Identification by Raman Spectroscopy of Various Weak Oxygen-bridged Donor–Acceptor Adducts of Arsenic and Antimony Pentafluorides; a Reversal of the Usual Lewis Acidities of these Pentafluorides towards Sulphuryl Fluoride

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The compounds POF_3, SO_2, SOF_2, and COF_2 form 1 : 1 oxygen-bridged adducts with AsF_5 and SbF_5 as shown from their Raman spectra obtained at various temperatures. The base strength of the donors appears to decrease in the given order. Sulphuryl fluoride behaves as a still weaker base; however, Raman spectra show the formation of an oxygen-bridged 1 : 1 adduct with AsF_5, but not SbF_5, a reversal of the usual Lewis acidities.

In order to confirm the vibrational assignments for $PF_3{\cdot}AsF_5$,[1] adducts formed by AsF_5 and SbF_5 with other weak bases (SO_2, SOF_2, COF_2, and SO_2F_2) were investigated using low-temperature Raman spectroscopy, and those of $POF_3{\cdot}AsF_5$ and $POF_3{\cdot}SbF_5$ [2] were re-investigated. During the progress of this work the vibrational spectrum of $SO_2{\cdot}SbF_5$ was reported.[3]

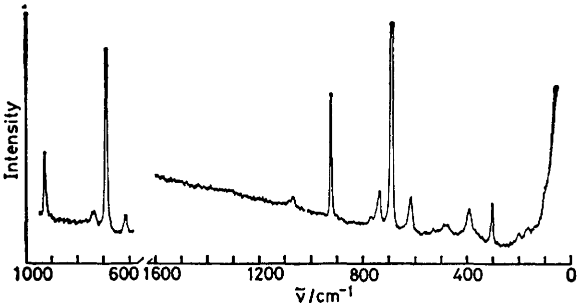

FIGURE 1 Raman spectra of solid $POF_3{\cdot}AsF_5$ at room temperature

X-Ray single-crystal studies clearly show that $SO_2{\cdot}SbF_5$,[4] $POCl_3{\cdot}SbCl_5$,[5] and a variety of related [5,6] complexes are bonded *via* O$\rightarrow$Sb bonds. High-resolution ^{19}F n.m.r. data [7-9] show that $L(SbF_5)_n$ (L = SO_2, SOF_2, SO_2ClF, or COF_2; n = 1 or 2) are oxygen bonded and the n.m.r. evidence is consistent with adduct formation between L and AsF_5; however, fine structure was not observed for the arsenic derivatives and therefore unambiguous structural information was not obtained.[7] Complex formation was reported not to occur between SO_2F_2 and AsF_5 [7] or SbF_5.[8]

The Raman spectra of all the adducts described below are consistent with the formation of L$\rightarrow$MF$_5$ donor–acceptor adducts *via* an oxygen bridge. The adduct $SO_2F_2{\cdot}AsF_5$ was detected; however, no evidence was obtained for the corresponding $SO_2F_2{\cdot}SbF_5$, a reversal at low temperature of the usual Lewis acidities of AsF_5 and SbF_5.

EXPERIMENTAL

Reagents.—Unless otherwise specified, the reagents and apparatus were as described in ref. 1. Errors in wavenumbers are *ca.* $\pm 3\ cm^{-1}$. Phosphoryl fluoride (Ozark-Mahoning) and COF_2 (Pierce) were used without purification. Non-condensable gases were removed from SOF_2 (Peninsular Chemresearch).

Sample Preparations.—The Raman samples of $L{\cdot}MF_5$ (L = POF_3, SO_2, SOF_2, COF_2, or SO_2F_2; M = As or Sb)

