Vibrational Spectra of Fluorocarbon–Group V Derivatives. Part II.[†] The Compounds $CF_3{\cdot}PX_2$ where X = Halogen or Hydrogen

By **J. David Brown, Robert C. Dobbie, and Brian P. Straughan,*** Department of Inorganic Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU

The gas-phase i.r. and liquid-phase Raman spectra of the phosphines $CF_3{\cdot}PX_2$ (X = H, F, Cl, Br, or I) have been recorded. The observed bands have been assigned on the basis of C_s symmetry. However, there is substantial mixing of the internal co-ordinates of vibration, and so simple group-frequency correlations cannot be made for all of the bands. The coupling of vibrations is less severe in the case of CF_3PH_2.

SINCE the first preparation of trifluoromethyl derivatives of phosphorus(III) there has been a steady flow of papers describing the synthesis of many compounds with chemical properties quite unlike their hydrocarbon analogues. Despite the availability of several series of related compounds, remarkably few studies of structure or physical properties have been reported. In most cases, analysis of the vibrational spectra has been restricted to the identification of some characteristic i.r. group frequencies, although an early attempt by Beg and Clark [1] to assign the i.r. spectra of some trifluoromethylphosphines deserves mention. More detailed studies of the i.r. and Raman spectra of $CF_3{\cdot}PCl_2$ [2] and of $[(CF_3)_2P]_3N$ [3] have been published and Bürger and Grobe and their co-workers have reported a thorough investigation of the vibrational spectra of compounds $(CF_3)_3M$ where M = P, As, or Sb.[4]

With the advent of the laser as a Raman light source, the difficulties in obtaining sufficient quantities of the compounds for Raman spectroscopy have been overcome. It seemed important to select a simple but fairly extensive series of phosphine derivatives to attempt to assign the fundamental vibrations and to investigate the applicability of the concept of group frequencies. A study of this nature was also required to assist in the assignment of the vibrational spectra of some bridged biphosphine compounds which are being studied in these laboratories. We have accordingly studied the compounds $CF_3{\cdot}PX_2$ and $(CF_3)_2{\cdot}PX$ (where X = F, Cl, Br, I, or H). We now record and discuss the spectra of the phosphines containing one trifluoromethyl group.

RESULTS AND DISCUSSION

If the $-CF_3$ group assumes a symmetrical configuration with respect to the position of the $-PX_2$ group then the molecules will belong to point group C_s and 15 active fundamentals will be allowed. Nine will belong to species a' (R, pol; i.r.) and six are of species a'' (R, dp; i.r.). There are no inactive fundamentals.

Several factors assist in the assignment of the observed bands. In the first place, the assignments are simplified considerably by assuming that the vibrational frequencies for the CF_3 group are in similar positions to those observed in the spectra of the trifluoromethyl halides.[5] This assumption is reasonable based on some approximate force constant calculations for the present series of molecules. Our calculations indicate that considerable mixing of vibrations does occur but the bands which are located for all the compounds in the regions 1129—1222, 740—745, and 520—555 cm^{-1} can be described as essentially CF_3 stretching, CF_3 symmetric deformation, and CF_3 symmetric and antisymmetric deformation modes respectively. A modified valence force field was used and force constants were transferred from PX_3 [6] and CF_3X [5] molecules. The values of the stretching force constant (f_r) and stretch–stretch interaction (f_{rr}) were adjusted (while the ratio $f_r : f_{rr}$ was kept the same as in

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[†] Part I, R. C. Dobbie and B. P. Straughan, *Spectrochim. Acta*, 1971, **27**, *A*, 255.

[1] M. A. A. Beg and H. C. Clark, *Canad. J. Chem.*, 1962, **40**, 393.

[2] J. E. Griffiths, *Spectrochim. Acta*, 1965, **21**, 1135.

[3] P. J. Hendra, R. A. Johns, C. T. S. Miles, C. J. Vear, and A. B. Burg, *Spectrochim. Acta*, 1970, **26**, *A*, 2169.

