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Halogen Pentafluoride-Lewis Acid Adducts[1]

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Vibrational spectra have been recorded for the known adducts $ClF_5 \cdot AsF_5$, $ClF_5 \cdot xSbF_5$ ($x = 1.08$ and 1.36), $BrF_5 \cdot 2SbF_5$, and $IF_5 \cdot SbF_5$. Furthermore, the new adduct $BrF_5 \cdot AsF_5$ has been prepared. It is marginally stable at −95°. The spectra of the ClF_5 adducts are consistent with predominantly ionic structures containing the ClF_4^+ cation. The spectrum of ClF_4^+ is very similar to that of isoelectronic SF_4 thus indicating a pseudo-trigonal-bipyramidal structure of symmetry C_{2v}. All fundamentals have been assigned and a valence force field has been computed for ClF_4^+. The vibrational spectra of $IF_5 \cdot SbF_5$ and $BrF_5 \cdot 2SbF_5$ are compatible with the predominantly ionic structures $IF_4^+SbF_6^-$ and $BrF_4^+Sb_2F_{11}^-$, respectively, established by X-ray diffraction data. Tentative assignments are given for BrF_4^+ and IF_4^+. The ^{19}F nmr spectra of $BrF_5 \cdot 2SbF_5$ and $IF_5 \cdot SbF_5$ in HF solution are also reported.

Introduction

Halogen fluorides exhibit amphoteric character. By combining with strong Lewis acids, they can form cations containing one F^- ion less than the parent molecule. In recent years these salts have received much attention, and numerous papers dealing with their syntheses and structures have been published.[2] Whereas the structures of the halogen mono-, tri-, and heptafluoride adducts are reasonably well established, much less is known about the complexes of the halogen pentafluorides.

Chlorine pentafluoride combines with Lewis acids such as AsF_5,[3] SbF_5,[3,4] and PtF_5.[5,6] Ionic structures containing the ClF_4^+ cation were suggested;[3,5] however, no supporting data were presented. Recently, the ^{19}F nmr spectrum of $ClF_5 \cdot 1.36SbF_5$ in HF-AsF_5 solution was studied.[7] The observation of two resonances of equal intensity at low field is strong evidence for the presence of a ClF_4^+ cation having a pseudo-trigonal-bipyramidal structure of symmetry C_{2v}, analogous to that found[8,9] for isoelectronic SF_4.

Bromine pentafluoride forms with SbF_5 the adduct, BrF_5 $2SbF_5$.[10] A brief report on the ^{19}F nmr spectrum of the solid and melt has been published[11] indicating the presence of two different kinds of fluorine ligands; however, the observed area ratio was in poor agreement with that expected for the postulated[11] structure $BrF_4^+Sb_2F_{11}^-$. Recently, the crystal structure of $BrF_5 \cdot 2SbF_5$ has been determined establishing[12] its predominantly ionic nature. After completion of our study,[1] Surles and coworkers have reported[13] the Raman spectra of $BrF_4^+Sb_2F_{11}^-$ and of BrF_5 in SbF_5 solution and proposed a tentative assignment for BrF_4^+. Solutions of BrF_5 in SbF_5 were shown[13] to be highly conductive suggesting an ionic formulation for the $BrF_5 \cdot SbF_5$ adduct.

Iodine pentafluoride forms 1:1 adducts with SbF_5[14] and PtF_5.[15] Recently, the crystal structure of $IF_5 \cdot SbF_5$ has independently been studied by X-ray diffraction by two groups.[16,17] Unfortunately, $IF_5 \cdot SbF_5$ tends to form twin crystals[17] thus rendering the structural determination somewhat difficult. Both groups suggest for $IF_5 \cdot SbF_5$ a mainly ionic structure containing a distorted trigonal-bipyramidal IF_4^+ cation of symmetry C_{2v} and an SbF_6^- anion distorted from symmetry O_h. However, several interesting questions such as the difference in bond length between the axial and equatorial IF bonds remain unresolved. Shamir and Yaroslavsky have reported[18] in a preliminary communication the Raman spectra of a number of adducts including that of $IF_5 \cdot SbF_5$. However, their experimental data are incomplete and, therefore, their conclusions are little convincing.

Experimental Section

Apparatus. The materials used in this work were manipulated either in a well-passivated (with ClF_3) 304 stainless steel vacuum system equipped with Teflon FEP U traps or in the dry nitrogen atmosphere of a glove box. Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%).

The Raman spectra of the solids were recorded with a Spex Model 1400 spectrophotometer. The green (5145 Å) or the blue (4880 Å) line of a Coherent Radiation Laboratory Model 52 Ar ion laser and the red (6328 Å) line of a Spectra-Physics Model 125 He–Ne laser were used as exciting lines. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or clear Teflon FEP or Kel-F capillaries (1–4 mm i.d.) were used as sample containers. For the capillaries the transverse viewing–transverse excitation technique was applied. The Raman spectra of the HF solutions were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line. The samples were contained in Teflon FEP capillaries which were also used for the ^{19}F nmr spectra.

The infrared spectra of the solids were recorded on a Beckman Model IR-7 with CsI interchange and Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm^{-1} as dry powders between AgCl or AgBr plates or thin (2 mils) Teflon FEP sheets. Compensation for bands due to the Teflon FEP window material was achieved by placing an empty cell in the reference beam. Screw-cap metal cells with Teflon FEP gaskets were used as window holders. The low-temperature infrared spectrum of $ClF_5 \cdot AsF_5$ was taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl. Temperature cycling of the

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(1) Presented in part at the 6th International Symposium on Fluorine Chemistry, Durham, England, July 1971.

(2) For a recent review on interhalogen cations, for example, see R. J. Gillespie and M. J. Morten, *Quart. Rev., Chem. Soc.*, **25**, 533 (1971).

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(13) T. Surles, A. Perkins, L. A. Quarterman, H. H. Hyman, and A. I. Popov, *J. Inorg. Nucl. Chem.*, **34**, 3561 (1972).

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(15) N. Bartlett and D. H. Lohman, *J. Chem. Soc.*, 619 (1964).

