AOX_4 coordination. SOF_4 does have this structure,[22] and while the VSEPR theory is not always dependable for transition metal compounds, one might expect it to hold at least for the d^0 molecules $MoOF_4$ and WOF_4. However, if just electron-pair repulsions are considered ("points-on-a-sphere" model), the energy difference between the trigonal-bipyramidal (C_{2v}) and square-pyramidal (C_{4v}) symmetries is only slight; in fact, the Berry "pseudorotation" of trigonal-bipyramidal molecules proceeds, *via* a low potential barrier, through just such a C_{4v} intermediate.[29,30] For heavy atoms with large valence shells, the electron-pair interaction may be very small, resulting in a negligible energy difference between the two structures.[28] If ligand repulsions are important in determining the stereochemistry, the C_{4v} structure may then be favored, and the metal oxytetrafluorides appear to be such a case. According to the models of Table III, for C_{2v} symmetry there are two $O\cdots F$ contacts of 2.47 Å (and in the C_{3v} model there are three such contacts), while for C_{4v} symmetry all four $O\cdots F$ distances are 2.68 Å. The four closest $F\cdots F$ distances, on the other hand, are only slightly different: 2.60 Å for C_{2v} *vs.* 2.56 Å for C_{4v}. Another case in which nonbonded interactions are important in determining the stereochemistry of transition metal compounds is that of the chromyl halides,[31] for which the X–Cr–X angles are larger than the O=Cr=O angles, contrary to the predictions of VSEPR theory. For the sulfuryl halides, however, the reverse is true, and their stereochemistry is determined by the electron-pair repulsions alone.

The motion that would convert the C_{4v} structure of the oxytetrafluorides into C_{2v} symmetry is that of the B_2 bending fundamental, ν_6. Because of the apparently small energy difference between the two symmetries, one would expect this mode to have an abnormally small force constant and large amplitude[30] and perhaps to exhibit a perturbed rotational contour. This fundamental is only Raman active, however, and its observation in the vapor phase would be difficult.[32]

Registry No. $MoOF_4$, 52049-90-8; WOF_4, 52049-91-9; $ReOF_4$, 52152-11-1.

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[29] E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).

[30] R. R. Holmes, *Accounts Chem. Res.*, 5, 296 (1972).

[31] C. D. Garner, R. Mather, and M. F. A. Dove, *J. Chem. Soc., Chem. Commun.*, 633 (1973).

[32] Note Added in Proof. L. E. Alexander, I. R. Beattie, A. Bukovszky, P. J. Jones, C. J. Marsden, and G. J. Van Schalkwyk [*J. Chem. Soc., Dalton Trans.*, 81 (1974)] have recently reported a parallel study of $MoOF_4$ and WOF_4. Vapor density measurements indicated that the gases are essentially monomeric, although there was evidence for polymer formation in WOF_4 (only). Infrared and Raman spectra of the vapor and matrix-isolated species were interpreted as strongly suggesting C_{4v} symmetry. In the Raman spectrum of WOF_4, one band at 328 cm^{-1} was described as weak and broad; this may be the B_2 fundamental that converts C_{4v} symmetry to C_{2v} (see our Discussion). (Alexander, *et al.*, used a numbering system that interchanges the B_1 and B_2 designations relative to our notation. Further confusion arises from their assignment of the 328-cm^{-1} band to B_2 (our B_1) in their text, and to B_1 (our B_2) in their Table 4.)

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The XeF_3^+, $XeOF_3^+$, and XeO_2F^+ Cations. Preparation and Characterization by Fluorine-19 Nuclear Magnetic Resonance Spectroscopy

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The preparation of the salts $XeF_3^+SbF_6^-$, $XeF_3^+Sb_2F_{11}^-$, $XeOF_3^+SbF_6^-$, $XeOF_3^+Sb_2F_{11}^-$, and $XeO_2F^+Sb_2F_{11}^-$ is described. The ^{19}F nmr spectra of solutions of these salts in excess SbF_5 show that the XeF_3^+, $XeOF_3^+$, and XeO_2F^+ ions are present in these solutions. The spectra are consistent with a T-shaped structure of the trigonal-bipyramidal AX_3E_2 type for XeF_3^+ and an AX_4E type structure with the same arrangement of the fluorines and an oxygen replacing one of the equatorial line pairs, for $XeOF_3^+$.

