Preparation and Characterization of Tetrafluorophosphonium(V) Hexadecafluorotriantimonate(V), $[PF_4][Sb_3F_{16}]$, the Adduct Arsenic Pentafluoride–Trifluorophosphine (1/1), and the Redox Reactions of Trifluorophosphine with Arsenic, Antimony, and Bismuth Pentafluoride

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Phosphorus pentafluoride and SbF_5 form a 1 : 3 adduct the vibrational spectrum of which is consistent with the formulation $[PF_4][Sb_3F_{16}]$. The 1 : 1 donor–acceptor adduct formed at −130 °C between PF_3 and AsF_5 has been characterized by Raman spectroscopy. The adduct is in equilibrium with its dissociated components between −130 and −78 °C; however, a redox reaction occurs at $\geqslant -78$ °C. Phosphorus trifluoride also undergoes redox reactions with antimony and bismuth pentafluorides.

COMPLEXES between phosphorus trifluoride and transition metals are well known;[1-3] PF_3 also forms weak complexes with strong main-group[2] Lewis acids, *e.g.* $PF_3{\cdot}BH_3$,[2,4] $PF_3{\cdot}B(BF_2)_3$,[5] and $PF_3{\cdot}AlCl_3$.[6]

Various two-co-ordinate phosphorus cations have been reported.[7-10] Thomas *et al.*[11] have prepared salts of $[P(NMe_2)_2]^+$ and $[PCl(NMe_2)]^+$, but attempts to identify $[PF(NMe_2)]^+$ and $[PF_2]^+$ were not successful. However, other workers[12] reported that $PF_3{\cdot}AsF_5$ and $PF_3{\cdot}SbF_5$ were stable at −78 °C and room temperature, respectively, and these adducts were formulated as $[PF_2][AsF_6]$ and $[PF_2][SbF_6]$, with cation–anion interaction, on the basis of their vibrational spectra. The latter systems have been reinvestigated and the results are presented below.

In an attempt to determine the nature of the solid produced in the reaction of PF_3 with SbF_5, PF_5 was found to react with SbF_5 to form a 1 : 3 adduct formulated as $[PF_4][Sb_3F_{16}]$. Phosphorus pentafluoride's ability to act as a fluoride-ion acceptor is well known;[13] however, since its discovery by Thorpe[14] in 1875 there have been no reports of it acting as a Lewis base. A preliminary account of part of this work has been reported.[15]

EXPERIMENTAL

Reagents and Apparatus.—Unless otherwise stated, apparatus and materials and techniques were as given in refs. 16—18, and starting materials purified and characterized by routine methods. Raman spectra were obtained using a Spex Ramalab RS2 spectrometer with the green 5 145 Å exciting line and a slit width of 4 cm^{-1}, unless otherwise specified. Low-temperature Raman spectra were recorded using a variable-temperature assembly. The interior of the non-silvered Dewar was first cooled to at least −100 °C, and then the sample, at −196 °C, was quickly introduced.

Reaction of PF_3 *with* AsF_5 *at* −78 °C.—Phosphorus trifluoride and AsF_5 (50 cm^3, 2 atm) † were condensed separately into a Kel-F vessel, and warmed to −78 °C. In 30 min the vapour pressure was 1 atm in 60 cm^3, and the volatiles were PF_5, PF_3, and AsF_5. In a series of separate experiments, double the amounts of PF_3 and AsF_5 were allowed to react for 7 min, 1, 6.75, and 9.25 h, at −78 °C. Volatiles at −78 °C were removed and the AsF_3 residue identified. The reduction of AsF_5 to AsF_3 was found to be 70, 80, 94, and 100%, respectively, based on the weight of PF_3 added and AsF_3 produced.

The reaction was also followed by ^{19}F n.m.r. spectroscopy in SO_2F_2 and SO_2ClF solvents. A redox reaction was observed to proceed at −60 to −55 °C, after 0.5 h, and increased with time.