(16) (a) H. W. Baird and H. F. Giles, preliminary data abstracted in *Acta Crystallogr., Sect. A*, **25**, S3, S115 (1969); (b) private communication; refinement of data of ref 16a resulted in the following geometry for IF_4^+: $r_{eq} = 1.78$, $r_{ax} = 1.87$ Å; $\angle_{eq} = 101$, $\angle_{ax} = 156°$.

(17) N. Bartlett, private communication. IF_4^+ geometry: $r_{eq} = 1.79$, $r_{ax} = 1.81$ Å; $\angle_{eq} = 107$, $\angle_{ax} = 153°$.

(18) J. Shamir and I. Yaroslavsky, *Isr. J. Chem.*, **7**, 495 (1969).

internal window *in vacuo* was essential to obtain spectra free of unreacted starting materials.

The ^{19}F nmr spectra were recorded at 56.4 MHz on a Varian high-resolution nmr spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the side-band technique with an accuracy of ±1 ppm relative to the external standard $CFCl_3$.

Preparation of the ClF_5 Adducts. The purification of ClF_5, SbF_5, AsF_5, and HF and the preparation of the $ClF_5 \cdot$(Lewis acid) adducts has previously been described.[3] Since the melting point and the composition of the $ClF_5 \cdot SbF_5$ samples varied somewhat with the method of preparation, three different samples were investigated. Sample I had the composition $ClF_5 \cdot 1.08SbF_5$ and showed first signs of melting at 88°. It was prepared by adding an SbF_5-HF solution to excess ClF_5. Sample II had the composition $ClF_5 \cdot 1.36SbF_5$ and was prepared by combining SbF_5 dissolved in HF with an excess of ClF_5 at −196° followed by warm-up to 25° and removal of volatile material *in vacuo*. It showed first indications of partial melting at ~35°. With increasing temperature, however, the sample solidified again showing the onset of a second melting at 88°. Sample III had the same composition as sample II and was prepared by treating a part of sample II with excess ClF_5 in a Monel cylinder at 50° for 48 hr with agitation. It melted at about 33° to form a milky, highly viscous liquid. The synthesis of the $ClF_4^+PtF_6^-$ and $ClF_6^+PtF_6^-$ mixture has previously been described.[6]

Preparation of $BrF_5 \cdot 2SbF_5$. Bromine pentafluoride (from The Matheson Co.) was treated with F_2 at ambient temperature until the material was colorless. It was purified by fractional condensation through two traps kept at −64 and −95°. The material retained in the −95° trap showed no detectable impurities in the infrared spectrum.

Bromine pentafluoride (112.3 mmol) was condensed at −196° into a passivated 100-ml Monel cylinder containing 68.8 mmol of SbF_5. The cylinder was heated for 3 days at 120°. Subsequently, unreacted BrF_5 (78.3 mmol) was removed *in vacuo* at ambient temperature leaving behind a white, crystallinic solid. Consequently, BrF_5 (34.0 mmol) had reacted with SbF_5 (68.8 mmol) in a mole ratio of 1:2.02 producing the complex $BrF_5 \cdot 2SbF_5$.

Preparation of $BrF_5 \cdot AsF_5$. Bromine pentafluoride (4.42 mmol) was combined with AsF_5 (13.15 mmol) at −196° in a Teflon FEP U trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 1200 mm, the mixture was cooled again to −196°. This procedure was repeated several times until the reaction was complete. Unreacted AsF_5 (8.77 mmol) was removed *in vacuo* at −95° leaving behind a white solid which melted at higher temperature to form an almost colorless liquid. Prolonged pumping on the adduct at −95° resulted in the removal of additional small amounts of AsF_5 indicating that the adduct has a slight dissociation pressure even at −95°. The infrared spectrum of the gas obtained by exhaustive dissociation of the solid showed BrF_5 and AsF_5 in a 1:1 mole ratio. Based on the above given material balance, BrF_5 (4.42 mmol) had combined with AsF_5 (4.38 mmol) in a mole ratio of 1:0.99 producing the complex $BrF_5 \cdot AsF_5$.

Preparation of $IF_5 \cdot SbF_5$. This product was prepared as previously described.[14] The material was a white, crystallinic solid. The material balance was as expected for a 1:1 adduct. *Anal.* Calcd for $ISbF_{10}$: I, 28.9; Sb, 27.8; F, 43.3. Found: I, 29.4; Sb, 27.4; F, 43.0.

Liquid IF_5 and gaseous AsF_5 when combined at 20° with stirring did not form a stable adduct.

Results and Discussion

Syntheses and Properties. The preparation of the ClF_5 adducts has previously been discussed.[3] In the BrF_5-SbF_5 system we could not isolate a 1:1 adduct even when employing a large excess of BrF_5 and temperatures above 100° in the synthesis. The $BrF_5 \cdot 2SbF_5$ complex is a white crystallinic solid. It can be stored in Teflon FEP containers without appreciable decomposition. Exposure to small amounts of moisture or reactive surfaces produces a pink to deep red color due to the formation of Br_2^+ salts.[2] Single crystals of $BrF_5 \cdot 2SbF_5$ can be readily grown by slow sublimation at temperatures slightly higher than ambient. The results of a single-crystal X-ray diffraction study on $BrF_5 \cdot 2SbF_5$ have been reported[12] elsewhere. With AsF_5, however, BrF_5 does form a 1:1 adduct, but its thermal instability preempted its use for structural studies. Upon melting, the complex forms a colorless liquid. If impure BrF_5 is used in the synthesis, the color of the liquid is an intense burgundy red indicating the presence of Br_2^+ ions.[2] The fact that AsF_5 and SbF_5 combine with BrF_5 in different mole ratios might be explained by the pronounced tendency of SbF_5 to form polymeric anions such as $Sb_2F_{11}^-$.

Our data obtained for $IF_5 \cdot SbF_5$ confirm Woolf's reports.[14] Single crystals of $IF_5 \cdot SbF_5$ were grown by slow sublimation at 40°. A single-crystal X-ray diffraction study in our laboratory was discontinued when we learned about the work[15] of Baird and Giles. The fact that AsF_5, a weaker Lewis acid than SbF_5, does not form a stable adduct with IF_5 is not surprising. As previously pointed out,[19] halogen pentafluorides possess an energetically favorable pseudooctahedral structure and show little tendency to form the energetically less favorable pseudo-trigonal-bipyramidal XF_4^+ cations.

