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STRUCTURE OF MONO-DEUTERATED PHOSPHINE.

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STRUCTURE OF MONO-DEUTERATED PHOSPHINE

by

LeRoy Alfred Schaum, Jr.

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A Thesis Submitted to the Faculty of the  
DEPARTMENT OF CHEMISTRY  
In Partial Fulfillment of the Requirements  
For the Degree of  
MASTER OF SCIENCE  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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This thesis has been approved on the date shown below:

Stephen G. Kukolich  
S. G. KUKOLICH  
Professor of Chemistry

April 16, 1982  
Date

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## ABSTRACT

The structure of mono-deuterated phosphine,  $\text{PH}_2\text{D}$ , has been determined using high-resolution microwave spectroscopy.

Six rotational transitions were observed, the two lowest transitions in J providing sufficient information to determine the effective structure of the molecule. The transitions observed and their respective frequencies in MHz are:  $2_{02} \rightarrow 2_{12}$ ,  $35142.07 \pm 0.03$ ;  $2_{12} \rightarrow 2_{11}$ ,  $18070.93 \pm 0.02$ ;  $3_{03} \rightarrow 3_{13}$ ,  $28158.50 \pm 0.03$ ;  $4_{04} \rightarrow 4_{14}$ ,  $20815.33 \pm 0.03$ ;  $5_{05} \rightarrow 5_{15}$ ,  $14246.69 \pm 0.01$ ; and  $6_{06} \rightarrow 6_{16}$ ,  $9121.37 \pm 0.01$ .

Assuming the molecule is a rigid-rotor and the constancy of structural values with isotopic substitution, a bond distance of 1.418 Å and a bond angle of  $93.36^\circ$  has been determined.

## CHAPTER 1

### INTRODUCTION

Microwave spectroscopy is recognized as an extremely effective tool in structural studies of simple inorganic molecules in the gas phase. The transition frequencies corresponding to changes in the rotational energies of a molecule can be related to its moments of inertia, and depending on the complexity of the molecule and the number of observed lines, the structure of the molecule can be elucidated.

This thesis reports on the structure of mono-deuterated phosphine,  $\text{PH}_2\text{D}$ . Previous structural studies on this molecule have been conducted by Stevenson (1940), Loomis and Strandberg (1951), and Nielsen (1952). All of these workers used information obtained partly from infra-red studies. Sirvetz and Weston (1953) were the first workers to determine the structure of  $\text{PH}_2\text{D}$  from microwave studies of the molecule.

The present study was initiated in order to identify transitions in the molecule exhibiting hyperfine structure (line splittings) which could then be examined in more detail on the molecular beam maser.

Phosphorus is located directly below nitrogen in the periodic table and of particular interest would be the observation of inversion splitting in  $\text{PH}_2\text{D}$ , as is readily observed in mono-deuterated ammonia,  $\text{NH}_2\text{D}$  (Weiss and Strandberg, 1951). None of the six lines reported in

this study exhibited hyperfine structure as measured in the Stark cell spectrometer. Nevertheless, the data obtained in this study has been used to refine the structural parameters reported for  $\text{PH}_2\text{D}$  and expand the data base of observed transitions in the molecule by reporting three new transitions currently unreported in the literature.

## CHAPTER 2

### THEORY

A total of six Q-branch ( $\Delta J = 0$ ) transitions in  $\text{PH}_2\text{D}$  were observed during the course of this study. Due to the lack of splitting in these lines, the data obtained were used to derive the P-H bond distance and H-P-H bond angle. The following discussion describes how this derivation was made possible based upon the experimental data obtained.

If one makes the usual "first-order" approximation that  $\text{PH}_2\text{D}$  is a rigid rotor and that the molecular structure is unaffected by isotopic substitution, the two independent quantities that will describe the molecule are the bond distance,  $r$ , and the bond angle,  $\theta$ . In order to determine these two unknowns, it is necessary to have two known quantities about the molecule that can be expressed in terms of the bond distance and the bond angle. This may be expressed as

$$f_1(r, \theta) = X_1 \quad (2-1)$$

$$f_2(r, \theta) = X_2 \quad (2-2)$$

where  $X_1$  and  $X_2$  are numerical quantities depending on  $r$  and  $\theta$ , calculated from experimental data. It is clear that the problem basically is of the classic "two equations and two unknowns" variety.

Conveniently, there exist two rotational parameters which meet the requirements placed on  $X_1$  and  $X_2$ . Consider the following

expression giving the energy of any asymmetric rotor (Harmony, 1972, p. 191):

$$E(J_{K_{-1} K_{+1}}) = \frac{1}{2}h(A+C)J(J+1) + \frac{1}{2}(A-C)E_{K_{-1} K_{+1}}^J(\kappa) \quad (2-3)$$

The term  $E(J_{K_{-1} K_{+1}})$  represents the energy of a rotational level of total angular momentum  $J$  having values  $K_{-1}$  and  $K_{+1}$  for the projection of  $J$  on the molecule-fixed  $Z$  axis in the prolate symmetric rotor and oblate symmetric rotor limits, respectively. The term  $E_{K_{-1} K_{+1}}^J(\kappa)$  is the so-called "reduced" energy where  $\kappa$  is defined

$$\kappa = \frac{2B-A-C}{A-C} \quad (2-4)$$

and is called Ray's asymmetry parameter (Gordy and Cook, 1970, p. 163). The terms  $A$ ,  $B$ , and  $C$  are the rotational constants of the molecule and are expressed as

$$A = \frac{h}{8\pi^2 I_a} \quad B = \frac{h}{8\pi^2 I_b} \quad C = \frac{h}{8\pi^2 I_c} \quad (2-5)$$

where  $I_a$ ,  $I_b$ , and  $I_c$  are the moments of inertia of the molecule with respect to the molecule-fixed principal axis system. The asymmetry parameter may assume values

