

The Raman Spectra and Molecular Constants of Phosphorus Trifluoride and Phosphine*

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The Raman frequencies of $\text{PF}_3(l)$ were found to be $\omega_1(1)$, 890 cm^{-1} ; $\omega_2(1)$, 531 cm^{-1} ; $\omega_3(2)$, 840 cm^{-1} ; and $\omega_4(2)$, 486 cm^{-1} , indicating a regular pyramid structure of the molecule. Three frequencies were observed for $\text{PH}_3(l)$: 2306 cm^{-1} , 1115 cm^{-1} and 979 cm^{-1} . With the aid of electron diffraction data the standard virtual entropies of

$\text{PF}_3(g)$, $\text{PCl}_3(g)$, $\text{AsF}_3(g)$, and $\text{AsCl}_3(g)$ at 25°C are calculated to be 64.2, 74.7, 69.2, and 78.2 cal./deg., respectively; that of $\text{PH}_3(g)$ is estimated to be 50.5 cal./deg. These data lead to the following free energies of formation at 25°C: $\text{AsCl}_3(g)$, -62,075 cal.; $\text{PH}_3(g)$, 2750 cal.; $\text{PCl}_3(g)$, -62,220 cal.

INTRODUCTION

THE thermodynamic constants and molecular structure of the volatile fluorides are most readily obtained, at the present time, from the results of Raman spectra and electron diffraction experiments. The free energy and entropy values so determined are not as accurate as those calculated from more complete spectroscopic data, but in general they are about as reliable as those resulting from equilibrium measurements. Then too, comparisons of the Raman frequencies and molecular sizes for a series of analogous substances give a measure of relative bond strengths and point to possible generalizations regarding bond angles and molecular shapes.

In the present paper are presented the results of an investigation on the Raman spectra of phosphorus trifluoride and phosphine, together with a discussion of their thermodynamic quantities and molecular structures.

We wish to express here our indebtedness to Dr. L. O. Brockway and Mr. F. T. Wall for permitting us to use as yet unpublished results of electron diffraction experiments made on phosphorus trifluoride, arsenic trifluoride and arsenic trichloride.

EXPERIMENTAL

The phosphorus trifluoride was prepared by the direct reaction between arsenic trifluoride and phosphorus trichloride.¹ The two liquids are not

miscible, and the reaction is slow, but its rate was increased by adding a few drops of antimony pentachloride and by warming the mixture to 35°. In this manner 20 cc of liquid phosphorus trifluoride (m.p. -160°, b.p. -95°) was prepared in two hours. The resulting material was fractionated repeatedly and condensed into a Raman tube which was then sealed. To obtain the spectrum the tube was placed in a Dewar flask containing alcohol and solid carbon dioxide. The Dewar flask was silvered over one-half of its circumference in such a way that it formed a semi-cylindrical mirror.

Phosphine was prepared by treating calcium phosphide with water. A train of gas absorption bottles containing concentrated hydrochloric acid and water served to convert the lower phosphorus hydrides into phosphine. The gas was thoroughly dried by passing it repeatedly through traps cooled with solid carbon dioxide. The resulting material was condensed into a Raman tube which was then sealed off and placed in the above-described Dewar flask which contained alcohol and solid carbon dioxide.

Both the phosphorus trifluoride and phosphine were present as liquids under their own vapor pressures of 2 to 4 atmospheres. Good photographs were obtained in one and one-half to three hours with a water-cooled mercury arc in Pyrex as a source of radiation. The spectrum from gaseous phosphorus trifluoride was also photographed by using the 2537A line of mercury as a source of radiation. Three Raman lines were obtained. Considerable decomposition of the gas took place with the formation of a yellow solid.

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¹ Ruff, *Die Chemie des Fluors*, p. 28, Springer, Berlin, 1920.

TABLE I. *The Raman spectra and molecular constants of phosphorus trifluoride, phosphine and analogous trihalides.*

Sub-stance	$\omega_1(1)$ (cm^{-1})	$\omega_2(1)$ (cm^{-1})	$\omega_3(2)$ (cm^{-1})	$\omega_4(2)$ (cm^{-1})	M-X (A)	X-X (A)	β	$I_1 \times 10^{40}$ ($\text{g} \cdot \text{cm}^2$)	$I_2 \times 10^{40}$ ($\text{g} \cdot \text{cm}^2$)	S^*_{298} cal./ deg.
PH_3^\dagger	2306(10)	979(2)		1115(1)	(1.45)	(2.23)	(100°)	(8.26)	6.22	50.5 ± 1
PF_3	890(10)	531(3)	840(10)	486(3)	1.56	2.37	99°	176.0	106.6	64.2 ± 2
$\text{PF}_3(\text{g})$	893(5)		851(5)	487(7)						
$\text{PCl}_3(2)$	510(10)	257(10)	480(2)	190(10)	2.02	3.09	100°	558.3	314.7	74.7 ± 3
$\text{AsF}_3(3)$	707(10)	341(2)	644(9)	274(4)	1.73	(2.65)	(100°)	220.0	144.8	69.2 ± 2
$\text{AsCl}_3(2)$	410(10)	193(6)	370(6)	159(8)	2.18	3.36	101°	661.8	402.0	78.2 ± 3