Gas-phase Reaction between PF_3 *and* AsF_5 *at Room Temperature.*—Phosphorus trifluoride (0.17 atm in the volume of the line and i.r. cell) was condensed and isolated in the side arm of the i.r. cell. An equal amount of AsF_5 was introduced into the cell, and its spectrum taken. The valve separating the AsF_5 and PF_3 was opened. The spectrum of the reaction products was immediately taken and showed the presence of PF_3, AsF_5, PF_5, and AsF_3. The conversion was *ca.* 50, 95, and 100% in 7 min, 1, and 3 h, respectively based on calibration of the i.r. absorption intensity of PF_5 at known concentrations.

Preparation of Raman Samples of PF_3–AsF_5.—The samples were prepared by condensing pre-weighed stoicheiometric amounts of PF_3 and AsF_5 into sample tubes which were flame-sealed under vacuum. The components were mixed by warming gradually from −196 to −78 °C (briefly), with mixing. The sample was then stored at −196 °C. The compound was a solid at −130 °C and a solid–liquid mixture at −78 °C.

Reaction of PF_3 *with* SbF_5.—In a typical reaction, PF_3 (0.26 g) was condensed onto SbF_5 (1 g) in a Kel-F tube. In 1 h the vapour pressure had decreased from 760 to 645 mmHg at room temperature in a volume of 63 cm^3. The compounds PF_3 and PF_5 were present in the gas phase and the relative amount of the latter increased with time. After 2 d the volatiles (700 mmHg) were removed by pumping for 10 min. The white solid left had a weight decrease of 6% relative to that of SbF_5 added, and only had a broad intense i.r. absorption at 500—700 cm^{-1} in the Sb–F stretching region.

Reaction between PF_3 *and* SbF_5 *in* SO_2F_2 *at* −45 °C.—Phosphorus trifluoride (1.68 g) was condensed onto a mixture of SbF_5 (4.87 g) and SO_2F_2 (9.24 g), then the mixture was kept at −45 °C for 3 d. The volatiles at −45 °C (PF_3, SO_2F_2) were distilled off leaving a white paste which had a weight increase of 0.18 g relative to SbF_5 added and had some vapour pressure at room temperature. The volatiles contained PF_5 and SO_2F_2, but no PF_3. The i.r. spectrum of the white paste had a weak absorption at

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† Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

1 160 cm^{-1}, indicating formation of $[PF_4][Sb_3F_{16}]$ (see below), and a very intense peak in the Sb–F stretching region.

Reaction between PF_3 *and* SbF_5 *in* WF_6.—Phosphorus trifluoride (0.25 g) was condensed onto a mixture of SbF_5 (4.87 g) and WF_6 (7.89 g) and stirred at room temperature. The volatile contained PF_5 and WF_6, but no PF_3 after 18 h. The sample was evacuated to constant weight. A Raman spectrum of the white solid residue (1.13 g corresponding to $SbF_3 : SbF_5 = 1.0 : 1.0$) showed peaks in the Raman corresponding to $SbF_3{\cdot}SbF_5$ (form A) of Gillespie *et al.*[19,20]

Attempted Identification of $PF_3{\cdot}SbF_5$ *by Raman Spectroscopy*.—Phosphorus trifluoride (0.06 g) was condensed onto SbF_5 (0.63 g) in the form of a thin film on the wall of the sample tube, and flame-sealed. The Raman spectrum taken at room temperature, 10 min after the sample was removed from liquid N_2, showed peaks attributable to $[PF_4][Sb_3F_{16}]$ a small amount of SbF_5, and probably $SbF_3(SbF_5)_x$.[19-23]

Vapour Pressure of $[PF_4][Sb_3F_{16}]$.—The vapour pressure above $[PF_4][Sb_3F_{16}]$ was measured using a Validyne AP10 pressure gauge with 0—100 and 0—1 000 mmHg transducers calibrated for direct read out from a model CD transducer indicator. Pressures were obtained as the temperature was increased. The data for 0—23 °C were fitted by least squares yielding equation (1). The measured

$$\log_{10}(P/\text{mmHg}) = 11.4 - (2\,740/T) \qquad (1)$$

pressures were, for example, 139 ± 2, 24 ± 1, and 16 ± 1 mmHg at 23, 0.1, and -23 °C, respectively. The experiment was repeated and the same results obtained within experimental error.

