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[(FXe)2O2S(O)F]+[AsF6]-

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Contribution from the Department of Chemistry, Princeton University, Princeton, N.J., 08540, The University of California, and the Lawrence Berkeley Laboratory, Berkeley, California, 94720.

FLUOROSULFATES AND PERCHLORATES OF XENON(II) AND THE SALT [(FXe)2O2S(0)F]t[AsF6]−

by

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ABSTRACT

The fluorine ligands of xenon difluoride may be substituted, one at a time, by other electronegative species. Interaction of the difluoride with the appropriate molar quantity of anhydrous acid, below 0°, yields the monofluorosulfate, FXeOSO2F, which is a colorless solid, m.p. 36.6°, the bis-fluorosulfate, Xe(OSO2F)2, which is a pale yellow solid, m.p. 43-45°, the monoperchlorate, FXeOClO3, which is a colorless solid, m.p. 16.5° and a yellow solid, which decomposes below 0°, which is probably the bis-perchlorate, Xe(OClO3)2. All of these xenon difluoride derivatives are thermodynamically unstable and dismutate spontaneously above 0°, the
major products being as represented by the equations:

\[ 2FXeOSO_2F \rightarrow XeF_2 + Xe + S_2O_6F_2; \]
\[ Xe(OSO_2F)_2 \rightarrow Xe + S_2O_6F_2; \]
\[ 2FXeOCIO_3 \rightarrow XeF_2 + Cl_2O_7 + \frac{1}{2}O_2 + Xe; \]
\[ Xe(OClO_3)_2 \rightarrow Xe + Cl_2O_6 + O_2. \]

Although solid products have been obtained from the interaction of XeF_2 with methyl- and trifluoromethyl-sulfuric acids, the stoichiometries of which suggest FXeOR species, they are explosive and have not been well characterized. FXeOSO_2F can be vacuum sublimed at 20°. The bis-fluorosulfate, which is not volatile at 20°, is of lower thermal stability. Single crystals are primitive monoclinic with \( a = 7.8, b = 13.5, c = 6.7 \ \text{Å} \) (all \( \pm 0.1 \ \text{Å} \)), \( \beta = 96° \).

Vibrational spectroscopic evidence indicates that the xenon(II) atom is two coordinated in each of these compounds, the structural formulae being: \( F\cdot Xe\cdot O\cdot S(0)_2\cdot F \); \( F\cdot S(0)_2\cdot O\cdot Xe\cdot O\cdot S(0)_2\cdot F \) and \( F\cdot Xe\cdot O\cdot ClO_3 \). The vibrational spectra indicate that although the Xe atom in \( Xe(OSO_2F)_2 \) is symmetrically coordinated, the molecule is not centrosymmetric.

FXeOSO_2F does not combine with excess XeF_2 to form a \([Xe_2F_3]^+\) salt, as do the FXeMF_6 compounds. The products of the reactions \( XeF^+MF_6^- + FSO_2OH \) (M = Ru, As, Sb), in HF, may be \([XeOSO_2F]^+[MF_6]^-\) salts, but except for the Sb compound they are labile at room temperature. They have not been structurally characterized. The new salt, \([(FXe)OSO_2F]^+[AsF_6]^-\) has been prepared and is sublimable without change. Vibrational spectra indicate that the cation is the symmetrical \([(FXe)OSO_2F]^+\) species. Efforts to prepare \([(FXe)_2O_2CCF_3]^+\) have led to immediate oxidation of the acid:

\[ [Xe_2F_3]^+ [AsF_6]^-. + 2CF_3COOH \rightarrow 2HF + 2Xe + 2CF_4 + 2CO_2 + AsF_5. \]
Hydrogen chloride is also readily oxidized:

\[
[Xe_2F_3]^+[AsF_6]^– + HCl \rightarrow HF + \frac{1}{2} Cl_2 + \frac{1}{4} AsF_5 + \frac{3}{4} [Xe_2F_3]^+[AsF_6]^–
\]

INTRODUCTION

The fluorides and substituted fluorides of xenon are thermodynamically stable\(^1\), whereas the oxides are highly endothermic\(^2\). This difference is largely a consequence of the bond energy of molecular \(O_2\) being greater than that of \(F_2\) (110 versus 37 kcal mole\(^{-1}\)) although the bond energy for Xe-0 is less than for Xe-F. There is no indication that a neutral xenon chloride will be kinetically stable enough to persist at ordinary temperatures, although the matrix isolation work of Pimentel and his coworkers\(^3\) has established that xenon dichloride can be made from the elements in a glow discharge. The bonding in chlorides and other halides is significantly weaker\(^1,3\) than in the fluorides\(^4\). The experimental evidence therefore suggests that only the most electronegative ligands can generate the bond strength essential to ensure the persistence of noble-gas compounds under ordinary temperatures and pressures and this view is also supported by theoretical considerations\(^5\).

Earlier studies, in these laboratories, involving xenon difluoride as an oxidative fluorinator\(^6\), suggested that the fluorosulfate ligand could make an effective bond to xenon. We therefore sought xenon fluorosulfates and perchlorates, by metathesis from the difluoride:

\[
XeF_2 + HA \rightarrow FXeA + HF; \quad FXeA + HF \rightarrow XeA_2 + HF.
\]

Independent investigation, by Musher\(^7\), into the possibility of xenon esters,
Xe(OR)₂, demonstrated that acetates and trifluoroacetates could be prepared. Musher suggested that fluorosulfates and related compounds would also be preparable.

Both the perchlorate and fluorosulfate ligands are strongly electron attracting and the generation of hydrogen fluoride (a very thermochemically favorable compound⁻), gave promise of a forward reaction. The syntheses are effective if the stoichiometry, temperature and hydrogen fluoride removal are properly controlled. The monosubstituted compounds are more stable than the disubstituted and are, therefore, more easily made and handled than the latter. A brief description of the monosubstituted compounds has already been given⁹, and the crystal and molecular structure of FₓeOSO₂F is given in the accompanying paper¹⁰. The chemical and physical behavior of the fluorosulfates and perchlorates show that they are derivatives of bicovalent xenon(II) and the preliminary chemical evidence suggests that they will be effective fluorosulfonating and perchloronating reagents, respectively.

The moderate thermal stability of the xenon fluorosulfates suggested that trifluoromethyl sulfates and even the methyl sulfates might be preparable. Although reactions to produce these compounds did proceed, under control, at temperatures of -20° or lower, the solid products usually detonated at or below room temperatures. The interaction of XeF₂ with a slight molar excess of HOSO₂CF₃ in HF has yielded a solid product which vibrational spectroscopic evidence indicates is CF₃SOₓeF₃.

Since work in these laboratories¹¹ and independent work by Peacock and his coworkers¹², has established XeF₂ to be a fluoride ion donor we have tried to make the (XeOSO₂F)⁺ salts by the interactions FₓeOSO₂F⁺.
MF\textsubscript{5} (M = Ru, As, Sb). The products of these reactions are (except for the Sb system) labile and remain ill-defined, but the new complex cation, [(F\textsubscript{xe}O\textsubscript{2})\textsubscript{2}S(O)F]\textsuperscript{+}, has proved to be easy to generate and is relatively stable thermally.

**Experimental Section**

**Materials.** Xenon difluoride was obtained by the method of Streng and Streng\textsuperscript{13} and Holloway\textsuperscript{14} as modified by Williamson\textsuperscript{15}. Previous analytical, x-ray and spectroscopic examination in these laboratories has confirmed that this method yields high purity XeF\textsubscript{2}\textsuperscript{15}. Fluorosulfonic acid obtained from K and K Laboratories, Inc., Plainview, N.Y., was purified by distillation under ordinary pressure followed by a high vacuum distillation. The purified acid was a colorless liquid, b.p. 164°. Perchloric acid was prepared from commercial 70\% perchloric acid, by adding a five-fold excess of conc. H\textsubscript{2}SO\textsubscript{4} followed by distillation at 10 torr. Trifluormethyl sulfonic acid, obtained from The Chemical Division of the 3M Company, St. Paul, Minn., was distilled prior to use. Methylsulfonic acid was obtained from Eastern Chemical Corp., Paquannock, N.J. and was distilled prior to use. Arsenic pentafluoride was obtained from the Ozark Chemical Co., and antimony pentafluoride was prepared by fluorination of antimony trioxide in an inclined glass tube. Ruthenium pentafluoride was prepared by fluorinating the metal in a Monel bomb at 200°.

**Apparatus.** The derivatives of xenon difluoride were prepared in Kel-F tubes provided with Kel-F valves. The tubes were made by drilling approximately 3" lengths of 5/8" diameter Kel-F rod to preserve a 1/8" wall thickness. This tube was threaded at the neck and provided with a rounded
lip to effect a tight ring seal when screwed into the valve. The valve was fashioned after a conventional V-stem, packed, valve. The vacuum dried Kel-F tubes were loaded with XeF$_2$ in a Vacuum Atmospheres Corporation Drilab. Manipulations involving volatile reactants or products were carried out on a vacuum line constructed of 1/3" nickel tubing linked by Monel Swagelock fittings and Monel Whitey valves and capable of a vacuum of 10$^{-5}$ torr or better.

