Vibrational Spectra of Fluorocarbon–Group V derivatives. Part III.[1] The Compounds $(CF_3)_2PX$ where X = Halogen or Hydrogen

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The gas phase i.r. and liquid phase Raman spectra of the phosphines $(CF_3)_2PX$ (X = H, F, Cl, Br, I) have been recorded, and the observed fundamentals assigned on the basis of C_s symmetry. Coupling of the vibrational modes of the same symmetry class has been noted.

ALTHOUGH trifluoromethyl-substituted phosphines have been known for some time, thorough investigation of their vibrational spectra has begun only recently. The spectra of the compounds CF_3EH_2,[2] $(CF_3)_2EH$ (E = P or As; X = H or D),[3] and $(CF_3)_3E$ (E = P, As, or Sb)[4] have been recorded and analysed in detail, the assignments being supported by force-constant calculations. Evidence has been obtained[5] from vibrational spectroscopy for the existence of the diphosphine, $(CF_3)_2P\cdot P(CF_3)_2$, and diarsine, $(CF_3)_2As\cdot As(CF_3)_2$, in the *trans*-conformation in the gaseous and liquid phases. In a previous paper of this series, the i.r. and Raman spectra of the compounds CF_3PX_2 (X = H, F, Cl, Br, or I) were reported[1] and the validity of the concept of group frequencies was discussed. In this paper the gas and liquid phase spectra of the related series of compounds $(CF_3)_2PX$ (X = H, F, Cl, Br, or I) are presented for the first time and assignments are proposed for the observed bands based on the C_s point group. The results described in Part II[1] and here were required for the study[6] of the more complex spectra obtained for a series of bisphosphine derivatives containing two $P(CF_3)_2$ groups.

RESULTS AND DISCUSSION

If the $-CF_3$ groups assume a symmetrical configuration with respect to the position of the P– halogen group then the molecules will belong to point group C_s and 24 active fundamentals will be allowed. Thirteen will belong to species a' (R, pol; i.r.) and eleven are of species a'' (R, dp; i.r.).† There are no inactive fundamentals.

The assignment of the observed spectra is simplified by assuming that the vibrational frequencies for the $-CF_3$ groups are in similar positions to those observed in the spectra of the trifluoromethyl halides[7] and CF_3PX_2 compounds[1] where X = halogen or hydrogen. That this assumption is reasonable follows from some approximate force constant calculations for the present series of molecules, using a modified valence force field as described.[1] Considerable mixing of the internal coordinates of vibration is prevalent in the low-frequency modes but our calculations show that the bands located for all the compounds in the regions 1115—1228, 715—752, and 524—582 cm^{-1} can be described as essentially CF_3 stretching, CF_3 symmetric deformation, and CF_3 antisymmetric deformation modes respectively, in agreement with the results of similar calculations for $(CF_3)_2PH$ carried out by others.[3]

The observed data for the five compounds and proposed assignments, excluding the two allowed torsional modes, are given in the Table. Only the more interesting or unusual features of the spectra will be discussed in detail. Many of the very weak features could be assigned to specific overtones or combination bands when a good numerical fit could be obtained. There is no other basis for these particular assignments.

Bis(trifluoromethyl)phosphine, $(CF_3)_2PH$.—Our data and assignments are in good agreement with those of

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† R = Raman-active, i.r. = i.r.-active, pol = polarized, dp = depolarized.

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[3] H. Bürger, J. Cichon, J. Grobe, and F. Höfler, *Spectrochim. Acta*, 1973, **29A**, 47.

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[5] H. Bürger, J. Cichon, R. Demuth, J. Grobe, and F. Höfler, *Z. anorg. Chem.*, 1973, **396**, 199.

[6] R. C. Dobbie, M. J. Hopkinson, and B. P. Straughan, unpublished work.

[7] 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.

Bürger and co-workers.[3] As in the case of CF_3PH_2, the i.r. spectrum is complicated in the P–H stretching region by the presence of several weak overtone and combination bands (see Table). The assignment is clear from the Raman spectrum because the overtone and combination bands are too weak to be observed and the spectrum exhibits a single polarized line at 2358 cm^{-1}. The two P–H deformation modes are clearly resolved in both spectra at 812 and 856 cm^{-1}. The Raman depolarization ratios leave no doubt that the lower frequency band is due to the symmetric deformation and it is interesting to note that the relative positions of these two bands reverse for the halides (see Figure). The remainder of the vibrational spectrum must be due to the $(CF_3)_2P$ skeleton and despite the mixing possibilities discussed earlier, it is clear from the Figure that the positions of these modes are not substantially altered when the hydrogen atom is replaced by a halogen.

Bis(trifluoromethyl)fluorophosphine, $(CF_3)_2PF$.—The P–F symmetric stretching vibration is easily assigned to the very strong i.r. band at 850 cm^{-1} and the corresponding line in the Raman spectrum is polarized as expected. The in-plane and out-of-plane deformation modes can be readily located by comparing the spectra of $(CF_3)_2PF$ and $(CF_3)_2PH$ (see Figure). The symmetric deformation of the fluoride lies very close to the P–C stretch at 455 cm^{-1} but a distinct shoulder can be resolved in the Raman spectrum at 463 cm^{-1}. The remainder of the spectrum has been interpreted in terms of skeletal modes.

