

"Forbidden" Millimeter-Wave Transitions in Arsine¹

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A millimeter-wave spectrometer having a sensitivity of $4 \times 10^{-10} \text{ cm}^{-1}$ in the 2-mm region has been used for observation of the "forbidden" transitions $J \rightarrow J, K = \pm 4 \rightarrow \pm 1$ and $J \rightarrow J, K = \pm 5 \rightarrow \pm 2$ in AsH_3 . A comprehensive computer analysis was made of the frequencies measured in this work together with available microwave frequencies of other transitions. This analysis provides accurate values of the rotational constants, nuclear quadrupole couplings, and effective structural parameters of the molecule. The spectral constants B_0 and C_0 (in MHz) are 112 470.597 and 104 884.665, respectively.

I. INTRODUCTION

In a previous paper (1) we reported observations of forbidden $\Delta K = \pm 3$ microwave transitions in PH_3 and PD_3 . Our measurements of $K = 3 \rightarrow 0$ transitions in PH_3 and $K = 3 \rightarrow 0$ and $K = \pm 4 \rightarrow \pm 1$ transitions in PD_3 confirmed the assignments of the lower-frequency $K = \pm 2 \rightarrow \mp 1$ transitions of PH_3 and of PD_3 reported by Chu and Oka (2), and improved significantly the molecular constants, especially C_0 . A similar investigation is here described for arsine.

Transitions in AsH_3 obeying the $\Delta J = 0, \Delta K = \pm 3$ selection rules were first observed by Chu and Oka (2). They reported eight transitions obeying the selection rules $\Delta J = 0, K = \pm 2 \rightarrow \mp 1, \Delta F = 0$ in the frequency range of 21.16 to 21.84 GHz. The large As quadrupole coupling splits the $K = \pm 2 \rightarrow \mp 1$ line into two doublets, each component of which is an unresolved doublet. Chu and Oka combined their value of C_0 with the known value of B_0 (3) and with other information to obtain the zero-point effective, the zero-point average, and the equilibrium structures. Recently, Olson *et al.* (4) reported their observation of "perturbation-allowed" transitions of the type $\Delta |K - l| = \pm 3$ in the ν_1 and ν_3 infrared bands of AsH_3 . They combined their $\Delta |K - l| = \pm 3$ infrared measurements with the $K = \pm 2 \rightarrow \mp 1$ microwave measurements of Chu and Oka and with the normally allowed $\Delta K = 0$ microwave measurements of Helminger *et al.* (3) to obtain both a set of ground state molecular constants and an associated zero-point-effective structure. Olson *et al.* then used the constants for the ν_2 and ν_4 bands given by Sarka, *et al.* (5) with their constants for the ν_1 and ν_3 bands to determine the equilibrium structure. Our detection of the $K = \pm 4 \rightarrow \pm 1$ and the $K = \pm 5 \rightarrow \pm 2$ forbidden transitions was assisted by a preliminary prediction of their frequencies from the results of Helminger *et al.*, of Olson *et al.*, and of Chu and Oka.

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The need for observation of the higher $K = \pm 4 \rightarrow \pm 1$ and $K = \pm 5 \rightarrow \pm 2$ millimeter-wave transitions described in this paper was indicated by Chu and Oka (2), 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 very weak transitions such as these in the shorter millimeter-wave region, we designed an exceptionally sensitive millimeter-wave spectrometer, which is described in the earlier paper (1).

The Q -branch $\Delta K = \pm 3$ transitions represent only one class of forbidden transitions in symmetric top molecules included in the general theory of Watson (6, 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. 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 AsH_3 , the rotation about the b -axis of inertia induces a small dipole moment ($\approx 3.938 \times 10^{-5}$ D) perpendicular to the symmetry axis which leads to a slight admixture of the K levels and a breakdown of the familiar $\Delta K = 0$ selection rule. The threefold symmetry about the c -axis limits this admixture to K levels differing by three units. 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 , PD_3 , and AsH_3 which already have permanent dipole moments 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 in CH_4 , SiH_4 , and GeH_4 have been observed by Rosenberg *et al.* (11–14) in the far-infrared region. Kreiner *et al.* (15) have used Laser-Stark spectroscopy to measure the distortion-induced dipole moment of GeH_4 . Forbidden transitions of CH_4 in the ground vibrational state have also been detected in the microwave region by Holt *et al.* (16). At a recent symposium, Kagann *et al.* (17) reported their observations of over 140 Q -type $\Delta K = \pm 3$ microwave transitions in OPF_3 .

