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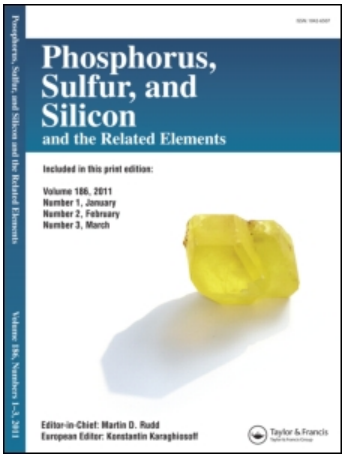

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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To cite this Article Griffiths, James E. , Carter Jr, Richard P. and Holmes, Robert R.(1995) 'MOLECULAR STRUCTURES OF PCl_4F, PCl_3F_2, PCl_2F_3, AND PF_5: INFRARED AND LOW - TEMPERATURE RAMAN VIBRATIONAL SPECTRA', Phosphorus, Sulfur, and Silicon and the Related Elements, 98: 1, 11 — 31
To link to this Article: DOI: 10.1080/10426509508036938
URL: http://dx.doi.org/10.1080/10426509508036938

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Phosphorus, Sulfur, and Silicon, 1995, Vol. 98, pp. 11–31
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MOLECULAR STRUCTURES OF PCl_4F, PCl_3F_2, PCl_2F_3, AND PF_5: INFRARED AND LOW-TEMPERATURE RAMAN VIBRATIONAL SPECTRA*†

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(Received 30 March 1964)

Molecular structures of PCl_4F, PCl_3F_2, PCl_2F_3, and PF_5 are derived from vapor-state infrared spectra (2000–250 cm^{-1}) and low-temperature liquid-state Raman displacements ($\Delta\nu$ = 50–1200 cm^{-1}) together with qualitative polarization measurements. All of the compounds appear to have a basic trigonal bipyramidal framework. The spectra of PCl_4F are best interpreted in terms of a C_{3v} structure in which the fluorine atom occupies an axial site; in PCl_3F_2 (D_{3h} point group) the fluorine atoms also assume axial positions. For PCl_2F_3, the symmetrical D_{3h} structure is shown to be incorrect. Available evidence supports the C_{2v} structure in which the fluorine atoms appear in one equatorial and two axial sites. Phosphorus pentafluoride is found to have a regular trigonal bipyramidal structure. Complete vibrational assignments are made in terms of the normal modes and thermodynamic functions are evaluated for PCl_5, PCl_3F_2, and PF_5.

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The phosphorus (v) chlorofluorides, PCl_nF_{5-n}, are especially interesting because they exist in low-temperature forms which slowly rearrange at room temperature to solid modifications. Some evidence has been accumulated which shows that the solid modifications are ionic and the "low-temperature" forms are molecular.[1] Moreover, a study of the relative coordination tendencies shows that the low-temperature forms behave as typical Lewis acids in molecular addition compound formation with pyridine.[2]

With the recent development of suitable syntheses of the molecular forms,[3] a detailed study of their structures became attractive. It was anticipated that these substances would have trigonal bipyramidal structures similar to that observed by electron diffraction for PCl_5[4] and PF_5.[5] In fact an early electron-diffraction investigation[5] supports a trigonal bipyramidal structure for PCl_2F_3 in which the fluorine atoms assume equatorial positions and the chlorine atoms occupy axial sites. However, interpretation of recent low-temperature ^{19}F NMR results shows a preference for a trigonal bipyramidal structure for PCl_2F_3 wherein the chlorine atoms are equatorial and the fluorine atoms occupy one equatorial and the two axial sites.[6]

Since positional isomerization is a possibility in PCl_4F and PCl_3F_2 as well (the synthesis of $PClF_4$ has not been published at this time), it was felt that the complete infrared and Raman vibrational spectra of the compounds in the series would aid

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*Pentacoordinated Molecules. III. Previous paper: R. R. Holmes, W. P. Gallagher and R. P. Carter, Jr., *Inorg. Chem.*, **2**, 437 (1963).

†Presented in part before the Division of Inorganic Chemistry, 147th National Meeting of the American Chemical Society, Philadelphia, Pennsylvania, April 1964.

in resolving the stereochemical aspects. Several studies of the vibrational spectrum of PCl_5 exist[7,8] but only incomplete infrared studies of PF_5 have been reported.[9,10] To allow a more thorough correlation of the data, a study of PF_5 was included in this work.

EXPERIMENTAL

Materials

The mixed halides PCl_4F, PCl_3F_2, and PCl_2F_3 were made by the low-temperature chlorination of PCl_2F, $PClF_2$, and PF_3, respectively,[3] in a Pyrex glass vacuum system. Stopcocks and ground glass joints were lubricated with Kel-F grease. The PCl_2F and $PClF_2$ were prepared and purified according to a previous procedure.[3] In the preparation of PCl_2F_3, commercial PF_3 (Columbia Organic Chemicals Company) was used after fractionation and in some cases was subjected to a chemical treatment which has been shown to remove small amounts of impurities yielding a mass spectroscopically pure product.[11] Chlorine gas (The Matheson Company) was dried over phosphorus pentoxide coated glass beads at $-78°$ *in vacuo* and fractionated before use.

No impurities were evident in the Raman spectra of the compounds. However, because of possible reactions of the chlorofluorides with the infrared cell windows and the slow conversion of the samples to solid forms at room temperature, it was expected that impurities would develop during infrared spectral measurements. This occurred in varying degrees for all compounds except PCl_3F_2 which proved to be remarkably stable.

Relatively pure phosphorus pentafluoride (Columbia Organic Chemicals Company) was subjected to fractional vaporization and condensation in a glass vacuum system in which stopcocks were lubricated with Kel-F grease. Physical measurements on a tensimetrically homogeneous sample gave the following results: molec. wt. 126.3, calc. 126.0; vapor pressure at $-111.6°C$, 54.6 mm, lit.[12] 50.5 mm. No impurities could be detected in the Raman spectrum of the liquid and only small amounts of POF_3 were found with infrared absorption measurements. Reaction of PF_5 with the Pyrex gas cells at room temperature may account for the latter.

Raman Spectra

To record the Raman spectra of the phosphorus chlorofluorides in the liquid state and to avoid their conversion to solid modifications it was necessary to build a low-temperature cell. The final design, shown in Figure 1, consists of an unsilvered Dewar form whose end tapers to fit snugly into the circular brass alignment cone of the Cary Model 81 spectrophotometer. The extreme end of the taper has parallel optical flats to minimize reflection losses and distortion of the scattered light.

The sample tube was made from 7-mm-o.d. Pyrex tubing and a bend served to prevent the liquid from escaping the cooled section of the cell. Samples were condensed in such tubes *in vacuo* and after sealing were stored at $-78°C$ until used.

In operation, the sample tube was placed in the precooled apparatus. Cooling

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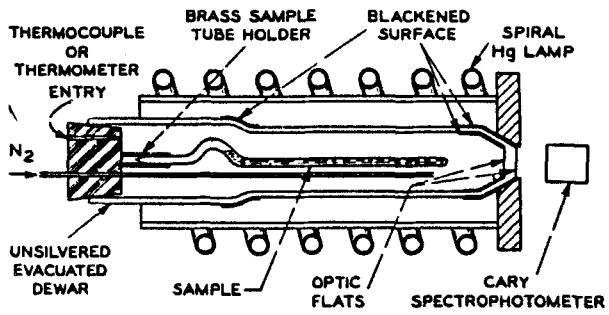

FIGURE 1 Low-temperature Raman cell for a Cary Model 81 spectrophotometer.

was provided by passing dry nitrogen gas through a copper coil immersed in liquid nitrogen and then to the nitrogen inlet of the cell assembly. By regulating the gas flow with a flowmeter, any desired temperature could be maintained from room temperature down to $-160°C$. With this arangement temperature fluctuations could be held to within $\pm 1°C$. No solid formation was noticed during any of the measurements.

