

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

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A comprehensive investigation of both the allowed and the forbidden rotational spectra of the phosphine molecule,  $\text{PH}_3$ , in the ground vibrational state is described. The new experimental microwave investigation covers the frequency region from 300 to 1070 GHz.

### INTRODUCTION

Recently, there has been a renewal of interest in investigations of the spectra of small molecules with a high degree of symmetry. In the present paper experimental investigation of both allowed and forbidden lines of the submillimeter wave absorption spectrum of  $\text{PH}_3$  is described with a brief study of the symmetry properties of the energy levels of this molecule. On the basis of the results obtained here and microwave data on the phosphine molecule available in the literature we have obtained a set of 17 molecular constants and determined a new upper limit for inversion splitting in the ground state of this molecule. This new limit is smaller by a factor of 20 than the previous value.

### 1. EXPERIMENTAL DETAILS

The rotational spectrum of the phosphine molecule in the frequency range 300–1070 GHz was observed by using the submillimeter microwave spectrometer RAD (1) and submillimeter frequency synthesizer (SFS) (2); in the high-frequency region (higher than 600 GHz) one more BWO automatic frequency control (AFC) loop was added and it used the SFS signal as a reference.

The absorption cell was kept at room temperature, and the pressure in it amounted to 0.4 Torr of  $\text{PH}_3$  for measurements of the allowed transitions and 0.8–1 Torr of  $\text{PH}_3$  for the forbidden transitions. Portions of the spectrum with the forbidden and allowed transitions of  $\text{PH}_3$  are displayed in Figs. 1 and 2, respectively. The measured frequencies of the  $Q$ -branch forbidden transitions  $J \leftarrow J, |K| = 2 \leftarrow 5$  and the allowed  $R$ -branch transitions  $J = 3 \leftarrow 2, K \leftarrow K$  and  $J = 4 \leftarrow 3, K \leftarrow K$  are presented in Table I together with the formerly known experimental data from Refs. (3–6). Our experimental errors indicated in Table I include not only those of measurements (consideration of which may be seen

<sup>1</sup> The results of this paper were partially reported at the V-th International Seminar on High Resolution Infrared Spectroscopy, Liblice (near Prague, Czechoslovakia), 1978, paper A2.

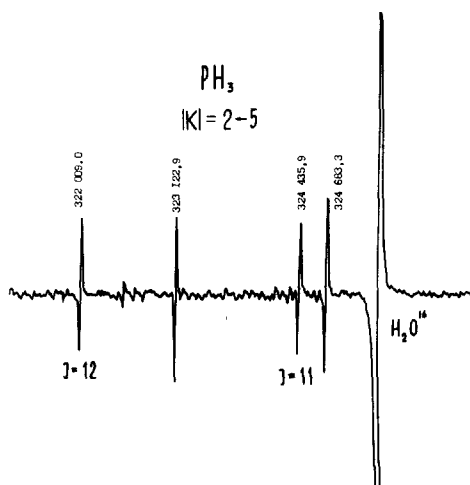


FIG. 1. A part of a record of the submillimeter wave spectrum of PH<sub>3</sub> containing the forbidden lines of the *Q*-branch  $K = \pm 2 \leftarrow \pm 5$ ,  $J \leftarrow J$  with  $J = 11$  and  $J = 12$ . Here are also present two nonassigned lines, measured frequencies of which are given in the figure. On the right is H<sub>2</sub><sup>16</sup>O line present as impurity. The lines are recorded in the form of derivative from absorption profile.

in Ref. (7)) but also the possible shifts of transition frequencies due to pressure. In this case we used the value of the pressure shift of the transition  $J = 1 \leftarrow 0$  in the ground vibrational state measured by us earlier (8), which equals +0.56 MHz/Torr.

Finally, we note that we measured also the self-broadening for the forbidden transition  $|K| = 2 \leftarrow 5$ ,  $J = 11$ . It has the value  $(5.4 \pm 0.6)$  MHz/Torr HWHM. This agrees well with the self-broadening parameter for the allowed transition measured in Ref. (8) and appreciably differs from that used in other papers (4, 5).

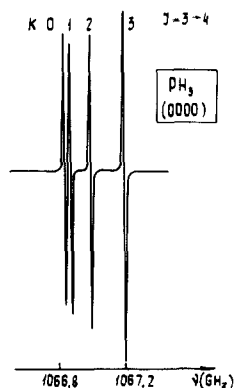


FIG. 2. A part of a record of the submillimeter wave spectrum of PH<sub>3</sub> at frequencies higher than 1 THz ( $10^{12}$  Hz) containing lines of the allowed transitions of the *R*-branch  $J = 4 \leftarrow 3$ ,  $K \leftarrow K$ . The lines are recorded in the form of derivative from absorption profile.

