Lawrence Berkeley National Laboratory
LBL Dissertations

Title
PERFLUORO CATIONS OP THE NON-METALLIC ELEMENTS

Permalink
https://escholarship.org/uc/item/84h8109z

Author
Gibler, Donald D.

Publication Date
1973-04-01

Thesis/dissertation

eScholarship.org Powered by the California Digital Library
University of California

LBL-1157

# PERFLUORO CATIONS OF THE NON-METALLIC ELEMENTS

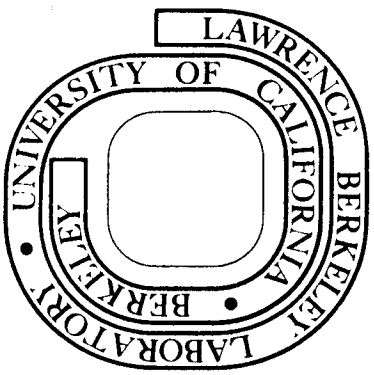
Donald D. Gibler
(Ph.D. Thesis)

April 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

**For Reference**

**Not to be taken from this room**




LBL-1157

## DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 3 8 0 0 0 9 0



# PREFACE

## ACKNOWLEDGMENTS

My acquaintance with the persons in the following list has prospered the completion of this theses, and while they are in no way accountable for any of its defects, each is responsible in some measure for whatever merit it possesses.

Ethel May Gibler

Neil Bartlett

Chris Adams

Al Bulliner

Mark Gennis

Fritz Sladky

Donald Stewart

Carol Walters

Allan Zalkin

The portion of this work done at Princeton was supported by NSF monies (1966-69) and the portion completed at the University of California, Lawrence Berkeley Laboratory was supported by Atomic Energy Commission grants (1969-72). Many thanks are due to both the funding agencies and these two great universities.

PERFLUORO CATIONS OF THE NON-METALLIC ELEMENTS

TABLE OF CONTENTS

Page Number

PREFACE . . . . . iii

LIST OF TABLES . . . . . vi

LIST OF ILLUSTRATIONS . . . . . vii

ABSTRACT . . . . . 1

I. INTRODUCTION . . . . . 4

II. PRINCIPAL EXPERIMENTAL WORK . . . . . 4

A. The Crystal Structure of $XeRuF_7$ . . . . . 4

B. Crystallographic Findings: $SAsF_9$ . . . . . 7

C. The Crystal Structure of $SBF_7$ . . . . . 8

D. Experiments with $IF_7$ and $IF_5$ to Determine Their Relative Fluoride Ion Donating Abilities . . . . . 11

E. The Crystal Structure of $IF_4^+SbF_6^-$ . . . . . 14

III. SURVEY OF DONOR FLUORIDES OF GROUPS VI-VIII . . . . 17

A. Introduction . . . . . 17

B. The Noble Gas Fluorides . . . . . 17

C. The Chlorine Fluorides . . . . . 23

D. The Bromine Fluorides . . . . . 26

E. The Iodine Fluorides . . . . . 27

F. The Fluorides of the Sulfur Subgroup . . . . . 31

IV. A THERMODYNAMIC MODEL . . . . . 38

V. MISCELLANEOUS EXPERIMENTS . . . . . 50

A. A New Synthesis of $IOF_5$ . . . . . 50

B. The Interaction of $NO_2F$ with $IrF_6$ . . . . . 52

TABLE OF CONTENTS - Continued

Page Number

C. The Preparation of $NO_2^+WOF_5^-$ . . . . . .55

D. $AsF_5 + PF_5$ / $PF_4^+AsF_6^-$ . . . . . .55

VI. APPENDICIES

A. Computer Programs and Some Pertinent Equations Relating to the Crystallographic Work . . . . . .56

B. Observed and Calculated Structure Factors for $XeF^+RuF_6^-$ . . . . . .59

C. Observed and Calculated Structure Factors for $SF_3^+BF_4^-$ . . . . . .60

D. Observed and Calculated Structure Factors for $IF_4^+SbF_6^-$ . . . . . .61

VII. REFERENCES . . . . . .62-69

VIII. TABLES . . . . . .70-85

IX. ILLUSTRATIONS. . . . . .86-99

# LIST OF TABLES


Page Number

I. Final Positional and Thermal Parameters for $XeF_5^+RuF_6^-$ . . . . . 71

II. Sulfur and Arsenic Postional Parameters for $SF_3^+AsF_6^-$ . . . . . 72

III. Final Positional and Thermal Parameters of $SF_3^+BF_4^-$ . . . . . 73

IV. Final Positional and Thermal Parameters of $IF_4^+SbF_6^-$ . . . . . 74

V. Known Fluoride Donor-Acceptor Complexes. . . . . 75-76

VI. Bonding in Some $XeF_2$ Derivatives. . . . . 77

VII. Interatomic Distances (Å) and Angles (Deg.) for $XeF^+RuF_6^-$ . . . . . 78

VIII. Interatomic Distances (Å) and Angles (Deg.) for $IF_4^+SbF_6^-$ . . . . . 79

IX. Interatomic Distances (Å) and Angles (Deg.) for $(SF_3)(BF_4)$. . . . . 80

X. A Comparison of $SF_3^+$ and Some Other $MF_3$ Species. 81

XI. Calculated $\Delta H_{diss}$ for Some $F^-$ Donor-Acceptor Complexes. . . . . 82

XII. Tensimetry of $IrF_6 + NO_2F$. . . . . 83

XIII. X-Ray Powder Data for $NO_2^+IrF_6^-$. . . . . 84

XIV: X-Ray Powder Data for $NO_2^+WOF_5^-$. . . . . 85

# LIST OF ILLUSTRATIONS


Page Number

Figure 1: The $XeF^{+}RuF_6^{-}$ Structural Unit. . . . . 87

Figure 2: Stereoscopic View to Show Packing of the $XeFRuF_6$ Units in the Crystal Lattice. . . . . 88

Figure 3a: The $XeF_5^{+}$ and $RuF_6^{-}$ Structural Units and the Coordination of $XeF_5^{+}$. . . . . 89

Figure 3b: The Molecular Structure of $XeF_5^{+}[AsF_6]^{-}$. . . 90

Figure 4: Molecular Geometries of $XeF_5^{+}$, $IF_5$, $TeF_5^{-}$. . 91

Figure 5: Molecular Geometries of $ClF_2^{+}$, $SF_2^{+}$, $ClO_2^{-}$.. 92

Figure 6: Molecular Geometries of $BrF_4^{+}$, $SeF_4$. . . . . 93

Figure 7: Molecular Geometries of $IF_4^{+}$, $TeF_4$, $SbF_4^{-}$. . 94

Figure 8: Packing Diagram of $SF_3^{+}BF_4^{-}$. . . . . 95

Figure 9: The $SF_3$ Cation.. . . . . 96

Figure 10: Plot of Bond Length -vs- the Logarithm of the Stretching Force Constant for Some S-F Bonds.. . . . . 97

Figure 11: Comparison of Raman Spectra of $SF_3^{+}BF_4^{-}$. . . 98

0 0 0 0 3 8 0 0 0 4



# PERFLUORO CATIONS OF THE NON-METALLIC ELEMENTS

Donald D. Gibler

## ABSTRACT

Many of the fluorides of groups VI to VIII interact with powerful fluoride ion acceptors to form salts of which $XeF^+RuF_6^-$, $SF_3^+BF_4^-$ and $IF_4^+SbF_6^-$ are representative examples. The crystal structures of these three salts have been determined from three dimensional X-Ray single crystal scintillation counter data.

Crystals of $XeF^+RuF_6^-$ are monoclinic, space group $\underline{P}2_1/\underline{n}$ [an alternate setting of $\underline{P}2_1/\underline{c}$ ($C_{\underline{2h}}^5$), with $\underline{a}$ = 7.991, $\underline{b}$ = 11.086, $\underline{c}$ = 7.250 (all ± .006 Å), $\underline{\beta}$ = 90.68 ± .05°, $\underline{V}$ = 642.2 Å$^3$, $\underline{z}$ = 4, and $\underline{d_c}$ = 3.78 g cm$^{-3}$. Full matrix least-squares refinement using 1044 independent reflections with $I > 2\sigma(I)$ yielded a conventional R factor of .07. The structural unit is an $XeF^+RuF_6^-$ ion pair. The internuclear separation in the cation Xe-F(1) = 1.872(17) Å. The remaining fluorine atoms form a distorted octahedral coordination about the ruthenium atom, with one, F(2), making a close approach to the xenon atom, Xe-F(2) = 2.182(15) Å. The associated Ru-F(2) bond [1.919(13) Å] is somewhat longer than the other ruthenium fluorine bonds (mean distance 1.80 Å). The angle F(1)-Xe-F(2) [177.08(1.23)°] is essentially linear. The angle Xe-F(2)-Ru = 137.19(46)°.

$SF_3^+BF_4^-$ crystallizes as clear colorless plates in the orthorhombic space group $\underline{Pnma}$ ($D_{\underline{2h}}^{16}$) with $\underline{a}$ = 9.599(3) Å, $\underline{b}$ = 5.755(3) Å, $\underline{c}$ - 8.974(3) Å, $\underline{d_c}$ = 2.34 g cm$^{-3}$, $\underline{z}$ = 4, and $\underline{V}$ = 495.8 Å$^3$. Full matrix least-squares refinement using 700

independent reflections having $I > 2\sigma(I)$ converged to a weighted R factor of .04. The structure consists of discrete $SF_3^+$ and $BF_4^-$ ions. The $SF_3^+$ ion exhibits $C_{3v}$ symmetry within experimental error, the S-F bond distances being two at 1.495(2) Å, and one at 1.499(2) Å, and bond angles 97.62(7)° and (twice) 97.39(12): the structure provides no evidence for bridge bonding of cation to anion. The closest non-bonding S-F contacts are 2.593(3) Å.

The $IF_4^+SbF_6^-$ structure was determined using a twinned crystal. This crystal exhibited the symmetry of space group $P4/n$ ($C_{4h}^3$) with $a = b = 5.875$ Å, $c = 10.332$ Å (all ± .005 Å), $V = 356.61$ Å$^3$, $z = 2$, and $d_c = 4.085$ g cm$^{-3}$. For structure refinement it was necessary to introduce a disorder. This is consistent with the observation that the single crystals of $ISbF_{10}$ are orthorhombic, not tetragonal. Crystals employed for data collection were, in all cases, twinned about $c$. The final conventional R factor of .07 was obtained using 504 data and involved a twofold disorder of the fluorine atoms in the general positions of S.G. $P4/n$. The structure consists of discrete $IF_4^+$ and $SbF_6^-$ ions. The $IF_4^+$ ion, a $C_{2v}$ symmetry species, has two bonds [I-F(5)] at 1.811(17) Å and two [I-F(6)] at 1.792(25) Å. The angle F(5)-I-F(5) = 153.26° and the angle F(6)-I-F(6) = 106.04°. The $SbF_6^-$ unit departs slightly from $O_h$ symmetry.

The thermodynamic stability of the salts formed by the interaction of non-metal fluorides with $BF_3$, $PF_5$, $AsF_5$, and $SbF_5$ is discussed in terms of a modified Born-Haber cycle. The enthalpy for the process $[AF_{x-1}]^+[MF_{y+1}]^-(c) \rightarrow AF_{x(g)} + MF_{y(g)}$ has been evaluated using the cycle and are estimated to be reliable to ± 5 kcal/mole.

Chemical studies have established $IF_7$ to be superior to $IF_5$ as a fluoride ion donor. The preparation and properties of the new compounds $IF_6^+MF_6^-$ (M = Ir, Pt, and Ru) are described.

Exploitation of the good $F^-$ donor properties of $IF_7$ and the poor $F^-$ donor properties of $IOF_5$ has yielded an improved synthesis of $IOF_5$.

The preparation and properties of $NO_2^+WOF_5^-$ and $NO_2^+IrF_6^-$ are described.

# I. INTRODUCTION

The majority of the fluorides of groups VI-VIII form adducts with per-fluoro Lewis acids such as $AsF_5$, $BF_3$, or $SbF_5$. The purpose of this thesis is to further elucidate the nature of these adducts and to investigate their relative stabilities. Four principal experimental contributions are presented: (1) chemistry establishing $IF_7$ as a better fluoride ion donor than $IOF_5$ and $IF_5$, and the structural investigations of (2) $XeF^+RuF_6^-$, (3) $IF_4^+SbF_6^-$, and (4) $SF_3^+BF_4^-$. The findings from these investigations are incorporated in a survey of adduct forming behavior of related fluorides of krypton, xenon, chlorine, bromine, iodine, sulfur, selenium, and tellurium. The experimental evidence presented in this survey is used as a basis for the formulation of these adducts as salts of general formula $[EF_x]^+[MF_y]^-$; this permits a modified Born-Haber cycle to be used as a basis for a discussion of the relative stability of such salts. In spite of some rather bold extrapolations the model considered conforms satisfactorily to the present experimental observations.

# II. PRINCIPAL EXPERIMENTAL WORK

## A. The Crystal Structure of $XeRuF_7$

Crystal Preparation.- Crystals of the xenon difluoride-ruthenium pentafluoride complex were prepared by the fusion of minute quantities of powder in thin walled quartz capillaries. The powdered compound, prepared by direct fusion of $XeF_2$ and $RuF_5$ in a Kel-F tube at 120C was loaded into the capillaries under nitrogen atmosphere in a Vacuum Atmospheres Corp. dry box. The capillaries

were distributed along a glass tube placed in a cylindrical heater which provided a temperature gradient along the axis of the tube. Crystals formed most successfully in the temperature range from 100 to 120°.

Crystal Data.- $XeRuF_7$ (mol. wt. = 365.36) is monoclinic with $\underline{a}$ = 7.991, $\underline{b}$ = 11.086, $\underline{c}$ = 7.250 (all ± .006Å), $\underline{\beta}$ = 90.68 ± .05°, $\underline{V}$ = 642.2 $Å^3$, $\underline{z}$ = 4, $\underline{d}_c$ = 3.78 g $cm^{-3}$ and F(000)= 636.30. Single crystal precession photographs established the following conditions limiting possible reflections h k ℓ, none, h 0 ℓ, h + ℓ = 2n; and 0 K 0, K = 2n. These indicated the space group $\underline{P2_1/n}$ (an alternate setting of S.G. No. 14 in the International Tables[1]). The equivalent positions for this setting are: x, y, z; -x, -y, -z; 1/2 + x, 1/2 - y, 1/2 + z; 1/2 - x, 1/2 + y, 1/2 - z.

