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Raman Spectral Studies of α-$XeF_3^+SbF_6^-$, β-$XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}^-$, $XeF_3^+AsF_6^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}^-$, and $XeO_2F^+Sb_2F_{11}^-$

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We have studied the reactions of SbF_5 with XeF_4, $XeOF_4$, and XeO_2F_2 and also the reaction of AsF_5 with XeF_4. The Raman spectra of the solid products and their solutions in HF or SbF_5 indicate that they may be formulated as the salts α-$XeF_3^+SbF_6^-$, β-$XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}$, $XeF_3^+AsF_6^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}$ and $XeO_2F^+Sb_2F_{11}^-$. Complete assignments of the spectra have been made for the cations. These assignments are consistent with the known T-shaped structure of XeF_3^+ and they indicate that $XeOF_3^+$ has a structure based on a trigonal bipyramid with the oxygen and one of the fluorines occupying two of the equatorial positions and that XeO_2F^+ has a pyramidal structure. The Raman spectra also provide evidence for the existence of fluorine bridges between the cation and the anion in these compounds. In the SbF_6^- compounds the O_h symmetry of the isolated anion is reduced by the fluorine bridges and in the majority of the compounds bands are observed which may reasonably be assigned to the vibrations of the Xe---F---M bridge. As the crystal structures of $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$ are known, it was possible to carry out a factor-group analysis in these cases which accounts well for all the bands observed in the Raman spectra of the solids.

Introduction

A large number of complexes of XeF_2 and XeF_6 have been prepared with a variety of strong Lewis acids,[1] e.g., pentafluorides such as SbF_5 and RuF_5, and it has been established by several techniques, including Raman and ^{19}F NMR spectroscopy and x-ray crystallography that these complexes have ionic structures in which the cations are XeF^+ [2-5] and XeF_5^+ [5-14] or the fluorine-bridged cations $Xe_2F_3^+$ [2,3,7,15] and $Xe_2F_{11}^+$.[10,16,17] There has been, however, a marked lack of information on possible similar complexes of XeF_4 and the oxyfluorides $XeOF_4$ and XeO_2F_2. Indeed, because XeF_4 was found not to form stable complexes with AsF_5,[18] IrF_5,[18] and RuF_5,[19] it was concluded by Bartlett and co-workers that XeF_4 is a weaker base than either XeF_2 or XeF_6. Nevertheless, there was some evidence that XeF_4 and $XeOF_4$ do form complexes with SbF_5. Cohen and Peacock[20a] reported that xenon tetrafluoride or mixtures of xenon tetrafluoride and difluoride dissolve in antimony pentafluoride with gas evolution to give green solutions. On removing the solvent at 25 °C they obtained an easily decomposed white solid in addition to the yellow $XeF_2{\cdot}2SbF_5$ complex, but they were unable to isolate the white compound in a pure state. They assumed that it was the adduct $XeF_4{\cdot}2SbF_5$, but the composition was never determined. Some conductivity evidence[20b] has been given for compound formation between XeF_4 and PF_5 and between AsF_5 and SbF_5. However, the conclusions from this work that SbF_5 forms the compounds $2XeF_4{\cdot}SbF_5$ and $XeF_4{\cdot}4SbF_5$ are not in agreement with subsequent work. Several years ago, Selig[21] reported the formation of the stable complex $XeOF_4{\cdot}2SbF_5$, but no structural information was obtained for this compound. There has been no previous information on complexes of XeO_2F_2.

We have now shown that XeF_4, $XeOF_4$, and XeO_2F_2 all form complexes with antimony pentafluoride and that these complexes contain the cations XeF_3^+, $XeOF_3^+$, and XeO_2F^+. XeF_4 also forms a rather unstable complex with AsF_5.

Preliminary reports of our results have been given in two brief communications.[22,23] Since then we have published[24] the details of the x-ray crystallographic determination of the structure of β-$XeF_3^+SbF_6^-$ and of the preparation and ^{19}F NMR spectra of solutions of the cations XeF_3^+, $XeOF_3^+$, and XeO_2F^+.[25] Subsequent to our preliminary communications, Bartlett and co-workers published their determination of the structure of $XeF_3^+Sb_2F_{11}^-$ [26] and also a paper on the preparation and Raman spectra of XeF_3^+ and $XeOF_3^+$ salts.[27] The x-ray crystallographic studies have shown that β-$XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$ both contain the T-shaped XeF_3^+ cation, which is strongly fluorine-bridged to the anion. The present paper reports the Raman spectra of α- and β-$XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}^-$, and $XeO_2F^+Sb_2F_{11}^-$. Assignments of the vibrational spectra have been made for the cations XeF_3^+, $XeOF_3^+$, and XeO_2F^+. In the cases of β-$XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$, factor-group analyses of the spectra based on the known crystal structures have been carried out.

Results and Discussion

The Complexes $XeF_4{\cdot}SbF_5$ and $XeF_4{\cdot}2SbF_5$. These two complexes are readily prepared by direct reaction between XeF_4 and SbF_5 at room temperature, the latter by using an excess of SbF_5 and the former by fusing $XeF_4{\cdot}2SbF_5$ with an excess of XeF_4 at 80 °C.[25] The compounds are stable yellow and pale yellow-green solids, respectively.

Another form of $XeF_4{\cdot}SbF_5$ may be prepared from SbF_5 and excess XeF_4 in anhydrous HF. Crystallization from solution at room temperature followed by removal of excess solvent and XeF_4 under vacuum yielded pale yellow-green crystalline $XeF_4{\cdot}SbF_5$. We designate the high-temperature form, prepared at 80 °C, α-$XeF_3^+SbF_6^-$ and the room-temperature form β-$XeF_3^+SbF_6^-$. The Raman spectra of the compounds $XeF_3^+Sb_2F_{11}^-$, $XeF_3^+AsF_6^-$, and α- and β-$XeF_3^+SbF_6^-$ are given in Table I and Figures 1 and 2.

The spectra are consistent with the ionic structures $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$ which have now been established by x-ray crystallography.[24,26] The XeF_3^+ ion is T shaped with C_{2v} symmetry and has a structure which is quite similar to that of the "isoelectronic" molecules ClF_3 and BrF_3. Six normal modes, all Raman and infrared active, are expected for the XeF_3^+ cation with C_{2v} symmetry, namely, three a_1 modes, two b_1 modes, and and one b_2 mode. Assignments for these modes and also for the anion modes are given in Table I. They are made on the basis of published spectra for the anions and the spectra of related molecules including, in

Table I. Raman Spectra and Assignments for α-$XeF_3^+SbF_6^-$, β-$XeF_3^+SbF_6^-$, $XeF_3^+AsF_6^-$, and $XeF_3^+Sb_2F_{11}^-$