**X-ray powder photographs.** Thin walled 0.3 mm diameter quartz capillaries were dried under vacuum and loaded under dry nitrogen in a glove bag, this operation being carried out in a cold room at ~ 0°. The capillaries were sealed by drawing down in a small flame, the sample being kept cold at all times. X-ray powder photographs were taken, using graphite 'crystal' monochromatized Cu K$_\alpha$ radiation, on a G.E. Precision Camera. The powder samples were maintained at ~ 0° by a stream of cold dry nitrogen.

**Raman spectra.** The microcrystalline solids and a sample of liquid S$_2$O$_6$F$_2$ were each contained in sealed thin walled 1 mm diameter Pyrex glass capillaries for Raman Spectroscopy. The spectrometer employed a Spectra-Physics Model 125 He/Ne laser in conjunction with a Spex Model 1400 double monochromator.

**Infrared spectra.** A gas tight Kel-F cell fitted with AgCl windows was used for all condensed phase spectra. The powdered solids were dusted on to the inner surfaces of the windows, the same precautions being taken as for x-ray sample preparation. A Perkin-Elmer 137 Infracord was used over its full range of 4000-400 cm$^{-1}$.

**Xenon(II) fluoride fluorosulfate, FXeOSO$_2$F.**

**Preparation.** An equimolar amount of fluorosulfonic acid was added to a
known weight of xenon difluoride contained in a Kel-F tube and valve assembly. The mixture, initially at -75°, rapidly yielded a colorless solution when warmed to 0°. Hydrogen fluoride was removed in a dynamic vacuum with the mixture held at 0°. A colorless solid, m.p. 36.6°, remained. The evolved hydrogen fluoride was trapped, weighed, and titrated with base. One mole of HF was evolved per mole of acid brought into interaction with XeF₂. Several syntheses were followed gravimetrically. In all cases the hydrogen fluoride evolution and the yield of product was in accord with the overall reaction: XeF₂ + HOSO₂F → FXeOSO₂F + HF. Typically, XeF₂ (0.728 g, 4.3 mM) plus HOSO₂F (0.430 g, 4.3 mM) gave FXeOSO₂F (1.040 g, 4.2 mM) of volatiles (0.125 g, mainly HF, but containing traces of Xe, S₂O₅F₂ and S₂O₆F₂, the latter being identified from infrared spectra). In an experiment in which an excess of XeF₂ was employed, the same white solid, m.p. 36.6°, was obtained on removing excess XeF₂ in a dynamic vacuum (for 0.5 hr) at 20°: XeF₂ (4.95 mM) + HOSO₂F (3.60 mM) → FXeOSO₂F (3.60 mM) + HF (3.7 mM).

Some Properties of FXeOSO₂F. - A small sample at ~ 20° was completely transferred in a dynamic vacuum, after several hours, to a U-tube cooled at -75°. Well formed crystals were obtained in this way. This provided for the crystal structure determination reported in the accompanying paper. That the single crystals were representative of the bulk material was proved by a complete indexing of the x-ray powder data given in Table I.

The colorless solid, on melting at 36.6°, produced a pale yellow-green liquid which evolved xenon and within an hour appeared to be completely decomposed according to the equation:
2FXeOSO₂F → XeF₂ + S₂O₆F₂ + Xe. A ¹⁹F n.m.r. study of the melt confirmed this observation. Both the xenon difluoride and the peroxysulfuryldifluoride produced in this decomposition were pure. This decomposition also occurs spontaneously in the solid at room temperature with a half-life of ~ 2 days at 20° and the transformation has been followed crystallographically, single crystals of the FXeOSO₂F having decomposed, on X-irradiation at room temperature, to yield a colorless liquid (S₂O₆F₂) and well-formed crystals which were established by precession photography to be of xenon difluoride. The S₂O₆F₂ was identified by its characteristic infrared spectrum¹⁷, with strong bands at 1490, 1246, 846 (PQR) and 752 cm⁻¹, and by its ready thermal dissociation to the colored OSO₂F radical.

A preliminary survey of the chemical properties of FXeOSO₂F show that it is a fluorosulfonating agent, very like S₂O₆F₂. All reactions are accompanied by brisk evolution of xenon gas. Thus sulfur trioxide interacted with the solid to generate S₂O₆F₂: FXeOSO₂F + 3SO₃ → S₂O₆F₂ + Xe; sulfur dioxide on the other hand yields S₂O₅F₂: FXeOSO₂F + SO₂ → S₂O₅F₂ + Xe, as supported by the infrared spectrum¹⁶ of the gaseous product.

The vibrational spectra for FXeOSO₂F are given in Table II.

**Xenon(II) Bis-fluorosulfate, Xe(OSO₂F)₂**

**Preparation.** - The preparation of Xe(OSO₂F)₂ was similar to that for FXeOSO₂F. Xenon difluoride and fluorosulfonic acid in a 1:2 mole ratio were transferred to a Kel-F reactor and maintained at -75° for 1/2 hour. To complete the reaction the yellow solution was allowed to warm to 0°. Traces of gaseous xenon were detected when the mixture was cooled to -75°. The volatiles, removed in a dynamic vacuum at temperatures below 0°, were trapped and weighed. An infrared spectrum showed the volatiles to be
HF, with < 4 mole % $S_2O_6F_2$^16. Again, the number of moles of HF evolved corresponded to the number of moles of HOSO$_2$F introduced and was in agreement with the overall reaction $XeF_2 + 2HOSO_2F = Xe(OSO_2F)_2 + 2HF$.

In a representative preparation, $XeF_2$ (0.731 g, 4.3 mM) and HOSO$_2$F (0.864 g, 8.64 mM) gave 1.371 g of yellow solid, (4.2 mM $Xe(OSO_2F)_2$) and 0.212 g of volatiles, which contained 8.7 mM HF. When the molar ratio of the two reactants was between 1 and 2, a yellow liquid remained on removal of HF at 0°. This liquid (presumably a mixture of $FXeOSO_2F$ and $Xe(OSO_2F)_2$), slowly evolved xenon gas, even at 0°.

Some properties of $Xe(OSO_2F)_2$—The Raman spectrum is compared with those of $FXeOSO_2F$ and $Xe(OSO_2F)_2$ in Table III. Single crystals of $Xe(OSO_2F)_2$ were obtained by slow evaporation of a HF solution and fragmentary precession photograph data, from such a crystal, provided for the indexing of the x-ray powder data given in Table IV. Unlike $FXeOSO_2F$, $Xe(OSO_2F)_2$ appears to be involatile at room temperature. A small sample of $Xe(OSO_2F)_2$ under a dynamic vacuum at 20°, slowly decomposed but none of the compound collected in the limbs of a U-tube, cooled at -75°, provided to trap it.

$Xe(OSO_2F)_2$ is a yellow solid which gives a yellow melt at 43-45°. The melt decomposes slowly, but quantitatively: $Xe(OSO_2F)_2 \rightarrow Xe + S_2O_6F_2$. The solid decomposes similarly if kept at 20° for a few hours. In one experiment $Xe(OSO_2F)_2$ (0.5 g) was allowed to decompose in a Kel-F reactor and the xenon was pumped out at -75°. Vapor pressure measurements on the remaining liquid and the infrared spectrum, of a gaseous sample at 20°, corresponded to data given previously for $S_2O_6F_2$^17. The infrared spectrum proved that other sulfur fluorides and oxyfluorides were absent. Samples of $S_2O_6F_2$ obtained in this way melted sharply at -51.6°, a value 4° higher.
than that previously given\textsuperscript{17}.

The \textit{bis}-fluorosulfate dissolves in both IF\textsubscript{5} and BrF\textsubscript{3}. These solutions decompose very slowly at room temperature and even at 40° the xenon evolution is at a much lower rate than in the case of pure Xe(OSO\textsubscript{2}F)\textsubscript{2}. The solution in IF\textsubscript{5} decomposed according to the equation Xe(OSO\textsubscript{2}F)\textsubscript{2} → Xe + S\textsubscript{2}O\textsubscript{6}F\textsubscript{2}. The BrF\textsubscript{3} solution yielded SO\textsubscript{2}F\textsubscript{2} as well as Xe and S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} and a viscous residue. Raman spectroscopy showed the last to be similar to the product of irradiation of a BrF\textsubscript{3} - S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} mixture and demonstrated the presence of -SO\textsubscript{3}F groups in the product.

\textbf{Xe(II) fluoride perchlorate}

\textbf{Preparation}.—Perchloric acid (0.294 g, 2.93 mM) was condensed into a Kel-F reactor containing XeF\textsubscript{2} (0.477 g, 2.82 mM) and allowed to warm first to -110° and after 10 minutes to -60°. The reaction was completed by warming to 0° at which temperature volatiles (0.991 g) were removed in a dynamic vacuum and trapped. The infrared spectrum of the volatiles showed them to consist mainly of HF with traces of Cl\textsubscript{2}O\textsubscript{7}, ClO\textsubscript{2} and ClO\textsubscript{3}F, the last being in smallest concentration. The solid residue (0.680 g) corresponded to 2.72 mM of FXeOC1O\textsubscript{3}. The colorless solid melted sharply at 16.5° decomposing simultaneously to yield a liquid which rapidly turned from yellow to red. The infrared spectrum of the gaseous products of decomposition was accounted for completely assuming the main product to be Cl\textsubscript{2}O\textsubscript{7}, with some ClO\textsubscript{2} and traces of FClO\textsubscript{3}. Xenon and oxygen were also present.