Attempted Preparations of Adducts PF_5–BiF_5, –NbF_5, *and* –TaF_5, *and* AsF_5–SbF_5 *and* –BiF_5.—The systems PF_5–BiF_5, –NbF_5, –TaF_5, AsF_5–SbF_5, and AsF_5–BiF_5 were similarly investigated. The vapour pressure was constant during the reaction, and the products were found to be the same as the starting materials.

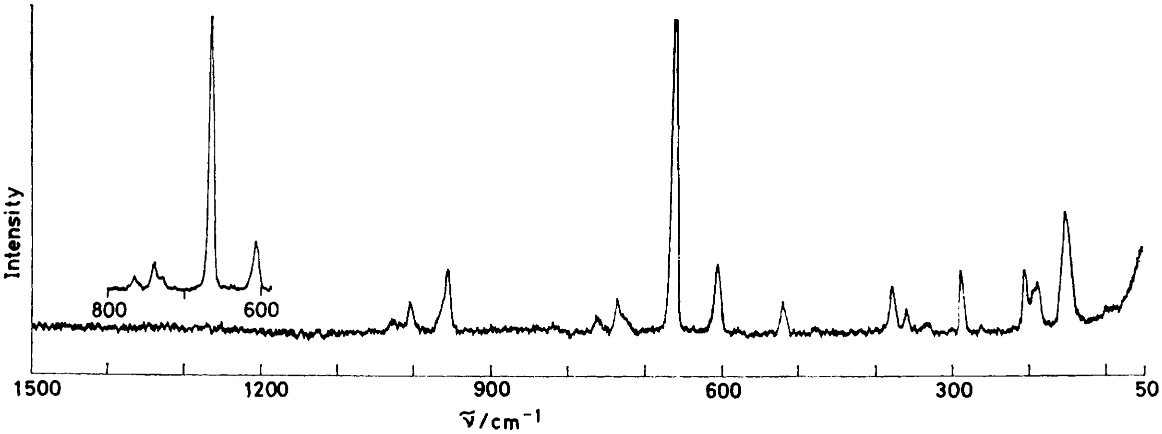

FIGURE 1 Raman spectra of solid $PF_3{\cdot}AsF_5$ at *ca.* -162 °C

A Raman spectrum of $PF_3 : SbF_5 = 3.4 : 1$, taken at -135 °C after standing at -45 °C for 8 d, showed peaks attributed to the starting material, as did that of $PF_3 : SbF_5 : SO_2F_2 = 2.5 : 3 : 1$ held at -45 °C for 8 d.

Reaction of PF_3 *with* BiF_5.—In a typical experiment, PF_3 (1.07 g) was condensed onto BiF_5 (1.55 g) in a Monel vessel. The vapour pressure remained constant and after 3 d the volatiles contained only PF_3. The reaction vessel was then heated for 5 d at 80 °C with the upper part of the vessel cooled with air. The gaseous product contained PF_5 and PF_3. Volatiles were removed leaving BiF_3 (1.37 g).

Preparation of $[PF_4][Sb_3F_{16}]$.—In a typical experiment PF_5 (3.62 g, 28.74 mmol) was condensed onto SbF_5 (4.65 g, 21.45 mmol) in a Pyrex glass bulb (60 cm^3). The mixture was repeatedly thermally cycled between room temperature and -196 °C. After 2.5 d the excess of PF_5 was removed by pumping, with the reactor held at -78 °C. The weight of solid (5.62 g) corresponded to the formation of an adduct with mol ratio $PF_5 : SbF_5 = 1 : 2.8$, assuming the weight increase was the amount of PF_5 consumed. The compounds PF_5 and SbF_5 were separated by fractional distillation in a closed system recovering 6.70 mmol of PF_5 and 21.70 mmol of SbF_5. The experiment was repeated ten times with various ratios of starting materials (PF_5 always in excess) including one carried out in a Parr bomb (50 cm^3; SbF_5, 5.38 g; PF_5, 38.44 g). Adducts of $PF_5 : SbF_5$ ratio *ca.* 1 : 3 were obtained in all cases.