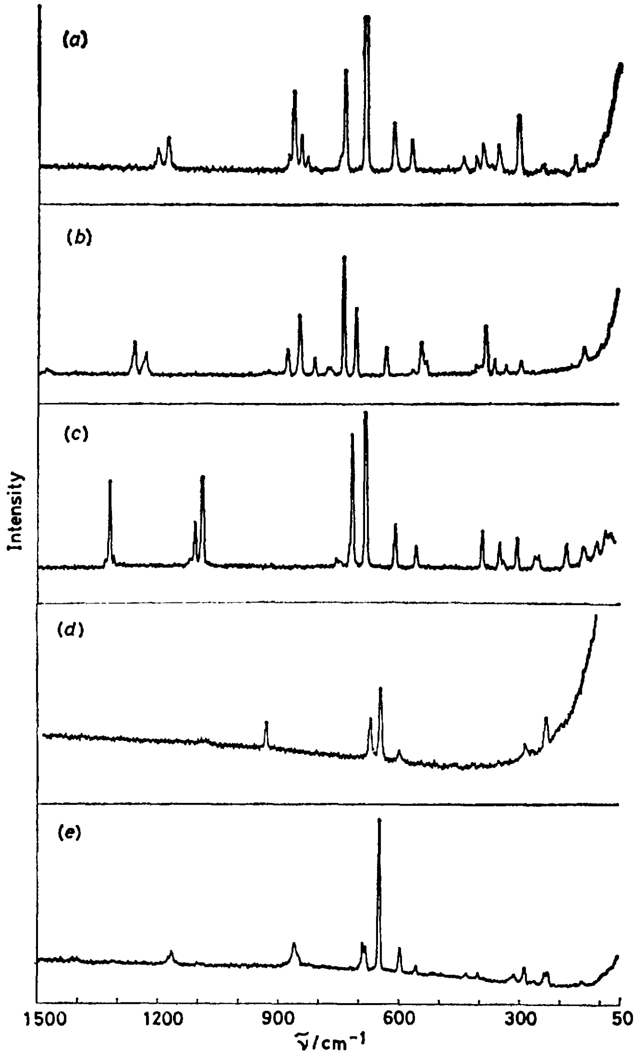

FIGURE 2 Raman spectra of (*a*) $SOF_2{\cdot}AsF_5$ (*ca.* −162), (*b*) $SO_2F_2{\cdot}AsF_5$ (*ca.* −162), (*c*) $SO_2{\cdot}AsF_5$ (*ca.* −162), (*d*) $POF_3{\cdot}SbF_5$ (r.t.), and (*e*) $SOF_2{\cdot}SbF_5$ (*ca.* −162 °C). In (*b*) dissociated SO_2F_2 and AsF_5 are observed and wavenumbers are listed in SUP 22500. For (*c*) see also footnote *j* in Table 1