Freq, cm^{-1}					
α-$XeF_3^+SbF_6^-$	β-$XeF_3^+SbF_6^-$	$XeF_3^+AsF_6^-$	XeF_3^+ assignments		$XeF_3^+Sb_2F_{11}^-$ freq, cm^{-1}
643 (100)[a]	663 (100), 643 (56)	643 (85)	$\nu_1(a_1)$	$\nu(Xe-F_e)$	655 (39)
573 (88)[a]	564 (94), 576 (94)	571 (100)	$\nu_2(a_1)$	$\nu_{sym}(Xe-F_a)$	583 (100)
205 (2)	199 (2), 212 (3)		$\nu_3(a_1)$	$\delta_{sym}(F_a-Xe-F_a)$	209 (6)
609 (9)	604 (21), 612 (25)	607 (38), 608 (58)	$\nu_4(b_1)$	$\nu_{asym}(Xe-F_a)$	619 sh
305 sh	318 (2), 335 (2)	316 (18)	$\nu_5(b_1)$	$\delta_{asym}(F_a-Xe-F_a)$	305 sh
			$\nu_6(b_2)$	$\delta(XeF_3)$, out of plane	

Freq, cm^{-1}					
α-$XeF_3^+SbF_6^-$	β-$XeF_3^+SbF_6^-$	$XeF_3^+AsF_6^-$	MF_6^- (C_{4v}) assignments		$Sb_2F_{11}^-$ freq, cm^{-1}
664 (4)	659 (34)	672 (12)	$\nu_1(a_1)$	$\nu(MF_a)$	717 (3)
649 (9)	629 (44)	629 (6)	$\nu_2(a_1)$	$\nu_{sym}(MF_4)$	700 (21)
557 (<1)	624 (65)	590 (2)	$\nu_5(b_1)$	$\delta_{sym}(MF_4)$, out of plane	677 (48)
449 (18)	514 (25)	465 (18)	$\nu_4(a_1)$	$\nu(M---F)$	644 (14)
688 (27)	689 (6)	714 (18)	$\nu_8(e)$	$\nu_{asym}(MF_4)$	651 sh
270 (8)	271 (5)	418 (4)	$\nu_3(a_1)$	$\delta_{sym}(MF_4)$, out of plane	634 (72)
362 (<1)	360 (11)	353 (4)	$\nu_{11}(e)$	$\delta(F---MF_4)$	629 sh
		342 (15)	$\nu_7(b_2)$	$\delta_{sym}(MF_4)$, in plane	586 sh
289 sh	287 (2)	386 (11)			578 sh
284 (4)		384 (4)	$\nu_9(e)$	$\delta(F_a-MF_4)$	550 (39)
186 (2)					541 sh
299 sh	296 (8)		$\nu_6(b_1)$	$\delta_{sym}(MF_4)$, out of plane	489 (5)
232 (1)	257 (1)		$\nu_{10}(e)$	$\delta_{asym}(MF_4)$, in plane	360 (10)
108 (8)	129 (11), 138 (13)	158 (4), 106 (3)		$\nu(Xe---F)$	336 sh
155 (4)				$\delta(Xe---F---M)$	334 (14)
					329 (7)
					293 sh
					280 (5)
					267 sh
					233 (7)
					224 sh
					220 sh

[a] In a solution of $XeF_3^+Sb_2F_{11}^-$ in SbF_5 only ν_1 and ν_2 of XeF_3^+ were observed at 640 and 570 cm^{-1}, in addition to peaks due to SbF_5, and both were found to be polarized.

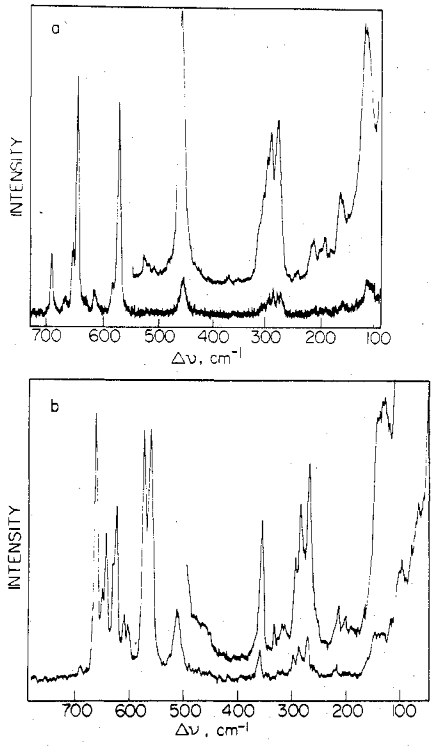


Figure 1. Raman spectra of (a) α- and (b) β-$XeF_3^+SbF_6$ at room temperature.

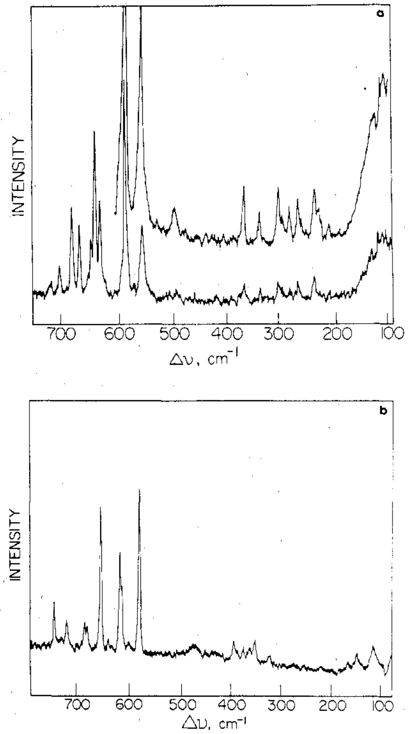


Figure 2. Raman spectra of (a) $XeF_3^+Sb_2F_{11}^-$ at −81 °C and (b) $XeF_3^+AsF_6^-$ at −100 °C.

particular, ClF_3,[28] BrF_3,[28] IF_3,[29] and the xenon fluorides XeF_2[30] and XeF_4.[31] The Raman spectrum of β-$XeF_3^+SbF_6^-$ is similar to that of the α modification but differs in that each line assigned to XeF_3^+ is split into a doublet. As will be shown later, this doubling of the lines can be reasonably attributed to factor-group splitting.

The assignments of the Xe–F stretching vibrations ν_1, ν_2, and ν_4 seem quite certain, but those of the three bending modes are more tentative because of the weakness of the observed

Table II. Comparison of Vibrational Frequencies (cm^{-1}) of XeF_3^+, ClF_3, BrF_3, and IF_3

$XeF_3^{+\,a}$	$ClF_3^{\,b}$		$BrF_3^{\,b}$			Assignment
Raman (solid)	Raman	IR	Raman	IR	$IF_3^{\,c}$ IR	(C_{2v})
644 (12)	752.1 744.7 } p, s	742 760 } s	675 p, s	688 682 } s	640 628 } s	$\nu_1(a_1)$
583 (100)	529.3	522 538 } m	552 p, vs	547 557 } w	550 mw	$\nu_2(a_1)$
209 (6)	321 337 } p, w	328 s	233^c p, w	242 s	228 m	$\nu_3(a_1)$
618 sh		702 vs	612 vvw	604 614 621 } vs	480 vs	$\nu_4(b_1)$
305 sh	431 dp, w	442 w		342 350 359 } vw	331 m	$\nu_5(b_1)$
		328		242 s	240 245 } s	$\nu_6(b_2)$

^{a} $XeF_3^+Sb_2F_{11}^-$; this work. ^{b} Reference 28. ^{c} Reference 29.

bands and overlap with anion bands. The two strongest bands at 643 and 573 cm^{-1} in the spectrum of α-$XeF_3^+SbF_6^-$ can be assigned to the Xe–F equatorial stretching mode $\nu_1(a_1)$ and the symmetrical Xe–F axial stretching mode $\nu_2(a_1)$, respectively. As expected, both of these peaks are strongly polarized in SbF_5 solution. These bands cannot be due to XeF_4, which has Raman bands at 543 and 502 cm^{-1}, nor are they due to XeF^+, which has a single strong band at 619 cm^{-1}.[2]

In the case of the Raman spectrum of β-$XeF_3^+SbF_6^-$, ν_1 and ν_2 can be reasonably assigned to the doublets at 663, 643 and 564, 576 cm^{-1}, respectively. It is to be noted that the average values of 653 and 570 cm^{-1} are close to the values observed for ν_1 and ν_2 of the α modification.