Preparation of Raman Samples of PF_5–SbF_5.—A Raman sample of $[PF_4][Sb_3F_{16}]$ was prepared *in situ* as above. The weight of the sample corresponded to $PF_5 : SbF_5 = 1 : 2.9$. The Raman spectrum was recorded on a Cary model 82 spectrometer.

The polarization measurements were obtained from a sample of ratio $PF_5 : SbF_5 = 1 : 8$ which was prepared by condensing the stoicheiometric amounts into a sample tube. A homogeneous liquid sample was obtained by gentle heating. A sample of $SOF_4{\cdot}3SbF_5$ was similarly prepared, and Raman spectra obtained using a Spex 1400 spectrometer.

RESULTS AND DISCUSSION

Raman Spectrum of $PF_3{\cdot}AsF_5$.—The Raman spectrum of solid $PF_3{\cdot}AsF_5$ obtained at *ca.* -162 °C is given in Figure 1. The assignments given in Table 1 are made by comparison with the vibrational spectra of PF_3,[24] $PF_3{\cdot}BH_3$,[25] $[Ni(PF_3)_4]$,[26] $SClF_5$,[27-29] $S(CF_3)F_5$,[27] $SeClF_5$,[30] $TeClF_5$,[31] $MeCN{\cdot}AsF_5$,[32] and other $L{\cdot}AsF_5$[33] (L = POF_3, COF_2, SOF_2, or SO_2F_2) adducts.

The local symmetry of the $P{\cdot}AsF_5$ moiety in $PF_3{\cdot}AsF_5$ is considered to be C_{4v}.[27,32,33] For the purpose of comparison and convenience, we follow the description given for $SeClF_5$ by Christe *et al.*[30] for the $P{\cdot}AsF_5$ moiety. The peaks at 605, 663, 736, and 763 cm^{-1} are readily assigned as ν_5, ν_2, ν_1, and ν_8, respectively, of P·AsF_5, by comparison with the Raman spectra of related species. ν_9 and ν_{10} are assigned at 381 and 291 cm^{-1}; however, the assignments could be reversed as discussed by Byler and Shriver,[32] $\nu_{sym}(PF_3)$ (A_1) and $\nu_{asym}(PF_3)$ (E) are assigned at 953 and 1 003, 1 027 cm^{-1}. The splitting of the E mode may be attributed to the lower symmetry in the solid state. The increase of $\nu(PF_3)$ in the adduct, relative to that in PF_3 [24] (ν_{sym} at 892, ν_{asym} at 840 cm^{-1}), is consistent with an increase of the positive character on phosphorus accompanying lone-pair donation from phosphorus to arsenic and an increase in P–F bond strength. It is possible that in $PF_3{\cdot}AsF_5$ there is no back donation of electron density accounting for the higher ν_{sym},ν_{asym}-(PF_3) stretching frequencies relative to those observed for simple transition-metal PF_3 complexes.[1,26]

TABLE 1

Raman spectrum (cm^{-1}) [a] of $PF_3{\cdot}AsF_5$

		Species [b]	Assignments
1 027	(6)	E	PF_3 asym str.
1 003	(10)		
953	(28)	A_1	PF_3 sym str.
763	(5)	E (ν_8)	AsF_4 asym str.
736	(13)	A_1 (ν_1)	AsF′ str.
728	(sh)		?
663	(100)	A_1 (ν_2)	AsF_4 sym str.
605	(23)	B_1 (ν_5)	AsF_4 sym out-of-phase str.
519	(10)	A_1	PF_3 sym def.
381	(16)	E (ν_9)	F′AsF_4 wag
365	(5)	A_1 (ν_3)? E ?	AsF_4 sym out-of-plane def. PF_3 asym def.
338	(5)	B_2 (ν_7)?	AsF_4 sym in-plane def.
291	(14)	E (ν_{10})	AsF_4 asym in-plane def.
263	(2)		?
208	(16)	E	PF_3 rock
191	(12)		
155	(38)	A_1 (ν_4) E (ν_{11})	AsP str. PAsF_4 wag

[a] Relative intensities (0—100) are given in parentheses. [b] Vibrations in parentheses are those referred to P·AsF_5 moiety (C_{4v} symmetry) only.

