angle is 147°.[3] It would seem that this angle is rather easily distorted by packing considerations and that its exact value is perhaps not highly significant. It is perhaps influenced by the intermolecular contact Xe-F(7) which is not present in the $XeF_3^+Sb_2F_{11}^-$ structure.

We conclude that the structure of $XeF_3^+SbF_6^-$ is essentially ionic, but that there is a weak covalent interaction between the two ions by a fluorine bridge and that both the ions are slightly distorted by this interaction. In particular, the Sb-F(1) bond that is involved in this bridging interaction is slightly longer than the other Sb-F bonds and there is a corresponding distortion of the bond angles from the ideal angle of 90°. There are also two weak intermolecular interactions between pairs of $XeF_3^+SbF_6^-$ units which thus form cyclic dimers. The directions of these interactions again indicate that they may be regarded as weak covalent bonds. The similarity of all the parameters of XeF_3^+, including the Sb-F-Xe bridging distances, in both the SbF_6^- and $Sb_2F_{11}^-$ compounds (Table III) implies that there is an almost identical interaction between the SbF_6^- and $Sb_2F_{11}^-$ anions and the XeF_3^+ cation.

Acknowledgments. We thank the National Research Council of Canada for financial support of this work and for a scholarship to G. J. S.

Registry No. $XeF_3^+SbF_6^-$, 39797-63-2.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1690.

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Fluorine-19 Nuclear Magnetic Resonance and Raman Spectroscopic Study of the $(FXe)_2SO_3F^+$ Cation. Preparation and Characterization of $(FXe)_2SO_3F^+AsF_6^-$

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Received October 4, 1973 AIC30723Q

The reaction of the $Xe_2F_3^+$ cation with HSO_3F has been studied in solution by ^{19}F nmr spectroscopy and shown to give rise to the cation $(FXe)_2SO_3F^+$. The compound $(FXe)_2SO_3F^+AsF_6^-$ has also been prepared and studied in BrF_5 solution by ^{19}F nmr and in the solid phase by Raman spectroscopy. The cation is shown to contain the fluorosulfate group in the bridging position.

Introduction

A number of xenon(II) compounds have been prepared by substitution of a highly electronegative ligand for one or both of the fluorines in xenon difluoride.[1-8] The fluorine-bridged cations $Xe_2F_3^+$ [9,10] and $Kr_2F_3^+$ [11] are now well-established species both in the solid phase and in solution. It was therefore of interest to determine if electronegative groups other than fluoride could also form similar bridged species. We describe in this paper the preparation and characterization by ^{19}F nmr and Raman spectroscopy of the fluorosulfate-bridged cation $(FXe)_2SO_3F^+$. We have previously given a preliminary report of the ^{19}F nmr parameters of this ion[12] and Bartlett and coworkers[8] have reported on an independent preparation of $(FXe)_2SO_3F^+AsF_6^-$ and its Raman spectrum. The present work which includes a more detailed analysis of the Raman spectrum of $(FXe)_2SO_3F^+AsF_6^-$ than reported previously as well as a detailed ^{19}F nmr investigation of the formation and decomposition of the $(FXe)_2SO_3F^+$ cation in HSO_3F solution proves that the SO_3F group is indeed situated in the bridging position.

Results and Discussion

^{19}F Nmr Spectroscopy. In an attempt to obtain the ^{19}F nmr spectrum of $Xe_2F_3^+$ from solutions of the compounds $Xe_2F_3^+SbF_6^-$ and $Xe_2F_3^+AsF_6^-$ in HSO_3F, it was found that the spectrum changed with time and apparently several species were formed. It was evident that $Xe_2F_3^+$ undergoes a reaction in fluorosulfuric acid although its spectrum can be obtained in BrF_5 solution in which it is stable.[10]

If the ^{19}F nmr spectrum of either compound in HSO_3F solution is measured at −95°, immediately after its preparation at approximately −40°, it shows a high-field peak, A, accompanied by ^{129}Xe satellites (Figure 1a and Table I). This peak cannot be assigned to XeF_2, $FXeSO_3F$, or $Xe_2F_3^+$ [10] and must be due to a new species which we propose to be $(FXe)_2SO_3F^+$. On the basis of its chemical shift and the absence of a $^{129}Xe-^{19}F$ coupling constant, a second high-field peak, B, may be assigned to HF. These assignments are supported by the observation of a peak, A′, in the F-on-S region of the spectrum in addition to that due to the solvent. The integrated relative intensities of the MF_6^- (C), HF, and F-on-Xe environments were 6:1:2, respectively. Unfortunately, the