Data Collection.- Diffraction data were collected on a Picker automatic four-circle diffractometer with a fine focus Mo anode tube. The crystal used was an irregularly shaped roughly oval tablet ~ 0.3 × 0.2 × 0.1 mm. There were no well defined faces. The mosaic spread of the crystal was examined by omega scans of strong reflections on each of the principal reciprocal lattice axes and found to be acceptable. Twelve high angle reflections were centered at a take-off angle of ~ 3°, and were used in a least-squares refinement of cell parameters. Data were collected at a take-off angle of 3° by the two theta scan technique at a scan rate of 1° per minute. The scan width was ± 0.85° from 2θ(calc.) for $\alpha_1$ and $\alpha_2$ peaks respectively. The crystal and detector were stationary for the ten second background counts which were offset 0.5° from the 2θ scan limits. The X-ray beam was monochromatized with a graphite crystal. Automatic

attenuators were inserted when the peak intensity exceeded 10,000 c.p.s. A pulse height analyzer was used to reduce noise.

Two unique data sets, the -h, k, ± ℓ and the h, k, ± ℓ were collected for $2\theta \leq 60°$. Intensities of two standards were collected at intervals of every 60 reflections. A total of 4136 intensities were recorded which averaged to yield a data set of 1887 independent reflections.

Structure Refinement.- The positions of the heavy atoms were determined from a three dimensional Patterson synthesis. The peak intensities did not support unequivocal assignment of the xenon or ruthenium atoms to the two sets of positions. Both possibilities were subjected to least-squares refinement and although the agreement factor was roughly the same for the two cases one showed large temperature factor anomalies. A difference Fourier based on the other case revealed six peaks, assignable to fluorine atoms, in a near octahedral disposition about the Ru atom, with a seventh peak, attributable to a F atom, approximately 2 Å away from the Xe atom. Another least-squares refinement including these fluorine atoms resulted in a conventional R factor of 0.20 which improved to 0.13 when the heavy atoms were allowed anisotropic temperature factors. Further full matrix refinements with all atoms anisotropic gave $R = 0.09$, $R_2 = 0.11$.

Examination of the observed and calculated structure factors showed that the poorest agreement occurred with the low-angle high intensity reflections. Since absorption and extinction corrections could not be reliably made, the lower angle data ($\sin\theta/\lambda \leq 0.20$) was given zero weight in the final least-squares refinements as

were data having $I \leq 2\sigma(I)$. This procedure resulted in R = 0.07, $R_2$ = 0.08 and a standard deviation for an observation of unit weight of 1.28. The number of non-zero weighted data in this refinement was 1044. The positional and thermal parameters, reported in the Table I, are from this refinement. The $F_o$ and $F_c$ data for $XeFRuF_6$ are given in Appendix II.

B. Crystallographic Findings: $SAsF_9$

Crystal Preparation.- Single crystals of the 1:1 $SF_4$:$AsF_5$ adduct were prepared by sublimation of minute quantities of the material in quartz capillaries. Precession photographs were obtained for the zero, first, second, and third layers on the principal axes.

Crystal Data.- $SAsF_9$ (mol. wt. 277.89) is orthorhombic with $a$ = 20.375(3), $b$ = 8.508(3), $c$ = 11.224(3) Å, $V$ = 1945 Å$^3$, $z$ = 12, $d_c$ = 2.84 g cm$^{-3}$, and the effective volume per fluorine atom is 18 Å$^3$. The diffraction symmetry was found to be mmm C_c_ which is consistent with three space groups $Cmc2_1$, $C2cm$, and $Cmcm$. Accurate cell dimensions were obtained by examination of high angle reflections along each of the principal reciprocal axes.

Partial Solution of the Structure.- A complete data set was obtained for two crystals. No obvious systematic discrepancies were observed between the two sets. A Patterson synthesis provided a solution for the heavy atom positions in the space group $Cmc2_1$. Of 1530 accessible reflections in the more complete data set only 487 were greater than $3\sigma$, and the backgrounds proved rather large and irregular. The placement of all fluorines would require greater than 100 parameters in the least-squares matrix. As a result of

this poor data to parameter ratio the positions of the fluorine atoms in the structure could never be adequately defined in spite of the fact that the weighted R could be lowered to 0.07 with arsenic atoms alone anisotropic. Table II indicates the sulfur and arsenic positions used in the most successful refinements. The sulfur:arsenic coordination is 6:6 and is similar to that in NiAs with each sulfur located near the center of a distorted trigonal prism of arsenic atoms.

C. The Crystal Structure of $SBF_7$.

Crystal Preparation.- The adduct $SF_4 \cdot BF_3$ was prepared by co-condensation of $SF_4$ (excess) and $BF_3$ in a Monel can provided with a teflon-gasketed lid. Sulfur tetrafluoride was obtained from Ozark-Mahoning Co., Tulsa, Okla., and $BF_3$ from Matheson Company, Inc., East Rutherford, N.J. Both were used without purification. The colorless solid was transferred to quartz capillaries in a Vacuum Atmospheres Corp. Dri-Lab with a nitrogen atomosphere. The capillaries were sealed by drawing down in a small flame. Crystals were grown by sublimation, by establishing small temperature gradients in the capillaries at ~ 60°. Most of the crystals grown by this technique proved to be twinned when examined under the polarizing microscope. Even crystals which appeared to be satisfactory under microscopic examination showed poor mosaic quality when examined on the diffractometer. Omega scans of representative diffraction peaks from the crystal finally chosen for data collection revealed a major peak with two satellites. The satellites contributed approximately 10% towards the total intensity for the most unfavorable of several reflections scanned.

The crystal was roughtly rectilinear with dimensions .4 x .2 x .2 mm.

Crystal Data.- $SBF_7$ (mol. wt. 265.56) is orthorhombic with $a$ = 9.599(3), $b$ = 5.755(3), $c$ = 8.974(3) Å, $V$ = 495.8 Å$^3$, $z$ = 4, $d_c$ = 2.34 g cm$^{-3}$ and F(000) = 336.52. The unit cell volume satisfies Zachariason's criterion for close-packed fluoride lattices, since the effective volume per fluorine atom is 17.7 Å$^3$.[2] Single crystal photographs confirmed the diffraction symmetry found for $SF_4 \cdot BF_3$ by Calvert et al.[3] The structure was successfully refined in the centrosymmetric space group Pnma.

X-Ray Measurements, $SF_3BF_4$.- Diffraction data were collected on a Picker automatic four circle diffractometer equipped with a fine focus Mo anode tube. As previously noted, the omega scans of the crystal were not entirely satisfactory. Accurate cell dimensions were obtained by determining the 2θ angle for the MoK$\alpha_1$ peak of the reflection of highest angle observable along each of the principal axes. Intensity data were collected by the θ-2θ scan technique at a scan rate of one degree per minute. The poor mosaic quality of the crystal required a scan width of two degrees. Background counts were offset from the scan limits by 0.5 degrees, and each count lasted 10 seconds. The radiation was monochromatized with a graphite crystal (2θ = 11.8°). Automatic attunuators were inserted when the beam intensity exceeded 10,000 c.p.s. Three standards were checked every one hundred reflections.

A complete set of -h k ℓ reflections was collected to a 2θ of 65° and a portion of the h -k -ℓ set also. A sorted averaged set of 980 unique reflections was obtained from 1240 intensity measurements. Of these 700 having $I \leq 2\sigma(I)$ were given non-zero

weighting in the least-squares refinement.

Structure Refinement.- A Patterson synthesis revealed the position of the sulfur atom but the least-squares refinement, with the sulfur atom alone, gave R = .50 [$R = \Sigma|(F_o)-(F_c)|/(F_o)$]. We were still not certain of the space group at this point and so ran WILSON to check statistical inequalities. These were not conclusive but indicated strongly that Pnma (No. 62 in the International Tables)[1], the centric group was correct. A set of E values produced by this program were subsequently used in MULTAN, a recently developed direct methods program. Two sets of phases generated by the program looked promising and a Fourier synthesis was produced from each, neither of which indicated a full structure. Several trial structures, indicated by these Fourier syntheses, were refined by least-squares. The best refinement R = 0.43 was achieved using the sulfur (four fold) position indicated by the Patterson synthesis, along with an eight-fold set and a four-fold set of fluorine atoms. A Fourier syntheses produced with the phases generated by this refinement, revealed that the four-fold fluorine atom set was misplaced, but the positions of the other atoms were clearly indicated. Subsequent isotropic refinement gave R = 0.10 and incorporation of anisotropic temperature factors, for all atoms, reduced R to 0.043. The largest residual density revealed by a difference Fourier at this point was 0.96 $e/\AA^3$, near the S atom position. The positional and thermal parameters and the average root-mean-square displacements from this refinement are reported in Table III. The final value of $R_2$ = 0.058, and R (including zero weighted data) = 0.063. The standard deviation of an

observation of unit weight was 1.32. The largest shift of any parameter, divided by the estimated standard deviation on the last cycle, was less than 0.0003.

D. Experiments with $IF_7$ and $IF_5$ to Determine Their Relative Fluoride Ion Donating Abilities.

Materials.- $IF_5$ was obtained from Matheson Corp., East Rutherford, N.J. It was purified by exposure to fluorine at ~ 500 torr followed by trap-to-trap distillation. $IF_7$ was prepared by fluorination of $IF_5$ or $HgI_2$ at 250° in Monel vessels (all tempreatures in °C). $AsF_5$ was obtained from Ozark-Mahoning, Tulsa, Okla. Ruthenium, platinum and iridium were obtained from Englehard Industries, Menlo Park, Edison, N.J. The metals were converted to their fluorides by direct fluorination in Monel cans fitted with Teflon gasketed lids. $IF_6^+AsF_6^-$ was prepared by condensation of $IF_7$ and $AsF_5$ in Monel vessels fitted with Teflon gasketed lids.

Attempted Syntheses of $IF_5 \cdot AsF_5$.- An excess of $AsF_5$ was condensed onto 11.6 g $IF_5$ in a Kel-F trap. The mixture was warmed and cooled alternately to bring the $AsF_5$ to a liquid state. When complete solution of the $IF_5$ was indicated the trap was maintained at -35° while the $AsF_5$ was removed under dynamic vacuum. A clear liquid remained in the trap upon warming to ambient temperature. The mass of the liquid was 11.3 g and the vapor pressure was identical to that of pure $IF_5$. There was no evidence for any adduct formation between $IF_5$ and $AsF_5$ at temperatures equal to or above -35°. Subsequent removal of the $IF_5$ under vacuum revealed no solid residue.

Interaction of $IF_6^+AsF_6^-$ With $IF_5$.- This experiment was conducted several times with no indication of any exchange to produce $IF_4^+AsF_6^-$. In a typical run $IF_6^+AsF_6^-$ (1.763 g) in a Pyrex trap was treated with 5 ml. of liquid $IF_5$. Solution was complete at ambient temperature. The trap was transferred to the vacuum line and slowly evacuated. The white crystalline material remaining behind weighed 1.461 g. Both single crystal and X-ray powder patterns confirmed the material to be pure $IF_6^+AsF_6^-$. The infrared spectrum of the starting material and the recovered material were obtained as powders pressed between AgCl plates. They too, were identical, showing the characteristic absorptions due to $IF_6^+AsF_6^-$ at 960(s) and 795(m).[4]

Interaction of $IF_5$ with $MF_5$ (M = Ir, Os or Pt).- These experiments were condicted in Pyrex traps since the solutions obtained frequently cracked Kel-F traps. The pentafluorides of osmium, iridium, and platinum were all found to be soluble in hot $IF_5$. Upon complete solution the traps were evacuated to dryness. Each remaining material was examined by X-ray powder photography and was found to be identical to the original metal pentafluoride.

Interaction of $IF_5$ with $NO^+PtF_6^-$.- This investigation was conducted in a manner identical to the preceding experiments. Again the residue on removal of $IF_5$ solvent displayed an X-ray powder pattern identical to the starting solute.

Preparation of $IF_6^+PtF_6^-$.- $PtI_2$ (1.5 g) was placed in a prefluorinated 110 ml monel can fitted with a Teflon gasgeted, water cooled lid. Fluorine was admitted slowly to a pressure of

150 pounds and the can was heated at 300° overnight. Upon cooling and removal of excess fluorine the can was opened in the drybox (nitrogen atmosphere). The lid held a bright yellow sublimate. X-ray powder patterns of the material were identical to those of the material prepared by Lohmann[5] by reaction of $O_2^+PtF_6^-$ with $IF_5$ and characterized by him as $IF_4^+PtF_6^-$. A Raman spectrum was obtained which suggested the proper formulation to be $IF_6^+PtF_6^-$.

| | RAMAN FREQUENCIES | | | | | |
|---|---|---|---|---|---|---|
| $IF_6^+PtF_6^-$ | | $IF_6^+$ in $AsF_6^-$ Salt [4] | | $PtF_6^-$ in $NO^+$ Salt [6] | |
| 240 | s* | | | 249 | m* |
| 346 | m | 340 | m* | | |
| 575 | mw | | | 572 | mw |
| 638 | vs | | | 647 | s |
| 705 | ms | 708 | s | | |
| 726 | w | 732 | w | | |

* Relative intensities: s = strong, w = weak, m = medium, v = very

Preparation of $IF_6^+IrF_6^-$ and $IF_6^+RuF_6^-$.- Iridium or ruthenium powder, molecular iodine and fluorine (in excess) were reacted under conditions similar to those in the above experiment. In each case the X-ray powder pattern showed the material to be isomorphous with the $IF_6^+PtF_6^-$ salt prepared from $PtI_2 + F_2$.