Introduction

Although a large number of complexes of XeF_2 and XeF_6 with fluoride acceptor molecules have been reported[1,2] no such complexes of XeF_4, $XeOF_4$, or XeO_2F_2 had been characterized prior to the work described here. There had been an early report of an unstable xenon tetrafluoride–antimony pentafluoride complex which was believed to have the composition $XeF_4 \cdot 2SbF_5$; however, no analytical or other conclusive evidence in support of this formulation had been published.[3] An early report[4] that XeF_4 interacts with SbF_5 or TaF_5 to form XeF_2 adducts is erroneous. These adducts were most probably obtained because the XeF_4 was contaminated with XeF_2. More recently Martin[5] has claimed the complexes $2XeF_4 \cdot SbF_5$ and $XeF_4 \cdot 4SbF_5$ but again they were not characterized. Bartlett and coworkers have reported that XeF_4 does not form stable adducts with either AsF_5 or IrF_5 in bromine pentafluoride solution[6] or with RuF_5.[7] Consequently, they concluded that the fluoride ion donor ability of XeF_4 is far inferior to that of either XeF_2 or XeF_6. However, as we have shown, XeF_4 does, in fact, readily form the adducts $XeF_4 \cdot SbF_5$ and $XeF_4 \cdot 2SbF_5$, which may be formulated, at least approximately, as the ionic salts $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$. Since our preliminary report[8] of our

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[1] F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

[2] J. H. Holloway, "Noble-Gas Chemistry," Methuen, London, 1968, Chapter 4, p 157.

[3] B. Cohen and R. D. Peacock, *J. Inorg. Nucl. Chem.*, 28, 3056 (1966).

[4] A. J. Edwards, J. H. Holloway, and R. D. Peacock, *Proc. Chem. Soc., London*, 275 (1963).

[5] D. Martin, *C. R. Acad. Sci., Ser. C*, 1145 (1969).

[6] N. Bartlett and F. Sladky, *J. Amer. Chem. Soc.*, 90, 5316 (1968).

[7] D. Gibler, B. Morrell, N. Bartlett, and A. Zalkin, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 13–17, 1971, No. FLUO 1.

[8] R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Chem. Commun.*, 1543 (1971).

^{19}F nmr and Raman spectroscopic evidence for XeF_3^+ Bartlett and coworkers[9] have reported the preparation of $XeF_3^+SbF_6^-$ and $XeF_3^+Sb_2F_{11}^-$ and also an X-ray crystallographic study of $XeF_3^+Sb_2F_{11}^-$.[10] We have completed a similar X-ray crystallographic study of $XeF_3^+SbF_6^-$.[11]

Xenon oxide tetrafluoride was shown to form the adduct $XeOF_4 \cdot 2SbF_5$ several years ago[12] but its structure was not investigated at that time. In a preliminary publication of our results[13] we showed that the ^{19}F nmr spectrum of a solution of $XeOF_4 \cdot 2SbF_5$ in excess SbF_5 and the Raman spectrum of the solid adduct clearly indicated the presence of the $XeOF_3^+$ ion.[13] More recently Bartlett and his coworkers[9] have published a report of the preparation of the adducts $XeOF_4 \cdot SbF_5$ and $XeOF_4 \cdot 2SbF_5$ and of their Raman spectra, which are also consistent with their formulation as salts of the $XeOF_3^+$ cation.

Other than the decomposition of XeO_2F_2 to XeF_2 and oxygen[14] no reactions of XeO_2F_2 have been reported prior to the present work in which it has been shown that XeO_2F_2 reacts with SbF_5 to give the XeO_2F^+ cation.[13]

In this paper the details of the preparation of a number of complexes of XeF_4, $XeOF_4$, and XeO_2F_2 with SbF_5 together with a study of the ^{19}F nmr spectra of their solutions in SbF_5 are presented. These spectra show the formation of the ions XeF_3^+, $XeOF_3^+$, and XeO_2F^+ in these solutions and provide information on the structures of the cations.