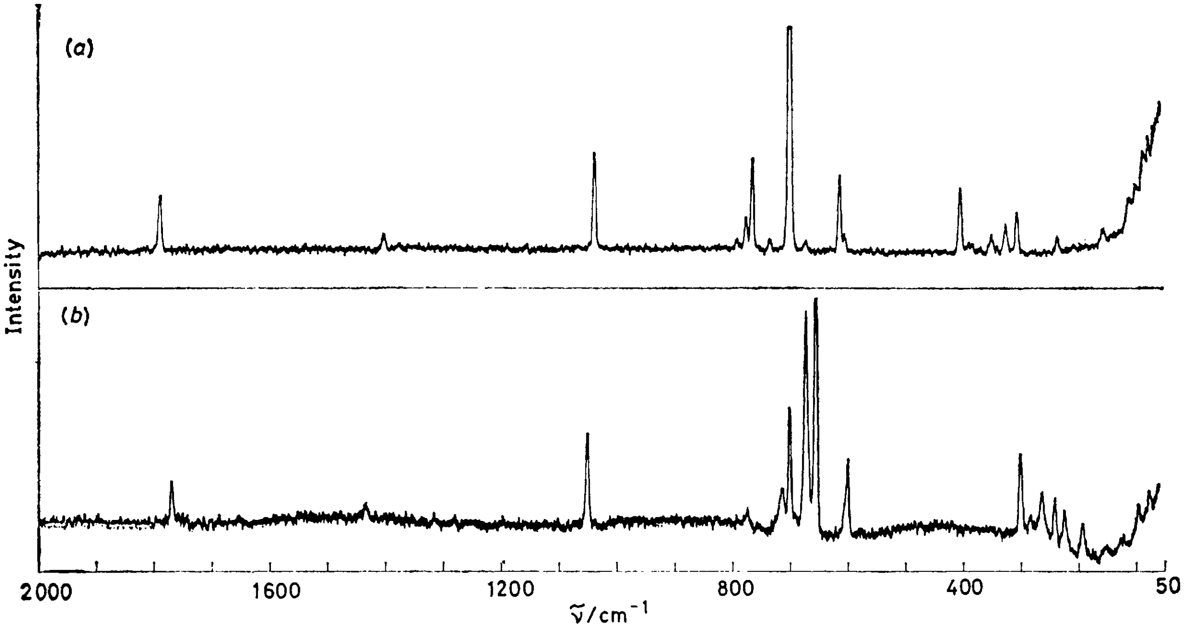

FIGURE 3 Raman spectra of (*a*) solid COF$_2$·AsF$_5$ (*ca.* −162 °C) and (*b*) solid COF$_2$·SbF$_5$ (*ca.* −162 °C)

were prepared by condensing pre-weighed stoicheiometric amounts in 1 : 1 (error ±5%) mol ratios of starting materials into a Raman tube (outside diameter 5 mm), and flame sealed.

The final appropriate slush baths in which the sample components gave a uniform liquid were: SO$_2$F$_2$·AsF$_5$ (−78), COF$_2$·AsF$_5$ (−45), SO$_2$·AsF$_5$ and SOF$_2$·AsF$_5$ (−22), COF$_2$·SbF$_5$ (0), SOF$_2$·SbF$_5$ (37), POF$_3$·AsF$_5$ (45), and SO$_2$·SbF$_5$ (75 °C). Samples of SOF$_2$·SbF$_5$ and SO$_2$·SbF$_5$ became supercooled liquids at room temperature, enabling polarization measurements to be obtained.

The adducts POF$_3$·AsF$_5$, SOF$_2$·SbF$_5$, and SO$_2$·SbF$_5$ were kept at ambient temperature after mixing, other samples being gradually cooled and stored at −196 °C.

Attempted Preparation of Xe·AsF$_5$, NF$_3$·AsF$_5$, AsF$_3$·AsF$_5$, N$_2$O·AsF$_5$, PF$_5$·AsF$_5$, PF$_3$·PF$_5$, WF$_6$·SbF$_5$, *and* SO$_2$F$_2$·SbF$_5$. —Raman samples of Xe·AsF$_5$, NF$_3$·AsF$_5$, AsF$_3$·AsF$_5$, N$_2$O·AsF$_5$, PF$_5$·AsF$_5$, PF$_3$·PF$_5$, WF$_6$·SbF$_5$, and SO$_2$F$_2$·SbF$_5$ were prepared similarly. Samples of WF$_6$·SbF$_5$ and SO$_2$F$_2$·SbF$_5$ were well mixed at room temperature before cooling. Raman spectra were taken at *ca.* −162 °C (except SO$_2$F$_2$·SbF$_5$ at *ca.* −137 °C). The Raman spectra showed only the superposition of the reactants.

RESULTS AND DISCUSSION

The Raman spectra of solid L·MF$_5$ (M = As or Sb, L = POF$_3$, SO$_2$, SOF$_2$, COF$_2$, or SO$_2$F$_2$) are given in Figures 1—3. Raman spectra were also obtained in the

TABLE 1

Tentative assignments of bands (cm^{-1}) attributed to P·AsF$_5$, O·AsF$_5$, N·SbF$_5$, and O·SbF$_5$ moieties in the Raman spectrum [a] of various L·AsF$_5$ and L·SbF$_5$ adducts assuming C_{4v} symmetry