Due to the small liquid range of PF_5 (mp, $-91.6°$; bp, $-84.8°C$) a hazard existed if the temperature of any part of the Raman cell rose above the boiling point during the course of the measurement. By using a modified sample tube (Figure 2) incorporating a ballast bulb and a cold-storage bulb, no difficulty was encountered. Phosphorus pentafluoride was condensed in Bulb A and sealed at B. After alignment in the Raman cell within the lamp housing of the spectrophotometer, Bulb A was immersed in an ethyl acetate slush bath ($-83.6°C$) providing a temperature slightly above the normal boiling point of PF_5. On cooling the Raman cell to a lower temperature ($-90°C$), PF_5 slowly condensed until the sample tube was filled to the hump shown in Figure 2. The temperature was then raised to $-86°C$ and the Raman measurements were made.

Raman displacements from the 4358 Hg line are expected to be accurate to ± 3 cm^{-1} for the sharper lines. Measurements at $\Delta\nu < 200$ cm^{-1} always employed

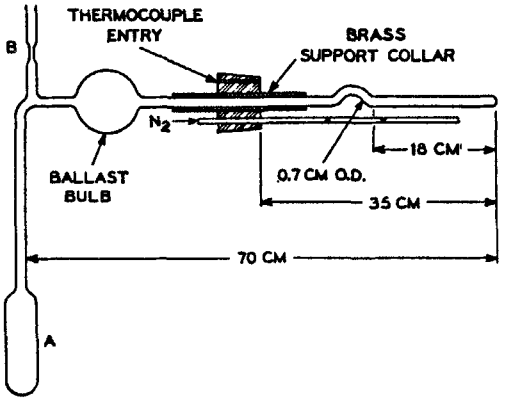

FIGURE 2 Low-temperature sample cell for liquid PF_5.

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single-beam operation to eliminate instrument ghosts. In all of the experiments, however, a weak ghost appeared at about 170 cm^{-1} and this is attributed to the geometry of our sample rather than to an intrinsic property of the instrument. It could arise from the spectrophotometer *seeing* the walls or the rounded end of the small-diameter sample tube. Other experiments using 19 or 22 mm o.d. sample tubes in which the round ends were shielded from the exciting light rendered the ghost vanishingly weak and no problems were encountered to within 35–50 cm^{-1} of the exciting line, even at high amplification.

Infrared Spectra

Infrared spectra were recorded in the 2000–250 cm^{-1} range with a Perkin-Elmer Model 421 spectrophotometer. Frequency accuracy is better than ± 3 cm^{-1} throughout and is based upon calibrations with the known rotational bands of H_2O, NH_3, and CO_2.[13,14] Samples were confined in 10-cm gas cells fitted with KBr and CsI windows but these were subject to chemical attack by some of the compounds and had to be frequently repolished. The effect was minimized in some cases by admixing argon with the gas under study. The far-infrared spectrum (250–120 cm^{-1}) of PF_5 in the vapor phase was observed with a Perkin-Elmer Model 301 spectrophotometer. The gas was held in a glass cell with polyethylene windows and the frequency calibration (± 1 cm^{-1}) for this measurement was done simultaneously using the known pure rotational spectrum of HCl gas.[15]

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RESULTS

The expected numbers of infrared- and Raman-active fundamentals for various molecular structures are given in Table I. Infrared and Raman spectra are shown for PF_5 (Figures 3 and 4), PCl_2F_3 (Figure 5), PCl_3F_2 (Figure 6), and PCl_4F (Figure 7) and the corresponding data are summarized in Tables II, III, IV, and V. A Raman spectrum of $POCl_3$ is shown in Figure 8 because of its importance in the interpretation of the spectrum of PCl_4F. The fundamental frequencies of each of the molecules are collected in Tables VI (PF_5), VII (PCl_2F_3), VIII (PCl_3F_2), and IX (PCl_4F). The fundamental vibrations of PCl_2F_3 in terms of a C_{2v} structure are given in Table X.

TABLE I

Activity of fundamental modes

Point group	Funda-mentals	Raman	Infrared	R–ir coincidences
D_{3h}	8	6(2*p*)	5	3
C_{4v}	9	9(3*p*)	6	6
C_{3v}	8	8(4*p*)	8	8
C_{2v}	12	12(5*p*)	11	11
C_s	12	12(8*p*)	12	12

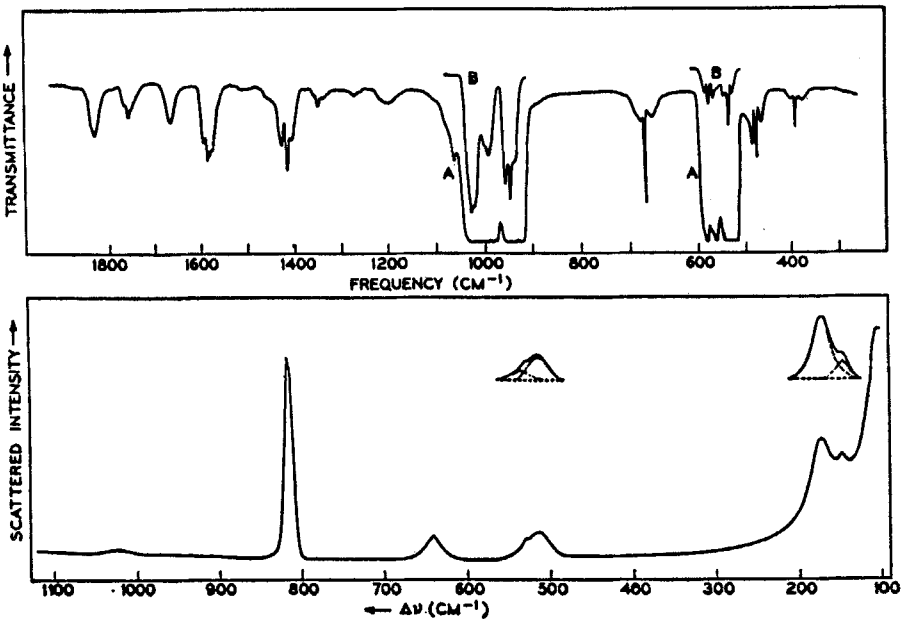

FIGURE 3 Infrared and Raman spectra of PF_5. Infrared (top): (A) p = 37 cm, l = 10 cm; (B) p = 1 cm, l = 10 cm; temperature 25°C. Raman (bottom): slit 10 cm^{-1}, ampl. 3000, temperature −86° ± 1°C; single beam.

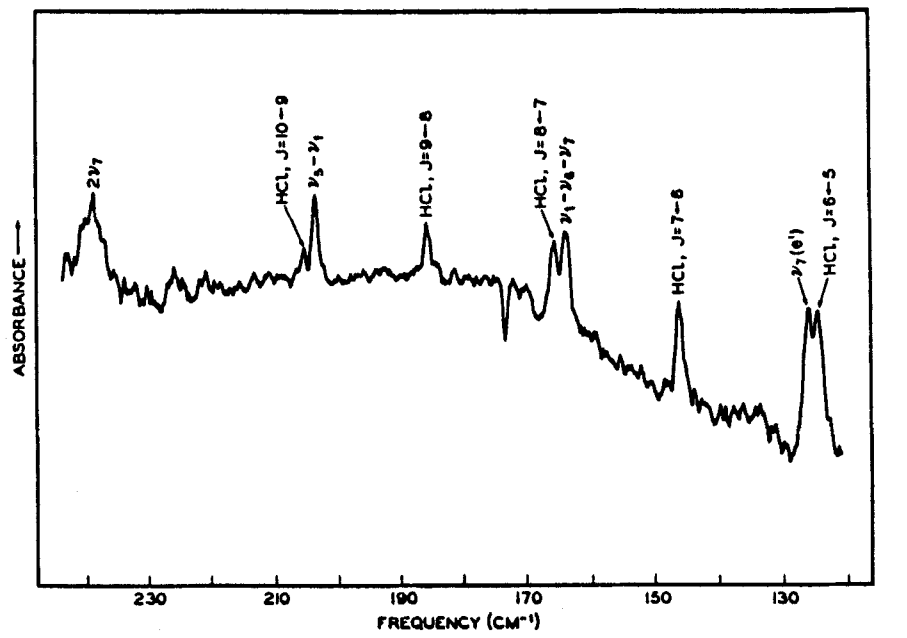

FIGURE 4 Far-infrared spectrum of PF_5. (PF_5 + HCl): p = 34.5 cm, l = 10.0 cm, temperature 25°C.

