"Forbidden" Rotational Spectra of Symmetric-Top Molecules: PH₃ and PD₃[1]

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A millimeter-wave spectrometer having a sensitivity of 4×10^{-10} cm^{-1} in the 2-mm region has been constructed for observation of extremely weak millimeter-wave spectra of gases. It has been used to measure $J \to J$, $K = 0 \leftarrow 3$ transitions in PH$_3$ and $J \to J$, $K = 0 \leftarrow 3$ as well as $K = \pm 1 \leftarrow \pm 4$ transitions in PD$_3$. The B_0 and C_0 spectral constants (in MHz) are: for PH$_3$, $B_0 = 133\ 480.15 \pm 0.12$ and $C_0 = 117\ 488.85 \pm 0.16$; for PD$_3$, $B_0 = 69\ 471.10 \pm 0.03$ and $C_0 = 58\ 974.37 \pm 0.05$. The effective ground-state values obtained for the bond angle and bond length are: for PH$_3$, r_0 (Å) $= 1.420_0$ and $\alpha_0(°) = 93.34_5$; for PD$_3$, r_0 (Å) $= 1.417_6$ and $\alpha_0(°) = 93.35_9$. The corresponding zero-point-average values were calculated to be: for PH$_3$, r_z (Å) $= 1.4269_9 \pm 0.0002$ and $\alpha_z(°) = 93.228_7$; for PD$_3$, r_z (Å) $= 1.4226_5 \pm 0.0001$ and $\alpha_z(°) = 93.256_7 \pm 0.004$. For both species, the equilibrium values are r_e (Å) $= 1.4115_9 \pm 0.0006$ and $\alpha_e(°) = 93.32_8 \pm 0.02$.

1. INTRODUCTION

The pure rotational transitions normally observed for symmetric-top molecules conform to the selection rules $\Delta J = \pm 1$, $\Delta K = 0$. As a result of their axial symmetry, there is no off-axis component of the permanent dipole moment to couple a radiation field with the rotation about the symmetry axis. Hence, resonance radiation does not normally induce changes in the K quantum number which measures the angular momentum about this axis. Consequently, the moment of inertia for rotation about the symmetry axis, and the associated centrifugal distortion constants, cannot be obtained from the normal rotational spectra.

As a result of theoretical developments and notable advancements in the experimental techniques for spectral detection, it has become possible to detect rotational transitions in the ground vibrational state corresponding to changes in the energy of rotation about the symmetry axis of symmetric-top molecules, i.e., changes in the K quantum number. For molecules with C_{3v} symmetry, such as PH$_3$ and PD$_3$ which are reported here, the observable transitions—forbidden in the normal theory—correspond to K changes of ± 3.

The possibility of $\Delta K = \pm 3$ changes in molecules of C_{3v} symmetry was apparently first recognized in 1967 by Hanson (1). The basic theory for such transitions was later contributed by Watson (2). These transitions were first detected as pure rotational spectra in 1973 by Chu and Oka (3), who observed $\Delta J = 0$, $K = \pm 1 \leftarrow \mp 2$ transitions in PH$_3$ occurring in the 43.7 to 47.4 GHz region. In 1974 they reported (4) similar

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measurements of $\Delta J = 0$, $K = \pm 1 \leftarrow \mp 2$ transitions for PD_3 in the 29.9 to 30.8 GHz region, and for AsH_3 in the 21.2 to 21.8 GHz region. Chu and Oka were helped in their measurements by the line frequency predictions based on the previous observation of $\Delta(K - l) = \pm 3$ vibration–rotation transitions of PH_3 and AsH_3 by Maki, Sams, and Olson (5). Likewise, our detection (6) of the higher-frequency $K = 0 \leftarrow 3$ forbidden transition of PH_3 and PD_3 was assisted by a preliminary prediction of their frequencies from the results of Maki et al. as well as those of Chu and Oka.

The need for observation of these higher K transitions described in this paper was indicated by Chu and Oka (4), who reported that their spectrometer was not sufficiently sensitive at the higher frequencies to detect them. Measurements of these transitions confirm the assignments of the frequencies measured by Chu and Oka and provide increased accuracy in the values of the spectral constants, particularly those influenced by the distortion caused by rotation about the symmetry axis. For observation of weak transitions such as these in the shorter millimeter-wave region, we designed the exceptionally sensitive millimeter-wave spectrometer described below.