		Temperature [a]	A_1				B_1		B_2	E			
Compound	State	(θ_c/°C)	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}
SClF$_5$ [b]	l	r.t.[c]	833 (2)	704 (30)	603 (2)	403 (100)	625 (7)		505 (2)	927 (2)	584 (1)	442 (8)	271 (6)
SeClF$_5$ [d]	l	r.t.	721 (18)	656 (100)	443 (22)	385 (85)	636 (6)		380	745 (3)	424 (4)	336 (12)	213 (14)
TeClF$_5$ [e]	l	r.t.	708 (31)	659 (100)	312 (8)	413 (77)	651 (8)		302 (5)	726 (6)	327 (9)	259 (17)	167 (18)
MeCN·AsF$_5$ [f]	s	22	715 (46)	673 (100)	365 (6)	270 (6)	603 (10)			740 (2)	384 (12)	325 (17)	239 (10)
PF$_3$·AsF$_5$ [g]	s	−162	736 (13)	663 (100)	365 (5)	155? (38)	605 (23)		338 (5)	763 (5)	381 (16)	291 (14)	155? (38)
POF$_3$·AsF$_5$	s	r.t.	735 (15)	688 (100)	374 (5)	200 (3)	619 (15)			772 (3)	394 (15)	303 (10)	
	l	45	733 (38)	688 (100)	374 (6)	197 (6)	615 (11)				394 (14)	305 (19)	
COF$_2$·AsF$_5$	s	−162	765 (18)	701 (100)	351 (6)		615 (16)		328 (7)	776 (7)	406 (13)	308 (9)	238 (4)
	l	−50	773 (27)	709 (100)	349 (6)		626 (10)		323 (1)		413 (12)	301 (11)	
SOF$_2$·AsF$_5$	s	−162	736 (38)	688 (100)	357 (11)		615 (18)			748 (sh)	395 (10)	307 (24)	249 (3)
	l	−34	733 (54) [h]	699 (100)	349 (11)		623 (8)			761 (28)	390 (13) [h]	302 (15)	
SO$_2$F$_2$·AsF$_5$	s	−162	772 (8) [i]	709 (71)	339 (5)		622 (sh)			778 (8)	400 (8)	300 (14)	
SO$_2$·AsF$_5$ [j]	s	−162	716 (45)	683 (100)	351 (9)		610 (18)		324 (1)	{756 (3) {746 (3)	394 (12) 381 (1)	309 (12)	265 (6) 254 (6)
	l	−23	732 (28) [h]	695 (100)	350 (13)		620 (5)		323 (1)	754 (sh)	404 (9)	304 (6)	248 (<1)
MeCN·SbF$_5$ [k]	s	22	673 (40)	646 (60)	290 (10)	277 (sh)?	602 (10)				290 (10)	183 (10)	261 (sh)
COF$_2$·SbF$_5$	s	−162	673 (82) [l]	658 (100)	285 (5)	265 (14)	600 (23)		242 (14)	716 (19) 701 (29)	303 (28)	194 (14)	226 (14)
	l	−1		665 (100) [m]	300 (9)	266 (13)	607 (10) [n]		234 (16)	714 (55) [o]	300 (9)	185 (2)	234 (16)
SOF$_2$·SbF$_5$	s	−162	681 (16)	646 (100)	289 (16)	266 (5)	599 (20)			688 (18)	321 (13)	231 (12)	239 (12)
	l	r.t.	670 (sh)	653 (100)	297 (24)	277 (9)	604 (10)			695 (sh)	297 (24)	232 (23)	232 (23)
POF$_3$·SbF$_5$	s	r.t.	678 (52)	654 (100)	290 (12)	274 (4)	606 (14)					239 (31)	239 (31)
SO$_2$·SbF$_5$ [p]	s	r.t.	664 (100)	645 (70)	295 (22)	266 (7)	600 (26)	149? (11)	248? (4.5)	697 (3) 691 (2)	310? (4)	199? (8)	232? (16)
	l	r.t.	695 (14)	650 (100)	295 (14)	268 (6)	600 (9)	146? (3)			331? (2)	200? (5)	230? (9)

[a] Relative intensities in parentheses (0—100). [b] Raman bands quoted from ref. 14, assignments from ref. 16. For all ClMF$_5$ species ν_4 refers to M$-^{35}$Cl stretch only. [c] The temperatures quoted were obtained from a thermistor situated behind the sample, and therefore the temperatures of the samples under irradiation are likely to be higher than that indicated here and in Tables 2 and 3. [d] Ref. 13. Raman bands quoted. [e] Ref. 16. Raman bands quoted. [f] Refs. 11 and 12. [g] Ref. 1. [h] Overlaps with dissociated AsF$_5$. [i] Alternatively, ν_1 may be hidden underneath the intense uncomplexed AsF$_5$ peak at 739 cm^{-1}. [j] Different Raman spectra of SO$_2$·AsF$_5$ (*ca.* 1 : 1 mol ratio) in the solid state were also obtained. [k] Refs. 10—12. [l] Includes δ_{asym}(FCO). [m] Overlaps with dissociated SbF$_5$, SbF′ str., and δ_{asym}(FCO). [n] Probably includes FCO sym def. [o] Overlaps with dissociated SbF$_5$. [p] Refs. 3 and 12. The Raman spectra of the solid, supercooled liquid, and SO$_2$ solution of the SO$_2$·SbF$_5$ adduct obtained in our work are the same as those reported in these references, within experimental error.