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Table I. ^{19}F Nmr Parameters for the $(FXe)_2SO_3F^+$ Cation and Related Systems

Solute (m)	Solvent[b]	Time at room temp, hr	Temp, °C	$(FXe)_2SO_3F^+$			XeF^+		δ,[a] ppm			$FXeSO_3F$	
				δ,[a] ppm		$J_{^{129}Xe-^{19}F}$, Hz	δ,[a] ppm	$J_{^{129}Xe-^{19}F}$, Hz	$S_2O_6F_2$	MF_6^-	HF	δ,[a] ppm	$J_{^{129}Xe-^{19}F}$, Hz
$Xe_2F_3^+AsF_6^-$ (0.92)	HSO_3F	0.00	−91	−44.6	220.7	6330				63.4	180.9		
		1.08	−91	−44.7	222.1	6380	242.1	~6690	−39.1	63.4	181.6		
		1.58	−97	−44.7	221.2	6340	243.1	6630	−39.2	64.1	181.1		
		1.92	−96				243.8	6610	−39.1	64.5	182		
		2.25	−97				243.8	6620	−39.3	65	177		
		2.75	−97				244.1	6650	−39.2	73			
$XeF^+AsF_6^-$ (0.46)			−96				243.8	6615		64.4			
$Xe_2F_3^+SbF_6^-$ (0.42)	HSO_3F	0.00	−95	−44.7	220.0	6380	226.5	6480		123.2	181.9		
		0.05	−95	−44.8	221.9	6400	229.6	6490		124.7	181.4		
		0.25	−95	−44.7	220.9	6400	236.2	6590	−39.1	122.5	180.7		
		0.50[c]	−95	−44.8	221.1	6360	241.1	6620	−39.5	122.2	181.1		
		1.00	−95				243.0	6640	−39.1	122.4	181.4		
		1.42	−95				243.5	6670	−38.8	123.6	181.2		
$XeF^+SbF_6^-$ (0.70)	HSO_3F		−93				242.5	6620		123.2			
$(FXe)_2SO_3F^+AsF_6^-$ (2.22)	BrF_5		−59	−44.4	221.9	6470				60.9			
$XeF^+AsF_6^-$ (1.0) $K^+SO_3F^-$ (0.5) [d]	HSO_3F		−97	−44.8	220.1	6400			−39 sh	63.0	179.7	196.3	6020
$XeF^+AsF_6^-$ (1.0) $K^+SO_3F^-$ (1.4) [d]	HSO_3F		−67						−39 sh		181.6	196.2	6020

[a] With respect to external $CFCl_3$. [b] HSO_3F, −40.8 ppm; BrF_5, −269.9 (F_a) and −133.5 (F_e) ppm, $J_{FF} = 75$ Hz. [c] Peaks attributed to $F_5SbSO_3F^-$ and $Sb_2F_{11}^-$ begin to appear in the F-on-Sb and F-on-S regions of the spectrum. [d] Peaks were also observed at −47.2 and −42 (sh) ppm which are assigned to $S_2O_5F_2$ and $Xe(SO_3F)_2$, respectively; a peak due to $FXeSO_3F$ could not be observed due to overlap with the solvent line.

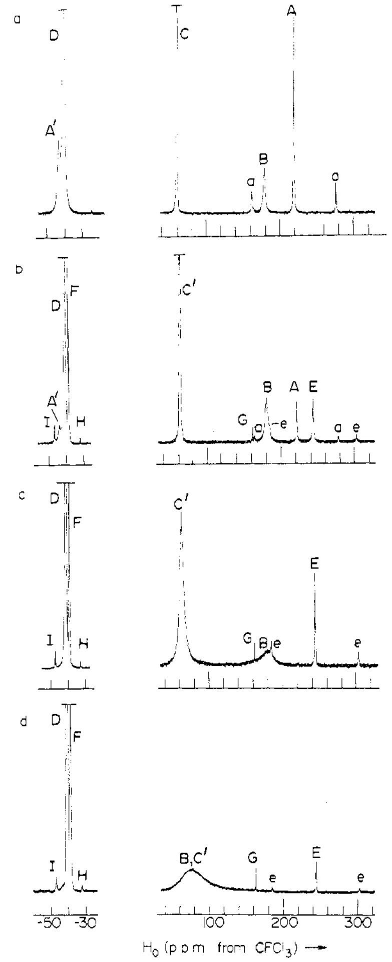
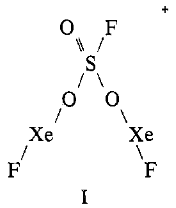