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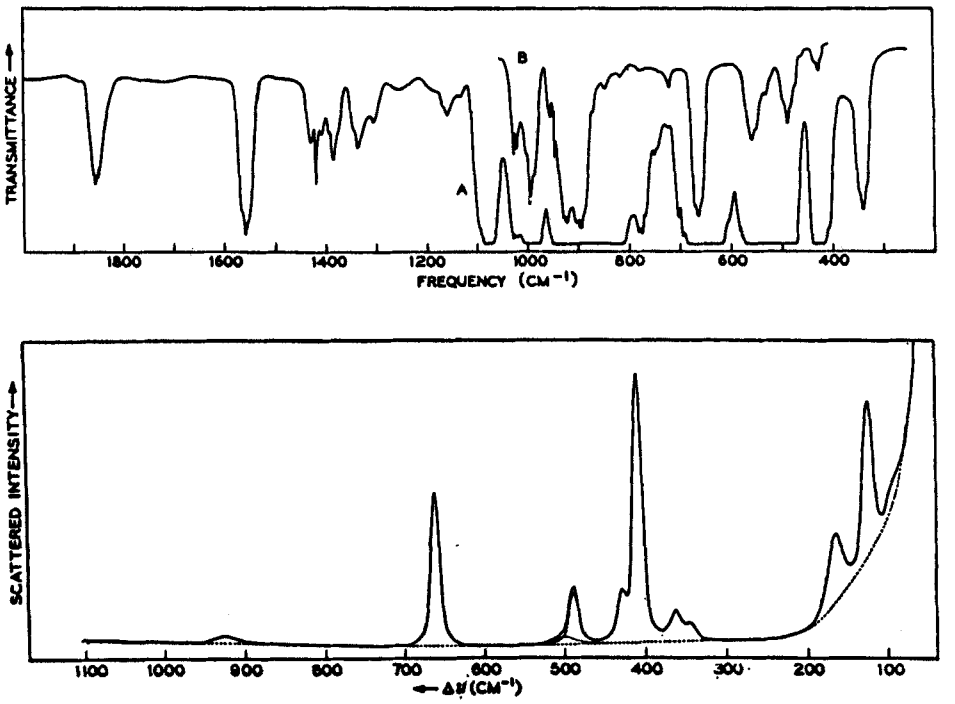

FIGURE 5 Infrared and Raman spectra of PF_3Cl_2. Infrared (top): (A) p = 68 cm, (B) p = 0.4 cm, l = 10 cm; temperature 25°C. Raman (bottom): slit 10^{-1} cm, ampl. 3000, temperature −40°C; single beam.

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Bond lengths which are used in the evaluation of moments of inertia appear in Table XI and the thermodynamic values for the compounds appear in Table XII. Finally, a correlation chart interrelating the fundamental frequencies is shown in Figure 9.

SELECTION RULES AND ASSIGNMENTS

The structural framework for all of the molecules under study is most probably the trigonal bipyramid with distortions from this being possible for some of the mixed chlorofluoride molecules. Depending on the relative positions of the chlorine and fluorine atoms, the molecules may belong to the D_{3h}, C_{3v}, C_{2v} or possibly the C_s point groups. The tetragonal pyramidal structure (C_{4v} point group) is another possibility and is considered for the PCl_4F molecule. The number and activities of the fundamentals for each of the models are listed in Table I.

Although accurate bond lengths and angles cannot be determined from the vibrational spectra alone, the basic structures are tractable from the data on the number, activity and polarizations of the observed fundamentals. Specific details for individual molecules appear in the following sections.

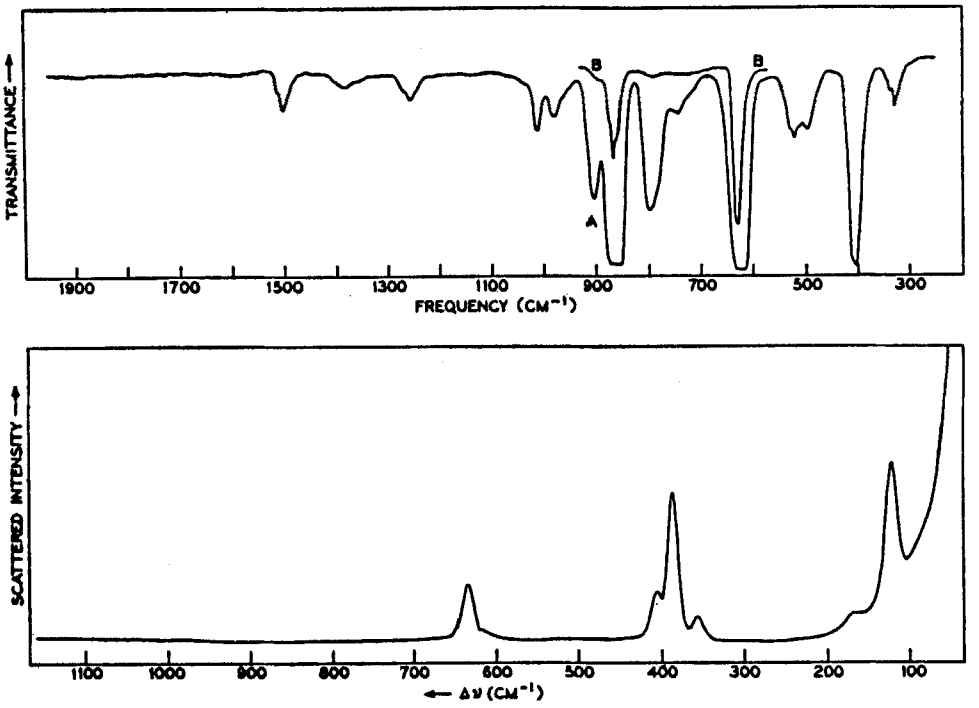

FIGURE 6 Infrared and Raman spectra of PF_2Cl_3. Infrared (top): (A) $p \approx 20$ cm, $l = 10$ cm; (B) $p \approx 2$ cm, $l = 10$ cm; temperature 25°C. Raman (bottom): slit 10 cm^{-1}, ampl. 3000, temperature −40°C; single beam.

I. PF_5

There does not appear to be any doubt that PF_5 belongs to the D_{3h} point group.[5] The two polarized lines at 817 and 640 cm^{-1} in the Raman spectrum (Figure 3 and Tables II and VI) clearly belong to the a_1' species and the depolarized line at 514 cm^{-1} which has no counterpart in the infrared is assigned to $\nu_3(e'')$. It follows that the two infrared bands at 945 and 576 cm^{-1}, which are not observed in the Raman spectrum are $\nu_3(a_2'')$ and $\nu_4(a_2'')$, respectively. The remaining lines at 1025 and 534 in the liquid-state Raman spectrum and at 1026.4, 533, and 126 cm^{-1} (Figure 4) in the infrared can be confidently assigned to the e' fundamentals ν_5, ν_6, and ν_7. The ν_7 fundamental was not observed in the Raman spectrum because of the unusually high background intensity near the exciting line. The observation of an additional lamp ghost at 145 cm^{-1} suggested that the background intensity arose from some undesirable construction feature in the sample tube or from an imperfect alignment of the tube. Additional experiments with empty sample tubes and with the arrangement shown in Figure 2 after the PF_5 was recondensed in Bulb A confirmed that the line at 145 cm^{-1} was not due to liquid PF_5.

