

## Submillimeter Spectrum and Spectroscopic Constants of the Arsine Molecule in the Ground Vibrational State<sup>1</sup>

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The submillimeter spectrum of the arsine molecule,  $\text{AsH}_3$ , of both the allowed  $R$ -branch transitions ( $J + 1 \leftarrow J$ ,  $J = 0, 1, 2, 3$ ) and forbidden transitions of the  $Q$  branches,  $|K| = 4 \leftarrow 7$ ,  $5 \leftarrow 8$ ,  $6 \leftarrow 9$ , is investigated in the frequency range from 220 to 900 GHz. Weak absorption lines were observed by using the spectrometer RAD with sensitivity increased by a nontunable cavity cell. On the basis of the results obtained and microwave data available in the literature the rotational spectrum of the arsine molecule in the ground state is analyzed.

### INTRODUCTION

The present interest in investigations of microwave spectra of small molecules with a high degree of symmetry is associated basically with a study of "forbidden" rotational electric dipole transitions. In spite of this, such transitions in the submillimeter wave region were observed only for two molecules,  $\text{NH}_3$  (1, 2) and  $\text{PH}_3$  (3). This fact can be explained by a rather low sensitivity of the methods used earlier in this region. In the present paper an experimental investigation of both allowed and weak "forbidden" rotational electric dipole transitions of  $\text{AsH}_3$  in the ground vibrational state in the frequency range from 200 up to 900 GHz is described. Weak lines were observed and measured by increasing (by an order of magnitude, on the average) the sensitivity of the scanning microwave spectrometer RAD (4) using a large (in comparison with the wavelength) nontunable cavity with practically merged modes (5). On the basis of the results obtained and microwave data available in the literature we have obtained a complete and accurate set of spectroscopic constants for the ground state of this molecule.

### EXPERIMENTAL DETAILS

The rotational spectrum of the arsine molecule in the frequency range 220-900 GHz was observed by using the submillimeter microwave spectrometer RAD with a system for precise frequency measurement (4). The nuclear hyperfine structure in the rotational spectrum of  $\text{AsH}_3$  required certain experimental conditions. Particularly, in the presence of closely located hyperfine quadrupole components we have to measure frequencies of line centers of the  $R$ -branch regular transitions  $J + 1 \leftarrow J$ ,  $K \leftarrow K$  at relatively low pressures—of some hundredths of a Torr when

<sup>1</sup> The results of this paper were partially reported at the Vth All-Union Symposium on Molecular Spectroscopy of High and Superhigh Resolution, Novosibirsk, 1980.

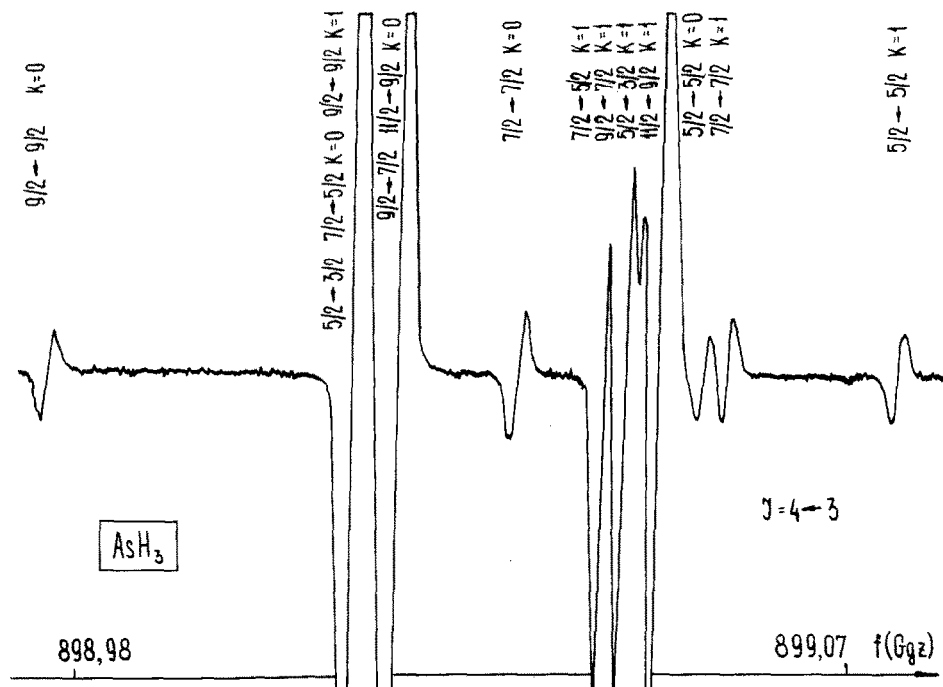


FIG. 1. A part of a record of the submillimeter wave spectrum of the arsine molecule containing the lines of the  $R$ -branch transition  $J = 4 \leftarrow 3$ ,  $K \leftarrow K$  in the ground vibrational state at pressure  $p \approx 0.08$  Torr and time constant  $\tau \approx 1$  sec. The lines are recorded in the form of derivative of absorption profile.