^{19}F Nmr Spectra. The ^{19}F nmr spectrum of $ClF_5 \cdot 1.36SbF_5$ in acidified HF has previously been discussed.[7] The observation of two signals of equal intensity at −256 and −274 ppm, respectively, relative to $CFCl_3$ below −60° is strong evidence for a ClF_4^+ cation having two nonequivalent sets of two fluorine ligands.[7]

The ^{19}F nmr spectrum of $BrF_5 \cdot 2SbF_5$ in HF or HF-AsF_5 solution showed, between +20 and −80° for the BrF part of the spectrum, a single resonance at −197 ppm relative to external $CFCl_3$. In the HF-SbF region at 20° a very broad unresolved common peak centered at about 130 ppm was observed indicating fast exchange between the solvent and the anion. In more dilute solutions the HF-$Sb_2F_{11}^-$ signal shifted to about 150 ppm and gained in relative intensity whereas the chemical shift of the BrF_4^+ resonance remained constant. At lower temperatures (−60 to −80°) the peak in the SbF region started to separate into several peaks at about 76, 93, 120, and 127 ppm. Whereas the identity of these peaks could not definitely be established, the chemical shifts of some of them are similar to those (93, 120, and 142 ppm) previously found for $Sb_2F_{11}^-$ in HF solution.[20] The chemical shift of −197 ppm found for BrF_4^+ in HF differs significantly from that (−167 ppm) reported by Meinert and Gross for the melt.[11] This discrepancy might be caused by the different environment.

A solution of $IF_5 \cdot SbF_5$ in HF exhibited between +20 and −80° only one signal at 133 ppm indicating rapid exchange between all species present. Acidification of the solvent with AsF_5 did not influence the exchange rates sufficiently to cause a separation into individual signals.

The fact that the inter- and intramolecular exchange rates decrease in the order $IF_5 \cdot SbF_5 > BrF_5 \cdot 2SbF_5 > ClF_5 \cdot SbF_5$ might be explained by the decreasing size and polarizability of the corresponding halogen pentafluorides.

Vibrational Spectra. The vibrational spectra of the halogen pentafluoride-Lewis acid adducts are shown in Figures 1-10. The infrared spectrum of the $ClF_4^+PtF_6^-$ and $ClF_6^+PtF_6^-$ mixture has previously been given[6] and, hence, is not shown here. The observed frequencies are listed in Tables I and II.

Since the ionic nature and structure of the Lewis acid adducts of ClF_5, BrF_5, and IF_5 have been established by X-ray diffraction,[12,16,17] nmr,[7] and conductivity studies,[13] the discussion of their vibrational spectra can be kept relatively short. The main objective of this study is to demonstrate that the vibrational spectra are consistent with the known

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(20) R. J. Gillespie and K. C. Moss, *J. Chem. Soc. A*, 1170 (1966); M. Azeem, M. Brownstein, and R. J. Gillespie, *Can. J. Chem.*, 47, 4159 (1969).

Table I. Vibrational Spectra of $ClF_5 \cdot$(Lewis acid) Adducts and Their Assignments Compared to That[a] of SF_4

Obsd freq (cm^{-1}) and rel intens[b]								Assignment (point group)[c]	
SF_4(g)		$ClF_5 \cdot AsF_5$[f]		$ClF_5 \cdot SbF_5$[g]			$ClF_4^+PtF^-$ $ClF_6^+PtF_6^-$[h]		
					Raman				
Ir[d]	Raman[e]	Ir	Raman	Ir	Solid	HF soln	Ir	XF_4 (C_{2v})	YF_6 (O_h)
1744 vw 1617 vw		1600 vw, br						$\nu_1 + \nu_8$ (B_2)	
		1390 vw							720 + 671
1281 w		1340 vw		1335 w			1330 w, br	$\nu_2 + \nu_6$ (B_1)	$\nu_1 + \nu_3$ (F_{1u})
867 s	865 (0+)	827 s	830 (2.5)	825 s, sh	822 (2.5)	825 sh	790 vs	ν_8 (B_2)	
891 s	888 (9.0)	796 vs	799 (10)	803 vs	802 (10)	802 (10)		ν_1 (A_1)	
730 vs	730 (0+)							ν_6 (B_1)	
		720 vs	711 (0.3)	669 vs	670 (0.5–2.5)		670–620 vs		ν_3 (F_{1u})
		699 s	695 (0.3)	648 vs	653 (8.6)	656 (8)			ν_1 (A_{1g})
		673 ms	671 (8.0)						
		584 m 576 mw	579 (4)	579 w	583 (0.6–4)				ν_2 (E_g)
558 m	553 (10)	568 w	567 (6.5)		568 (5.5)	574 (5.5)		ν_2 (A_1)	
		553 w							ν_2 (E_g)
532 ms	532 (4.0)	536 mw	538 (2.5)	535 ms*	534 (5)*	537 (1)*	545 s, br*	ν_7 (B_2) and	ν_2 (E_g)*
464 vw	475 (1.2)	511 ms**	519 (1)	510 sh	515 (0.2)	515 (0+)	500 s	ν_3 (A_1) and	ν(AsFAs)**
	414 (0+)		473 (1)		475 (0.4)	475 (0.4)		ν_5 (A_2)	
353 ms	350 (0+)	395 s	399 (0.6)	386 m			383 s	ν_9 (B_2)	
				280 s			271 s		ν_4 (F_{1u})
			372 (2.7)		279 (1.4)	277 (1)			ν_5 (F_{2g})
226 w	223 (1.0)		237 (1.1)		235 (0.5)	245 sh		ν_4 (A_1)	

[a] R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, **54**, 344 (1971). [b] Uncorrected Raman intensities. [c] Assignments for the anion bands are made assuming for simplicity octahedral symmetry, although in most cases the actual symmetry is expected to be lower than O_h. [d] I. W. Levin and C. V. Berney, *J. Chem. Phys.*, **44**, 2557 (1966). [e] K. O. Christe and W. Sawodny, *ibid.*, **52**, 6320 (1970). [f] The low-temperature infrared spectrum indicates the presence of substantial amounts of $As_2F_{11}^-$. [g] The listed frequencies are those obtained for $ClF_5 \cdot 1.08SbF_5$. The relative intensities of the 670-, 583-, and to a lesser extent the 534-cm^{-1} Raman bands varied, indicating different degrees of deviation of SbF_6^- from symmetry O_h or slight inhomogeneity of the sample. [h] Reference 6.