The remaining infrared bands were assigned to combinations and overtones of the fundamentals and to four of the six fundamentals expected for the POF_3 impurity. One band at 989 cm^{-1} was not positively identified. In addition, slow attack of the CsI cell windows by PF_5 resulted in the gradual growth of two bands.[16]

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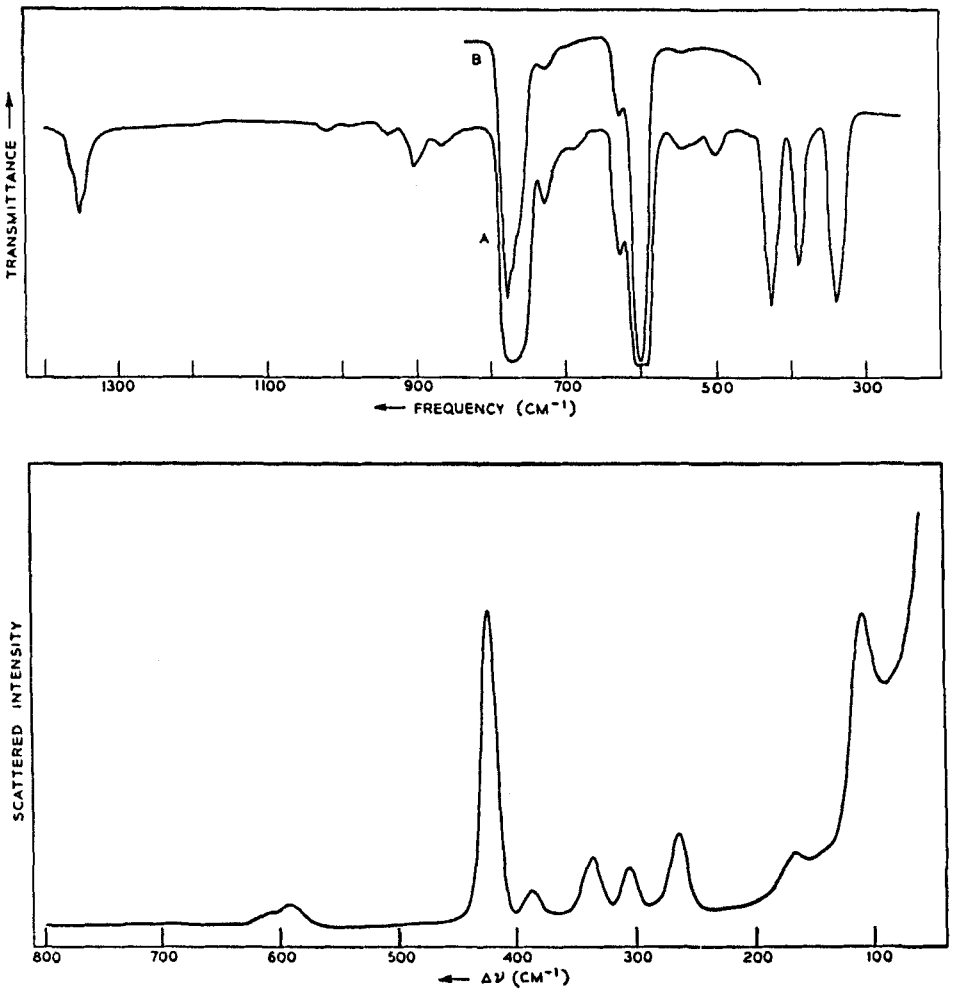

FIGURE 7 Infrared and Raman spectra of $PFCl_4$. Infrared (top): (A) $p \approx 10$ cm, $l = 10$ cm; (B) $p \approx 2$ cm, $l = 10$ cm; temperature 25°C. Raman (bottom): slit 10 cm^{-1}, ampl. 1000, temperature −40°C; single beam.

II. PCl_2F_3

Electron-diffraction results[5] favor the trigonal bipyramid having a D_{3h} symmetry for PCl_2F_3 but interpretations of low-temperature NMR measurements give preference to the trigonal bipyramid (C_{2v} symmetry) in which the Cl atoms occupy equatorial sites.[6] As Table I shows, it should be possible to distinguish readily between the two models on the basis of the number, activities, and the Raman depolarization ratios of the fundamentals.

A total of nine lines[17] are observed in the Raman spectrum of PCl_2F_3 (Figure 5) over the temperature range −20° to −120°C and two of these at 343 and 427 cm^{-1} correspond in frequency to fundamentals of POF_3 and $POClF_2$, respectively.[9,18] Samples of PCl_2F_3 were synthesized using commercial PF_3 which might

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TABLE II

Vibrational spectrum of PF_5[a]

ir (gas)[b]		Raman (liq.)[c]			
cm^{-1}	I	cm^{-1}	I	pol.	Assignment
126	m	...	...	...	$\nu_7(e')$
...		145	11	...	"ghost"
164	w	...	...	...	$\nu_1-\nu_6-\nu_7=157(A_1'+A_2'+E')$
...		169	...	...	"ghost"
205	w	...	...	...	$\nu_6-\nu_7=207(E')$
240	w	...	...	...	$2\nu_7=252(A_1'+E')$
375	*P* w				
388	*Q* w	...	...	...	$\nu_6-\nu_5=386(E')$
397	*R* w				
459	*P* w				
473	*Q* w	...	...	...	$\nu_5(POF_3)$
481	*R* w				
484	wsh	...	...	...	$\nu_6(POF_3)$
...		514	13	dp	$\nu_8(e'')$
526	*P* m				
533	*Q* m	534	5	(dp)	$\nu_6(e')$
548	*R* m				
565	*P* m				
575.5	*Q* m	...	...	...	$\nu_4(a_2'')$
584.5	*R* m				
...		640	14	p	$\nu_3(a_1')$
652	*P* w				
666	*Q* w	...	...	...	$\nu_6+\nu_7=660(A_1'+A_2'+E')$
675	*R* w				
...		817	100	p	$\nu_1(a_1')$
857.5	*P* w				
870.4	*Q* w	...	...	...	$\nu_2+2\nu_7=880(A_2''+E'')$?; $\nu_3(POF_3)$
879.2	*R* w				
933.8	*P* vs				
944.8	*Q* vs	...	...	...	$\nu_3(a_2'')$
955.3	*R* vs				
989	m	...	...	...	?
1019.7	*P* vs				
1026.4	*Q* vs	1025	2	(dp)	$\nu_5(e')$
1034	*R* vs				
1061	vvw	...	...	...	$2\nu_5=1066(A_1'+E')$
1198	vwb	...	...	...	$\nu_1+\nu_5-\nu_7=1203(E')$
1271	vvw	...	...	...	$\nu_5+2\nu_7=1266(A_1'+A_2'+2E')$
1335	*P* vvw				
1346	*Q* vvw	...	...	...	$\nu_1+\nu_6=1350(E')$
1355	*R* vvw				
1403	*P* w				
1415	*Q* w	...	...	...	$\nu_1(POF_3)$
1424	*R* w				
1457	vvw	...	...	...	$\nu_1+\nu_5=1459(E')$
1573	*P* w				
1584	*Q* w	...	...	...	$\nu_2+\nu_5=1585(A_2'')$
1593	*R* w				
1665	w	...	...	...	$\nu_2+\nu_6=1666(E')$
1755	*Q* w	...	...	...	$\nu_1+\nu_3=1762(A_2'')$
1764	*R* w				
1830	w	...	...	...	$\nu_1+\nu_6=1843(E')$
2030	w	...	...	...	$2\nu_3=2052(A_1'+E')$

[a] p = polarized; dp = depolarized; s = strong; m = medium; w = weak; v = very; sh = shoulder.

[b] In addition to the bands listed, two others *grew* on the windows and are attributed to $\nu_1(f_{1u})$ = 828 and $\nu_4(f_{1u})$ = 559 cm^{-1} of the PF_4^- ion.

[c] Raman intensities are relative to the strongest *line* being equal to 100.

have contained POF_3 and $PClF_2$ impurities. However, using a sample which was purified by a method known to yield mass spectroscopically pure phosphorus trifluoride,[11] Raman spectra of the resulting PCl_2F_3 showed no differences. Therefore, the observed lines are considered to arise from PCl_2F_3 only.