The antisymmetric X–F axial stretch $\nu_4(b_1)$ for BrF_3 and ClF_3 occurs at a frequency between those for ν_1 and ν_2. For this reason this mode, which is expected to have a low intensity in the Raman spectrum, is assigned to the peak at 609 cm^{-1} in the α phase and to peaks at 604 and 612 cm^{-1} in the β phase. The $\nu_5(b_1)$ mode has been assigned to the weak bands at 431, 350, and 331 cm^{-1} in the Raman spectrum of gaseous ClF_3[28] and the infrared spectra of BrF_3[28] and IF_3,[29] respectively. This mode is tentatively assigned to the shoulder observed at 305 cm^{-1} for $XeF_3^+Sb_2F_{11}^-$ and α-$XeF_3^+SbF_6^-$ and at 318, 335 cm^{-1} for β-$XeF_3^+SbF_6^-$. It has been pointed out by Claassen et al.[28] that $\nu_3(a_1)$ and $\nu_6(b_2)$ of ClF_3 and BrF_3, which may be approximately described as in-plane and out-of-plane bends, respectively, of the near-linear F–X–F part of the molecule, might be expected to lie close together in frequency. In the Raman spectra of both ClF_3 and BrF_3, $\nu_6(b_2)$ was too weak to be observed and is presumably also too weak to be observed in the Raman spectra of the XeF_3^+ salts. This mode, however, appears as a strong infrared band at 240 and 245 cm^{-1} in IF_3. The F–Xe–F axial symmetric bend, $\nu_3(a_1)$, is assigned to the weak bands observed at 205 cm^{-1} for α-$XeF_3^+SbF_6^-$ and at 199 and 212 cm^{-1} for β-$XeF_3^+SbF_6^-$. For ClF_3, BrF_3, and IF_3, ν_3 has been assigned to bands at 337–321, 233, and 228 cm^{-1}, respectively. Table II compares the vibrational frequencies for XeF_3^+, BrF_3, and ClF_3.

The remaining bands in the spectrum arise from the anion and from the Xe---F part of the fluorine bridge. Although an SbF_6^- anion of O_h symmetry would be expected to give rise to three Raman-active bands $a_{1g} + e_g + t_{2g}$, additional bands arising from the anion in both α-$XeF_3^+SbF_6^-$ and β-$XeF_3^+SbF_6^-$ are observed in the Raman spectrum. A reasonable assignment for the anion modes can be made by taking account of the fact that one of the fluorines of SbF_6^- is involved in a fluorine bridge. Gillespie and Schrobilgen[33] have previously demonstrated that the AsF_6^- and SbF_6^- anion modes of the fluorine-bridged XeF^+ and KrF^+ salts may be satisfactorily assigned on the basis of C_{4v} symmetry. Thus the anion is best written as $(F_5Sb{-}{-}{-})F^-$ and is assumed to have C_{4v} symmetry. Any slight effect of the nonlinearity of the Sb---F---Xe bridge is ignored in this interpretation. For C_{4v} symmetry, 11 normal modes of vibration are predicted, namely, 4 a_1, 2 b_1, b_2, and 4 e, all of which are Raman active. As an aid to the assignment of the vibrational modes of SbF_6^- (C_{4v} symmetry), the spectra of a number of related octahedral molecules and monosubstituted derivatives as well as the correlation diagram for the normal modes of an SbF_6^- anion of O_h symmetry going to the distorted $(F_5Sb{-}{-}{-}F)^-$ anion[33] have been relied upon. Assignments for the SbF_6^- anion modes of α-$XeF_3^+SbF_6^-$ and β-$XeF_3^+SbF_6^-$ as well as $XeOF_3^+SbF_6^-$ are based on these model compounds and similar assignments for $XeF^+SbF_6^-$ [33] and $KrF^+SbF_6^-$.[33] The spectra provide no evidence for a symmetry lower than C_{4v}, e.g., C_s, C_1, or C_{2v}, since a total of 15 normal modes would be expected under these symmetries.

The $\nu_4(a_1)$ and $\nu_{11}(e)$ modes may be, at least approximately, described as ν(Sb---F) and δ(F---SbF_4), respectively, and are of particular significance since they are directly associated with the fluorine-bridge interaction. It has previously been noted that treatment of the MF_6^- ion in terms of O_h symmetry cannot account for the observation of a weak band that invariably occurs in the region 450–500 cm^{-1} in most, if not all, of the AsF_6^-, SbF_6^-, IrF_6^-, and PtF_6^- salts of XeF^+ and KrF^+.[33] This band has been attributed to the bridging M---F stretch (ν_4). Owing to the increased length of the M---F bridge bond, the stretching frequency of this bond is significantly lower by ca. 150–250 cm^{-1} than $\nu_1(a_{1g})$ in the undistorted anion. Both $\nu_8(e)$ and $\nu_3(a_1)$ have frequencies that are similar to their O_h counterparts, $\nu_3(t_{1u})$ and $\nu_4(t_{1u})$, respectively, and are therefore assigned on the basis of their NO^+ and alkali metal salts.[33] The bridging M---F stretch and F---MF_4 bend have been previously assigned for $XeF^+AsF_6^-$,[2] $XeF^+SbF_6^-$,[2] and $KrF^+MF_6^-$ (M = As, Sb, Pt).[33] In the spectra of $XeF^+SbF_6^-$ and $XeF^+Sb_2F_{11}^-$ [2,33] the bands in the region of 450 cm^{-1} have been attributed to the stretching vibration of the Sb---F bond of the Sb---F---Xe bridge and it seems reasonable, in the present case, to assign the bands observed at 449 and 514 cm^{-1} for α-$XeF_3^+SbF_6^-$ and β-$XeF_3^+SbF_6^-$ to this same vibration ($\nu_4(a_1)$). This frequency is too low to be attributed to a normal Sb–F bond and it is not reasonably assigned to XeF_3^+. Moreover, this low frequency for an Sb---F bond is consistent with the abnormal length of this bond. A number of xenon–fluorine stretching frequencies have been found to correlate well with the bond length.[2,10] Therefore, it might be expected that the Xe---F bridge bond in $XeF_3^+Sb_2F_{11}^-$, which is longer (2.50 Å) than that in $XeF^+Sb_2F_{11}^-$ (2.35 Å), would have a lower frequency than in $XeF^+Sb_2F_{11}^-$. The bond length–stretching frequency correlation suggests a value in the region of 200 cm^{-1}. Any of the frequencies 232,

Table III. Correlation Diagram for the XeF_3^+ Modes of $XeF_3^+Sb_2F_{11}^-$

Free ion C_{2v}		Site C_1		Crystal^a C_i	Activity
$2\nu_1, 2\nu_2, 2\nu_3$, 2T	a_1		a_g	$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$, 3T, 3R	Raman
$2\nu_4, 2\nu_5$, 2T, 2R	b_1	a			
2R	a_2				
$2\nu_6$, 2T, 2R	b_2		a_u	$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$, 3T, 3R	Ir

^{a} Crystal space group $P\bar{1}$.