II. EXPERIMENTAL DETAILS

The millimeter-wave spectrometer and the experimental procedure used in these measurements are described in the earlier paper (1). The high sensitivity of this spectrometer ($\approx 4 \times 10^{-10}$ cm^{-1} at 144 GHz for a time constant of 1 sec) made possible the measurement of these weak $\Delta K = \pm 3$ transitions with an estimated accuracy of three parts in 10^7 .

III. 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 $\psi_{J,K\pm 3}$ in the ground vibrational state. The term in the Hamiltonian responsible for the interaction may be ex-

pressed (18) as

$$H' = \frac{\hbar^4 \tau_{xxxx}}{4} [(J_+^3 + J_-^3)J_z + J_z(J_+^3 + J_-^3)], \quad (1)$$

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

In the absence of the perturbing H' term, the rotational levels are all doubly degenerate for each value of K , ($K \neq 0$). The energy levels corresponding to $K \neq 3$ are raised or lowered, but they remain degenerate with symmetry E . The $K = 3$ level, however, is split into A_1 and A_2 components. The designations A_1 , A_2 , and E indicate the symmetry of the rovibrational wavefunction (excluding spin). In the case of AsH_3 , each of the energy levels is split further into $(2I + 1)$ components by the quadrupole interaction of the $\text{As}(I = \frac{3}{2})$ nucleus. The symmetry selection rules for Q -type $\Delta K = \pm 3$ transitions (19) are $+\leftrightarrow -$, along with $A_1 \leftrightarrow A_2$, or $E \leftrightarrow E$.

The formulas giving the energy levels may be expressed (20, 21) for $K \neq 3$ as:

$$\begin{aligned} \frac{E(F, J, K)}{h} &= G(J, K) + \frac{1}{2}[C_N + (C_K - C_N)K^2/J(J+1)] \\ &\times [F(F+1) - I(I+1) - J(J+1)] - eQq \left[3 \frac{K^2}{J(J+1)} - 1 \right] Y(J, \frac{3}{2}, F) + \left[\frac{\hbar^4 \tau_{xxxx}}{4h} \right]^2 \\ &\times \left\{ \frac{(2K-3)^2[J(J+1) - K(K-1)][J(J+1) - (K-1)(K-2)][J(J+1) - (K-2)(K-3)]}{G(J, K) - G(J, K-3)} \right. \\ &\left. + \frac{(2K+3)^2[J(J+1) - K(K+1)][J(J+1) - (K+1)(K+2)][J(J+1) - (K+2)(K+3)]}{G(J, K) - G(J, K+3)} \right\}; \quad (2) \end{aligned}$$

and for $K = 3$ as

$$\begin{aligned} \frac{E^-(F, J, 3)}{h} &= G(J, 3) + \frac{1}{2}[C_N + (C_K - C_N)K^2/J(J+1)] \\ &\times [F(F+1) - I(I+1) - J(J+1)] - eQq \left(3 \frac{K^2}{J(J+1)} - 1 \right) Y(J, \frac{3}{2}, F) \\ &+ \left(\frac{\hbar^4 \tau_{xxxx}}{4h} \right)^2 \frac{81[J(J+1) - 12][J(J+1) - 20][J(J+1) - 30]}{G(J, 3) - G(J, 6)} \\ &+ \left\{ h_0 - 18 \left(\frac{\hbar^4 \tau_{xxxx}}{4h} \right)^2 / [G(J, 0) - G(J, 3)] \right\} \\ &\times J(J+1)[J(J+1) - 2][J(J+1) - 6], \quad (3) \end{aligned}$$

