Preparation of $XeOF_3^+ \cdot Sb_2F_{11}^-$ and $XeO_2F^+ \cdot Sb_2F_{11}^-$. ^{19}F Nuclear Magnetic Resonance and Raman Spectra of $XeOF_3^+$ and XeO_2F^+

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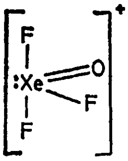
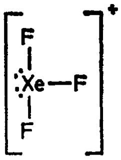
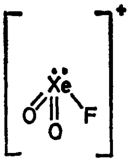
Summary The ^{19}F n.m.r. spectra of solutions in SbF_5 and the Raman spectra of the solids show that the compounds $XeOF_4 \cdot 2SbF_5$ and $XeO_2F_2 \cdot 2SbF_5$ have the ionic structures $XeOF_3^+ \cdot Sb_2F_{11}^-$ and $XeO_2F^+ \cdot Sb_2F_{11}^-$, that the $XeOF_3^+$ ion has the expected trigonal bipyramidal AX_4E type structure and that the XeO_2F^+ ion has a pyramidal structure analagous to the isoelectronic XeO_3.

XENON OXIDE tetrafluoride is known to form the adduct $XeOF_4 \cdot 2SbF_5$ which is a non-volatile white solid melting at *ca.* 70°.[1] The structure of this adduct has not been investigated although it seemed reasonable to suppose that it might be the ionic compound $XeOF_3^+ \cdot Sb_2F_{11}^-$. $XeOF_4$ was prepared by the reaction of equimolar amounts of $XeOF_6$ and H_2O in solution in HF. The solution of XeF_4 in HF


(I)


(II)


(III)

was added to an excess of SbF_5. The solvent and excess SbF_5 were then removed under vacuum and the solid product pumped to constant weight at room temperature. The weight of the product and the elemental analyses were in excellent agreement with the expected composition $XeOF_4{\cdot}2SbF_5$. The adduct was sparingly soluble in SbF_5 at 50° but the solubility was considerably enhanced by the addition of XeF_2 to the solution. A similar effect of XeF_2 on the solubility of XeF_4 in SbF_5 has been noted previously.[2] The solution containing $XeOF_4{\cdot}2SbF_5$ and XeF_2 could be supercooled to 5° long enough to obtain an n.m.r. spectrum. Both solutions gave a ^{19}F n.m.r. spectrum consisting of an AX_2 spectrum in the F-on-Xe region with a slight second order perturbation and accompanying ^{129}Xe satellites (Figure). The spectrum is consistent with the expected structure for the $XeOF_3^+$ cation (I) in which the lone-pair, an oxygen atom and a fluorine atom occupy the equatorial positions of a trigonal bipyramid and two fluorine atoms occupy the axial positions. The structure is thus very similar to that of the isoelectronic IOF_3 molecule. The n.m.r. parameters are given in Table 1.

TABLE 1

^{19}F *N.m.r. parameters for the fluoro- and oxyfluoro-cations of* Xe^{VI} *in* SbF_5 *solvent*

Cation	Chemical shift[a] (p.p.m.)	J_{FF} (Hz)	$J_{^{129}Xe-^{19}F}$ (Hz)	Temp. (°C)	Molal conc. of cation
XeF_5^{+}[b]	A-231·7	175·7	1512	35	(XeF_5^+) = 0·251
	X_4-108·8		143·1		
$XeOF_3^+$	A-195·1	103·0	983	5	$(XeOF_3^+)$ = 0·699
	X_2-147·1		434		(XeF^+) = 1·10
XeO_2F^+	-199·4		79·7	5	[c]

[a] With respect to external $CFCl_3$. [b] Ref. 3. [c] Prepared by dissolving 0·354 g of XeO_2F^+–$XeF^+Sb_2F_{11}^-$ mixture in 1·75 g of SbF_5.