[4] H. Bürger, J. Cichon, J. Grobe, and F. Hofler, *Spectrochim. Acta*, 1972, **28**, *A*, 1275.

[5] P. R. McGee, F. F. Cleveland, A. G. Meister, and C. E. Decker, *J. Chem. Phys.*, 1953, **21**, 242; R. C. Taylor, *J. Chem. Phys.* 1954, **22**, 714.

[6] K. Kuchitsu, T. Shibata, A. Yokozeki, and C. Matsumura, *Inorg. Chem.*, 1971, **10**, 2587; T. R. Manley and D. A. Williams, *Spectrochim. Acta*, 1965, **21**, 1773.

CF_3X and PX_3) to give frequencies which matched the observed band positions.

Secondly the Raman depolarization ratios for the liquid samples enable one in principle to distinguish between a' and a'' species. However, the mixing which occurs among the lower-frequency fundamentals of the same character species gives rise to some unexpected ratios.

Finally the i.r. spectra in the vapour phase exhibit some well-resolved *PQR* branches for the hydride, fluoride, and chloride molecules. The different contours of these bands can be correlated with changes in the dipole moment along the three principal inertial axes, and hence they assist in the band assignments.

TABLE 1

Observed frequencies and assignments for $CF_3{\cdot}PH_2$

I.r. (gas)		Raman (liquid)			
cm⁻¹	Intensity	cm⁻¹	Intensity	pol.	Assignments
—	—	289	$\frac{1}{2}$	dp	PCF_3 def. a''
—	—	323	$\frac{1}{2}$	?	PCF_3 def. a'
415 *PQR*(17) *	m	419	9	pol	PC str. a'
522	w	527	$\frac{1}{2}$	dp?	$2CF_3$ defs. $a' + a''$
742 *PQR*(17)	mw	741	8	pol	CF_3 def. a'
821 *PQR*(18)	s	823	1	pol	PH_2 def. (+2 × 419) a'
840 *PQR*(22)	s	842	1	dp	PH_2 def. a''
990	w	—	—	—	Combination
1069 *PQR*(17)	ms	1068	$\frac{1}{2}$	pol?	PH_2 def. a'
1150 *PQR*?	vvs	1138	$\frac{1}{2}$	pol?	CF_3 str a'
1175	vvs	—	—	—	CF_3 str a''
1185 *PQR*(17)	vvs	1184	$\frac{1}{2}$	pol?	CF_3 str a'
2280	w	—	—	—	2 × 1150
2325	s	2338	10	pol	PH_2 str a'
2350	sh	2360	sh		PH_2 str a''

* The values in parentheses are the observed *PR* separations in cm⁻¹.

TABLE 2

Observed frequencies and assignments for $CF_3{\cdot}PF_2$

I.r. (gas)		Raman (liquid)			
cm⁻¹	Intensity	cm⁻¹	Intensity	pol	Assignments
—	—	197	1	dp	PF_2 twist + CF_3 rock
—	—	282	6	pol	PF_2 def. a'
—	—	324	1	dp?	PC str + CF_3 rock + PF_2 twist
389 *PQR*(12) *	s	387	6	pol	PF_2 def. a'
463 *PQR*(11)	s	460	2	pol?	PC str + CF_3 rock + PF_2 twist
555 *PQR*(11)	s	555	1br		2 × 282 + CF_3 def. a''
561 *PQR*(16)	s				CF_3 def. a''
590	w				
744 *PQR*(12)	w	745	10	pol	CF_3 def. a'
848sh	w	850	3sh	dp?	PF_2 str a''
864 *PQR*(11)	s	861	3	pol	PF_2 str a'
1160	vvs	1153	$\frac{1}{2}$		CF_3 str a'
1170sh		1166	$\frac{1}{2}$		CF_3 str a''
1222	vvs	1222	$\frac{1}{2}$		CF_3 str a'
1280sh		—			
1300	m	—			

* The values in parentheses are the observed *PR* separations in cm⁻¹.

The observed data and suggested assignments for the five compounds are in Tables 1—5. The Figure is a line diagram which summarizes all the Raman data and also illustrates the trends in vibrational frequencies. Only the more interesting and unusual features of the spectra concerned with the C–PX_2 skeleton will now be discussed in detail.