$$-1 \leq \kappa \leq +1$$

where  $-1$  corresponds to a prolate symmetric rotor and  $+1$  to an oblate symmetric rotor. This term serves as a useful indicator of the degree of asymmetry in a molecule. Finally, by convention, the principal

axes a, b, and c are always correlated with X, Y, and Z in such a way that guarantees

$$A \geq B \geq C$$

Using Eqn. (2-3), the difference in energy between two rotational levels having energies  $E(J_{K-1, K+1})$  and  $E(J_{K'-1, K'+1})$  is given by

$$E(J_{K'-1, K'+1}) - E(J_{K-1, K+1}) = \frac{A-C}{2} \times [E_{K'-1, K'+1}^J(\kappa) - E_{K-1, K+1}^J(\kappa)] \quad (2-6)$$

assuming  $E(J_{K'-1, K'+1}) > E(J_{K-1, K+1})$ , where A and C are rotational constants of the molecule previously defined in Eqn. (2-5). Fortunately, for low values of the total angular momentum J, closed-form expressions are available for values of the reduced energy,  $E_{K-1, K+1}^J(\kappa)$ , in terms of the asymmetry parameter (Gordy and Cook, 1970, p. 178).

We are now at a point where the two rotational parameters allowing a set of equations like (2-1) and (2-2) to be written may be identified. Study of Eqn. (2-6) reveals that both  $\frac{A-C}{2}$  and  $\kappa$  may be calculated directly from the experimental measurement of two different rotational transitions.

These terms correlate with  $X_1$  and  $X_2$  of Eqns. (2-1) and (2-2), respectively. Where, however, does the explicit functional dependence on the bond distance and bond angle originate? Both  $\frac{A-C}{2}$  and  $\kappa$  are expressed in terms of the rotational constants of the molecule which were defined in Eqn. (2-5). These rotational constants, in turn,

depend upon the values of the moments of inertia evaluated in the molecule-fixed principal axis system having its origin at the center of mass of the molecule. In this coordinate system, the moment of inertia matrix possesses only diagonal elements which can be expressed as (Gordy and Cook, 1970, p. 497):

$$\begin{aligned} I_x &= \sum_i M_i (y_i^2 + z_i^2) \\ I_y &= \sum_i M_i (x_i^2 + z_i^2) \\ I_z &= \sum_i M_i (x_i^2 + y_i^2) \end{aligned} \quad (2-7)$$

The coordinates  $x$ ,  $y$ , and  $z$  then may be expressed in terms of  $r$  and  $\theta$ , with considerable simplification occurring due to the assumptions that all bond distances and all bond angles in the molecule are the same.

Summarizing the above discussion, it has been shown that to evaluate the structure of  $\text{PH}_2\text{O}$  as a rigid, asymmetric rotor it is necessary to evaluate the asymmetry parameter  $\kappa$ , and  $\frac{A-C}{2}$  from experimental data. Using Eqn. (2-6), energy level differences involved in an allowed transition are dependent upon the value of  $\frac{A-C}{2}$  and the difference in the reduced-energy terms of the rotational levels involved. For transitions involving low  $J$  values, these terms may be written in closed form as a function of  $\kappa$ . This allows an expression to be written for a particular low- $J$  transition frequency that involves a dependence only on  $\kappa$  and  $\frac{A-C}{2}$ . In order to solve for these two

unknowns, it is necessary to measure transition frequencies from two experimentally observed lines. Once these parameters have been evaluated, they may be expressed in terms of  $r$  and  $\theta$ , allowing the bond distance and angle to be evaluated.

The values of  $r$  and  $\theta$  obtained by this method are effective values, uncorrected for vibrational effects, and a consequence of the initial assumption that the molecule is a rigid-rotor. A discussion of vibrational contributions to effective structural values is provided by Gordy and Cook (1970, pp. 524-532). An additional effect unaccounted for in the rigid-rotor approximation is the effect of centrifugal distortion. As the molecule rotates, bond angles change and bond distances elongate, particularly in rotational levels of high  $J$ . Experimentally, one observes a displacement in line position from what the rigid-rotor model predicts, generally becoming greater as  $J$  increases. This study minimizes the effect of centrifugal distortion on the derived molecular structure by using the two lowest  $J$  lines observed in the calculation. A rigorous theoretical treatment of this effect is also available in Gordy and Cook (1970, pp. 205-235).

## CHAPTER 3

### EXPERIMENTAL

Experimentally, the principal difficulties encountered when studying rotational transitions using microwave spectroscopy are measuring transition frequencies accurately and obtaining narrow line-width spectra of acceptable intensity. The discussion that follows describes how the spectrometer used in this study addresses these areas.

#### Frequency Measurement

In order to make use of the extremely high resolution displayed by microwave spectra, techniques for making highly accurate frequency measurements must be employed in a conventional microwave spectrometer. Following the selection of a suitable reflex klystron, which produces microwave radiation in the frequency range of interest, gross tuning is accomplished by adjusting the dimensions of a resonant cavity inside the source. The effect of these cavity adjustments is periodically monitored using a wavemeter. This meter is basically another resonant cavity with adjustable dimensions calibrated in frequency units. The klystron output is fed into the wavemeter and then into a diode detector which generates a DC output. This frequency is then read directly off the wavemeter, allowing further adjustments to be made to the klystron's output in order to attain the operating point

desired. This method allows fairly rapid tuning of the microwave oscillator; however, it is not sufficiently accurate for this high resolution experimental work.