Numbers in parentheses adjoining frequency values are relative intensities. Numbers in parentheses adjoining ω 's are multiplicities. M-X and X-X are interatomic distances. β is the bond angle formed by two X-atoms and the M-atom. I_1 and I_2 ($= I_3$) are moments of inertia about the symmetry axis and the axis \perp symmetry axis, respectively. S^*_{298} is the virtual entropy of the vapor at one atmosphere and 25°C.

† In the case of phosphine the assignment of frequencies is provisional.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of the experiments are presented in Table I together with various derived quantities. For comparison the corresponding values for phosphorus trichloride, arsenic trifluoride and arsenic trichloride are also given.

The assignment of the frequencies of the trifluoride to the modes of vibration was made by comparison of the spectrum from the trifluoride with that from the trichloride. In the latter case the assignment is based on polarization experiments.² The lines ω_2 and ω_4 are quite sharp and narrow while ω_1 and ω_3 are broad with a width of about 30 cm^{-1} each. The three lines found for gaseous PF_3 are all sharp.

If the atoms in phosphorus trifluoride occupy the corners of a regular triangular pyramid then the four lines ω_1 , ω_2 , ω_3 and ω_4 are permitted by the Raman selection rules.^{3,4} Any deviation from regularity of the structure would lead to splitting of the frequencies ω_3 and ω_4 which have multiplicities of two each, and no splitting was observed. Since four lines were observed it may be concluded that the regular triangular pyramidal structure is to be ascribed to phosphorus trifluoride. The results of the electron diffraction experiments are in complete agreement with this conclusion.

Although the Raman selection rules permit four lines in the case of phosphine if it is assumed, as is probably correct, that the atoms occupy the

corners of a regular triangular pyramid, only three were observed. That at 2306 cm^{-1} was remarkably intense and fairly sharp; another at 979 cm^{-1} was much weaker and quite sharp, while the third line at 1115 cm^{-1} was weaker still and somewhat diffuse. These lines correspond closely to three bands observed in the infrared,⁵ namely, 2327, 990–992.5 and 1121 cm^{-1} , the lack of perfect agreement being doubtless due to the fact that the Raman frequencies were obtained from the liquid, while the infrared absorption bands were obtained from the gas. If one assumes with Fung and Barker that the two bands at 990 and 992.4 cm^{-1} are fundamentals, then the Raman line 979 cm^{-1} consists of two unresolved fundamentals. In this manner the fourth permitted Raman frequency would be accounted for. Under this assumption Fung and Barker were led to the conclusion that the phosphine molecule is a spherical top, and since the moment of inertia about the axis perpendicular to the symmetry axis⁶ is $6.22 \times 10^{-40} \text{ g} \cdot \text{cm}^2$ the phosphorus bond angle would be $88\frac{1}{2}^\circ$.

However, from Table I it is seen that the bond angles in PCl_3 , PF_3 and AsCl_3 are 100°, 99° and 101°, respectively, and the results of Barnes, Benedict and Lewis⁷ on ND_3 and NH_3 yield an angle of 108° for NH_3 . These facts indicate that the bond angle is nearly an invariant for the trivalent compounds of the fifth group elements. According to this empirical generalization the bond angle in phosphine would be about 100°, and the molecule becomes a symmetrical top with a moment of inertia about the symmetry

² Cabannes and Rousset, *Ann. de physique* **19**, 229 (1933). The internuclear distances for PCl_3 are due to Wierl, *Ann. d. Physik* **8**, 521 (1931).

³ Yost and Sherborne, *J. Chem. Phys.* **2**, 125 (1934).

⁴ Debye, *The Structure of Molecules*, Blackie and Son, Ltd., London, 1932. Cf. the article by Placzek, p. 86. E. B. Wilson, Jr., *J. Chem. Phys.* **2**, 432 (1934).

⁵ Fung and Barker, *Phys. Rev.* **45**, 238 (1934).