Results and Discussion

The crystalline salt $XeF_3^+Sb_2F_{11}^-$ was prepared by the reaction of XeF_4 with an excess of SbF_5

$$XeF_4 + 2SbF_5 \rightarrow XeF_3^+Sb_2F_{11}^- \qquad (1)$$

Xenon tetrafluoride is soluble in redistilled antimony pentafluoride at 50° to give a yellow-green solution which crystallizes at lower temperatures. Removal of excess SbF_5 under vacuum at room temperature yields a yellow crystalline solid which is stable at room temperature. The combining ratio and elemental analyses were consistent with the formulation of this compound as $XeF_3^+Sb_2F_{11}^-$. In contrast, Cohen and Peacock,[3] who used XeF_4 that was probably significantly contaminated with XeF_2, reported that XeF_4 or mixtures of XeF_4 and XeF_2 dissolve in antimony pentafluoride with gas evolution to give green solutions. Upon removal of excess SbF_5 these authors reported that they obtained an easily decomposed white solid, which was presumed to be $XeF_4 \cdot 2SbF_5$, and a yellow solid, which was presumed to be $XeF_2 \cdot 2SbF_5$. It is likely that the yellow solid reported by Cohen and Peacock was really a mixture of $XeF^+Sb_2F_{11}^-$ and $XeF_3^+Sb_2F_{11}^-$, and although the nature of the easily decomposed white solid is not clear, it is certain that it was not $XeF_3^+Sb_2F_{11}^-$.

Two modifications of the 1:1 adduct $XeF_4 \cdot SbF_5$ were found. The high-temperature α modification was prepared by warming an excess of XeF_4 with $XeF_3^+Sb_2F_{11}^-$ in an evacuated glass ampoule to 80°. Removal of excess XeF_4 under vacuum at 80° yielded a pale yellow-green solid which had an elemental analysis corresponding to $XeF_3^+SbF_6^-$. A second form of $XeF_3^+SbF_6^-$, the low-temperature β modification, was prepared by allowing SbF_5 to react with excess XeF_4 in anhydrous HF at 0°. Crystallization from HF solution at room temperature followed by removal of excess solvent and XeF_4 under vacuum yielded pale yellow-green crystals which were suitable for a single-crystal X-ray structure analysis.[11]

Although an excess of XeF_4 was used in the preparation of $XeF_3^+SbF_6^-$, no evidence was obtained for the formation of an $Xe_2F_7^+$ salt although both $Xe_2F_3^+$ and $Xe_2F_{11}^+$ are known. Bartlett and coworkers[9] obtained a similar negative result.

The preparation of $XeOF_4$ by the reaction of equimolar amounts of XeF_6 and H_2O may be safely and conveniently carried out in HF solution. Addition of the resulting solution to an excess of SbF_5 followed by removal of the solvent and unreacted SbF_5 under vacuum yielded a white solid having an elemental analysis in excellent agreement with the composition $XeOF_3^+Sb_2F_{11}^-$. The 1:1 adduct $XeOF_3^+SbF_6^-$ was prepared by the interaction of SbF_5 with an excess of liquid $XeOF_4$ at room temperature. Removal of excess $XeOF_4$ under vacuum yielded a stable white solid which had an elemental analysis in agreement with the formulation, $XeOF_3^+SbF_6^-$.

Xenon dioxide difluoride was generated in HF solution in a manner analogous to that used for the preparation of $XeOF_4$ by the reaction of XeF_6 with twice the molar amount of water. Reaction of the resulting solutions with excess SbF_5 followed by removal of the solvent and excess SbF_5 under vacuum yielded a light yellow solid. The presence in the Raman spectrum of an intense band at 619 cm^{-1} in addition to lines attributable to the XeO_2F^+ cation and the $Sb_2F_{11}^-$ anion indicated that this material contained a significant amount of $XeF^+Sb_2F_{11}^-$,[14] which is, itself, a yellow solid when pure. The formation of this product is consistent with the fact that during the final stages of pumping off HF and excess SbF_5 from the reaction mixture the product was for a time dissolved in what was essentially pure SbF_5 in which it is unstable and slowly evolves oxygen gas. The decomposition of the XeO_2F^+ cation proceeds according to eq 2

$$XeO_2F^+ \rightarrow XeF^+ + O_2 \qquad (2)$$

and is analogous to that of XeO_2F_2[15] which is also thermodynamically unstable and slowly decomposes to XeF_2 and O_2. The problem of decomposition was circumvented by allowing stoichiometric amounts of SbF_5 and XeO_2F_2 to react in HF solution. Pumping this solution to dryness at room temperature led to the formation of a white solid which had an elemental analysis and a combining ratio corresponding to $XeO_2F^+Sb_2F_{11}^-$. The overall reaction corresponding to the formation of $XeO_2F^+Sb_2F_{11}^-$ is

$$XeO_2F_2 + 2SbF_5 \rightarrow XeO_2F^+Sb_2F_{11}^- \qquad (3)$$

The solid compound was also somewhat unstable at room temperature and was found to be essentially completely decomposed after 2 months to $XeF^+Sb_2F_{11}^-$. The decomposition of a sample sealed in a glass capillary was monitored by Raman spectroscopy. Exposure of solid $XeF^+Sb_2F_{11}^-$ to 150 atm of oxygen gas at room temperature for 8 hr and subsequent examination of the sample by Raman spectroscopy gave no evidence that reaction 2 is reversible under these conditions.

