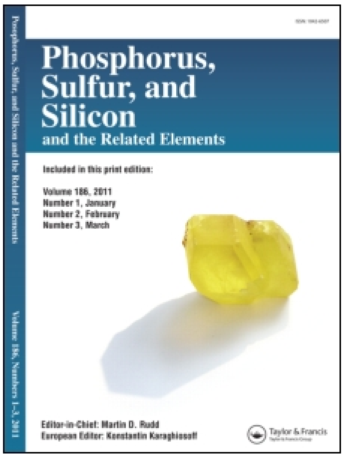

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MOLECULAR STRUCTURE OF PC1F$_4$: INFRARED SPECTRUM, LOW-TEMPERATURE RAMAN SPECTRUM, AND GAS-PHASE DIPOLE MOMENT: PENTACOORDINATED MOLECULES. IX

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MOLECULAR STRUCTURE OF $PClF_4$: INFRARED SPECTRUM, LOW-TEMPERATURE RAMAN SPECTRUM, AND GAS-PHASE DIPOLE MOMENT: PENTACOORDINATED MOLECULES. IX*

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The vapor-state infrared spectrum (2000–250 cm^{-1}) and liquid-state Raman displacements ($\Delta\nu$ = 50–1200 cm^{-1}) of $PClF_4$ are reported. The vapor-state electric dipole moment of $PClF_4$ was obtained from a study of the temperature variation of the dielectric constant over the range −68° to −2°. The resulting value is 0.78 ± 0.01 D. The induced polarization is 13.7 ± 0.4 cc. Interpretation of the vibrational data as well as the dielectric data and ^{35}Cl pure quadrupole resonance frequency support the conclusion that the structure of $PClF_4$ is a trigonal bipyramid (C_{2v} point group) with the chlorine atom located at an equatorial site.

The infrared and Raman spectra of all members of the phosphorus (V) chlorofluorides PCl_nF_{5-n} have been reported[1] previously except for $PClF_4$. Analysis of the vibrational data and results of dielectric,[2] pure quadrupole, and nuclear magnetic resonance measurements[3] have shown that the molecular forms[4] of these compounds exist in a trigonal bipyramidal framework with the fluorine atoms showing a preference for axial sites.

Recently we have synthesized[5] $PClF_4$ and have obtained the corresponding data to allow its structure to be determined.

EXPERIMENTAL

Materials

The compound $PClF_4$ was synthesized by low-temperature fluorination of the molecular form of PCl_2F_3 using SbF_3 as the fluorinating agent.[5] PCl_2F_3 was prepared *in vacuo* according to a modification[6] of a previous procedure.[7] The preparations were carried out in a Pyrex glass vacuum system. Stopcocks and ground-glass joints were lubricated with Kel-F grease.

No impurities were evident in the Raman spectrum. However, because of possible reaction with the cell materials and disproportionation of $PClF_4$ to PF_5 and PCl_2F_3 observed[5] in the gas phase, small amounts of the latter in addition to POF_3 were detected in the infrared measurements.

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Spectra

To avoid disproportionation of $PClF_4$ to PCl_2F_3 and PF_5 it was necessary to record the Raman spectrum of the liquid at low temperatures. A previous Raman cell design[1] was modified to allow precise centering of the liquid-sample tube. This was accomplished by properly constricting the inner wall of the cell at the end tapering toward the optical flats. The constriction was such to allow use of 7- to 9-mm-o.d. sample tubes.

To avoid the hazards of pressure buildup, if any, caused by disproportionation of that part of the $PClF_4$ vapor (producing the more volatile PF_5) which would be exposed to room temperature during the recording of the Raman spectrum, the sample cell arrangement and procedure discussed[1] previously for PF_5 was used here. The measurement was performed at about −100°C. However, neither a trace of PF_5 nor of any other impurity was evident in the Raman spectrum.