Figure 1. ^{19}F nmr spectrum of a solution of $(FXe)_2SO_3F^+AsF_6^-$ (0.92 *m*) prepared by dissolving $Xe_2F_3^+AsF_6^-$ in HSO_3F at −78°. Spectra were recorded at −97° in a glass tube: (a) initial spectrum; (b)-(d) spectra after warming to 25° for 1.58, 2.25, and 2.75 hr, respectively. Peak assignments: (A) $(FXe)_2SO_3F^+$ and (a) ^{129}Xe satellites, (B) HF, (C) AsF_6^-, (C′) AsF_5-AsF_6^-, (D) HSO_3F solvent, (E) XeF^+ and (e) ^{129}Xe satellites, (F) $S_2O_6F_2$, (G) SiF_4, (H) FSO_3F, (I) $S_2O_5F_2$.

F-on-S environment could not be accurately integrated in HSO_3F solvent owing to severe overlap with the solvent peak. The integrated relative intensities are consistent with the very rapid formation of $(FXe)_2SO_3F^+$ from $Xe_2F_3^+$ at low temperature according to the reaction

$$Xe_2F_3^+ + HSO_3F \rightarrow (FXe)_2SO_3F^+ + HF \qquad (1)$$

The ^{19}F nmr spectrum is attributed to the fluorosulfate-bridged structure I, which gives rise to only one F-on-Xe(II) resonance in the nmr spectrum, rather than to the fluorine-bridged structure II which would give an AX or AB spectrum for the F-on-Xe(II) environments.



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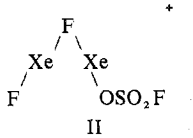

II

Preparation of $(FXe)_2SO_3F^+AsF_6^-$. The formation of the $(FXe)_2SO_3F^+$ cation was confirmed by preparing the compound $(FX)_2SO_3F^+AsF_6^-$ by the reaction of stoichiometric amounts of $Xe_2F_3^+AsF_6^-$ and HSO_3F in HF solution. After removal of the solvent under vacuum, a pale yellow, almost white, crystalline solid was obtained with an analysis very close to that expected for the compound $(FXe)_2SO_3F^+AsF_6^-$. When this compound was dissolved in BrF_5, it gave an nmr spectrum consisting of three lines of relative intensities 1:6:2 in the F-on-S, F-on-As, and F-on-Xe(II) regions, respectively. The chemical shifts, ^{129}Xe-^{19}F coupling constant, and relative intensities are in excellent agreement with those for the HSO_3F solution of $(FXe)_2SO_3F^+$ (Table I).

The cation $(FXe)_2SO_3F^+$ can also be formed by the reaction of XeF^+ and SO_3F^- at −78° in HSO_3F solvent according to eq 2. Addition of $K^+SO_3F^-$ to a solution of $XeF^+AsF_6^-$

$$2XeF^+AsF_6^- + K^+SO_3F^- \rightarrow (FXe)_2SO_3F^+AsF_6^- + K^+AsF_6^- \qquad (2)$$

in HSO_3F gave the same ^{19}F nmr peaks as have been attributed to $(FXe)_2SO_3F^+AsF_6^-$ (Table I). The $(FXe)_2SO_3F^+$ cation can react further with an additional mole of SO_3F^- according to eq 3 causing the $(FXe)_2SO_3F^+$ peaks to disappear leaving

$$(FXe)_2SO_3F^+AsF_6^- + K^+SO_3F^- \rightarrow 2FXeSO_3F + K^+AsF_6^- \qquad (3)$$

peaks due to $FXeSO_3F$, $Xe(SO_3F)_2$, and HF (Table I). The latter two species arise from reaction 4. The AsF_6^- peak is

$$FXeSO_3F + HSO_3F \rightarrow Xe(SO_3F)_2 + HF \qquad (4)$$

not observed on addition of excess SO_3F^- presumably because $K^+AsF_6^-$ has very low solubility in HSO_3F at −67°.