The Q-branch $\Delta K = \pm 3$ transitions represent only one class of forbidden transitions in symmetric molecules included in the general theory of Watson et al. (2, 7) and others (8, 9). Oka (10) has recently written an excellent review of the experimental and theoretical developments of this relatively new type of spectra. It should be mentioned that forbidden transitions of symmetric-top molecules in vibrationally excited states were theoretically predicted many years earlier by Mizushima and Venkateswarlu (11), before sufficiently sensitive spectrometers were available for their detection. In the ground vibrational state the off-axis dipole moment which couples the radiation field to the rotation is induced by centrifugal distortion. The selection rules are determined by the molecular symmetry. In the molecules studied here, the rotation about the b axis of inertia induces a small dipole moment perpendicular to the symmetry axis which leads to a slight admixture of the K levels and a breakdown of the $\Delta K = 0$ selection rule. The threefold symmetry about the c axis limits this admixture to K levels differing by 3. It is of interest that centrifugal distortion due to rotation about the symmetry axis can likewise generate a small dipole component along the symmetry axis. This component is of no particular consequence in molecules such as PH_3, which already has a permanent dipole moment along the symmetry axis, but it can give rise to forbidden $\Delta J = \pm 1$ transitions in molecules such as CH_4, which has no permanent dipole moment. In fact, $\Delta J = 1$ rotational transitions of CH_4, SiH_4, and GeH_4 have been observed by Rosenberg et al. (12–15) in the far-infrared region. Forbidden transitions of CH_4 in the ground vibrational state have also been detected in the microwave region by Holt, Gerry, and Ozier (16). These and other forbidden spectra of symmetric-top molecules are treated in Oka's review (10). He also reports that he and his associates have recently detected $\Delta K = \pm 3$ transitions of NH_3 with an infrared laser (17).

2. EXPERIMENTAL DETAILS

The microwave spectrometer used in these measurements has: for the millimeter-wave source, a klystron-driven harmonic generator; for the absorption cell, a high-Q Fabry–Perot transmission cavity (semiconfocal arrangement); and for millimeter-wave

detection, an indium–antimonide detector operated at 1.6 K. The power from the harmonic generator is injected into the cavity by way of a small, rectangular aperture (0.075 × 0.034 in.) in the center of the flat, circular mirror. The power level in the cavity is monitored by radiation from another small, rectangular aperture in the same plate, the output from which is channeled to the indium–antimonide detector. The Q of the resonant cavity mode as indicated by the $\nu_0/\Delta\nu$, the resonant frequency divided by the half-width of the Lorentzian mode shape, is approximately 600 000 at 140 GHz.

In operation, the resonant cavity is filled with the absorbing sample of gas to a pressure of about 15 to 25 μm. The klystron is tuned so that the proper harmonic coincides with the predicted absorption frequency, and the cavity is adjusted to resonate at that frequency. The klystron harmonic is then locked to the peak of the cavity resonance, and the cavity is tuned through the molecular absorption line. The drop in the monitored power resulting from the change in the loaded Q of the cavity corresponds to the detected spectral line.