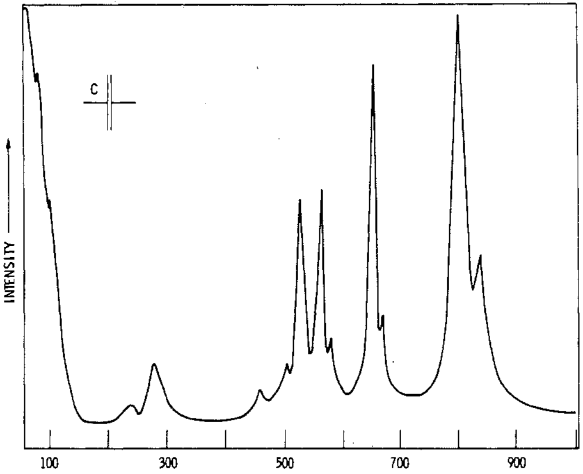

Figure 1. Raman spectrum of solid $ClF_5 \cdot 1.08SbF_5$ (sample I) contained in a Teflon FEP capillary. Exciting line was 5145 Å. C indicates spectral slit width.

ionic structures, to define the principal bands of the $HalF_4^+$ cations, and to examine the plausibility of the given assignments by comparison with the known spectra of isoelectronic chalcogen tetrafluorides and by force field computations.

Chlorine Pentafluoride Adducts. The infrared spectra of the $ClF_5 \cdot xSbF_5$ adducts are relatively insensitive to changes in the ClF_5:SbF_5 combining ratio owing to the relative broadness of the bands due to the Sb-F vibrations (see Figure 3). In the corresponding Raman spectra (Figures 1 and 2), however, slight changes in the composition of the adducts or in the procedures used for their preparation may cause significant changes. As expected, sample I, having the composition $ClF_5 \cdot 1.08SbF_5$, shows the simplest spectrum. With increasing SbF_5 content and tempering, features attributable to polymeric anions such as $Sb_2F_{11}^-$ become more pronounced. Similarly, the low-temperature infrared spectrum of the $ClF_5 \cdot AsF_5$ adduct (Figure 5) indicates the presence of the $As_2F_{11}^-$ anion.[21,22] However, the $As_2F_{11}^-$ anion is much less stable than $Sb_2F_{11}^-$ resulting in the facile removal of the second AsF_5 molecule under the conditions[3] used for the synthesis of the Raman sample (1:1 adduct).

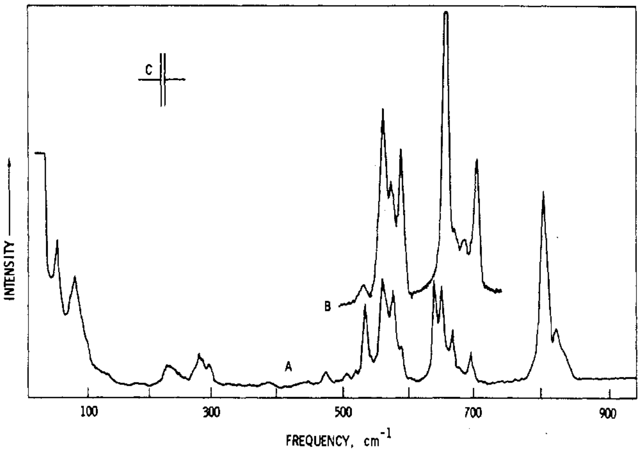

Figure 2. Raman spectrum of solid $ClF_5 \cdot 1.36SbF_5$. Traces A and B show samples II and III, respectively. Kel-F capillaries were used as containers with 5145-Å excitation.

The vibrational assignments for ClF_4^+ in point group C_{2v} (see Table I) were made by analogy with isoelectronic SF_4[23-26]

(21) K. O. Christe and W. Maya, *Inorg. Chem.*, **8**, 1253 (1969).

(22) P. A. W. Dean, R. J. Gillespie, R. Hulme, and D. A. Humphreys, *J. Chem. Soc. A*, 341 (1971).

(23) I. W. Levin and C. V. Berney, *J. Chem. Phys.*, **44**, 2557 (1966).

(24) K. O. Christe and W. Sawodny, *J. Chem. Phys.*, **52**, 6320 (1970).

(25) R. A. Frey, R. L. Redington, and A. L. K. Aljibury, *J. Chem. Phys.*, **54**, 344 (1971).

Table II. Vibrational Spectra of $BrF_5 \cdot 2SbF_5$ and $IF_5 \cdot SbF_5$ Compared to Those of SeF_4 and TeF_4

Obsd freq (cm^{-1}) and rel intens[a]						Obsd freq (cm^{-1}) and rel intens[a]				
SeF_4[b]		$BrF_5 \cdot 2SbF_5$					$IF_5 \cdot SbF$			
		Solid		HF soln		TeF_4[c]	Solid		HF soln	Tentative assignment for
Ir	Raman	Ir	Raman	Raman	Tentative assignment for XF_4 in C_{2v}	Ir	Ir	Raman	Raman	XF_4 in C_{2v}
723 s	724 w, sh	730 sh	736 sh		ν_8 (B_2)	695 m	728 sh	729 (9)	704 (10)	ν_1 (A_1)
744 ms	749 vs, p		723 (10)	680 sh	ν_1 (A_1)	682 m	719 m	720 (1.6)		ν_8 (B_2)
622 vs		690 vs	704 (2.4)		ν_6 (B_1) + $Sb_2F_{11}^-$ (?)		691 sh	693 (2.2)	663 (8)	SbF_6^- + ν_6(B_1)
		655 vs	660 sh	660 (10)	$Sb_2F_{11}^-$	587 s	668 sh	662 (10)		
		645 sh	651 (6.9)				655 vs			
				600 sh						
	574 s, p	606 mw	606 (4.8)	575 (5)	ν_2 (A_1)		625 m, sh	625 (3)		
		568 m	555 (3.3)		$Sb_2F_{11}^-$	572 vw		614 (4)	609 (9)	ν_2 (A_1)
		540 mw	545 sh	540 (1)			567 w, sh	569 (1.5)	570 sh	SbF_6^-
		488 ms		490 (1)	Sb-F-Sb		520 vw, sh	521 (1.3)		
405 m	400 w	419 m		426 (2)	ν_7 (B_1)	333 w	388 mw	385 (0.8)		ν_7 (B_1)
	366 m, p		385 (0.5)		ν_3 (A_1)	293 mw	345 w	341 (0.4)	325 sh	ν_3 (A_1)
250 vw		369 mw	369 (0.5)	363 (5)	ν_9 (B_2)		311 w	316 (0.2)		ν_9 (B_2)
			295 (1)	280 sh	$Sb_2F_{11}^-$			299 (0.9)		SbF_6^-
			264 (0.7)				288 m	285 (0+)	280 sh	
			230 (0.5)	235 (0+)			263 mw	259 (0.5)	250 sh	
160 vw	162 w, p		219 (0.2)		ν_4 (A_1)			151 (0.4)		ν_4 (A_1)
			45 (1.5)		Lattice mode			72 (1)		Lattice modes
								42 (6)		