TABLE I
Observed Frequencies and Calculated Intensities for the AsH₃ Transitions

Transition	Observed Frequency ν (MHz)	ν Obs- ν Calc	a_{\max} (calc) (10^{-10} cm ⁻¹)
<u>Normal Rotational Transitions</u>			
<u>J → J + 1 K → K F → F' (a)</u>			
J = 0 K = 0 F = 3/2 → 5/2	224 937.78	-0.01	
0 0 3/2 → 3/2	224 896.85	-0.02	
0 0 3/2 → 1/2	224 969.88	0.02	
1 0 5/2 → 7/2	449 792.43	0.02	
1 0 5/2 → 5/2	449 751.38	0.00	
1 0 3/2 → 3/2	449 821.08	0.02	
1 0 1/2 → 3/2	449 748.06	-0.01	
1 1 5/2 → 7/2	449 813.69	0.03	
1 1 3/2 → 5/2	449 772.90	-0.01	
1 1 1/2 → 3/2	449 823.85	-0.05	
<u>Forbidden Rotational Transitions</u>			
<u>J → J K = ± 2 → ∓ 1 F → F' (b)</u>			
J = 9 F = 15/2	21 835.96	0.01	1.7
10 17/2	21 827.60	-0.10	1.9
10 19/2	21 824.66	0.29	
11 19/2	21 402.76	0.08	2.0
11 21/2	21 399.84	-0.07	
12 21/2	21 161.96	-0.14	1.9
12 23/2	21 159.68	-0.07	
<u>J → J K = ± 4 → ± 1 F → F' (c)</u>			
J = 8 F = 15/2	110 694.86	0.03	13.7
9 19/2	109 737.88	-0.11	17.9
9 21/2	109 758.26	-0.04	17.9
9 15/2	109 761.53	-0.03	17.9
10 21/2	108 694.21	0.00	20.8
10 19/2	108 696.65	0.04	20.8
10 23/2	108 710.90	0.06	20.8
10 17/2	108 713.34	0.09	20.8

(continued)

and

$$\frac{E^+(F, J, 3)}{h} = G(J, 3) + \frac{1}{2}[C_N + (C_K - C_N)K^2/J(J+1)]$$

$$\times [F(F+1) - I(I+1) - J(J+1)] - eQq \left(3 \frac{K^2}{J(J+1)} - 1 \right) Y(J, \frac{3}{2}, F)$$

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

$$- h_0(J(J+1)[J(J+1) - 2][J(J+1) - 6], \quad (4)$$

where

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

$$- D_K K^4 + H_{JJK} J^2(J+1)^2 K^2 + H_{JKK} J(J+1)K^4$$

$$+ L_{JJKK} J^2(J+1)^2 K^4 + H_K K^6 + L_{JJJK} J^3(J+1)^3 K^2. \quad (5)$$

TABLE I—Continued

Transition			Observed Frequency ν (MHz)	ν Obs- ν Calc	a_{\max} (calc) (10^{-10} cm^{-1})
J → J K = ±4 → ±1 F → F (c) (continued)					
11		23/2	107 564.50	0.02	22.1
11		21/2	107 566.25	-0.05	22.1
11		25/2	107 578.28	-0.05	22.1
11		19/2	107 580.14	-0.02	22.1
12		25/2	106 354.89	-0.02	21.5
12		23/2	106 356.38	0.04	21.5
12		27/2	106 366.72	0.09	21.5
12		21/2	106 368.17	0.11	21.5
13		27/2	105 072.41	-0.06	19.4
13		25/2	105 073.65	0.06	19.4
13		29/2	105 082.50	-0.02	19.4
13		23.2	105 083.61	-0.03	19.4
14		29/2	103 725.04	-0.06	16.3
14		27/2	103 725.85	-0.16	16.3
14		31/2	103 733.80	0.00	16.3
14		25/2	103 734.66	-0.06	16.3
15		31/2	102 322.08	0.00	12.9
15		29/2	102 322.95	0.13	12.9
15		33/2	102 329.74	0.05	12.9
J → J K = ±5 → ±2 F → F (c)					
J =	8	F = 17/2	155 785.04	0.07	20.3
	8	15/2	155 791.36	0.02	20.3
	8	19/2	155 820.52	-0.02	20.3
	8	13/2	155 826.92	0.01	20.3
	9	19/2	154 443.53	0.10	28.4
	9	17/2	154 448.00	0.02	28.4
	9	21/2	154 471.86	-0.03	28.4
	9	15/2	154 476.40	-0.04	28.4
	10	21/2	152 972.59	-0.07	34.7
	10	19/2	152 975.92	-0.10	34.7
	10	23/2	152 995.93	0.01	34.7
	10	17/2	152 999.27	-0.03	34.7

(continued)

The $Y(J, I, F)$ which appears in the contribution from the quadrupole interaction may be expressed as:

$$Y(J, I, F) = \frac{\frac{3}{4}C(C+1) - I(I+1)J(J+1)}{2I(2I-1)(2J-1)(2J+3)}, \quad (6)$$

where

$$C = F(F+1) - I(I+1) - J(J+1), \quad \text{and where } \mathbf{F} = \mathbf{J} + \mathbf{I}. \quad (7)$$

($I = \frac{3}{2}$ in the case of AsH_3 considered here.) The $K = 3$ levels contain the term $\pm h_0 J(J+1)[J(J+1) - 2][J(J+1) - 6]$, first derived by Nielsen and Dennison (22) in their explanation of the anomalous effects in $K = 3$ lines observed by early microwave spectroscopists. Unfortunately, we were unable to evaluate the splitting constant h_0 for AsH_3 because the frequencies of the Q -type $K = 3 \rightarrow 0$ series occur below the operating range of our spectrometer.