To achieve control of the klystron frequency by the cavity, a 2.6 kHz sine wave is superimposed on the klystron reflector to sweep the harmonic back and forth across the center of the cavity resonance. The signal produced at the detector (with the loop opened) changes phase by 180° as the klystron is tuned through the cavity resonance. This detector signal is processed by a phase-lock-in amplifier which generates a correction voltage with the proper phase-and-time response to lock the klystron harmonic to the peak of the cavity resonance. Thus, as the cavity is tuned by movement of the curved mirror in and out, the klystron harmonic and the cavity resonance track together. In practice, the amplitude of the 2.6 kHz stabilizing signal is reduced to about 40 mV, or less, to keep most of the harmonic power within the envelope of the cavity-response curve.
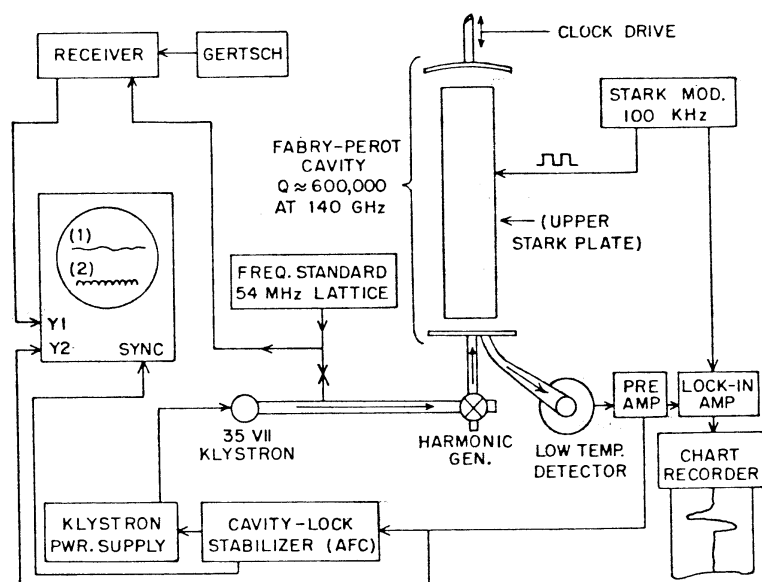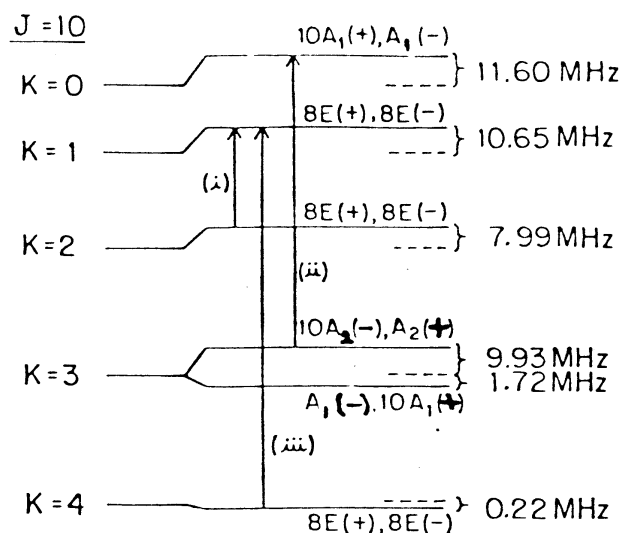

Fig. 1. Diagram of spectrometer.

ROTATIONAL ENERGY LEVELS OF PD₃

Fig. 2. Energy level diagram of the first five K states for $J = 10$ of PD₃ showing the energy shifts caused by the $\mathcal{H}'$ perturbation, the $K = 3$ splitting, the level symmetry (under particle exchange), and the nuclear spin degeneracy. The transition indicated by (i) is that measured by Chu and Oka (4). Those indicated by (ii) and (iii) were measured in this work.

The inside of the cavity is fitted with Stark-modulation plates which are positioned well out of the microwave field to avoid lowering the Q. A square-wave generator is used to produce Stark modulation of the absorption line at 100 kHz. As the clock-driven cavity tunes through the absorption, the detector signal is processed by a phase-lock-in amplifier referenced to the 100-kHz signal. The   line-shape signal from the amplifier is displayed on the chart recorder (see Fig. 1). After exploratory scans to establish the shape of the line, the peak of the cavity response is tuned to the center of the absorption-line contour, and the corresponding klystron frequency is measured with a frequency standard monitored by station WWVB. Repeated measurements are made for each direction of approach to the line center. The accuracy achieved for the line-frequency measurements is estimated to be 1 part in 10^8. The sensitivity of our spectrometer ($\approx 4 \times 10^{-10}$ cm^{-1} at 144 GHz for a time constant of 1 sec) enables us to measure the weak $\Delta K = \pm 3$ transitions with this high precision. The factors limiting the sensitivity appear to be the degree of klystron stability, the power available from the harmonic generator, and the extraneous vibrations of the cavity end plates.

3. THEORETICAL BACKGROUND

As a result of centrifugal distortion, the rotational wavefunction $\psi_{J,K}$ of a molecule having C_{3v} symmetry mixes slightly with the wavefunction $\psi_{J,K\pm3}$ in the ground vibrational state. The term in the Hamiltonian responsible for the interaction may be ex-

pressed (*18*) as

$$\mathcal{3C}' = (\hbar^4 \tau_{xxxx}/4)[(J^2_+ + J^2_-)J_x + J_x(J^2_+ + J^2_-)], \tag{1}$$

where τ_{xxxx} is a centrifugal distortion constant and J_x, J_+, and J_- are rotational operators.

In the absence of the perturbing $\mathcal{3C}'$ term, the rotational levels are all doubly degenerate for each value of K ($K \neq 0$). Figure 2 illustrates the effect of the perturbation on the $J = 10$ energy levels in PD_3. The energy levels corresponding to $K \neq 3$ are raised or lowered, but they remain degenerate with symmetry E. The $K = 3$ level is, however, split into A_1 and A_2 components. The $+$ and $-$ signs indicate the parity of the total wavefunction. The symmetry assignments A_1, A_2, and E indicate the symmetry of the rovibrational wavefunction (excluding spin) for an interchange of two hydrogens. The integer preceding the symmetry assignment (A_1, A_2, or E) indicates the nuclear statistical weight of the state. The symmetry selection rules for Q-type $\Delta K = \pm 3$ transitions (19) are $+ \leftrightarrow -$, along with $A_1 \leftrightarrow A_2$,   or $E \leftrightarrow E$.