Raman displacements from the 4358-Hg line were recorded with a Cary Model 81 spectrophotometer and are considered accurate to ± 3 cm^{-1} for the sharper lines. Weak and broad instrument ghosts appeared at about 145 and 170 cm^{-1} with the latter being the stronger of the two. Qualitative polarization measurements were obtained with the use of cross and axial Polaroid cylinders which fitted around the outside of the Raman Dewar cell. To check on the effects of geometry, the Raman spectrum of both PF_5 previously recorded with a different Cary 81 spectrophotometer and CCl_4 were studied in the cell arrangement used for $PClF_4$ as well as the polarization of the CCl_4 lines.

The gas-phase spectrum of $PClF_4$ was recorded in the range 2000–400 cm^{-1} with a Perkin-Elmer Model 337 grating Infracord and in the range 2000–250 cm^{-1} with a Perkin-Elmer Model 421 spectrophotometer. The former was calibrated with polystyrene and the latter with ammonia and H_2O vapor. A 10-cm gas cell fitted with AgCl, KBr, or CsI windows was used. Both Pyrex and Monel metal cells were used.

Argon was mixed with the $PClF_4$ for some of the runs to minimize decomposition to PF_5 and PCl_2F_3 and cell attack. Even so, some weak bands were attributable to PF_5 and PCl_2F_3. Their presence was confirmed by obtaining repeat spectra of the same sample as a function of time. With a sample having a pressure of a few mm, the bands assigned to $PClF_4$ completely disappeared in 3–4 h in the beam of the 421 while PF_5 bands were seen to grow as well as POF_3 bands, the latter less so than the former. At higher sample pressures small amounts of disproportionation products made themselves evident.

After conditioning of the cell with the $PClF_4$, reproducible spectra were obtained in the pressure region from 2 to 500 mm. The frequency accuracy is ± 2 cm^{-1}.

Dielectric Measurements

The dielectric measuring assembly, cell-bath housing, and operating procedure have been described[2] in connection with vapor-state dielectric measurements of PCl_3F_2 and PCl_2F_3 performed in this laboratory. The manually nulled quartz spiral Bourdon gauge used to measure pressure was replaced by a Texas Instruments automatically servonulled quartz spiral Bourdon unit. As a result the time of the measurement on a sample at a particular temperature and pressure was reduced to about a minute. In order to keep the time down in the earlier study,[2] the measurement was a two-man operation. Any effects due to the slow conversion of $PClF_4$ to PF_5 and PCl_2F_2 observed near room temperature accordingly would be minimized. As noted,[2] temperature equilibrium is reached in a minute or so on the first addition of sample to the evacuated cell and almost instantaneously on successive additions or removals. To further minimize any sample contamination due to instability the measurements were confined to temperatures below 0° (range, −68° to −2°C).

At each temperature several series of capacitance-versus-pressure readings were made in the range 10 to 270 mm. Several samples were used and measurements were made as a function of both increasing and decreasing temperature. A different portion of a particular sample was used at each temperature. Analysis of the results showed no systematic differences which might indicate lack of homogeneity. The pressure readings recorded were good to ±0.01 mm. The temperature was held constant to ±0.01° and determined with a Pt resistance thermometer.

A new Pyrex cell was constructed which was similar to that used before but had a conductive Nesa coating applied to all exterior portions instead of a silver coating. The latter served as a shield from external capacitive coupling in the three-terminal system used. The replaceable capacitance of the cell determined as before with ammonia gas was 188.3 ± 1.0 pF.

RESULTS

Dipole Moment of $PClF_4$

Table I lists the polarization P for $PClF_4$ as a function of temperature. Average values of P determined from measurements on three different samples are listed. The polarizations are reproducible to about ±0.07 cc.

Calculation of the dipole moment from a least-squares treatment of the data in Table I gave 0.78 ± 0.01 D. The same result is obtained if individual values are used. The temperature-independent polarization is 13.7 ± 0.4 cc. The limits of uncertainty are those associated with the standard deviation in the slope of the least-squares line and the standard deviation in the intercept.

TABLE I

Temperature variation of the molar polarization of $PClF_4$.

T (°C)	P (cc)
−68.38	32.24
−59.45	31.25
−48.30	30.48
−37.28	29.60
−24.82	28.94
−12.04	28.28
−1.57	27.52

INFRARED AND RAMAN SPECTRA

Infrared and Raman spectra of $PClF_4$ are shown in Figures 1 and 2. The frequencies, relative intensities, states of polarization, and suggested assignments are given in Table II. The assignments are made on the basis of C_{2v} symmetry, the justification for which is discussed below.