Table IV. Correlation Diagram for the XeF_3^+ Modes of β-$XeF_3^+SbF_6^-$

Free ion C_{2v}		Site C_1		Crystal^a C_{2h}	Activity
$4\nu_1, 4\nu_2, 4\nu_3$, 4T	a_1		a_g	$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$, 3T, 3R	Raman
4R	a_2	a	b_g	$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$, 3T, 3R	Raman
$4\nu_4, 4\nu_5$, 4T, 4R	b_1		a_u	$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$, 3T, 3R	Ir
$4\nu_6$, 4T, 4R	b_2		b_u	$\nu_1, \nu_2, \nu_3, \nu_4, \nu_5, \nu_6$, 3T, 3R	Ir

^{a} Crystal space group $P2_1/n$.

205, or 186 cm^{-1} for α-$XeF_3^+SbF_6^-$ could be reasonably assigned to this mode, and tentative assignments of the bands at 232 cm^{-1} in the α salt and the band at 257 cm^{-1} in β-$XeF_3^+SbF_6^-$ to this mode were made. The remaining bands, 155 and 108 cm^{-1} (for α-$XeF_3^+SbF_6^-$) and 129 and 138 cm^{-1} (for β-$XeF_3^+SbF_6^-$) are assigned to bending of the Xe---F–Sb bridge or to lattice modes. One somewhat puzzling feature of the spectra of α- and β-$XeF_3^+SbF_6^-$ is the difference in the frequencies of the $\nu_4(a_1)$ mode. The higher frequency observed for β-$XeF_3^+SbF_6^-$ implies a shorter Sb---F bond and a longer Xe---F bond. A knowledge of the structure of the α phase is evidently essential to a complete understanding of the solid-state vibrational spectrum.

Factor-Group Analyses of the Raman Spectra of β-$XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$. Since the x-ray structures of $XeF_3^+Sb_2F_{11}^-$ and β-$XeF_3^+SbF_6^-$ are known, factor-group analyses were made in order to aid in the assignment of the XeF_3^+ bands. The correlation method, in which the free ion symmetry is correlated to the site symmetry and subsequently to the factor group isomorphous with the space group, was used in both cases. A discussion of the correlation method may be found in an article by Carter[34] and in the work of Fateley et al.[35] The correlation diagrams for the XeF_3^+ modes in $XeF_3^+Sb_2F_{11}^-$ and β-$XeF_3^+SbF_6^-$ are given in Tables III and IV, respectively. The correlations have been determined by consulting the published tables.

From the space group data for $XeF_3^+Sb_2F_{11}^-$ and the correlation diagram (Table III) it can be seen that each pair of internal modes is divided under factor-group symmetry C_1 into an a_g and an a_u mode. Since the unit cell is centrosymmetric, the rule of mutual exclusion applies, and the Raman-active modes are infrared inactive and vice versa. Consequently only one line per normal mode is expected for XeF_3^+ and for $Sb_2F_{11}^-$ in the Raman spectrum as was observed. Lines due to the $Sb_2F_{11}^-$ anion were identified by comparison with the spectra of $XeF^+Sb_2F_{11}$ and related compounds.

For β-$XeF_3^+SbF_6^-$, it is particularly noteworthy that, unlike α-$XeF_3^+SbF_6^-$, each cation line of β-$XeF_3^+SbF_6^-$ is further split into a doublet (Table I and Figure 1). The free XeF_3^+ cation possesses C_{2v} symmetry and therefore already exhibits the maximum number of 6 Raman- (infrared-) active bands, 3 a_1 + 2 b_1 + b_2. Consequently, lowering the site symmetry of XeF_3^+ in crystalline β-$XeF_3^+SbF_6^-$ would not be expected to give rise to additional bands in the Raman or infrared spectrum. It must, therefore, be concluded that the observed splitting of the XeF_3^+ modes is the result of vibrational coupling (factor-group splitting) of the cation modes in the unit cell of β-$XeF_3^+SbF_6^-$. The correlation of the free XeF_3^+ ion under C_{2v} symmetry to the species under C_1 site group symmetry and C_{2h} factor-group symmetry in β-$XeF_3^+SbF_6^-$ is shown in Table IV. It may be seen that each normal mode of the free XeF_3^+ ion will give rise to two Raman-active internal modes, an a_g mode and a b_g mode, under C_{2h} factor-group symmetry. In the case of $\nu_2(a_1)$, $\nu_4(b_1)$, and $\nu_5(b_1)$ this splitting of the normal modes into doublets is readily apparent (Table I and Figure 1). The assignment of $\nu_1(a_{1g})$ is complicated by the fact that additional lines arising from the anion appear in the same spectral region. While it is clear that a maximum of two of the bands can be assigned to the factor-group split $\nu_1(a_1)$ mode, the assignments that are given are not entirely unambiguous.

Reaction of XeF_4 with Excess AsF_5. The Raman spectrum of the yellow product obtained when excess AsF_5 was condensed onto XeF_4 at −100 °C is given in Table I and Figure 2. Two strong bands at 643 and 571 cm^{-1} clearly indicate the presence of the XeF_3^+ cation. The other bands may be attributed to excess AsF_5 and to an AsF_6^- having C_{4v} symmetry, presumably because of the formation of a fluorine bridge with XeF_3^+. As excess AsF_5 was used, there is the possibility of the formation of the $As_2F_{11}^-$ anion which has previously been identified by its ^{19}F NMR spectrum in solution at low temperature.[36] However, all of the observed bands may be attributed to XeF_3^+, AsF_5, and excess AsF_6^-, and although some $As_2F_{11}^-$ may have been present, no convincing evidence for this species could be obtained from the Raman spectrum.

The intensity of the doublet band at 607, 608 cm^{-1} is unexpectedly high if it is assumed that it arises only from $\nu_4(b_1)$ of XeF_3^+ since this is generally of relatively low intensity (see Figure 1). Moreover on warming the mixture briefly to room temperature and then again running the low-temperature spectrum it was found that the 608-cm^{-1} band together with a band at 679 cm^{-1} increased in intensity and an additional band appeared at 338 cm^{-1} while the 643- and 571-cm^{-1} bands of XeF_3^+ decreased in intensity. The three bands which increased in intensity are identical with three strong bands of the spectrum of $XeF^+AsF_6^-$ [2] and indicate that some decomposition of the XeF_3^+ occurs even at low temperature. The nature of this decomposition is not certain. It could simply be represented as in eq 1 but no direct evidence for F_2 was

$$XeF_3^+AsF_6^- \rightarrow XeF^+AsF_6^- + F_2 \qquad (1)$$

obtained. Alternatively there might be a disproportionation to XeF^+ and XeF_5^+, although no clear evidence for XeF_5^+ was obtained from the Raman spectrum.