Each unperturbed energy level of a symmetric-top molecule is normally doubly degenerate for each nonzero value of K. It is necessary to form linear combinations of $\psi_{J,+K}$ and $\psi_{J,-K}$ in order to obtain wavefunctions which have the proper symmetry for an exchange of two of the hydrogens. The new wavefunctions for PH_3, $\psi^+_{J,K}$ and $\psi^-_{J,K}$, are defined in terms of the wavefunctions $\psi_{J,+K}$ and $\psi_{J,-K}$ and the nuclear wavefunctions $\alpha\beta\beta$, $\alpha\beta\alpha$, etc. (where α and β stand for spin up and spin down, respectively) as follows (*20*): for $K \neq 0$ or a multiple of 3,

$$\psi^{\pm}_{J,K} = (1/6^{\frac{1}{2}})[\psi_{J,+K}(\beta\alpha\alpha + \alpha\beta\alpha e^{2\pi i K/3} + \alpha\alpha\beta e^{4\pi i K/3})$$
$$\pm \psi_{J,-K}(\beta\alpha\alpha + \alpha\beta\alpha e^{-2\pi i K/3} + \alpha\alpha\beta e^{-4\pi i K/3})] \tag{2}$$

and

$$\psi^{\pm}_{J,K} = (1/6^{\frac{1}{2}})[\psi_{J,+K}(\alpha\beta\beta + \beta\alpha\beta e^{2\pi i K/3} + \beta\beta\alpha e^{4\pi i K/3})$$
$$\pm \psi_{J,-K}(\alpha\beta\beta + \beta\alpha\beta e^{-2\pi i K/3} + \beta\beta\alpha e^{-4\pi i K/3})]; \tag{3}$$

for $K = 0$,

$$\psi^+_{J,0} = (1/3^{\frac{1}{2}})\psi_{J,0} \begin{Bmatrix} \beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta \\ \alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha \end{Bmatrix}, \tag{4a}$$

and for $K = 3$

$$\psi^{\pm}_{J,K} = (1/6^{\frac{1}{2}})(\psi_{J,+K} \pm \psi_{J,-K}) \begin{Bmatrix} \alpha\alpha\alpha \\ \beta\beta\beta \\ \beta\alpha\alpha + \alpha\beta\alpha + \alpha\alpha\beta \\ \alpha\beta\beta + \beta\alpha\beta + \beta\beta\alpha \end{Bmatrix}. \tag{4b}$$

The similar wavefunctions for PD_3 are more complicated because of the spin value $I = 1$ for D.

The formulas giving the energy levels may be expressed (*21, 22*) for $K \neq 3$ as:

$$\frac{E(J,K)}{h} = F(J,K)$$

$$+ \left(\frac{\hbar^4\tau_{zzzz}}{4h}\right)^2 \left\{ \frac{(2K-3)^2[J(J+1) - K(K-1)][J(J+1) - (K-1)(K-2)][J(J+1) - (K-2)(K-3)]}{F(J,K) - F(J,K-3)} \right.$$

$$\left. + \frac{(2K+3)^2[J(J+1) - K(K+1)][J(J+1) - (K+1)(K+2)][J(J+1) - (K+2)(K+3)]}{F(J,K) - F(J,K+3)} \right\} ; \quad (5)$$

and for $K = 3$ as

$$\frac{E^-(J,3)}{h} = F(J,3) + \left(\frac{\hbar^4\tau_{zzzz}}{4h}\right)^2 \left\{ \frac{81[J(J+1) - 12][J(J+1) - 20][J(J+1) - 30]}{F(J,3) - F(J,6)} \right.$$

$$\left. + \left[h_0 - \frac{18(\hbar^4\tau_{zzzz}/4h)^2}{F(J,0) - F(J,3)} \right] J(J+1)[J(J+1) - 2][J(J+1) - 6] \right\}, \quad (6)$$

and

$$\frac{E^+(J,3)}{h} = F(J,3) + \left(\frac{\hbar^4\tau_{zzzz}}{4h}\right)^2 \left\{ \frac{81[J(J+1) - 12][J(J+1) - 20][J(J+1) - 30]}{F(J,3) - F(J,6)} \right.$$