Preparation of $IF_7^+RuF_6^-$.- Ruthenium pentafluoride (.357 mmole) was immersed in $IF_7$ liquid at 80° for about 3 hours. The trap (Kel-F) was cooled and evacuated to dryness under vacuum at room

temperature. The increase in weight of the reaction vessel and its contents indicated a $RuF_5$:$IF_7$ combining ratio of 1:1.04. X-ray powder patterns were almost the same as those obtained from the product of the $PtI_2 + F_2$ reaction. $RuF_5 \cdot IF_7$ did not melt sharply and decomposed in the range 135-140°.

$IF_6^+RuF_6^-$, Crystallographic Investigations.- Repeated attempts to sublime $IF_6^+RuF_6^-$ in quartz capillaries only resulted in the formation of $RuF_5$ crystals. However, $BrF_5$ was found to be a good solvent for the compound. By slow removal of $BrF_5$ from the solution at -20°, single crystals of $IF_6^+RuF_6^-$ were obtained. For the several single crystals examined, the mosaic spread was, unfortunately, not of sufficient quality to justify a complete structure determination. The diffraction symmetry and systematic absences were determined from precession photographs. This data obtained on Poloroid film using Mo radiation is listed below. A pseudo A centering of the two heavy atoms is indicated by a well defined pattern of strong reflections for which h = 2n and K + l = 2n.

Crystal Data.- $IF_6^+RuF_6^-$ crystallizes in the monoclinic space group $P2_1/n$, an alternate setting of $P2_1/c$ ($C_{2h}^5$), with $a$ = 9.81, $b$ = 7.61, $c$ = 5.80 (all ± .01 Å), $\beta$ = 107°50' ± 5', $V$ = 432.4 Å$^3$, $z$ = 2, volume per fluorine atom = 17.2 Å$^3$ and $d_c$ = 3.50 g cm$^{-3}$.

E. The Crystal Structure of $ISbF_{10}$.

Preparation of $IF_5 \cdot SbF_5$.- $SbF_5$ (6.4826 g) was placed in Kel-F trap. An excess of $IF_5$ was added under a nitrogen atmosphere. Gravimetry indicated the combining ratio $IF_5$:$SbF_5$ = 1:1.07. This

confirms the preparation of the 1:1 $IF_5 \cdot SbF_5$ adduct first reported by Woolf[7].

Crystal Preparation.- Crystals were prepared by sublimation of minute quantities of the adduct in quartz capillaries in the approximate range of 80-100°. Examination of crystals under the microscope revealed a characteristic cruciform marking on the 0 0 1 face and the nature of the disorder revealed by the structure determination suggests that the crystal used for data collection was twinned along the extinction axis. The crystal selected for data collection was a rectangular prism with dimensions: 0.09 × 0.08 × 0.15 mm. Examination of several crystals by the precession method showed them to be tetragonal with systematic absences for h k 0, $h + k \neq 2n$. The photographs (on Polaroid film) suggested Laue symmetry 4/mmm, but the final structural refinement was accomplished in the Laue group 4/m.

Crystal Data.- $ISbF_{10}$ (mol. wt. 438.63) is tetragonal with $a = b = 5.875 \pm .005$, $c = 10.332 \pm .005$ Å, $d_c = 4.085$ g cm$^{-3}$, $V = 356.61$ Å$^3$, $z = 2$, and F(000) = 388. The effective volume per fluorine atom is consistent with Zachariason's criterion[2] for close packed fluoride lattices, V(F) = 17.8 Å$^3$. The space group we refined the structure in is P4/n.

Data Collection.- The crystal was mounted on a General Electric XRD 5 diffractometer with the phi axis coincident with the crystallographic a axis. Data were collected with the crystal and counter stationary. Standard reflections were observed periodically and non-statistical variations in their intensities

were not observed. The variation in intensity of the h 0 0 reflections as a function of phi was examined and became the basis for an empirical absorption correction.[8] Of 621 intensities accessible in the range $0 < 2\theta < 60°$, 504 were larger than six counts above background and were used for the structure refinement. The largest intensity (13,082 counts) recorded was the 1 1 0 reflection. Backgrounds were not used in the estimation of $\sigma(I)$, so the formula of Appendix I now is:

$$\sigma(I) = \{I + [.05(I)]^2\}^{1/2}$$

Structure Refinement.- The Patterson synthesis was solved for heavy atom positions which were consistent with both P4/n and P4/nmm. Subsequent least-squares refinement yielded R = 0.14. The constraint of the heavy atoms to lie on the four fold axis of the unit cell implied that an $IF_4$ unit was present which was either square pyramidal, square planar, or disordered. A succession of difference fouriers and least-squares refinements indicated a disorder of all fluorine atoms in general positions, with half F atom occupancy of the eight fold positions. The best of many efforts in both possible space groups indicates P4/n to be the appropriate space group for the crystal studied. The final R factor for 504 data with the temperature factors for all atoms isotropic was .077. The final positional and thermal parameters are given in Table IV.

Subsequent investigation of omega scans of several crystals indicate that the crystal used in the structure refinement here presented was probably twinned and that the true unit cell is

orthorhombic with a very nearly equal to b. The separation of reflections from the twins was not sufficient to justify data collection. The indicated lattice constants are a = 8.290, b = 8.339, c = 10.337 (all ± .008 Å). Attempts are underway to grow crystals from solution ($IF_5$ or HF) in hopes of avoiding the twinning consistently present in those grown by sublimation.

## III. SURVEY OF DONOR FLUORIDES OF GROUPS VI-VIII.

### A. Introduction.

The following review is not meant to be exhaustive, but to provide a context for the discussion and elaboration of the significance of the experimental work just described. It is also meant to provide a prelude and justification for the thermodynamic arguments concerning these and similar materials presented in Section IV.

A table of known complexes (Table V) will be presented in Section VIII. Complexes involving more than one fluoride donation per acceptor molecule have been omitted, both from the Table and the review. The compounds are discussed in the order their respective cations appear in this Table.

### B. The Noble Gas Fluorides.

Krypton Difluoride as a Fluoride Ion Donor.- The only well characterized $KrF_2$ adduct known is the 1:2 $KrF_2 \cdot 2SbF_5$ complex. This adduct was first reported by Selig and Peacock[9]. They reported infra-red absorptions at 813 and 600-700 $cm^{-1}$. Raman spectra obtained by McKee[10] in these laboratories show a marked resemblance to those of $XeF^+Sb_2F_{11}^-$, the crystal structure of

which has been done by Peacock et al.[11] There is no crystallographic data available, although powder diffraction patterns are similar to those of $XeF^+Sb_2F_{11}^-$ [10].

Xenon Difluoride as a Fluoride Ion Donor.- The chemistry of xenon difluoride as a fluoride ion donor has been extensively investigated by Bartlett and Sladky[12]. They present firm gravimetric and vibrational spectroscopic data for the existence of 1:1 $XeF_2 \cdot MF_5$ adducts in which M = As, Ir, Ru, Os, and Pt. The arsenic pentafluoride adduct decomposes at ambient temperature to $Xe_2F_3^+ AsF_6^-$, the crystal structure of which has been completed[13]. The existence of a 1:1 $XeF_2 \cdot SbF_5$ complex has been inferred from phase studies by Maslov[14]. R. Mews had isolated this compound and shown it to be isomorphous to $XeF^+RuF_6^-$ by means of X-ray powder photography[122]. The $XeF_2 \cdot 2MF_5$ adducts with M = Pt, Ir, or Ru[12] and Sb or Ta[15] have also been investigated. Bartlett and Sladky[12] report Raman data on all of these materials except the $XeF_2 \cdot 2TaF_5$ adduct. In all cases a characteristic frequency between 621 and 600 $cm^{-1}$ may be assigned to a xenon-fluorine stretch. The $XeF_2 \cdot 2SbF_5$ showed the highest Xe-F stretching frequency of 621 $cm^{-1}$. Interpreted in terms of an isolated $XeF^+$ ion, this correlates quite well with the isoelectronic IF molecule, e.g.,

| | $XeF^+$ | Ref. | IF | Ref. |
|---|---|---|---|---|
| bond length | 1.84 | 11 | 1.906 | 16 |
| $\nu$ | 621 | 12 | 610 | 17 |
| f md./Å | 3.7 | 12 | 3.6 | 18 |

In spite of the large number of 1:1 $XeF_2 \cdot MF_5$ adducts prepared no crystal structure had been successfully concluded on any of them. The spectroscopic investigations suggested a high degree of similarity among the Xe-F bonds in all of these materials and that in the crystallographically characterized $XeF^+Sb_2F_{11}^-$. However, the frequencies were often split in the 1:1 adducts and were all somewhat lower than in the $Sb_2F_{11}^-$ salt. A crystal structure of the $XeF_2 \cdot RuF_5$ adduct was undertaken to determine the degree of similarity or difference in the xenon-fluorine bonds in each type of species. Since the powder patterns of all of the platinum-metal pentafluoride adducts were virtually identical this structure determination could be considered to apply satisfactorily to all. The ruthenium adduct was preferred because the relatively low atomic number of ruthenium favors a more accurate structure determination using X-ray diffraction data. The structure solution has been described in the experimental section. A description and comparison of this structure to those of other Xe(II) species follows.

The crystal structure of $XeF^+RuF_6^-$: Description of Structure.- A computer drawn visualization of one formula unit of the structure is shown in Figure 1. The xenon-ruthenium distance in this unit is 3.819(3). The ruthenium atom is surrounded by six fluorine atoms in a near octahedral array. One of these fluorine atoms, designated F2 in the drawings, is at a significantly longer distance [1.919(13)] from the ruthenium atom than the other five (mean distance 1.80 Å). This fluorine atom (F2) also makes the closest approach of these six fluorine atoms (bonded to ruthenium)

to the xenon atom, with an approach of 2.182(15) Å. The atom designated F1 lies 1.872(17) Å from the xenon atom and is greater than 3 Å from its next nearest neighbor. The F1-Xe-F2 angle is essentially linear at 177.08(1.23). The Xe-F2-Ru angle is 137.19(46).

The structure consists of an array of these formula units separated by van der Waals' distances. The xenon atom has as its closest non-bonded neighbors fluorines bonded to ruthenium and vice versa. A stereographic view of the packing of 10 formula units is shown in Figure 2.

The Structure of $XeRuF_7$ and its Relationship to Other $XeF_2$ Adducts.- A discussion of the bonding in $XeF_2$ is helpful in determining the best formulation of $XeRuF_7$ and other $XeF_2$ adducts. The weight of the evidence favors a single electron bond for each Xe-F linkage as opposed to the more traditional electron pair bond description.

Pimentel[19] and Rundle[20] have proposed a molecular orbital scheme using a xenon 5p atomic orbital and a 2p atomic orbital from each fluorine. Combination of these produces three molecular orbitals; one bonding (+F-, -Xe+, +F-), one non-bonding (+F-, , -F+) and one anti-bonding (+F-, +Xe-, +F-). There are four electrons (two from the xenon orbital and one each from the fluorine orbitals) to populate these molecular orbitals. Consequently the two lowest m.o.'s (the bonding and non-bonding ones) are filled, and since only the two electrons in the bonding orbital contribute to bonding, each Xe-F bond is a one electron bond with a formal bond order of 0.5 assuming a bonding order of

unity for an electron pair bond.

The model of Bilham and Linnet[21] proposes that each fluorine shares one of the xenon atom's electrons, thus creating an octet of electrons about each atom. The Xe-F linkage is, as in the Pimentel and Rundle case, a single electron bond.

Coulson[22] favors a valence bond treatment involving a resonance hybrid of the two canonical forms $F^-(XeF)^+$ and $(FXe)^+F^-$. This permits the retention of a classical octet for each ion species. Again one bonding electron pair must serve for two XeF bonds.

If one of the fluorine atoms in $XeF_2$ is replaced by a ligand (L) more electronegative than fluorine itself the canonical form $(F\text{-}Xe)^+L^-$ will have greater weight than the $F^-(Xe\text{-}L)^+$ canonical form. As L becomes increasingly more electronegative the $(F\text{-}Xe)^+L^-$ form will be expected to predominate almost entirely, and the Xe-F bond in this case will be a classical electron pair bond with a bond order of unity. Pauling[23] has given an empirical equation relating bonding length to bond order,

$$r(\tfrac{n}{2}) = r(1) - .60 \log \tfrac{n}{2}$$

where n is the bond order and r is the bond length. Application of this equation (assuming n = 1/2 for Xe-F in $XeF_2$) to the terminal Xe-F bonds of several $XeF_2$ derivatives yields the bond orders shown in Table VI, which also notes the steady increase in $\nu$(Xe-F) accompanying the decrease in bond length as the substituted ligand becomes increasingly electronegative. The indicated bond order of .8 for the 1.87 Å Xe-F bond justifies a very much greater

weighting for $(FXe)^+(RuF_6)^-$ than the alternative $F^-(XeFRuF_5)^+$ or $F^-(XeF)^+RuF_5$. Also, the observed spectroscopic evidence is in good agreement with an $XeF^+RuF_6^-$ formulation, and indeed was used to predict the principal features of the structure prior to this work[12]. On these bases the $XeF^+RuF_6^-$ formulation is preferred.

In an $XeF^+$ cation, one would expect that the six non-bonding electrons would tend to be distributed about the edge of the base of a cone, the axis of which is the xenon-fluorine interatomic vector (as in a Linnett quartet description). If such were the case the polarizing power of the xenon atom would also be greatest along this axis, that being the direction least shielded by electron density. Consequently an anion would find this the most favorable direction of approach for maximizing interionic attractive forces and minimizing repulsive forces. This explains why the linear geometry of $XeF_2$ is undistorted in these materials, even though the bond distances alter markedly.

Xenon Tetrafluoride as a Fluoride Ion Donor.- $XeF_4$ has been reported to form adducts with $SbF_5$[24,25]. No firm structural evidence is available for the material. $AsF_5$ does not form a stable complex with $XeF_4$. This fact has proven to be of use in the separation of mixtures of the binary xenon fluorides[26].

Xenon Hexafluoride as a Fluoride Ion Donor.- Xenon hexafluoride forms stable $XeF_5^+$ salts with $AsF_5$[27], $IrF_5$[26], $RuF_5$[28], and $PtF_5$[26]. Less well characterized $SbF_5$ and $BF_3$ adducts are also in the literature[29,27].