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TABLE III

Vibrational spectrum of PCl_2F_3[a]

ir (gas)		Raman (liq.)[b]			
cm^{-1}	I	cm^{-1}	I	pol.	Assignment
...	...	95	6	...	"ghost"
...	...	124	36	dp	$\nu_8(a_1)$, $\nu_{12}(b_2)$
...	...	145	1	...	"ghost"
...	...	165	14	...	"ghost"
338	m	343	6	(dp)	$\nu_9(b_1)$
368	vvw	363	10	dp	$\nu_8(a_2)$, $\nu_9(b_1)$
407	wsh	407	100	p	$\nu_4(a_1)$
427	ms	427	15	dp	$\nu_7(b_1)$
460	vw	...	...	...	$\nu_3+\nu_9=462(B_1)$
488	s	488	20	(p)	$\nu_3(a_1)$
500	vwb	500	3	(dp)	$\nu_{11}(b_2)$
528	wsh	...	...	...	$\nu_4+\nu_5=531(A_1)$; $\nu_4+\nu_{12}=531(B_2)$
568	w	...	...	...	$\nu_9+2\nu_5=586(B_1)$; $\nu_9+2\nu_{12}=586(B_1)$
665	vs	660	63	p	$\nu_2(a_1)$
742 747	vw	...	...	...	$\nu_4+\nu_9=745(b_1)$
767 772 778	w	...	...	...	$\nu_4+\nu_8=775(B_1)$
818	w	...	...	...	$2\nu_4=814(A_1)$
885	sh	...	...	...	$\nu_3+\nu_7+\nu_9=889(A_1)$
893	vs	...	...	...	$\nu_3+\nu_4=895(A_1)$
902	w	...	...	...	$\nu_1(a_1)$
925	vs	924	2	dp	$\nu_{10}(b_2)$
990	m	...	...	...	(POF_3 impurity)
1025	w	...	...	...	(SiF_4 impurity)
1069	w	...	...	...	$\nu_3+\nu_4=1072(A_1)$
1159	w	...	...	...	$2\nu_4+\nu_9=1152(B_1)$
1258	vvw	...	...	...	$\nu_4+2\nu_7=1261(A_1)$
1307	vw	...	...	...	$2\nu_3+\nu_9=1314(B_1)$
1335	w	...	...	...	$\nu_4+\nu_{10}=1332(B_2)$
1385	w	...	...	...	$\nu_9+\nu_{10}+\nu_{12}=1387(B_1)$
1415	w	...	...	...	(POF_3 impurity)
1502	vvw	...	...	...	$\nu_2+\nu_3+\nu_9=1521(B_1)$
1554	ms	...	...	...	$\nu_2+\nu_3+\nu_4=1560(A_1)$
1590	vvw	...	...	...	$\nu_2+\nu_{10}=1590(B_2)$
1855	ms	...	...	...	$2\nu_{10}=1850(A_1)$

[a] p = polarized; dp = depolarized; s = strong; m = medium; w = weak; v = very; sh = shoulder.
[b] Raman intensities are relative to the strongest line being equal to 100. When the polarization measurement is uncertain, parentheses are used.

The total number of observed lines immediately eliminates the symmetrical D_{3h} model from consideration. In order to interpret the spectrum on the basis of a C_{2v} model, however, it is useful to start from a hypothetical D_{3h} structure. If the axial Cl—P—Cl bonds in the D_{3h} model are bent away from one of the equivalent equatorial fluorine atoms bisecting the angle defined by the phosphorus atom and the other two fluorine atoms, and if the bisected angle is increased to a value greater than 120°, the resulting structure belongs to the C_{2v} point group. Moreover, if the bisected F—P—F angle is increased to 180° and the Cl—P—Cl angle is

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TABLE IV
Vibrational spectrum of PCl_3F_2[a]

ir (gas)		Raman (liq.)[b]			
cm^{-1}	I	cm^{-1}	I	pol.	Assignment
...	...	122	82	dp	$\nu_7(e')$
...	...	168	...	...	"ghost"
328	m	...	...	...	$\nu_4(a_2'')$
...	...	357	17	dp	$\nu_8(e'')$
...	...	387	100	p	$\nu_2(a_1')$
404	vs	408	33	dp	$\nu_6(e')$
...	...	445	vw	...	$\nu_4+\nu_7=450(E'')$
498	w	502	vw	...	$\nu_2+\nu_7=509(E')$
522	w	...	...	...	$\nu_6+\nu_7=526(A_1'+A_2'+E')$
625	vs	609	4	dp	$\nu_6(e')$
...	...	633	38	p	$\nu_1(a_1')$
742	w	...	...	...	$\nu_6+\nu_7=747(A_1'+A_2'+E')$
797	m	...	...	...	$\nu_2+\nu_6=795(E')$
867	vs	...	...	...	$\nu_3(a_2'')$
903	w	...	...	...	$\nu_2+\nu_6+\nu_7=913(A_1'+A_2'+E')$; $2\nu_2+\nu_7=896(E')$
1017	w	...	...	...	$\nu_1+\nu_2=1020(A_1')$
1255	w	...	...	...	$\nu_1+\nu_6=1258(E')$
1382	w	...	...	...	$\nu_1+\nu_6+\nu_7=1380(A_1'+A_2'+E')$
1500	m	...	...	...	$\nu_1+\nu_3=1500(A_2'')$

[a] p = polarized, dp = depolarized; s = strong; m = medium; w = weak; v = very.
[b] Raman intensities are relative to the strongest line being equal to 100.

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decreased to 120°, the structure is just that suggested by the nuclear magnetic resonance results[6] and the inversion process is the one proposed by Berry[19] to account for rapid fluorine exchange in PF_5.

In any case, the result of changing the structure from one of D_{3h} to one of C_{2v} symmetry is that the degeneracies of the e' and e'' modes in the former are removed giving $a_1 + b_2$ and $a_2 + b_1$ modes, respectively, for the latter. This is summarized in Table X where the twelve fundamentals of the C_{2v} structure are listed in terms of their species and an idealized description of the motions involved. The relationship between the species of the C_{2v} modes to those expected for a D_{3h} model is also given. The molecular framework is oriented so that the Cl—P—Cl atoms are in the xz plane and therefore the axis of least moment of inertia lies in that plane and the axis of the intermediate moment of inertia coincides with the $C_2(z)$ axis.

The infrared band at 925 and its weak shoulder at 902 cm^{-1} correspond to the weak and diffuse Raman line at 924 cm^{-1} and may be assigned to $\nu_{10}(b_2)$ and $\nu_1(a_1)$, respectively (Figure 5, Table III). The strong infrared band at 665 cm^{-1} and the polarized liquid state Raman line at 660 cm^{-1} is confidently assigned to ν_2 by comparison with somewhat similar assignments made for $PF_5(\nu_2 = 640\ cm^{-1})$ and $PCl_3F_2(\nu_1 = 633\ cm^{-1})$. In the 500 cm^{-1} region of the spectrum, two lines are evident in the Raman effect at 488 and at about 500 cm^{-1}. In the infrared a strong absorption occurs at 488 cm^{-1} but an unresolved weak band at about 500 cm^{-1} is less evident because of strong overlapping by the 488 cm^{-1} band. On the basis of

a D_{3h} structure $\nu_6(e')$ is expected to occur in this frequency range and therefore the frequencies 488 and 500 cm^{-1} are assigned to $\nu_3(a_1)$ and $\nu_{11}(b_2)$, respectively, in the C_{2v} model.

The depolarized line at 427 cm^{-1} and the intense polarized line at 407 cm^{-1} in the Raman effect coincide with the strong band at 427 cm^{-1} and the weak shoulder centered at 407 cm^{-1} in the infrared spectrum and are assigned to the antisymmetric and symmetric PCl_2 stretching vibrations $\nu_7(b_1)$ and $\nu_4(a_1)$, respectively.

The low intensity of ν_4 in the infrared as compared with the rather high intensity of this fundamental in the Raman effect may be a reflection of a rather large Cl—P—Cl angle. The intensity of the infrared absorption band for this type of vibration is expected to go to zero as the angle approaches 180°.

In keeping with our model approximation $D_{3h} \rightarrow C_{2v}$, we expect the remaining fundamentals to arise from $\nu_4(a_2'') \rightarrow \nu_9(b_1)$, $\nu_8(e'') \rightarrow \nu_6(a_2) + \nu_8(b_1)$, and $\nu_7(e') \rightarrow \nu_5(a_1) + \nu_{12}(b_2)$. Since five fundamentals remain to be assigned and only three lines are available for this, we must conclude that our model is in error or that the expected changes in the spectra are too small to be observed. The high number of infrared and Raman coincidences and the total number of Raman lines clearly eliminate a structure of higher symmetry than C_{2v}. On the other hand, the fact that the intensity of the 500 cm^{-1} Raman line compared with the 488 cm^{-1} line is very small and the observation that the 902 line was not detected in the Raman effect offers support for the second conclusion. On this basis the weak Raman line at 363 cm^{-1} (368 in the infrared) is assigned to $\nu_6(a_2)$ and $\nu_8(b_1)$ and the line at 343 cm^{-1} (338 cm^{-1} in the infrared) is attributed to $\nu_9(b_1)$. The remaining line at 124 cm^{-1}, for which we have no infrared data, is considered to arise from $\nu_5(a_1)$ and $\nu_{12}(b_2)$. It has been tacitly assumed that in going from the D_{3h} to the C_{2v} structure the frequencies of the fundamentals, in cases where the splitting of degeneracies occurred, would not be shifted greatly. Our analysis seems to indicate that this is a reasonable assumption.