$$\left. - h_0 J(J+1)[J(J+1) - 2][J(J+1) - 6] \right\}, \quad (7)$$

where

$$F(J,K) = B[J(J+1) - K^2] + CK^2 - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4$$

$$+ H_{JJK}J^2(J+1)^2K^2 + H_{JKK}J(J+1)K^4 + L_{JJKK}J^2(J+1)^2K^4 + L_{JJJK}J^3(J+1)^3K^2. \quad (8)$$

These $K = 3$ levels contain the term $\pm h_0 J(J + 1)[J(J + 1) - 2][J(J + 1) - 6]$, first derived by Nielsen and Dennison (23) in their explanation of the anomalous effects in $K = 3$ lines observed by early microwave spectroscopists. The total splitting of the $K = 3$ levels is

$$\Delta\nu = [E^-(J, 3) - E^+(J, 3)]/h$$

$$= \left[2h_0 - \frac{18(h^4\tau_{xxxx}/4h)^2}{F(J, 0) - F(J, 3)} \right] J(J + 1)[J(J + 1) - 2][J(J + 1) - 6]. \quad (9)$$

The part of Eq. (9) that is enclosed in brackets is not a constant because of the presence of the $F(J, 0) - F(J, 3)$ expression in the denominator. The denominator $F(J, 0) - F(J, 3)$ is a power series in $J(J + 1)$:

$$F(J, 0) - F(J, 3) = 9(B - C)\left[1 + \frac{9D_K}{B - C} + \frac{D_{JK} - 9H_{JKK}}{B - C}J(J + 1) \right.$$

$$\left. - \frac{H_{JJK} + 9L_{JJKK}}{B - C}J^2(J + 1)^2 - \frac{L_{JJJK}}{B - C}J^3(J + 1)^3 \right]. \quad (10)$$

It is not sufficient to retain only the first term, $9(B - C)$. We found that a simultaneous, least-squares fit of the available data for normal transitions and forbidden transitions for the molecular constants did not converge properly unless the full expression was used.

The line strengths of the forbidden $\Delta K = \pm 3$ transitions (1, 2) are given by

$$S = \tfrac{1}{4}(\theta^{xx}{}_x)^2{}_{\text{eff}}(J \mp K)(J \mp K - 1)(J \mp K - 2)$$

$$\times (J \pm K + 1)(J \pm K + 2)(J \pm K + 3)(2J + 1)/J(J + 1) \quad (11)$$

where

$$(\theta^{xx}{}_x)_{\text{eff}} = \theta^{xx}{}_x + \hbar^4\tau_{xxxx}\mu_z/[2h(B - C)] \quad (12)$$

is the effective dipole moment inducing the transition. The term,

$$\theta^{xx}{}_x = 2(B)^2\left[\frac{a^{xx}{}_3}{\nu^2{}_3}\left(\frac{\partial\mu_x}{\partial Q_3}\right) + \frac{a^{xx}{}_4}{\nu^2{}_4}\left(\frac{\partial\mu_x}{\partial Q_4}\right)\right], \quad (13)$$

is an induced dipole component which results from admixture of the ground vibrational state with excited vibrational modes. This contribution, first recognized by Watson (2), is called vibrational intensity borrowing by Oka (10). The last term results from centrifugally induced mixing of rotational levels of the ground vibrational state. This contribution to the forbidden transitions, first derived by Hansen (1), is called rotational intensity borrowing by Oka (10). In this expression τ_{xxxx} is the centrifugal distortion constant in $\mathcal{3C}'$ of Eq. (1), μ_z is the permanent dipole moment, and C and B are the spectral constants with reference to the symmetry axis and the perpendicular axis, respectively.

For the present molecules, the contribution of the vibrational intensity borrowing is small in comparison with that of the rotational intensity borrowing. For PH$_3$, Chu and Oka (4) calculated that $\theta^{xx}{}_x = 1.6 \times 10^{-5}$ D and that the centrifugally induced moment, the second term of Eq. (12), is 8.3×10^{-5} D. The relative contributions of these mo-

ments to the forbidden line strengths, Eq. (12), is $(1.6/8.3)^2 = 0.037$. Thus, for PH_3 in the ground vibrational state, the contribution of the vibrational mixing to the intensities of the $\Delta K = \pm 3$ transitions is negligible in comparison with that from rotational mixing. Chu and Oka also estimate that the centrifugal rotational intensity borrowing is the dominant term for PD_3.