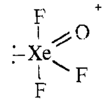
In another experiment in which all of the excess AsF_5 was pumped off at −78 °C new peaks appeared in the spectrum at 500 and 544 cm^{-1} which can reasonably be attributed to XeF_4. Thus it appears that in the absence of excess AsF_5 $XeF_3^+AsF_6^-$ also decomposes to XeF_4 and AsF_5.

Raman Spectra of the Salts $XeOF_3^+SbF_6^-$ and $XeOF_3^+Sb_2F_{11}^-$. In a brief communication, we have presented ^{19}F NMR and Raman evidence for the $XeOF_3^+$ cation.[23] Subsequent to the completion of this work, Bartlett and co-workers[27] published a paper on the preparation and Raman spectrum of $XeOF_3^+SbF_6^-$ and $XeOF_3^+Sb_2F_{11}^-$. Our Raman spectra are generally in agreement with those of Bartlett et al.[27] but are somewhat more complete. We also give a more detailed assignment of the spectra than that presented by these authors.

The ^{19}F NMR spectrum of the $XeOF_3^+$ cation is consistent with the expected structure (I) in which a lone pair, an oxygen

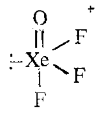
Table V. Raman Spectra of $XeOF_3^+SbF_6^-$ and $XeOF_3^+Sb_2F_{11}^-$ (Frequencies in cm^{-1})

$XeOF_3^+SbF_6^-$ (solid, −83 °C)		$XeOF_3^+SbF_6^-$ (~1 *m* HF soln)		$XeOF_4$ (0.8 *m* SbF_5 soln)	$XeOF_3^+Sb_2F_{11}^-$ (solid, −83 °C)		Assignments for $XeOF_3^+$ (C_s)	
944 (23)		942 p (100)		942 p, m	942 (70)		$\nu_1(a')$	$\nu(Xe{=}O)$
632 (32) 629 (34)		637 p (59)		634 p, m	635 (90)		$\nu_2(a')$	$\nu(Xe-F_e)$
348 (3) 337 (7)					334 (11)		$\nu_3(a')$	$\delta_{sym}(XeOF_e)$ in-plane bend
589 (41) 590 (100)		586 p (70)		589 p, m	601 (100) 594 (73)		$\nu_4(a')$	$\nu_{sym}(Xe-F_a)$
206 (2)					199 (4)		$\nu_5(a')$	$\delta_{asym}(XeOF_e)$ in-plane rock
194 (<1)							$\nu_6(a')$	$\delta_{sym}(Xe-F_a)$
618 (15) 612 sh		612 (<1)			617 (15)		$\nu_7(a'')$	$\nu_{asym}(XeF_a)$
366 (8)		365 (<1)			356 (14)		$\nu_8(a'')$	$\delta_{asym}(XeOF_e)$
324 (9) 319 sh					319 (12)		$\nu_9(a'')$	$\tau(XeOF)$
SbF_6^- (C_{4v})		$XeOF_4$		SbF_5	$Sb_2F_{11}^-$			
667 sh	$\nu_1(a_1)$	920 p (15)	$\nu_1(a_1)$	717 p, vs	703 (39)			
660 (6)		567 p (47)	$\nu_2(a_1)$	669 p, vs	700 sh			
646 sh	$\nu_2(a_1)$	531 dp (<1)	$\nu_5(b_2)$	300 w	687 sh			
640 sh		SbF_6^-		267 s	686 (8)			
563 (3)	$\nu_5(b_1)$			220 s	663 (3)			
547 (20)		650 p (12)	$\nu_1(a_{1g})$	185 w	643 (12)			
505 (14)	$\nu_4(a_1)$	287 sh	$\nu_5(t_{1g})$	120 s	629 sh			
523 (<1)		269 sh			576 sh			
696 (34)	$\nu_8(e)$				564 (12)			
685 sh					555 (8)			
261 sh	$\nu_3(a_1)$				547 (12)			
	$\nu_{11}(e)$				301 (4)			
366 (8)	$\nu_7(b_2)$				297 (10)			
283 (2)	$\nu_9(e)$				256 (8)			
280 (2)					243 (9)			
194 (<1)	$\nu_6(b_1)$				228 (8)			
308 sh	$\nu_{10}(e)$				222 sh			
					475 (4)	$\nu(Sb\text{- - -}F)$		
					138 (8)	$\delta(Xe\text{- - -}F\text{- - -}Sb)$		



I

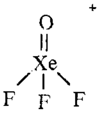
atom, and a fluorine atom occupy equatorial positions and two fluorine atoms occupy the axial positions of a trigonal bipyramid.[25,32] The ^{19}F NMR spectrum does not, however, give a conclusive proof of structure I as structure II is also con-



II

sistent with the NMR spectrum. The spectra of the compounds $XeOF_3^+Sb_2F_{11}^-$ and $XeOF_3^+SbF_6^-$ are given in Table V and Figure 3.

Nine normal modes are expected for the $XeOF_3^+$ ion with C_s symmetry, namely, 6 a' and 3 a'', all of which are Raman and infrared active. The observed spectra have been assigned by comparison with the spectra of $ClOF_3$[37] which has been interpreted in terms of a C_s structure analogous to I and that of XeF_3^+. The remaining structural possibility for the $XeOF_3^+$ ion would be the tetrahedral structure III which would be



III

expected if the lone pair of the xenon were sterically inactive. For this molecular geometry (C_{3v} symmetry) six fundamentals, all Raman and infrared active, are expected. The observation of eight of the nine lines expected for C_s symmetry, as well as the observation of three xenon–fluorine stretching frequencies, whereas only two are predicted for C_{3v} symmetry,

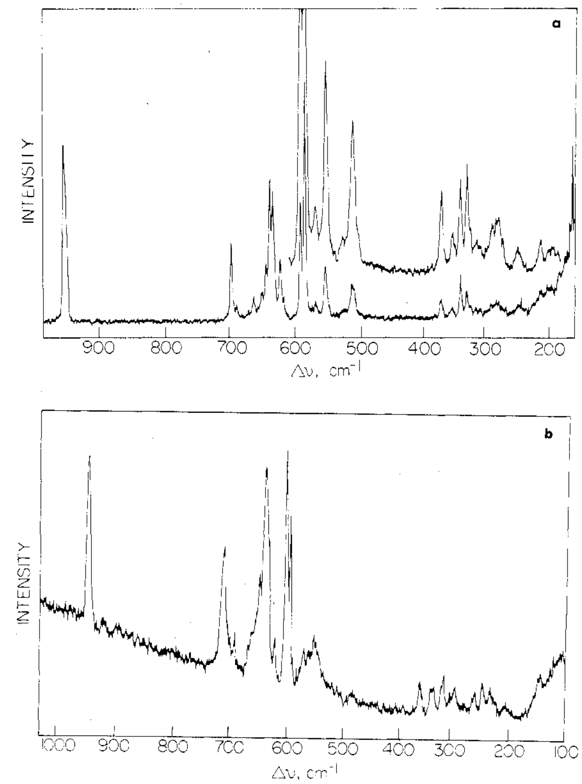


Figure 3. Raman spectra of (a) $XeOF_3^+SbF_6^-$ and (b) $XeOF_3^+$-$Sb_2F_{11}^-$ at −85 °C.