The symmetric P–Ni stretch in the stable $[Ni(PF_3)_4]$ [26] occurs at 195 cm^{-1}; therefore it is reasonable to assign ν_4 to the weaker P–As stretch in the labile $PF_3{\cdot}AsF_5$ adduct as the band at 155 cm^{-1}. The medium intensity of this peak also supports the assignments, since other peaks in the region observed for related species are weak.

The Raman spectrum is therefore consistent with the donor–acceptor formulation $PF_3{\cdot}AsF_5$ rather than $[PF_2][AsF_6]$.[12]

Behaviour of $PF_3{\cdot}AsF_5$ *above* −130 °C.—The Raman spectrum of a sample of ratio $PF_3 : AsF_5 = 1 : 1$ at −130 °C showed peaks attributable to the adduct only; however, at −112 and −78 °C the individual compounds PF_3 and AsF_5 were present, the dissociation increasing with increase in temperature. A sample of ratio $PF_3 : AsF_5 = 1 : 3$ was kept at −78 °C for 3 h. The Raman spectrum showed a mixture of PF_5, AsF_5, AsF_3, and the adduct $PF_3{\cdot}AsF_5$. Therefore, the following equilibrium takes place between −130 and −78 °C, and a redox reaction occurred at ⩾ −78 °C, the extent of reaction increasing with time:

$$PF_3{\cdot}AsF_5 \xrightleftharpoons{\text{between } -130 \text{ and } -78^\circ\text{ C}} PF_3 + AsF_5$$

$$\xrightarrow{\geqslant -78^\circ\text{C}} PF_5 + AsF_3$$

It appears that AsF_5 is a poorer acceptor toward PF_3 than either B_2H_6 [3] or $AlCl_3$.[6]

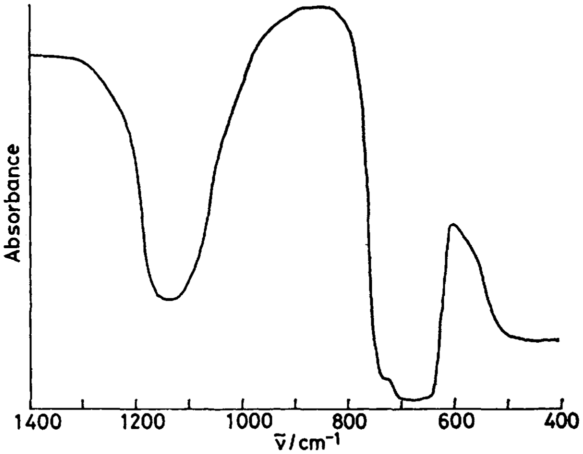

FIGURE 2 Infrared spectrum of $[PF_4][Sb_3F_{16}]$

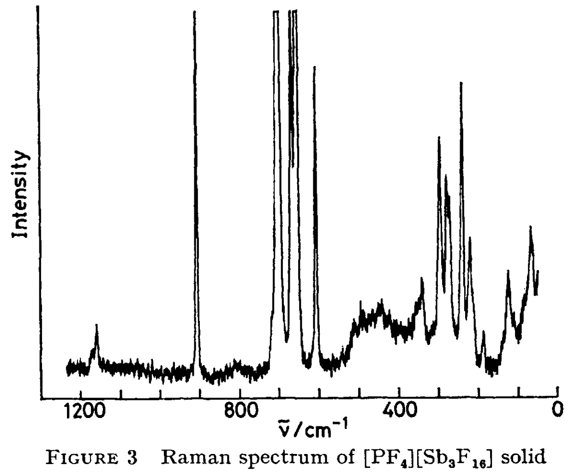

FIGURE 3 Raman spectrum of $[PF_4][Sb_3F_{16}]$ solid

The Raman results showing a redox reaction between PF_3 and AsF_5 at ⩾ −78 °C are supported by the ^{19}F n.m.r. experiments, the large-scale reactions, and the reaction carried out between PF_3 and AsF_5 in an i.r. cell at room temperature. It was previously reported [12] that $PF_3{\cdot}AsF_5$ was stable at −78 °C, and dissociated into its constituents at room temperature. The redox reaction involving components in their standard and other states is allowed ($\Delta H = -356$ kJ mol^{-1} at 25 °C).[34-38]