Accurate frequency measurements are made by locking the klystron's output to a harmonic of a very stable 10-mHz crystal oscillator. Following the selection of a suitable crystal in the vicinity of 10 MHz, the tenth harmonic of the crystal frequency is generated and sent to a frequency counter. A portion of this 100 MHz signal is also sent to a frequency synchronizer, which generates harmonics of this signal up into the microwave region. These harmonics are mixed with a portion of the klystron's output. A 30-mHz IF is produced here and accurately maintained by referencing it to a 30-mHz signal generated from the stable 10-mHz crystal oscillator. A block diagram of the frequency measurement system is given in Figure 1. At this point, the 10-mHz crystal oscillator is locked to the klystron's output. Any change in source frequency will force the frequency synchronizer to send a correcting signal to the klystron's reflector as it tries to maintain a 30-mHz difference between the appropriate crystal harmonic and the klystron's output. Tuning of the source is accomplished by applying a voltage ramp to the crystal oscillator, changing its frequency and causing the klystron's output to change as just described. The accuracy of the frequency counter is periodically verified by monitoring station WWVB operated by the National Bureau of Standards.

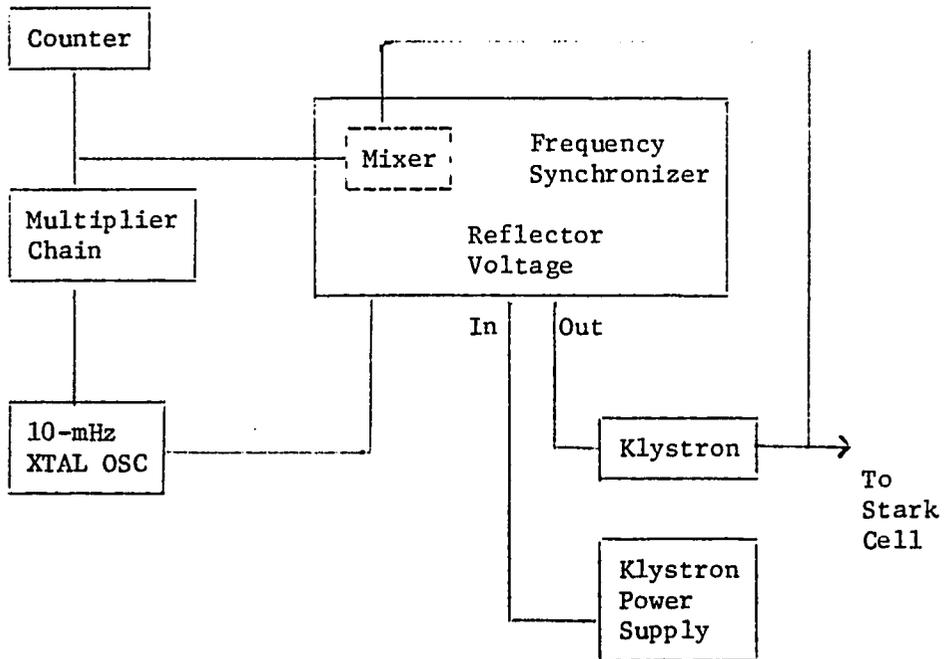


Figure 1. Frequency measurement block diagram.

### Sample Handling

After a microwave transition has been located, a great deal of effort is spent on obtaining spectra that possess as low a line width as possible. This allows a more precise determination of the center frequency of the transition being studied. Several line-broadening mechanisms affect the spectra obtained from a conventional microwave spectrometer and are discussed below.

#### Doppler Broadening

This effect arises from the velocity of the molecules contained in the waveguide relative to that of the source radiation. If a molecule at rest has a transition frequency  $\nu_0$ , the frequency at which a transition will occur when it is moving with velocity  $V$  relative to the radiation is (Gordy and Cook, 1970, p. 44)

$$\nu = \pm \nu_0 \left(1 + \frac{V}{C}\right) \quad (3-1)$$

where  $C$  is the speed of light. A sample of gas-phase molecules will possess a Maxwell velocity distribution and associated frequency shifts. The contribution of these Doppler shifts to the observed line-widths has been shown to be (Gordy and Cook, 1970, p. 45)

$$2(\Delta\nu)_d = 7.15 \times 10^{-7} \left(\frac{T}{M}\right)^{1/2} \nu_0 \quad (3-2)$$

where  $T$  is the absolute temperature and  $M$  corresponds to the molecular weight in amu's. The term  $2(\Delta\nu)_d$  identifies the increase in the full width at half maximum (FWHM) of a line due to Doppler broadening.

This effect generally must be tolerated in the course of experiments using conventional microwave spectrometers.

#### Wall Collisions

Johnson and Strandberg (1952) have shown that an increase in a transition's FWHM due to collisions with waveguide walls may be approximated by

$$2(\Delta\nu) = 10\left(\frac{1}{a} + \frac{1}{b} + \frac{1}{c}\right)\left(\frac{T}{M}\right)^{\frac{1}{2}} \quad (3-3)$$

where a, b, and c are the dimensions of the waveguide measured in centimeters, T is the absolute temperature, M is the molecular weight, and  $2(\Delta\nu)$  is in kHz. This effect is usually negligible except for certain high frequency experiments employing waveguides having high cutoff frequency values.

#### Pressure Broadening

Pressure broadening is generally the predominant line-broadening mechanism in conventional microwave spectroscopy. Arising mainly from transition-inducing intermolecular collisions, rigorous treatment of this effect is complex and available in the literature (Anderson, 1949). Further information including a comparison of various theoretical models is presented in Townes and Schawlow (1955, pp. 338-366).

One of the results obtained from these theories is that a reduction in line-width may be obtained by lowering the sample cell pressure.

Experimentally, once a spectral line has been located, the pressure is gradually decreased to obtain as narrow a line as possible while still preserving acceptable line intensity.

The spectrometer used in this study utilizes a mechanical fore-pump followed by a diffusion pump to minimize the line-broadening effects of pressure. Further reductions in pressure are obtained by using a liquid nitrogen trap to condense the more volatile species. Operating pressures typically were 10 microns or less during the course of an experiment.

#### Signal Detection

The sample size used in measuring rotational lines leads to extremely small power absorptions at a transition frequency. The Stark effect, as well as sophisticated detection electronics, is used to improve the sensitivity of the technique and the quality of the spectra obtained.