rules out structure III. From the vibrational spectrum it should be possible to distinguish between structures I and II. For structure I, one xenon–equatorial fluorine and two xenon–axial fluorine stretching frequencies should be observed. For structurally related molecules, the frequencies have been found to decrease in the order $\nu(\text{Xe–F}_e) > \nu_{\text{asym}}(\text{Xe–F}_a) > \nu_{\text{sym}}(\text{Xe–F}_a)$ and a pattern of bands having the intensities strong, weak, strong should also be seen. For structure II, in which there is only one axial fluorine and two equatorial fluorine atoms, it is anticipated that the frequencies would decrease in the order $\nu_{\text{asym}}(\text{Xe–F}_e) \approx \nu_{\text{sym}}(\text{Xe–F}_e) > \nu(\text{Xe–F}_a)$ and the pattern of intensities should be weak, strong, strong. It is clear that the $XeOF_3^+$ cation has the spectrum expected for structure I.

It is expected that the xenon–equatorial fluorine stretching mode, ν_2, would have a higher frequency than the xenon–axial fluorine symmetric stretching mode, ν_4, owing to the anticipated shorter xenon–equatorial fluorine bonds. Accordingly, ν_2, is assigned to the peaks appearing at 632, 629 and at 635 cm^{-1} for $XeOF_3^+SbF_6^-$ and $XeOF_3^+Sb_2F_{11}^-$, respectively. The Xe=O stretching frequency, ν_1, is assigned to the 944- and 942-cm^{-1} bands in the 1:1 and 1:2 salts, respectively. This peak occurs at a significantly higher frequency than the corresponding mode in the parent molecule $XeOF_4$, which has a frequency of 919 cm^{-1}.

Polarization measurements on an HF solution of $XeOF_3^+SbF_6^-$ showed that the bands assigned to ν_1, ν_2, and ν_4 were strongly polarized. Strongly polarized bands were also found for these modes in a spectrum of $XeOF_4$ in SbF_5 solution (Table V).

The remaining high-frequency band, ν_7, which may be approximately described as the antisymmetric xenon–axial fluorine stretch, might be expected to have a frequency similar to that of the corresponding ν_4 mode in XeF_3^+, i.e., 618 cm^{-1}. Generally for this type of molecule ν_7 has a frequency between those of X–F$_e$, ν_2, and symmetric X–F$_a$, ν_4. It seems reasonable to attribute the bands at 618 and 612 cm^{-1} in $XeOF_3^+SbF_6^-$ and the 617-cm^{-1} band in $XeOF_3^+Sb_2F_{11}^-$ to ν_7. A comparison of the $XeOF_3^+$ bands with those of $ClOF_3$ and IOF_3 is given in Table VI. Although the Raman spectrum of IOF_3 exhibits more lines than are expected for a monomeric IOF_3 molecule, the comparison is nevertheless interesting and useful. The five remaining bands of $XeOF_3^+$ must be assigned to deformational modes. Three of these modes, ν_3, ν_8 and ν_9, all involve motions of the double-bonded oxygen atom and should give rise to bands which have no counterpart in the XeF_3^+ spectrum; however, the bands arising from ν_5 and ν_6, which involve motions of the F$_a$–Xe–F$_a$ part of the molecule, should have similar frequencies to the analogous modes of XeF_3^+, and they are therefore expected to occur in the region of 200 cm^{-1} and are assigned to the two bands at 206 and 194 cm^{-1}, respectively, in $XeOF_3^+SbF_6^-$. In $XeOF_3^+Sb_2F_{11}^-$ only one band in this region was observed at 199 cm^{-1}.

In the case of $XeOF_3^+SbF_6^-$, three sets of doublets were observed in the 300–360-cm^{-1} region. In the parent molecule, $XeOF_4$, ν_8, the Xe=O bending mode, occurs at 362 cm^{-1},[38] while the symmetric (ν_2) and asymmetric (ν_4) bending modes of XeO_3 have been assigned to bands at 344 and 317 cm^{-1}, respectively.[39] Partly on the basis of force constant calculations Christe[37] assigned ν_8, for $ClOF_3$, to a higher frequency than ν_3. The same order is used here and ν_8 is assigned to the band at 366 cm^{-1}, while ν_3 is assigned to the bands at 348 and 337 cm^{-1} in the 1:1 salt. The torsional mode, ν_9, is assigned to the bands at 324 and 319 cm^{-1}. Similar assignments are also made for $XeOF_3^+Sb_2F_{11}^-$. The doublets observed in the spectra of $XeOF_3^+SbF_6^-$ must be due to factor-group splitting, but no space group data are yet available to support this view. Since more lines are observed than can be accommodated under O_h symmetry, a better assignment for the SbF_6^- modes may be made on the basis of C_{4v} symmetry. A band at 505 cm^{-1}, which is not otherwise easily accounted for, may be reasonably assigned to $\nu_4(a_1)$, the stretching vibration of the Sb–F bond in the Sb–F---Xe bridge. The band at 241 cm^{-1} is tentatively attributed to the other half of this bridge, ν(Xe---F). Similar assignments have been made for the compound $XeOF_3^+Sb_2F_{11}^-$. Finally, the low-frequency bands at 150 and 112 cm^{-1} may be attributed to the bending motions of the fluorine bridge or to external modes. It should also be pointed out that for $XeOF_3^+SbF_6^-$, the assignment of the bands appearing at 366 and 194 cm^{-1} can be made by assuming the former band to arise from a coincidence between $\nu_8(a'')$ of $XeOF_3^+$ and $\nu_7(b_2)$ of SbF_6^- and the latter to arise from a coincidence of $\nu_6(a')$ of $XeOF_3^+$ and $\nu_6(b_2)$ of SbF_6^-, respectively.

Table VI. Vibrational Spectra of $XeOF_3^+$ and Related Molecules (cm^{-1})

$XeOF_3^+$ [a] Raman	IOF_3 [b] Raman	$ClOF_3$ Raman[c]	$ClOF_3$ Ir[d]	Assignment
	919 (9), [e]			
	911 (13)			
	899 (16)			
944 (23)	878 (100)	1222 (15) p	1228, 1224 s	$\nu_1(a')$
	851 (7)	1211 (5) p	1218, 1213	
634 (32)	650 (93)	694 (26) p	701, 684 s	$\nu_2(a')$
629 (34)	630 (4)	686 sh p	676, 666	
348 (3)	343 (7)	489 (10)	491 ms	$\nu_3(a')$
337 (7)				
589 (41)	543 (84)	482 (100)	481 ms	$\nu_4(a')$
580 (100)				
206 (2)	213 (1)	319 (1)	323 m	$\nu_5(a')$
			313 m	
194 (<1)	191 (1)	224 (4)	230 mw	$\nu_6(a')$
618 (15)	506 (3)		652 d	$\nu_7(a'')$
612 sh	515 (15)		641 vs	
366 (18)	374 (4)	500 (10)	501 ms	$\nu_8(a'')$
324 (9)	319 (2)	414 (2) dp	412 w	$\nu_9(a'')$
319 sh				
	302 (4) [e]			
	296 (15)			
	172 (16)			
	104 (9)			
	72 (10)			
	60 (23)			

[a] $XeOF_3^+SbF_6^-$, solid. [b] Solid; R. J. Gillespie and J. P. Krasznai, unpublished observations. [c] Gas; ref 38. [d] Solid, low-temperature matrix; ref 38. [e] Not assigned.