X-ray powder photographs of FXeOC1O\textsubscript{3} showed some similarity to those of FXeOOSO\textsubscript{2}F but indicated that the compounds were not isomorphous. The powder data is given in Table V. The vibrational spectra for FXeOC1O\textsubscript{3} are given in Table VI.
Xe(II) bis-perchlorate. - In an attempt to prepare Xe(OClO₃)₂ a small amount of FXeClO₄ was transferred to a Kel-F reactor and an equimolar amount of HClO₄ condensed on to it. This mixture which was shaken initially at -11°, then at -60° for several minutes generated a yellow solid and HF. The latter was largely removed at -50°. On warming to 0° the yellow solid rapidly changed to a red liquid. Xe, O₂, Cl₂O, and traces of ClO₂ and FCIO₃ were liberated as the gaseous products of decomposition. The residual red liquid detonates when heated and corresponds to the description of the chlorine oxide described as Cl₂O₆₁⁹.

Although on those occasions when care has been taken to carry out the HClO₄ + XeF₂ interaction at low temperatures, and HF has been removed at low temperatures, there have been no explosions, on other occasions, when rapid warm up of the reactants has been permitted, very strong detonations have occurred.

 Attempted Preparation of Xenon(II) Perchlorate Fluorosulfate, O₃ClOXeOSO₂F. The synthesis of O₂ClOXeOSO₂F was attempted both by adding perchloric acid to FXeOSO₂F and fluorosulfonic acid to FXeClO₃ in a manner similar to that used for the bis-perchlorate preparation. Although the products of the interactions showed no gas evolution at -60° and yielded a colorless solution in anhydrous HF, removal of volatiles produced a yellow solid which rapidly yielded a red liquid and simultaneously evolved xenon and oxygen, even below 0°. Infrared spectra of the vapor from this product showed S₂O₆F₂ and various chlorine oxides to be present. There was no indication of mixed oxides or peroxide (e.g., O₃ClO-OSO₂F). The product indeed behaved like a mixture of Xe(OSO₂F)₂ and Xe(OClO₃)₂.

 Interaction of XeF₂ with Some other Protonic Acids. HCl. - Xenon difluoride did not interact with pure HCl at -78° but addition
of anhydrous HF produced a red-brown coloration at \(-100^\circ\). Xenon was evolved even at \(-100^\circ\) and quantitative recovery of the Xe was obtained at \(-50^\circ\). The interaction proceeded according to the equation:

\[
\text{XeF}_2 + \text{HCl} \rightarrow \frac{1}{2}\text{XeF}_2 + \frac{1}{2}\text{Cl}_2 + \text{HF}.
\]

\(\text{CF}_3\text{SO}_2\text{OH}\) (CAUTION!). \(\text{XeF}_2\) (4.73 mM) was condensed onto the acid which was in slight excess for a 1:1 reaction (5.52 mM). The mixture was contained in the usual Kel-F reactor. Anhydrous HF (6 ml) was added by vacuum distillation and the stirred mixture was slowly (~ 1 hr) brought to 0\(^\circ\) and held at that temperature for 2 hours. Slight gas evolution occurred in this time and infrared spectroscopy, of the gas, indicated the presence of \(\text{C}_2\text{F}_6\). The solvent was removed between \(-40^\circ\) and \(-30^\circ\). The remaining solid was colorless at \(-80^\circ\) but yellow at 0\(^\circ\). The residue, after 3 hours under dynamic vacuum, weighed 1.06 g (theoretical yield for \(\text{FXeOSO}_2\text{CF}_3\), allowing for ready decomposition of the bis compound, = 1.18 g). The Raman spectrum given in Table II is compatible with the formulation \(\text{FXeOSO}_2\text{CF}_3\). The solid decomposed slowly at 0\(^\circ\) and rapidly between 40 and 60\(^\circ\) (no melting up to 60\(^\circ\)). The major gaseous products were \(\text{CF}_4\) and Xe.

Efforts to prepare \(\text{FXeOSO}_2\text{CF}_3\) with \(\text{XeF}_2\) rich or exact 1:1 mixtures of the reactants, yielded very unstable solid products, which decomposed slowly at 0\(^\circ\) to yield the gaseous products \(\text{SO}_2\text{F}_2\), \(\text{CF}_4\) and Xe. In all cases the solids detonated on warming up to room temperature.

\(\text{CH}_3\text{SO}_2\text{OH} \cdot \text{XeF}_2\) (9.45 mM) was condensed onto the acid (9.77 mM) and the neat mixture was warmed slowly to \(-15^\circ\), at which temperature a yellow color developed at the interface between the two solids. Gas slowly evolved at \(-15^\circ\) and on warming the mixture to 0\(^\circ\), to hasten the interaction of the two solids, very fast gas evolution occurred, which was not arrested by cooling in...
liquid nitrogen. Detonation occurred. A similar reaction, carried out
in HF, generated a colorless clear solution at -65° (6.74 m mole XeF₂ and
6.69 mM CH₃SO₂OH in 4 ml HF). Slight gas evolution occurred on warm-up
to ~ -40°, at which point a faint yellow color also developed. The solvent
was removed between -50 and -20°. The solid which remained was pale yellow
at 0° and slowly yielded gaseous products (~ 0.02 m mole min⁻¹). It
detonated on warming to room temperature.

ClSO₂OH. Addition of XeF₂ (3.0 mM) to the acid (3.0 mM) followed by warm-
up to -78° led to a vigorous reaction to yield a pale yellow solution and
much gas, which contained 3 mM Xe. Chlorine gas was the other identifiable
gaseous product. Similar interaction of acid with XeF₂, but in a 2:1 molar
ratio (4.18 mM ClSO₂OH, 2.09 mM XeF₂) generated Xe (2.1 mM) and Cl₂ (2.15 mM),
even at -95°. The less volatile liquid residue proved to be HSO₃F, this
indicating the overall reaction to be:

XeF₂ + 2ClSO₂OH → Xe + Cl₂ + FSO₂OH.

(CF₃)COH. XeF₂ (4.3 mM), interacted with gas evolution, with the acid
(4.33 mM) at 0°. (No reaction occurred below that temperature.) The
reaction accelerated with time and gave a colorless solution. Xenon was
removed under vacuum at -130° and amounted to (4.33 mM).

Attempts to Prepare [XeOSO₂F]⁺MF₆⁻ Salts.

[XeF]⁺[SbF₆]⁻ was prepared by adding XeF₂ (4.22 mM) to a solution of SbF₅
(40.7 mM) in HF (10 ml). This mixture was stirred for 4 hours at 0°, by
which time a clear pale yellow solution had formed. The HF was removed in
a dynamic vacuum at 0° to leave a pale yellow solid. The powder photograph
indicated isomorphism with [FXe]⁺[RuF₆]⁻ and was indexed on the basis of
an orthorhombic unit cell of dimensions: a = 11.2, b = 8.0, c = 7.5 Å.
(all ± 0.1 Å). The Raman spectrum showed the presence of \( \text{Xe}_2\text{F}_3^+\text{SbF}_6^- \)
(as anticipated from the slight excess of XeF\(_2\) over the 1:1 stoichiometry) but the other bands were entirely attributable to \([\text{XeF}]^+\text{[SbF}_6^-\)\]. The Raman bands (in cm\(^{-1}\), with relative intensities and assignments in parentheses, are as expected on the basis of previous studies\(^{11}\) of XeF\(^+\)MF\(_6^-\) salts:

\[
\begin{align*}
668(13, \nu\text{Sb-F}), & \quad 651(3, \nu\text{Sb-F}), & \quad 643(6, \nu\text{Sb-F}), & \quad 624(3, \nu\text{Sb-F}), & \quad 612(25, \nu\text{Xe-F}), & \quad 607(\text{sh}, \nu\text{Xe-F}), \quad 595(\text{sh}, \nu\text{Sb-F}), & \quad 591(\text{sh}, \nu\text{Xe}_2\text{F}_3^+ \text{impurity}) , \\
581(\text{sh}, \nu\text{Xe}_2\text{F}_3^+ \text{impurity}), & \quad 470(2 \text{ broad}, \nu\text{Sb-F}), & \quad 290(5, \nu\text{Sb-F}), & \quad 270(4, \nu\text{Sb-F}).
\end{align*}
\]

\([\text{XeF}]^+\text{[SbF}_6^-\) and FSO\(_2\text{OH}\) (5.44 mM and 6.1 mM respectively) were dissolved in HF (10 ml) with stirring at 0° for 4 hours to give a yellow-green solution. The solvent was removed in a dynamic vacuum, at -30° to leave a yellow-green solid. Xenon evolution during all manipulations to this point amounted to < 0.5 mM. The weight of residue amounted to 2.4 g, whereas that anticipated for \([\text{XeSO}_3\text{F}]^+\text{[SbF}_6^-\) is 2.5 g. The solid gave a unique powder photograph but the Raman spectrum was of poor quality and the great reactivity of the compound towards the AgCl plates rendered the infrared spectra valueless. A similar solid, having an identical x-ray powder pattern, was prepared by mixing equimolar proportions of the neat reactants at 48° for 48 hours.