Table III lists the number and activity of fundamentals for C_{2v} as well as other possible point groups. Structural models are shown in Figure 3.

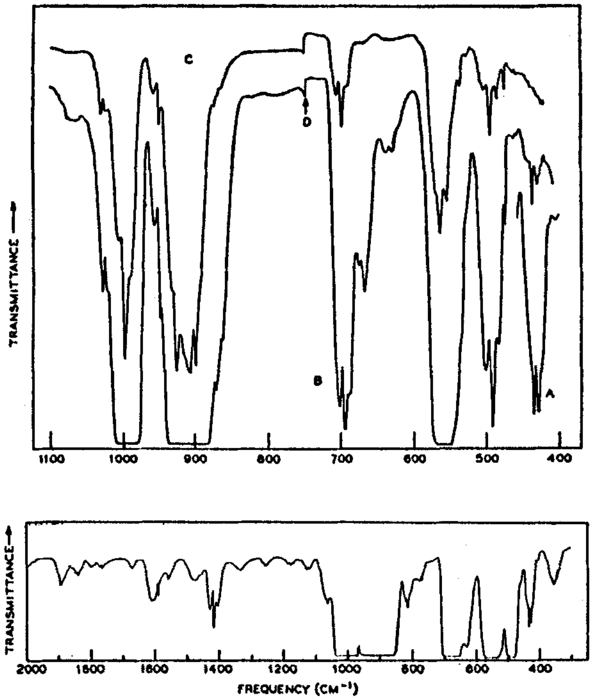

FIGURE 1 Infrared spectrum of $PClF_4$ at 25°C. Top: PE Model 337 grating Infracord, (A) $p = 30$ cm, (B) $p = 3$ cm, (C) $p = 0.5$ cm, $l = 10$ cm, (D) filter change. Bottom: PE421 spectrophotometer, $p = 20$ cm.

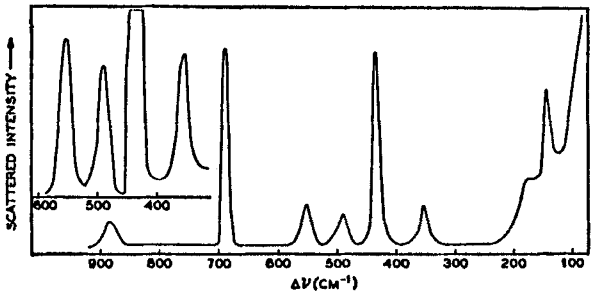

FIGURE 2 Raman spectrum of $PClF_4$ at -100°C, slit 10 cm^{-1}, amplification 1275, single slit; (insert) slit 10 cm^{-1}, amplification 1500, doublet slit.

TABLE II

Vibrational spectrum of $PClF_4$.[a]