^{19}F Nmr Spectroscopy. Cohen and Peacock[3] reported that the nmr spectra of solutions of XeF_4 contained other peaks due to fluorine on xenon in addition to the peak that arises

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(9) D. E. McKee, C. J. Adams, and N. Bartlett, *Inorg. Chem.*, 12, 1722 (1973).

(10) D. E. McKee, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 12, 1713 (1973).

(11) P. Boldrini, R. J. Gillespie, P. Ireland, and G. J. Schrobilgen, *Inorg. Chem.*, in press.

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(13) R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 607 (1972).

(14) R. J. Gillespie and B. Landa, *Inorg. Chem.*, 12, 1383 (1973).

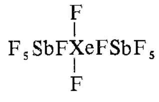
(15) J. L. Huston, *J. Phys. Chem.*, 71, 339 (1967).

Table I. ^{19}F Nmr Parameters for XeF_3^+, $XeOF_3^+$, and XeO_2F^+ in SbF_5 Solvent

Solutes (molality)	Temp, °C	Species	Chem shift,[a] ppm	J_{FF}, Hz	$J_{^{129}Xe-^{19}F}$, Hz
XeF_4 (0.20) XeF_2 (0.50)	26	XeF_3^+	A −23.0 B_2 −38.7	174	2440 2620
		XeF^+	291.5		7260
		SbF_5, $Sb_2F_{11}^-$	112.5		
$XeOF_3^+Sb_2F_{11}^-$ (0.70) XeF_2 (1.10)	5	$XeOF_3^+$	A −195.1 X_2 −147.1	103	983 434
		XeF^+	294.5		7295
		SbF_5, $Sb_2F_{11}^-$	118.7		
$XeO_2F^+Sb_2F_{11}^-$ $XeF^+Sb_2F_{11}^-$ mixture[b]	5	XeO_2F^+	−199.4		80
		XeF^+	289.5		7215
		SbF_5, $Sb_2F_{11}^-$	110 vb		

[a] With respect to external $CFCl_3$. [b] Prepared by dissolving 0.35 g of $XeO_2F^+Sb_2F_{11}^-$–$XeF^+Sb_2F_{11}^-$ mixture (composition unknown) in 1.75 g of SbF_5.

from XeF_2 and which has subsequently been shown to be due to XeF^+.[16] These new lines which were reported to consist of two sets of triplets were attributed to a Xe(IV) species with two bridging and two nonbridging fluorines (I). Poorly

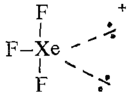


$$F_5SbF\overset{F}{\underset{F}{Xe}}FSbF_5$$

I

resolved sets of small peaks, which occurred symmetrically on each side of the center group of lines, were also observed and were attributed to ^{129}Xe–^{19}F coupling in the XeF_4–SbF_5 complex. The ^{129}Xe–^{19}F coupling constant was estimated to be approximately the same for both fluorine-on-xenon environments, *i.e.*, 4000 Hz. No chemical shifts or fluorine–fluorine coupling constants were quoted for the Xe(IV) species.