Table 2

Tentative assignments of bands (cm^{-1}) attributed to the Lewis bases (PF_3, POF_3, or COF_2) in complexes with AsF_5 and/or SbF_5

Compound	PF_3 [a]	$PF_3{\cdot}AsF_5$ [a]	POF_3		$POF_3{\cdot}AsF_5$		$POF_3{\cdot}SbF_5$	COF_2		$COF_2{\cdot}AsF_5$		$COF_2{\cdot}SbF_5$	
State [b]	l	s	s	l	s	l	s	s	l	s	l	s	l
θ_c/°C	−122	−162	−142	−22	r.t.	45	r.t.	−132	−96	−162	−50	−162	−1
$\nu_{sym}(PF_3)$	876 [c] (100)	953 (28)	881 (100)	874 (100)	925 (28)	918 (39)	937 (29)						
$\nu_{asym}(PF_3)$	826 (100)	1 027 (6) 1 003 (10)	986 (17)	984 (4)	1 085 (2) 1 071 (4)	1 067 (3)	1 085 (1)						
$\nu(PO)$			1 399 (1) 1 382 (11) 1 369 (2) 1 361 (1)	1 394 (21)	1 305 (1)	1 300 (5)							
$\delta_{sym}(PF_3)$	484 (20)	519 (10)	475 (25)	472 (30)	485 (8)	485 (5)	468 (4)						
$\delta_{asym}(PF_3)$	347 (12)	365 (5)	491 (7)		534 (2)	533 (2)	552 (2)						
$\rho_r(PF_3)$		208 (16) 191 (12)	343 (25)	337 (16)									
$\nu(CO)$								1 906 (26)	1 945 (22) [d] 1 902 (67)	1 788 (12)	1 835 (12)	1 770 (9)	1 803 (6)
$\nu_{sym}(CF_2)$								980 (100)	968 (100)	1 037 (20)	1 016 (21)	1 050 (28)	1 057 (4) [e] 1 043 (6) [e]
$\nu_{asym}(CF_2)$								1 253 (4)	1 261 (2)	1 402 (5)	1 394 (1)	1 436 (4)	1 430 (<1)
$\delta_{sym}(FCO)$								587 (13)	587 (10)	606 (4)	626 (10)	606 (sh)	
$\delta_{asym}(FCO)$								626 (22)	624 (17)	673 (4)		[f]	[f]
$\pi(OCF_2)$								767 (12)	771 (8)	792 (3)		774 (6)	777 (3)

[a] Ref. 1. [b] l = Liquid, s = solid. [c] Intensities in parentheses are relative to those given in Table 1 for the corresponding adducts. [d] Combination band enhanced by Fermi resonance (see ref. 21). [e] Two peaks could arise from the presence of $COF_2{\cdot}SbF_5$ and possibly $COF_2{\cdot}Sb_2F_{10}$. [f] Probably overlaps with SbF_5 peaks (see Table 1).

liquid phase (Tables 1—3). Polarization measurements were obtained for all adducts except $POF_3{\cdot}SbF_5$ and supported the assignments given in the Tables. For most adducts some dissociation into the components was observed at the temperature at which polarization measurements were obtained (Table 1). Dissociation of the adducts into constituents was reversible in all cases.