PF_3–SbF_5 *System*.—The salt $[PF_4][Sb_3F_{16}]$ was observed in the Raman spectrum of a sample of PF_3–SbF_5 obtained 10 min after removal from liquid N_2, indicating that a redox reaction occurs at room temperature or below.

Raman spectra of PF_3–SbF_5 and PF_3–SbF_5–SO_2F_2 taken at −135 °C after being held at −45 °C showed peaks attributable to the starting materials. This suggests the absence of formation of ' $PF_3{\cdot}SbF_5$ ' at this temperature and is further evidence for the lack of an extensive redox reaction under these conditions. Evidence for the reported $[PF_2][SbF_6]$ [12] was not obtained. However, a redox reaction occurs between PF_3(g) and SbF_5(l) at room temperature. The redox reaction yielding SbF_3(s) and PF_5(g) is allowed [35,36,38-40] ($\Delta H = -207$ kJ mol^{-1} at 25 °C). The reaction is, however, complicated by the further reaction of the products with SbF_5(l) to form $[PF_4][Sb_3F_{16}]$ and SbF_3-$(SbF_5)_x$.[19-23]

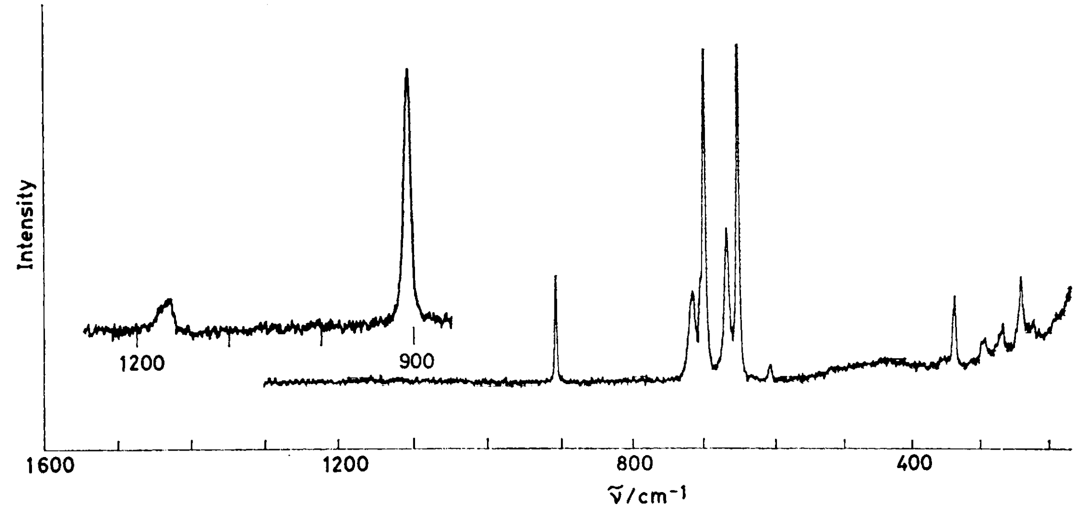

FIGURE 4 Raman spectra of a liquid sample of ratio $PF_5 : SbF_5 = 1 : 8$

Preparation of $[PF_4][Sb_3F_{16}]$.—This salt is prepared quantitatively from SbF_5 and excess of PF_5 at room temperature according to equation (2). The white solid has a vapour pressure of PF_5 of 139 ± 2 mmHg at 23 °C.