The line strengths of the forbidden $\Delta K = \pm 3$ transitions (6, 23) are given by

$$S = \frac{1}{4}(\theta_x^{xx})_{\text{eff}}^2 (J \mp K)(J \mp K - 1)(J \mp K - 2)(J \pm K + 1)(J \pm K + 2) \\ \times (J \pm K + 3)(2J + 1)/J(J + 1), \quad (8)$$

TABLE I—Continued

Transition		Observed Frequency ν (MHz)	ν Obs- ν Calc	a_{\max} (calc) (10^{-10} cm $^{-1}$)	
J → J	K = ±5 → ±2	F → F	(c) (continued)		
11		23/2	151 380.19	-0.02	38.0
11		21/2	151 382.73	-0.03	38.0
11		25/2	151 399.62	0.02	38.0
11		19/2	151 402.07	-0.10	38.0
12		25/2	149 674.47	-0.02	37.9
12		23/2	149 676.46	-0.02	37.9
12		27/2	149 690.90	-0.01	37.9
12		21/2	149 692.95	0.06	37.9
13		27/2	147 865.05	0.06	34.8
13		25/2	147 866.70	0.14	34.8
13		29/2	147 879.07	0.02	34.8
13		23/2	147 880.72	0.09	34.8
14		29/2	145 962.56	0.07	29.7
14		27/2	145 963.82	0.05	29.7
14		31/2	145 974.66	-0.02	29.7
14		25/2	145 975.96	-0.01	29.7
15		31/2	143 979.43	-0.10	23.7
15		29/2	143 980.44	-0.14	23.7
15		33/2	143 990.14	-0.07	23.7
15		27/2	143 991.25	-0.00	23.7
16		33/2	141 930.83	0.02	17.8
16		31/2	141 931.74	0.07	17.8
16		35/2	141 940.26	0.04	17.8
16		29/2	141 941.05	-0.03	17.8

(a) P. Helminger, E. Beeson, Jr., and W. Gordy, Ref. 3.

(b) Chu and Oka, Ref. 2. One frequency from this reference was omitted.

(c) Present work.

where

$$(\theta_x^{xx})_{\text{eff}} = \theta_x^{xx} + \hbar^4 \tau_{xxxx} \mu_z / [2h(B - C)] \quad (9)$$

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

$$\theta_x^{xx} = 2(B)^2 \left[\frac{a_3^{xx}}{\nu_3^2} \left(\frac{\partial \mu_x}{\partial Q_3} \right) + \frac{a_4^{xx}}{\nu_4^2} \left(\frac{\partial \mu_x}{\partial Q_4} \right) \right], \quad (10)$$

is an induced dipole component which results from admixture of the ground vibrational state with excited vibrational modes. The last term of Eq. (9) results from centrifugally induced mixing of rotational levels of the ground vibrational state. In this expression, τ_{xxxx} is the centrifugal distortion constant in H' of Eq. (1), μ_z is the permanent dipole moment, and C and B are the spectral constants with respect to the symmetry axis and the perpendicular axis, respectively.

The contribution of the "vibrational intensity borrowing" [first term in Eq. (9)] is small in comparison with that of the "rotational intensity borrowing" [second term in Eq. (9)] (2). For PH_3 , the relative contribution of these two terms to the forbidden line strengths, Eq. (8), is $(1.6/8.3)^2 = 0.037$, and it is estimated that the relative contribution is even smaller in AsH_3 . Thus, for AsH_3 in the ground vibrational state the contribution of the vibrational mixing to the intensities of the $\Delta K = \pm 3$ transitions