$XeF_6$ has been shown to be a better fluoride donor than $XeF_2$ by the preference of $XeF_5^+$ salt formation from 1:1:1 mixtures of

$XeF_2$, $XeF_6$, $AsF_5$[26]. $XeF_6$ cannot be displaced from its salts by an excess of $IF_7$. This indicates that $XeF_6$ is a roughly comparable to better fluorine donor than $IF_7$[26].

The structures of both $XeF_5^+AsF_6^-$ [30] and $XeF_5^+PtF_6^-$ [28] are known. Recently the structure of $XeF_5^+RuF_6^-$ (isostructural to the $PtF_6$ salt) has been completed with better precision than was obtained for the Pt salt[31]. In both cases, see Figures 3a and 3b, the geometry of the $XeF_5^+$ unit is the same. But in the case of the arsenic salt the number of fluoride "bridges" to the cation is three while in the platinum and ruthenium salts the number is four. It may be seen by comparison with the parameters for $IF_5$ and $TeF_5^-$ (Figure 4) that this cation also exhibits a marked similarity to its isoelectronic neighbors. This extends even to the relative shortening of the axial bonds and the repulsive effect of the non-bonding valence electron pair resulting in an $F_{ax}$-E-$F_{eq}$ angle of ~ 80°, which is surprisingly constant for all three species.

C. The Chlorine Fluorides.

$ClF_3$ as a Fluoride Ion Donor.- The interaction of $ClF_3$ with the Lewis acids $BF_3$, $PF_5$, $AsF_5$ and $SbF_5$ was first studied by Pavlath[32] in 1954. The findings were not published in the open literature until 1965 when conductomeric and freezing points studies[33] were presented which supported the adducts formulation as $ClF_2^+$ salts. Infrared and Raman investigations[34,35] tended to confirm the presence of essentially isolated cations and anions in $ClF_2^+AsF_6^-$, $ClF_2^+SbF_5^-$, and $ClF_2^+BF_4^-$. There is some disagreement among authors as to the assignment of $\nu_2$ for $ClF_2^+$, but whichever set of values is chosen for the

fundamental frequencies of the cation, they are found to be present in each of the three salts with only minor variations.

| | | $ClF_2^+AsF_6^-$ (34,35) | $ClF_2^+BF_4^-$ (34,35) | $ClF_2^+SbF_6^-$ (34) |
|---|---|---|---|---|
| $ClF_2^+$ | $\nu_1$ | 806 or 811 809 | 788 or 798 798 | 805 or 809 |
| | $\nu_2$ | 384 or 544 | 373 or 537 396 | 387 |
| | $\nu_3$ | 821 or 818 | 808 or 813 | 830 |

Both authors agree that interactions with the anions, i.e., bridging fluorine bonds, must be weak.

Subsequently, A. J. Edwards and coworkers have reported[36] the crystal structure of $ClF_2^+SbF_6^-$. He argues for the existence of weak fluorine bridges linking the $ClF_2^+$ and $SbF_6^-$ units. The strongest evidence on which this is based is the existence of a very much distorted square planar configuration of fluorines about the chlorine atom. This indicates, according to Edwards, a pseudo-six coordination about the chlorine, i.e., six chlorine electrons plus 4 electrons from the bridging fluorines plus 2 electrons from bonding fluorines, for a total of six electron pairs. However, the fact that only one antimony-fluorine bond of the $SbF_6$ unit is significantly longer than the others argues against this information.

A comparison of the $ClF_2$ unit in Edwards' structure and the isoelectronic relatives $SF_2$ and $ClO_2^-$ (see Figure 5) is illuminating. The striking similarity of all three species strongly

suggests that the bonding in each must be similar. Simple electrostatic repulsion of the ligands adequately describes the increase in bond angle as the relative amount of electron density in those ligands increases. This similarity coupled with reluctance of chlorine to form six-coordinate species, strongly suggests that the $ClF_2$ unit in this structure is indeed a well isolated $ClF_2^+$ cation. This ion may be visualized as pseudo tetrahedral, with 2 non-bonding electron pairs and 2 fluorine ligands about the Cl atom. The close approach of the fluorine ligands of the $SbF_6^-$ anion in the plane of the fluorines bound to chlorine and approximately opposite them is consistent with a tendency to avoid the two lone pairs located on the chlorine atom, and simultaneously, minimizes the cation-anion distance to achieve a better lattice energy. Therefore, all of the significant structural characteristics can be explained adequately in terms of the ionic formulation, $ClF_2^+SbF_6^-$, which must be considered at least as valid as the polymeric fluorine bridged structure.

<u>$ClF_5$ as a Fluoride Ion Donor</u>.- $ClF_5$, like several other pseudo octahedral (5 F ligands and a non-bonding valence-electron pair) molecules is a notably poor fluoride donor. Two adducts stable at ambient temperatures have been reported; $ClF_4^+PtF_6^-$ and $ClF_4^+SbF_6^-$ [37,38]. Structural evidence is lacking on both materials. Christe and coworkers have reported I.R. and Raman spectra for $ClF_4^+SbF_6^-$ as well as the low temperature spectrum of $ClF_4^+AsF_6^-$ which is completely dissociated at ambient temperatures. He interprets these in terms of a $ClF_4^+$ cation showing $C_{2v}$ symmetry, indicating a valence bond-pseudo-trigonal-bipyramidal cation with a lone pair

of electrons occupying an equatorial position[38]. The characterization of the $ClF_4^+PtF_6^-$ materials rests primarily on a chemical analysis, and since the indexed powder pattern of the material indicates a probable effective volume per fluoride ion of only 16.8 $Å^3$, I consider the identification as only tentative at this point.

D. The Bromine Fluorides

$BrF_3$ as a Fluoride Ion Donor.- $BrF_3$ is a poorer fluoride ion donor than $ClF_3$, for it does not form a stable complex with $BF_3$. The adduct of $BrF_3$ with $SbF_5$ was first reported in 1949 by Woolf and Emeleus[39]. A crystal structure investigation of the material by Edwards and coworkers was first reported in 1967[40]. Once again, as in the $ClF_2^+SbF_6^-$ case, Edwards has invoked strong fluorine bridging to account for the distortions of the $SbF_6^-$ from a strictly octahedral geometry. The arguments for a simple ionic model based on valence pair bonding within ions hold here just as they did in the $ClF_2^+$ case. In fact, Christe and Schack report vibrational spectra of both $BrF_2^+SbF_6^-$ and $BrF_2^+AsF_6^-$ showing that the characteristic $BrF_2^+$ frequencies can be assigned in spite of complex spectra due to the distorted nonoctahedral anions[41]. They state that the spectra of the material is best interpreted in terms of discrete $BrF_2^+$ and $SbF_6^-$ ions. The $BrF_2^+$ cation shows a bond angle of 95° and a bond length of 1.70(02) Å in the $SbF_6^-$ salt[40]. The fundamental frequencies observed for the $BrF_2^+$ species in the $AsF_6^-$ and $SbF_6^-$ salts agree well. These facts indicate that, as may be expected, the positively charged bromine atom, shielded only by its two fluorine ligands and two lone pairs, does exert a powerful electrostatic effect on the negative fluorine ligands of

the anions, thus reducing their symmetry. They do not, however, require a polymeric bonding model to be adequately dealt with. On the contrary, the remarkable similarity of the $BrF_2^+$ frequencies indicates that the less polarizable cation possesses a fixed geometry unique to itself and independent of the counter ion present in the crystal.

| Raman Spectra[41] | $BrF_2^+AsF_6^-$ | $BrF_2^+SbF_6^-$ |
|---|---|---|
| $\nu_1$(intensity) | 705(10) | 706(10) |
| $\nu_2$(intensity) | 362(2.0) | 360(1.8) |
| $\nu_3$(intensity) | 702(sh) | 703(3) |

$BrF_5$ as a Fluoride Ion Donor.- The only fluoride ion acceptor capable of forming a complex with $BrF_5$ is $SbF_5$. Christe and Lind[42] have recently completed a low-precision structure of $BrF_4^+Sb_2F_{11}^-$. The $BrF_4^+$ ion shows the apprximately $C_{2v}$ symmetry exhibited by its isoelectronic neighbor $SeF_4$[43], as shown in Figure 6. This geometry is that predicted by electron pair repulsion theory for a five electron pair molecule-cation. The ability of $ClF_5$ to form $ClF_4^+$ $PtF_6^-$ suggests that it may be a slightly better fluoride donor than $BrF_5$. $BrF_5$ is certainly a poorer donor than $BrF_3$.

E. The Iodine Fluorides

Prior Work on the Fluoride Donor Behavior of $IF_5$ and $IF_7$.- The only known compound of $IF_5$ in which it behaves as a fluoride donor is the 1:1 $SbF_5$:$IF_5$ prepared by Woolf in 1950[7]. A compound characterized as $IF_5 \cdot PtF_5$ had been reported in 1962[5], but our

experimental work refutes the previous characterization. The Raman spectrum of $IF_4^+SbF_6^-$ has been shown to contain 9 lines attributable to the $IF_4$ unit which is consistent with a $C_{2v}$ symmetry species[44].

Seel and Detmer reported compounds of $IF_7$ with powerful fluoride acceptors ($IF_7 \cdot AsF_5$, $IF_7 \cdot 3SbF_5$, and $IF_7 \cdot BF_4$) in 1958.[45] The Raman spectrum of $IF_6^+AsF_6^-$ has established the ionic formulation for that material[4]. No crystal structure on either material has been published, although Beaton does report a solution for $IF_6^+AsF_6^-$ based on powder data and an assumed space group[46]. The $IF_7 \cdot BF_4$ adduct is completely dissociated at room temperature at atmospheric pressure and has a dissociation pressure of 10 mm at -60°[45].

No investigation into the relative fluoride donating capability of these two molecules had been attempted. No single crystal investigations had been reported. Therefore, the experimental work previously described and next to be discussed was undertaken.

Discussion of the Experimental Investigations of the Fluoride Ion Donating Behavior of $IF_5$ and $IF_7$.- The results of the experimental work described in Section IID establishe several facts. Iodine heptafluoride is superior to iodine pentafluoride as a fluoride ion donor. It forms 1:1 adducts with the pentafluorides of arsenic, iridium, platinum and ruthenium, whereas, $IF_5$ forms 1:1 adduct only with $SbF_5$. This is contrary to the situation of the other halogen fluorides in which the highest valent compound is always the poorer fluoride donor. However, it is in agreement with the observation that the six electron pair coordination

seems to possess remarkable stability. As previously noted, $XeF_6$ is a better donor than $XeF_4$, and $IOF_5$ is a very much poorer donor than $IF_7$ (it forms no adduct with even $SbF_5$[46]). The group VI hexafluorides also fall in this category.

The reported [5] $IF_4^+PtF_6^-$ is in error. The analytical data were certainly misleading, but it may be that prefluorination of the $IF_5$ to remove reduced iodine impurity, resulted in a mixture of $IF_5$ and $IF_7$, and this was the major reason for the mistake. The similarity of the vibrational frequencies for $IF_6^+$ observed in the hexafluorometallates to those found in $IF_6^+AsF_6^-$ suggests strongly that the $IF_6^+$ ion has octahedral symmetry in all these materials.

Description of the Structure of $IF_4^+SbF_6^-$.- The structure consists of alternating $IF_4$ and $SbF_6$ units stacked along the fourfold axes of the unit cell. Both of these units are disordered by a rotation about the fourfold axis of 25° for the $SbF_6$ unit and 90° for the $IF_4$ unit. Thus of eight 1/2 occupancy fluoride atoms lying off the fourfold axis within bonding distance of each of the heavy atoms, only four are used to form a unique unit. The $SbF_6$ units each contain atoms F(1), F(2) and either four F(3) or four F(4) with bond distances of 1.801(23), 1.856(18), 1.878(23) and 1.923(22) Å, respectively. The F-Sb-F angles within a unique unit are all 90° within a single standard deviation. The unique $IF_4$ unit is formed by taking two opposite fluorine atoms from each of sets F(5) and F(6) to produce an $IF_4$ unit having $C_{2v}$ symmetry, with bond distances: I to F(5) 1.811(17), and F(6) 1.729(25) Å. The F(5)-I-F(5) angle = 153.27° and the F(6)-I-F(6) angle = 107.04°.

The nearest non-bonded neighbors of the iodine atom are four fluorine atoms from set F(3) or set F(4) wh ch approach off the symmetry axis at distances of 2.709(22) and 2.674(21) Å, respectively. All fluorine-fluorine contacts between units are 2.6 Å or larger. Interatomic distances and angles are shown in Table VIII.

Discussion of the $IF_4^+SbF_6^-$ Structure.- The validity of the ionic formulation for $IF_4^+SbF_6^-$ is firmly established by the structure. The range of bond lengths in the $SbF_6^-$ unit (1.86 ± .06 Å) are close to those found[47] in lithium hexafluoroantimonate (1.877 ± .006 Å). The $IF_4^+$ geometry is that expected according to a simple valence bond model for a species bearing 10 electrons on the central atom. The closest anion-fluorine contacts made to the iodine lie off the symmetry axis of the ion. This combined with the observed geometry of the cation itself strongly suggests the presence of a sterically active lonepair of electrons belonging to the iodine atom and lying along that axis.

The sequence of isoelectronic structures $SbF_4^-$, $TeF_4$, and $IF_4^+$ are illustrated in Figure 7. A steady shrinkage of bond lengths as the residual positive charge on the central atom increases is evident. More striking perhaps, is the near equivalence of the axial and equatorial bonds in the $IF_4^+$ unit. This may be a consequence of the positively charged iodine pulling its lone pair of electrons closer to the bonding pairs. This would force the axial fluorines down, forcing in turn the equatorial fluorines apart, resulting in both a larger equatorial bond length and angle, as is the case. However, this near equivalence of

axial and equatorial bonds may be an artifact of the disordered structure. A comparison of $IF_5$ and $IF_4^+$ further illustrates the bond shortening which accompanies fluoride ion donation.

| $IF_5$ in $IF_5 \cdot XeF_2$[50] | | $IF_4^+$ | |
|---|---|---|---|
| $I\text{-}F_{ax}$ | 1.817(1) | $I\text{-}F_{eq}$ | 1.792(25 |
| $I\text{-}F_{eq}$ | 1.873(5) | $I\text{-}F_{ax}$ | 1.811(17) |

Note that if the iodine atom is considered to have only five electrons available for bonding, the $I\text{-}F_{ax}$ in $IF_5$ can be represented as I:F whereas $IF_{eq}$ would be I·F. In $IF_4^+$, $I\text{-}F_{eq}$ = I:F and $I\text{-}F_{ax}$ = I·F in this representation. The difference between the lengths of the postulated one and two electron bonds in this case is not nearly so large as we have seen for Xe-F one and two electron bonds in $XeF_2$ and $XeF^+$. This may be a consequence of the difference in the oxidation states of the xenon and iodine atoms.