the collision width of spectral lines approaches the Doppler one. However, with decrease in pressure with acoustic detector sensitivity decreases ( $p_{\text{optim}} \approx 1$  Torr). Due to this, observation and measurement of frequencies of hyperfine quadrupole components of  $\text{AsH}_3$  lines were impossible in some cases, especially for weak transitions obeying the  $\Delta F = -1$  selection rules. Besides, the absorption coefficient of "forbidden" electric dipole transitions of arsine in the ground vibrational state in the frequency range used is at best  $\gamma_{\text{max}} \sim 10^{-8} \text{ cm}^{-1}$ . Thus, the method of increasing the sensitivity of the submillimeter scanning spectrometer RAD by an absorption cell in the form of a nontunable cavity (5) was adopted. As a result, sensitivity corresponding to the minimum detectable absorption coefficient (when  $S/N = 1$ )  $\gamma_{\text{min}} \approx 6 \times 10^{-10} \text{ cm}^{-1}$  was achieved for the average radiation source power 10 mW and time constant  $\tau \approx 1$  sec.

All measurements were carried out at room temperature and the pressure in the absorption cell was as a rule  $p \approx 0.02$ – $0.08$  Torr when measuring frequencies of allowed transitions and  $p \approx 0.5$  Torr for "forbidden" transitions. Examples of records of allowed and "forbidden" rotational transitions are given in Figs. 1, 2, and 3. It is easy to see that hyperfine quadrupole components are located very close to one another and some of them are not resolved. Since the accuracy of measuring absorption peaks is better than the spectrometer resolution, the identification of the peak frequency with the frequency of one of the spectral lines forming the peak

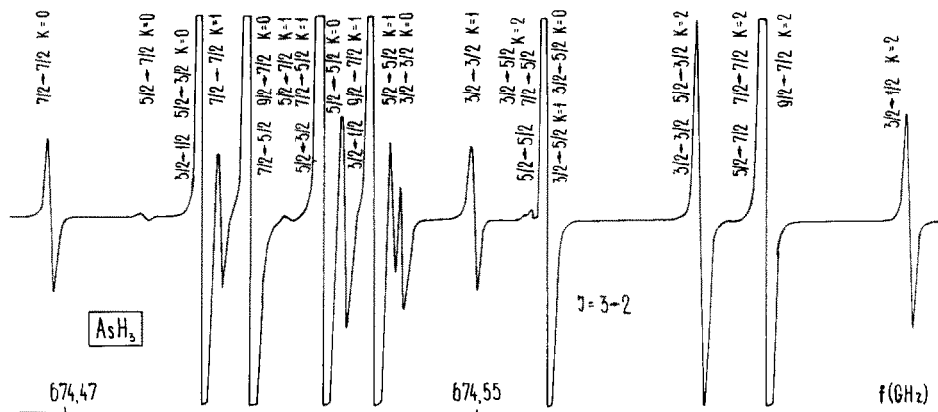


FIG. 2. A part of a record of the submillimeter wave spectrum of the  $\text{AsH}_3$  molecule containing the lines of the  $R$ -branch transition  $J = 3 \leftarrow 2$ ,  $K \leftarrow K$  in the ground state at pressure  $p \approx 0.12$  Torr and time constant  $\tau \approx 1$  sec. The lines are recorded in the form of derivative of absorption profile.

or neglecting the peak shift due to the influence of wings of the neighboring lines can lead to significant errors in the treatment of the spectrum. Thus, during the processing of the measurements a correction of spectral line positions was performed (see Appendix).

In the ground state of  $\text{AsH}_3$  we measured (Table I) 51 frequencies of the  $R$  branch allowed transitions ( $J + 1 \leftarrow J$ ,  $K \leftarrow K$ ,  $\Delta F = 0, \pm 1$ ) with  $J = 0, 1, 2$ , and 3 and 46 frequencies of "forbidden" transitions of three  $Q$  branches ( $J \leftarrow J$ ,  $\Delta F = 0$ ) with  $|K| = 4 \leftarrow 7, 5 \leftarrow 8$ , and  $6 \leftarrow 9$ . The "forbidden" spectrum of arsine in the ground vibrational state was investigated in the range from 240 to 340 GHz. Figure 3 displays the rotational lines of the  $Q$  branch with  $|K| = 6 \leftarrow 9$  and  $J = 10, 11, 12$ . The observed dependence of frequency spacings both between the doublets and between the lines within doublets on the quantum number  $J$  for  $\text{AsH}_3$  was used to make assignments when the data available in the literature (9-11) led to errors in predicted submillimeter frequencies of "forbidden" transitions  $\Delta K = 3$  comparable with distances between neighboring  $J$  lines in each  $Q$  branch.