Bis(trifluoromethyl)chlorophosphine, $(CF_3)_2PCl$.—The proposed assignments for the molecule are given in the Table. The band positions follow the expected pattern except for the region 500—600 cm^{-1} where two very strong i.r. bands are observed at 533 and 566 cm^{-1} and strong Raman lines lie at 532 (pol) and 570 (pol) cm^{-1}. In addition, the Raman spectrum exhibits weak shoulders at 559 and 582 cm^{-1}. The two shoulders, which are masked in the i.r. spectrum by the presence of the other two bands, can be assigned satisfactorily to the CF_3 antisymmetric deformation modes, since the latter appear in approximately these positions as weak features in the spectra of the other four compounds. The only other vibration expected for this region is the P–Cl symmetric stretch. While this vibration undoubtedly accounts for one of the strong bands discussed, the origin of the other is not so obvious. The Figure shows that the two bands appear only in chloride compound and the bands are too strong to be explained in terms of an impurity. The separation of the bands (48 cm^{-1}) is much too large for a chlorine isotope effect and so the most likely explanation seems to be a Fermi resonance interaction between the P–Cl symmetric stretch (*ca.* 550 cm^{-1}) and the first overtone of the fundamental which lies at 277 cm^{-1}. The first overtone would belong to character species *a*′ and hence could undergo intensity enhancement at the expense of the totally symmetric P–Cl stretch. The two vibrational levels would repel one another and the two strong bands at 532 and 570 cm^{-1} would result. We have

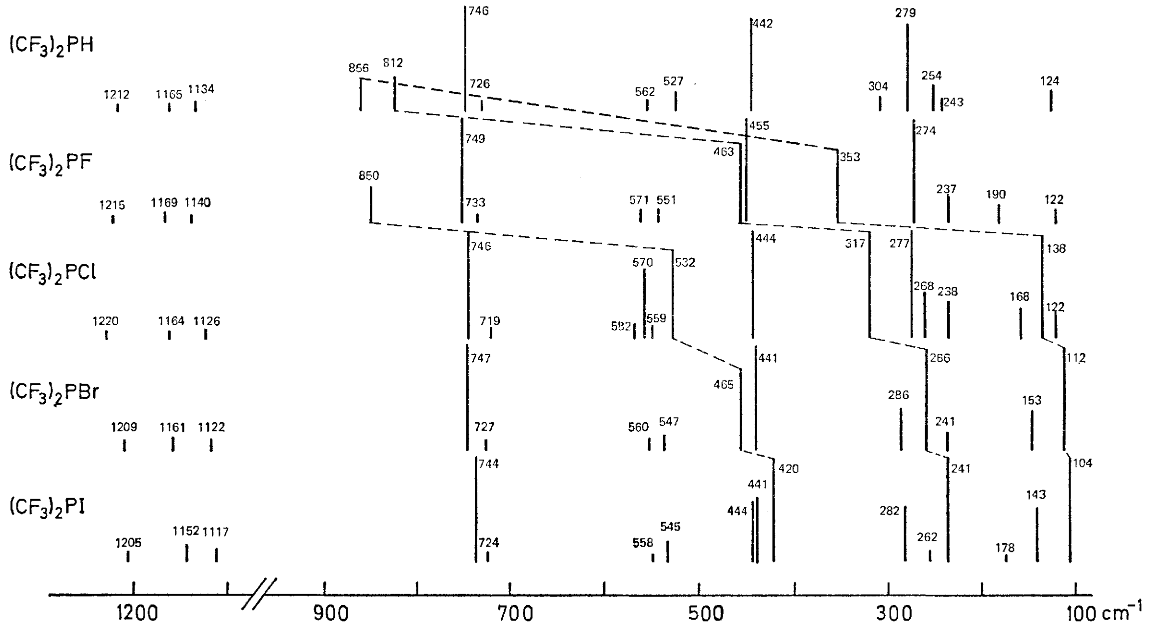
Observed frequencies and assignments for the compounds $(CF_3)_2PX$ where X = H, F, Cl, Br or I