The local symmetry of the $O{\cdot}MF_5$ (M = As or Sb) entities is considered as C_{4v},[1,10-12] and the description of the frequencies for OMF_5 is similar to that given for $SeClF_5$.[13] The modes ν_1, ν_2, ν_3, ν_5, ν_8, ν_9, and ν_{10} of the OMF_5 moiety (Table 1) are quite similar in intensity and frequencies, and can be readily assigned by comparison with similar molecules of C_{4v} symmetry.[1,10-16] The assignments of ν_4, ν_7, and ν_{11} are very tentative, and no attempt was made to assign ν_6 since it has not been observed for related molecules.[13] Low-frequency bands and some weak peaks were not assigned [see Supplementary Publication No. SUP 22500 (4 pp.)].* A normal-co-ordinate analysis of $SO_2{\cdot}SbF_5$ showed that it was difficult to definitely assign[17] a characteristic O–Sb stretch ν_4 because of a high degree of coupling with other skeletal vibrations.

Assignments of the donor group in the adducts are made by comparison with the free donors (Tables 2 and 3). The observed Raman frequencies for PF_3,[18,19] POF_3,[18,20] COF_2,[18,21] SOF_2,[22,23] SO_2F_2,[24] and SO_2[18,25] are consistent with literature values. Solid-state Raman spectra of POF_3 and COF_2 do not appear to have been reported. Splittings of some bands for which single peaks would be expected may be due to solid-state effects.

In liquid POF_3,[18,20] $\nu(PO)$ is observed at 1 344 cm^{-1}, whereas in $POF_3{\cdot}AsF_5$ it is shifted to 1 305 cm^{-1}, consistent with previous results.[2] The weakening of the co-ordinated bond is accompanied by a strengthening of the P–F bonds. Similar shifts in frequencies are observed for the other adducts (see Tables 2 and 3).

The relative Lewis basicity can be judged to be in the order of Lewis base strength $POF_3 > SO_2 > SOF_2 > COF_2 > PF_3 > SO_2F_2$ by the temperature at which the AsF_5 and SbF_5 adducts begin to dissociate (see SUP 22500) and is consistent with ^{19}F n.m.r. results.[7,8] The difference in the Raman shifts of the adducts relative to the unco-ordinated donor is also consistent with the formation of stronger SbF_5 adducts and with ^{19}F n.m.r. data.[7-9] However, the relative change in $\nu(SF_2)$ is ambiguous and the SO_2 vibrations occur at about the same frequencies.

In all cases the Raman spectra support an oxygen-bridged formulation of the adducts and the AsF_5 portions of the adducts are similar to that found for $PF_3{\cdot}AsF_5$, thus supporting the donor–acceptor[1] formulation of this adduct.

The ^{19}F n.m.r. spectrum indicated[7] the absence of complex formation between AsF_5 and SO_2F_2. However, $SO_2F_2{\cdot}AsF_5$ and components of equilibrium (1) were observed by Raman spectroscopy [Figure 2(*b*), Table 1] at −162 °C. The most intense peak in the

$$SO_2F_2 + AsF_5 \rightleftharpoons SO_2F_2{\cdot}AsF_5 \qquad (1)$$

complex (ν_2) is still observed at *ca.* −83 °C. The relatively strong peaks can be assigned to the adduct and these increase in intensity as the temperature is decreased, relative to those of the free ligand, and decrease as the temperature is increased.

It has been shown that the n.m.r. spectrum of the adduct $PF_3{\cdot}AlCl_3$[27] is very similar to that of the unco-ordinated ligands. The adduct $SO_2F_2{\cdot}AsF_5$ is weaker than $PF_3{\cdot}AlCl_3$; therefore, it may well be that, with fast exchange, the ^{19}F n.m.r. spectrum of $SO_2F_2{\cdot}AsF_5$ in equilibrium with dissociated species is similar to those of unco-ordinated SO_2F_2 and AsF_5. Raman spectroscopy is therefore a useful tool for the detection of weak adducts in equilibrium with their constituents.