The accuracy of measurement for allowed transitions equals 50 to 100 KHz depending on intensity and for "forbidden" transitions of 300 KHz. Frequencies of the transitions after correction are presented in Tables IA and B. These frequencies which we call experimental ones correspond to the positions of maxima of "infinitely narrow lines" and are related to the measured frequencies as  $\nu_{\text{exp}} = \nu_{\text{meas}} + \delta_{\text{cor}}$ . A small increase of errors of experimental frequencies in comparison with the errors of measured frequencies is caused by errors in calculation of  $\delta_{\text{cor}}$ . It is seen from Table I that the value  $\delta_{\text{cor}}$  can be compared with the error of the measured frequency. Curly brackets in Table I show unresolved groups of hyperfine components. In this case the given experimental frequency  $\nu_{\text{exp}}$  refers to the strongest line of this group. It should be stressed that for calculation of  $\delta_{\text{cor}}$  we measured simultaneously both the center frequency of each absorption peak and its width.

Note that the measured self-broadening parameter of  $\text{AsH}_3$  equals  $\Delta\nu = 3.4(3)$  MHz/Torr HWHM (6) and the pressure self-shift determined for separate hyperfine quadrupole components of the transition  $J = 1 \leftarrow 0$  is equal to  $\delta\nu = 0.15(2)$  MHz/Torr (7). The dependence of the self-shift of the arsine molecular lines on the quantum number  $J$  is investigated in Ref. (8); in general, the self-shift parameter decreases with increasing  $J$ .

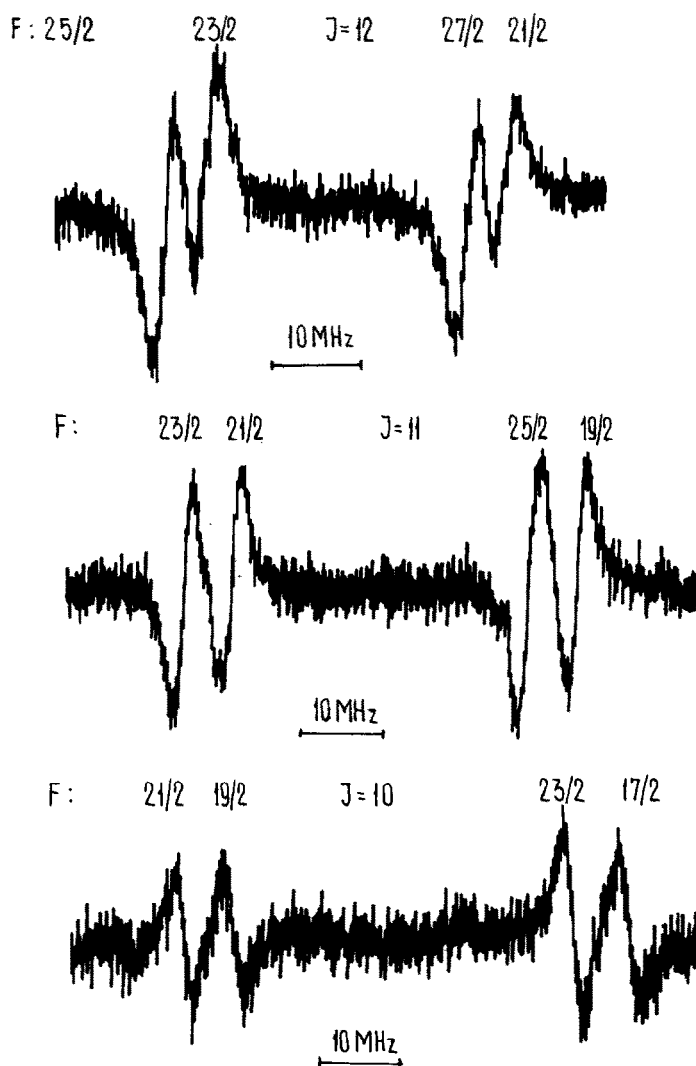


FIG. 3. A part of a record of the submillimeter wave spectrum of the  $Q$ -branch  $|K| = 6 \leftarrow 9$  "forbidden" electric dipole transitions with  $J = 10, 11, 12$  of the  $\text{AsH}_3$  molecule in the ground state obtained at the cell in the form of a nontunable cavity ( $p \approx 0.5$  Torr, time constant  $\tau \approx 1$  sec). The lines are recorded in the form of derivative of absorption profile.