TABLE 3

Observed frequencies and assignments for $CF_3{\cdot}PCl_2$

I.r. (gas)		Raman (liquid)			
cm⁻¹	Intensity	cm⁻¹	Intensity	pol	Assignment
—	—	135	3	dp }	PCl_2 twist a''
—	—	160	4	dp }	CF_3 rock a''
—	—	203	4	pol	PCl_2 def. a'
—	—	246	$\frac{1}{2}$		PC str + CF_3 rock a'
—	—	295	10	pol	PCl_2 def. a'
—	—	390	$\frac{1}{2}$		
428 *PQR*(14) *	s	424	3	pol	PC str + CF_3 rock a'
470	vw	—	—		
517	sh	515	7	pol	PCl_2 str a'
527 *PQR*(11)	s	524	sh		PCl_2 str a''
545 *PQR*(12)		548	4	pol	$2CF_3$ def. $a' + a''$
—	—	592	$\frac{1}{2}$		2 × 295 = 590
720	w	720	$\frac{1}{2}$		203 + 515 = 718
745 *PQR*(10)	w	742	4	pol	CF_3 def. a'
1006	vw				
1030	vw				2 × 515 = 1030
1100	vw				2 × 548 = 1096
1151	vs	1143	$\frac{1}{2}$		CF_3 str } $a' + a''$
1175	m	1165	sh		CF_3 str }
1200 *PQR*(11)	vs	1195	$\frac{1}{2}$		CF_3 str a'

* The values in parentheses are observed *PR* separations in cm⁻¹.

TABLE 4

Observed frequencies and assignments for $CF_3{\cdot}PBr_2$

I.r. (gas)		Raman (liquid)			
cm⁻¹	Intensity	cm⁻¹	Intensity	pol	Assignment
—	—	109sh	5	dp }	CF_3 rock a'' +
—	—	116	9	dp }	PBr_2 twist a''
—	—	151	6	pol	PBr_2 def. a'
—	—	248	$\frac{1}{2}$		PC str + CF_3 rock a'
—	—	260	10	pol	PBr_2 def. a'
388	m	385	$\frac{1}{2}$		PC str + CF_3 rock a'
424	m	421	9	pol	PBr_2 str a'
438	m	434	2		PBr_2 str a''
524	w	523	3	dp?	CF_3 def. a'' + 2 × 260
540	m	543	$\frac{1}{2}$		CF_3 def. a'
743 *PQR*(10) *	m	741	3	pol	CF_3 def. a'
864	w	—	—		
1004	w	—	—		
1028	w	—	—		
1085	mw	—	—		
1110	m	—	—		
1142	vs	1131	$\frac{1}{2}$		CF_3 str } $a' + a''$
1160	sh	1156	sh		CF_3 str }
1190 *PQR*(10)	vs	1184	$\frac{1}{2}$		CF_3 str a'
1240	w	—	—		
1284	w	—	—		

* The values in parentheses are the observed *PR* separations in cm⁻¹.

$CF_3{\cdot}PH_2$.—Our data and assignments are in good agreement with those of Bürger and his co-workers [7] (see Table 1). Two $-PH_2$ stretching vibrations are observed

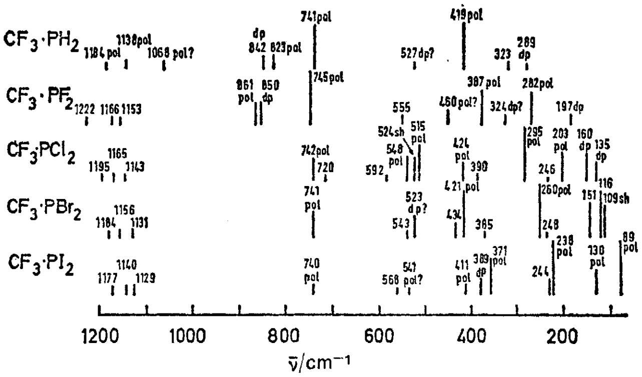
[7] H. Bürger, J. Cichon, R. Demuth, and J. Grobe, personal communication.