Decomposition of $(FXe)_2SO_3F^+$. The $(FXe)_2SO_3F^+$ cation is not stable in excess HSO_3F at room temperature and slowly decomposes, liberating xenon gas. The stepwise decomposition was studied in detail by nmr spectroscopy and the spectral changes are summarized in Table I and Figure 1a-d. Upon warming HSO_3F solutions of the cation to room temperature for a few minutes and again recording the spectrum at −95°, it was found that the F-on-Xe and F-on-S peaks assigned to $(FXe)_2SO_3F^+$ decreased in intensity with time and eventually disappeared. A new F-on-Xe(II) signal appeared just to high field of $(FXe)_2SO_3F^+$. The new peak, however, shifted to high field in the case of the SbF_6^- salt and the magnitude of the ^{129}Xe-^{19}F coupling constant increased as the $(FXe)_2SO_3F^+$ signal decreased in intensity, approaching the chemical shift and coupling constant associated with $XeF^+SbF_6^-$ dissolved in HSO_3F (Table I). In contrast, the AsF_6^- salt gave a ^{129}Xe-^{19}F coupling constant and chemical shift which varied only slightly throughout the decomposition and which corresponded to that of $XeF^+AsF_6^-$ dissolved in HSO_3F (Table I). The HF peak also increased in intensity and three new peaks appeared in the F-on-S region of the spectrum; the most intense peak, which grew most rapidly, is assigned to $S_2O_6F_2$ (−39.1 ppm)[13,14] while the weaker peaks are assigned to $S_2O_5F_2$ (−47.3 ppm)[13,14] and FSO_3F (−32.6 ppm).[13] The spectral changes can, for the most part, be attributed to a further reaction of $(FXe)_2SO_3F^+$ with an additional mole of HSO_3F according to the equation

$$(FXe)_2SO_3F^+ + HSO_3F \rightarrow XeF^+ + Xe + S_2O_6F_2 + HF \qquad (5)$$

The variable chemical shift and ^{129}Xe-^{19}F coupling constant observed for XeF^+ during the decomposition of $(FXe)_2SO_3F^+SbF_6^-$ can be attributed to fluorine exchange between XeF^+ and HF or SbF_6^- environments. Exchange of XeF^+ with $(FXe)_2SO_3F^+$ is ruled out by the constant chemical shift

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Table II. Raman Spectra of $FXeSO_3F$, $Xe(SO_3)_2$, and $(FXe)_2SO_3F^+AsF_6^-$

Freq, cm^{-1}			Freq, cm^{-1}		Freq, cm^{-1}		
$FXeSO_3F$[a]	$Xe(SO_3F)_2$[a]	Assignment	$(FXe)_2$-$SO_3F^+AsF_6^-$	Assignment	IO_2SO_3F[c]	$(CH_3)_2Sn$-$(SO_3F)_2$[d]	$SbF_4^-$$SO_3F$[e]
1378 (2)[b]	1408 (3)[b]	SO_2 asym str (a″)	1342 (8)	S=O str (a′)	1335	1350	1430
1193 (1)	1226 (3)[b]	SO_2 sym str (a′)	1084 (2)	SO_2 asym str (a″)	1182[b]	1180	1216
989 (2)[b]	947 (4)[b]	S–OXe str (a′)	1032 (8)	SO_2 sym str (a′)	1047[b]	1076[b]	1080
798 (2)[b]	818 (<1)	S–F str (a′)	871 (3)	S–F str (a′)	843	827	890
598 (7)[b]	605 (8)[b]	SO_2 bend (a′)	691 (2)	AsF_6^-, $\nu_1(a_{1g})$			
			677 (11)				
528 (150)[b]		Xe–F str (a′)	629 (15)	S=O wag (a′)	615	620	
553 (2)	539 (1)	S–F wag (a′)	594 (8)	SO_2 bend (a′)	603	590	
			582 (52)	Xe–F asym str (a″); Xe–F sym str (a′)			
434 (2)	436 (5)	Xe–O str (a′)	571 (100)				
			566 (36)				
			554 (82)				
392 (2)	385 (1)	SO_2 rock (a″)	576 sh	AsF_6^-, $\nu_2(e_g)$			
253 (10)	254 (19)[b]	F–S–O bend (a′)	540 (3)	S–F wag (a′)	562	554	
			400 (6)	Xe–O asym str (a″); Xe–O sym str (a′)			
239 (4)		O–Xe–F bend (a″)	395 (3)				
179 (3)		SO_2F torsion (a′)	392 (2)	SO_2 rock (a″)	459	417	
107 (6)	116 (3)	S–OXe torsion (a″)	364 (4)	AsF_6^-, $\nu_5(t_{2g})$			
			255 (3)	SO_2F torsion (a″)	310	304	
			245 (1)	O–Xe–F sym in-plane and out-of-plane bends (a′); O–Xe–F asym in-plane and out-of-plane bends (a″)			
			240 (1)				
			193 (4)	Xe–O–S sym in-plane and out-of-plane bends (a′); Xe–O–S asym. in plane and out-of-plane bends (a″)			
			162 (4)				
			138 (3)				