[a] Uncorrected Raman intensities. [b] Best values and assignments were taken from K. Ramaswamy and S. Jayaraman, *Indian J. Pure Appl. Phys.*, 8, 625 (1970); L. E. Alexander and I. R. Beattie, *J. Chem. Soc., Dalton Trans.*, 1745 (1972); C. J. Adams and A. J. Downs, *Spectrochim. Acta, Part A*, **28**, 1841 (1972). [c] From the last reference given in footnote *b*.

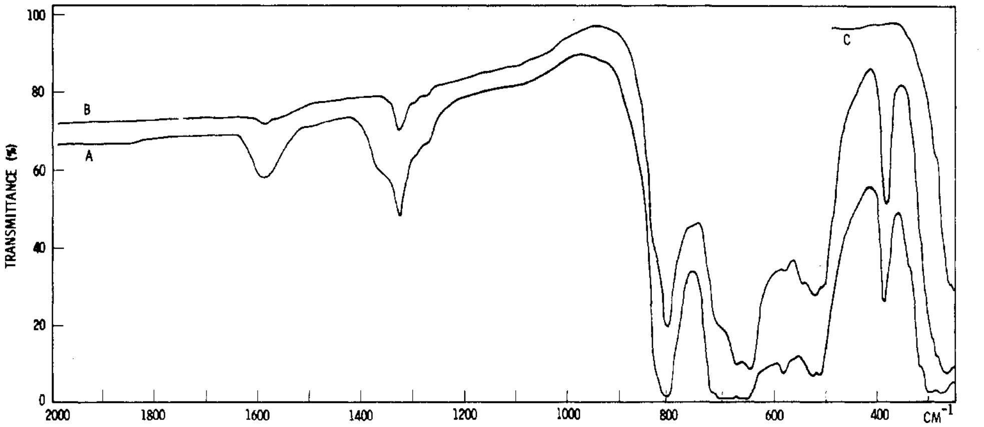

Figure 3. Infrared spectra of solid $ClF_5 \cdot xSbF_5$ as dry powder between AgBr plates: trace A, sample II; trace B, sample I; trace C, AgBr window background.

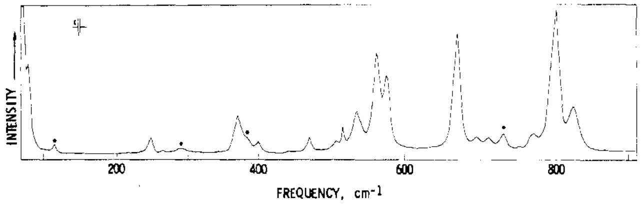

Figure 4. Raman spectrum of solid $ClF_5 \cdot AsF_5$ contained in a Teflon FEP capillary. Exciting was line 5145 Å. Bands marked by an asterisk are due to the Teflon tube.

and by comparison with the known spectra of compounds containing AsF_6^-,[21,27-29] $As_2F_{11}^-$,[21,22] SbF_6^-, and $Sb_2F_{11}^-$ [20,28,30-33] anions. In solids, the deviation of the spectra of these anions from those expected for the isolated octahedral ions is very common. It can be caused by effects such as site symmetry lowering, slight distortion of the octahedrons owing to crystal packing and anion-cation interac-

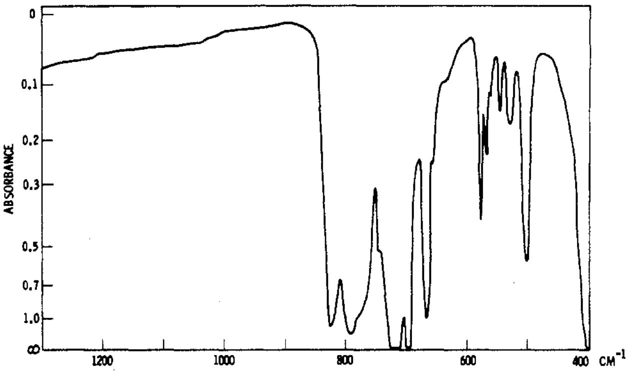

Figure 5. Low-temperature infrared spectrum of solid $ClF_5 \cdot AsF_5$. Window material AgCl.