In attempting to repeat Cohen and Peacock's work, the spectrum of a solution of XeF_4 in SbF_5 was obtained at 50°. The spectrum showed several poorly resolved peaks to low field of an intense broad peak in the fluorine-on-antimony region. The poor resolution was presumably due to fluorine exchange among the F-on-Sb and F-on-Xe(IV) environments. Attempts to slow the exchange by recording the spectrum at lower temperature resulted in crystallization of the sample. It was found, however, that a mixture of XeF_2 and XeF_4 is quite soluble in SbF_5 at room temperature. The enhanced solubility of XeF_4 in SbF_5 solutions containing XeF_2 is apparently due to the increased ionizing power of the solvent resulting from the presence of the XeF^+ and $Sb_nF_{5n+1}^-$ ions. The room-temperature ^{19}F nmr spectrum of the solution was similar to that recorded at 50° in pure SbF_5 except that resolution of the low-field peaks was considerably enhanced (Figure 1). The low-field F-on-Xe region of the spectrum consists of an AB_2 spectrum with ^{129}Xe satellites and not of an A_2X_2 (A_2B_2) pattern as previously reported by Cohen and Peacock. The two ^{129}Xe–^{19}F coupling constants are similar (∿2500 Hz), but they are considerably smaller than 4000-Hz couplings reported in the previous work. The ^{19}F nmr parameters obtained in the present work are listed in Table I. The spectrum is consistent with the expected C_{2v} geometry for the XeF_3^+ cation (II) in which two lone pairs occupy the equatorial positions of a trigonal-bipyramidal arrangement of five electron pairs[17] as in ClF_3[18,19] and BrF_3.[20] The relative chemical shifts of the A and B parts of the spectrum are consistent with the suggested geometry; *i.e.*, the B (axial) fluorines occur at lower field than the A (equatorial) fluorine as in the case of ClF_3.[21]



II

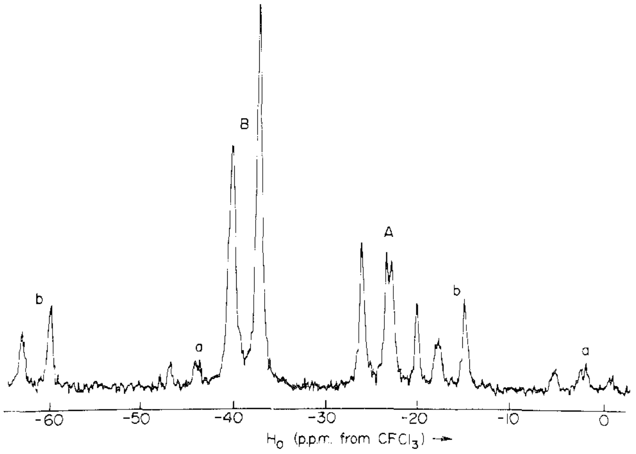


Figure 1. The ^{19}F nmr spectrum (56.4 MHz, 26°) of the XeF_3^+ cation (0.20 *m* XeF_4 and 0.50 *m* XeF_2 in SbF_5 solution): (A) axial fluorines and (a) ^{129}Xe satellites; (B) equatorial fluorine and (b) ^{129}Xe satellities.

The adduct $XeOF_4 \cdot 2SbF_5$ is sparingly soluble in SbF_5 at 50°, but the solubility is 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 above. The solution containing $XeOF_4 \cdot 2SbF_5$ and XeF_2 could be supercooled to 5° long enough to obtain a well-resolved nmr spectrum. At higher temperatures fluorine exchange among F-on-Xe(VI) and F-on-Sb environments caused exchange broadening of the lines. In addition to lines attributable to fluorine on antimony and to XeF^+, these solutions gave a ^{19}F nmr spectrum in the F-on-Xe(VI) region consisting of an AX_2 spectrum with a slight second-order perturbation and accompanying ^{129}Xe satellites (Figure 2). The spectrum is consistent with the expected structure for the $XeOF_3^+$ cation (III) in which the lone pair, the oxygen atom, and a fluorine atom occupy the equatorial positions of a trigonal bipyramid and two fluorine atoms occupy the axial positions,[17] as has been

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(16) R. J. Gillespie, A. Netzer, and G. J. Schrobilgen, *Inorg. Chem.*, 13, 1455 (1974).

(17) R. J. Gillespie, "Molecular Geometry," Van Nostrand-Reinhold, London, 1972.

(18) D. F. Smith, *J. Chem. Phys.*, 21, 609 (1953).

(19) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, 21, 602 (1953).

(20) D. W. Magnuson, *J. Chem. Phys.*, 27, 223 (1957).

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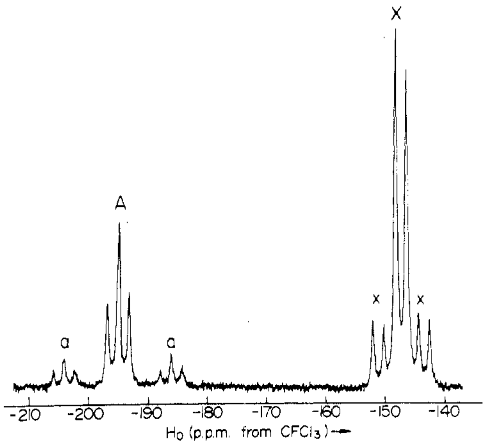
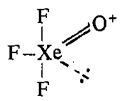
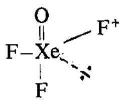