TABLE I

Experimental and Calculated (Treatment with  $L_J \neq 0$ ) Values of Transition Frequencies of the AsH<sub>3</sub>-Molecule in the Ground Vibrational State: Allowed Rotational Transitions:  
 $J + 1 \leftarrow J, K \leftarrow K, F^1 \leftarrow F$

Transition			Exp. Frequency	Calc. Frequency	$\delta_{\text{corr}}$	E - C
J K	F' $\leftarrow$ F	(MHz)	(MHz)	(KHz)	(KHz)	
0 0	3/2	3/2	224 896.858(50)	224 896.875(32)		- 17
0 0	5/2	3/2	224 937.813(50)	224 937.800(30)		13
0 0	1/2	3/2	224 969.911(50)	224 969.907(32)		4
1 0	3/2	1/2	449 748.038(50)	449 748.057(21)		- 19
1 0	5/2	5/2	449 751.364(50)	449 751.384(21)		- 20
1 1	5/2	3/2	449 772.879(50)	449 772.900(20)		- 21
1 0	3/2	5/2	449 780.19(10)	449 780.164(22)		27
1 0	5/2	3/2				
1 0	7/2	5/2	449 792.435(50)	449 792.413(18)	14	36
1 1	5/2	5/2				
1 1	3/2	5/2				
1 1	1/2	3/2	449 807.28(10)	449 807.327(19)	39	- 5
1 1	7/2	5/2	449 813.672(50)	449 813.662(19)		10
1 0	3/2	3/2	449 821.094(50)	449 821.088(19)		6
1 1	3/2	1/2	449 823.910(50)	449 823.914(18)		- 4
1 1	1/2	1/2	449 844.082(50)	449 844.084(21)		- 2
1 0	1/2	3/2	449 861.60(10)	449 861.591(30)		7
2 0	7/2	7/2	674 468.847(50)	674 468.834(20)		13
2 0	5/2	7/2	674 487.47(10)	674 487.441(26)		29
2 0	3/2	1/2				
2 0	5/2	3/2	674 499.654(50)	674 499.690(13)	42	6
2 1	7/2	7/2	674 503.647(50)	674 503.631(17)		16
2 0	7/2	5/2				
2 0	9/2	7/2	674 509.933(50)	674 509.969(17)	46	10
2 1	5/2	7/2	674 517.52(10)	674 517.491(26)	- 25	- 5
2 1	5/2	3/2				
2 1	7/2	5/2	674 524.194(50)	674 524.334(14)	113	- 27
2 0	5/2	5/2	674 528.423(50)	674 528.470(16)	15	- 32
2 1	3/2	1/2				
2 1	9/2	7/2	674 534.498(50)	674 534.603(17)	42	- 63
2 1	5/2	5/2	674 538.178(50)	674 538.194(15)	8	- 8
2 0	3/2	3/2	674 540.008(50)	674 540.088(18)	36	- 43
2 1	3/2	3/2	674 554.177(50)	674 554.169(16)		7
2 2	3/2	5/2				
2 2	5/2	5/2				
2 2	7/2	5/2	674 567.83(10)	674 567.861(19)		- 35
2 1	3/2	5/2				
2 0	3/2	5/2				
2 2	3/2	3/2				
2 2	5/2	3/2	674 596.774(50)	674 596.802(16)	42	14
2 2	5/2	7/2				
2 2	9/2	7/2	674 608.604(50)	674 608.622(19)	18	0
2 2	7/2	7/2				
2 2	3/2	1/2	674 637.388(50)	674 637.359(20)		29
3 0	9/2	9/2	898 977.638(50)	898 977.604(23)		34
3 0	5/2	3/2				
3 0	7/2	5/2	899 013.911(50)	899 013.916(16)	33	27
3 1	9/2	9/2				
3 0	9/2	7/2				
3 0	11/2	9/2	899 018.805(50)	899 018.844(19)	49	10
3 0	7/2	7/2	899 032.516(50)	899 032.523(20)		- 7
3 1	7/2	5/2	899 043.08(10)	899 043.101(14)	- 14	- 30
3 1	9/2	7/2	899 045.33(10)	899 045.318(15)	- 11	5
3 1	5/2	3/2				
3 1	11/2	9/2	899 049.41(10)	899 049.489(17)		- 83
3 0	5/2	5/2	899 054.17(10)	899 054.208(23)	17	- 16
3 1	7/2	7/2	899 056.95(10)	899 056.961(18)		- 10
3 1	5/2	5/2	899 077.26(10)	899 077.293(21)		- 37
3 2	9/2	9/2				
3 2	9/2	7/2	899 125.180(50)	899 125.214(15)	17	- 17
3 2	7/2	9/2				
3 2	7/2	7/2				
3 2	7/2	5/2	899 130.75(10)	899 130.813(14)	31	- 31
3 2	11/2	9/2	899 141.57(10)	899 141.581(17)		- 12
3 2	5/2	7/2				
3 2	5/2	5/2				
3 2	5/2	3/2	899 146.914(50)	899 146.973(14)	27	- 32
3 3	7/2	7/2	899 253.433(50)	899 253.424(28)	- 6	2
3 3	9/2	7/2	899 258.914(50)	899 258.902(22)		13
3 3	5/2	5/2	899 262.85(10)	899 262.918(25)	22	- 51
3 3	7/2	5/2	899 277.534(50)	899 277.529(21)		6
3 3	11/2	9/2	899 295.604(50)	899 295.596(23)		8
3 3	9/2	9/2	899 309.31(10)	899 309.231(37)		75
3 3	5/2	3/2	899 314.019(50)	899 314.020(24)		- 1