$(CF_3)_2PH$		$(CF_3)_2PF$		$(CF_3)_2PCl$		$(CF_3)_2PBr$		$(CF_3)_2PI$		
I.r. (gas)	Raman (liquid)	I.r. (gas)	Raman (liquid)	I.r. (gas)	Raman (liquid)	I.r. (gas)	Raman (liquid)	I.r. (gas)	Raman (liquid)	Assignments
	124dp		122		122dp?					CF_3 asym rocks + PC_2 def. (2*a*″ + *a*′)
	243		190		168pol?		153pol?		143pol	
ca. 250w	254dp		237dp		238dp		241dp			
					268sh				262dp	
	279pol		274pol	275w[a]	277pol[a]		266pol[c]		282pol	CF_3 rock (*a*′)
							286dp			CF_3 rock (*a*″)
ca. 300w	304									CF_3 rock (*a*′)
440vs	442pol	455vs	455pol	444vs	444pol	441s	441pol	440vs	441 444 dp?	PC_2 strs. (*a*′ + *a*″)
524m	527dp	541w	551dp		559		547dp	545m	545dp	CF_3 def. (*a*″)
				566vs[b]	570pol[b]					PCl str (*a*″) + 2 × 277
561m	562dp	568m	571dp		582	558	560dp	561m	558dp	CF_3 def. (*a*″)
715w	726	727vw	733	717w	719	722w	727	718w	724	CF_3 def. (*a*″)
749vs[d]	746pol	752w[d]	749pol	750m[d]	746pol	748vs	747pol	746s[d]	744pol	CF_3 def. (*a*′)
809vs	812pol		463	318w[a]	317pol[a]		266pol[c]		241pol	PX def. (*a*′)
855vs	856dp		353dp		138dp		112dp		104dp	PX def. (*a*″)
1124 1128 vvs	1134	1132 1136 vvs		1134 1139 vvs	1126	1120msh		1120ssh	1117	CF_3 strs. (3*a*′ + 3*a*″)
1137 1143 vvs		1144 1149 vvs	1140			1136vvs	1122	1134vvs	1129	
1177vvs	*ca.* 1165	1177vvs	1169	1170vvs	1164	1164vvs	1161	1164vvs	1152	
1209vvs	1212	1203m		1194s		1206vvs	1209	1206vvs	1205	
		1228vvs	1215	1216vvs	1220					
2360s	2358pol	850vs	850pol	533vs[b]	532pol[b]	466s	465pol	419vs	420pol	PX str. (*a*′)

[a] Strong mixing of the internal co-ordinates takes place. [b] Fermi-resonance interaction occurs, see text. [c] These two fundamentals are considered to be coincident. [d] These fundamentals exhibit *PQR* structures centred on the reported values.

The i.r. spectra of the compounds exhibit additional features which may be assigned to overtone or combination bands. The positions of these bands are as follows: $(CF_3)_2PH$ 500vwsh, 1270vw, 1338vw, 2262m, 2297w, 2387w, 2419w; $(CF_3)_2PF$ 509vw, 692vw, 810wsh, 905vw, 980w, 1026vw; $(CF_3)_2PCl$ 680vvw, 1090s, 1275s, 1300ssh, 1315msh; $(CF_3)_2PBr$ 702vw, 858vvw, 880vvw, 984vvw, 1025vvw, 1187wsh, 1254w, 1278w, 1290w, 1382wbr; $(CF_3)_2PI$ 474sh, 658vw, 679vw, 839vw, 881vw, 981vw, 1024w, 1090msh, 1186msh, 1254vw, 1274vw, 1287vw, 1300vw cm^{-1}.

assigned the band at 277 cm^{-1} to a mixed mode involving the internal co-ordinates of the P–Cl symmetric deformation and the symmetric CF_3 rock. Both these vibrations are expected to occur at approximately this frequency and both modes belong to character species *a'*. Finally the antisymmetric P–Cl deformation can be assigned to the strong depolarized Raman line at 138 cm^{-1}.



Raman spectra (positions and intensities) for the series $(CF_3)_2PX$

Bis(trifluoromethyl)bromophosphine, $(CF_3)_2PBr$ *and Bis(trifluoromethyl)iodophosphine,* $(CF_3)_2PI$.—The Table lists the observed vibrational data and proposed assignments for the bromide and iodide compounds. The bands above 500 cm^{-1} can be assigned by analogy with the hydride and fluoride compounds. The low-frequency Raman spectra for both compounds exhibit three intense bands due to motions of the highly polarizable halogen atoms and the resulting frequency trends can be seen in the Figure. The remaining prominent bands in the spectra can be easily accounted for in terms of $(CF_3)_2P$– skeletal modes.

EXPERIMENTAL

Iodobis(trifluoromethyl)phosphine was prepared by the direct reaction of CF_3I, iodine, and red phosphorus.[8] The other halogenophosphines were obtained from $(CF_3)_2PI$ by exchange reactions, and $(CF_3)_2PH$ by the action of anhydrous hydrogen iodide and mercury.[9] The purity of the samples was checked by molecular weight and vapour pressure measurements and by ^{19}F n.m.r. spectroscopy; no significant impurities were detected. I.r. spectra of gaseous samples were recorded on Perkin-Elmer 125 (4000—400 cm^{-1}) and 457 (400—250 cm^{-1}) spectrometers in 10 cm cells. Raman spectra of liquid samples, sealed in glass capillaries, were obtained on a modified Cary 81 spectrometer, using a Coherent Radiation 52 krypton ion gas laser as the radiation source. The samples were examined with both 6471 and 5320 Å radiation.

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