TABLE I

Measured and Calculated (Treatment "A") Values of Transition Frequencies of the  $\text{PH}_3$  Molecule in Its Ground Vibrational State

Transition	Meas. Freq. (MHz) $\nu_m$ ( $\Delta\nu_m$ )	Calc. Freq. (MHz) $\nu_c$ ( $\Delta\nu_c$ )	$\nu_m - \nu_c$ (kHz)
Allowed Rotational Transitions			
<u>J+1 ← J   K ← K</u>			
J=0   K=0	266 944.52 (4) <sup>a</sup>	266 944.52 (4)	0
1   0	533 794.32 (20)	533 794.33 (16)	- 10
1   1	533 815.01 (25)	533 815.00 (16)	10
2   0	800 456.26 (20) <sup>b</sup>	800 456.18 (12)	80
2   1	800 487.03 (20)	800 487.10 (12)	- 70
2   2	800 579.93 (20)	800 579.94 (12)	10
3   0	1 066 835.85 (20)	1 066 835.91 (10)	- 60
3   1	1 066 876.90 (20)	1 066 876.98 (10)	- 80
3   2	1 067 000.33 (20)	1 067 000.28 (10)	50
3   3	1 067 206.26 (20)	1 067 206.18 (10)	80
Forbidden Rotational Transitions			
<u>J ← J   K ← ±1 ← ±2</u>			
J=6	47 391.16 (56) <sup>c</sup>	47 390.92 (15)	240
7	47 178.66 (36)	47 179.11 (13)	- 450
8	46 939.04 (24)	46 939.09 (11)	- 50
9	46 671.48 (16)	46 671.678(89)	- 198
10	46 377.80 (24)	46 377.778(74)	22
11	46 058.52 (12)	46 058.391(69)	129
12	45 714.84 (20)	45 714.611(76)	229
13	45 347.64 (24)	45 347.620(92)	220
14	44 958.68 (28)	44 958.6 <sup>o</sup> (12)	- 10
15	44 549.88 (24)	44 549.17 (15)	- 290
16	44 119.80 (52)	44 120.49 (22)	- 690
17	43 671.08 (56)*	43 674.16 (35)	-3080
<u>J ← J   K ← 0 ← 3</u>			
J=3	143 701.63 (10) <sup>d</sup>	143 701.548(69)	82
4	143 331.01 (10)	143 331.085(54)	- 75
5	142 869.93 (10)	142 869.917(43)	13
6	142 319.00 (10)	142 318.971(41)	29
7	141 679.05 (10)	141 679.018(44)	32
8	140 950.44 (10)	140 950.488(46)	- 48
9	140 133.10 (10)	140 133.258(46)	- 158
10	139 226.51 (10)	139 226.413(46)	97
J=11	138 228.01 (10)	138 227.964(49)	26
12	137 134.66 (10)	137 134.654(54)	6
13	135 941.42 (10)	135 941.448(57)	- 28
14	134 641.42 (10)	134 641.396(89)	24
<u>J ← J   K ← 2 ← 5</u>			
J=6	333 839.95 (50) <sup>b</sup>	333 840.16 (36)	- 210
7	332 344.95 (50)	332 345.39 (27)	- 440
8	330 651.65 (50)	330 651.50 (22)	150
9	328 764.43 (50)	328 764.20 (21)	230
10	326 690.32 (50)	326 689.85 (22)	470
11	324 435.91 (50)	324 435.50 (23)	410
12	322 008.98 (50)	322 008.83 (23)	150
13	319 417.85 (50)	319 418.15 (24)	- 300
14	316 671.85 (50)	316 672.38 (25)	- 530
15	313 780.44 (50)	313 781.01 (27)	- 570
16	310 754.78 (50)	310 754.13 (43)	650
Molecular Beam Resonance Transitions			
<u> K  = 3 splitting</u>			
J=3	0.062 25 (20) <sup>e</sup>	0.062 058 (6)	0.192
4	0.434 09 (20)	0.434 020(29)	0.070
5	1.734 13 (20)	1.734 154(78)	-0.024
6	5.195 70 (20)	5.195 58 (13)	0.120
7	12.969 00 (20)	12.969 08 (13)	-0.080
8	28.442 50 (20)	28.442 50 (18)	0
9	56.855 00 (20)	56.854 99 (20)	0.010

Note. a—Helminger and Gordy (3), b—the present paper, c—Chu and Oka (4), d—Helms and Gordy (5) e—Davies *et al.* (6).