TABLE IB

Forbidden Rotational Transitions:  $J-J$ ,  $F-F$ 

Transition		Exp.Frequency	Calc.Frequency	$\delta_{\text{corr}}$	E - C
J	F	(MHz)	(MHz)	(KHz)	(KHz)
$K = \mp 1 \leftarrow \pm 2$ (b)					
12	25/2	21 159.68(40)	21 159.56(18)		120
12	23/2				
12	27/2	21 161.96(40)	21 161.91(18)		52
12	21/2				
11	23/2	21 399.84(30)	21 399.93(13)		88
11	21/2				
11	25/2	21 402.76(30)	21 402.70(13)		61
11	19/2				
10	21/2	21 624.66(30)	21 624.52(13)		140
10	19/2				
10	23/2	21 627.60(30)	21 627.85(13)		- 250
10	17/2				
9	19/2	21 832.56(50)	21 832.11(17)		450
9	17/2				
9	21/2	21 835.96(40)	21 836.18(17)		- 220
9	15/2				
$K = \pm 4 \leftarrow \pm 7$ (a)					
12	25/2	238 898.90(30)	238 890.79(15)	- 162	- 53
12	23/2	238 901.69(30)	238 901.92(15)	204	- 25
12	27/2	238 924.57(30)	238 924.58(15)	- 124	- 129
12	21/2	238 927.46(30)	238 927.74(15)	243	- 42
11	23/2	241 635.26(30)	241 635.06(11)	- 95	104
11	21/2	241 639.13(30)	241 639.09(11)	- 98	142
11	25/2	241 665.69(30)	241 665.53(12)	- 76	76
11	19/2	241 669.77(30)	241 669.60(12)	106	279
10	21/2	244 187.16(30)	244 187.09(10)	- 44	32
10	19/2	244 192.21(30)	244 192.39(10)	56	- 118
10	23/2	244 223.64(30)	244 223.66(11)	- 34	- 56
10	17/2	244 228.84(30)	244 229.00(10)	66	- 91
9	19/2	246 541.79(30)	246 542.05(12)	- 250	
9	17/2	246 549.07(30)	246 549.21(12)	- 138	
9	21/2	246 586.65(30)	246 586.75(13)	- 97	
9	15/2	246 594.36(30)	246 593.96(13)	405	
$K = \pm 5 \leftarrow \pm 8$ (a)					
12	25/2	285 276.12(30)	285 275.99(13)	- 112	17
12	23/2	285 279.52(30)	285 279.70(13)	136	- 44
12	27/2	285 306.54(30)	285 306.47(13)	- 90	- 13
12	21/2	285 309.94(30)	285 310.21(13)	165	- 106
11	23/2	288 551.76(30)	288 551.66(10)	- 59	41
11	21/2	288 556.50(30)	288 556.42(10)	- 64	146
11	25/2	288 587.73(30)	288 587.68(11)	- 47	3
11	19/2	288 592.31(30)	288 592.48(11)	85	- 90
10	21/2	291 604.97(30)	291 604.77(13)		193
10	19/2	291 610.84(30)	291 611.03(13)	36	- 159
10	23/2	291 648.04(30)	291 648.00(14)		40
10	17/2	291 654.14(30)	291 654.30(14)	42	- 126
$K = \pm 6 \leftarrow \pm 9$ (a)					
13	27/2	329 075.75(30)	329 075.64(15)	- 137	- 25
13	25/2	329 078.76(30)	329 079.03(15)	176	- 95
13	29/2	329 105.95(30)	329 105.78(16)	- 119	51
13	23/2	329 109.27(30)	329 109.21(16)	160	213
12	25/2	333 154.90(30)	333 154.73(13)	- 82	88
12	23/2	333 158.83(30)	333 159.00(13)	- 95	- 75
12	27/2	333 189.96(30)	333 189.89(13)	- 63	1
12	21/2	333 194.01(30)	333 194.21(13)	111	- 94
11	23/2	336 989.02(30)	336 989.15(11)	- 36	- 165
11	21/2	336 994.41(30)	336 994.64(11)	51	- 176
11	25/2	337 030.59(30)	337 030.70(12)	- 108	
11	19/2	337 036.05(30)	337 036.24(12)	58	- 132
10	21/2	340 560.47(30)	340 560.40(12)		67
10	19/2	340 567.77(30)	340 567.62(12)		144
10	23/2	340 610.52(30)	340 610.27(14)		243
10	17/2	340 617.81(30)	340 617.55(13)		259
9	19/2	343 851.64(30)	343 851.87(21)	- 227	
9	15/2	343 922.62(30)	343 922.66(21)	- 35	