An extended version[10] of a previously published correlation of stretching frequency and bond lengths for XeF bonds[2] may be used to predict the Xe–F bond lengths in $XeOF_3^+$ which have not up till now been determined by X-ray crystallography. The predicted values are Xe–F$_e$ = 1.82 Å and Xe–F$_a$ = 1.88 Å.

In an HF solution of $XeOF_3^+SbF_6^-$ (Table V), the appearance of additional Raman bands at 920, 567, and 537 cm^{-1}, which are due to $XeOF_4$, demonstrates that some formation of $XeOF_4$ occurs by solvolysis of $XeOF_3^+$ according to

$$XeOF_3^+ + 2HF \rightleftarrows XeOF_4 + H_2F^+ \qquad (2)$$

XeF_5^+ has been shown to undergo an analogous solvolysis,[10] i.e.

$$XeF_5^+ + 2HF \rightleftarrows XeF_6 + H_2F^+ \qquad (3)$$

Raman Spectrum of $XeO_2F^+Sb_2F_{11}^-$. The Raman spectrum of solid $XeO_2F^+Sb_2F_{11}^-$ is given in Figure 4 and in Table VII together with the spectrum of XeO_2F_2. The XeO_2F^+ cation is expected to have the typical trigonal-pyramidal geometry

Table VII. Raman Spectra (cm^{-1}) of Solid $XeO_2F^+Sb_2F_{11}^-$ and XeO_2F_2

XeO_2F^+-$Sb_2F_{11}^-$ [a]	Assignment	XeO_2-F_2 [b]	Assignment
923 (38)	$\nu_5(a'')$ $\nu(XeO_2)$ asym str	902 w	$\nu_6(b_1)$ $\nu(XeO_2)$ asym str
867 (100)	$\nu_1(a')$ $\nu(XeO_2)$ sym str	845 vs	$\nu_1(a_1)$ $\nu(XeO_2)$ sym str
693 sh	$Sb_2F_{11}^-$	578 w	$\nu_8(b_2)$ $\nu(XeF_2)$ asym str
688 (34)		490 s	$\nu_2(a_1)$ $\nu(XeF_2)$ sym str
647 (15)		333 ms	$\nu_3(a_1)$ $\delta(XeO_2)$ sym bend
630 (23)			
623 (23)		324[c] s	$\nu_7(b_1)$ XeF_2 sym bend out of plane
587 sh			
574 sh		313 ms	$\nu_9(b_2)$ XeO_2 rock
518 (15)		223 vw	$\nu_5(a_2)$ torsion
580 (58)	$\nu_2(a')$ $\nu(Xe{-}F)$	198 w	$\nu_4(a_1)$ $\delta(XeF_2)$ sym bend in plane
334 (23)	$\nu_4(a')$ $\delta(XeO_2)$ sym bend		
326 (7)	$Sb_2F_{11}^-$		
267 (15)			
244 (15)			

[a] The spectrum was recorded at −107 °C in a glass tube.
[b] Liquid; H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *J. Chem. Phys.*, 49, 253 (1968). [c] Solid, infrared low-temperature matrix.

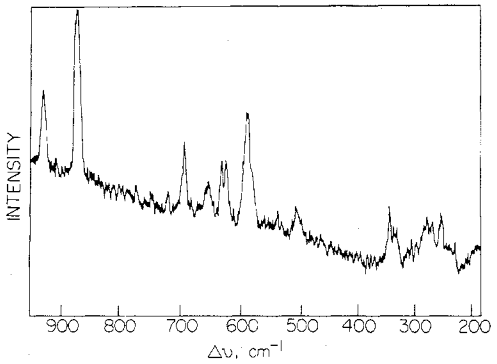
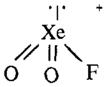


Figure 4. Raman Spectrum of $XeO_2F^+Sb_2F_{11}^-$ at 107 °C.

of an AX_3E molecule, similar to that found for XeO_3, and to have C_s symmetry, i.e.



Under C_s symmetry, six fundamental vibrations are predicted for the XeO_2F^+ cation. All modes are infrared and Raman active. These modes are approximately described as the XeO_2 symmetric and antisymmetric stretches ($\nu_1(a')$ and $\nu_5(a'')$), XeO_2 bend ($\nu_4(a')$), Xe–F stretch ($\nu_2(a')$), and Xe–F in-plane and out-of-plane deformations ($\nu_3(a')$ and $\nu_6(a'')$).

A reasonable assignment of the observed bands was made by comparison with the related halogen oxyfluorides ClO_2F,[40] BrO_2F,[41] and IO_2F,[42] as well as with the pyramidal anions SOF_2^- [40] and $SeOF_2^-$.[40] The intense peak at 867 cm^{-1} is assigned as the XeO_2 symmetric stretch, $\nu_2(a')$, while the weaker peak at 923 cm^{-1} is assigned to the XeO_2 antisymmetric stretching mode, $\nu_5(a'')$. The intense band at approximately 580 cm^{-1} is assigned to the Xe–F stretching frequency, $\nu_1(a')$, while the band at 334 cm^{-1} is assigned to $\nu_4(a')$, the symmetric XeO_2 bending mode. In XeO_2F_2 the latter mode has been found to occur at 333 cm^{-1}. The remaining bands in the spectrum are characteristic of $Sb_2F_{11}^-$.

No bands could be attributed to the symmetric ν_3 and antisymmetric ν_6, FXeO deformational modes. They are undoubtedly weak and are most likely obscured by $Sb_2F_{11}^-$ bands. It is noteworthy that the frequencies observed for XeO_2F^+ are higher than the corresponding frequencies for the parent XeO_2F_2 molecule just as the frequencies of XeF_3^+ and $XeOF_3^+$ are higher than those of XeF_4 and $XeOF_4$. The effect of the positive charge is undoubtedly to increase the effective electronegativity of the xenon and thereby decrease the polarity and increase the strength of all the bonds in the molecule.