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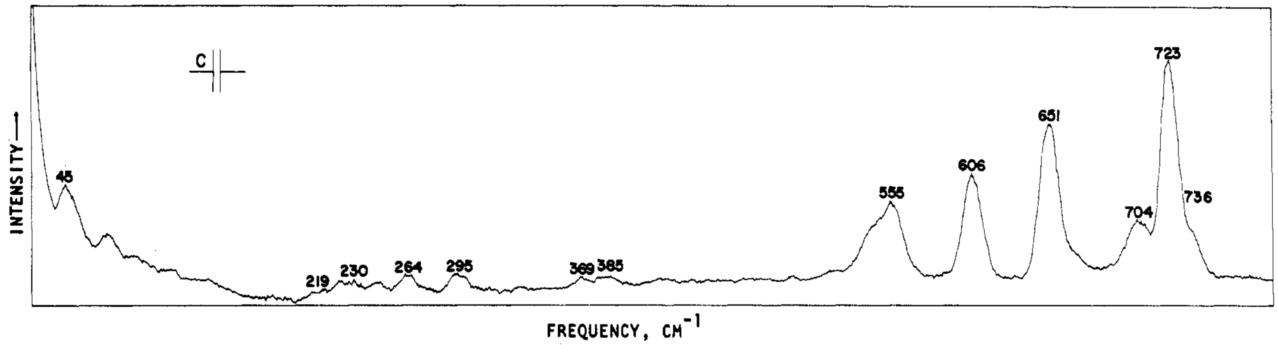

Figure 6. Raman spectrum of solid $BrF_5 \cdot 2SbF_5$ contained in a glass tube with a hollow inside glass cone. Exciting line was 5145 Å using the axial viewing-transverse excitation technique.

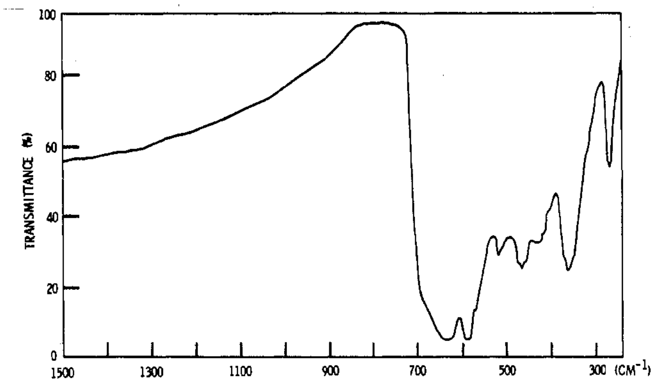

Figure 7. Infrared spectrum of solid $BrF_5 \cdot 2SbF_5$ as a dry powder between AgCl plates.

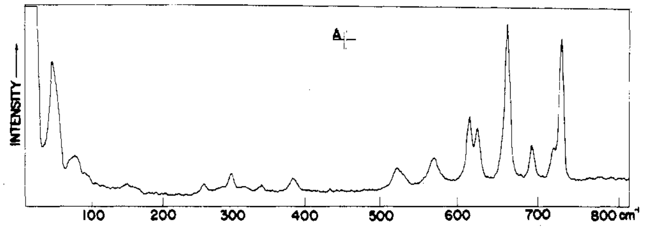

Figure 8. Raman spectrum of solid $IF_5 \cdot SbF_5$ contained in a glass tube with a hollow inside glass cone using 5145-Å excitation.

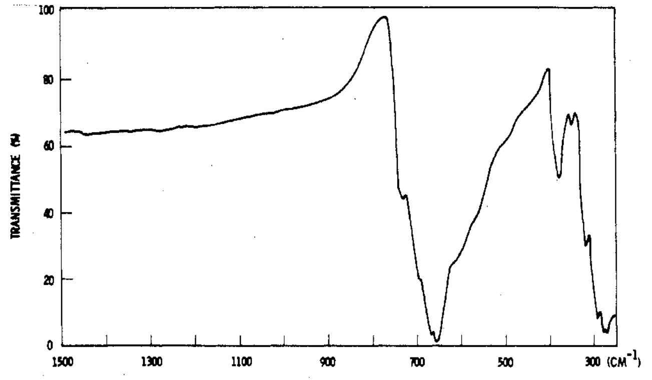

Figure 9. Infrared spectrum of solid $IF_5 \cdot SbF_5$ as a dry powder between AgBr plates.

tion, and the tendency to form polymeric anions. Unfortunately, the splittings, frequencies, and relative intensities of these bands strongly vary from compound to compound. Therefore, reliable assignments for the cations require the recording of spectra of adducts containing different anions or of solution spectra which usually show the bands characteristic of the unperturbed ions. Contrary to the highly symmetric octahedral XF_6^- anions, the ClF_4^+ cation of symmetry C_{2v} should be very little influenced by solid-state effects because it possesses already its maximum number ($3n - 6 = 9$) of modes.

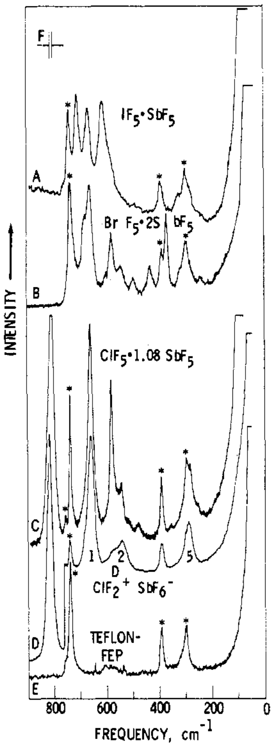

Figure 10. Raman spectra of HF solutions of $IF_5 \cdot SbF_5$ (trace A), $BrF_5 \cdot 2SbF_5$ (trace B), $ClF_5 \cdot 1.08SbF_5$ (trace C), and $ClF_2^+SbF_6^-$ (trace D; the numbers indicate ν_1, ν_2, and ν_5 of octahedral SbF_6^-) in Teflon FEP capillaries using 4880-Å excitation. Trace E shows the spectrum of an empty capillary; Teflon bands are marked by and asterisk. F indicates spectral slit width.

For the ClF_5 adducts sufficient experimental data (see Table I) are available to distinguish the anion from the cation bands. As can be seen, the spectrum of ClF_4^+ is very similar to that of isoelectronic SF_4.[23,24] This close resemblance is comparable to that found for the isoelectronic pairs SF_2O-ClF_2O^+,[34] SF_2O_2-$ClF_2O_2^+$,[35] SF_6-ClF_6^+,[6] and SF_5^--ClF_5[36] and, therefore, is not surprising. For ClF_4^+, the assignment to the individual modes was made by analogy with SF_4. For SF_4, the assignment of Frey, *et al.*,[25] was used which was recently confirmed[26] by mean-square amplitudes of vibration and force field computations.