Spectroscopic Constants of the AsH<sub>3</sub> Molecule in the Ground Vibrational State and Their Correlation Matrix for Treatment with  $L_I \neq 0$ 

B	112 470.61500(2340)	MHz	1											
C	104 884.0805 (1264)		0.184	1										
D <sub>J</sub>	2 931.2155(54749)		0.9721	0.178	1									
D <sub>JK</sub>	- 3 723.793 (475) KHz		-0.004	-0.045	-0.011	1								
D <sub>K</sub>	3 357.18 (446)		-0.001	0.9629	0.000	-0.105	1							
H <sub>J</sub>	546.60 (45115)		0.9433	0.174	0.99406	-0.009	0.000	1						
H <sub>JJK</sub>	- 1 277.51 ( <b>1492</b> )		-0.001	-0.743	-0.003	0.398	-0.785	-0.002	1					
H <sub>JKK</sub>	1 623.73 ( <b>4020</b> )		-0.001	0.844	0.000	-0.149	0.857	0.000	-0.9536	1				
H <sub>K</sub>	- 370.0 (392)		0.000	0.767	0.000	-0.039	0.832	0.000	-0.388	0.446				
L <sub>J</sub>	- 3.611 ( <b>11604</b> ) Hz		-0.9243	-0.169	-0.9860	0.012	0.000	-0.99821	0.003	0.000				
L <sub>JJJK</sub>	- 0.39592( <b>6096</b> )		0.000	0.580	0.002	-0.323	0.604	0.002	-0.9287	0.854				
L <sub>JJKK</sub>	1.405 (111)		0.000	-0.273	0.000	0.157	-0.270	0.000	0.656	-0.578				
L <sub>JKKK</sub>	- 1.361 (233)		0.000	-0.793	0.000	0.053	-0.815	-0.001	0.613	-0.734				
L <sub>K</sub>	- 0.252 (186)		0.000	-0.163	0.000	-0.230	0.000	-0.096	0.143					
O <sub>K</sub>	105.35 (395)		0.066	0.023	0.030	0.041	0.005	0.029	0.005	0.005				
O <sub>N</sub>	111.87 (948)	KHz	0.034	-0.011	0.031	-0.006	-0.018	0.032	0.022	-0.026				
eqQ	- 162.6431 (532) MHz		0.053	-0.014	0.047	-0.045	-0.017	0.044	0.007	-0.020				

Before the present work, microwave data on measured frequencies of the following rotational transitions of AsH<sub>3</sub> in the ground vibrational state available in literature were: (1) the allowed transition  $J = 1 \leftarrow 0$  and some strongest components of the transition  $J = 2 \leftarrow 1$  (9) (2) "forbidden" transitions of the  $Q$  branch  $K = \pm 1 \leftarrow \mp 2$  ( $9 \leq J \leq 12$ ) (10) (3) "forbidden" transitions of two  $Q$  branches  $|K| = 1 \leftarrow 4$  ( $8 \leq J \leq 15$ ) and  $|K| = 2 \leftarrow 5$  ( $8 \leq J \leq 16$ ) (11). Our measurements of allowed transitions are more extensive than those in Ref. (9), completely cover the latter, and agree well with the data of Ref. (9) wherever comparison can be made. Thus, for the sake of uniformity, we used only our data on allowed transitions in evaluating molecular constants. We also used all measurements of the  $Q$ -branch "forbidden" transitions  $K = \pm 1 \leftarrow \mp 2$  (10), and these data are included in Table

H <sub>K</sub>	1								
L <sub>J</sub>	0.000	1							
L <sub>JJJK</sub>	0.214	-0.001	1						
L <sub>JKKK</sub>	0.051	-0.001	-0.884	1					
L <sub>JKKK</sub>	-0.585	0.000	-0.306	-0.127	1				
L <sub>K</sub>	-0.652	-0.001	0.022	0.056	-0.223	1			
C <sub>K</sub>	0.002	-0.030	-0.000	-0.007	-0.001	-0.002	1		
C <sub>N</sub>	-0.007	-0.032	-0.033	0.048	-0.012	0.018	0.301	1	
eqQ	-0.009	-0.043	-0.011	0.015	0.011	0.000	-0.072	0.121	1

TABLE III

Spectroscopic Constants of the AsH<sub>3</sub> Molecule in the Ground Vibrational State and Their Correlation Matrix for Treatment with  $L_J = 0$