Extra lines in the Raman effect might also arise from intermolecular interactions in the condensed state. This does not appear to be the case, however, because we could not detect any change in the spectrum of a pure sample of PCl_2F_3 in the temperature range −20° to −120°C or in a solution containing 25% by volume of PCl_2F_3 in isopentane in the range −40° to −144°C.

III. PCl_3F_2

The Raman spectrum of PCl_3F_2 is particularly simple largely because there were no impurities detected and the observed spectrum is fully in agreement with D_{3h} symmetry.

As before the polarized lines at 633 and 387 cm^{-1} are assigned to $\nu_1(a_1')$ and $\nu_2(a_1')$ and the depolarized line at 357 cm^{-1} which does not appear in the infrared is assigned to $\nu_8(e'')$. The remaining three Raman lines at 609, 408, and 122 cm^{-1} (625 and 404 cm^{-1} in the infrared) can be attributed to ν_5, ν_6, and ν_7, respectively. Two fundamentals, which appear in the infrared spectrum at 867 and 328 cm^{-1} but not in the Raman effect, must be assigned to $\nu_3(a_2'')$ and $\nu_4(a_2'')$, respectively. The remaining bands in both spectra (Figure 6, Table IV) were readily assigned to combinations of the fundamentals except for a weak band at 903 cm^{-1} in the

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TABLE V

Vibrational spectrum of PCl_4F[a]

ir (gas)		Raman (liq.)[b]			
cm^{-1}	I	cm^{-1}	I	pol.	Assignment
...	...	110	47	dp	$\nu_8(e)$
...	...	167	8	...	"ghost"
...	...	265	30	p	$\nu_4(a_1)$
297	w	302	16	dp	$\nu_7(e)$
339	s	337	20	dp	$\nu_6(e)$
388	ms	384	10	p	$\nu_5(a_1)$
427	s	422	100	p	$\nu_3(a_1)$
...	...	485	1	...	$POCl_3$ impurity
500	w	...	...	...	$\nu_3+\nu_8=498(E)$
541	w	...	...	...	$\nu_2+\nu_8=537(E)$
601	vs	592	8	dp	$\nu_4(e)$
626	m	612	4	dp	$\nu_4+\nu_8=604(E)$; $\nu_3+2\nu_8=608(A_1+E)$ $\nu_3+2\nu_8=647(A_1+E)$
686	w	...	...	...	$\nu_3+\nu_7=685(E)$
725	m	...	...	...	$\nu_2+\nu_7=724(E)$; $\nu_4+\nu_7=727(A_1+A_2+E)$
778	vs	...	...	...	$\nu_1(a_1)$
867	w	...	...	...	$2\nu_5=854(a_1)$
902	m	...	...	...	$\nu_4+\nu_7=898(A_1+A_2+E)$
937	w	...	...	...	$\nu_4+\nu_6=940(A_1+A_2+E)$
1025	w	...	...	...	$\nu_2+\nu_6=1026(E)$ or SiF_4
1200	vw	...	...	...	$2\nu_6=1204(A_1+E)$
1352	m	...	...	...	$\nu_1+\nu_4+\nu_7=1350(E)$

[a]p = polarized; dp = depolarized; s = strong, m = medium; w = weak; v = very; sh = shoulder.
[b]Raman intensities are relative to the strongest line being equal to 100.

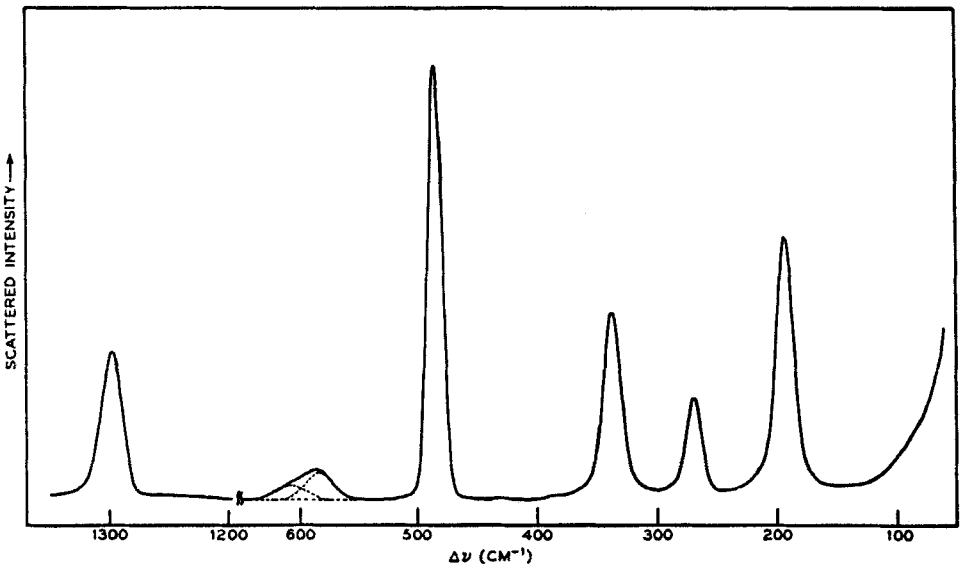

FIGURE 8 Raman spectrum of $POCl_3$. Slit 10 cm^{-1}, ampl. 500, temperature 25°C; single beam.

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TABLE VI
Fundamental frequencies of PF_5[a]

No.	Mode description	Activity	Species	Assignment
1	PF_3 sym. stretch	R, (p); —	a_1'	817
2	PF_2 sym. stretch			640
3	PF_2 antisym. stretch	—; ir	a_2''	945
4	PF_3 sym. out-of-plane bend			576
5	PF_3 antisym. stretch	R, (dp); ir	e'	1026
6	PF_3 in plane bend			533
7	PF_2 antisym. axial bend			126
8	Rocking	R, (dp);—	e''	514

[a] Gas-phase values are used when available.

TABLE VII
Fundamental frequencies of PCl_2F_3[a]

No.	Species	Freq.	No.	Species	Freq.
1	a_1	902	7	b_1	427
2	a_1	665	8	b_1	368
3	a_1	488	9	b_1	338
4	a_1	407	10	b_2	925
5	a_1	124	11	b_2	500
6	a_2	368	12	b_2	124

[a] Gas-phase values are used when available.

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infrared. Although the frequency of this is correct for the $\nu_4(e)$ fundamental of POF_3, the strong $\nu_1(a_1)$ band of POF_3 was not observed. Tentatively, the band at 903 cm^{-1} is assigned to $\nu_2 + \nu_6 + \nu_7 = 913$ or to $2\nu_2 + \nu_7 = 896$ cm^{-1} or to both.

IV. PCl_4F

If the trigonal bipyramidal structure is retained in PCl_4F, the molecule would belong to the C_{3v} or to the C_{2v} point group depending on whether the fluorine atom occupies an axial or an equatorial site. In the first structure, the equatorial chlorine atoms may or may not be coplanar with the phosphorus atom. By analogy with SF_5Cl,[20] one would not expect exact coplanarity but, regardless of this, the point group would not change.

An examination of the Raman spectrum (Figure 7, Table V) reveals nine lines (and one "lamp ghost" at 167 cm^{-1}), one of which is extremely weak ($\Delta\nu = 485$ cm^{-1}) and is identified with a $POCl_3$ impurity. Since this is the most intense line in the spectrum of $POCl_3$, others are not expected to be observable (Figure 8). In addition to the remaining eight-line spectrum, one more band at 778 cm^{-1} in the infrared spectrum is strong enough to be considered as a fundamental. Although

TABLE VIII
Fundamental frequencies of PCl_3F_2[a]

No.	Mode description	Activity	Species	Assignment
1	Sym. PF_2 stretch	R(p);—	a_1'	633
2	Sym. PCl_3 stretch			387
3	Antisym. PF_2 stretch	—; ir	a_2''	867
4	Out-of-plane PCl_3 bend			328
5	Antisym. PCl_3 stretch	R(dp); ir	e'	625
6	PCl_3 in-plane bend			404
7	PF_2 axial bend			122
8	Rocking	R(dp);—	e''	357

[a] Gas-phase frequencies are used when available.

this exceeds by one the number of bands expected for a C_{3v} structure (and is short by three the number expected for a C_{2v} structure), the following analysis is based upon an assumed C_{3v} model. Consideration of the alternate C_{2v} and C_{4v} models is deferred until the discussion section of this paper.