Hughes and Wilson (1947) were the first workers to report the incorporation of Stark modulation in microwave spectroscopy. Making use of the perturbation on molecular energy levels effected by an applied electric field, the Stark effect effectively switches molecules into and out of resonance, allowing a modulation of the absorbed power. This is accomplished by bisecting lengthwise the sample-cell waveguide with an electrode insulated electrically from its walls. A 10-kHz high voltage square wave is applied to this electrode during the course of an experiment. If the source output corresponds to a

transition frequency of the molecule under study, power will be absorbed in the "field-off" condition. In the presence of an electric field, however, the energy difference between the two rotational levels changes. This causes microwave power to be absorbed at a different frequency leading to the frequent appearance of "Stark lobes" on the recorded spectra.

Detection of the modulated power absorption is accomplished utilizing a microwave crystal detector. The output of this detector is fed to a high-Q bandpass filter tuned to the modulation frequency.

Signal amplification and detection are performed by a lock-in amplifier incorporating phase-sensitive detection. Following amplification, the signal is chopped and integrated. The DC output from the integrator is amplified further and recorded on a strip chart recorder. Figure 2 presents a block diagram of the detection electronics used in this study.

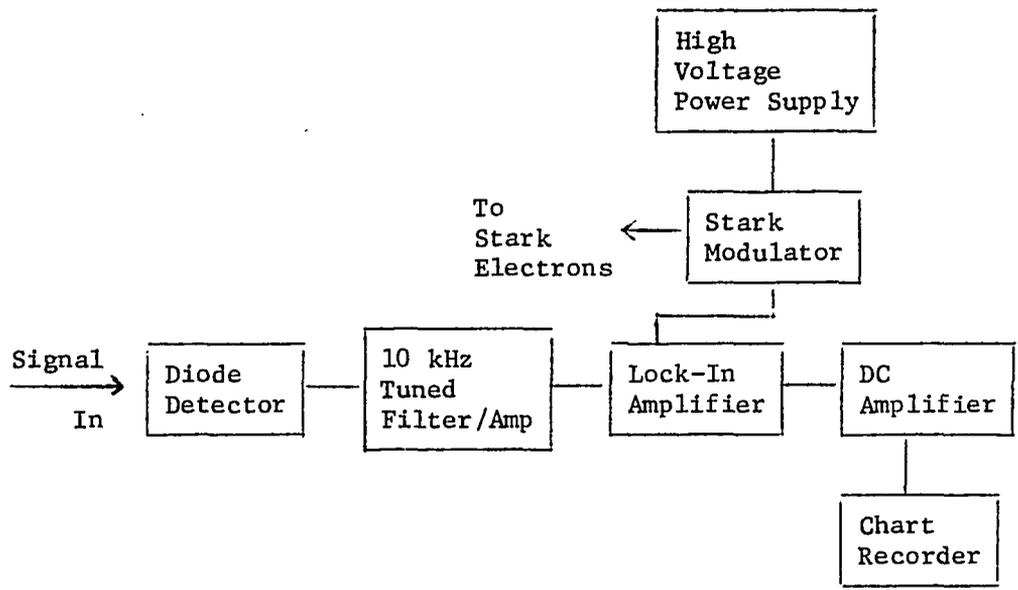


Figure 2. Detection electronics block diagram.

## CHAPTER 4

### RESULTS AND ANALYSIS

A total of six Q-branch ( $\Delta J = 0$ ) transitions of  $\text{PH}_2\text{D}$  were measured in this study, including three previously unreported in the literature. The two lowest J transitions were used to calculate the rigid rotor structural parameters of the molecule in order to minimize the effects of centrifugal distortion. The transitions measured, their frequencies and line-widths, previously reported work, and rigid rotor predictions (RR) are presented in Table 1.

Both of the  $J = 2$  lines were used to calculate the asymmetry parameter  $\kappa$  and  $\frac{A-C}{2}$ , using the following expressions for the transition frequencies.

$$\nu_{2_{02}} \quad \nu_{2_{12}} = \frac{A-C}{2} [-\kappa - 3 + 2(\kappa^2 + 3)^{\frac{1}{2}}] = 35142.07 \text{ MHz} \quad (4-1)$$

$$\nu_{2_{12}} \quad \nu_{2_{11}} = \frac{A-C}{2} [3(\kappa + 1)] = 18070.93 \text{ MHz} \quad (4-2)$$

Elimination of  $\frac{A-C}{2}$  leads to a value for  $\kappa$  of  $-0.741290 \pm 0.000001$ .

The indicated accuracy of this value was obtained from the errors associated with the transition frequency measurements. Substitution of this value in Eqn. (4-2) leads to a value for  $\frac{A-C}{2}$  of  $23283.4 \pm 0.1$  MHz with the indicated error limits again being due to the uncertainty associated with the transitions' line center. Sirvetz and Weston (1953) reported values of  $-0.741384$  and  $23292.6$  MHz,

Table 1.

Transition Center Frequencies, Line-Widths, Previous  
Work, and Theoretical Predictions

| Transition                  | $\nu$ (mHz)*        | FWHM (kHz) | SW** (mHz) | RR*** (mHz) |
|-----------------------------|---------------------|------------|------------|-------------|
| $2_{03} \rightarrow 2_{12}$ | $35142.07 \pm 0.03$ | 114        |            | 35162.59    |
| $2_{12} \rightarrow 2_{11}$ | $18070.93 \pm 0.02$ | 104        | 18070.96   | 18071.49    |
| $3_{03} \rightarrow 3_{13}$ | $28158.50 \pm 0.03$ | 146        | 28158.53   | 28202.47    |
| $4_{04} \rightarrow 4_{14}$ | $20815.33 \pm 0.03$ | 94         | 20815.38   | 20882.89    |
| $5_{05} \rightarrow 5_{15}$ | $14246.69 \pm 0.01$ | 67         |            | 14332.04    |
| $6_{06} \rightarrow 6_{16}$ | $9121.37 \pm 0.01$  | 55         |            | 9214.34     |

\*Error bars correspond to  $\pm 3\sigma$ .