4. RESULTS

Twelve $K = 0 \leftarrow 3$ transitions of PH_3 as well as ten $K = \pm 1 \leftarrow \pm 4$ and five $K = 0 \leftarrow 3$ transitions in PD_3 were measured. The observed frequencies are given in Tables I and II. Displacement in positions of lines of PH_3 caused by the Nielsen–Dennison splitting (23) of the $K = 3$ levels (105 MHz for $J = 10$ in PH_3) increased the difficulty of their detection. This splitting does not occur in the transitions observed by Chu and Oka (4), but it has been directly observed for PH_3 by Davis et al. (24) in a molecular beam resonance experiment. Location of the $K = 0 \leftarrow 3$ transitions would have been even more difficult were it not for our access to their molecular beam measurements.

The $\Delta K = \pm 3$ transitions exhibit a rapid change in the observed intensity with increasing value of J. Figure 3 illustrates the calculated intensity profile (see Eq. (14)). This variation is due partly to the increase in the rotationally induced coupling moment with J and partly to the variation in the population of J states. At the temperature of the observation, 300 K, the intensity reaches a maximum for $J = 10$. The solid vertical bars in Fig. 3 correspond to transitions that we have measured. The dashed vertical bars representing calculated lines have been included for better indication of the trend. Figure 4 shows actual recordings of two lines.

The peak absorption coefficients listed in Tables I and II were calculated from the formula,

$$\alpha(\text{cm}^{-1}) = \frac{1.147 \times 10^{-13}}{\Delta\nu T^{\frac{5}{2}}} \nu^2_0 \left(1 - \frac{h\nu_0}{2kT}\right)$$

$$\times \exp(-E_{J,K}/kT)[(B^2C)^{\frac{1}{2}}g_K g_I S[(J, K \pm 3) \leftarrow (J, K)]], \quad (14)$$

where the line-strength factor S is given by Eq. (11), $T = 300$ K, g_I is the reduced nuclear statistical weight factor (25), g_K is the statistical weight factor for each K level, and $\Delta\nu = 20$ MHz is the line breadth at a pressure of 1 Torr. This value for the $\Delta\nu$ is the same as that used by Chu and Oka (4) for PH_3. Other factors included in the numerical constant are described in Ref. (25).

We had little difficulty in detecting the $J = 3$, $\Delta J = 0$, $K = 0 \leftarrow 3$ transition which has a predicted intensity of only 7×10^{-10} cm⁻¹. From comparisons of the signal-to-noise ratios for the four weaker lines of PH_3 and PD_3 with the calculated line intensities given in Tables I and II, we estimate the sensitivity of our spectrometer to be approximately 4×10^{-10} cm⁻¹.

A combined computer analysis was made of the available frequencies for different types of transitions measured by us and by others as listed in Tables I and II. The analysis consisted of a least-squares fitting of 10 molecular constants to the observed frequencies of PH_3 and 9 to those of PD_3. The program calculates the difference in the energy levels by use of Eqs. (5)–(8) with assumed values of the molecular constants.

TABLE I
Observed Frequencies and Calculated Intensities for the PH₃ Transitions

Transition	Observed Frequency ν (MHz)	ν Obs - ν Calc	α_{max} (Calc) (10^{-9} cm^{-1})
Normal Rotational Transitions			
$J + 1 \leftarrow J \quad K \leftarrow K$ (a)			
$J = 0 \quad K = 0$	266 944.52	0.00	
1 0	533 794.32	0.00	
1 1	533 815.01	0.00	
Forbidden Rotational Transitions			
$J \leftarrow J \quad K = \mp 1 \leftarrow \pm 2$ (b)			
$J = 6$	47 391.16	0.41	2.2
7	47 178.66	-0.27	3.4
8	46 939.04	0.09	4.5
9	46 871.48	-0.14	5.3
10	46 377.80	-0.03	5.7
11	46 058.52	-0.05	5.5
12	45 714.84	-0.05	5.0
13	45 347.84	-0.07	4.2
14	44 958.68	-0.14	3.3
15	44 548.88	0.04	2.4
16	44 119.80	0.53	1.6
17	43 671.08	-0.32	1.1
$J \leftarrow J \quad K = 0 \leftarrow 3$ (c)			
$J = 3$	143 701.63	-0.09	0.7
4	143 331.01	-0.13	3.4

TABLE I (continued)

