamma \), one is able to obtain an average spacing between successive component lines for which \( J = K \). This spacing in the R branch is then

\[
2 \left( 1 - \gamma \right) \alpha = \gamma.
\]

If one of the Teller parameters \( \gamma_\alpha \) or \( \gamma_\gamma \) can be found, it is possible to determine the other by use of the relation

\[
\gamma_\alpha + \gamma_\gamma = \frac{\Gamma_{gg}}{2\Gamma_{ss}} - 1.
\]

Once knowing the Teller parameters, a quantity \( \gamma \) is
determined by
\[
\xi_i = \left[ \frac{I_{ii} \xi_i}{2 L_{xx}} - \xi_i \right] / \left[ 1 + \xi_i \right]
\]
and the relation of \( \xi_i = 1 / \xi_i \), and all the quantities to fill out the equation of Dennison are now available,
\[
[m k'(\omega_i^2\omega_i^2)] - [m k'(\omega_i^2\omega_i^2)] = \frac{(k'k') \left[ m_{ii} \omega_i^2 + m_{ij} \omega_j^2 \right]}{(\xi_i^2 + \xi_i)} \quad [n]
\]
The derivation of this equation from the fine structure of the perpendicular bands is made possible by the relation of \( \xi_i \) to the potential constant squared,
\[
\xi_i = \frac{2m B R^2}{\mu \lambda \left( \mu / \lambda - \beta \right)^2}
\]
When the normal frequencies are expressed in terms of the observed band centers and an anharmonic term, Dennison's equation \([a]\) provides a second relationship in the two unknowns \( \omega_i \) and \( \omega_j \) by means of which the value of these quantities can be determined. The normal frequencies can be found from the equations
\[
\omega_i = \nu_i (1 + \alpha_i) \quad \omega_i' = \nu_i' (1 + \frac{\beta_i}{\epsilon_i} \alpha_i)
\]
\[
\omega_\nu = \nu_\nu (1 + \alpha_\nu) \quad \omega_\nu' = \nu_\nu' (1 + \frac{\beta_\nu}{\epsilon_\nu} \alpha_\nu).
\]
The potential constants \( \alpha \), \( \beta \), and \( \gamma \) can be obtained from
\[
\lambda_i + \lambda_\nu = \frac{\alpha}{m k} + \frac{\beta}{m}
\]
\[
\lambda_i' + \lambda_\nu' = \frac{\alpha}{m k'} + \frac{\beta}{m'}.
\]
* A derivation of this equation appears in (33).
A positive sign is assigned to $\beta$ because the bonding is primarily of the valence type and the analysis of the near infrared spectrum is complete. The geometry of the molecule and the six potential constants are known.

The effects of centrifugal stretching on the spectra of molecules was first noted by Wright and Randall (1) when they observed a divergence from the 2B spacing of the rotation lines in the far infrared. Slawsky and Dennison (13) have worked out this problem for the XY$_3$ molecules, and their theoretical work was used to obtain the predicted spectra.

The energy expression which Slawsky and Dennison found for these molecules is as follows:

$$W_{\frac{J}{K}} = \frac{\hbar}{2I_B} \left( \frac{J}{I_A} - \frac{1}{I_3} \right) \frac{h}{\hbar} K - \left( \frac{2}{I_B} \right) J(J+1) + 2 \left( \frac{1}{I_B} \right) J(J+1) + 2 \left( \frac{1}{I_B} \right) J(J+1).$$

The $\mathcal{P}$'s in this expression are functions of the potential constants of the molecule and two distances within the molecule. They are as follows:

$$\mathcal{P}_1 = \mathcal{G} \left\{ \frac{a_{12} c}{a B - c^2} + \frac{a_{23} c}{a B - c^2} + \frac{a_{31} c}{a B - c^2} \right\},$$

$$\mathcal{P}_2 = \frac{1}{2} \left( \frac{2}{I_B} \right) \mathcal{G} \left\{ \frac{a_1^2}{3 (a B - c^2)} \right\}.$$
The two internal dimensions of the molecule are the distance of a Y atom from the symmetry axis and the distance of the plane of the three Y atoms from the center of gravity of the molecule. Once the potential constants and the geometries of the molecules are known, the \( P' \)s can be found and the energy levels determined.