\([\text{XeF}]^+\text{[RuF}_6^-\) (1.36 mM) prepared as previously described, was mixed with HSO\(_3\text{F}\) (1.41 mM) in HF (2 ml) with stirring, at 0°, for 5 hours. The \([\text{XeF}]^+\text{[RuF}_6^-\) appeared to dissolve and a second crystalline phase appeared at the surface of the solution, which assumed a yellow tint. Removal of the HF at 0° yielded a yellow solid, which rapidly turned red-brown, and
rapidly decomposed with gas evolution, xenon and sulfur oxyfluorides being formed.

\[ \text{[XeF]}^+\text{[AsF}_6^-] \text{ was prepared by dissolving AsF}_5 (10.87 \text{ mM}) \text{ and XeF}_2(10.4 \text{ mM}) \]

in HF (5 ml) and FSO_2OH (10.6 mM) was condensed into this mixture which

was allowed to warm to 0°. It was maintained with vigorous stirring at 0°

for 2 hours then for a further 2 hours at ~20°. The solution became

greenish but some colorless solid remained out of solution. More solid

precipitated on cooling to -40°, at which temperature the HF was removed

in a dynamic vacuum. The greenish solid, which remained, rapidly become

brown on warm up to -30°, at which point the solid melted and evolved gas.

Eventually, with removal of volatiles (AsF_5, Xe, SO_2F_2 and S_2O_6F_2), under
dynamic vacuum, a residue of 1.84 g of \[(\text{FXe})_2\text{O}_2\text{S(0)F}]^+\text{[AsF}_6^-\] (see below) remained.

The preparation of \[(\text{FXe})_2\text{O}_2\text{S(0)F}]^+\text{[AsF}_6^-\]: XeF_2 (7.8 mM) and FSO_2OH

(4.38 mM) were condensed in HF (6 ml) and stirred at 0° for 4 hours.

AsF_5 (4.2 mM) was added to the solution, which was held at -78°. This HF

solution was almost colorless, although a second yellowish phase was

observed at the bottom of the Kel-F container. The HF was removed between

-30 and 0°C, to leave a pale yellow solid (2.14 g). Traces of SO_2F_2 were

present in the gaseous products. Under vacuum, at room temperature, the

solid became colorless. The Raman spectrum showed the materials to be

mainly \[(\text{FXe})_2\text{O}_2\text{S(0)F}]^+\text{[AsF}_6^-\] with some \[\text{Xe}_2\text{F}_3]^+\text{[AsF}_6^-\] impurity. This

composition is entirely consistent with the stoichiometry of the starting

materials since the XeF_2 concentration was less than required for the

ideal interaction:

\[ \text{FXeOSO}_2\text{F} + \text{XeF}_2 + \text{AsF}_5 \rightarrow [(\text{FXe})_2\text{O}_2\text{S(0)F}]^+\text{[AsF}_6^-\] . \]
A purer product was obtained from the \([\text{FXe}]^+\text{[AsF}_{6}]^-\) - H\text{FSO}_2\text{OH} interaction described above and from the interaction of equimolar quantities of \(\text{Xe(OSO}_2\text{F)}_2\) and \(\text{AsF}_5\) in HF. This latter reaction generated a colorless crystalline solid at 0°, but removal of HF between -40 and -50° yielded a dark brown liquid which evolved \(\text{SO}_2\text{F}_2\), \(\text{AsF}_5\) and HF, under a dynamic vacuum, for 15 hours at -40°, to yield a colorless solid, which Raman spectroscopy proved to be a mixture of \(\text{Xe(OSO}_2\text{F)}_2\) and \([\text{(FXe)}_2\text{O}_2\text{S(O)}\text{F}]^+\text{[AsF}_{6}]^-\). Warming this mixture to 40° destroyed the former but not the latter.

The Raman spectrum (Table VII) and the effectiveness of the stoichiometry \(2\text{XeF}_2 + \text{FSO}_2\text{OH} + \text{AsF}_5\) in forming the product, together, provide strong support for the formulation \([\text{(FXe)}_2\text{O}_2\text{S(O)}\text{F}]^+\text{[AsF}_{6}]^-\).

**Analysis.** Several samples from different preparations were analysed for xenon. This was accomplished by sealing samples of the solid in preweighed quartz x-ray capillaries, which were then inserted into a conventional combustion tube of a Dumas nitrometer. The nitrometer was previously purged with xenon. Found: Xe, sample (a): 45.8; 45.4; sample (b) 45.4; 45.5%. Required for \(\frac{4}{3}\text{AsS}_2\text{Xe}_2\): Xe, 44.6%. Unfortunately, the sample capillaries could not be evacuated prior to closing and therefore contained small, but imprecisely known, volumes of nitrogen. Thus the xenon analysis by this method should be high. The greatest possible error, (if the capillary volume of nitrogen were present), would introduce a 3% excess to the xenon analysis. Since the samples, in each case, occupied approximately half the capillary volume, it is probable that the analyses were high by approximately half this amount. On this basis, the xenon analysis, by the Dumas nitrogen method, gives findings in excellent accord with expectations.

**Properties of \([\text{(FXe)}_2\text{O}_2\text{S(O)}\text{F}]^+\text{[AsF}_{6}]^-\).** The Raman spectrum of the colorless
The solid is represented in Table VII. It is remarkably similar to that of $[\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^-$. Surprisingly, the solid is sublimable, at $\sim 20^\circ$, in a dynamic vacuum. The Raman spectrum shows only traces of $[\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^-$. The solid decomposes above $64^\circ$ at ordinary pressures and yields $\text{S}_2\text{O}_6\text{F}_2$, $\text{Xe}$ and $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$ in accord with the equation:

$$[(\text{FXe})_2\text{O}_2\text{S}(0)\text{F}]^+[\text{AsF}_6]^- \rightarrow \frac{3}{4} [\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^- + \frac{1}{4} \text{AsF}_5 + \frac{1}{2} \text{Xe} + \frac{1}{2} \text{S}_2\text{O}_6\text{F}_2$$

The solid interacts rapidly with dry CH$_3$CN. The attempted preparation of $[(\text{FXe})_2\text{O}_2\text{CCF}_3]^+[\text{AsF}_6]^- \quad \text{CF}_3\text{COOH (2.25 mM) was added at } -196^\circ \text{ to a solution of } \text{Xe}_2\text{F}_3^+\text{AsF}_6^- \quad \text{(2.22 mM) in HF (5 ml). As soon as the mixture melted on warm up, a vigorous interaction occurred and was complete within 1 or 2 minutes. The volatile products, which were removed under vacuum at } 20^\circ, \text{ proved to be CF}_4, \text{ CO}_2, \text{ and Xe. The residue proved to be pure } [\text{Xe}_2\text{F}_3]^+\text{AsF}_6^- \quad \text{(0.32 g). If allowance is made for the volatility of } [\text{Xe}_2\text{F}_3]^+\text{AsF}_6^- \quad \text{, these observations are in accord with the overall reaction:}$

$$[\text{Xe}_2\text{F}_3]^+\text{AsF}_6^- + \text{CF}_3\text{COOH} \rightarrow \text{CF}_4 + \text{CO}_2 + \text{HF} + \frac{1}{2} \text{AsF}_5 + \text{Xe} + \frac{1}{2} [\text{Xe}_2\text{F}_3]^+\text{AsF}_6^-.$$

HCl (2.26 mM) was added to a solution of $[\text{Xe}_2\text{F}_3]^+\text{AsF}_6^- \quad \text{(2.26 mM) in HF (5 ml) at } -80^\circ. \text{ Evolution of Xe and Cl}_2 \text{ gas occurred above } -40^\circ \text{ and removal of the volatiles at this temperature left only a residue of } [\text{Xe}_2\text{F}_3]^+\text{AsF}_6^- \quad \text{. Evidently the decomposition proceeded according to the equation:}$

$$[\text{Xe}_2\text{F}_3]^+\text{AsF}_6^- + \text{HCl} (\text{HF}) \rightarrow \frac{1}{2} \text{Cl}_2 + \frac{1}{2} \text{Xe} + \frac{1}{4} \text{AsF}_5 + \frac{3}{4} [\text{Xe}_2\text{F}_3]^+\text{AsF}_6^-.$$
DISCUSSION

Preparative. - Our studies have demonstrated that the F ligands of XeF₂ may be substituted, one at a time by highly electronegative ligands. At least for the -OSO₂F and -OC₁₀₃ ligands there is no tendency for the mono-substituted derivatives to dismutate (i.e., 2FXeOR ≠ XeF₂ + Xe(OR)₂), since the FXeOR compounds may be obtained pure by mixing the reactants in 1:1 molar ratio:

\[ \text{XeF}_2 \text{HOR} \rightarrow \text{FXeOR} + \text{HF}. \]

On the other hand, we have failed to generate the unsymmetrical compounds:

\[ \text{FXeOR} + \text{HOR}' \rightarrow \frac{1}{2}\text{Xe(OR)}_2 \] + \[ \frac{1}{2}\text{Xe(OR')}_2 \].

It is not known whether the production of an equimolecular mixture of Xe(OSO₂F)₂ and Xe(OC₁₀₃)₂ is a consequence of lower solubility of one or both of the symmetrical compounds relative to the unsymmetrical compound, or whether the symmetrical compounds are energetically more favorable (perhaps from greater resonance stabilization) than the unsymmetrical. Presumably the intermolecular ligand exchange is provided for by some solvolysis by the hydrogen fluoride.