ir (gas)		Raman (liq.)[b]				ir (gas)		Raman (liq.)[b]			
cm^{-1}	I	cm^{-1}	I	Pol.	Assignment (C_{2v})	cm^{-1}	I	cm^{-1}	I	Pol.	Assignment (C_{2v})
		144	63	(p)	$\nu_5(a_1), \nu_9(b_1)$	(910) 921 927	P vs Q vs R vs				$\nu_7(b_1)$
356	w	355	28	dp	$\nu_6(a_2), \nu_{12}(b_2)$	945	m				$2\nu_3(POF_3) = 946$; PF_5
427 434	mw mw	435	100	p	$\nu_4(a_1)$	954	m				$\nu_3+\nu_6(POF_3) = 956$
459 472	P mw Q m				$\nu_3(POF_3) = 473$[c]	986 994 1002	P vs Q vs R vs				$\nu_4(POF_3) = 994$
481 490 499	P s Q s R s	490	27		$\nu_8(b_1)$	1019 1026 1038	P m Q m R m				PF_5
		(510)	4		$\nu_3(a_1)$	1063	w				$\nu_5+\nu_7 = 1065(B_1)$
522 531 542	P m Q m R m				PF_5[d]	1120 1129	P vw Q vw				$2\nu_{11} = 1120(A_1)$
551 560[e] 567	P vs Q vs R vs	553	31	(dp)	$\nu_{11}(b_2)$	1176 1186 (1194)	P vw Q vw R vw				$\nu_2+\nu_8 = 1181(B_1)$
618 626 634	P mw Q mw R mw				?	1257	vw				$\nu_2+\nu_{11} = 1251(B_2)$
665 672	Q m R m				PCl_2F_3[d]	1335	vw				$\nu_4+\nu_{10} = 1337(B_2)$
685 691 700	P s Q s R s	689	94	p	$\nu_2(a_1)$	1405 1417 1428	P mw Q mw R mw				$\nu_1(POF_3) = 1418$
730 738 746	P vw Q vw R vw				PCl_2F_3	1476	vw				$\nu_4+\nu_6(POF_3) = 1477$
765 771 778	P vw Q vw R vw				PCl_2F_3	1558	vw				$\nu_4+2\nu_{11} = 1554(A_1)$
808 817 825	P w Q w R w				$\nu_5+\nu_6(POF_3) = 819$	1590	vw				$\nu_1+\nu_2 = 1586(A_1)$ $\nu_2+\nu_{10} = 1594(B_2)$
859 869	P m Q m				$\nu_2(POF_3) = 873$	1608	vw				$\nu_2+\nu_7 = 1612(B_1)$ or $\nu_8+2\nu_{11} = 1610(B_1)$
895	vs	884	22		$\nu_1(a_1)$	1795	vw				$2\nu_1 = 1790(A_1)$
903	vs				$\nu_{10}(b_2)$	1893	vw				
						1995	vw				$2\nu_4(POF_3) = 1988$

[a] p denotes polarized; dp, depolarized; s, strong; m, medium; w, weak; v, very.

[b] Raman intensities are relative to the strongest line being equal to 100 and were obtained using a planimeter.

[c] Frequencies and assignments of POF_3 fundamentals are taken from H. Selig and H. H. Claassen, J. Chem. Phys. 44, 1404 (1966).

[d] See Ref. 1.

[e] Presence of PF_5 at 575 cm^{-1} causes asymmetry to the high-frequency side of the 560-cm^{-1} band.

TABLE III

Activity of fundamental modes for various models.

Point group	Fundamentals	Raman	Infrared	R–ir coincidences
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

For the C_{2v} symmetry the selection rules say that only the a_2 vibration is infrared inactive and of the binary combinations only $a_1a_2 = A_2$ and $b_1b_2 = A_2$ are not allowed in the infrared.

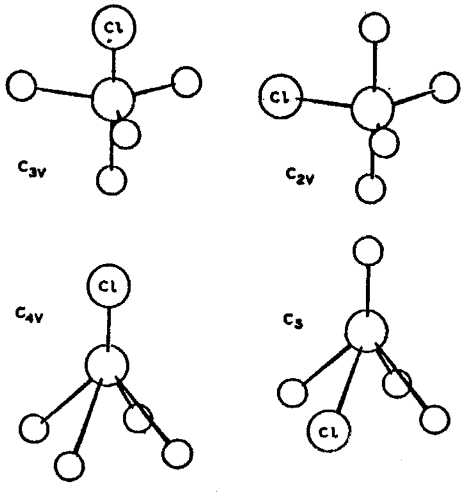

FIGURE 3 Structural models for $PClF_4$.

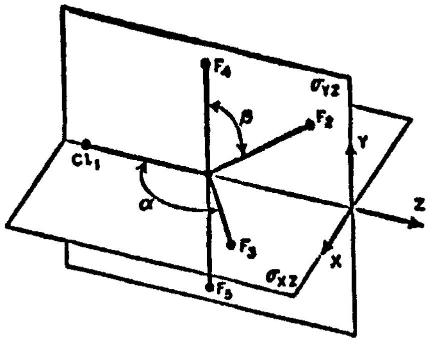

FIGURE 4 Coordinates for $PClF_4$ (C_{2v} point group).