No polarization measurements could be obtained in SbF_5 solution owing to rapid decomposition. It was also found that even solid $XeO_2F^+Sb_2F_{11}^-$ slowly decomposed according to eq 4 over a period of months to give $XeF^+Sb_2F_{11}^-$ and oxygen.

$$XeO_2F^+ \rightarrow XeF^+ + O_2 \qquad (4)$$

The decomposition of the XeO_2F^+ cation in SbF_5 solution and of solid $XeO_2F^+Sb_2F_{11}^-$ was monitored by Raman spectroscopy. It was found that peaks at 923, 867, 580, and 334 cm^{-1} decreased in intensity relative to the anion peaks and a new peak appeared at 615 cm^{-1} which may be attributed to XeF^+.[2]

It is concluded that the Raman spectrum of the complex $XeO_2F_2{\cdot}2SbF_5$ is consistent with the "ionic" formulation $XeO_2F^+Sb_2F_{11}^-$ and that XeO_2F^+ has a pyramidal geometry. No direct evidence for fluorine bridging was obtained in this case as any possible lowering of the symmetry of $Sb_2F_{11}^-$ by the formation of a fluorine bridge cannot be detected in view of the complicated nature of the spectrum of $Sb_2F_{11}^-$ which has not yet been fully interpreted and assigned. Moreover, any bands due to the vibrations of a fluorine bridge are likely to be hidden under one or more of the rather large number of bands of $Sb_2F_{11}^-$.

Experimental Section

Xenon tetrafluoride and xenon hexafluoride were prepared from xenon and fluorine according to the methods described by Malm and Chernick.[43] Both fluorides were purified by heating with dry sodium fluoride as described by Sheft et al.[44] Pure liquid $XeOF_4$ was made by the interaction of solid XeF_6 with a glass surface at room temperature.[45] Both $XeOF_4$ and XeO_2F_2 were conveniently generated in HF solution by the interaction of XeF_6 with 1 or 2 mol of water, respectively.[25] β-$XeF_3^+Sb_2F_{11}^-$ was prepared by the interaction of XeF_4 with excess SbF_5 at −50 °C.[25] α-$XeF_3^+SbF_6^-$ was prepared by treating $XeF_3^+Sb_2F_{11}^-$ with an excess of XeF_4 at 80 °C.[25] The reaction of excess XeF_4 with SbF_5 in HF solution at room temperature gave $XeF_3^+SbF_6^-$.[25]

$XeOF_3^+Sb_2F_{11}^-$ was prepared by treating an HF solution of $XeOF_4$ with an excess of SbF_5 while $XeOF_3^+SbF_6^-$ was prepared by dissolving SbF_5 in an excess of liquid $XeOF_4$ at room temperature.[25] $XeO_2F^+Sb_2F_{11}^-$ was prepared by dissolving a stoichiometric amount of SbF_5 in a solution of XeO_2F_2 in HF and pumping to dryness at room temperature.[25]

In the study of the XeF_4–AsF_5 system approximately 0.2 g of XeF_4 was transferred to a heavy-walled glass NMR tube and excess AsF_5 was condensed onto XeF_4 at −196 °C. The tube was allowed to warm up to −64 °C and maintained at this temperature for 2 h before the Raman spectrum of the resulting yellow solid was recorded under a layer of liquid AsF_5 at −80 °C. In an identical experiment, excess AsF_5 was pumped off at −78 °C prior to recording the Raman spectrum of the solid.

Raman Spectra. The Raman spectra were obtained with a Spex Industries Model 1400 spectrometer using the 5145-Å radiation from a Spectra Physics Model 164 argon ion laser. Low-temperature spectra were recorded by placing the sample tube inside a glass tube surrounded by an evacuated jacket, silvered except at the center. Liquid nitrogen was boiled off from a Dewar and passed through the tube. The temperature was monitored with a copper–constantan thermocouple positioned in the stream just ahead of the sample region. The Raman shifts are estimated to be accurate to ±2 cm^{-1}.

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Registry No. $XeF_3^+SbF_6^-$, 39797-63-2; $XeF_3^+AsF_6^-$, 58815-32-0; $XeF_3^+Sb_2F_{11}^-$, 39797-62-1; $XeOF_3^+SbF_6^-$, 39797-65-4; $XeOF_3^+$-

$Sb_2F_{11}^-$, 39797-64-3; $XeO_2F^+Sb_2F_{11}^-$, 52078-91-8; $XeOF_4$, 13774-85-1; SbF_5, 7783-70-2; IOF_3, 19058-78-7; XeO_2F_2, 13875-06-4.

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Preparation and Characterization of $2KrF_2{\cdot}SbF_5$, $KrF_2{\cdot}MF_5$ (M = Sb, Ta), and $KrF_2{\cdot}2MF_5$ (M = Sb, Ta, Nb): the $[Kr_2F_3]^+$ and $[KrF]^+$ Cations[1]

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The new adducts $2KrF_2{\cdot}SbF_5$, $KrF_2{\cdot}MF_5$ (M = Sb, Ta), and $KrF_2{\cdot}2MF_5$ (M = Ta, Nb) have been prepared and characterized, and $2KrF_2{\cdot}TaF_5$ has been obtained in solution. Raman spectra of these adducts and the already known $KrF_2{\cdot}2SbF_5$ are interpreted in terms of the molecules having fluorine-bridged (Kr···F···M) contributions to the bonding as well as contributions from ionic formulations such as $[Kr_2F_3]^+[MF_6]^-$ and $[KrF]^+[MF_6]^-$ (M = Sb, Ta) and $[KrF]^+[M_2F_{11}]^-$ (M = Sb, Ta, Nb). Thermal decomposition studies on some of the adducts have produced evidence for other new adducts which can be conveniently formulated as $[xKrF_2{\cdot}KrF]^+[Ta_2F_{11}]^-$ and $[xKrF_2{\cdot}KrF]^+[Nb_2F_{11}]^-$ (where x is probably equal to 1), in which the additional KrF_2 units appear to be weakly associated with the cationic parts of the adducts.

Introduction

The difficulty in preparing large-scale samples of KrF_2 and the fact that the compound is said to decompose readily at room temperature[3] has impeded progress with its chemistry. Until our own[1] and Gillespie and Schrobilgen's recent work[4] the only established krypton compound, other than KrF_2 itself, was $KrF_2{\cdot}2SbF_5$.[5a] This has recently been characterized by Bartlett and his co-workers as the salt $[KrF]^+[Sb_2F_{11}]^-$.[5b]

Other information on krypton difluoride chemistry has been published by Russian workers.[6,7] In an extensive review on krypton difluoride they briefly mentioned krypton difluoride adducts of the types $KrF_2{\cdot}MF_5$ (M = Sb, Ta), $KrF_2{\cdot}2MF_5$ (M = Sb, Ta, Nb), and $2KrF_2{\cdot}MF_4$ (M = Ti, Sn) but no details of preparation or characterization were reported.[6] In another paper, however, the same authors claimed that $KrF_2{\cdot}2SbF_5$ is the only compound formed in the KrF_2–SbF_5–BrF_5 system.[7]

We have investigated the reactions of KrF_2 with NbF_5, TaF_5, and $[BrF_4]^+[Sb_2F_{11}]^-$ in BrF_5 solution and the thermal decompositions of the materials which can be separated. The solid adducts $2KrF_2{\cdot}SbF_5$, $KrF_2{\cdot}MF_5$ (M = Sb, Ta), and $KrF_2{\cdot}2MF_5$ (M = Ta, Nb) have been prepared and characterized by gravimetry and Raman spectroscopy for the first time and evidence for $2KrF_2{\cdot}TaF_5$ has been observed in so-