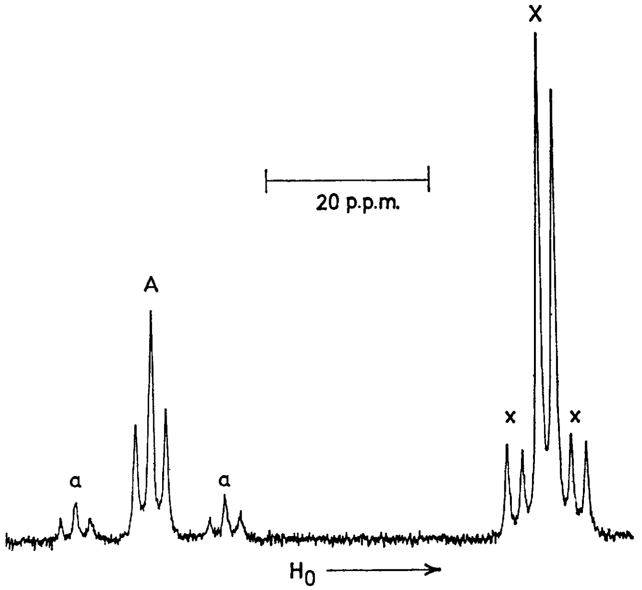


FIGURE. ^{19}F *N.m.r. spectrum* (5°, 56·4 *MHz*) *of the* $XeOF_3^+$ *cation in a solution having the molal composition* $(XeOF_3^+)$ 0·699, (XeF^+) 1·10. (*A*) *equatorial fluorine and* (*a*) ^{129}Xe *satellites;* (X) *axial fluorines and* (x) ^{129}Xe *satellites.*

The Raman spectrum of the solid adduct $XeOF_4{\cdot}2SbF_5$ is also consistent with the formulation $XeOF_3^+{\cdot}Sb_2F_{11}^-$ since, in addition to the bands expected for the $Sb_2F_{11}^-$ ion, we also observed bands at 942 cm^{-1}, which may be attributed to the Xe=O stretch, and at 634, 589, and 554 cm^{-1}, which may be attributed to the Xe–F equatorial stretch and the symmetric and asymmetric stretches Xe–F axial, respectively. Comparison with the spectra of the isoelectronic IOF_3 molecule and with XeF_3^+ and $XeOF_4$ also supports these assignments. The Xe–F frequencies are very close to those of XeF_3^+ which has the very similar structure (II) with a lone pair replacing the doubly-bonded oxygen.

TABLE 2

Observed Raman frequencies and assignments for $XeOF_3^+$ *and* XeO_2F^+ *and related species*

Vibrational mode		Frequency (cm^{-1})			
		$XeOF_3^+$	IOF_3[a]	XeF_3^{+}[b]	$XeOF_4$[c]
$Xe^{I}{=}O$ stretch		942	883	—	919
Xe^{I}–F eq. stretch		634	657	643	
					566[f]
Xe^{I}–F ax. stretch	sym.	589	550	584	
					530[g]
	asym.	554[e]	515	549[e]	
		XeO_2F^+	IO_2F[a]	XeO_2F_2[d]	
$Xe^{I}{=}O$ stretch	sym.	865	807	850	
	asym.	924	866	882	
Xe^{I}–F stretch		595	550	537	

[a] Ref. 4. [b] Ref. 3. [c] Ref. 5. [d] Ref. 6. [e] Because of other peaks in this region of the spectrum this assignment must be regarded as tentative. [f] Xe–F sym. stretch. [g] Xe–F asym. stretch.

No adducts of XeO_2F_2 with SbF_5 have so far been reported. A solution of XeO_2F_2 in HF was prepared by adding water to a solution of XeF_6 in a 2:1 mol ratio. This solution was added at low temperature to an excess of SbF_5 and the mixture warmed to room temperature and pumped to constant weight. The weight of the yellow solid product corresponded to the composition $XeO_2F_2{,}1{\cdot}8SbF_5$. The solid dissolved readily in SbF_5 at room temperature to give a yellow-green solution which slowly evolved a gas which appeared to be oxygen. Cooling to 5° caused the gas evolution to cease and caused the colour of the solution to intensify to a dark green. The ^{19}F n.m.r. spectrum of the solution consisted of a very broad and intense line due to F-on-Sb, a strong XeF^+ line with accompanying ^{129}Xe satellites and an intense new single line with a small Xe–F coupling which is assigned to XeO_2F^+. The Xe–F coupling in XeO_2F^+ is the smallest that has been observed up to the present time. The n.m.r. parameters are summarised in Table 1. The chemical shifts of the Xe^{VI} fluorocations are to much lower field than the Xe^{IV} and Xe^{II} fluorocations and the Xe–F coupling constant is also much smaller and of opposite sign. These n.m.r. parameters will be discussed in detail in a forthcoming publication. The evolution of oxygen gas is presumably due to the decomposition

$$XeO_2F^+ \xrightarrow{SbF_5} XeF^+ + O_2$$

The presence of XeF^+ in solution as a consequence of this decomposition is probably responsible for the apparently large solubility of $XeO_2F^+{\cdot}Sb_2F_{11}^-$ in SbF_5.

The Raman spectrum of the yellow solid showed, in addition to the lines due to $Sb_2F_{11}^-$, a single Xe–F stretch at 595 cm^{-1} and two frequencies in the Xe=O region at 865 cm^{-1} and 924 cm^{-1} which may be assigned to the symmetric and asymmetric stretches of the XeO_2 group (Table 2). The n.m.r. and Raman spectra are consistent with the expected trigonal pyramidal geometry for the XeO_2F^+ ion (III).

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