in the i.r. spectrum at 2325 (a') and 2350 (a'') cm^{-1}. The spectrum in this region is complicated by the presence of a CF overtone ($2 \times 1150 = 2300$ cm^{-1}) but the situation is clarified by the Raman spectrum which resolves the $-PH_2$ antisymmetric stretch more easily, while the CF overtone is too weak to be observed. The three $-PH_2$ deformation modes are clearly observed in both the i.r. and Raman spectra at 1069, 840, and 821 cm^{-1}. The gas-phase i.r. spectrum shows prominent *PQR* structure for all three bands and the *PR* separations are consistent with the assignment of the 821 and 1069 cm^{-1} absorptions to parallel bands of a near symmetric top while 840 cm^{-1} must represent a perpendicular type band. *PR* separations have been calculated [8] by use of accurate values of the molecular dimensions found by microwave spectroscopy,[9] giving a value of 14 cm^{-1} for the parallel bands and 21 cm^{-1} for the perpendicular bands, in reasonable agreement with the observed values.

TABLE 5

Observed frequencies and assignments for $CF_3{\cdot}PI_2$

I.r. (gas)		Raman (liquid)			
cm^{-1}	Intensity	cm^{-1}	Intensity	pol	Assignments
—	—	89	10	pol	PI_2 def. a'
—	—	130	3	pol	CF_3 rock
—	—	238	10	pol	PI_2 def. a'
—	—	244	sh		CF_3 rock
—	—	371	6	pol	PI_2 str a'
395	vs	389	2	dp	PI_2 str a''
410	s	411	1	pol	PC str a'
—	—	541	$\frac{1}{2}$		CF_3 def. } $a' + a''$
—	—	568	$\frac{1}{2}$		CF_3 def.
740	mw	740	1	pol	CF_3 def. a'
1129	vvs	—	—		CF_3 str a'
1140	vvs	—	—		CF_3 str a''
1151	sh	—			
1177	vvs				CF_3 str a'



Raman spectra, showing positions and intensities, for the series $CF_3{\cdot}PX_2$

The most difficult modes to assign in all of the spectra are the P–C stretching (a') and the two $-CF_3$ rocking modes ($a' + a''$). Force-constant calculations indicate that considerable mixing of the internal co-ordinates of vibration occurs, especially with those of the appropriate symmetry involving the bending of the PX_2 group. The assignments are most clear-cut for the hydride where an essentially P–C stretching mode is observed as a strong polarized band at 419 cm^{-1} and the two rocking modes lie below this position at 323 (a') and 289 (a'') cm^{-1}. Thus one can satisfactorily account for all of the fundamentals except the torsional mode, which is expected to be weak in both the i.r. and Raman spectra.

$CF_3{\cdot}PF_2$.—The frequencies and assignments for this compound are in Table 2. The $-PF_2$ stretching vibrations are easily discernible in the i.r. spectrum as a strong absorption feature centred on 846 cm^{-1}, which partially resolves into two overlapping *PQR* contours. The Raman spectrum of the pure liquid establishes the presence of two modes at 861 (pol) and 850 (dp) cm^{-1}.

The spectrum below 500 cm^{-1} can be interpreted in terms of localised group frequencies. However our force-constant calculations indicate that the low-frequency bending modes involve significant motions of all the atoms in the molecule and so the use of group labels is an oversimplification. We have indicated this situation in Table 2 as appropriate.

$CF_3{\cdot}PF_2$ and the other halides studied exhibit several i.r. bands with prominent *PQR* contours which could be useful aids to assignment but unfortunately the accurate geometry of the molecules is unknown.