Failure to prepare FXeCl or XeCl₂ by substitution of the F ligands of XeF₂:

\[ \text{HCl} + \text{XeF}_2 \rightarrow \frac{1}{2}\text{XeF}_2 + \text{HF} + \frac{1}{2}\text{Cl}_2 \]

or of Xe₂F₃⁺:

\[ [\text{Xe}_2\text{F}_3]^+[	ext{AsF}_6]^− + \text{HCl} \rightarrow \text{HF} + \frac{1}{2}\text{Cl}_2 + \frac{1}{2}\text{Xe} + \frac{1}{4}\text{AsF}_5 + \frac{3}{4}[\text{Xe}_2\text{F}_3]^+[	ext{AsF}_6]^− \].
indicate that the chlorine ligand is too readily oxidized to molecular chlorine, for Xe-Cl compounds to be preserved under normal conditions of temperature and pressure. It is of interest, here, that chlorine is also liberated in the interaction of chlorosulfonic acid with XeF₂:

\[ \text{XeF}_2 + 2\text{HOSO}_2\text{Cl} \rightarrow \text{Xe} + \text{Cl}_2 + 2\text{HOSO}_2\text{F}. \]

This may simply be a consequence of HCl generation:

\[ \text{HF} + \text{HOSO}_2\text{Cl} \rightarrow \text{HOSO}_2\text{F} + \text{HCl}. \]

The difficulties experienced in preparing Xe(II) derivatives of the trifluoromethyl and methyl-sulfates show, that even when bound species are generated, it is not always possible to preserve, what are frequently thermodynamically unstable compounds, at room temperature. The gaseous decomposition products of the mono-trifluoromethylsulfate, FXeOSO₂CF₃, are mainly carbon tetrafluoride and xenon, which suggests the overall change:

\[ \text{FXeOSO}_2\text{CF}_3 \rightarrow \text{Xe} + \text{CF}_4 + \text{SO}_3. \]

In our one successful preparation, slight excess of acid was employed and the reaction was accompanied by evolution of a gas which contained C₂F₆ (no CF₄). This is consistent with the formation of an unstable bis compound, Xe(OSO₂CF₃)₂. If this material were to decompose similarly to Xe(OSO₂F)₂, the peroxide CF₃O₂S·O·O·SO₂CF₃ would be the product. The latter however, has been reported by Noftle and Cady, to undergo exothermic decomposition to perfluoroethane, sulfur trioxide and trifluoromethanesulfonate. It may be that the explosive decomposition of samples
from our other acid-rich preparations were triggered by this decomposition. The appearance of CF₄ and the absence of C₂F₆ in the thermal decomposition of FXeOSO₂CF₃ suggests that the SO₃CF₃ radical is not an important decomposition species but indicates rather that there is fluorine attack at the S-C bond, perhaps intra-molecularly. Evidently much the same kind of attack occurs in the system XeF₂ + CF₃COOH (1:1 molar ratio in HF), which liberates gases (including CF₄) even at -25°. The trifluoroacetate group is very effectively fluorinated when attempts are made to substitute into the Xe₂F₃⁺ ion:

\[ \text{Xe}_2F_3^+ + \text{AsF}_6^- + \text{CF}_3\text{COOH} \rightarrow \quad \text{HXF}_2\text{CO}_2\text{CF}_3^+ + [\text{AsF}_6^-] \rightarrow \]

\[ [\text{XeF}]^+ [\text{AsF}_6]^- + \text{Xe} + \text{CF}_4 + \text{CO}_2 \]

The work of Eisenberg and DesMarteaux²² and Sladky²³ has already established the instability of the trifluoroacetates.

The number of ligands which will satisfy the high electronegativity requirements for bonding to a xenon atom and yet be capable of withstanding fluorine atom attack, must be small. Fluorosulfate and perchlorate evidently are good ligands but the pentafluoroorthotellurate ligand -O-TeF₅, as demonstrated by Sladky, appears to be the best so far.²⁴

Structure and Properties.- The vibrational spectroscopic data, given in Tables II, III and VI, indicate that the binding of the xenon atom to its ligands, in the FXeOR or Xe(OR)₂ compounds, is comparable to that in XeF₂. The stretching modes \(\nu(Xe-F)\) and \(\nu(Xe-O-)\) are mixed in FXeOSO₂F and FXeOCIO₃. They appear at 521 and 433 cm⁻¹ in the fluorosulfate and at 525 and 505 cm⁻¹ in the perchlorate. It seems from these frequencies, that in neither case is the bonding very different from that in XeF₂ where \(\nu_{sym} = 495\) and
Furthermore, the observed Xe-O stretching frequency in Xe(OSO$_2$F)$_2$, $\nu$(Xe-O)$_{sym}$ = 436 cm$^{-1}$, is not only comparable to the XeF and XeO stretching frequencies in FXeOSO$_2$F, but is remarkably similar to the $\nu$(I-O)$_{sym}$ = 441 cm$^{-1}$ observed recently by Aubke and his coworkers for I(OSO$_2$F)$_4^-$.

The preference of the XeF$_2$·2MF$_5$ derivatives for the structure FXe$^+[F_2M$-F-MF$_5]$$^-$, raised the possibility of the bisfluorosulfate being FXe$^+$(O$_3$S-OSO$_2$F)$^-$ but the vibrational spectroscopic evidence does not support this formulation. As the data in Table III demonstrate, the fluorosulfate group in Xe(OSO$_2$F)$_2$ is similar in character to that in FXeOSO$_2$F, although less anion-like. It is seen, however, that each -SO$_3$F band of the FXeOSO$_2$F spectrum is represented in the spectrum of Xe(OSO$_2$F)$_2$ by a close doublet. This is consistent with a structure in which the xenon atom is bound to two -OSO$_2$F groups in a non-centrosymmetric assembly.

If, in keeping with all known Xe(II) structures (see reference 10), the xenon atom is linearly coordinated in oxygen, -O-Xe-O-, the spectra required that the molecule, at least in the solid state, have a gauche or cis configuration. The comparison of the Xe(OSO$_2$F)$_2$ spectrum with that of S$_2$O$_6$F$_2$ is also of interest. The singularity of the -SO$_3$F modes in the Raman, show it to be a centrosymmetric molecule. Evidently the -SO$_3$F groups in this molecule are less SO$_3$F$^-$-like than in Xe(OSO$_2$F)$_2$.

Incidentally, it should also be noted that the stretching frequency of the peroxide bond $\nu$(O-O) = 798 cm$^{-1}$, is low and is compatible with the ready dissociation of S$_2$O$_6$F$_2$:

$$\text{FS(O)}_2\cdot\text{O-OS(O)}_2\cdot\text{F} \rightarrow 2\text{FSO}_3^-.$$
This may be associated with the high electron withdrawing capability of the \(-\text{OS}_2\text{F}\) group, which presumably prevents the location of appreciable electron density in the peroxide bond.

The fluorosulfate decompositions proceed quantitatively as follows:

\[
2\text{XeOS}_2\text{F} \rightarrow \text{XeF}_2 + \text{S}_2\text{O}_6\text{F}_2 + \text{Xe} \\
\text{Xe(OS}_2\text{F)}_2 \rightarrow \text{Xe} + (\text{SO}_3\text{F})_2 . 
\]

The perchlorate decompositions are much more complex and although it is possible that \((\text{ClO}_4)_2\) or \(\text{ClO}_4^-\) may be initial products of the decomposition, there is presently no evidence to support the existence of either species in the products of the reactions. The clean nature of the fluorosulfate dismutations may in part rest on the high stability of the \(\text{SO}_3\text{F}\) radical.\(^{17}\) It is reasonable to postulate the \(\text{XeF}^-\) radical as the other initial product of decomposition. If this radical occurs, it must be stable towards either dissociation into atoms or mutual annihilation,

\[
\text{i.e., } 2\text{XeF}^- \neq 2\text{Xe} + \text{F}_2 ,
\]

since neither fluorine nor \(\text{FOSO}_2\text{F}\) is detected in the decomposition products.

The thermochemical bond energy of \(\text{XeF}^-\) must not exceed that in \(\text{XeF}_2\), however, if the \(\text{XeF}\) radical is to disproportionate spontaneously

\[
2\text{XeF}^- \rightarrow \text{Xe} + \text{XeF}_2 ,
\]

since the entropy change is slightly unfavorable for \(\text{XeF}_2\) formation in this reaction.\(^{27}\) Therefore, if the \(\text{XeF}^-\) radical is an intermediate in the \(\text{FXeOS}_2\text{F}\) decomposition, the bond energy must be < 32 kcal mole\(^{-1}\) to be
compatible\(^1\) with process (3) and > 18 kcal mole\(^{-1}\) to account for the absence of fluorine\(^{28}\) [Equation (2)]. It is pertinent that the \(\text{XeF}^+\) radical has also been postulated\(^{11}\) as an intermediate, which disproportionates, in the redox reaction:

\[
3\text{XeF}^+\text{OsF}_6^- \rightarrow \text{XeF}_3^+\text{OsF}_6^- + 2\text{OsF}_6 + \text{Xe}.
\]

**Bonding.**—In the valence-bond description of \(\text{XeF}_2\), Coulson\(^{56}\) has emphasized the dominance of the canonical forms \((\text{F-Xe})^+\text{F}^-\) and \(\text{F}^-(\text{Xe-F})^+\) in the resonance hybrid. This representation accounts well for the polarity\(^{-1}\) \(\text{F}_x\text{Xe}_y\text{F}_z\), indicated by nmr\(^{29}\), Mossbauer\(^{30}\), ESCA\(^{31}\) and thermodynamic data.\(^{32}\) It is particularly impressive that the enthalpy of sublimination derived for the \(\text{XeF}_2\) case, by Rice and his coworkers\(^{32}\) in 1963, on the basis of the charge distribution\(^{1}\) \(\text{F}_x\text{Xe}_y\text{F}_z\), is 13.3 kcal mole\(^{-1}\), whereas the experimental value reported\(^{33}\) in 1968 is 13.2 kcal mole\(^{-1}\). It should be recognised that the Coulson valence-bond model is not, in the final analysis, significantly different from the Rundle\(^{34}\) and Pimentel\(^{35}\) three-center molecular orbital description or the Bilham and Linnett-one-electron-bond description\(^{36}\), but it does provide for a more straightforward estimation of thermodynamic stabilities of compounds than the other approaches do.