The selection rules for the rotational spectrum are \( \Delta J = \pm 1, \Delta K = 0 \) and the frequencies of the transitions to be observed are thus given by

\[
\nu = \frac{\hbar^2}{2I_\theta} \left[ 2J + \sqrt{(P_2 - P_3) J} - \sqrt{P_1 P_3^3} + \sqrt{(P_1 - P_3 - 2P_3)} J \right] \]

It is from this formula that the expected rotational spectra were predicted.
APPENDIX II

NOTES ON PREPARATION OF GASES

These gases should be prepared only in a hood. Be sure the hood is functioning properly. Keep the doors of the hood as nearly closed as possible at all times.

It is necessary to have provisions made so that it is possible to equalize the pressure in every part of the generating system at all times. It is desirable that this plan conserves the gas. It is not advisable to let the gases go unconfined.

Phosphine

Calcium phosphide may be kept in a freshly filled desiccator. This retards the hydrolyzation because the atmosphere about it is confined. It appears as though the drying agent is dried by this procedure. The generating system must be airtight. The pressure within the generator must be closely watched as the yield (87 per-cent) is high and the pressure can become excessively high in a short time if the drying tube should plug. Only the coarsest drying agent is usable while working with commercial calcium phosphide. A portion of the drying agent should be left in front of the main section of the drying tube upon which some of the impurities resulting from the
reaction may be deposited prior to a place where such action might hinder the gas flow. When finished, the generating system should not be opened to the air until it has been evacuated and the system has been flushed out a few times with the inert carrier gas otherwise the residual phosphine will burn. If this is partially confined at atmospheric pressure, the glass will be broken. A copper sulfate solution turns black when phosphine is bubbled through it. This serves as a good pressure indicator and neutralizer at a position where the phosphine gas is not wanted. $P_2H_2$ and $P_2H_4$ may be formed at the same time $PH_3$ is produced in the above reaction. These gases are spontaneously explosive. An explosion is the only indication of their presence.

**Arsine**

The success that was had in making $AsD_3$ from sodium arsenide suggests that this method of Saunders (52) might be used in preparing $AsH_3$.

In the usual method of preparing $AsH_3$ from $As_2O_3$, the normality of the acid is critical. An excess of acid causes a reduction of the arsine formed and a deficiency reduces the yield. HCl of 0.2 normality works quite well.

It is fortunate that the $As_2O_3$ is only slightly soluble so that with due care it can be weighted and measured safely. A fraction of a gram of $As_2O_3$ is lethal.
However, this insolubility causes arsenic trioxide to precipitate out of the solution if it is placed in the freshly boiled HCl. This difficulty can be circumvented by putting a larger portion of dry As₂O₃ in with the magnesium turnings. It should be remembered that 0.2 normal solution is desired and that a drop of 0.2 normal solution on say 100 cc of solution already spent in the generator does not carry the reaction on at the rate it began. Arsenic gas is extremely poisonous. One bubble, as in water, has been fatal.

Stibine

The best yield, 14 percent, of stibine should be obtained from a magnesium antimony, about 80 - 20, alloy. Because of the difficulty in preparing this alloy, it was not used.

The next best yield, ten to twelve percent, of stibine is given by a zinc antimony alloy, about 80 - 20. This is the alloy used. A physical mixture is not sufficient. The two metals must be alloyed. Because of the difference of their melting temperature and because of the ease with which antimony sublimes, it is imperative that relatively large pieces of antimony be melted and that these be smothered as much as possible with the zinc while being heated. The mixture must not be stirred until just before pouring. Antimony vapors are poisonous.
A weak, about 0.2 normal acid, is dropped on the turnings of the alloy to generate stibine. Too strong an acid will cause reduction of the stibine produced. This is shown by a black deposit on the walls of the generator.

A simple test as to whether stibine has been produced is to leave the generating system partially evacuated over night. This results in a fairly complete coating of the distributing system with a shiny antimony mirror.

A third method of generating stibine is similar to that used for arsine. Antimony trioxide, $\text{Sb}_2\text{O}_3$, is put in acid solution and dropped on a hydrogen generating metal. Freshly boiled acid should be used. The $\text{Sb}_2\text{O}_3$ precipitates out at certain normality. A proper mixture can be obtained by putting some $\text{Sb}_2\text{O}_3$ and water in the generator with the metal and dropping the remainder on it.

A fourth method to prepare stibine was attempted. A lead antimony alloy was made and the resultant turnings were treated with acetic acid. The yield from this method was negligibly small.

In general, the purity of the gases seem best if the reaction is carried on at atmospheric pressure. The addition of a drying tube between the generating system and the absorption cell is not too desirable as drying tubes block at times. A drying agent placed directly in the cell was the most efficient means of drying the gases.
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