Transition	Observed Frequency ν (MHz)	ν Obs - ν Calc	α_{max} (Calc) (10^{-9} cm^{-1})
5	142 869.93	0.05	8.8
6	142 319.00	0.12	17.1
7	141 679.05	0.13	27.2
8	140 950.44	0.02	37.1
9	140 133.10	-0.14	44.8
10	139 226.51	0.07	48.5
11	138 228.01	-0.03	47.9
12	137 134.86	-0.02	43.5
13	135 941.42	0.00	36.6
14	134 641.42	0.02	28.6
Molecular Beam Resonance Transitions (d)			
$K = 3$ Splittings			
$J = 3$	0.062	0.000	
4	0.434	-0.002	
5	1.734	-0.007	
6	5.198	-0.016	
7	12.969	-0.027	
8	28.483	-0.025	
9	56.855	0.031	

(a) P. Helminger and W. Gordy, Phys. Rev. 188, 100 (1969).
(b) Chu and Oka, Ref. 4.
(c) Present work.
(d) Davies, et al., Ref. 24.

TABLE II (continued)

Transition	Observed Frequency ν (MHz)	ν Obs - ν Calc	α_{max} (Calc) (10^{-9} cm^{-1})
$J \to J$ $K = 0 \to 3$ (c)			
$J = 9$	93 498.65	-0.04	2.2
10	93 265.70	0.02	3.0
11	93 009.29	-0.08	3.7
12	92 729.42	-0.02	4.3
13	92 425.42	0.05	4.7
$J \to J$ $K = \pm 1 \to \pm 4$ (c)			
$J = 9$	155 957.87	-0.02	7.8
10	155 573.65	0.00	10.7
11	155 153.32	0.01	13.6
12	154 697.68	0.15	16.1
13	154 207.02	0.00	18.0
14	153 682.42	-0.08	19.0
15	153 124.72	-0.07	19.1
16	152 534.73	-0.02	18.4
17	151 913.22	-0.04	16.9
18	151 261.35	0.09	14.9

(a) P. Helminger and W. Gordy, Phys. Rev. 188, 100 (1969).
(b) Chu and Oka, Ref. 4.
(c) Present work.

TABLE II
Observed Frequencies and Calculated Intensities for the PD₃ Transitions

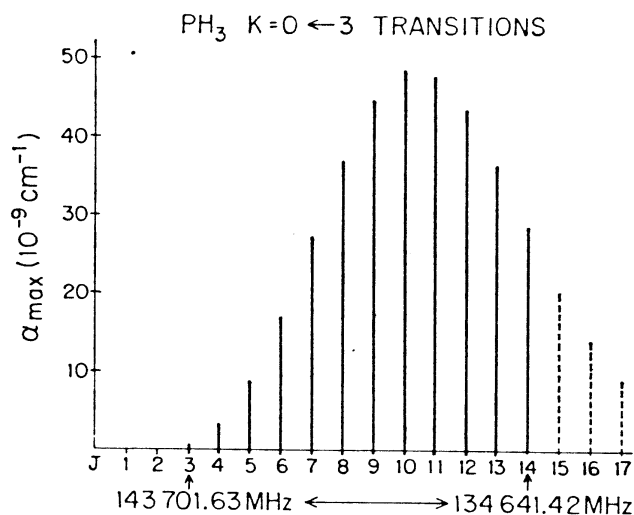| Transition	Observed Frequency ν (MHz)	ν Obs - ν Calc	α_{max} (Calc) (10^{-9} cm^{-1})
Normal Rotational Transitions			
$J+1 \to J$ $K \to K$ (a)			
$J = 0$ $K = 0$	138 938.17	0.06	
1 0	277 851.71	-0.01	
1 1	277 856.93	-0.04	
2 0	416 716.39	0.03	
2 1	416 724.18	-0.03	
2 2	416 747.81	0.01	
Forbidden Rotational Transitions			
$J \to J$ $K = \mp 1 \to \pm 2$ (b)			
$J = 13$	30 805.64	0.18	0.79
14	30 700.67	-0.04	0.82
15	30 587.40	0.06	0.82
16	30 471.50	-0.02	0.78
17	30 347.32	-0.11	0.71
18	30 217.40	0.16	0.62
19	30 081.32	0.15	0.53
20	29 939.20	0.22	0.43

FIG. 3. Calculated intensities for the $K = 0 \leftarrow 3$ lines observed in the present work (solid lines) and for some not observed (dotted lines).