$$PF_5(g) + \tfrac{3}{n}(SbF_5)_n(l) \longrightarrow [PF_4][Sb_3F_{16}]\ (s) \qquad (2)$$

The compounds PF_5 and SbF_5 were quantitatively recovered by fractional distillation. The value for ΔH (dissociation) of 52 ± 3 kJ mol^{-1} can be obtained from equation (1) and presumably is associated with equations (3), (4), (5), and (6) and others that are similar.

$$4[PF_4][Sb_3F_{16}] \longrightarrow PF_5(g) + 3[PF_4][Sb_4F_{21}] \qquad (3)$$

$$5[PF_4][Sb_4F_{21}] \longrightarrow PF_5(g) + 4[PF_4][Sb_5F_{26}] \qquad (4)$$

$$2[Sb_nF_{5n+1}]^- \longrightarrow [Sb_{n-1}F_{5(n-1)+1}]^- + [Sb_{n+1}F_{5(n+1)+1}]^- \qquad (5)$$

$$[Sb_nF_{5n+1}]^- \longrightarrow [Sb_{n-1}F_{5(n-1)+1}]^- + \tfrac{1}{n}(SbF_5)_n(l) \qquad (6)$$

It is noted that the Raman spectrum of $PF_5{\cdot}8SbF_5$ (Figure 4, Table 2) is not dissimilar to a superposition of $[PF_4][Sb_3F_{16}]$ and $(SbF_5)_n$(l). Inhomogeneity and solidification of SbF_5 at 8.3 °C [34,41] also complicate the system particularly at lower temperatures where the experimental points were not fitted by equation (1). The low value of ΔH is consistent with the observation that excess of PF_5 was needed for the reaction to go to completion. We were unable to obtain evidence for $[PF_4]$-$[SbF_6]$ or $[PF_4][Sb_2F_{11}]$.

Vibrational Spectra of $[PF_4][Sb_3F_{16}]$.—The i.r. and Raman spectra of the title compound are shown in Figures 2 and 3 and a Raman spectrum of a sample of ratio $PF_5 : SbF_5 = 1 : 8$ is shown in Figure 4. The assignments are given in Table 2.

Assignments of $[PF_4]^+$ are made by comparison with the isoelectronic tetrahedral SiF_4,[42,43] $[NF_4]^+$,[44] CF_4,[42,45] and $[BF_4]^-$ [42,44] of T_d symmetry. The strong i.r.

TABLE 2

Vibrational spectra (cm^{-1}) of $[PF_4][Sb_3F_{16}]$

$[PF_4][Sb_3F_{16}]$		$PF_5 : SbF_5 = 1 : 8$	
Raman	I.r.[a]	Raman	Tentative assignments
1 170vw 1 160vw	1 160s,br	1 165 [dp]	$\nu_3(F_2)$ PF asym str.
908s		908 [p]	$\nu_1(A_1)$ PF sym str.
800vvw			?
	733sh		
		717 [p]	
709 (sh)		707 (sh) [b]	
703vs	690s,br	701 [p]	Sb–F str.
670s		670 [p]	
657vs		657 [p]	
609m		608 [dp]	
520—		520—	Sb–F–Sb bridging str.
380vw,br	450m,br	380 [b]	
360vw			
342vw		342 [p]	
297m		294 [dp]	
281w			
271w		266 [dp]	Sb–F bendings and def.
240m		240 [dp]	
222w		220 [dp]	
188vw			
125w			
70w			lattice vibration

[a] It is possible that the compound might well have lost PF_5 on sample preparation and the i.r. may be that of $[PF_4]$-$[Sb_3F_{16}]{\cdot}xSbF_5$. [b] Polarization measurement uncertain.

absorption at 1 160 cm^{-1} is in the P–F stretching region which is assigned as $\nu_3(F_2)$. The weak doublet at 1 170 and 1 160 cm^{-1} (broad, singlet, depolarized in the liquid phase) in the Raman supports this assignment. The intense, well polarized, Raman peak at 908 cm^{-1} in the P–F stretching region is assigned as $\nu_1(A_1)$. The P–F stretching frequencies were similar in intensity, but at higher energy, than the corresponding bands of SiF_4, and are similar to those of $[NF_4]^+$ (see Table 3).