F. The Fluorides of the Sulfur Subgroup.

The Hexafluorides.- No adducts of any of the hexafluorides of the sulfur subgroup with fluoride ion acceptors has been reported. This is certainly not too surprising in the case of sulfur haxafluoride since the enthalpy change for the reaction[48] $SF_6 \rightarrow SF_5^+ + F^-$ is 272 Kcal $mole^{-1}$. The corresponding values for $SeF_6$ and $TeF_6$ are not known, but in view of the much readier hydrolysis and lower thermal stability[49] of $TeF_6$ vis a vis $SF_6$ it would seem a much more likely candidate for $F^-$ donation, and the nonexistence of compounds such as $TeF_5^+SbF_6^-$ may be due more to a lack of preparative effort than to an inherent instability.

The Tetrafluorides.- Bartlett reported the existence of several adducts of $SF_4$, $SeF_4$ and $TeF_4$ in 1956[51]. A more detailed paper[52] in 1961 described the following adducts: $SF_4 \cdot BF_3$, $SF_4 \cdot AsF_5$, $SF_4 \cdot SbF_5$, $SeF_4 \cdot AsF_5$, $SeF_4 \cdot SbF_5$, $SeF_4 \cdot BF_3$ and $TeF_4 \cdot SbF_5$. It was shown further that selenium tetrafluoride would displace sulfur tetrafluoride from the $SF_4$ adducts. The relative donating ease of $TeF_4$ was not established, but, if a smooth trend down the period exists, the fluoride donating capabilities lie in the sequence $TeF_4 > SeF_4 > SF_4$. This would be analogous to the sequence observed for the halogen tri- and pentafluorides in which the higher atomic number member of each series is also the most ready fluoride donor (see Section IV). $SF_4 \cdot IrF_5$ and $SF_4 \cdot OsF_5$ adducts have also been characterized[53] as well as a low temperature $SF_4 \cdot PF_5$ adduct reported on the basis of vibrational spectroscopic data alone[54]. Selenium tetrafluoride has been shown to form adducts with $OsF_5$[52], $IrF_5$[52], and $NbF_5$[55].

Infrared and conductivity investigations by Seel and Detmer supported an ionic formulation ($SF_3^+BF_4^-$) for the $SF_4 \cdot BF_3$ compound. Gillespie and his coworkers, in an extensive vibrational spectroscopic study[54] of $SF_4$ adducts with $SbF_5$, $AsF_5$, $PF_5$ and $BF_3$, concluded that these materials were ionic in a gross sense, but there was good evidence for relatively strong fluorine bridging between cations and anions. Another study by Evans and Long[56] reports, "the spectra of the molten complexes $SF_4 \cdot SbF_5$, $SeF_4 \cdot SbF_5$ and $SeF_4 \cdot AsF_5$ can be interpreted in terms of the ionic formulations $SeF_3^+SbF_6^-$, $SeF_3^+SbF_6^-$ and $SeF_3^+AsF_6^-$". They could reach no

decision on the correct formulation for the $TeF_4 \cdot SbF_5$ adduct from their spectra.

Other comments on the probable correct formulation of these materials mounted. Cotton and George reviewed theoretical considerations favoring ionic formulations. Muetterties and his coworkers[58], while admitting the validity of an ionic formulation also allowed, on the basis of solution - nmr studies, that the $SF_4 \cdot BF_3$ adduct could be a fluorine bridged dimer or polymer.

Single crystal x-ray structural investigations of $SeF_4 \cdot NbF_5$ and $SeF_4 \cdot 2NbF_5$ have now been reported by Edwards and his coworkers. They state[59] that the structures can best be described as derived largely from the ionic formulations $[SeF_3]^+[Nb_2F_{11}]^-$ and $SeF_3^+NbF_6^-$, with some contribution from fluorine bridging between anions and cations to produce a much distorted octahedral coordination of Se by F atoms. However, once again, in spite of postulated fluorine bridging the geometry of the cationic unit $SeF_3^+$ is remarkably similar to its isoelectronic neighbor $AsF_3$ with the characteristically shortened bonds in the cation.

| | $SeF_3^+$ [59] | $AsF_3$ [60] |
|---|---|---|
| bonds | 1.67, 1.64, 1.66(2) Å | 1.7063 ± .0006 Å |
| angles | 94.0, 93.9, 94.6(1.7)° | 96.1 ± .050° |

Apart from the limited information provided by powder diffraction patterns on $SF_4 \cdot MF_5$ compounds[52,61,62] (M = Sb, Os, Ir, Ru), the only other crystallographic data on the $SF_4$ adducts was the space group information provided by Calvert[3] and his coworkers

from single crystal studies of $SF_4 \cdot BF_3$. Although they suggested that the $SF_4 \cdot BF_3$ structure might be the anti $NH_4IO_3$ structure they did not undertake a complete structural analysis. In view of the lack of definitive structural analysis on the $SF_4$ adducts a single crystal x-ray diffraction investigation was undertaken on the $SF_4 \cdot BF_3$ adduct.

Description of the $SF_3^+BF_4^-$ Structure.- The atomic arrangement is shown in Figure 8. The sulfur atoms and the boron atoms lie in mirror planes. Each sulfur atom has three close fluorine atom neighbors. This $SF_3$ unit is illustrated in Figure 9, which illustrates that, although the site symmetry of the sulfur atom is only $C_s$, the unit as a whole possesses $C_{3v}$ symmetry. The boron atom has four close fluorine atom neighbors. This unit is approximately tetrahedral.

Each sulfur atom is roughly equidistant from three fluorine atoms (designated F3 and F5) of three different $BF_4$ groups at distances of 2.624(2)(twice) and 2.593(3) Å. The closest approach of the other fluorine atom in the $BF_4$ group (designated F4) to a sulfur atom is 3.111(5) Å. The boron-fluorine distances in the $BF_4$ unit are equal within experimental error. However, the F-B-F angles which involve the fluorine atom designated F4 are slightly smaller than those which do not. Significant interatomic distances and angles are tabulated in Table IX. This structure is not the antitype of that reported[63] for $NH_4^+IO_3^-$ as was thought likely by Calvert[3], et al. Indeed, the entire arrangement appears to be simply dictated by the closest packing of $C_{3v}$ symmetry $SF_3$ species and tetrahedral $BF_4$ species.

Discussion of the $SF_3^+BF_4^-$ Structure.- On chemical grounds we can formulate the sulfur species as $SF_3^+$ and the boron species as $BF_4^-$ and, furthermore, we can anticipate that the sulfur atom of the $SF_3$ group will be the effective center of positive charge.

Since fluorine atoms are highly electron attracting, they should be neutral if not slightly negative in net charge, even in the $SF_3^+$ ion. On the F atom side of the $SF_3^+$ ion it is, therefore, reasonable to suppose that the positive charge would be more effectively screened than on the sulfur side. However, the nonbonding valence electron pair of S(IV) will provide appreciable screening on the three-fold axis, if, as might be expected, it occupies a spacially directed orbital (e.g. an $sp^3$ hybrid). Such steric activity of the 'non-bonding pair' suits the arrangement observed in this structure, since the F ligands of the $BF_4^-$ make their close approach to the sulfur atom well off the $\underline{c}_3$ axis and also avoid the F ligands of the $SF_3^+$ to the maximum extent. The fluorine atom arrangement about each sulfur atom is, therefore, that of a trigonally distorted octahedron, with three F atoms bound and 3 (of 3 separate $BF_4^-$) attracted electrostatically.

Although the $BF_4^-$ departs slightly from the tetrahedral ideal, the B-F interatomic distances 1.377(3)(twice), 1.393(5) and 1.397(4) (mean 1.386(6)) are not significantly different within the set, and and in excellent agreement with the mean values (uncorrected for librational motion) for $NaBF_4$[64](1.398 0.05 Å), $KBF_4$[65](1.386(6)), and $NH_4BF_4$[66] (1.382(6)).

However, the polarizing power of the sulfur atom is evidenced by the small angular distortions in the $BF_4$ unit. The positively charged sulfur atom attracts the F3 and F5 atoms of the $BF_4$ unit

most causing the F5-B-F5 and F3-B-F5 angles to be greater than tetrahedral. These distortions from tetrahedral symmetry are of no greater degree than those seen in the aforementioned tetrafluoroborate salts.

The $SF_3^+$ species is very similar to its isoelectronic relative $PF_3$[67] (see Table X). The most striking feature of this resemblance is the equality of the apical angles F-S-F and F-P-F. Presumably the higher nuclear charge of the sulfur atom is responsible for the S-F interatomic distance being 0.07 Å shorter than the P-F distance. The maintainance of the constant shape, despite bond length change, appears to be the rule for cation and isoelectronic neutral molecule pairs. It is not surpirsing that the non-bonding valence-electron-pair in the cation should be more contracted, and hence have greater repulsive-interaction effect, than in the neutral molecule, but the preservation of constant shape indicates that the bonding electrons are affected to a like extent.

The full refinement of the crystal structure of $[SF_3]^+[BF_4]^-$ and the partial solution of the structure of $[SF_3]^+[AsF_6]^-$ (see Section IIC) each show the anion occupying a lattice site of symmetry lower than $\underline{T}_{\underline{d}}$ and $\underline{O}_{\underline{h}}$, respectively. The anionic vibrational frequencies of these two compounds lie close to those found for the anions in other salts or in solution, but the spectra clearly show "site effects", viz. the splitting of degenerate fundamentals [$\nu_2(e_g)$ of $AsF_6^-$] and the breakdown of gross selection sites so that $\nu_3(t_{1u})$ of $AsF_6^-$ is observed in the Raman spectrum of $[SF_3]^+[AsF_6]^-$, as are $\nu_1(a_1)$ and $\nu_2(e)$ of $BF_4^-$ in the

infrared spectrum of $[SF_3]^+[BF_4]^-$ [54]. These effects are small, and certainly originate in unit-cell dynamics and in the slight deviation of the ions from structural regularity rather than in extensive interionic fluorine-bridging interactions, as proposed by Gillespie[27]; we note that comparable "site effects" are seen in the spectra of the alkali metal tetrafluoroborates[123].

The bond length in the $SF_3^+$ species is the shortest recorded so far for a S-F bond. This, at least in part, may be attributed to appreciable net positive charge of the sulfur atom, and the low coordination number (hence weaker interligand repulsions). Although the bond in $SF_3^+$ is even shorter ( ~ 0.05 Å) than the equatorial bond in $SF_4$ (1.545 Å) it is dramatically shorter ( ~ 0.15 Å) than the axial bonds in the latter (1.646 Å)[68]. These findings are in harmony with the view that the axial $SF_4$ bonds are effectively single-electron bonds, and the equatorial bonds, electron-pair bonds[69]. (Donation of fluoride ion: $SF_4 \rightarrow SF_3^+ \cdot F^-$ generates a cation in which all bonds are electron pair bonds). Indeed the bond stretching force constants give further support to these views.

The S-F stretching force constant for $SF_3^+$ we find to be 5.67 md $Å^{-1}$, which is comparable to the value of 5.2 md $Å^{-1}$ for the S-F equatorial stretching force constant of $SF_4$ and approximately twice the value of 2.8 md $Å^{-1}$ derived for the axial bonds in that molecule[70].

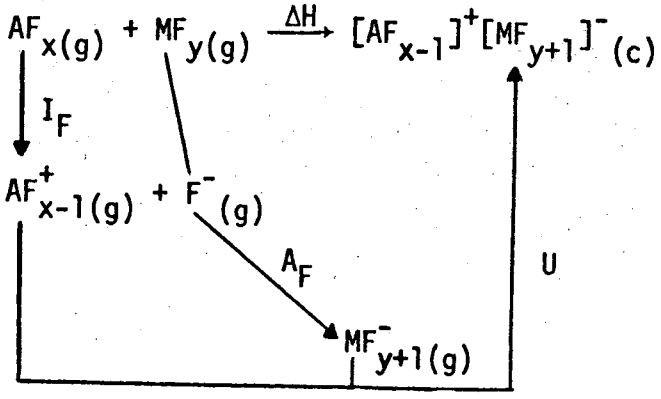
The logarithm of the stretching force constants and the bond lengths of several S-F bonds are compared to those of the $SF_3^+$ cation according to the relationship discovered by Herschbach and

Laurie[71] in Figure 10. The relatively high strength of the bonding in the $SF_3^+$ species is quite marked.

In summary, the structure determination has established the proper formulation of $SBF_7$ to be $SF_3^+BF_4^-$. The $SF_3^+$ cation, the only perfluorosulfur cation established, possesses the shortest sulfur-fluorine bonds yet observed. An ionic formulation $SF_3^+AsF_6^-$ for the $SF_4 \cdot AsF_5$ adduct is given further credence due to the similarity of vibrational frequencies attributable to the $SF_3^+$ species in that material and in $SF_3^+BF_4^-$.

## IV. A THERMODYNAMIC MODEL

The structural and spectral evidence presented in the preceding sections support the formulation of virtually all complexes of the powerful fluoride ion acceptors with the fluorides of groups VI to VIII as ionic materials. A modified Born-Haber cycle is then a logical theoretical construct for a discussion of the thermodynamics of such complexes. The cycle considered here will be of the following type.




The enthalpy of dissociation of the fluoride ion donor into a singly charged cation and a fluoride ion is designated by $I_F$.