\*\*From M. H. Sirvetz and R. E. Weston, J. Chem. Phys. **21**, 898 (1953).

\*\*\*Predictions based on the rotational constants calculated from structural parameters given by Sirvetz and Weston (1953).

respectively, using the  $2_{12} \rightarrow 2_{11}$  and  $3_{03} \rightarrow 3_{13}$  transitions. Discrepancies between the two results can be attributed to the different transitions used in the calculation. As Table 1 indicates, there is a 60-mHz difference between the rigid-rotor prediction and the observed transition frequency of  $3_{03} \rightarrow 3_{13}$  line used along with the  $2_{12} \rightarrow 2_{11}$  line in the structural calculations by SW. The present study, while also using the  $2_{12} \rightarrow 2_{11}$  transition in the calculation, uses a lower J line as the other known quantity. Presumably, this reduces the effect of centrifugal distortion on the calculated rigid-rotor parameters leading to more accurate results. It is interesting to note from Table 1 that the  $2_{02} \rightarrow 2_{12}$  transition is shifted by only 20 mHz when compared with the rigid-rotor prediction.

Using the values of  $\kappa$  and  $\frac{A-C}{2}$  calculated above, it is possible to solve for the bond distance,  $r$ , and angle  $\theta$ , in  $\text{PH}_2\text{D}$ . Moment and product of inertia expressions are set up with respect to an arbitrary coordinate system fixed in the molecule. Judicious selection of the axes for this coordinate system results in an inertial tensor which can be written as a 3 x 3 matrix in block diagonal form. This matrix consists of one 2 x 2 sub-matrix, and one already diagonal term. The elements of these matrices are listed below:

$$I_{xx} = r^2 \cos^2 \theta' (m_D + 2m_H) + r^2 \sin^2 \theta' (1.5m_H) - \frac{[r \cos \theta' (-m_D - 2m_H)]^2}{M} \quad (4-3)$$

$$I_{yy} = r^2 \sin^2 \theta' (m_D + \frac{m_H}{2}) + r^2 \cos^2 \theta' (m_D + 2m_H) - \frac{[r \sin \theta' (m_D - m_H)]^2}{M} - \frac{[r \cos \theta' (-m_D - 2m_H)]^2}{M}$$

$$I_{zz} = r^2 \sin^2 \theta' (m_D + 2m_H) - \frac{[r \sin \theta' (m_D - m_H)]^2}{M}$$

$$I_{xy} = 0$$

$$I_{yz} = 0$$

$$I_{xz} = [r^2 \sin \theta' \cos \theta' (-m_D + m_H)] + \frac{[r \sin \theta' (m_D - m_H)][r \cos \theta' (-m_D - 2m_H)]}{M}$$

where  $m_D$  and  $m_H$  are the masses of deuterium and hydrogen in amu's and  $M$  is the molecular weight of  $\text{PH}_2\text{D}$  in amu's. The angle  $\theta'$  in these expressions is the angle formed by the P-H bond and the " $C_3$ " axis of the molecule. This angle is related to the bond angle of the molecule  $\theta$  by (Gordy and Cook, 1970, p. 503)

$$\sin \frac{\theta}{2} = \frac{\sqrt{3}}{2} \sin \theta'$$

Subsequent diagonalization of this sub-matrix results in expressions for the principal moments of inertia of the molecule in terms of  $r$  and  $\theta$ .

Once expressions for the principal moments of inertia have been established from Eqns. (4-3), they are substituted into the formulas for the rotational constants (Eqns. 2-5) and then into the

expression for  $\kappa$  (Eqn. 2-4). This leads to a value of  $93.36^\circ$  for the bond angle. To compute  $r$ ,  $\frac{A-C}{2}$  is expressed in terms of the principal moments of inertia leading to a value of 1.418 Å. The accuracy of these numbers in describing the effective structure of the molecule is estimated to be  $\pm 0.001$  Å and  $\pm 0.01^\circ$  for the bond distance and angle, respectively. Table 2 lists other reported values for the structure of phosphine available in the literature.

The bond distances and angles listed in Table 2 are effective values, uncorrected for the effects of vibration. As such, they tend to be somewhat larger than so-called equilibrium structures where bond distances and angles correspond to the molecule being at the minimum of the potential energy curve, i.e., free from zero-point vibrational effects. For example, Helms and Gordy (1977) reported values of 1.420 Å and  $93.36^\circ$  for the effective bond distance and angle in  $\text{PH}_3$ . Corresponding equilibrium values were reported by these workers to be 1.4116 Å and  $93.33^\circ$ .

As evidenced by Table 2, excellent agreement exists between the results of this study and previous microwave work on  $\text{PH}_3$ ,  $\text{PH}_2\text{D}$ , and  $\text{PD}_3$ . While the lower J lines used here in the structural computations theoretically lead to improved rigid-rotor parameters, practically the effect is virtually negligible.