We can appreciate from Figure 1, that the ionization potential of the noble-gas atom is a key indicator of bonding prospects. Size and electron affinity of the ligand are also important. The lower the ionization potential, the less energy is required from the steps

\[
\Delta H(\text{electron-pair})(G^+ + L \rightarrow GL^+) ; \Delta H(\text{electrostatic})(G^+L^+ + L^- \rightarrow (L-G^+L^-)g)
\]

and \(R(\text{resonance})\), to ensure a bound species \(GL_2\). If \(L\) is sufficiently electronegative \((G-L)^+\) will be stable with respect to \(G\) and \(L^+\) and
\[ \Delta H(\text{electron-pair bond}) \text{ will be an exothermic term. Again if } L \text{ is sufficiently electronegative } (L-G)^+L^- \text{ will be stable with respect to } L-G \text{ and } L \text{ (note that electrostatic energy is lost in this change) but it is also clear that the smaller } L \text{ is, the more exothermic will } \Delta H(\text{electrostatic}) \text{ be, and the more favorable will be the conditions for bonding. The instability of } XeCl_2 \text{ can now be appreciated in terms of this model. It should first be noted that chlorine electron-pair bonds, with typical elements, are energetically less favorable than fluorine bonds}^{37,28} \text{ (thus the bond energies for ICl and I-F are 58 and 67 kcal mole}^{-1}, \text{ respectively). Furthermore, the chlorine atom and ion are much bigger than their fluorine counterparts.}^{37} \text{ The energy of ion-pair formation, } \Delta H(\text{electrostatic}), \text{ is therefore less exothermic than in the fluoride case. If we take the observed interatomic distance of 2.0 Å in } XeF_2, \text{ as a measure of the interionic distance in the ion pair, we would estimate the interionic distance in } XeCl_2 \text{ to be } \sim 2.4 \text{ Å. The attraction energies associated with these distances are 166 and 138 kcal mole}^{-1}, \text{ respectively. Although the electron affinity of chlorine is 3 kcal mole}^{-1} \text{ greater than for fluorine}^{28}, \text{ this is the only term in the cycle which is more favorable for the chlorine case and the summation indicates that the enthalpy of formation of } XeCl_2(g) \text{ from the gaseous atoms would be less favorable than for } XeF_2, \text{ by 34 kcal mole}^{-1}, \text{ with } \Delta H_{at}(XeF_2) = 65 \text{ and } \Delta H_{at}(XeCl_2) \sim 31 \text{ kcal mole}^{-1}. \text{ These values are in harmony with the stretching force constants given by Nelson and Pimentel, which are } k_r = 1.32 \text{ mdyne/Å for } XeCl_2 \text{ and } k_r = 2.6 \text{ mdyne/Å for } XeF_2. \text{ Since the strong-acid anions are highly electronegative, it seemed likely that they would be good ligands for the heavier noble-gases. However, these multiatom ligands, while conferring advantages from their high} \]
electron affinities, are nevertheless sizeable species. The ion-pair energy $\Delta H(\text{electrostatic})$ for species such as $\text{FXe}^+\text{ClO}_4^-$ or $\text{FXe}^+\text{SO}_3^-$ could be as much as $40$ kcal mole$^{-1}$ less than for $\text{F-Xe}^+$, since the lattice energies of Rb and Cs perchlorates are $\sim 40$ kcal mole$^{-1}$ less than for the corresponding fluorides. Therefore, even though the electron affinity of $\text{ClO}_4(g)$ is greater than for $\text{F}(g)$ and even though the electron-pair bond in $(\text{XeOClO}_3)^+$ may be as favorable as in $(\text{Xe-F})^+$, the overall energetics could well be less favorable than for $\text{XeF}_2$, simply because of the large ligand size. This may account for the disappointing thermal stability of the fluorosulfates and perchlorates.

The dominance of the $(\text{F-Xe})^+(\text{SO}_3^F)^-$ canonical form over the $(\text{FO}_2\text{SO}-\text{Xe})^+\text{F}^-$ form in the resonance hybrid, indicated by the crystal structure, calls for comment. At the outset it should be noted that the first canonical form alone is less appropriate than in the case of the $\text{XeF}_2/\text{RuF}_5$ compound, where $(\text{F-Xe})^+(\text{RuF}_6)^-$ is judged to be of overwhelming importance compared with $^-(\text{Xe-F-RuF}_5)^+$ or $^+(\text{Xe-F})^+\text{RuF}_5$. The ability of the hexafluororuthenate(V) to form a $\text{Xe}_2\text{F}_3^+$ salt, and the failure of $\text{FXeOSO}_2$ to do likewise, gives a chemical justification for this differentiation of the compound types. The $(\text{FO}_2\text{SO}-\text{Xe})^+\text{F}^-$ canonical form is therefore judged to be significant. It is a fair assumption that the ion-pair attraction and repulsion energies of this form are approximately the same as for $(\text{F-Xe})^+(\text{SO}_3^F)^-$. The high electron affinity of $\text{SO}_3^F$ relative to $\text{F}$ will tend to favor the latter canonical form. Evidently, the electron-pair-bond energy in $(\text{FO}_2\text{SO}-\text{Xe})^+$, of the
(F₀₂SO-Xe)⁺F⁻ form, would need to exceed the (Xe-F)⁺ bond energy, in the (FXe)⁺(OSO₂F)⁻ form, by the difference in the SO₃F and F electron affinities, for the two forms to have comparable weight in the resonance hybrid.

Similar considerations provide for an understanding of the low thermal stability of the (Xe-OSO₂F)⁺(MF₆)⁻ and related salts. Clearly the lattice energy for such salts will be less favorable than for (Xe-F)⁺(MF₆)⁻ where U has been estimated to be approximately -115 kcal mole⁻¹.¹¹b Electron or F⁻ transfer will occur if the cation has sufficiently high affinity and the lattice energy is sufficiently low. Previous work¹¹ has shown that the compound (FXe)⁺(AsF₆)⁻ is thermally unstable with respect to F⁻ abstraction from the anion:

$$2\text{FXe}^+\text{AsF}_6^- \rightarrow \text{Xe}_2\text{F}_3^+\text{AsF}_6^- + \text{AsF}_5^-$$

It may be that the fate of the xenon fluorosulphate cation in the hexa-fluoroarsenate is similar:

$$3\text{FXeOSO}_2\text{F} + \text{AsF}_5 \rightarrow ((\text{FXe})_2\text{O}_2\text{SOF})^+(\text{AsF}_6)^- + \text{Xe(OSO}_2\text{F})_2^-$$

The close similarity of the vibrational spectra of ((FXe)₂O₂SOF)⁺(AsF₆⁻) and ((FXe)₂F)⁺(AsF₆⁻), compared in Table VII, indicates that the F-Xe bond is similar in the two cations. The higher electron affinity of the SO₃F group, relative to F, favors its location in the bridging position of the cation, the (F-Xe)⁺(SO₃F)⁻(Xe-F)⁺ canonical form therefore being the anticipated dominant one.
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The following Tables are not to be reproduced in the regular edition:

 Tables I
      IV
      V
REFERENCES


20. Although XeF+[SbF 6 ]− is monoclinic, a = 7.991, b = 11.086, c = 7.250 Å (all ± 0.006 Å) β = 90.68 ± 0.05°; space group P21/n, the departure from orthorhombic symmetry is not revealed by our Debye Scherrer photographs. It is probable that the true unit cell of XeF+[SbF 6 ]− is also monoclinic.
27. The Standard entropies for gaseous Xe (S°, 40.5 e.v.) and XeF2 (S°, 62.0 e.v.) are known and that for XeF+ can be taken to be essentially the same as for IF (S°, 56.5 e.v.)
30. C. L. Chernick, C. E. Johnson, J. G. Malm, G. J. Perlow, and M. R. Perlow,
37. L. Pauling, "The Nature of the Chemical Bond", Cornell University
38. The perchlorates and fluorosulfates of the alkali metals are usually
    isostructural (all usually in space group Pnma). Thus for KCIO₄,
    \(a = 8.83, b = 5.65, c = 7.24 \text{ Å} \) (N. V. Mani, Proc. Indian Acad. Sci.,
    46A 143 (1957)); for KSO₃F, \( a = 8.62, b = 5.84, c = 7.35 \) (K. O'Sullivan,
    R. C. Thompson, and J. Trotter, J. Chem. Soc., A, 2026 (1967)); and
    for KBF₄, \( a = 8.66, b = 5.48, c = 7.03 \) (G. Brunton, Acta Cryst., B25
    2161 (1969)). A Thermochemical radius of 2.1 Å has been advocated
    (A. H. Sharpe, "Halogen Chemistry" Vol. 1, V. Gutmann, ed., Academic
    calculations, using the second Kapustinskii equation, from which,
    \( U(\text{RbBH}_4) = 149 \) and \( U(\text{CsBH}_4) = 144 \text{ kcal mole}^{-1} \). It is probable, in
    view of the slightly greater size of ClO₄⁻ and SO₃F⁻ relative to Br₄⁻,
that the lattice energies for the Rb and Cs salts of these anions will be a little less than the values quoted for Br$_4^-$. The lattice energies, quoted by Sharpe, for RbF and CsF are 186 and 179 kcal mole$^{-1}$ respectively.