$CF_3{\cdot}PCl_2$.—The assignments are listed in Table 3 and they follow a familiar pattern down to *ca.* 530 cm^{-1}. The results are also in good agreement with the work of Griffiths.[2] The $-PCl_2$ stretching modes are observed at 524 (a') and 515 (a'') cm^{-1} and below this frequency one expects to observe the P–C stretching vibration. However, the latter mode is particularly affected by mixing and cannot be assigned to one frequency. There are five fundamental modes ($3a' + 2a''$) to be allocated to the five Raman bands below 300 cm^{-1}. We have assigned the two strongly polarized bands at 295 and 203 cm^{-1} to essentially $-PCl_2$ symmetric bending motions but the other low-frequency modes are highly coupled (see Table 3).

$CF_3{\cdot}PBr_2$ and $CF_3{\cdot}PI_2$.—Tables 4 and 5 list the observed vibrational data and suggested assignments. The bands above 450 cm^{-1} can be assigned by analogy with the previous compounds but the low-frequency Raman spectra reveal several very intense bands for both compounds. The intensity of the low-frequency bands is not unexpected since modes involving the highly polarizable bromine and iodine atoms will give rise to strong Raman lines in this region. In addition to the two $-PX_2$ stretching modes, group theory predicts that three $-PX_2$ deformation fundamentals will be both i.r.- and Raman-active and these can be readily located by their high intensity. However, the CF_3 rocking modes *etc.*, which are also expected to lie in this low region by analogy with the $CF_3{\cdot}PH_2$ and $CF_3{\cdot}PF_2$ compounds, apparently exhibit unusually intense Raman bands, *e.g.*, at 244 cm^{-1} in $CF_3{\cdot}PI_2$ and at 109 and 248 cm^{-1} in $CF_3{\cdot}PBr_2$. The enhanced intensities become obvious if one compares the intensity of the CF_3 symmetric deformation mode at *ca.* 740 cm^{-1} for the five compounds under investigation.

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[8] W. A. Seth Paul and G. Dijkstra, *Spectrochim. Acta*, 1967, **23**, *A*, 2861.

[9] I. M. Y. Wang, C. O. Britt., A. H. Cowley, and J. E. Boggs, *J. Chem. Phys.*, 1968, **48**, 812.

With the same instrument conditions and allowance for the slight variation in sample volume, the intensity at *ca.* 740 cm^{-1} does not alter significantly over this whole series, while the bands which might be considered as $-CF_3$ rocking modes gain appreciably in intensity. This observation strongly suggests that the internal co-ordinates of the P–C stretching and CF_3 rocking modes are mixed with the phosphorus–halogen deformation fundamentals and the involvement of the polarizable halogen atoms leads to the overall enhancement of intensities for the Raman bands below 450 cm^{-1}.

The trend of $-PX_2$ bending frequencies (see Figure), and also approximate calculations, make it likely that the $-PI_2$ twisting mode (a'') remains unobserved in the Raman spectrum. This band is expected to occur at *ca.* 50 cm^{-1} but could not be detected, presumably owing to the proximity to the exciting line.

EXPERIMENTAL

Di-iodotrifluoromethylphosphine was prepared by heating a mixture of CF_3I, iodine, and red phosphorus in a sealed tube.[10] The other halogeno-compounds were obtained from $CF_3{\cdot}PI_2$ by exchange reactions,[10,11] and $CF_3{\cdot}PH_2$ by the action of anhydrous hydrogen iodide and mercury.[12] The compounds were purified by careful vacuum fractionation and their identity confirmed by molecular-weight and vapour-pressure measurements and in some cases by ^{19}F n.m.r. spectroscopy. I.r. spectra of gaseous samples were recorded on Perkin-Elmer model 125 and 457 spectrometers in 10 cm glass cells fitted with appropriate alkali-metal halide windows. Raman spectra of liquid samples, contained under pressure in sealed glass capillary tubes, were obtained on a modified Cary model 81 spectrometer, with a Coherent Radiation model 52 krypton ion gas laser as the radiation source. The samples were examined with both 6471 and 5320 Å radiation.

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[11] V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii, *Zhur. obshchei Khim.*, 1959, **29**, 3957; A. B. Burg and J. E. Griffiths, *J. Amer. Chem. Soc.*, 1960, **82**, 3514.

[12] R. G. Cavell and R. C. Dobbie, *J. Chem. Soc. (A)*, 1967, 1308.