While it is possible to calculate the effective rotational constants of the molecule from its structure, a more accurate and direct method would be to include a low J,  $\Delta J = \pm 1$  transition. If a line of this type were to be included in the analysis, the

Table 2.  
Comparison of Reported Phosphine Structures

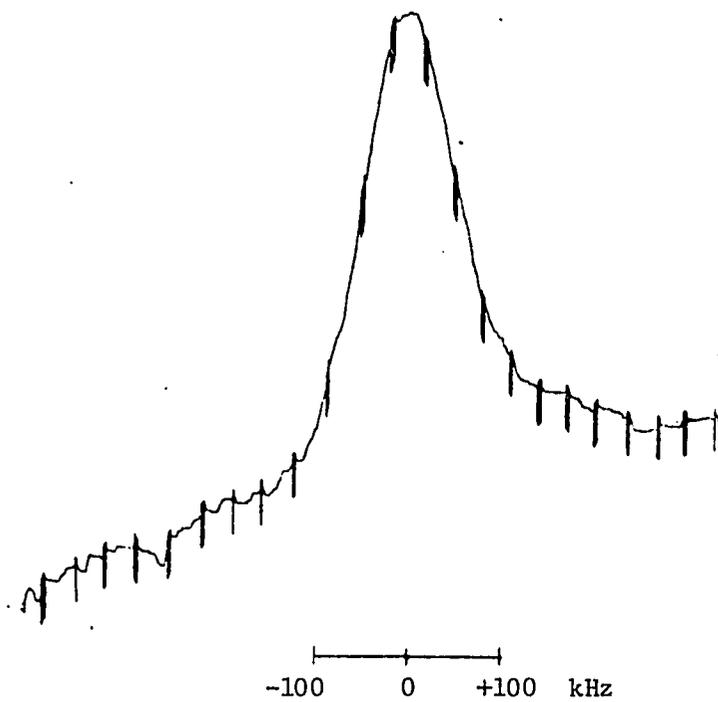
| Reference | Bond Distance<br>(angstroms) | Bond Angle<br>(degrees) | Comments  |
|-----------|------------------------------|-------------------------|---|
| 1         | 1.4177                       | 93.36                   | Microwave study on PH <sub>2</sub> D                                    |
| 2         | 1.419                        | 93.5                    | Combined microwave and IR data on PH <sub>3</sub> and PH <sub>2</sub> D |
| 3         | 1.424                        | 93.8                    | Data based on PH <sub>3</sub> IR studies                                |
| 4         | 1.420                        | 93.34                   | Forbidden-transition study on PH <sub>3</sub>                           |
| 4         | 1.418                        | 93.36                   | Forbidden-transition study on PH <sub>3</sub>                           |
| 5         | 1.418                        | 93.36                   |   |

- References:
1. M. H. Sirvets and R.E. Weston, J. Chem Phys. 21, 898 (1953).
  2. C. C. Loomis and M. W. P. Strandberg, Phys. Rev. 81, 798 (1951).
  3. H. H. Nielson, J. Chem. Phys. 20, 759 (1952).
  4. D. A. Helms and W. Gordy, J. Mol. Spectrosc. 66, 206 (1977).
  5. This study.

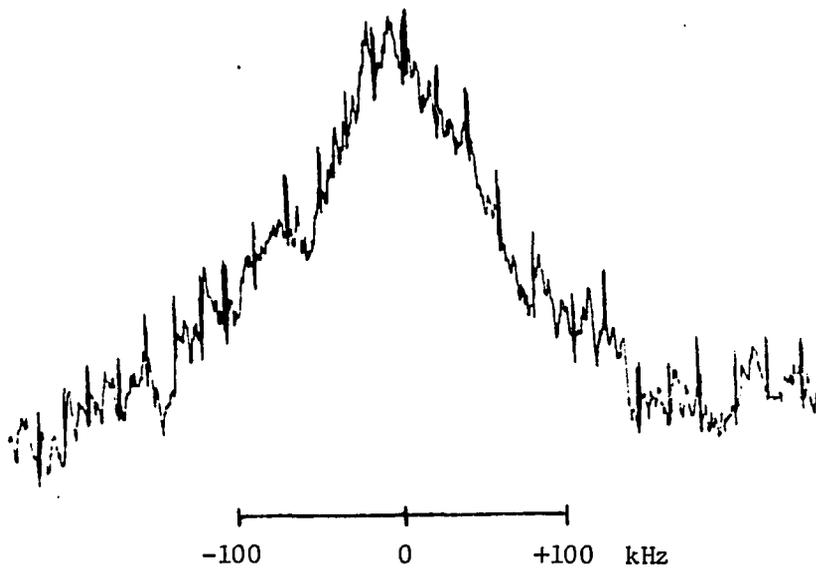
rotational constants could be directly determined from the frequencies of three transitions (see Eqn. 2-3). The lowest  $\Delta J = \pm 1$  line accessible to the spectrometer used in this study is the  $5_{50} \rightarrow 6_{15}$  transition predicted to have a rigid-rotor frequency of 45 GHz. Due to its relatively high J value, though, centrifugal distortion effects could render the rotational constants calculated by this method less accurate than what would be obtained by using the values of r and  $\theta$  reported here.

This study has confirmed earlier, lower resolution microwave work on the structure of  $\text{PH}_2\text{D}$ . A basis for future high resolution molecular beam experiments has also been provided by the accurate measurement of a number of higher J transitions in  $\text{PH}_2\text{D}$ . Future work on this molecule could consist of observing  $\Delta J = \pm 1$  lines to evaluate the rotational constants, an experiment which has not of yet been performed. Measuring a number of additional transitions in the molecule would allow an accurate treatment of centrifugal distortion to be performed.