[a] R. J. Gillespie and B. Landa, *Inorg. Chem.*, 12, 1383 (1973). [b] Denotes the average frequency and/or the total intensity. [c] H. A. Carter and F. Aubke, *Inorg. Chem.*, 10, 2296 (1971). [d] P. A. Yeats, J. R. Sams, and F. Aubke, *ibid.*, 11, 2634 (1972). [e] R. J. Gillespie and R. A. Rothenbury, *Can. J. Chem.*, 42, 416 (1964).

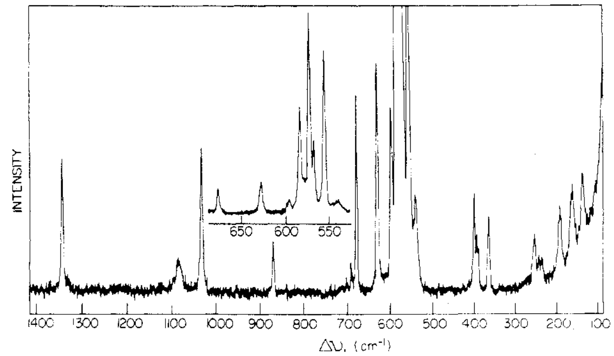

Figure 2. Raman spectrum (−90°) of solid $(FXe)_2SO_3F^+AsF_6^-$ contained in a glass sample tube.

and coupling constant observed for $(FXe)_2SO_3F^+$ throughout the decomposition (Table I). Fluorine exchange would entail the making and breaking of Xe-F bonds, leading to a single exchange-averaged environment exhibiting no ^{129}Xe-^{19}F coupling in the fast-exchange limit. An intermediate rate of fluorine exchange, however, would not lead to complete collapse of such a large ^{129}Xe-^{19}F coupling and would cause the chemical shift and coupling constant to decrease with increasing exchange rate. Fluorine exchange is apparently slower in the case of the AsF_6^- salt and this may be due to either a difference in the relative base strengths of AsF_6^- and SbF_6^- or the difference in the concentrations of the solutions.

Solutions of XeF^+ are also not stable at room temperature and their reaction according to eq 6 comprises the second

$$XeF^+MF_6^- + 2HSO_3F \rightarrow Xe + MF_5 + S_2O_6F_2 + 2HF \qquad (6)$$

step in the overall decomposition of $(FXe)_2SO_3F^+$ in HSO_3F solvent. The formation of MF_5 in these systems is indicated by rapid fluorine exchange among AsF_6^-, AsF_5, and HF environments to give a single broad exchange-averaged peak (Figure 1c, d) in the case of the AsF_6^- salt and by a steady increase in the intensity of the lines due to $SbF_5SO_3F^-$ and $Sb_2F_{11}^-$ throughout the decomposition of the SbF_6^- salt.[10]

Raman Spectroscopy. The laser Raman spectrum of the product of the reaction of $Xe_2F_3^+AsF_6^-$ with HSO_3F was studied at low temperature and it provides further support for our conclusion that this compound can be formulated as $(FXe)_2SO_3F^+AsF_6^-$ with the cation containing a bridging fluorosulfate group. Although Bartlett, *et al.*,[8] did not publish a diagram of the room-temperature spectrum, a comparison of their observed frequencies and intensities with ours indicates that our low-temperature spectrum (Figure 2) was better resolved. The frequencies of the bands observed in the spectrum and their proposed assignments are given in Table II together with the spectra of some related compounds.