Figure 2. The ^{19}F nmr spectrum (56.4 MHz, 5°) of the $XeOF_3^+$ cation (0.70 *m* $XeOF_3^+Sb_2F_{11}^-$ and 1.10 *m* XeF_2 in SbF_5 solution): (A) equatorial fluorine and (a) ^{129}Xe satellites; (X) axial fluorines and (x) ^{129}Xe satellites.

observed for the isoelectronic $ClOF_3$[22] and IOF_3[23] molecules. Structure IV cannot be ruled out on the basis of the ^{19}F nmr results alone, although it is inconsistent with the predictions of the VSEPR theory[17] and with the Raman spectrum.[24] Although Pilipovich and coworkers[25] have shown that the high-resolution spectrum of $ClOF_3$ is a single line, a more recent study of the transverse relaxation as a function of the temperature and frequency by Alexandre, *et al.*,[26] has shown that two different fluorine environments are present in $ClOF_3$. As in the case of $XeOF_3^+$, the resonance of the axial fluorines of $ClOF_3$ is at higher field than that of the equatorial fluorine. The nmr parameters are given in Table I.

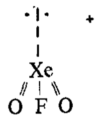


III



IV

Dissolution of a mixture of $XeO_2F_2 \cdot 2SbF_5$ and $XeF_2 \cdot 2SbF_5$ in SbF_5 at room temperature gave a yellow-green solution which slowly evolved oxygen gas. Cooling to 5° caused gas evolution to cease and caused the color of the solution to intensify to a dark green. The ^{19}F nmr spectrum of the solution consisted of a very broad and intense line due to fluorine on antimony, a strong XeF^+ line with accompanying ^{129}Xe satellites, and an intense new single line at low field with a small ^{129}Xe-^{19}F coupling which can only reasonably be assigned to XeO_2F^+ (V). The ^{129}Xe-^{19}F coupling in XeO_2F^+ is the smallest that has been observed up to the present time. The nmr parameters are summarized in Table I.



V

Correlation of the ^{129}Xe-^{19}F Coupling Constant and ^{19}F Chemical Shift. We have previously noted that a nearly linear correlation exists between the ^{19}F chemical shift and the ^{129}Xe-^{19}F coupling constants of the xenon fluorides and oxyfluorides and their cations, and the XeF_3^+, $XeOF_3^+$, and XeO_2F^+ cations conform to this relationship.[27] It seems likely that the observed trend, a decrease in the ^{19}F chemical shift with decreasing coupling constant, can be rationalized if differences in the nmr parameters are determined mainly by the same term. In the case of the ^{19}F chemical shift, differences are determined mainly by the paramagnetic term of the screening tensor, $\sigma_p{}^{AA}$. By second-order perturbation theory[28] $\sigma_p{}^{AA}$ can be expressed in terms of ground-state molecular orbitals and is inversely proportional to a mean excitation energy ΔE, *i.e.*

$$(\sigma_p{}^{AA})_{av} = \frac{-e^2\hbar^2}{2m^2c^2(\Delta E)}\langle r^{-3}\rangle_{2p}(Q_{AA})_{av} + \sum_{B(\neq A)}(Q_{AB})_{av} \tag{4}$$

where $\langle r^{-3}\rangle_{2p}$ is the mean inverse cube of the 2p-orbital radial function on fluorine, $(Q_{AA})_{av}$ is a charge density term for fluorine, and

$$\sum_{B(\neq A)}(Q_{AB})_{av}$$

is a F-Xe π-bond order term. The terms Q_{AB}, which can only occur if the xenon atom possesses available p atomic orbitals, contain the $p\pi$-$p\pi$ contribution to the chemical shift.

Similarly, if the Fermi contact contribution for Xe-F spin-spin coupling is assumed to be dominant, the reduced coupling constant K_{AB} can be expressed in terms of the δ_A-δ_B bond order and the mean excitation energy[29]

$$K_{AB} = \frac{2}{9}\frac{e^2h^2}{m^2c^2(\Delta E)}(s_B|\delta(\mathbf{r}_B)|s_B)(s_A|\delta(\mathbf{r}_A)|s_A)(P_{s_As_B})^2 \tag{5}$$

where $P_{s_As_B}$ is the MO bond order between the 5s orbital of xenon and the 2s orbital of fluorine.