APPENDIX  
TRANSITION FREQUENCIES

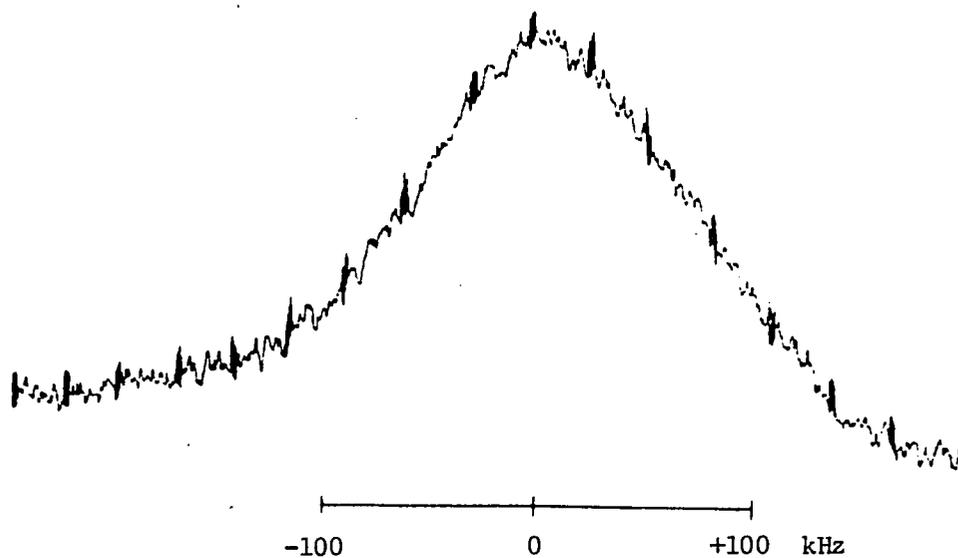
$2_{02} \rightarrow 2_{12}$  Transition

Frequencies shown are relative to the line center at 35142.07 MHz.

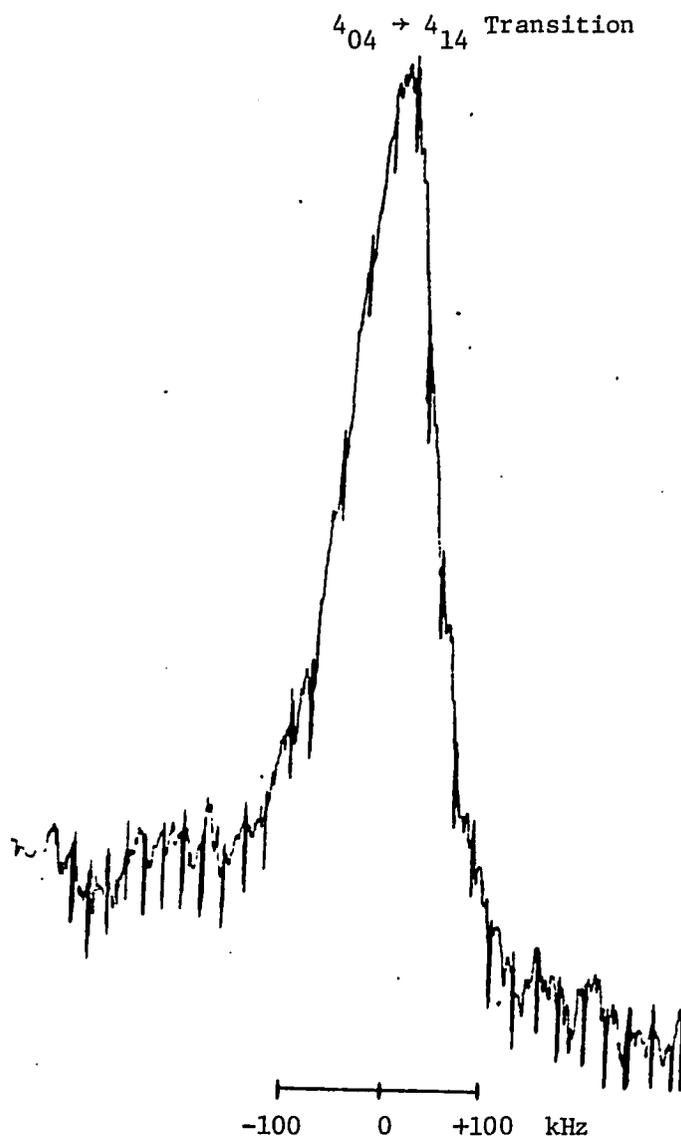
$2_{12} \rightarrow 2_{11}$  Transition

Frequencies shown are relative to the line center at 18070.93 mHz.

