

## The Raman Spectrum of Arsenic Trifluoride and the Molecular Constants of $\text{AsF}_3$ , $\text{AsCl}_3$ and $\text{PCl}_3$

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The Raman spectrum of  $\text{AsF}_3$  was found to consist of four lines with the frequencies  $\omega_1(1)$ , 707;  $\omega_2(1)$ , 341;  $\omega_3(2)$ , 644; and  $\omega_4(2)$ , 274  $\text{cm}^{-1}$ . The selection rules require a pyramidal molecule. Electron diffraction data for  $\text{AsF}_3$ ,  $\text{AsCl}_3$  and  $\text{PCl}_3$  are used to establish the bond angles. The entropies of the three trihalides were calculated, and the standard free energies of formation of  $\text{AsCl}_3(l)$  and  $\text{AsCl}_3(g)$  were determined to be  $-65,190$  cal. and  $-62,718$  cal., respectively, at  $25^\circ$ .

### INTRODUCTION

THE volatile fluorides have not received much attention with respect to their molecular structures and thermodynamic properties. Since fluorine<sup>1</sup> is extremely electronegative in character, it is of considerable interest to determine how this behavior is reflected in internuclear distances and binding forces. Furthermore, no readily reversible reactions involving fluorine have yet been found, and it becomes accordingly necessary to resort to indirect methods to evaluate entropies and free energies. In this paper are described the results of a study of arsenic trifluoride with respect to such considerations. For comparison, the properties of the trichlorides of arsenic and phosphorus are included.

### EXPERIMENTAL

Arsenic trifluoride (B.P.  $63^\circ$ ) was prepared by distilling a mixture of arsenic trioxide, calcium fluoride and concentrated sulfuric acid.<sup>2</sup> The resulting material was fractionated in vacuum in an all-glass apparatus and then vacuum-distilled into the Raman tube. It was found that the trifluoride does not attack glass so readily when moisture is excluded. An appreciable pressure of silicon tetrafluoride does develop during the course of a day, however, and the liquid trifluoride slowly becomes turbid. It was observed that considerable triboluminescence develops if

a tube containing the compound is placed in liquid air and then removed and allowed to warm.

Fair photographs of the Raman lines were obtained in ten minutes and excellent ones in half an hour. The mercury-arc lamp used consisted of a long (30 cm) narrow U-tube of 8 mm Pyrex tubing equipped with electrodes sealed in at right angles near the open end. By means of a stopper and wax the lamp was enclosed in a glass jacket through which water was circulated. This type of lamp burns equally well in a vertical or nearly horizontal position; and, since it is kept cool with water, the Raman tube itself does not require cooling.

Electron diffraction experiments were made on  $\text{AsF}_3$  and  $\text{AsCl}_3$  by Dr. L. O. Brockway of this Laboratory, and we are greatly indebted to him for the results. A detailed account of the investigation will be published later by Professor Pauling and Dr. Brockway.

### EXPERIMENTAL RESULTS AND DISCUSSION

In Table I are presented the results of the experiments together with various derived quantities. The Raman frequencies for  $\text{AsCl}_3$  and  $\text{PCl}_3$  are due to Bhagavantam<sup>3</sup> and the internuclear distances for  $\text{PCl}_3$  to Wierl.<sup>4</sup>

The fluorides are generally assumed to be highly ionic in character, and this might lead to the supposition that the fluoride ions in arsenic

<sup>1</sup> Yost and Hatcher, *J. Chem. Ed.* **10**, 330 (1933).

<sup>2</sup> Ruff, *Die Chemie des Fluors*, p. 27, Julius Springer, Berlin, 1920.

<sup>3</sup> See Kohlrausch, *Der Smekal-Raman-Effekt*, p. 195 Julius Springer, Berlin, 1931.

<sup>4</sup> Wierl, *Ann. d. Physik* [5] **8**, 521 (1931).

TABLE I. Raman frequencies and molecular constants of  $AsF_3$ ,  $AsCl_3$  and  $PCl_3$ .

	$\omega_1(1)$ ( $cm^{-1}$ )	$\omega_2(1)$ ( $cm^{-1}$ )	$\omega_3(2)$ ( $cm^{-1}$ )	$\omega_4(2)$ ( $cm^{-1}$ )	$M-X$ ( $\text{Å}$ )	$X-X$ ( $\text{Å}$ )	$\phi$	$\beta$	$I_1$ ( $\times 10^{40}$ )	$I_3$ ( $\times 10^{40}$ )	$S_{298}^*$ (cal./deg.)
$AsF_3$	707(10)	341(2)	644(9)	274(4)	1.65	(2.47)	(60°)	(97°)	192.0	36.3	73.9 $\pm$ 1
$AsCl_3$	410(10)	193(6)	370(6)	159(8)	2.20	3.27	59	96	625.4	93.3	84.0 $\pm$ 3
$PCl_3$	510(10)	257(10)	480(2)	190(10)	2.04	3.18	64	101	590.4	31.7	78.6 $\pm$ 2

Numbers in parentheses adjoining frequency values are relative intensities. Numbers adjoining the  $\omega$ 's are multiplicities.  $M-X$  = Distance between As or P and halogen nuclei.  $X-X$  = Distance between halogen nuclei.  $\phi$  = Angle between altitude and edge of pyramid.  $\beta$  = Bond angle formed by two halogen atoms and As or P.  $I_1$  = Moment of inertia about symmetry axis.  $I_3 (= I_2)$  = Moment of inertia about axis  $\perp$  symmetry axis.  $S_{298}^*$  = Virtual entropy of vapor at 25° and one atmosphere.

trifluoride would so repel each other that they would lie in the same plane as the central arsenous ion. Since, however, four distinct Raman lines are observed, the selection rules<sup>5</sup> exclude the plane structure.