The linear relationship between $J_{^{129}Xe-^{19}F}$ and $\delta_{^{19}F}$ is therefore apparently explicable if the variation of each of these two parameters is due largely to the variation in the mean excitation energy ΔE.

Experimental Section

Xenon tetrafluoride and xenon hexafluoride were prepared from xenon, 99.9% (Matheson), and fluorine (Matheson) according to the methods described by Malm and Chernick.[30] Both fluorides were purified by heating with dry sodium fluoride, the method is essentially that described by Sheft, *et al.*[31] Pure liquid $XeOF_4$ was made by the interaction of solid XeF_6 with a glass surface at room temperature.[32]

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. In typical experiments *ca.* 1.4 g of XeF_6 was transferred under vacuum to preweighed Kel-F cold traps fitted with Teflon valves and dissolved in *ca.* 2.0 g of HF. A stoichiometric amount of distilled water was weighed out in a Kel-F tube which was subsequently equipped with a Kel-F head and Teflon valve. The water was then slowly pumped into the cold trap containing a frozen solution (−196°) of XeF_6 in HF. The distillation was periodically interrupted and the

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contents of the trap warmed to room temperature and remotely agitated from behind a suitable barricade. In this manner high local concentrations of water, which could lead to the production of significant quantities of XeO_3 and violent explosions, were avoided. The solutions were used immediately after their preparation to form the $XeOF_3^+$ and XeO_2F^+ salts as described below.

Preparation of $XeF_3^+Sb_2F_{11}^-$ and $XeF_3^+SbF_6^-$. A quantity of SbF_5 (3.773 g, 17.41 mmol) was added to 0.883 g (4.26 mmol) of XeF_4 in a glass ampoule. A Teflon valve was attached and the ampoule and contents was warmed to 50° to effect dissolution. The resulting yellow-green solution crystallized immediately upon cooling to room temperature. Excess SbF_5 was removed under vacuum at room temperature and pumping continued until constant weight was obtained (~36 hr). The final weight of product was 2.755 g and corresponded to $XeF_4 \cdot 2.03SbF_5$. The combining ratio as well as the elemental analyses is consistent with the formulation of this compound as $XeF_3^+Sb_2F_{11}^-$. *Anal.* Calcd: F, 41.51; Sb, 38.00; Xe, 20.49. Found: F, 41.22; Sb, 38.37; Xe, 20.75.

A quantity of $XeF_3^+Sb_2F_{11}^-$ (0.251 g, 0.391 mmol) was fused with XeF_4 (0.286 g, 1.381 mmol) for 1 hr at 80°. Excess XeF_4 was removed under vacuum at room temperature. The elemental analyses are consistent with the formulation $XeF_3^+SbF_6^-$. *Anal.* Calcd: F, 40.33; Sb, 28.71; Xe, 30.96. Found: F, 40.55; Sb, 28.32; Xe, 30.60.

Attempts were made to prepare $Xe_2F_7^+SbF_6^-$ by a method analogous to that used previously to prepare $Xe_2F_3^+SbF_6^-$.[16] In a typical experiment, 0.264 g (1.217 mmol) of SbF_5 in 5.565 g of HF was added to 0.504 g (2.324 mmol) of XeF_4 in a Teflon tube through a Kel-F Y piece. The XeF_4 dissolved at room temperature to give a bright yellow solution. The HF solvent was slowly pumped off at room temperature to give a pale yellow-green crystalline solid. A portion of the sample was transferred to a glass tube and examined by Raman spectroscopy and was shown to contain a significant amount of unreacted XeF_4. Excess XeF_4 was pumped off under vacuum at room temperature and a suitable crystal was selected from the remaining material and subjected to a single-crystal X-ray structure determination. The Raman spectrum of the crystal used in the structure analysis was identical with the spectrum of the bulk material. The results of the X-ray crystal structure determination, which has been published elsewhere,[11] show that this material was $XeF_3^+SbF_6^-$. No evidence for the formation of $Xe_2F_7^+SbF_6^-$ was obtained in the present work.