The infrared band at 778 cm^{-1} which lacked sufficient intensity to be observed in the Raman effect occurs at too high a frequency to be assigned to anything except $\nu_1(a_1)$, the P—F stretching fundamental. The most intense Raman line which is polarized and occurs at 422 cm^{-1} (427 cm^{-1} in the infrared) is assigned to the symmetric PCl_3 stretching vibration, $\nu_2(a_1)$. At lower frequency, a moderately intense polarized Raman line at 265 cm^{-1} appears to arise from the symmetric deformation of the PCl_3 unit. It is perhaps significant that this frequency is close to that observed for the similar fundamental in the spectrum of $POCl_3$ (267 cm^{-1}) and suggests that in PCl_4F, the three equivalent chlorine atoms are not coplanar with the phosphorus atom. The direction of the deviation from coplanarity, however, is not especially evident and therefore we do not offer speculations on the problem at this time. The Raman line at 384 cm^{-1} (388 cm^{-1} in the infrared) appears to be weakly polarized and therefore is assigned to the remaining nondegenerate fundamental, $\nu_3(a_1)$ which represents the axial P—Cl stretching mode.

The two low-frequency depolarized Raman lines at 302 cm^{-1} (297 cm^{-1} in the infrared) and at 110 cm^{-1} are assigned to $\nu_7(e)$ and $\nu_8(e)$, respectively. These are considered to represent complex rocking and bending motions, and in the absence of an accurate structure determiniation and verification using a normal coordinate analysis, further definition of the modes is impossible. A Raman line at 337 cm^{-1} appears to be depolarized and is assigned to the degenerate PCl_3 deformation mode $\nu_6(e)$. Much like $\nu_4(a_1)$, the frequency of this fundamental compares favorably with the frequency of the similar fundamental of $POCl_3$ [$\nu_5(e)$ = 337 cm^{-1}].

A weak pair of lines at 592 and 612 cm^{-1} in the Raman effect (601 and 626 cm^{-1} in the infrared) remain to be assigned. The most intense of these at 592 cm^{-1} is assigned to the remaining degenerate mode $\nu_5(e)$ which represents the antisymmetric PCl_3 stretching vibration. This also compares favorably with the frequency of the analogous fundamental in $POCl_3$, $\nu_4(e)$ = 583 cm^{-1}. The very weak Raman

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TABLE IX

Fundamental frequencies of PCl_4F[a]

No.	Mode description	Activity	Species	Assignment
1	P–F axial stretch	R(p); ir	a_1	778
2	PCl_3 sym. stretch			422
3	P–Cl axial stretch			388
4	PCl_3 sym. deformation			265
5	PCl_3 antisym. stretch	R(dp); ir	e	601
6	PCl_3 antisym. deform.			339
7	Rocking and bending			297
8	Rocking and bending			110

[a] Gas-phase frequencies are used when available.

TABLE X

Fundamental vibrations of PCl_2F_3[a]

Mode description[b]	Species a_1	a_2	b_1	b_2
PF stretching	$\nu_1(5)$	...	...	...
PF_2' stretching	$\nu_2(1)$	...	...	$\nu_{10}(5)$
PF_2' bending	$\nu_3(6)$	...	...	...
PF bending (yz)[c]	...	...	...	$\nu_{11}(6)$
PCl_2 stretching	$\nu_4(2)$	...	$\nu_7(3)$	...
PF bending (xz)[c]	...	...	$\nu_8(8)$	...
Cl_2PF_2' twist	...	$\nu_6(8)$	...	...
PF_2' wagging	...	...	$\nu_9(4)$	...
PF_2' rocking	...	...	...	$\nu_{12}(7)$
PCl_2 bending	$\nu_5(7)$	...	...	...

[a] Numbers in parentheses within the table represent the mode numbers according to the D_{3h} structure from which the modes in the C_{2v} structure are derived. Thus, $\nu_5(e')(D_{3h}) \rightarrow \nu_1(a_1) + \nu_{10}(b_2)(C_{2v})$.

[b] Primes refer to F atoms not on the $C_2(z)$ axis.

[c] (yz) and (xz) represents bending motions in the yz and xz planes, respectively.

TABLE XI

Bond distances of PCl_nF_{5-n} molecules

Molecule	r(P–F_{ax})	r(P–F_{eq})	r(P–Cl_{ax})	r(P–Cl_{eq})
PF_5[a]	1.57	1.57	...	...
PCl_3F_2[b]	1.59	...	...	2.04
PCl_5[c]	...	...	2.19	2.04

[a] From Ref. 5.

[b] Assumed values.

[c] From Ref. 4.

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TABLE XII

Thermodynamic functions for PX_nY_{5-n} compounds

T(°K)	$(H°-E_0°)/T$	$-(F°-E_0°)/T$	$S°$	$C_P°$
PF_5				
150	10.32	51.60	61.94	13.28
200	11.37	54.72	66.10	15.79
250	12.50	57.38	69.90	18.26
273.16	13.04	58.51	71.56	19.31
298.16	13.61	59.68	73.30	20.36
350	14.75	61.95	76.72	22.25
400	15.79	63.99	79.80	23.74
450	16.74	65.91	82.67	24.96
500	17.62	67.72	85.36	25.94
600	19.13	71.08	90.23	27.40
700	20.39	74.13	94.54	28.40
800	21.44	76.93	98.38	29.10
900	22.32	79.51	101.8	29.61
1000	23.07	81.90	105.0	29.99
PCl_3F_2				
150	11.36	55.34	66.71	16.57
200	13.10	58.85	71.96	19.92
250	14.74	61.95	76.71	22.52
273.16	15.44	63.29	78.75	23.49
298.16	16.15	64.68	80.85	24.40
350	17.49	67.38	84.89	25.91
400	18.62	69.79	88.43	27.00
450	19.60	72.04	91.66	27.83
500	20.46	74.16	94.63	28.47
600	21.87	78.02	99.91	29.37
700	22.99	81.48	104.5	29.95
800	23.89	84.62	108.5	30.34
900	24.62	87.48	112.1	30.63
1000	25.23	90.11	115.4	30.83
PCl_5				
150	12.79	57.89	70.71	19.56
200	14.94	61.88	76.84	22.99
250	16.80	65.43	82.24	25.31
273.16	17.56	66.95	84.52	26.12
298.16	18.31	68.52	86.85	26.84
350	19.66	71.57	91.25	27.98
400	20.75	74.27	95.04	28.75
450	21.68	76.77	98.47	29.32
500	22.46	79.10	101.6	29.74
600	23.73	83.32	107.1	30.32
700	24.70	87.06	111.8	30.68
800	25.47	90.41	115.9	30.93
900	26.08	93.45	119.5	31.09
1000	26.59	96.23	122.8	31.22

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line at 612 cm^{-1} must therefore be assigned as a combination band. Two possibilities are $\nu_4 + \nu_6 = 604(E)$ and $\nu_3 + 2\nu_8 = 608(A_1 + E)$ cm^{-1} each of which is suitable. Moreover, they are of the proper species so that their intensities could be enhanced and their frequencies shifted upward through a Fermi resonance interaction with the $\nu_5(e)$ fundamental. The previous comparison between some of the frequencies found here and in the spectrum of $POCl_3$ may be further extended. In the Raman spectrum of $POCl_3$, a band weaker in intensity than $\nu_4(e) = 583$ cm^{-1} occurs at 608 cm^{-1}. The combination $\nu_3 + \nu_5 = 606(E)$ adequately explains the weaker

band and its enhanced intensity is interpreted in terms of a Fermi resonance interaction between $\nu_3 + \nu_5$ and ν_4. This completes the vibrational analysis of the Raman spectrum. In the infrared, where the frequency ranges overlap with the Raman values, complete ir-R coincidences occur as required for the C_{3v} model. All additional infrared bands are satisfactorily interpreted in terms of combination bands.