\* This transition was not used in the treatment.

## 2. THEORY

*2.1. The Symmetry of Rotational States of a Phosphine Molecule*

To interpret experimental data, correct consideration of symmetry properties of the molecular energy states is necessary. There is no uniform approach to this problem yet, so we give a summary of our treatment used to classify the rotational state of a phosphine molecule. A more detailed description of the method will be published elsewhere (9).

A molecule is a multiparticle system. In the majority of cases it is not possible to solve exactly the problem of its stationary states. Thus we have to use perturbation theory methods. Passing to the zero approximation is performed by constructing a series of increasingly approximate models "enclosed" one in another until an exact solution of the model problem becomes possible. It is clear that for numerical calculation there must be continuity for transition between neighboring models, expressed by the possibility of describing the difference between them in the form of an expansion in a small parameter. In spite of this continuity requirement, the symmetry groups of the used models used are usually different, i.e., when passing from one model to another, symmetry is changed discontinuously. Therefore, to consider the solution evolution for transition between neighboring models it is necessary to use some matching conditions of symmetry properties of the solution. In other words, it is necessary to point out equivalent elements in these symmetry groups in relation to which the solution should be transformed in an identical manner. Following this treatment and using the molecular symmetry groups matchings suggested in Ref. (9) we obtain the classification scheme of rotational levels in Born-Oppenheimer approximation for the phosphine molecule ground state displayed in Fig. 3.

Consideration of this scheme permitted us to suggest a new method of studying the inversion splitting in the phosphine molecule. This problem is important because the pure inversion splitting in phosphine is small and all attempts to detect it failed (3, 6, 10). Presently, the most strict upper experimental limit of the inversion splitting in the ground state of PH<sub>3</sub> is 1 KHz. This limit is determined by the resolution of the spectrometer with a molecular beam used (6). This resolution is at present close to the limiting one; it is in fact defined by the time of flight of a molecule through an experimental device of reasonable size (11). So it is difficult now to expect significant improvement in the resolution of spectrometers, i.e., significant progress in studying the inversion in the phosphine molecule by means of direct observation of splitting.

However, use of the molecular symmetry properties permits the study of inversion motion by singling out and describing a small contribution to the experimentally observed (6)  $K$ -splitting of levels with  $|K| = 3$ .

One can easily see (9) that the levels with  $|K| = 3n$  ( $n = 1, 2, \dots$ ) split in the quasi-rigid approximation. It is important that this splitting "push apart" states with different behavior relative to inversion, so the inversion motion will contribute to the splitting. The sign of the inversion contribution changes with the parity of the rotational quantum number (9). Thus  $K$ -splittings of levels with  $|K| = 3$  will be "modulated" by the inversion contribution. The additional important

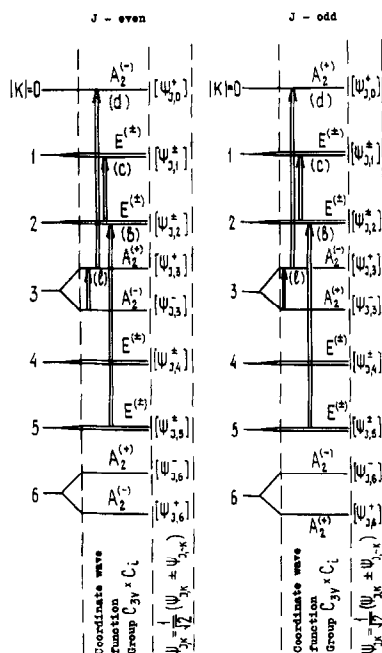


FIG. 3. Classification scheme of energy levels in the ground state of  $\text{PH}_3$ . Coordinate wave-functions in Born–Oppenheimer approximation are classified according to irreducible representations of the symmetry group  $C_{3v} \times C_i$ ;  $C_{3v}$ —molecular point group,  $i$ —inversion operation of the space coordinates of all particles. Wave functions  $\psi_{J,K}$  are considered in the basis in which one of the planes of reflection  $\sigma_v$  of the  $C_{3v}$  group coincides with the coordinate plane  $XZ$  ( $Z$  is the molecular axis of symmetry). Arrows show the experimentally observed  $Q$ -branch transitions; their legends correspond to those in Table I.

circumstance in the treatment is that the inversion splitting in the first approximation does not depend on the quantum numbers of the rotational state (13) whereas  $K$ -doubling depends strongly on these numbers (12). When using this approach, the “effective resolution” of the apparatus is essentially better than that determined only by the width of spectral lines for two reasons. First, the accuracy of measuring spectral line frequencies is determined by their width and the signal-to-noise ratio (14); second, information accumulates in a treatment of the whole ensemble of lines with the same model.