$3_{03} \rightarrow 3_{13}$  Transition

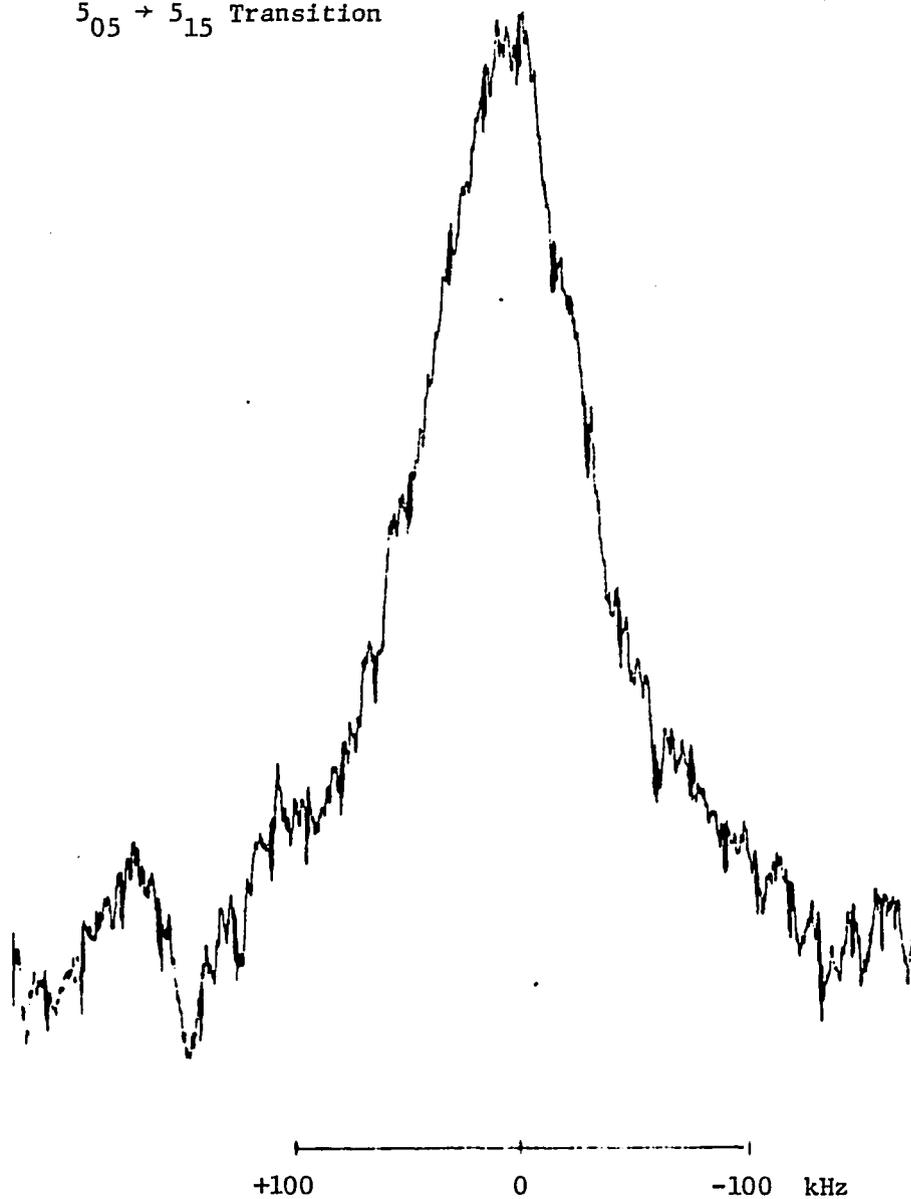


Frequencies shown are relative to the line center at 28158.33 MHz.

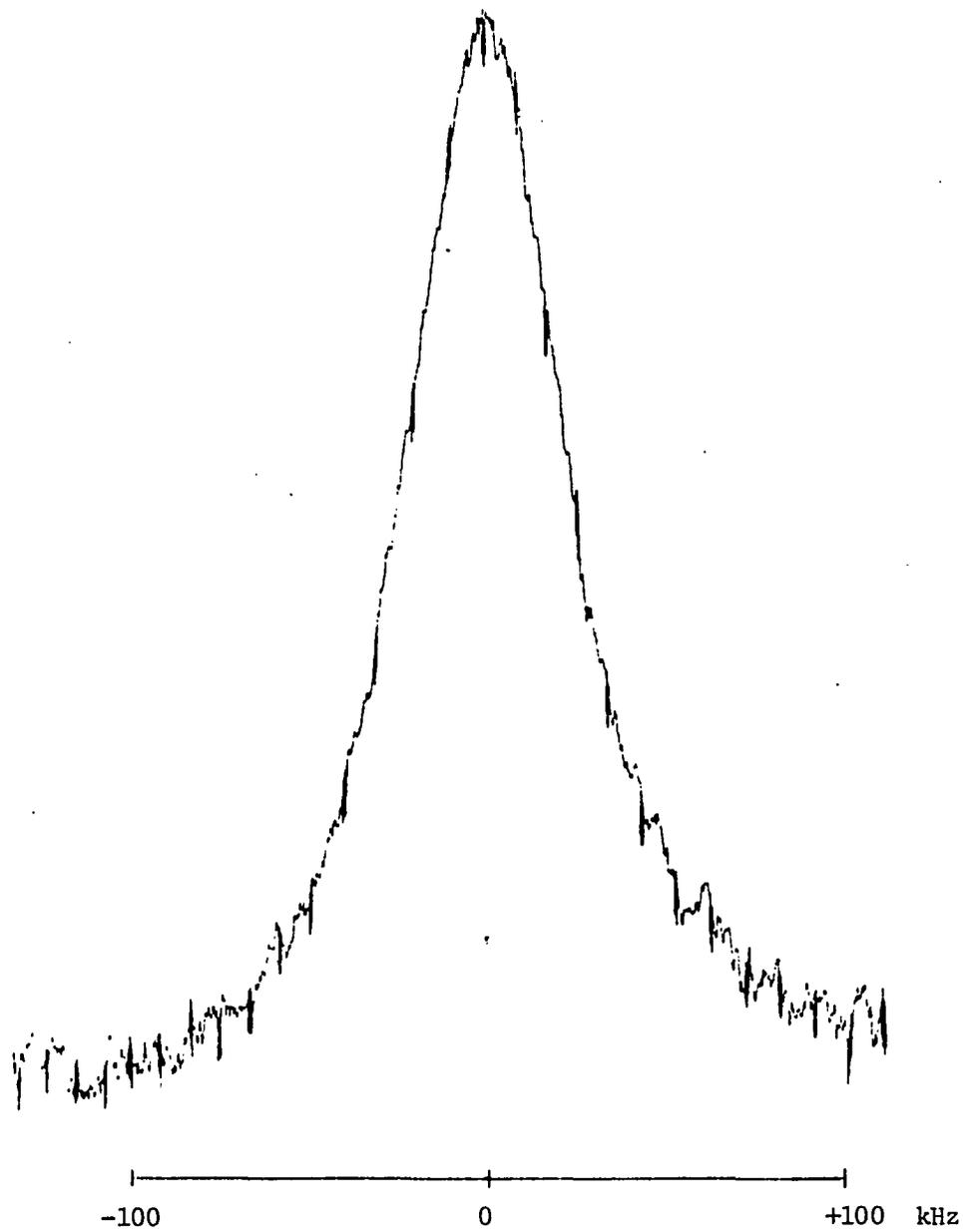


Frequencies shown are relative to the line center at 20815.33 MHz.

$5_{05} \rightarrow 5_{15}$  Transition



Frequencies shown are relative to the line center at 14246.69 mHz.

$6_{06} \rightarrow 6_{16}$  Transition

Frequencies shown are relative to the line center at 9121.37 mHz.

## LIST OF REFERENCES

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