39. The electron affinity of ClO$_4$ has been estimated from a Born-Haber cycle, employing a lattice energy calculation, to be 13.4 kcal mole$^{-1}$ (V. I. Medeneyev, L. V. Gurvich, V. N. Kondrat'ev, V. A. Medvedev and Ye. L Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities", St. Martin's Press, New York, 1966), whereas the electron affinity of F atom has been determined spectroscopically to be 79.5 ± 0.1 kcal mole$^{-1}$ (R. S. Berry and C. W. Reimann, J. Chem. Phys., 38, 1540 (1963)).

Table I. X-Ray Powder Data for FXeOS\(_2\)F (orthorhombic: 
a=9.88; b=10.00; c=10.13\AA; S. G. Pbc\(a\))

<table>
<thead>
<tr>
<th>(d_{\AA})</th>
<th>(10^4 1/d_{\text{obs}}^2)</th>
<th>(10^4 1/d_{\text{calc}}^2)</th>
<th>(h) (k) (L)</th>
<th>(I/I_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.03</td>
<td>395</td>
<td>390</td>
<td>002</td>
<td>60</td>
</tr>
<tr>
<td>4.56</td>
<td>481</td>
<td>497</td>
<td>021</td>
<td>80</td>
</tr>
<tr>
<td>4.09</td>
<td>596</td>
<td>600</td>
<td>121</td>
<td>50</td>
</tr>
<tr>
<td>3.588</td>
<td>777</td>
<td>790</td>
<td>022</td>
<td>100</td>
</tr>
<tr>
<td>3.554</td>
<td>792</td>
<td>799</td>
<td>202</td>
<td>60</td>
</tr>
<tr>
<td>3.375</td>
<td>878</td>
<td>891</td>
<td>123</td>
<td>60</td>
</tr>
<tr>
<td>3.042</td>
<td>1081</td>
<td>1080</td>
<td>113</td>
<td>30</td>
</tr>
<tr>
<td>3.018</td>
<td>1098</td>
<td>1100</td>
<td>131</td>
<td>20</td>
</tr>
</tbody>
</table>

\[2.777\] 1297 \{ 1277 023 \} 40

\[2.712\] 1360 1377 123 \} 80

\[2.705\] 1366 1387 213 \} 80

\[2.512\] 1585 1558 004 \} 30

\[2.474\] 1633 1638 400 40
<table>
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<tr>
<th>bands (cm$^{-1}$)</th>
<th>assignments</th>
<th>bands (cm$^{-1}$)</th>
<th>assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>253 s R</td>
<td>$\delta$(Xe-O-S)</td>
<td>236 vs R</td>
<td>$\delta$(Xe-O-S)</td>
</tr>
<tr>
<td>243 m R</td>
<td></td>
<td>316 w R</td>
<td>$\delta$(F-C-S)</td>
</tr>
<tr>
<td>395 mw R</td>
<td>$\rho$-w(S-F)</td>
<td>338 w R</td>
<td>+$\delta$(O-S-C)</td>
</tr>
<tr>
<td>433 s R</td>
<td>$\nu$(Xe-F)</td>
<td>369 s R</td>
<td>$\nu$(Xe-O)</td>
</tr>
<tr>
<td>518 vs IR</td>
<td>+$\nu$(Xe-O-)</td>
<td>534 s R</td>
<td>$\nu$(Xe-F)</td>
</tr>
<tr>
<td>521 vs R</td>
<td></td>
<td>539 w IR</td>
<td></td>
</tr>
<tr>
<td>531 m R</td>
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<td>505 sh R</td>
<td></td>
</tr>
<tr>
<td>536 m R</td>
<td></td>
<td>510 m IR</td>
<td></td>
</tr>
<tr>
<td>540 s R</td>
<td>$\delta$(O-S-O)</td>
<td>568 s R</td>
<td></td>
</tr>
<tr>
<td>584 mw R</td>
<td></td>
<td>570 w IR</td>
<td>$\delta$(O-S-O) +</td>
</tr>
<tr>
<td>597 w IR</td>
<td></td>
<td>582 s R</td>
<td>$\delta$(F-C-F)</td>
</tr>
<tr>
<td>614 m IR</td>
<td></td>
<td>595 m IR</td>
<td></td>
</tr>
<tr>
<td>616 mw R</td>
<td></td>
<td>636 w R</td>
<td></td>
</tr>
<tr>
<td>798 s IR</td>
<td>$\nu$(S-F)</td>
<td>771 w R</td>
<td>$\nu$(S-C)</td>
</tr>
<tr>
<td>800 w R</td>
<td></td>
<td>758 m IR</td>
<td></td>
</tr>
<tr>
<td>970 vs IR</td>
<td>$\nu$(S-O-)</td>
<td>840 m,br IR</td>
<td>$\nu$(C-F)</td>
</tr>
<tr>
<td>970 w R</td>
<td></td>
<td>922 m R</td>
<td>$\nu$(S-O bridge)</td>
</tr>
<tr>
<td>1197 w R</td>
<td>$\nu$(S-O$<em>{term}$)$</em>{sym}$</td>
<td>1143 w</td>
<td>$\nu$(C-F)</td>
</tr>
<tr>
<td>1210 vs IR</td>
<td></td>
<td>1120 m,br IR</td>
<td></td>
</tr>
<tr>
<td>1390 w R</td>
<td>$\nu$(S-O$<em>{term}$)$</em>{asy}$</td>
<td>1244 w R</td>
<td>$\nu$(S-O term)$_{sym}$</td>
</tr>
<tr>
<td>1393 s IR</td>
<td></td>
<td>1200 m,br IR</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1390 w R</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1390 w IR</td>
<td>$\nu$(S-O$<em>{term}$)$</em>{asy}$</td>
</tr>
</tbody>
</table>
References for Table II.

(a) The bands in the higher frequency range of 700-1400 cm\(^{-1}\) are assignable without much difficulty on the basis of comparisons with \(\text{FSO}_3^-\), \(\text{Xe(OSO}_2\text{F)}_2\) and \((\text{SO}_3\text{F})_2\) as illustrated in Table III, but the assignment of the \(\text{Xe-0}\) and \(\text{Xe-F}\) stretching was based on the assumption that the "symmetric" and "antisymmetric" F-Xe-O modes would be lower in frequency than 600 cm\(^{-1}\) (which characterizes the terminal XeF stretch in FXeRuF\(_6\) (where the XeF bond length is 1.88 Å)\(^{(b)}\)(c). It was also assumed that the Xe-F, Xe-0 stretching bands in the Raman would be intense, as in the \(\text{Xe}_2\text{F}_3^+\) salt spectra\(^{(c)}\).

(b) N. Bartlett, D. Gibler, M. Gennis, and H. Zalkin, to be published.


(d) Assignments for \(\text{FXeOSO}_2\text{CF}_3\) were made partly on the basis of comparison with \(\text{FXeOSO}_2\text{F}\) but also with reference to the Raman spectra of \(\text{KO}_3\text{SCF}_3\) and the hydrated acid. The potassium salt (which was prepared for us by Dr. C. J. Adams) and the acid both showed moderately strong bands at ~ 580 cm\(^{-1}\) (attributable to \(\delta(\text{O-S-O})\) or \(\delta(\text{F-C-F})\) and an intense pair of bands at ~ 320 and 350 cm\(^{-1}\) attributable to \(\delta(\text{F-C-S})\) or \(\delta(\text{O-S-C})\). These assignments, in which we were assisted by Dr. Adams, were important to our assignment of the \(\nu(\text{Xe-F})\) and \(\nu(\text{Xe-0})\) respectively.
Table III. Raman Frequencies and Assignments (a) for FXeOSO$_2$F, Xe(OSO$_2$F)$_2$ and S$_2$O$_6$F$_2$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v$(S-O term) asym</th>
<th>$v$(S-O term) sym</th>
<th>$v$(S-F)</th>
<th>$\delta$(O-S-O)</th>
<th>$\rho_w$(S-F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSO$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1287</td>
<td>1082</td>
<td>786</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FXeOSO$_2$F</td>
<td>1390w</td>
<td>1197w</td>
<td>970w</td>
<td>800w</td>
<td>616mw 536m 433s 395mw 253s</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe(OSO$_2$F)$_2$</td>
<td>1425w</td>
<td>1238mw</td>
<td>959mw</td>
<td>823w</td>
<td>601s 541w 436s 386mw 257vs 253vs</td>
</tr>
<tr>
<td></td>
<td>1417w</td>
<td>1219mw</td>
<td>946mw</td>
<td>815w</td>
<td></td>
</tr>
<tr>
<td>FO$_2$SOOSO$_2$F</td>
<td>1497mw</td>
<td>1251vs</td>
<td>880m</td>
<td>824s 798vs</td>
<td>598mw 527mw 485mw 392mw 299s</td>
</tr>
</tbody>
</table>

$w$ = weak, $m$ = medium, $s$ = strong, $v$ = very

$v$ = stretching, $\delta$ = deformation, $\rho_w$ = wagging ($\rho_w$(S-F) can also be written as $\rho_r$(SO$_3$)).
References for Table III.