THERMODYNAMIC FUNCTIONS

The thermodynamic functions were evaluated at a number of convenient temperatures for PF_5, PCl_3F_2, and PCl_5 using the usual methods of statistical mechanics. The data contained in this work and that of Taylor and Woodward[8] for PCl_5 were used. Bond lengths and angles which were employed in the calculations are summarized in Table XI and the thermodynamics values are collected in Table XII. Thermodynamic functions were not evaluated for PCl_2F_3 and PCl_4F because of the absence of reliable structural parameters.

DISCUSSION

Of the possible structures for the molecules studied in this work, the trigonal bipyramidal one appears to be totally consistent with all of the data. Moreover, the relative positions of the fluorine and the chlorine atoms results from an interpretation of the vibrational spectra.

Although the infrared and Raman spectra of PCl_2F_3 are interpreted in terms of a C_{2v} model in a trigonal bipyramidal structure, it is recognized that an alternate analysis could be presented in terms of a C_s structure in which the fluorine atoms occupy one axial and two equatorial sites. Since recently completed dipole moment,[21] ^{19}F nuclear magnetic resonance, and ^{35}Cl and ^{37}Cl quadrupole resonance studies[22] do not agree with this model and are in accord with the C_{2v} structure, further consideration of the least symmetrical model is not presented.

In order to establish if PCl_2F_3 exists as a mixture of isomeric forms in dynamic equilibrium or not, the temperature dependence of the frequencies and relative band intensities in the Raman effect was investigated. The lack of any detectable change in the spectrum from $-40°$ to $-120°C$ in the pure liquid (mp $-124°C$) or from $-20°$ to $-144°C$ in a 25% by volume isopentane solution excluded such a possibility.

Since the nuclear magnetic resonance results show evidence for intramolecular fluorine exchange[6,22] one might expect to observe this process spectroscopically. Conclusive evidence for a "pseudorotational process," as postulated by Berry[19] to explain the ^{19}F nuclear magnetic equivalence in PF_5, might be obtainable for PCl_2F_3 from a study of its pure rotational spectrum.

The spectrum of PCl_4F was especially important because of the three possible structures. Our interpretation favors the trigonal bipyramidal model in which the fluorine atom occupies an axial site. On the other hand, the total number of observed bands is also consistent with a tetragonal pyramidal model but the number of ir-R coincidences tends to eliminate this possibility. The remaining C_{2v} model

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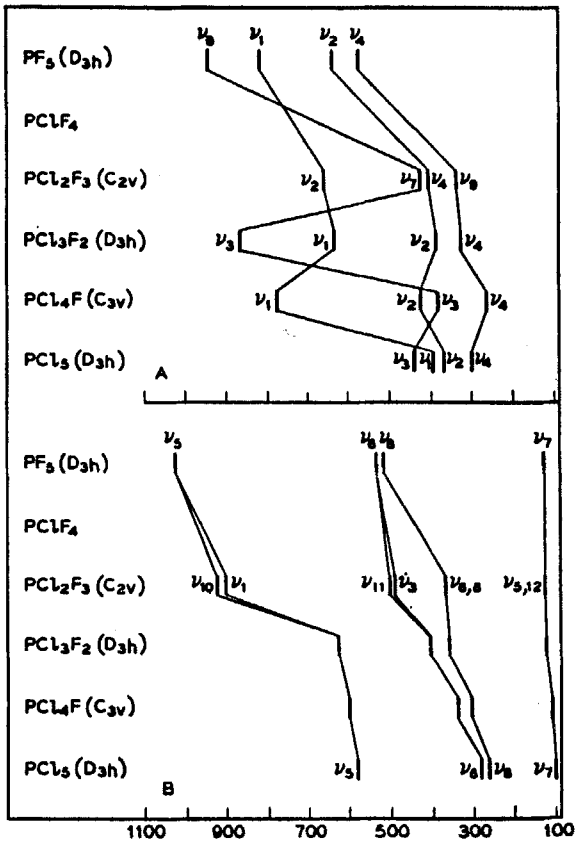

FIGURE 9 Correlation diagram for PCl_nF_{5-n} molecules. (a) Nondegenerate vibrations, (b) degenerate vibrations.

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in which the fluorine atom occupies an equatorial position is not so definitely excluded. The main difficulty with this model arises in the assignments connected with the P—Cl stretching modes. Two of the P—Cl bonds are expected to be longer than the other two and correspondingly one Cl—P—Cl angle is expected to approach 180° and the other to approach 120°.

The two symmetric P—Cl_2 stretching modes could probably be assigned to the Raman lines at 422 and 384 cm^{-1}. The antisymmetric PCl_2 stretching vibration associated with the smaller angle unit also is expected to occur in this frequency range and can be assigned along with the symmetric mode to the 422-cm^{-1} line (cf. PCl_2F_3). Because of the large Cl—P—Cl angle in the remaining PCl_2 unit, the antisymmetric stretching vibration is expected at a higher frequency. The line at 592 cm^{-1} seems to be too high for this by comparison with the spectrum of PCl_5 where this type of vibration occurs at about 450 cm^{-1}, only 80 cm^{-1} higher than the symmetric mode.[8] Assignment of the antisymmetric stretching fundamental in question to either the 422 or to the 384-cm^{-1} line implies a smaller Cl—P—Cl angle and also means that the 592- and 612-cm^{-1} lines must be explained in terms of combination bands. Although the latter is a possibility, it is unlikely that both

represent combinations. Furthermore, the total number of lines available for fundamentals is reduced to seven which means that there are only four lines available for the seven unassigned fundamentals. While accidental degeneracies of the kind required on the basis of this analysis are not without precedent, the argument becomes progressively less convincing when compared with the one presented for the C_{3v} structure.

The assignments made for chlorofluorides of pentavalent phosphorus are summarized in Figure 9. For added clarity the nondegenerate and degenerate vibrations have been separated. The frequency trends established among the nondegenerate vibrations support the assignments made for them. For example, the large frequency changes in the mode designated ν_3, representing an antisymmetric stretching of the axial P—X bonds,[23] in going from PF_5 to PCl_3F_2 reflect changes in the type of atoms which move during the particular vibration. The lines joining mode numbers, however, do not in all cases follow a particular type of vibration going through the complete series. This is a consequence of the numbering system used.[24] The frequencies of the degenerate vibrations require no special comment since anomalous behavior is absent.

The assignments for PCl_5 of Taylor and Woodward[8] were used in preference to those of Carlson[7] for two reasons. In the former, a weak band attributed to ν_2 was observed at a lower frequency than ν_1 which parallels the relative intensity and frequency observations made in this work in the spectrum of PF_5. Further arguments based on bond polarizability theory were also presented by Taylor and Woodward. The second and more convincing argument involves the assignments of ν_6 and ν_8. In Carlson's work $\nu_8 > \nu_6$ which is difficult to accept. In all of the pertinent molecules studied in the present work, $\nu_6 > \nu_8$ and the reverse requires a violation of the noncrossing rule for degenerate species.[24] The Raman spectrum of PCl_5 was not published, however, and therefore the problem of ν_2, ν_6, and ν_8 in PCl_5 may still be open to argument and possibly further study.

Although the vibrational spectrum of $PClF_4$ is not reported in this series, the correlation chart may serve as a useful guide to locating the fundamental frequencies. Other independent studies of the phosphorus (v) chlorofluorides discussed in this paper will be reported elsewhere.[21,22,25]

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ACKNOWLEDGEMENTS

We are grateful to Dr. G. E. Walrafen for the use of the Cary Model 81 spectrophotometer and to Dr. L. H. Sharpe and J. P. Luongo for access to the infrared instruments. Dr. T. D. Goldfarb kindly allowed us to use the far-infrared instrument at the State University of New York, Stony Brook and we are especially grateful to Dr. D. E. Irish for some of the early Raman measurements while a summer visitor at Bell Telephone Laboratories, Inc.

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17. One additional line at about 170 cm^{-1} is evident in all of the observed spectra and is attributed to a ghost. For convenience, this line is neglected in all discussion but it is shown in the individual spectra. Observations using empty sample tubes confirmed that the line is not due to the sample.
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