It seems, then, that either the electric field about the central atom is not spherically symmetric, or that the bonding is not as extremely ionic as might be supposed. The assumption of extreme ionic character suggested that, since the trifluoride has many nonpolar properties, the substance was a polymer. Careful vapor density measurements yielded a molecular weight of 133.4. The formula weight is 131.96; hence the vapor molecules are present as  $AsF_3$ . It must be concluded, therefore, that the bonding is not of the highly ionic type.

The results of the electron diffraction experiments are in accord with the assumption that the three fluorine atoms are at the corners of an equilateral triangle. Any deviation from this would lead to the splitting of the frequencies  $\omega_3(2)$  and  $\omega_4(2)$ , which have multiplicities of two, but no splitting was observed. The experimental evidence is, therefore, in agreement with the statement that, in arsenic trifluoride, the atoms are at the corners of a regular triangular pyramid with the arsenic atom at the vertex. Similar statements apply to the trichlorides of arsenic and phosphorus.

In order to assign the observed frequencies of arsenic trifluoride to the four possible modes of vibration (two of which are double), comparisons of the spectrum with those of the trichlorides of arsenic, antimony, and phosphorus<sup>3</sup> were made.

<sup>5</sup> Debye, *The Structure of Molecules*, Blackie and Son, Ltd., London, 1932. Cf. the article by Placzek, p. 86.

For the latter substances, the assignments have been based on the results of polarization experiments.

It is to be noted that the Raman frequencies for arsenic trifluoride are in all cases very close to 1.75 times the corresponding frequencies for the trichloride. This indicates that the binding constant for the As-F bond is roughly twice that for the As-Cl bond.

The F-F distance could not be determined from the results of the electron diffraction experiments. On the assumption of central forces only, Dennison<sup>6</sup> derived frequency formulae for the model in question, and these formulae show that the angle  $\phi$  (see table) is a function of  $\omega_1\omega_2/\omega_3\omega_4$  alone, and not of the binding constants. The value 46° was found for  $AsF_3$ , 39° for  $AsCl_3$ , and 51° for  $PCl_3$ . Since the two latter values are much lower than the observed ones, 59° and 64°, respectively (see Table I), it must be concluded that the formulae do not apply to the arsenic trihalides. Since the observed values of  $\phi$  for  $AsCl_3$  and  $PCl_3$  are equal within the limits of experimental error, we have chosen to make the assumption that for the trihalides of the phosphorus group elements the bond angles are an invariant. Some small deviations may result when very large atoms, such as iodine, are involved. In accordance with this assumption we have placed  $\phi = 60^\circ$  for arsenic trifluoride.

#### THERMODYNAMIC CONSTANTS

When entropy calculations are based on the use of Raman frequencies, errors of as much as

<sup>6</sup> Dennison, *Phil. Mag.* 1, 195 (1926).

3 cal./deg. may be expected when the vibrational entropy is large (10 to 20 cal./deg.).<sup>7</sup> In the table the uncertainties given are based on similar calculations for cases in which good heat-capacity data were available, and are meant to indicate what is believed to be the maximum possible error. In free energy calculations the resulting errors become 300 to 900 cal., which are comparable to those frequently encountered in calculations based on equilibrium data. The entropies derived from Raman spectra are often very useful, however, when it is desired to predict, with not too great precision, the tendency for reactions to take place.

The necessary thermal data for free energy calculations are available only for arsenic trichloride. The heats of formation of the liquid

and vapor are 71,390 cal. and 64,030 cal., respectively.<sup>8</sup> The vapor pressure<sup>9</sup> at 25° is 11.65 mm and the entropies of chlorine<sup>10</sup> and solid arsenic<sup>11</sup> are 53.31 cal./deg. and 8.4 cal./deg., respectively, at 25° and one atmosphere. From these data there results -65,190 cal. and -62,718 cal. for the standard free energies of formation of liquid and gaseous arsenic trichloride respectively at 25°. The error in the heats of formation is some 500 cal. and that due to the entropy of AsCl<sub>3</sub> is, at most, 900 cal. The free energy values are therefore in error by some 500 to 1400 cal.

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<sup>8</sup> Thomsen, Ber. **16**, 39 (1883). The heat of vaporization as determined by Baxter<sup>9</sup> is 7360 cal. at 25°.

<sup>9</sup> Baxter, Bezenberger and Wilson, J. Am. Chem. Soc. **42**, 1386 (1920).

<sup>10</sup> Giauque, J. Am. Chem. Soc. **54**, 1731 (1932).

<sup>11</sup> Anderson, J. Am. Chem. Soc. **52**, 2296 (1930).

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<sup>7</sup> Yost and Blair, J. Am. Chem. Soc. **55**, 2610 (1933).