⁶ Wright and Randall, *Phys. Rev.* **44**, 391 (1933).

⁷ Barnes, Benedict and Lewis, *Phys. Rev.* **45**, 347 (1934).

axis of 8.13×10^{-40} g·cm². The 990–992.4 cm⁻¹ band would then arise from a single fundamental vibration in which the phosphorus atom passes through the triangle formed by the hydrogen atoms as has been observed with ammonia.⁸ The fact that no doubling is observed in the pure rotation spectrum is due to the circumstance that the separation (approximately 0.0007 cm⁻¹) would be too small to be resolved. The fact that the fourth Raman line is not observed can be ascribed simply to a lack of sufficient intensity; this phenomenon is common in the case of molecules containing hydrogen.

THERMODYNAMIC CONSTANTS

The calculated entropies are given in the last column of Table I. The Raman frequencies obtained from liquids are generally lower than those obtained for the same substances in the gaseous states. The vibrational entropies calculated will, accordingly, be too great, and the magnitude of the deviations have been indicated in the table.

In the case of AsCl₃ complete thermal data are available for free energy calculations.⁹ For AsCl₃(l) and AsCl₃(g) the heats of formation are 72,470 cal. and 65,110 cal., respectively, and the calculated standard free energies of formation at 25° are -64,550 cal. and -62,075 cal., respectively. Equilibrium measurements in progress at this laboratory give a preliminary value of -58,500 cal. for AsCl₃(g). The agreement is satisfactory. No thermal data are available for AsF₃ and PF₃.

A number of determinations have been made of the heat and free energy of formation of phosphine but none of them are free from objections. The entropy of solid white phosphorus has not been determined. Preuner and Brockmüller¹⁰ have made equilibrium measurements on the reaction $P_4(g) = 2 P_2(g)$ over the temperature

range 800°–1200°. Duncan and Macrae¹¹ have made careful vapor pressure measurements on solid white phosphorus and the vapor is known to consist of P₄.

Herzberg¹² has determined both the moment of inertia and the vibrational energies of P₂ in the normal electronic state, thus making possible the calculation of a reliable value for the entropy. An estimate has been made of the empirical heat capacity equation for P₄. The results are as follows:

$$P_4(g) = 2 P_2(g) \quad (1)$$

$$\Delta H_{1000} = 33,800 \text{ cal.} \quad \Delta F_{1300}^\circ = 5110 \text{ cal.}$$

$$P_2(g), C_p = 7.4 + 0.001 T$$

$$S_{298}^* P_2(g) = 52.0 \text{ cal./deg.}$$

$$P_4(g), C_p = 10.0 + 0.003 T$$

$$\Delta H_T = 31,400 + 3.00 T - 0.0006 T^2$$

$$\Delta F_T^\circ = 31,400 - 3T \log_e T + 0.0006 T^2 + 481 T$$

$$\Delta H_{298} = 32,250 \text{ cal.} \quad \Delta F_{298}^\circ = 26,300 \text{ cal.}$$

$$4 P(s, \text{white}) = P_4(g) \quad (2)$$

$$\Delta H_{298} = 13,220 \text{ cal.} \quad \Delta F_{298}^\circ = 5850 \text{ cal.}$$

From these equations there is obtained the value 14.9 cal./deg. for the entropy of solid white phosphorus at 25°.

The reaction between P₄(g) and hydrogen to give phosphine has been studied by Ipatiew and Frost.¹³ They proved definitely that the reaction is reversible, but due to the experimental difficulties involved the heat of the reaction could not be determined as accurately as desired. Calorimetric determinations of the heat of formation of phosphine are not at all satisfactory. From the best existing data the following equations have been derived.

$$P_4(g) + 6H_2(g) = 4 PH_3(g) \quad (3)$$

$$\Delta H_{700} = -22,100 \text{ cal.} \quad \Delta F_{700}^\circ = 37,100 \text{ cal.}$$

$$PH_3(g), C_p = 8.04 + 0.0007 T + 5.1 \times 10^{-6} T^2$$

$$H_2(g), C_p = 6.50 + 0.0009 T$$

$$P_4(g), C_p = 10.0 + 0.003 T$$

$$\Delta H_T = -11,300 - 16.84 T - 0.0028 T^2 + 6.8 \times 10^{-6} T^3$$

⁸ Morse and Rosen, *Phys. Rev.* **42**, 210 (1932); Denison and Uhlenbeck, *ibid.* **41**, 313 (1932).