The cation $(FXe)_2SO_3F^+$ would be expected to possess C_s symmetry and therefore a total of 21 normal modes is predicted, 12 a′ and 9 a″, all of which are active in the Raman spectrum.

The sulfur-oxygen stretching frequencies are most readily assigned. The SO_3F^- ion (C_{3v} symmetry) has a symmetric SO_3 stretching mode, $\nu(a_1)$, at *ca.* 1080 cm^{-1} and the doubly degenerate antisymmetric stretching mode, $\nu_4(e)$, at *ca.* 1290 cm^{-1}.[15] The latter mode is split into two components for C_s symmetry resulting in three Raman-active vibrations. The vibrational frequencies due to the SO_3F group are compared with the corresponding modes for the fluorosulfate-bridged polymeric compounds IO_2SO_3F,[16] $(CH_3)_2Sn(SO_3F)_2$,[17] and SbF_4SO_3F.[18] The frequencies for the SO_3F

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(16) H. A. Carter and F. Aubke, *Inorg. Chem.*, 10, 2296 (1971).

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group in $(FXe)_2SO_3F^+$ agree quite well with those for these polymeric compounds.

The very high frequency (871 cm^{-1}) of the S-F stretching mode is also noteworthy and again indicates that the SO_3F group is in the central bridging position. If the SO_3F group were in a terminal position, the S-F stretching frequency would be expected to be close to those observed for $FXeSO_3F$ and $Xe(SO_3F)_2$, *i.e.*, 798 and 818 cm^{-1}, respectively. The S-F stretching frequency for bridging fluorosulfate groups, however, generally has a rather high value, *e.g.*, 890 cm^{-1} in SbF_4SO_3F.

Bands below 800 cm^{-1} are assigned by comparison with the spectra of the related fluorosulfates, $FXeSO_3F$ and $Xe(SO_3F)_2$ (Table II), and the AsF_6^- anion.[19] The bands at 554, 566, 571, and 582 cm^{-1} are assigned to Xe-F stretching frequencies as they are close to the Xe-F frequencies observed for XeF_2 and $FXeSO_3F$ and, like all the Xe-F bands previously observed, are relatively strong.[19] The origin of four strong lines instead of just two is not certain but it most probably arises from a solid state (factor group) splitting. The 395- and 400-cm^{-1} peaks in the spectrum of $(FXe)_2SO_3F^+$ are attributed to the Xe-O stretches. This is in agreement with Xe-O stretching modes assigned for $FXeSO_3F$ and $Xe(SO_3F)_2$ (Table II) and the Xe-O modes in the spectra of $FXeOTeF_5$ (457 cm^{-1}),[4] $Xe(OTeF_5)_2$ (434 cm^{-1}),[3] and $XeOTeF_5^+AsF_6^-$ (477 cm^{-1}).[5] Assignments of the low-frequency bending and torsional modes cannot be made with any degree of certainty, but plausible assignments are given.

Based on the frequencies of ν(Xe-F) and ν(Xe-O), an approximate assessment of the relative covalent character of the Xe-O bonds in $(FXe)_2SO_3F^+$ can be made. It is noteworthy that the Xe-F stretching frequencies are lower than those of $\mathit{F}Xe^+\cdots F\text{-}MF_5^-$ and $(\mathit{F}Xe)_2F^+$ [19] but are higher in frequency than that of $FXeSO_3F$. Parallel trends have also been noted for the ^{19}F chemical shifts, $^{129}Xe-^{19}F$ coupling constants, and Xe-F bond lengths of related Xe(II) species and lead to a predicted Xe-F bond length of 1.92 Å for $(FXe)_2SO_3F^+$.[10] This increase in the covalent character of the Xe-F bond relative to that of the monofluorosulfate leads to a corresponding decrease in the covalent character of the Xe-O bond and a corresponding decrease in the Xe-O stretching frequency, which is lower than that of either $FXeSO_3F$ or $Xe(SO_3F)_2$ (Table II). We therefore conclude that $(FXe)_2SO_3F^+$ is more ionic than either $FXeSO_3F$ or $Xe(SO_3F)_2$, *i.e.*, that there is a greater contribution from structures such as $(FXe)^+(SO_3F)^-(XeF)^+$ and $(FXeSO_3F)(XeF)^+$, but is less ionic than either $(FXe)_2F^+$ or $FXe^+\cdots F\text{-}MF_5^-$.