The energy associated with the formation of a bond between the fluoride ion acceptor (Lewis acid) and a fluoride ion is indicated by the Symbol $A_F$, and may be called the fluoride ion affinity of the Lewis acid. The lattice energy is indicated by the standard symbol, U.

The values of $I_F$ for the materials discussed here lie in the range of 200-250 kcal/mole. Experimentally these values are obtained from measurement of mass spectroscopic appearance potentials (A.P.) or from photoelectron spectroscopy (P.E.). The former method is reliable to ~ 5 kcal/mole and the latter to ~ 2 kcal/mole[72]. If the observed ionization process does not leave the cation in its ground electronic state the minimum energy charge coincident with cation formation is liable to be overestimated. The values available (derivable) from the literature for the enthalpy of the process $AF_x \rightarrow AF_{x-1} + F^-$ for the materials discussed here are listed below.

| $AF_x$ | $\Delta H$(kcal/mole) | Method | Ref. |
|---|---|---|---|
| $ClF_3$ | 215 | AP | 73 |
| $BrF_3$ | 231 | AP | 73 |
| $BrF_5$ | 243 | AP | 73 |
| $IF_5$ | 234 | AP | 73 |
| $XeF_2$ | 217 | PE | 74 |
| $XeF_4$ | 223 | PE | 74 |
| $XeF_6$ | 210 | PE | 74 |

$\Delta H$ for $AF_{x(g)} \rightarrow AF_{x-1(g)} + F^-(g)$

The values reported herein are given only to the nearest kcal/mole regardless of the claimed precision of the literature value.

The fluoride ion affinity is the most difficult number to obtain experimentally. A very indirect evaluation of the heat of formation of $K^+BF_4^-$ combined with lattice energy evaluations and the known ionization potential of potassium has led A. G. Sharpe[75] to a value of -91 kcal for the enthalpy of the reaction:

$$F^-(g) + BF_{3(g)} \rightarrow BF_4^-(g)$$

Sharpe's derivation is a persuasive one and his value is probably correct to within a few kcal/mole.

Vapor pressure dissociation measurements of several complexes have been done, leading to values for free energy of dissociation ($\Delta H_{diss}$) as a function of temperature for the process $AF^+_{x-1}MF^-_{y+1} \rightarrow AF_{x(g)} + MF_{y(g)}$.

| Compound | $\Delta H_{diss}$ kcal/mole$^{-1}$ | $\Delta S$(gibbs) | -300 $\Delta S$ (kcal/mole$^{-1}$) | Ref. |
|---|---|---|---|---|
| $SF_3^+AsF_6^-$ | +31 | +65 | 20 | 76 |
| $SF_3^+BF_4^-$ | +25 | +72 | 22 | 76 |
| $ClF_2^+BF_4^-$ | +24 | +80 | 24 | 77 |
| $ClF_2^+PF_6^-$ | +16 | +68 | 20 | 33 |
| $ClF_4^+AsF_6^-$ | +25 | +82 | 25 | 38 |

The data for the $SF_3^+$ salts is very reliable, having been obtained independently in two different laboratories. The vapor pressure of the last three compounds are all in excess of one atomsphere

at ambient temperatures, (25°).

Kapustinskii's second equation[78],

$$U_K = \frac{z_1 z_2 n 287.2}{r_c + r_a}\left(1 - \frac{.345}{r_c + r_a}\right)$$

[in which $U_K$ is the lattice energy (kcal/mole$^{-1}$) $z_1$ and $z_2$ the formal ionic charge; n the number of ions per formula unit;and $r_c$ and $r_a$ the ionic radii (Å) for the cation and anion], has been used as a starting point for the evaluation of lattice energies. Since the compounds here considered consist of rather large ions, an evaluation of the reliability of Kapustinskii's equation as compared to experimental values for the Cs halides are shown below. The ionic radii sum are those given by Wells[79], and the experimental lattice energies from Born Haber cycle evaluations by Cubicciotti[80].

| Salt | $U_{exp}$(kcal mole$^{-1}$) | $r_c + r_a$(Å) | $U_K$ (kcal mole$^{-1}$) | $U-U_K$ (kcal mole$^{-1}$) |
|---|---|---|---|---|
| CsF | 172 | 3.05 | 167 | 5 |
| CsCl | 154 | 3.50 | 148 | 6 |
| CsBr | 149 | 3.64 | 142 | 7 |
| CsI | 141 | 3.85 | 135 | 6 |

It was noted that $U_K$ was consistently less than $U_{exp}$. For the alkalai halides with smaller radii sums the agreement is much better, and it would appear that either the repulsive term in Kapustinskii's equation is over emphasized, or that van der Waals' forces are not properly being accounted for, probably the latter. In any case, since the radii sums dealt with in this discussion

are usually even larger (vide infra) than those given above, an arbitrary correction of 6% of $U_K$ has been added to $U_K$ for use in this work. It is notable that a detailed evaluation of the lattice energy of $K^+BF_4^-$ (cubic modification, K-B distance = 3.63 Å) by Altschuller[81] yielded the same value for the lattice energy, i.e., 152 Kcal/mole, as this modified Kapustinskii's equation.

The next problem is to define ionic radii for complex ions such as we have under consideration. Since the cations are certainly not spherically symmetrical, any radii must be considered merely a theoretical construct. However, the volume of one formula unit of a perfluoro complex salt may be reliably estimated in most cases by summing the number of fluorines and multiplying by 18 $Å^3$.[2] The reliability of this method is, of course, dependent on the heavy atoms bearing enough positive charge to shrink them to an insignificant volume, i.e., small enough to fit into the interstices of a close packed array of fluorine atoms. The crystallographic volumes per formula unit are compared to this calculated value for a number of materials below.

| Compound | $V_{exp}(Å^3)$ (Crystallographic) | $V_{calc.}(Å^3)$ (no. of F x 18 $Å^3$) | Ref. |
|---|---|---|---|
| $ClF_2^+SbF_6^-$ | 157 | 144 | 36 |
| $SF_3^+AsF_6^-$ | 162 | 162 | this work |
| $XeF_5^+PtF_6^-$ | 198 | 196 | 28 |
| $BrF_4^+Sb_2F_{11}^-$ | 271 | 270 | 42 |
| $IF_4^+SbF_6^-$ | 178 | 180 | this work |
| $IF_6^+AsF_6^-$ | 221 | 216 | 46 |

The volume of the $XeF^+$ salts is not given correctly by this method. Apparently the xenon atom contributes significantly to the molecular volume. However, if the volume of the $RuF_6^-$ anion is estimated as $6 \times 18$ $\mathring{A}^3$ = 108 $\mathring{A}^3$, then the volume of the $XeF^+$ cation will be 52 $\mathring{A}^3$. Since in reality the anionic fluorides of the above materials might be expected to be somewhat larger than cationic fluorines this must be considered as an upper limit on the $XeF^+$ cation volume.

Kapustinskii's equation[78] is based on a 6:6 packing in a NaCl type lattice array of ions. The effective volume of equal spheres in such an array is that of a cube with an edge twice that of the sphere's radius. This suggests using the cube root of the volume of an ion divided by 2 as a radius for use in Kapustinskii's equation, with the volume estimated as the number of fluorine atoms in the complex ion times 18 $\mathring{A}^3$. It should be mentioned that evaluation of the lattice energies have been carried out using a fluorine volume of 15 $\mathring{A}^3$ and 21 $\mathring{A}^3$ in the cation and anion respectively with little alteration in the resulting lattice energies. Following the procedure outlined, ionic radii and volumes for species $AF_x$, in which A is the central atom of a cation or anion, may be evaluated.

| | $AF_2$ | $AF_3$ | $AF_4$ | $AF_5$ | $AF_6$ | $XeF^+$ |
|---|---|---|---|---|---|---|
| v | 36 | 54 | 72 | 90 | 108 | 52 |
| r | 1.65 | 1.89 | 2.08 | 2.24 | 2.38 | 1.87 |

Summing ionic radii for the most common anion groupings, $MF_4^-$

$MF_6^-$, ($BF_4^-$, $AsF_6^-$, $PF_6^-$, $SbF_6^-$, etc.) gives the radii sums below.

| | $AF_2^+$ | $AF_3^+$ | $AF_4^+$ | $AF_5^+$ | $AF_6^+$ | $XeF^+$ |
|---|---|---|---|---|---|---|
| $MF_4^-$ | 3.73 | 3.97 | 4.16 | 4.32 | 4.46 | 3.95 |
| $MF_6^-$ | 4.03 | 4.27 | 4.46 | 4.62 | 4.76 | 4.25 |

Now the lattice energies themselves may be evaluated using the modified form of Kapustinskiis' second equation.

| | $AF_2^+$ | $AF_3^+$ | $AF_4^+$ | $AF_5^+$ | $AF_6^+$ | $XeF^+$ |
|---|---|---|---|---|---|---|
| $MF_4^-$ | 148 | 138 | 134 | 130 | 125 | 140 |
| $MF_6^-$ | 137 | 130 | 125 | 122 | 119 | 132 |

We are now in a position to evaluate the unknown quantities in some of the thermodynamic cycles. Since our most reliable heats of formation are for the $SF_3^+BF_4^-$ and $AsF_6^-$ salts the first unknown we will evaluate is the heat of dissociation $\Delta H(SF_{4(g)} \rightarrow SF_3^+(g) + F^-(g))$

| | $\Delta H(kcal/mole^{-1})$ |
|---|---|
| $SF_{4(g)} + BF_{4(g)} \rightarrow SF_3^+BF_4^-(c)$ | - 25 |
| $SF_3^+BF_4^-(c) \rightarrow SF_3^+(g) + BF_4^-(g)$ | + 138 |
| $BF_4^-(g) \rightarrow BF_3^+(g) + F^-(g)$ | + 91 |
| $SF_{4(g)} \rightarrow SF_2^+(g) + F^-(g)$ | + 204 |

Hence $H(SF_4(g) \rightarrow SF_3^+(g) + F^-(g)) = 204$ Kcal $mole^{-1} = IF(SF_4)$.

Next we determine the fluoride ion affinity of $AsF_5[A_F(AsF_5)]$.

| | $\Delta H(kcal/mole^{-1})$ |
|---|---|
| $AsF_{5(g)} + SF_{4(g)} \rightarrow SF_3^+AsF_6^-(c)$ | - 31 |
| $SF_3^+(g) + F^-(g) \rightarrow SF_{4(g)}$ | - 204 |
| $SF_3^+AsF_6^-(c) \rightarrow SF_3^+(g) + AsF_6^-(g)$ | + 130 |
| $AsF_{5(g)} + F^-(g) \rightarrow AsF_{6(g)}$ | - 105 |

$A_F(AsF_5) = -105$ kcal mole$^{-1}$

Next we evaluate $A_F(PF_5)$ from the heat of dissociation of $ClF_2^+PF_6^-$.

| | $\Delta H(kcal/mole^{-1})$ |
|---|---|
| $ClF_{3(g)} + PF_{5(g)} \rightarrow ClF_2^+PF_6^-(c)$ | - 16 |
| $ClF_2^+PF_6^-(c) \rightarrow ClF_2^+(g) + PF_6^-(g)$ | + 137 |
| $ClF_2^-(g) + F^-(g) \rightarrow ClF_{3(g)}$ | - 215 |
| $PF_{5(g)} + F^-(g) \rightarrow PF_6^-(g)$ | - 94 |

$A_F(PF_5) = -94$ kcal mole$^{-1}$

The stability to dissociation of $IF_4^+SbF_6^-$ at ambient temperatures strongly suggests a $\Delta H_{diss} \geq 20$ kcal mole$^{-1}$ for this material. This figure combined with $I_F(IF_5) = 234$ kcal mole$^{-1}$ and U = 125 kcal mole$^{-1}$ yields an upper limit on $A_F(SbF_5)$ of -129 kcal mole$^{-1}$.

$$A_F(SbF_5) \geq -129 \text{ kcal mole}^{-1} \quad .$$

Condideration of a similar energy cycle for $ClF_4^+AsF_6^-$ yielded $I_F(ClF_5)$.

| | $\Delta H(\text{kcal mole}^{-1})$ |
|---|---|
| $ClF_{5(g)} + AsF_{5(g)} \rightarrow ClF_4^+AsF_6^-(c)$ | - 25 |
| $ClF_4^+AsF_6^-(c) \rightarrow ClF_4^+(g) + AsF_6^-(g)$ | + 125 |
| $AsF_6^-(g) \rightarrow AsF_{5(g)} + F^-(g)$ | + 105 |
| $ClF_{5(g)} \rightarrow ClF_4^+(g) + F^-(g)$ | + 205 |

$I_F(ClF_5) = 205$ kcal mole$^{-1}$

Comparison of $I_F$ values for the halogen fluorides obtained experimentally or from these lattice energy cycles to a cycle based on the average bond energy (A.B.E.) and first ionization potential (I.P.) of the halogen atoms is of interest.

| | | $\Delta H(\text{kcal mole}^{-1})$ | Ref. |
|---|---|---|---|
| $ClF_5 \rightarrow ClF_4 + F$ | all reactants in gas phase. | + 36 = ABE | 82 |
| $ClF_4 \rightarrow ClF_4^+ + e$ | | + 300 = IP(Cl) | 75 |
| $F + e \rightarrow F^-$ | | - 80 = A(F) | 75 |
| $ClF_5 \rightarrow ClF_4^+ + F^-$ | | + 256 | |

Similar cycles for the other halogen fluorides (same ref. for corresponding portions of the overall reaction) allow the following comparison.

| Compound | (bond energy cycle) $I_F$(kcal mole$^{-1}$) | (from lattice energy cycle[a]/exp[b]) $I_F$(kcal mole$^{-1}$) |
|---|---|---|
| $ClF_5$ | 256 | 205[a] |
| $BrF_5$ | 238 | 243[b] |
| $IF_5$ | 225 | 234[b] |
| $ClF_3$ | 260 | 215[b] |
| $BrF_3$ | 241 | 231[b] |
| $IF_7$ | 216 | 204[a] (lower limit, vide infra) |

The discrepancy between the two sets of figures is obviously greatest for the chlorine fluorides. This may be due to either of two factors. The approximation of first bond breaking to the ABE is probably not accurate. Also, the reorganization energy coincident with hybridization of the atomic orbitals will surely affect the ionization potential of the central atoms. Nevertheless, there appears to be an unusual stabilizing effect operating for the formation of the chloro-cations.