B	112 470.608334(8928)	1									
C	104 884.0739 (1246)	MHz	0.074	1							
D <sub>J</sub>	2 929.5414 (9140)		0.9548	0.068	1						
D <sub>JK</sub>	- 3 723.791 (475)	KHz	0.018	0.048	0.003	1					
D <sub>K</sub>	3 357.180 (4457)		-0.001	0.9770	-0.001	-0.105	1				
H <sub>J</sub>	406.62 (2701)		0.9045	0.081	0.9871	0.055	0.007	1			
H <sub>JJK</sub>	- 1 277.50 (1492)		0.005	-0.753	0.000	0.398	-0.785	0.003	1		
H <sub>JKK</sub>	1 623.74 (4020)		-0.001	0.856	0.000	-0.149	0.857	0.009	-0.9536	1	
H <sub>K</sub>	- 370.0 (392)		-0.001	0.778	-0.001	-0.039	0.832	0.003	-0.389	0.446	
L <sub>JJJK</sub>	- 3.9595 (610)	Hz	-0.003	0.588	0.002	-0.323	0.604	0.004	-0.9287	0.854	
L <sub>JJKK</sub>	1.405 (111)		-0.001	-0.276	-0.003	0.157	-0.270	-0.011	0.656	-0.578	
L <sub>JKKK</sub>	- 1.361 (233)		0.002	-0.805	0.003	0.053	-0.815	-0.002	0.613	-0.734	
L <sub>K</sub>	- 0.252 (186)		-0.001	-0.166	-0.002	0.000	-0.230	-0.002	-0.096	0.143	
C <sub>K</sub>	105.32 (394)		0.099	0.018	0.005	0.042	0.005	-0.008	0.005	0.006	
C <sub>N</sub>	111.77 (947)	KHz	0.011	-0.017	-0.003	-0.005	-0.018	0.000	0.022	-0.026	
eqQ	- 162.6438 (531)	MHz	0.034	-0.022	0.027	-0.045	-0.017	0.017	0.007	-0.020	

$$L_J \leq 0.7 \text{ Hz}$$

I. Unfortunately we have not succeeded in fitting the results of measurements (11) for "forbidden" transitions of  $Q$  branches  $|K| = 1 \leftarrow 4$  and  $|K| = 2 \leftarrow 5$  within the quoted errors, thus they are not used by us in evaluating molecular constants. We cannot explain the reason of this poor fit; however, we consider it improbable that it lies in inadequacy of the model used or wrong assignment of our measured "forbidden" transitions. First, this model has been successfully applied (3) to describe a large number of high-precision measurements (both microwave and those obtained by a molecular beam spectrometer) of frequencies of transitions of the significantly more "nonrigid" phosphine molecule, PH<sub>3</sub>, in the ground vibrational state.<sup>2</sup> Second, removal of "forbidden" transitions measured in Ref. (10) from the treatment and those measured by us in the present paper (note that both of them

<sup>2</sup> The difference between the phosphine and arsine molecules caused by the arsine nuclear quadrupole structure is not essential in this case.

TABLE III—Continued

H <sub>K</sub>	1									
L <sub>JJJK</sub>	0.214	1								
L <sub>JJKK</sub>	0.051	-0.884	1							
L <sub>JKKK</sub>	-0.585	-0.306	-0.127	1						
L <sub>K</sub>	-0.653	0.022	0.056	-0.223	1					
C <sub>K</sub>	0.002	0.000	-0.007	-0.001	-0.002	1				
C <sub>N</sub>	-0.007	-0.033	0.043	-0.012	0.018	0.300	1			
eqQ	-0.009	0.011	0.015	0.011	0.000	-0.073	0.119	1		



are well described by the model used) does not improve the description of "forbidden" transitions measured in Ref. (11).<sup>3</sup>

Therefore, treatment of all experimental data on absorption line frequencies of the arsine molecule in the ground vibrational state given in Table I was performed within the limits of the semirigid symmetric-top model with  $K$ -doubling and hyperfine splittings due to quadrupole and magnetic interactions:

$$\begin{aligned}
 E(J, K, F) = & BJ(J+1) + (C-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 \\
 & - D_K K^4 + H_J J^3(J+1)^3 + H_{JJK} J^2(J+1)^2 K^2 + H_{JKK} J(J+1)K^4 + H_K K^6 \\
 & + L_J J^4(J+1)^4 + L_{JJK} J^3(J+1)^3 K^2 + L_{JJK} J^2(J+1)^2 K^4 + L_{JKK} J(J+1)K^6 \\
 & + L_K K^8 \pm (1/2)[\Delta_3 + \Delta_{3J} J(J+1)] \times J(J+1)[J(J+1) - 2][J(J+1) - 6] \delta_{|K|,3} \\
 & + eqQ \left[ \frac{3K^2}{J(J+1)} - 1 \right] \times Y(J, I, F) + \frac{1}{2} \left[ C_N + (C_K - C_N) \frac{K^2}{J(J+1)} \right] \\
 & \times [F(F+1) - J(J+1) - I(I+1)].
 \end{aligned}$$