Preparation of $XeOF_3^+Sb_2F_{11}^-$ and $XeOF_3^+SbF_6^-$. A solution containing 1.307 g (5.853 mmol) of $XeOF_4$ in 1.991 g of HF was poured through a Kel-F Y piece into a preweighed Teflon trap and valve assembly containing 3.516 g (16.22 mmol) of SbF_5. The HF solvent was pumped off at room temperature and pumping continued for 8 hr. The weight of the white solid remaining in the trap was 3.800 g and corresponded to the composition $XeOF_4 \cdot 1.965SbF_5$. The elemental analyses as well as the combining ratio support the formulation of this compound as $XeOF_3^+Sb_2F_{11}^-$. *Anal.* Calcd: F, 40.50; Sb, 37.07; Xe, 19.99. Found: F, 40.74; Sb, 37.34; Xe, 19.72.

The 1:1 compound $XeOF_3^+SbF_6^-$ was synthesized by allowing 0.529 g (2.439 mmol) of SbF_5 to react with 1.053 g (4.717 mmol) of liquid $XeOF_4$ at room temperature in a preweighed Teflon tube equipped with a Teflon valve. Excess $XeOF_4$ was recovered by pumping the liquid into a Kel-F cold trap assembly cooled to −196°. The resulting white solid was pumped on for 1 additional hr at room temperature. The elemental analyses are in accord with the formulation $XeOF_3^+SbF_6^-$. *Anal.* Calcd: F, 38.86; Sb, 29.84; Xe, 27.67. Found: F, 38.65; Sb, 28.03; Xe, 29.60.

Preparation of $XeO_2F^+Sb_2F_{11}^-$. The techniques used for the formation of the $XeO_2F^+Sb_2F_{11}^-$ were directly analogous to those employed in the synthesis of $XeOF_3^+Sb_2F_{11}^-$. In one experiment 1.392 g (6.914 mmol) of XeO_2F_2 dissolved in 1.550 g of HF was added to 6.452 g (29.77 mmol) of SbF_5. Pumping off the bulk of the solvent at room temperature yielded an SbF_5 solution of what was later shown to be XeO_2F^+. This solution was unstable at room temperature and slowly evolved oxygen gas. Pumping this solution to dryness yielded a light yellow product severly contaminated with $XeF^+Sb_2F_{11}^-$.[33] In another experiment, stoichiometric amounts of XeO_2F_2 (0.918 g, 4.563 mmol, dissolved in 1.185 g of HF) and SbF_5 (1.974 g, 9.11 mmol) were combined, mixed, and immediately pumped to dryness at room temperature. The product was a white solid and had a weight (2.891 g) corresponding to $XeO_2F_2 \cdot 2.00SbF_5$. The elemental analyses are also in agreement with the formulation $XeO_2F^+Sb_2F_{11}^-$. *Anal.* Calcd: F, 35.91; Sb, 38.35; Xe, 20.69. Found: F, 35.64; Sb, 38.67; Xe, 20.43. No Raman band attributable to XeF^+ was observed in material prepared by the latter method.

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Registry No. SbF_5, 7783-70-2; XeF_4, 13709-61-0; $XeF_3^+Sb_2F_{11}^-$, 39797-62-1; $XeF_3^+SbF_6^-$, 39797-63-2; $XeOF_4$, 13774-85-1; $XeOF_3^+Sb_2F_{11}^-$, 39797-64-3; $XeOF_3^+SbF_6^-$, 39797-65-4; XeO_2F_2, 13875-06-4; $XeO_2F^+Sb_2F_{11}^-$, 52078-91-8.

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[33] An intense Raman band at 619 cm^{-1} due to the Xe–F stretching mode of XeF^+ in $XeF^+Sb_2F_{11}^-$ was observed.

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Infrared and Raman Spectra of Trifluoromethyl Perchlorate

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The gas-phase infrared spectrum and the liquid-phase Raman spectrum of trifluoromethyl perchlorate have been recorded. The spectra show that CF_3OClO_3 contains a covalent monodentate perchlorato group. A total of 19 fundamental vibrations out of 21, expected for a model of symmetry C_s with hindered rotation, were observed and assigned.

Introduction

Few covalent perchlorates are known. Among these are free perchloric acid, $HOClO_3$, and its anhydride, $O_3ClOClO_3$, both of which have been known for many years.[1] More recently the halogen perchlorates $FOClO_3$,[2] $ClOClO_3$,[3] $BrOClO_3$,[4] $Cs^+Br(OClO_3)_2^-$,[5] $I(OClO_3)_3$,[6] and $Cs^+I(OClO_3)_4^-$ [6] have been reported. Alkyl perchlorates are also known but are very treacherous materials[1] and therefore have not been investigated extensively. While spectroscopic studies of O_3-

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