(a) For bands occurring at frequencies > 700 cm\(^{-1}\) the assignments were straightforward, as the Table itself indicates, but the \(\nu(Xe-O) + \nu(Xe-F)\) bands were chosen for FXeOSO\(_2\)F largely on the basis of their appreciable Raman intensity (bands in the region 600 - 400 cm\(^{-1}\) having been indicated by the structural features). For \(\nu(Xe-O)\) of Xe(OSO\(_2\)F)\(_2\) there was more difficulty, the choice being between 601 and 436 cm\(^{-1}\). The latter was chosen on the basis of a comparison with Sladky's findings\(^{(c)}\) for Xe(OTeF\(_5\))\(_2\) and Aubke and Carter's findings\(^{(d)}\) for I(OSO\(_2\)F)\(_4\).


Table IV. Partial X-Ray Powder Data for Xe(OSO₂F)₂

(Primitive monoclinic: a = 7.94, b = 13.7, c = 6.84 Å, β = 96°)

<table>
<thead>
<tr>
<th>dÅ</th>
<th>10⁴ l/d² obs.</th>
<th>10⁴ l/d² calc.</th>
<th>hkl</th>
<th>I/I₀</th>
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<tr>
<td>6.13</td>
<td>266</td>
<td>265</td>
<td>011</td>
<td>50</td>
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<tr>
<td>5.17</td>
<td>375</td>
<td>372</td>
<td>120</td>
<td>30</td>
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<tr>
<td>5.08</td>
<td>388</td>
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<td>4.65</td>
<td>462</td>
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<td>4.27</td>
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</tr>
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<td>3.993</td>
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<td>624</td>
<td>121</td>
<td>40</td>
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<td>3.951</td>
<td>641</td>
<td>640</td>
<td>200</td>
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<td>3.792</td>
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<td>70</td>
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<td>{809}</td>
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<td>90</td>
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<td></td>
<td></td>
<td>{825}</td>
<td>211</td>
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<tr>
<td>3.415</td>
<td>857</td>
<td>848</td>
<td>040,002</td>
<td>5</td>
</tr>
<tr>
<td>3.345</td>
<td>894</td>
<td>889</td>
<td>131</td>
<td>10</td>
</tr>
<tr>
<td>3.168</td>
<td>{981}</td>
<td>{112}</td>
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<tr>
<td></td>
<td>{985}</td>
<td>{211}</td>
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</table>

*Estimated visually
Table V. X-Ray Powder Data for FXeOClO₃

<table>
<thead>
<tr>
<th>dÅ</th>
<th>I/I₀</th>
<th>dÅ</th>
<th>I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.75</td>
<td>10</td>
<td>3.374</td>
<td>20</td>
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<tr>
<td>5.64</td>
<td>15</td>
<td>3.325</td>
<td>50</td>
</tr>
<tr>
<td>4.83</td>
<td>40</td>
<td>2.903</td>
<td>40</td>
</tr>
<tr>
<td>4.75</td>
<td>60</td>
<td>2.846</td>
<td>40</td>
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<tr>
<td>4.49</td>
<td>10</td>
<td>2.693</td>
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<tr>
<td>4.35</td>
<td>50</td>
<td>2.656</td>
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<tr>
<td>4.065</td>
<td>30</td>
<td>2.573</td>
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<td>3.657</td>
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<td>3.554</td>
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<td>2.423</td>
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<tr>
<td>3.510</td>
<td>100</td>
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<tr>
<td>3.467</td>
<td>40</td>
<td>2.345</td>
<td>50</td>
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Table VI. Vibrational Spectra and Assignments for FXeOClO$_3$

<table>
<thead>
<tr>
<th>FXeOClO$_3$ bands (cm$^{-1}$) assignments (b)</th>
<th>CIO$_4^-$ bands (cm$^{-1}$) assignments (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>202 m R $\delta$(F-Xe-O)</td>
<td></td>
</tr>
<tr>
<td>258 s R $\delta$(Xe-O-Cl)</td>
<td></td>
</tr>
<tr>
<td>505 vs IR $\nu$(Xe-F)</td>
<td></td>
</tr>
<tr>
<td>507 vs R $\nu$(Xe-F)</td>
<td></td>
</tr>
<tr>
<td>520 sh $\nu$(Xe-O-)</td>
<td></td>
</tr>
<tr>
<td>530 sh $\nu$(Xe-O-)</td>
<td></td>
</tr>
<tr>
<td>525 ms R</td>
<td></td>
</tr>
<tr>
<td>586 s IR</td>
<td>465 $\delta$(CIO$_2$)</td>
</tr>
<tr>
<td>593 w R</td>
<td>632 $\delta$(CIO$_2$)</td>
</tr>
<tr>
<td>614 R $\delta$(CIO$_3$)</td>
<td></td>
</tr>
<tr>
<td>620 vs IR $\nu$(CIO$_3$)</td>
<td></td>
</tr>
<tr>
<td>628 vs IR $\nu$(CIO$_3$)</td>
<td></td>
</tr>
<tr>
<td>638 R $\nu$(Cl-O-)</td>
<td></td>
</tr>
<tr>
<td>722 vs IR</td>
<td></td>
</tr>
<tr>
<td>726 w R</td>
<td></td>
</tr>
<tr>
<td>758 sh IR</td>
<td></td>
</tr>
<tr>
<td>754 w R</td>
<td></td>
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<tr>
<td>1014 mw R</td>
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<td>1018 vs IR $\nu$(Cl-O)$_{\text{sym}}$</td>
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</tr>
<tr>
<td>1032 vw R $\nu$(Cl-O)$_{\text{sym}}$</td>
<td>938 $\nu$(Cl-O)$_{\text{sym}}$</td>
</tr>
<tr>
<td>1048 sh IR</td>
<td></td>
</tr>
<tr>
<td>1202 mw R</td>
<td></td>
</tr>
<tr>
<td>1215 vs IR $\nu$(Cl-O)$_{\text{asym}}$</td>
<td></td>
</tr>
<tr>
<td>1243 vw R $\nu$(Cl-O)$_{\text{asym}}$</td>
<td>1119 $\nu$(Cl-O)$_{\text{asym}}$</td>
</tr>
<tr>
<td>1295 w IR</td>
<td></td>
</tr>
</tbody>
</table>
References for Table VI.

(a) Assignments are those given by R.E. Hester, and R.A. Plane, Inorg. Chem. 3, 769 (1964). The quoted frequencies are averages of those quoted by Hester and Plane.

(b) The four frequencies between 1000 and 1250 cm\(^{-1}\) must arise from terminal Cl-0 stretching, although only 3 stretching fundamentals are expected in this region for a single FXeOCl\(_3\) unit. Similarly the bands in the 590 - 770 cm\(^{-1}\) region can be assigned to deformation and rocking vibrations of the ClO\(_3\) group. In addition, the Cl-0-(bridging) stretch is expected to occur in this region. The remaining bands at lower frequency may be confidently assigned to motions involving significant displacement of the xenon atom. The appreciable intensity of these low frequency bands in the Raman is consistent with our experience that such motions give rise to intense Raman features. In view of the similar masses of oxygen and fluorine and the closeness of the frequencies assignable to Xe-F and Xe-0- stretch (507, 525 cm\(^{-1}\)) it is meaningless to assign one to Xe-F and the other to Xe-F. It is better to describe the modes as "symmetric" and "antisymmetric" F-Xe-O stretching, with the higher frequency attributable to the latter.
Table VII. Assignment of the Raman Spectrum of \((\text{FXe})_2 \text{O}_2 \text{S}(0)\text{F}^+\text{[AsF}_6^-\)
(bands in cm\(^{-1}\), relative intensities in parentheses)

\[
\begin{array}{lcl}
\text{[(FXe)_2F]^+[AsF}_6^-(a)} & \text{[(FXe)_2O_2S(0)F]^+[AsF}_6^-} & \text{[SO}_3\text{F]}^-(b)
\\
369(7)\nu_5(\text{AsF}_6^-) & ...... & 372(6)
\\
410(8) & ...... & 409\nu(\text{S-F})
\\
551(\text{sh}) & ...... & 566
\\
588(94)\nu(\text{XeF})_{\text{sym}} & ...... & 563(88)
\\
575(\text{sh})\nu_2(\text{AsF}_6^-) & ...... & 573(\text{sh})
\\
600(100)\nu(\text{XeF})_{\text{asym}} & ...... & 581(100)
\\
588(23) & ...... & 592
\\
633(12.5)
\\
683(19)\nu_1(\text{AsF}_6^-) & ...... & 685(13.5)
\\
875(2) & ...... & 786\nu(\text{S-F})
\\
1035(9) & \{ & 1082\nu(\text{S-0})_{\text{sym}}
\\
1090(3) & \} & \\
1350(5) & \} & 1287\nu(\text{S-0})_{\text{asym}}
\\
\end{array}
\]


In the case of XeF₂, E(F) is -80(a), ΔH(Electron pair bond) is -48(b) and the total bond energy(c) is -65 kcal mole⁻¹. Thus Σ(ΔH(electrostatic) + Resonance Energy) = -218 kcal mole⁻¹.

(a) Reference 39
(c) Reference 1.
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