The Raman spectrum of $SO_2F_2{\cdot}SbF_5$ taken at *ca.* −137 °C shows superimposition of the spectra of SO_2F_2 and SbF_5 (see SUP 22500). In particular, no new peaks attributable to bound SO_2F_2 were detected although we cannot completely rule out the possibility that they were

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 3

Tentative assignments of bands (cm^{-1}) attributed to the Lewis bases (SOF$_2$, SO$_2$F$_2$, and SO$_2$) in complexes with AsF$_5$ and/or SbF$_5$ [a]

Compound	SOF$_2$		SOF$_2$·AsF$_5$		SOF$_2$·SbF$_5$		SO$_2$F$_2$		SO$_2$F$_2$·AsF$_5$	SO$_2$		SO$_2$·AsF$_5$ [b]		SO$_2$·SbF$_5$ [c]	
State [d]	s	l	s	l	s	l	s	l	s	s	l	s	l	s	l
θ_c/°C	−162	−123	−162	−34	−162	r.t.[e]	−162	−95	−162	−135	−57	−162	−23	r.t.	r.t.[e]
ν_{sym}(SO)	1 319(9) 1 300(57) 1 292(41) 1 286(3)	1 304(100)	1 202(9) 1 176 (13)	1 226(32)	1 169(sh) 1 159(27) 1 155(sh)	1 188(17)	1 260(62)	1 259(43)	1 240(sh) [f] 1 234(42) [f]	1 147(100)	1 147(100)	1 119(4) [f] 1 108(15) [f] 1 090(42) [f]	1 121 [f](54)	1 109(13) [f] 1 088(19) [f]	1 100 [f](20)
ν_{asym}(SO)							1 480(2)	1 491(2)		1 341(4) 1 313(10)	1 332(4)	1 329(3) [g] 1 318(29) [g] 1 308(4) [g]	1 327 [g](11)	1 328(4) [g] 1 318(40) [g] 1 308(4) [g]	1 325 [g](22)
ν_{sym}(SF$_2$)	815(100) 798(21)	804(79)	875(4) 863(26)	858 [h](35)	857(39) 850(sh)	874(27)	848(100)	848(100)	879(34)						
ν_{asym}(SF$_2$)	722(32) 709(74)	719(40)	846(10) 830(3)	858 [h](35)	820(4)	838(13)	925(13) 905(3)	885(5)							
δ_{sym}(SF$_2$)	384(15)	382(11)	412(4)	404(19) [i]	406(5)		389(40)	388(19)	411(8)						
δ_{asym}(SF$_2$)	405(40)	398(22)	444(6)	434(4)	434(7)	430(8) [i]									
δ_{sym}(FSO)	539(15) 526(13)	528(28)	572(12)	562(9)	558(8)	559(5)									
δ_{sym}(SO$_2$) ρ_r(SO$_2$) ρ_r(SF$_2$)							549(45)	549(38)	568(7) 535(13)	524(5)	522(4)	559 [i](9)	545 [i](5)	539 [i](12)	539 [i](7)

[a] Intensities in parentheses and relative to those given in Table 1. [b] See footnote *j* in Table 1. [c] Refs. 3 and 12. [d] s = Solid, l = liquid. [e] Supercooled liquid at room temperature. [f] Bridging SO str. [g] Terminal SO′ str. [h] A very broad band probably includes both ν_{sym} and ν_{asym}. [i] OSO′ deformation.

obscured by SO_2F_2 and SbF_5, or were too weak to be observed. This suggests that there is no complex formation between SO_2F_2 and SbF_5, which agrees with the ^{19}F n.m.r. results.[8] Therefore SO_2F_2 is an inert diluent only in reactions involving SbF_5, not with AsF_5.

We were also unable to detect adduct formation between PF_3 and SbF_5,[1] although $PF_3 \cdot AsF_5$ was formed. Therefore AsF_5 behaves as a stronger acceptor than SbF_5 toward SO_2F_2 and PF_3,[1] a reversal of the usual relative acidities. It is possible that the reason for this lies in the fact that AsF_5 is a monomer in the gaseous and liquid states [28] (the Raman spectra of solid AsF_5 has peaks at 812w, 738vs, 636m, 386m, 366w, and 141w cm^{-1} at *ca.* −162 °C suggesting that it is monomeric in the solid state as well), whereas in the liquid, solution, and solid states SbF_5 is polymeric [29-34] and has an average degree of association of three at *ca.* 150 °C [34] in the gas phase indicating that the bridging bond is of appreciable energy. Therefore, in order to form an adduct, reasonably strong bridging bonds must be broken lowering the overall heat of reaction, and therefore very weak donors may form adducts with AsF_5 but not with SbF_5, even though the donor–acceptor bond may be itself stronger in the case of SbF_5.

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