The treatment performed by us of all the experimental data on absorption frequencies in the ground electronic and vibrational state of the phosphine molecule (see below) permitted us to lower the upper experimental limit of the inversion splitting in this state approximately by a factor of 20. It is natural that in the case of further accumulation and refinement of experimental information further progress in this direction will be possible.<sup>2</sup> Also, the method suggested above in which the properties of a molecular state symmetry permit one to substitute

<sup>2</sup> The magnetic hyperfine  $K$ -doublet structure when using transitions with  $\Delta J = \Delta K = \Delta F = 0$  may be neglected until the error of measuring their frequencies is much greater than the differences between hyperfine structures in two  $K$ -doublet states.

observation of spectral line splittings by observation of spectral line shifts, may evidently be applied to the study of other weak intramolecular interactions.

## 2.2. Determination of Spectroscopic Constants of the Phosphine Molecule in the Ground Vibrational State

Treatment of all the known experimental data (see Table I) on absorption line frequencies of the phosphine molecule in the ground vibrational state was performed within the limits of the semirigid symmetric-top model with *K*-doubling. The effective rotational Hamiltonian operator has the form

$$\begin{aligned} \hat{H} = & B\hat{P}^2 + (C - B)\hat{P}_z^2 - D_J\hat{P}^4 - D_{JK}\hat{P}^2\hat{P}_z^2 - D_K\hat{P}_z^4 + H_J\hat{P}^6 + H_{JK}\hat{P}^4\hat{P}_z^2 \\ & + H_{JKK}\hat{P}^2\hat{P}_z^4 + H_K\hat{P}_z^6 + L_J\hat{P}^8 + L_{JJK}\hat{P}^6\hat{P}_z^2 + L_{JJKK}\hat{P}^4\hat{P}_z^4 \\ & + L_{JKKK}\hat{P}^2\hat{P}_z^6 + L_K\hat{P}_z^8 + \frac{1}{2}(\Delta_3 + \Delta_J\hat{P}^2 + \Delta_{JJ}\hat{P}^4)(\hat{P}_+^6 + \hat{P}_-^6), \quad (1) \end{aligned}$$

where  $P$ ,  $P_z$  are the operators of the total angular momentum and its projection on to the axis of symmetry of the molecule, respectively;  $P_{\pm} = P_x \pm iP_y$ . Interpretation of quadratic and quartic constants is well known. Interpretation of sextic constants used here is considered in Ref. (12). Interpretation of the eighth- and tenth-order constants<sup>3</sup> is not obtained at present and the corresponding terms are introduced into the effective rotational Hamiltonian operator phenomenologically.

The inversion motion contribution was taken into account only for transitions between the *K*-doublet states with  $|K| = 3$ . Since the symmetric state in relation to the inversion operation corresponds to the "down" inversion shift and the anti-symmetric one to the "up" shift, the full splitting value is equal to

$$\begin{aligned} \Delta &= \Delta_{JK} - \Delta_i & J\text{—even,} \\ \Delta &= \Delta_{JK} + \Delta_i & J\text{—odd,} \end{aligned} \quad (2)$$

where  $\Delta_{JK}$  is the vibrational-rotational interaction contribution (having a magnitude strongly dependent on *J*, but a sign independent of *J*) and  $\Delta_i$  is the inversion motion contribution.

The algorithm used for the inverse spectroscopic problem solution is described in Ref. (1). The results of processing for the constants included in the rotational operator (1) are given in Tables IV and V. We could not determine well the inversion splitting constant  $\Delta_i$ ; but the result obtained sets an experimental limit for it is approximately 20 times lower than what was known before (6), namely,

$$\Delta_i = -8.4(418) \text{ Hz.} \quad (3)$$

The standard deviation of  $\pm 42$  Hz in Eq. (3) is consistent with that which would be estimated simply by taking the approximately  $\pm 200$  Hz measurement errors of the molecular beam data (6), multiplying by  $(2/7)^{1/2}$  to allow for subtraction of the beam measurements in pairs to obtain seven values for the splitting  $2\Delta$ , and then dividing by two to obtain a standard deviation for  $\Delta$ .