The rotational part of energy is represented in the same form as that for the ground state of  $\text{PH}_3$  (3) and the energy of hyperfine splittings is written in accordance with Ref. (12). The algorithm used for the inverse spectroscopic problem solution is described in Ref. (4). The set of spectroscopic constants obtained as well as their correlation coefficient matrix are presented in Table II. A search for constants  $\Delta_3$  and  $\Delta_{3J}$  has not been performed, since the experimental data obtained do not contain any information on the splitting of rotational levels due to  $K$  doubling. The frequencies of the transitions used in the fitting and calculated by the constants from Table II are given in Table I. Since we could not determine well the constant  $L_J$ , we also made the fitting for  $L_J = 0$ . The set of spectroscopic constants obtained in this variant as well as their correlation coefficient matrix are presented in Table III. After exclusion of the constant  $L_J$  refinement of the constants  $H_J$  and  $D_J$  strongly correlated with it takes place. This refinement has a physical meaning only when the real value of  $|L_J|$  does not exceed some limiting value (3). In this case the inequality  $|L_J| \leq 0.7$  Hz should be fulfilled.

#### APPENDIX

In the case of theoretical description of normally distributed statistically independent frequencies of isolated spectral lines, the principle of maximal confidence results in the following requirement on model parameter  $A_1, A_2 \dots A = A$

$$\varphi(A) = \sum_i \left[ \frac{\nu_i^{\text{exp}} - \nu_i^{\text{calc}}(A)}{\sigma_i} \right]^2 = \min. \quad (\text{A1})$$

Here  $\nu_i^{\text{exp}}, \nu_i^{\text{calc}}$  are experimental and theoretical values of the " $i$ th" spectral line,  $\sigma_i$  is the root mean square measurement error of  $\nu_i^{\text{exp}}$ . However, such a treatment

<sup>3</sup> The calculation within the limits of the model used in Ref. (11) and by the constants mentioned in Ref. (11) does not permit us to reproduce those small differences between theory and experiment for  $Q$  branches  $|K| = 1 \leftarrow 4, |K| = 2 \leftarrow 5$  given in Ref. (11).

can lead to essentially distorted results if the information is contained in the frequencies of the absorption peaks formed by overlapped spectral lines. Here the absorption profile is given by the superposition of profiles of separate lines. Assuming that the isolated line contour is described by the Lorentz curve, we obtain for the absorption profile

$$\gamma(\nu) = \sum_n \frac{\gamma_0^{(n)}}{1 + ((\nu - \nu_0^{(n)})/\Delta\nu)^2}, \quad (\text{A2})$$

where  $\gamma_0^{(n)}$ ,  $\nu_0^{(n)}$  are the maximum absorption coefficient and the center frequency of the "nth" isolated line, respectively. Let us suppose that the half-widths  $\Delta\nu$  are equal for all isolated lines. Theoretical analogs of absorption peak frequencies measured in the experiment do not coincide with  $\nu_0^{(n)}$ , but they are determined by the solutions of the equation

$$\frac{\partial\gamma}{\partial\nu} = \sum_n \gamma_0^{(n)} \frac{\nu - \nu_0^{(n)}}{[1 + (\nu - \nu_0^{(n)})/\Delta\nu]^2} = 0. \quad (\text{A3})$$

As a result the requirement on model parameters (A1) transforms to the form

$$\varphi = \sum_i \left( \frac{\nu_i^{\text{exp}} - \nu_i^{\text{calc}}(A) + \delta_i^{\text{cor}}}{\sigma_i^*} \right)^2 = \min, \quad (\text{A4})$$

where

$$\delta_i^{\text{cor}} = \sum_K \frac{\gamma_0^{(K)}}{\gamma_0^{(i)}} (\nu_i^{\text{exp}} - \nu_i^{\text{calc}}) \left\{ \frac{1 + ((\nu_i^{\text{exp}} - \nu_i^{\text{calc}})/\Delta\nu)^2}{1 + ((\nu_i^{\text{exp}} - \nu_K^{\text{calc}})/\Delta\nu)^2} \right\}^2, \quad (\text{A5})$$

$$\sigma_i^* = \left[ \sigma_i^2 + \left( \frac{\partial\delta_i^{\text{cor}}}{\partial\Delta\nu} \right)^2 \sigma_{\Delta\nu}^2 \right]^{1/2}. \quad (\text{A6})$$

When calculating  $\delta_i^{\text{cor}}$ , summation over  $K$  means summation over the lines affecting the position of the "ith" line. The shift of the line center was taken into account if it constituted more than one tenth of the measurement error of the corresponding absorption peak frequency. The value  $\sigma_i^*$  differs from  $\sigma_i$  and also takes into account the errors of calculation of  $\delta_i^{\text{cor}}$  caused by the errors in measurements of spectral line half-widths. A Computer program based on the given algorithm and used for treating the  $\text{AsH}_3$  spectrum is described in Ref. (13).

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