⁹ E. Peterson, *Zeits. f. physik. Chemie* **8**, 611 (1891); Baxter, Bezenberger and Wilson, *J. Am. Chem. Soc.* **42**, 1386 (1920); Yost and Sherborne, *J. Chem. Phys.* **2**, 125 (1934). In the latter article the moments of inertia and entropy values of AsCl₃, AsF₃ and PCl₃ are in error. These values as well as that for the free energy of formation of AsCl₃ have been recalculated and are given correctly in this paper.

¹⁰ Preuner and Brockmüller, *Zeits. f. physik. Chemie* **81**, 129 (1913).

¹¹ Duncan and Macrae, *J. Am. Chem. Soc.* **43**, 547 (1921).

¹² Herzberg, *Zeits. f. Physik* **69**, 548 (1931); *Phys. Rev.* **40**, 313 (1932).

¹³ Ipatiew and Frost, *Ber.* **63**, 1104 (1930).

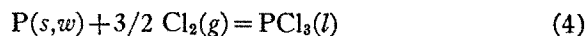
$$\Delta F^\circ_T = -11,300 + 16.48 T \log_e T + 0.0028 T^2 - 3.4 \times 10^{-6} T^3 - 41.3 T$$

$$\Delta H_{298} = -16,400 \text{ cal.} \quad \Delta F^\circ_{298} = 5155 \text{ cal.}$$

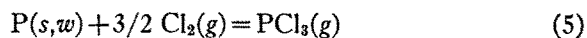
From these equations and the heat and free energy of vaporization of white phosphorus given above, a second value of 15.5 cal./deg. for the entropy of solid white phosphorus may be calculated. The close agreement between the two independent values is, in some measure, fortuitous, and, judging from the entropies of other solid substances of similar nature, both values are possibly too high. Until more accurate data are available we shall take 15.0 cal./deg. as the entropy of solid white phosphorus at 25°.

It is now possible to calculate the thermody-

amic constants for phosphorus trichloride. The heats of formation¹⁴ and vaporization¹⁵ of $\text{PCl}_3(l)$ are 75,900 cal. and -7620 cal., respectively, and the free energy of vaporization at 25° is 1080 cal. The following free energy equations may then be written:



$$\Delta H = -75,900 \text{ cal.} \quad \Delta F^\circ_{298} = -63,300 \text{ cal.}$$



$$\Delta H = -68,280 \text{ cal.} \quad \Delta F^\circ_{298} = -62,220 \text{ cal.}$$

¹⁴ Berthelot and Longuinine, *Ann. d. chim. phys.* (5) **6**, 307 (1875); Thomsen, *Ber.* **16**, 37 (1883); J. Ogier, *Comptes rendus* **87**, 210 (1878).

¹⁵ Regnault, *Mem. de l'acad. Sciences, France* **26**, 339 (1862).

On the Infrared and Raman Spectra of Methyl Compounds

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An analysis of the resonance interaction between the vibrations ν_1 and $2\nu_4$ in the methyl halide molecules explains the appearance of the very intense extra band in the infrared and Raman spectra of these molecules. This degeneracy is evidently characteristic of the methyl group. A number of molecules involving the methyl group and exhibiting the phenomenon of the extra band are listed.

THE infrared spectra of the methyl halides has been found by Bennett and Meyer¹ to consist of four single or parallel bands and three double or perpendicular ones. The frequency and intensity relations between them seem to preclude the possibility that any one is an harmonic; nevertheless, the molecule must have only nine degrees of freedom for vibration, and not ten as apparently indicated. The Raman spectra do not resolve this difficulty, but rather tend to emphasize it. Methyl chloride and methyl bromide each have strong Raman lines corresponding to the four single frequencies. Only a few of the double frequencies appear in Raman observations, and these lines are weak as would be expected from Placzek's theory.

The positions of the infrared bands observed in gaseous absorption, and of the Raman lines ob-

tained from the liquid, are listed in Table I. The designations by letter in the first column follow Bennett and Meyer, while the numerical subscripts are those of Dennison's analysis,² the even numbers corresponding to the double frequencies. Motions primarily involving the halogen atom are responsible for the frequencies ν_5 and ν_6 , while in first approximation ν_3 and ν_4 correspond to oscillations of the carbon and ν_1 and ν_2 to those of the three hydrogen atoms. Consequently, ν_4 , ν_2 and ν_1 are very insensitive to changes in mass of the fifth atom, and may be said to characterize the methyl radicle. There is no difficulty about the identification of *D* and *G* as ν_4 and ν_2 , respectively, but either *E* or *F* seems at first superfluous.

Analysis indicates that the harmonic of a perpendicular band consists of two components,

¹ Bennett and Meyer, *Phys. Rev.* **32**, 888 (1928).

² Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).