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Table III. Observed Frequencies (cm^{-1}), Approximate Description of Modes, and Computed Symmetry and Most Important Internal Force Constants[a] of ClF_4^+

					ClF_4^+	ClF_3[b]
A_1	ν_1	800	ν sym eq	$F_{11} = f_r + f_{rr}$	4.54	
				$F_{13} = \sqrt{2}f_{r\beta}$	0.24	
				F_{14}	0.05	
	ν_2	571	ν sym ax	$F_{22} = f_R + f_{RR}$	3.65	
	ν_3	510	δ sciss eq	$F_{33} = f_\beta$	2.65	
				F_{34}	−0.03	
	ν_4	237	δ sciss ax	$F_{44} = 0.31f_\alpha + 0.69f_\gamma$[c]	0.41	
A_2	ν_5	475	τ	$F_{55} = f_\alpha + f_{\alpha'''} - f_{\alpha'} - f_{\alpha''}$	2.08	
B_1	ν_6	795	ν asym ax	$F_{66} = f_R - f_{RR}$	3.23	
				$F_{67} = \sqrt{2}(f_{R\alpha} - f_{R\alpha'})$	0.50	
	ν_7	537	rocking	$F_{77} = f_\alpha - f_{\alpha''} + f_{\alpha'} - f_{\alpha'''}$	2.26	
B_2	ν_8	829	ν asym eq	$F_{88} = f_r - f_{rr}$	4.61	
				$F_{89} = \sqrt{2}(f_{r\alpha} - f_{r\alpha'})$	0.21	
	ν_9	385	δ sciss ax out of plane	$F_{99} = f_\alpha - f_{\alpha'''} - f_{\alpha'} + f_{\alpha''}$	2.54	
				f_r	4.58	4.19
				f_R	3.44	2.70
				f_{rr}	−0.04	
				f_{RR}	0.21	0.36

[a] Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch–bend interaction constants in mdyn/radian. [b] Reference 25. [c] In addition to interaction constants which are not listed.

In the spectra of the ClF_5 adducts, nine bands are found which might be attributed to ClF_4^+. Of these, the intense infrared and Raman bands at about 800 cm^{-1} obviously represent the symmetric equatorial ClF_2 stretching mode ν_1. The moderately intense Raman and strong infrared bands at about 825 cm^{-1} then must be the antisymmetric equatorial stretch ν_8. The symmetric axial stretch, ν_2, falls within the range of the ν_2 anion bands, but is clearly identified by the strong Raman band at 574 cm^{-1} in the HF solution. The antisymmetric axial stretching mode, ν_6, should be of very high intensity in the infrared and of very low intensity in the Raman spectrum. By comparison with other pseudo-trigonal-bipyramidal molecules such as ClF_3[37] or ClF_3O_2,[38] it should occur above 700 cm^{-1}. Since there is no additional yet unassigned strong infrared band above this frequency in all of the observed spectra, a coincidence with ν_1 must be assumed. The assignment of ν_4 and ν_9 to the bands at 237 and 385 cm^{-1}, respectively, is clear-cut and needs no further comment. This leaves us with three frequencies, 537, 515, and 475 cm^{-1}, for the assignment to ν_7, ν_3, and ν_5. Since the 475-cm^{-1} band appears to be inactive in the infrared spectrum, we ascribe it to ν_5 which ideally should be forbidden in the infrared spectrum. Based on their relative Raman intensities, when compared to those of SF_4, we prefer to assign ν_3 and ν_7 to 515 and 537 cm^{-1}, respectively. The assignments for ν_3, ν_7, and ν_5 are somewhat tentative. However, a reassignment of these three deformational modes should, owing to their similar frequencies, be of minor influence on the principal force constants.

Force Constants. The method used for the computation of the ClF_4^+ force field has previously been described.[38] The following geometry was assumed for ClF_4^+: $r(Cl\text{-}F_{eq}) = 1.57$, $R(Cl\text{-}F_{ax}) = 1.66$ Å; $\alpha(F_{ax}ClF_{eq}) = 90$, $\beta(F_{eq}ClF_{eq}) = 97$, $\gamma(F_{ax}ClF_{ax}) = 180°$. The symmetry coordinates were identical with those previously given[23,24] for isoelectronic SF_4, except for $S_3 = \Delta\beta$ and $S_4 = 0.2765\Sigma\alpha_i - 0.8332\gamma$, which are different owing to $\gamma = 180°$ in ClF_4^+ and were found numerically by a previously described[39] machine method.

A general valence force field for ClF_4^+ contains 17 symmetry force constants. Since only nine frequency values are available for their computation, a unique force field cannot be determined. Inspection of the G matrices of ClF_4^+ shows that in the A_1 block G_{12}, G_{23}, and G_{24} are zero and, therefore, F_{12}, F_{23}, and F_{24} can be neglected.[40]

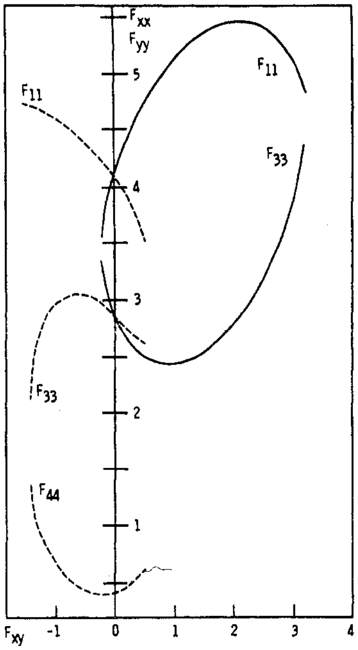

Figure 11. Force constant ellipses for ClF_4^+. The solid and broken curves represent the solutions for F_{11}, F_{33}, and F_{44} as a function of F_{34} and for F_{11} and F_{33} as a function of F_{13}, respectively. Dimensions are in mdyn/Å.