The value for $I_F(IF_7) \geq 204$ kcal mole$^{-1}$ is based on an assumption of $\Delta H \geq 0$ for

$$IF_7 + XeF_5^+AsF_6^- \rightarrow IF_6^+AsF_6^- + XeF_6$$

which Sladky[26] has shown does not proceed at normal temperatures

and pressures. The change in entropy must be very small here and has been assumed to be negligible.

We now have $I_F$ values for $XeF_x$ (x = 2,4,6), $ClF_x$ (x = 3,5), $BrF_x$ (x = 3,5), $IF_x$ (x = 5,7), and $SF_4$. These combined with the lattice energies and $A_F$ values for $SbF_5$, $AsF_5$, $PF_5$, and $BF_3$ allow the calculation of $\Delta H_{diss}$ of forty compounds. These are listed in Table XI along with an indication of whether or not the corresponding compound has been isolated. The reversal in the listing between $\Delta H_{diss}$ = -14 and -17 kcal/mole emphasizes the region of borderline stability. The marginal stability of $BrF_2^+$ $AsF_6^-$ may indicate some fluorine bridging, but in view of the spectral evidence supporting a distorted $AsF_6^-$ group one could also postulate an enhancement of lattice energy due to that distortion sufficient to place that material in the range of accessible compounds. Irregardless, if a $\Delta H_{diss}$ of 15 kcal $mole^{-1}$ is assigned as the minimum value capable of over-riding unfavorable entropy effects the cycle appears to be reliable to ± 4 kcal $mole^{-1}$. Woolf[83] has recently derived the $\Delta H_{diss}$ for $BrF_2^+SbF_6^-$ from calorimetric data on the heat of solution of $SbF_5$ in $BrF_3$ and his value, 44.5 kcal $mole^{-1}$, is in remarkable agreement with that calculated here. In view of the rather extensive and intensive research in this area it appears unlikely that any of the "compounds" in the unknown list will be isolated in the future.

An ordering of several of the transition metal pentafluorides relative to their fluoride ion acceptor capabilities can now be made. The $BrF_2^+$ salts of the transition metal pentafluorides show much greater thermal stability than $BrF_2^+AsF_6^-$. We may,

therefore, safely assume a $H_{diss} \geq 20$ kcal mole$^{-1}$ for these materials. Substituting this value in our cycle gives a minimum $A_F$ of -114 kcal/mole for $MF_5$ (M = Pt, Ru, Nb, Ta). Again, $XeF^+OsF_6^-$ and $XeF^+IrF_6^-$ are more stable than $XeF^+AsF_6^-$ which spontaneously decomposes to $Xe_2F_3^+AsF_6^-$ at ambient temperatures[2]. Since $IrF_5$ and $OsF_5$ have not been shown to form $BrF_3$ adducts we may place $A_F(IrF_5, OsF_5)$ between -114 and -105 kcal mole$^{-1}$. We now have the following sequence of fluoride ion affinities for the major acceptors.

| $F^-$ Acceptor | $A_F$(kcal mole$^{-1}$) |
|---|---|
| $SbF_5$ | - 129 |
| $TaF_5$ | - 114 |
| $NbF_5$ | - 114 |
| $PtF_5$ | - 114 |
| $RuF_5$ | - 114 |
| $IrF_5$, $OsF_5$ | $-105 \geq A_F \geq -114$ |
| $AsF_5$ | - 105 |
| $PF_5$ | - 94 |
| $BF_3$ | - 91 |

In conclusion, the enthalpies of dissociation derived from the cycle used here are highly consistent with experimental findings to date for the range of compounds under discussion The cycle provides a quantitative basis for the evaluation of the relative

fruitfulness of attempts to prepare new compounds. For example, all of the known hexafluoroarsenate V salts should have stable transition metal analogues for those metals whose pentafluorides have values of $A_F$ more negative than that of $AsF_5$. A glance at Table V(Section VIII) shows that this would represent a large number of new compounds, particularly in the niobium and tantalum cases. Some obvious gaps in our knowledge are demonstrated; e.g., what is the value of $A_F$ for $AuF_3$ and $BiF_5$? The usefulness to the synthetic chemist of accurate experimental $I_F$ values has been shown, and hopefully will prompt further investigations in that line. In summary, the model presented here correlates the existing data and marks some directions for future investigation.

## V. MISCELLANEOUS EXPERIMENTS

### A. A New Synthesis of $IOF_5$.

N. Bartlett and Levchuck[84] have reported the preparation of $IOF_5$ by the interaction of $IF_7$ with iodine pentoxide, glass, or water. Yields were generally unreliable and the oxyfluoride tended to be contaminated with $IF_7$, $SiF_4$ or other impurities. The results of their experiments did show, however, that $IOF_5$ may be prepared in the presence of water.

The existence of $IF_6^+AsF_6^-$ has been known since 1958[45]. The hexafluoroarsenate anion has been shown to have a peculiar stability to hydrolysis by W. L. Lockhart and his coworkers[85]. The combination of these two hydrolytic stabilities suggested a possible synthesis of $IOF_5$ by hydrolysis of the $IF_6^+AsF_6^-$ salt.

Materials.- $IF_7$ was prepared by fluorination of $HgI_2$. $AsF_5$ (Ozark Mahoning, Tulsa, Okla.) was combined with $IF_7$ to

yield $IF_6^+AsF_6^-$. NaF was reagent grade material from Baker Chemicals, Pillipsburg, N.J. A monel vacuum system was employed for transfer of gaseous materials. Reactions were carried out in monel vessels fitted with teflon gasketed removable lids. U.V. spectra were obtained in quartz cells. I.R. spectra were obtained in monel cells fitted with AgCl windows. Melting points were determined by the inability of the material contained in a quartz container to support a copper wire and were checked with a thermocouple. A Vacuum Atmospheres Corp. Drilab ($N_2$ atmosphere) was employed for the handling of $IF_6^+AsF_6^-$.

Procedure.- A weighed portion (.02 moles) of $IF_6^+AsF_6^-$ was transferred to a monel vessel ( ~ 200 ml) in the Drilab. An excess of NaF was added. The can was sealed and evacuated. It was then fitted with a tube and another valve containing a measured amount of distilled water. The can was cooled to liquid nitrogen temperature and the valve to the water supply opened and closed when the transfer of the water was complete (practically immediately). The water tube and valve were then removed. The can was re-attached to the vacuum system, cooled in a solid $CO_2$-acetone slush, and evacuated. Upon warming the gases remaining in the can were characterized. The resulting product was nearly pure $IOF_5$ containing traces of $SiF_4$ of unknown origin. Purity was confirmed by infrared and ultraviolet spectra and by the melting point, 5° ± 1°. Yields were approximately 40% based on initial $IF_7$ used in the preparation of the $IF_6^+AsF_6^-$.

Discussion.- The utilization of the stability of the $AsF_6^-$ ion to hydrolysis in the preparation of $IOF_5$ from $IF_6^+AsF_6^-$ has

been confirmed. The large number of salts formed by the hexafluoroarsenate species suggests that this may be a rewarding approach to other syntheses. The method here employed was found to be considerably improved by the prior cooling of the reaction vessel to -196°. This may be due to the physical state of the water (probably a frozen spray under these conditions), or the more adequate removal of heat from the reaction site inhibiting formation of lower oxyfluorides of iodine. The sodium fluoride is necessary to complex with HF formed in the reaction. The solid products remaining after the reaction were not characterized.

B. The Interaction of $NO_2F$ with $IrF_6$.

The observation by Jha and Rao[61,86] of oxidative fluorination of ONF to $ONF_3$ by $IrF_6$ suggested the possibility of a similar reaction between $NO_2F$ and $IrF_6$:

$$3NO_2F + 2IrF_6 \rightarrow 2(NO_2)^+(IrF_6)^- + NO(F)_2(OF)$$

$IrF_6$ did interact with $NO_2F$ but the hoped for oxyfluoride was not produced. Rather a 1:1 interaction with salt formation and fluorine elimination resulted:

$$NO_2F + IrF_6 \rightarrow (NO_2)^+(IrF_6)^- + 1/2\ F_2$$

the infrared spectra of the residual gases showed only traces of the starting materials and were noncondensible in a liquid nitrogen cold bath. The tensimetry of the reactions is shown in Table XII.

The solid product, $(NO_2)^+(IrF_6)^-$ is a white crystalline powder. The infrared spectra of the powder pressed between AgCl plates

shows the characteristic[87] absorbtion of $NO_2^+$ at 2360 $cm^{-1}$. The Raman spectra of the powder showed $\nu_1$ of $NO_2^+$ at 1402 $cm^{-1}$ and $\nu_1$, $\nu_2$, and $\nu_5$ of $IrF_6^-$ at 671, 566, and 253 $cm^{-1}$, respectively. Traces of $(NO)^+(IrF_6)^-$ were seen in the Raman spectra with the relative intensity of $NO^+$ to $NO_2^+$ being visually estimated as 3.5 to 55. Debye Scherrer X-ray powder photographs were obtained and indexed on the basis of an orthorhombic lattice (see Table XIII) with $\underline{a}$ = 7.20, $\underline{b}$ = 6.92 and $\underline{c}$ = 5.55 Å, and $\underline{V}$ = 276.52 $Å^3$. This volume is compatible with two formula units per unit cell if the cell volume is assumed to be effectively filled by the oxygen and fluorine atoms and their volume is assumed to be ~17.25 $Å^3$ each. The observation of intensities only for reflections having $h + k = 2n$ indicates a c-centering in the cell. This prompts a comparison of the associated primitive monoclinic cell to the pseudo-cubic cell of $(NO)^+(IrF_6)^-$:

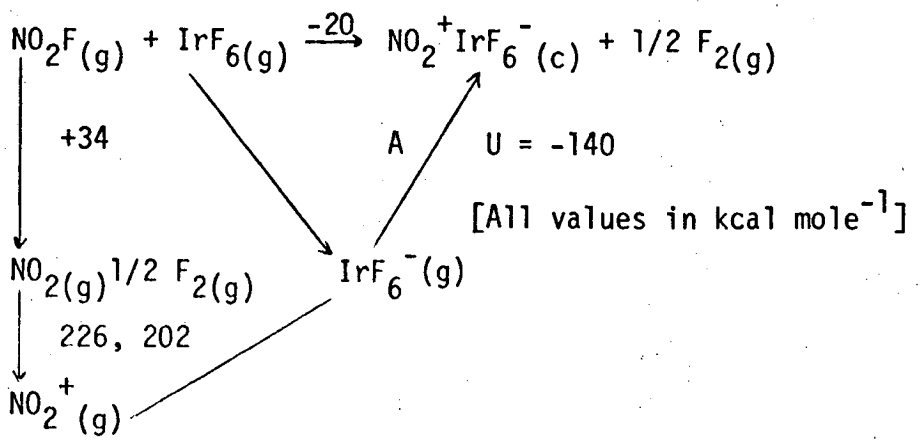
| $(NO_2)^+(IrF_6)^-$ | $(NO)^+(IrF_6)^-$ [88] |
|---|---|
| $\underline{a} = \underline{b} = 4.99$ Å | $\underline{a} = 5.057$ Å |
| $\underline{c} = 5.55$ Å | |
| $\underline{\alpha} = 92.3°$ | |
| $\underline{V} = 138$ $Å^3$ | $\underline{V} = 129$ $Å^3$ |

The molecular volume of $(NO_2)^+(IrF_6)^-$ lies midway between those of $RbIrF_6$ (129.8 $Å^3$) and $CsIrF_6$ (143.6 $Å^3$)[89,90]. Therefore, one can estimate an ionic radii for $NO_2^+$ relative to the Pauling ionic radii of Cs and Rb as

$$r^3(NO_2^+) = \frac{r^3(Rb) + r^3(Cs)}{2} = \frac{(1.48)^3 + (1.69)^3}{2}$$

$$r_{(NO_2^+)} = 1.59\ \text{Å}$$

It is interesting to note that a very similar result is obtained by (a) assigning the $IrF_6$ unit a valume of 108 $Å^3$, which is six times the average effective volume of a fluoride ion - ~ 18 $Å^3$; (b) assigning the residual volume to $(NO_2)^+$; (c) assuming a NaCl type packing so that the effective ionic radii are $V^{1/3}/2$. Using the above sequence the radii of $NO_2^+$ and $IrF_6^-$ would be 1.55 and 2.39 Å, respectively. Using the modified Kapustinskii equation previously described the resulting lattice energy is calculated as ~ 140 kcal/mole. It is probably safe to assume that a reaction that proceeds as rapidly as this one in the gas phase, and also has an unfavorable entropy change, has an enthalpy change of at least 20 kcal $mole^{-1}$. The N-F bond energy (34 kcal/mole) in $FNO_2$ is known[91]. The correct value of the first ionization potential of $NO_2$ is in some uncertainty, being set at 226 kcal/mole by two groups of workers[92,93] using photoionization techniques and at 202 kcal/mole by workers using photoelectron spectroscopy[94]. Consideration of the following cycle therefore places the lower limit of electron affinity of $IrF_6$ at either -140 or -116 kcal/mole.



C. The Preparation of $NO_2^+WOF_5^-$.

The interaction of $NO_2F$ with $WOF_4$ was investigated in an attempt to identify the reaction products obtained from the reaction between $NO_2$ and $WF_6$. The reaction between $NO_2F$ and $WOF_4$ is slow as gas-solid reactions often are, but if powdered $WOF_4$ is kept in contact with $NO_2F$ (~2 atm.) in a thoroughly dried pyrex container for several days, reaction does occur. Analysis of the product for tungsten and fluorine gave 51% tungsten and 26% fluorine. $NO_2^+WOF_5^-$ would require 54% W and 28% F. This formulation is supported by the Raman spectra which shows an absorbtion at 1405 $cm^{-1}$ characteristic of the $NO_2^+$ cation. The other bonds were assigned on the basis of a $WOF_5^-$ anion: 1037 $cm^{-1}$ ( W=O stretch), 696 $cm^{-1}$ (W-F stretch) and 326 and 316 $cm^{-1}$ (F-W-F bends). Infrared data reported[95] for $NO^+WOF_5^-$ include a W=O stretching frequency of 1005 $cm^{-1}$ and W-F stretching frequencies at 625 and 450 $cm^{-1}$. Upon prolonged storage the brown vapor of $NO_2$ gas over the sample stored in sealed pyrex tubes indicated a slow decomposition. The powder diffraction pattern is listed in Table XIV.