<sup>3</sup> The only tenth-order constant is  $\Delta_{JJ}$ . Its introduction is necessary because of the high accuracy of measured transition frequencies by the molecular beam spectrometer (6).



in differences between the measured and calculated frequencies of lines. But this is not a sufficient condition for exclusion of these constants. The problem is that after exclusion of the parameter  $L_J$  (or  $L_K$ ) refinements of the parameters  $D_J$ ,  $B$  (or  $D_K$ ,  $C$ , respectively) strongly correlated with it do not always have a physical sense. In fact, if we vary slightly the value of the parameter  $L_J$  (or  $L_K$ ) near the zero value, then parameters  $D_J$ ,  $B$  (or  $D_K$ ,  $C$ ) would also be varied. For preservation of the physical meaning of these refined constants the unknown value of the excluded parameter  $L_J$  (or  $L_K$ ) should not exceed some limiting value, chosen so as to maintain the values of constants  $D_J$ ,  $B$  (or  $D_K$ ,  $C$ ) within their new error limits. The condition of preserving the physical meaning of refined constants is more strict when we consider the parameter most strongly correlated with  $L_J$  (or  $L_K$ ). Mathematically this may be written in the form

$$\begin{aligned} |L_J| \cdot \left| \frac{(H_J)_A - (H_J)_B}{(L_J)_A} \right| &\leq (\sigma_{H_J})_B, \\ |L_K| \cdot \left| \frac{(H_K)_A - (H_K)_B}{(L_K)_A} \right| &\leq (\sigma_{H_K})_B \end{aligned} \quad (4)$$

where  $\sigma_X$  is the rms deviation of parameter  $X$ . Then

$$|L_J| \leq 3.7 \text{ Hz} \quad |L_K| \leq 23 \text{ Hz}. \quad (5)$$

The set of spectroscopic constants obtained as well as their correlation coefficient matrix are presented in Table III.

### 3. CONCLUSION

In view of the technological advances made in the submillimeter region, we have been able to observe a rather extended set of experimental data for PH<sub>3</sub>. This combined with the methods developed for treating the experimental results enabled us to remove some of the difficulties encountered in Refs. (5, 15) in interpreting the  $K$ -splitting. Also, the difference between experimental and calculated values for the frequencies is reduced by several orders of magnitude.

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### REFERENCES

1. A. F. KRUPNOV AND A. V. BURENIN, in "Molecular Spectroscopy: Modern Research" (K. Narahari Rao, Ed.), Vol. 2, pp. 93-126, Academic Press, New York, 1976.
2. S. P. BELOV, L. I. GERSHTEIN, A. V. MASLOVSKY, AND YU. P. SHANDRA, "All-Union Symposium on High and Superhigh Resolution Molecular Spectroscopy," abstracts of papers, pp. 243-246, Novosibirsk, 1978.
3. P. HELMINGER AND W. GORDY, *Phys. Rev.* **188**, 100-108 (1969).



4. F. Y. CHU AND T. OKA, *J. Chem. Phys.* **60**, 4612-4618 (1974).
5. D. A. HELMS AND W. GORDY, *J. Mol. Spectrosc.* **66**, 206-218 (1977).
6. P. B. DAVIES, R. M. NEUMANN, S. C. WOFSEY, AND W. KLEMPERER, *J. Chem. Phys.* **55**, 3564-3568 (1971).
7. B. A. ANDREEV, A. V. BURENIN, E. N. KARYAKIN, A. F. KRUPNOV, AND S. M. SHAPIN, *J. Mol. Spectrosc.* **62**, 125-148 (1976).
8. B. A. ANDREEV, S. P. BELOV, A. V. BURENIN, L. I. GERSHTEIN, A. F. KRUPNOV, A. V. MASLOVSKY, AND S. M. SHAPIN, *Opt. Spectrosc.* **44**, 620-621 (1978).
9. A. V. BURENIN AND V. N. MARKOV, *Izv. Vyssh. Uchebn. Zaved. Radiofiz.*, in press.
10. A. G. MAKI, R. L. SAMS, AND W. B. OLSON, *J. Chem. Phys.* **58**, 4502-4512 (1973).
11. N. RAMSAY, "Molecular Beams," IL, Moscow, 1960.
12. M. R. ALIEV AND J. K. G. WATSON, *J. Mol. Spectrosc.* **61**, 29-52 (1976).
13. W. GORDY AND R. L. COOK, "Microwave Molecular Spectra," Wiley-Interscience, New York, 1970.
14. Quantum electronics, Soviet Encyclopaedia, Moscow, 1969.
15. D. A. HELMS AND W. GORDY, *J. Mol. Spectrosc.* **69**, 473-481 (1978).