The influence of the remaining off-diagonal F terms on the diagonal F values was determined by computing their values as a function of the off-diagonal F terms. The resulting halves of the force constant ellipses are shown in Figures 11 and 12 and represent the possible mathematical solutions of the force field. It has previously been shown[40] that the most probable range for F_{xy} is limited by the extremal values F_{yy} and F_{xy} = minimum. Inspection of Figures 11 and 12 reveals that even with this constraint small variation of certain off-diagonal force constants can strongly influence the values of the diagonal force constants. Consequently, an uncertainty of about ±0.5 mdyn/Å should be assumed for

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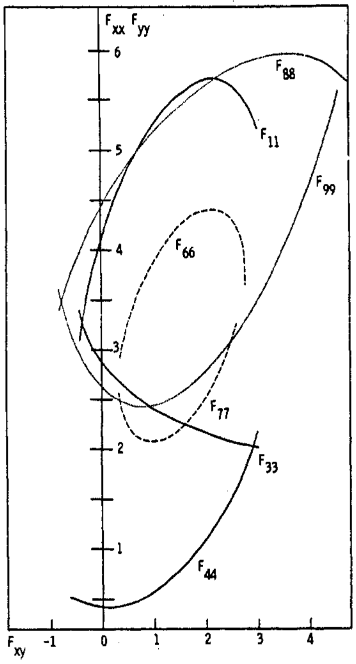

Figure 12. Force constant ellipses for ClF_4^+. The solid, broken, and dotted curves represent the solutions for F_{11}, F_{33}, and F_{44} as a function of F_{14}, for F_{66} and F_{77} as a function of F_{67}, and for F_{88} and F_{99} as a function of F_{89}, respectively.

the stretching force constants F_{11}, F_{66}, and F_{88}. However, in spite of these relatively larger uncertainties, Figures 11 and 12 clearly show that the symmetry force constants involving the equatorial bonds (*i.e.*, F_{11} and F_{88}) are significantly larger than those involving the axial bonds (*i.e.*, F_{22} and F_{66}). The frequencies used for the force constant computations of ClF_4^+ are listed in Table III, together with our preferred force field, obtained by the method of stepwise coupling.[41] The fact that ClF_4^+ and isoelectronic SF_4 show similar force fields is not surprising in view of their similar frequencies and *G* matrices.

The significant difference in covalent bond strength between equatorial (4.6 mdyn/Å) and axial (3.4 mdyn/Å) bonds in ClF_4^+ is in excellent agreement with a generalized bonding scheme previously discussed[42] for a large number of halogen fluorides. It suggests that the bonding in ClF_4^+ might be explained, as previously described for the related pseudo-trigonal-bipyramidal species ClF_3, ClF_3O,[39] and ClF_3O_2,[38] by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand) is mainly due to an sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semiionic three-center four-electron pp σ bond.[43-45]

$BrF_5 \cdot 2SbF_5$ Adduct. The predominantly ionic nature of $BrF_5 \cdot 2SbF_5$ has previously been established[12] by a single-crystal X-ray diffraction study. Owing to the large number of fundamentals expected for $BrF_4^+Sb_2F_{11}^-$ and to the inavailability of other salts containing the BrF_4^+ cation only tentative assignments can be made for BrF_4^+. These are listed in Table II and are based on comparisons with those reported for isoelectronic SeF_4[46-48] and those of other salts containing the $Sb_2F_{11}^-$ anion.[20,28,31,33,49] Our Raman spectrum[1] of solid $BrF_4^+Sb_2F_{11}^-$ has in the meantime been confirmed by Surles, *et al.*,[13] and the proposed assignments[1,13] agree for most of the fundamentals. Since the crystal structure of $BrF_4^+Sb_2F_{11}^-$ is known[12] and the assignments for BrF_4^+ are tentative, no force constant computations were carried out for BrF_4^+.

Table IV. Comparison of the Fundamental Vibrations (cm^{-1}) of ClF_4^+, BrF_4^+, and IF_4^+ with Those of Isoelectronic SF_4, SeF_4, and TeF_4, Respectively

		ClF_4^+	BrF_4^+	IF_4^+	SF_4	SeF_4	TeF_4
A_1	ν_1	800	723	704	891	749	695
	ν_2	571	606	609	553	574	572
	ν_3	510	385	341	475	366	293
	ν_4	237	216	151	226	162	[151][a]
A_2	ν_5	475			414		
B_1	ν_6	795	704	655	730	622	587
	ν_7	537	419	385	532	400	333
B_2	ν_8	829	736	720	867	723	682
	ν_9	385	369	316	353	250	[184.8][a]

[a] Computed values.

$IF_5 \cdot SbF_5$ Adduct. Two independent single-crystal X-ray diffraction studies[16,17] have shown that the $IF_5 \cdot SbF_5$ has the predominantly ionic structure $IF_4^+SbF_6^-$, although the bond lengths and angles found by the two groups for IF_4^+ differ somewhat. The observed vibrational spectrum of $IF_5 \cdot SbF_5$ (see Table II) is consistent with such a predominantly ionic structure. The bands were tentatively assigned by comparison with those of TeF_4,[48] which is isoelectronic with IF_4^+, and those reported for similar SbF_6^- salts[20,30] containing an SbF_6^- anion distorted from symmetry O_h.[50] Our Raman spectrum of $IF_5 \cdot SbF_5$ is in good agreement with that reported[18] by Shamir and Yaroslavski. However, their interpretation suffers from the incorrect assumption of an ideal octahedral SbF_6^- anion. As for $BrF_4^+Sb_2F_{11}^-$, the tentative nature of the IF_4^+ assignments does not warrant a force constant treatment.

In summary, all the experimental data, *i.e.*, X-ray diffraction data, vibrational and ^{19}F nmr spectra, and conductivity measurements, available for the halogen pentafluoride-Lewis acid adducts are consistent with predominantly ionic structures containing $HalF_4^+$ cations. The structure of these cations can be derived from a pseudo trigonal bipyramid with a free valence electron pair occupying one of the equatorial positions. Deviation from this structure increases, as expected, with increasing size and polarizability of the halogen central atom. This results in a decrease of the axial F-Hal-F angle and increasing F bridging from the ClF_5 to the IF_5 adducts. A comparison of the fundamentals assigned to the $HalF_4^+$ cations with those of the isoelectronic chalcogen tetrafluoride series (see Table IV) shows consistent trends and satisfactory agreement.

Acknowledgment. We are indebted to Dr. E. C. Curtis for assistance in the force constant computations, to Drs. D. Pilipovich, C. J. Schack, and R. D. Wilson for their help, and to Dr. D. Lawson for the use of the Raman spectrometer. K. O. C. is indebted to the Office of Naval Research for financial support.

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