With reference to Figure 4 the B_1 vibrations are taken to be those symmetric with respect to the XZ plane. The principal moments of inertia may be approximated for this symmetry on the basis of recent bond-distance information on PF_5[8,9] determined by electron diffraction. Assuming the following parameters, P—Cl_1, 2.04 Å; P—F_2, 1.52 Å; P—F_4, 1.57 Å; α, 120°; β, 90° the principal moments of inertia become, 265×10^{-40}, 368×10^{-40}, and 414×10^{-40} g-cm^2. The smallest inertial axis coincides with the C_2 axis, the largest with the X axis. The A_1 vibrations involve dipole changes parallel to the C_2 axis and hence should give rise to A-type band contours characteristic of asymmetric-top molecules. Correspondingly, the B_1 and B_2 vibrations giving dipole changes parallel to the X and Y axes should exhibit, respectively, C- and B-type band contours.

With reference to Badger's and Zumwalt's calculations[10] and using the moments of inertia estimated above, it is expected that the Q branch of the B-type bands should be more pronounced than that of the C type, but not especially so. Less difference might be expected between the A and C types. As seen in Figure 1, no major variations in contour are present for those bands which are not overlapping their neighbors.

By reason of the intensity and occurrence in overtones and combinations, seven bands in the infrared spectrum qualify as fundamentals. A weak band at 356 cm^{-1} in the infrared may be included as a fundamental because of its appearance in the Raman. The 144-cm^{-1} band, below the range of the infrared instrument, of moderate intensity in the Raman may be counted also. As mentioned above, broad instrument ghosts appear at 145 and 170 cm^{-1} with the latter being the stronger of the two. While experience has shown that these ghosts may be magnified somewhat by the particular sample under investigation, their relative intensities have never been observed to reverse. In Figure 2 the ghost band at 170 cm^{-1} is clearly evident in the Raman scattering. It is presumed that the lower intensity ghost is contributing slightly to the band observed at 144 cm^{-1}. As a result of the relatively large intensity observed for the latter band, it is included as a fundamental with considerable confidence. Consequently, nine bands are reasonably established as fundamentals. The Raman spectrum supports these as fundamentals except for the very strong bands at 903 and 921 cm^{-1} in the infrared; presumably their intensity is too low to be detected in the Raman under the conditions cited in the experimental section. On this basis, the structure having C_{4v} symmetry is ruled out. A total of six infrared-active fundamentals exist for this point group (Table III) while eight have been directly observed for $PClF_4$.

The total number of fundamentals allowed for the structure of C_{3v} symmetry is eight. This is one less than the number readily established as fundamentals and hence the C_{3v} point group appears as an unlikely representation. However, the latter may be considered to be a relatively weak argument against the likelihood of the C_{3v} configuration. A more severe criticism arises from an attempt at a vibrational assignment for this symmetry. In making such a fit one of the very strong infrared-active fundamentals would remain unassigned and $\nu_1(a_1)$, principally a PF_3 symmetric stretch, would appear at an unexpectedly high intensity in the infrared (one of the very strong bands centered around 900 cm^{-1}). The latter band in the C_{3v} point group should be intense in the Raman, which is not the case. The only band seen in this region is the least intense Raman line at 884 cm^{-1}. In addition, the 144-cm^{-1} band in the Raman which is most likely polarized would have to be assigned to a depolarized *e* mode. Further evidence against the C_{3v} symmetry is given in the discussion.

The difficulties cited above in attempting to fit the spectral data to the C_{3v} symmetry are removed by considering the more unsymmetrical representation, C_{2v}. For this symmetry a total of 12 fundamentals should exist and only nine have been accounted for.

In the related molecule, $CH_3PF_4(C_{2v})$, two separate vibrations attributable to PF_2 axial bending modes were not observed.[11] In fact, the splittings of the vibrations (e', e'') which are doubly degenerate in D_{3h} symmetry (PF_5) are not appreciably split in the region below 450 cm^{-1} in the infrared spectrum[11] of CH_3PF_4. The e' and e'' modes would be split into $a_1 + b_1$ and $a_2 + b_2$, respectively, by the change in symmetry from D_{3h} to C_{2v}. The infrared spectrum was not examined in the region of the 144-cm^{-1} fundamental but the 356 cm^{-1} is seen to be unresolved having a half-width at half-height of about 35 cm^{-1}. This band which is depolarized in the Raman and weak in the infrared is assigned to ν_6 and ν_{12} and would correspond to the doubly degenerate frequency e'' in D_{3h} symmetry. A separation of 15 cm^{-1}