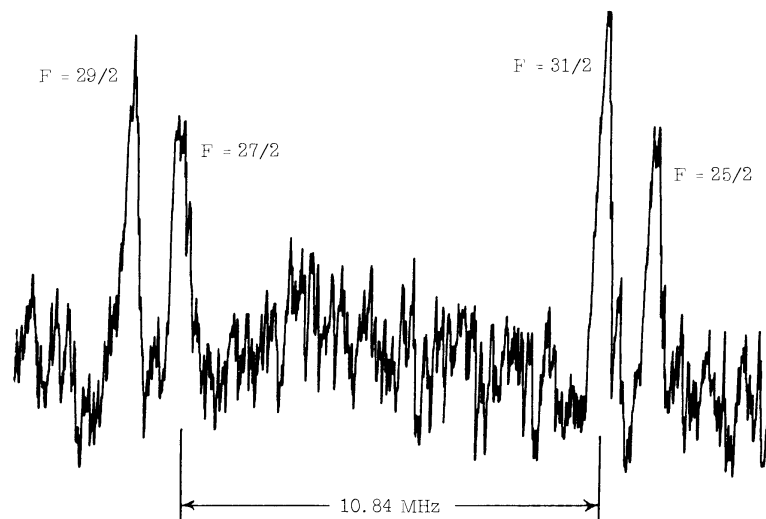


FIG. 1. Single scan of Q-type $K = \pm 5 \rightarrow \pm 2$ multiplet for $J = 14$.

is negligible in comparison with that from rotational mixing. We used the value of τ_{xxxx} from the analysis of the transition data to calculate the value of $(\theta_x^{xz})_{\text{eff}}$ used in the calculation of the intensities. The peak absorption coefficients, α_{max} , listed in Table I were calculated from the formula,

$$\alpha_{\text{max}}(\text{cm}^{-1}) = \frac{1.147 \times 10^{-13}}{\Delta\nu T^{\frac{1}{2}}} \nu_0^2 \left(1 - \frac{h\nu_0}{2kT} \right) \times \exp[-E(F, J, K)/kT] (B^2C)^{\frac{1}{2}} g_K g_n S[(F, J, K \pm 3) \leftarrow (F, J, K)], \quad (11)$$

where S is given by Eq. (8), $T = 300$ K, g_n is the reduced nuclear statistical weight

TABLE II
Molecular Constants

Molecular Constant	Value	Standard Deviation σ^*	
B_0	112 470.597	0.030	MHz
C_0	104 884.665	0.043	MHz
D_J	2.9257	0.0039	MHz
D_{JK}	-3.7164	0.0004	MHz
D_K	3.4126	0.0021	MHz
$(\hbar^4 \tau_{xxxx}/4h)$	0.679	0.003	MHz
H_{JJK}	-0.239	0.009	kHz
H_K	1.990	0.047	kHz
L_K	0.701	0.011	Hz
L_{JJK}	-1.729	0.067	Hz
C_{JJKK}	0.111	0.016	MHz
C_K	0.113	0.017	MHz
(eQq)	-162.58	0.11	MHz
$[\hbar^4 \tau_{xxxx} \mu_z / 2h(B-C)]$	3.938	0.017	10^{-5}D
r_0	1.5201381	0.0000002	\AA
α_0	91.975798	0.000006	($^\circ$)

* One standard deviation.

factor, 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 (2) for AsH_3 .

IV. RESULTS

Twenty-seven $K = \pm 4 \rightarrow \pm 1$ and thirty-six $K = \pm 5 \rightarrow \pm 2$ transitions were measured in this work. The observed frequencies are given in Table I. Figure 1 shows a chart recording of a single scan of the Q -type $K = \pm 5 \rightarrow \pm 2$ multiplet for $J = 14$. The quadrupole doublet is well resolved.

A combined computer analysis was made of the available frequencies for different types of transitions measured by us and by others as listed in Table I. The analysis consisted of a least-squares fitting of thirteen molecular constants to the observed frequencies of AsH_3 . The program calculates the difference in the energy levels by use of Eqs. (2)–(7) with assumed values of the molecular constants. Transition frequencies are calculated and compared to the measured transition frequencies to generate new estimates of the molecular constants. This iterative procedure is repeated by the computer until convergence is attained. The degree of fitting of the complete frequency set is shown by column 3 of Table I. The molecular constants for AsH_3 obtained from the combined analysis are listed in Table II.

The two independent zero-point-effective structural parameters for AsH_3 , r_0 and α_0 , were calculated from the B_0 and C_0 ; the resulting values are listed at the bottom of Table II. The standard deviations recorded for these values reflect only those uncertainties in the measurement of B_0 and C_0 and do not indicate the possible errors in the absolute values which depend on Planck's constant.

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