TABLE 3

Fundamental vibrational modes (cm^{-1}) of tetrahedral $[PF_4]^+$, $[NF_4]^+$, SiF_4, CF_4, and $[BF_4]^-$

Tetrahedral species	Ref.	Activity	ν_1 (A_1)	ν_2 (E)	ν_3 (F_2)	ν_4 (F_2)
$[PF_4]^+$	This work	Raman	908s		1 170vw 1 160vw	
		I.r.			1 160s	
$[NF_4]^+$	44	Raman	849s	450m	1 185w 1 153w	613s
		I.r.			1 162s	613s
SiF_4	42, 43	Raman	800s	268w	1 010w	390w
		I.r.			1 031vs	391s
CF_4	42, 45	Raman	908.5s	435m	1 234w	631.2m
		I.r.			1 241.2s	631.3m
$[BF_4]^-$	42, 44	Raman	778m	358w	1 065vw	535w
		I.r.			1 063s	529s

The P–F stretching frequency is the highest so far observed.[24-26,46] The isoelectronic $[SOF_3]^+$ contains very strong S–O and S–F bonds,[47,48] and exists as a discrete ion in solid $[SOF_3][AsF_6]$.[48] The ionic formulation $[PF_4]^+$ is therefore favoured although we cannot rule out the possibility of some weak anion–cation bridging.

It is expected that ν_2 and ν_4 of $[PF_4]^+$ would occur at *ca.* 300 and *ca.* 400 cm^{-1}, at slightly higher frequencies than those of the isoelectronic SiF_4[42,43] which are observed at 268 and 390 cm^{-1} (Table 3). After a careful comparison of both the position and relative intensities of vibrational spectra of the $[Sb_3F_{16}]^-$ anions in salts containing the counter ions $[IF_6]^+$,[49] $[ReF_6]^+$,[50] and $[SOF_3]^+$ (see Table 4) we were unable to assign ν_2 and ν_4 with any confidence.

TABLE 4

Raman spectrum (cm^{-1}) [a] of $[SOF_3][Sb_3F_{16}]$ [b]

*1 542*w	712m	*531*w	235m
1 265w	702s	*505*mw	219w
*1 064*w	690m	436vw	186vw
*1 057*w	676mw	*384*mw	140w
*908*m	662vs	290mw	126vw
850vw	607m	266w	112vw

[a] Italicized bands are assignable to $[SOF_3]^+$ (see ref. 47). [b] It is possible that $[SOF_3][Sb_3F_{16}]$ may be the average composition of the sample and the spectrum may be a superimposition of an equilibrium mixture of $[SOF_3][SbF_6]$, $[Sb_2F_{11}]^-$, $[Sb_3F_{16}]^-$, $[Sb_4F_{21}]^-$, *etc.*

Raman bands at ⩽700 cm^{-1} are similar, but not identical to, those of $[Sb_2F_{11}]^-$ [18,51-55] and may be due to the *trans*-bridged $[Sb_3F_{16}]^-$ isomer, previously found in $[Br_2][Sb_3F_{16}]$.[56,57] It is also possible that $[PF_4][Sb_3F_{16}]$ has a tetrameric structure similar to that of $BiF_5(SbF_5)_3$,[16,58] however, with very weak interaction between $[PF_4]^+$ and the *cis*-bridged $[Sb_3F_{16}]^-$.

Notwithstanding the difficulty of assigning the $[Sb_3F_{16}]^-$ peaks, the vibrational evidence suggests that $[PF_4]^+$ is essentially ionic, and therefore PF_5 acts as a fluoride-ion donor toward SbF_5. Various other less acidic fluorophosphonium(V) salts[46,59-62] have also been prepared. It is noted that SOF_4 containing formally S^{VI} is a better donor than PF_5 containing P^V. This may in part be due to the stability of the $[SOF_3]^+$ ion arising from the π-bond energy associated with the SO bond.[47,48]

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