was observed[11] for these frequencies (397, 412 cm^{-1}) in the CH_3PF_4 molecule. Assuming that the lowest frequency observed in the Raman at 144 cm^{-1} represents one of the axial bending modes or if close together in frequency and intensity the unresolved vibrations, ν_5 and ν_9, a total of 11 fundamentals have been accounted for. The assignment of 144 cm^{-1} to a PF_2 axial bend is in keeping with similar assignments in CH_3PF_4 (179 cm^{-1}),[11] $(CH_3)_2PF_3$ (184 cm^{-1}),[12] PCl_2F_3 (124 cm^{-1}),[13] all on C_{2v} symmetry, and $(CH_3)_3PF_2$ (190 cm^{-1})[12] and PCl_3F_2 (122 cm^{-1}),[1] both of D_{3h} symmetry. In PF_5 an assignment made for this vibration (126 cm^{-1})[1] is now believed to be in error.[14a] On the basis of a re-examination of the infrared spectrum of PFi, a low-intensity band ($p = 1$ atm, $l = 12$ cm) appearing at 300.6 cm^{-1} has been suggested for the PF_2 axial bend.[14b]

Considering further assignments, the two most intense lines in the Raman, 435 and 689 cm^{-1} are polarized, thus classifying them as a_1 species. These lines correspond to the 434-cm^{-1} band of moderate intensity and the strong band at 691 cm^{-1}, respectively, in the infrared and are easily classified as ν_4, a PCl stretching vibration, and ν_2, the PF_2 symmetric axial stretch. These bands again are in corresponding regions in related molecules. In PCl_3F_2 (D_{3h} symmetry) the symmetric PCl_3 stretch is at 387 cm^{-1}, in PCl_4F (C_{3v} symmetry), it is at 422 cm^{-1}.[1] The symmetric axial stretch in PCl_3F_2 is at 633 cm^{-1}, in PF_5 it is at 640 cm^{-1}.[1]

The most intense bands in the infrared spectrum appear at 895, 903, and 921 cm^{-1} and are most certainly PF stretching modes. A weak, somewhat broadened band appears at 884 cm^{-1} in the Raman spectrum. These bands would correspond to ν_1, ν_7, and ν_{10} but there is little to suggest the order of assignment since they are close in frequency and intensity although the highest frequency of the three, 921 cm^{-1}, probably is associated with the asymmetric equatorial stretch, ν_7. The band at 895 cm^{-1} is listed as ν_1 since there was a suggestion that the broad band at 884 cm^{-1} was polarized in the Raman. The 903-cm^{-1} band is assigned to ν_{10}.

The intense band in the infrared at 560 cm^{-1}, probably depolarized in the Raman (553 cm^{-1}), is assigned to ν_{11} representing an out-of-plane bending motion. The corresponding vibration in PF_5[1] appears at 576 cm^{-1}, in CH_3PF_4[11] at 538 cm^{-1}. The only other fundamental remaining in the infrared is the strong band at 490 cm^{-1} (490 cm^{-1} in the Raman also) and the suggested assignment is ν_8, an in

TABLE IV

Fundamental frequencies of $PClF_4$.

No.	Mode description	Activity	Species	Assignment
1	PF_2 stretch	R(p); ir	a_1	895
2	PF'_2 stretch			691
3	PF_2 in-plane bend			(510)
4	PCl stretch			434
5	PF'_2 bend			144
6	$PF_2F'_2$ twist	R(dp); ···	a_2	356
7	PF_2 stretch	R(dp); ir	b_1	921
8	$PClF_2$ in-plane bend			(490)
9	PF'_2 bend			144
10	PF'_2 stretch	R(dp); ir	b_2	903
11	$PClF_2$ out-of-plane bend			560
12	$PClF_2F'_2$ rock			356

plane bending vibration. The related frequencies in PF_5[1] and CH_3PF_4[11] are at 533 and 467 cm^{-1}, respectively. However, assignment of the 490-cm^{-1} band to ν_3 is equally likely. The frequencies ν_3 and ν_8 which represent a doubly degenerate e' mode in D_{3h} symmetry are separated by 47 cm^{-1} in CH_3PF_4.[11] An unassigned frequency of very weak intensity appearing as a shoulder in the Raman spectrum at about 510 cm^{-1} may possibly be ν_3. The latter frequency was not detected in the infrared but may be masked by the strong band appearing at 490 cm^{-1}.