Transition frequencies are calculated and compared to the measured transition frequencies to generate new estimates of the molecular constants. This iterative process is repeated many times by the computer until convergence is attained. The degree of fitting of the complete frequency set is shown by column 3 of Tables I and II. The molecular constants for PH_3 and PD_3 obtained from the combined analyses are listed in Table III. The constants h_0 and τ_{xxxx} for PD_3 are rather well determined since we were able to measure both the $K = \pm 1 \leftarrow \pm 4$ and $0 \leftarrow 3$ transitions. These same two constants for PH_3 are not nearly so well determined, because of their high statistical correlation and the lack of data from the $K = \pm 1 \leftarrow \pm 4$ transitions. The large uncertainties in the relative values of h_0 and the τ_{xxxx} do not appreciably limit the accuracy of the values of the other constants for PH_3.

There are only two independent structural parameters in PH_3 or PD_3, the bond angle and bond length. With the two measured moments, $I_b = h/8\pi^2 B_0$ and $I_c = h/8\pi^2 C_0$, an effective zero-point vibrational structure can be calculated for both species. The effective structural parameters thus derived are listed in Table IV. They are limited in
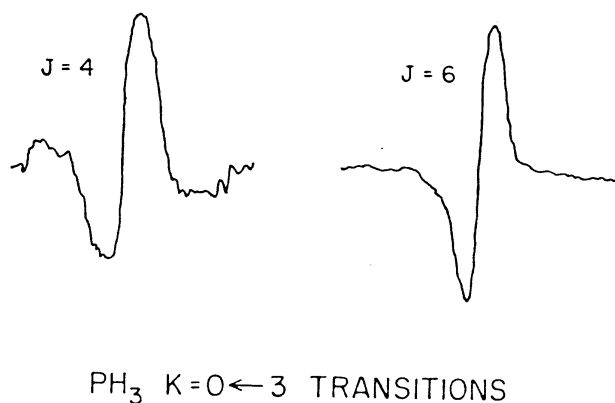

PH_3 $K = 0 \leftarrow 3$ TRANSITIONS

FIG. 4. Recordings of the $J = 4$ and $J = 6$, $K = 0 \leftarrow 3$, lines for PH_3 at 300 K.

TABLE III

Molecular Constants

Molecular Constant	PH$_3$	PD$_3$
B_0	133 480.15 $\pm$ 0.12 MHz	69 471.10 $\pm$ 0.03 MHz
C_0	117 488.85 $\pm$ 0.16 MHz	58 974.37 $\pm$ 0.05 MHz
D_J	3.947 $\pm$ 0.016 MHz	1.021 $\pm$ 0.002 MHz
D_{JK}	-5.132 $\pm$ 0.001 MHz	-1.312 $\pm$ 0.001 MHz
D_K	4.177 $\pm$ 0.011 MHz	1.023 $\pm$ 0.002 MHz
$\hbar^4 \tau_{xxxz}/4h$	0.62 $\pm$ 0.03 MHz	0.221 $\pm$ 0.005 MHz
H_{JJK}	-1.09 $\pm$ 0.04 kHz	-0.091 $\pm$ 0.004 kHz
h_0	67.6 $\pm$ 2.2 Hz	9.41 $\pm$ 0.22 Hz
L_{JJKK}	4.7 $\pm$ 0.7 Hz	
L_{JJJK}	0.52 $\pm$ 0.03 Hz	0.044 $\pm$ 0.005 Hz

accuracy by the uncorrected inertial defect. A second structure, the zero-point average structure (4) can also be calculated for each species from the observed B_0 and C_0 values. This structure was calculated by Chu and Oka for PH₃. We have recalculated the zero-point average values for the structural parameters with the B_0 and C_0 values derived from a computer analysis of the measured ground-state rotational transitions, as described above. The resulting parameters, listed in Table IV, are essentially the same as those obtained by Chu and Oka; the method used for calculation of the average

TABLE IV

Comparison of Different Structures for Phosphine

	Zero-point Effective[a]	Zero-point Average[b]	Equilibrium[b]
		PH$_3$	
r_{PH} (Å)	1.420$_0$	1.4269$_9$ $\pm$ 0.0002	1.4115$_9$ $\pm$ 0.0006
$\angle$HPH (°)	93.34$_5$	93.228$_7$ $\pm$ 0.005	93.32$_8$ $\pm$ 0.02
		PD$_3$	
r_{PD} (Å)	1.417$_6$	1.4226$_5$ $\pm$ 0.0001	1.4115$_9$ $\pm$ 0.0006
$\angle$DPD (°)	93.35$_9$	93.256$_7$ $\pm$ 0.004	93.32$_8$ $\pm$ 0.02

a. Uncorrected for inertial defects.

b. Calculated as described by Chu and Oka, Ref. 4.

structural values is the one they describe. Discussion of the significance or meaning of the various types of structures and methods for calculations of each type is given by Gordy and Cook (25).

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