Experimental Section

Materials. The preparation of $Xe_2F_3^+AsF_6^-$, $Xe_2F_3^+SbF_6^-$, and $XeF^+AsF_6^-$ as well as the purification of HF, HSO_3F, and BrF_5 has been described elsewhere.[10]

Preparation of $(FXe)_2SO_3F^+AsF_6^-$. In a typical preparation, 1.396 g (13.95 mmol) of HSO_3F dissolved in 10.95 g of HF was transferred by pouring through Kel-F and Teflon connections under vacuum to a Kel-F tube containing 7.116 g (13.99 mmol) of $Xe_2F_3^+AsF_6^-$. The HF was removed by pumping first at 0° and then at room temperature under vacuum. Continued pumping on the solid at room temperature indicated that the compound sublimes. The analytical results are in agreement with the proposed formulation, $(FXe)_2SO_3F^+AsF_6^-$. *Anal.* Calcd: F, 29.05; S, 5.45; As, 12.71; Xe, 44.62. Found: F, 29.29; S, 5.35; As, 12.56; Xe, 44.28.

Sample Preparation. All manipulations were carried out under anhydrous conditions on a vacuum line constructed from Monel, Kel-F, and Teflon or in a drybox. All preparative work was done in 15 cm × 2 cm o.d. Kel-F tubes (Argonne National Laboratory) equipped with Kel-F heads and Teflon valves.

Nmr and Raman samples were prepared and vacuum sealed in 5-mm o.d. medium-wall Pyrex nmr tubes attached to Teflon valves with $^1/_4$-in. Teflon nuts and ferrules. Bromine pentafluoride samples were prepared by distilling an appropriate quantity of BrF_5 into a sample tube containing the solute. Fluorosulfuric acid samples were prepared in a drybox by syringing the solvent into a sample tube containing the solute cooled to liquid nitrogen temperature. Samples were warmed briefly to −40° to effect dissolution and stored at −78° until the spectra could be recorded.

^{19}F Nmr Spectra. Fluorine nmr spectra were recorded on a Varian DA-60IL spectrometer operating at 56.4 MHz and modified as described previously[20] to record spectra from the first upper side band in field sweep unlock mode. The spectra were calibrated by the usual audio side band method using a Muirhead-Wigan D-890-A decade oscillator and referenced relative to external $CFCl_3$ by sample interchange. Side-band frequencies were checked with a General Radio Type 1191 frequency counter. A Varian V-4540 variable-temperature controller and variable-temperature probe were used to adjust the sample tube to the required temperature. The chemical shifts are estimated to be accurate to ±0.5 ppm.

Raman Spectra. The Raman spectrum of the solid was obtained with a Spex Industries Model 1400 spectrometer using the 5145-Å radiation from a Spectra Physics Model 164 argon ion laser. Spectra were recorded at −90° 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 spectrometer was calibrated by recording the mercury discharge lines over the spectral range of interest; the Raman shifts quoted are estimated to be accurate to ±2 cm^{-1}.

Acknowledgments. We thank the National Research Council of Canada for financial support of this work and for the award of a scholarship to G. J. S.

Registry No. HSO_3F, 7789-21-1; $Xe_2F_3^+AsF_6^-$, 21308-45-2; $(FXe)_2SO_3F^+AsF_6^-$, 39174-70-4; $Xe_2F_3^+SbF_6^-$, 12528-47-1; $XeF^+AsF_6^-$, 26024-71-5; $K^+SO_3F^-$, 13455-22-6; ^{129}Xe, 13965-99-6.

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