In any event the infrared and Raman spectra of $PClF_4$ have been reasonably interpreted in terms of the C_{2v} point group. While interpretation in terms of C_s symmetry is equally plausible, it will not be considered in view of other more convincing evidence against its likelihood discussed below. The frequency assignment and mode description for $PClF_4$ are listed in Table IV.

DISCUSSION

Analysis of the vibrational data show that the most symmetrical structure C_{4v} is inconsistent with the number and activity of the observed fundamentals for $PClF_4$. The C_{3v} symmetry is not as easily ruled out on the latter basis but difficulties are encountered in attempting a vibrational assignment for this case, while analysis in terms of the C_{2v} symmetry is entirely satisfactory. However, the spectral data do not allow a decision to be made between the C_{2v} symmetry and the less likely structure of C_s symmetry.

Comparison of the dipole moment of $PClF_4$ with the values observed for the other phosphorus (V) chlorofluorides shows that the assignment of the C_{2v} symmetry to $PClF_4$ is self-consistent. The value observed for $PClF_4$, 0.78 D, is close to the gas-state value observed[2] for PCl_2F_3 (0.68 D) shown[1,3,15] to be a trigonal bipyramid with the two chlorine atoms located in equatorial positions (C_{2v}). If, as an approximation, α and β (Figure 4) are taken as 120° and 90°, respectively, then vectorially the structures of $PClF_4$ and PCl_2F_3, each of C_{2v} symmetry, amounts to an equatorial P—F opposing an equatorial P—Cl bond dipole. The fact that the dipole moments are only 0.1 D apart supports the contention that they have the same symmetry. Small changes in electronic distribution and degrees of distortion between the two molecules could easily account for the difference.

The dipole moment of the trigonal bipyramidal structure of $PClF_4$ having an axial chlorine atom (C_{3v}) also, vectorially, may be considered in terms of an axial P—Cl opposing an axial P—F bond dipole. Such a consideration has been discussed[2] for PCl_4F where the gas-state dipole moment has been shown[16] to be exceedingly low, 0.21 D. The small value in PCl_4F is attributed primarily to the intrinsic differences in the weaker axial bonds compared to the equatorial bonds.[2] A similar low value might be expected if $PClF_4$ possessed C_{3v} symmetry.

The only pentacoordinated molecule shown to have a tetragonal pyramidal structure is antimony pentaphenyl in the solid state.[17] The structure approximates[17] that formed by starting with a trigonal bipyramid of regular geometry and bending the axial bonds toward one another while simultaneously widening the equatorial angle bisected by the plane in which the axial bonds are moving. The angles F_2—P—F_3 and F_4—P—F_5 (Figure 4) for this model would be 150° and the four adjacent bond angles would approach 94°. However, an estimate of the dipole moment of $PClF_4$ using the latter model is not possible for lack of appropriate dipole-moment values on this structural type.

A pure chlorine nuclear quadrupole measurement has been made on $PClF_4$. A value of 32.14 Mc/sec was obtained at 77°K for the ^{35}Cl isotope and is in the region (31.26 to 32.54 Mc/sec) found[3] for the ^{35}Cl NQR frequencies of equatorial chlorine atoms for the other members of the PCl_nF_{5-n} series. In PCl_4F possessing both equatorial and axial chlorine atoms, the axial ^{35}Cl NQR frequency was 28.99 Mc/sec compared to 32.54 Mc/sec for the equatorial sites.[3] Thus, further supporting evidence is provided by the pure quadrupole measurement that the chlorine atom is located at an equatorial site in $PClF_4$, assuming no change in structure occurs on going to the solid state, of course.

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