D. $AsF_5 + PF_5 \neq PF_4^+AsF_6^-$.

An equimolar mixture of $PF_5$ and $AsF_5$ in a monel can at a total pressure of ~ 1000 torr showed no lowering of vapor pressure. This indicates that $PF_5$ is a poorer fluoride donor than the isoelectronic molecules $SF_4$ and $ClF_3$.

# VI. APPENDICIES.

## A. Computer Programs and Some Pertinent Equations Relating to The Crystallographic Work.

The computer programs used in the course of the crystallographic work are listed and briefly described.

LESQ: An unpublished least-squares refinement program by A. Zalkin, Lawrence Berkeley Laboratories, Berkeley, California.

FORDAP: A Fourier plot program by A. Zalkin, Lawrence Berkeley Laboratories, Berkeley, California.

ORTEP: The Oak Ridge Thermal Ellipsoid Plot Program by C. K. Johnson, Oak Rodge National Laboratory, Oak Ridge, Tennessee.

WILSON: A Wilson plot and E calculating program of H. S. and M. L. Maddox revised by B. G. DeBoer and A. Zalkin for local (LBL) use.

MULTAN: A program for the automatic solution of crystal structures by Peter Main and Michael M. Woolfson, Department of Physics, University of York, York, England and Gabriel Germaine, University of Louvain, Louven, Belgium.

Some features common to the data handling and structure refinements for all of the structure determinations follow:

The data were corrected for Lorentz and polarization effects. The net intensity was calculated from

$$I = C - (B_1 + B_2)(T_c/2T_b)$$

in which C is the total recorded counts in scan time $T_c$ and $B_1$

$B_2$ are background counts for time $T_b$ each. The standard deviation of I is

$$\sigma(I) = [C + (T_c/2T_b)^2(B_1 + B_2) + (qI)^2]^{1/2}$$

in which q is an arbitrary factor usually on the order of 5% used to prevent the relative error for large counts becoming unrealistically small. The standard deviation of N equivalent reflections averaged together was:

$$\sigma_{AVE} = \frac{\sum_{i=1}^{N} [\sigma_i(I)]^2}{N}^{1/2}$$

unles $\sigma_{AVE}$ is less than the scatter of the N reflections in which case the formula applied was

$$\sigma(I)_{AVE} = \sum_{i=1}^{N} \Delta_i^2 \,^{1/2}/(N-1)$$

in which $\Delta_i$ is the difference between the average of N reflections and reflection i.

The standard deviation of the structure factor by the method of finite differences was taken as

$$\sigma(F) = F_o - [F_o^2 - s\,\sigma(I)/Lp]^{1/2}$$

in which s is the scaling factor in the equation

$$F_o = \frac{sI}{Lp}^{1/2}$$

For cases in which $I \leq \sigma(I)$,

$$\sigma(F) = [s\,\sigma(I)/Lp]^{1/2}$$

in which L and p are the Lorentz and polarization corrections. The least-squares program (LESQ) used in the refinements minimizes the function $R_2^2$:

$$R_2^2 = \Sigma w(\Delta F)^2/\Sigma w F_o^2$$

in which $F_o$ and $F_c$ are observed and calculated structure factors and $\Delta F$ is their difference. The weighting factor w is $1/[\sigma(F)]^2$ except that in some cases it may be set to zero for reflections that are less than three, two, or one $\sigma$. Scattering factors for neutral atoms were used[96]. The anisotropic temperature factor has the form

$$\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}\ell^2 - 2\beta_{12}hk - 2\beta_{13}h\ell - 2\beta_{23}k\ell).$$

The $B_{ij}$ values reported are related to the $\beta$'s in the preceeding equation:

$$B_{ij} = 4\beta_{ij}/a_i^* a_j^*$$

in which $a_i^*$ is the $i^{\underline{th}}$ reciprocal cell length.



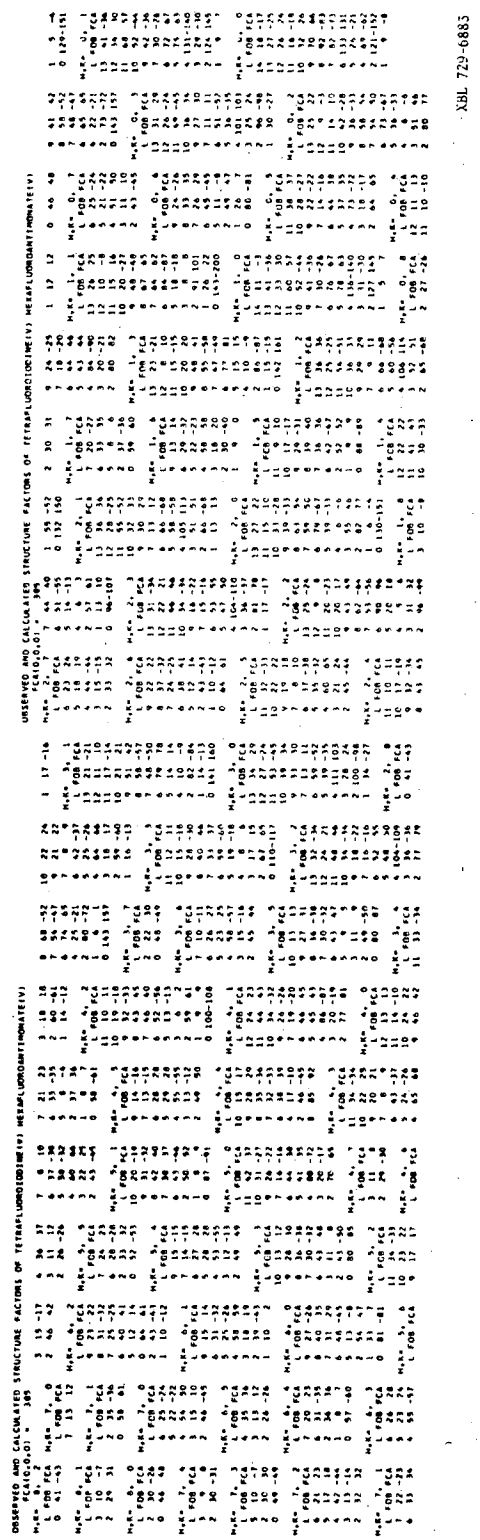
XBL-7211-7196

APPENDIX B: Observed and Calculated Structure Factors for $XeF^{+}RuF_{6}^{-}$



XBL-7211-7197

APPENDIX C: Observed and Calculated Structure Factors for $SF_3^+BF_4^-$



XBL 729-6885

APPENDIX D: Observed and Calculated Structure Factors for $IF_4^+SbF_6^-$

VII. REFERENCES.


1. The International Tables for X-ray Crystallography, Vol. 1, Kynoch Press, London, (1950).
2. W. H. Zachariason, Acta. Cryst. 2, 38 (1949).
3. L. D. Calvert and J. R. Morton, Acta Cryst. 17, 617 (1964).
4. K. O. Christe and W. Sawodny, Inorg. Chem. 6, 1983 (1967).
5a. N. Bartlett and D. H. Lohman, J. Chem. Soc., 5253 (1962).
5b. N. Bartlett, and D. H. Lohmann, J. Chem. Soc., 619 (1964).
6. As reported in reference 12, page 2183.
7. A. A. Woolf, J. Chem. Soc., 3678 (1950).
8. T. Ueki, A. Zalkin, and D. H. Templeton, Acta Crys. 19, 157 (1965).
9. H. Selig and R. D. Peacock, J. Amer. Chem. Soc. 86, 3895 (1964).
10. D. McKee, private communication.
11. V. M. McRae, R. D. Peacock, and D. R. Russell, Chem. Comm. 62 (1969).
12. F. O. Sladky, P. A. Bulliner and N. Bartlett, J. Chem. Soc. A, 2179 (1969).
13. F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer and A. Zalkin, Chem. Comm. 1048 (1968).
14. O. D. Maslov, et al., Zhur. Fiz. Khim., 41, 1832 (1967).
15. A. J. Edwards, J. H. Holloway, and R. D. Peacock, Proc. Chem. Soc. 275 (1963).
16. L. G. Cole and G. W. Elverum, Jr., J. Chem. Phys. 20, 1543 (1952).
17. R. A. Durie, Proc. Roy. Soc. A207, 388 (1951).

0 0 0 0 3 8 0 0 7 2 0



18. G. R. Somayajula, J. Chem. Phys. 33, 1541 (1960).

19. G. C. Pimentel, J. Chem. Phys. 19, 446 (1951).

20. R. E. Rundle, J. Amer. Chem. Soc. 85, 112 (1963).

21. J. Bilham and J. W. Linnett,Nature 201, 1323 (1964).

22. C. A. Coulson, J. Chem. Soc., 1442 (1964).

23. L. Pauling, The Nature of the Chemical Bond, 3rd Edition, Cornell University Press, Ithica, New York, 1960, p. 255.

24. B. Cohen and R. D.Peacock, J. Inorg. Nucl. Chem 28, 3056 (1966).

25. D. Martin, C. R. Acad. Sci. Paris, C, 1145 (1969).

26. N. Bartlett and F. Sladky, J. Amer. Chem. Soc. 90, 5316 (1968).

27. H. Selig, Science, 144, 537 (1964).

28. N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, Chem. Comm. 55, (1966).

29. G. Gard and G. H. Cady, Inorg. Chem. 3, 1745 (1964).

30. Work of F. Hollander, D. Templeton, M. Wechsburg and N. Bartlett reported in The Chemistry of Krypton, Xenon, and Radon, N. Bartlett and F. Sladky, publication of Lawrence Berkeley Laboratory, Berkeley, California, UCRL-19658.

31. N. Bartlett, B. Morrell, and A. Zalkin, private communication, not yet published.

32. A. E. Pavlath, Dissertation, Hungarian Academy of Science, Budapest, Hungary 1954.

33. K. O. Christe and A. E. Pavlath, Zeitschrift fur anorg. und allge. Chemie, 335, 210 (1965).

34. R. J. Gillespie and M. J. Morton, Inorg. Chem 9,616 (1970).

35. K. O. Christe and W. Sawodny, Inorg. Chem. 6, 313 (1967).

36. A. J. Edwards and R. J. L. Sill, J. Chem. Soc. A, 2697 (1970).

37. I. Q. Roberto and G. Mamantov, Inorganica Chimica Acta, Sept. 317 (1968).

38. K. O. Christe and D. Pilipovich, Inorg. Chem. 8, 391 (1969).

39. A. A. Woolf and H. J. Emeleus, J. Chem. Soc., 2865 (1949).

40. A. J. Edwards and G. R. Jones, Chem. Comm., 1304 (1967).

41. K. O. Christe and C. J. Schack, Inorg. Chem. 9, 2296 (1970).

42. M. P. Lind and K. O. Christe, Inorg. Chem. 11, 608 (1972).

43. I. C. Bowater, R. D. Brown, and F. K. Burden, J. Mol. Spec. 28, 454 (1968).

44. J. Shamir and I. Yaroslavsky, Israel Journal of Chem. 7, 495 (1969).

45. F. Seel and O. Detmer, Angew. Chem 70, 163 (1958).

46. S. P. Beaton, Ph.D. Thesis, University of British Columbia, Vancouver, B.C., Canada 1963.

47. J. H. Burns, Acta Cryst. 15, 1093 (1962).

48. V. H. Diebler and J. A. Walker, J. Chem. Phys. 44, 4405 (1966).

49. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry John Wiley and Sons, New York, 1962.

50. G. R. Jones, R. D. Burbank and N. Bartlett, Inorg. Chem. 9, 2264 (1970).

51. N. Bartlett and P. L. Robinson, Chem. and Ind. (London) 1351 (1956).

52. N. Bartlett and P. L. Robinson, J. Chem. Soc., 3417 (1961).

53. P. L. Robinson and G. J. Westland, J. Chem. Soc., 4481(1956).

0 0 0 0 3 8 0 2 1



54. M. McAzeem, M. Brownstein, and R. J. Gillespie, Can. J. Chem. 47, 4159 (1969).

55. A. J. Edwards and G. R. Jones, Chem. Comm., 346 (1968).

56. J. A. Evans and D. A. Long, J. Chem. Soc. A, 1688 (1968).

57. F. A. Cotton and J. W. George, J. Inorg. Nucl. Chem. 7, 397 (1958); 12, 386 (1960).

58. A. L. Oppeguard, W. L. Smith, E. L. Meutterties, and V. A. Englehard, J. Amer. Chem. Soc. 82, 3885 (1960).

59a. A. J. Edwards and G. R. Jones, J. Chem. Soc. A, 1491 (1970).

59b. ibid, 1891 (1970).

60. F. B. Clippard and L. S. Bartell, Inorg. Chem. 9, 205 (1970).

61. N. K. Jha, Ph.D. Thesis, University of British Columbia, Vancouver, B.C., Canada (1964).

62. R. Surfass, Senior Thesis, Princeton University, Princeton, New Jersey, 1967.

63. C. H. MacGillavry, and C. L. Panthaleon Van Eck, Rec. des Trans. Chim. des Pays-Bas, 62, 729 (1943).

64. G. Brunton, Acta Cryst., 1324, 1703 (1968).

65. G. Brunton, Acta Cryst B25, 2161 (1969).

66. A. P. Caron and J. L. Ragle, acta Cryst. B27, 1102 (1971).

67. S. Reichmann and F. Schreiner, J. Chem. Phys. 51, 2355 (1969).

68. W. M. Tolles, and W. D. Gwinn, J. Chem. Phys. 36, 1119 (1962).

69. R. E. Rundle, Record of Chemical Progress 23, 195 (1962).

70. I. W. Levin, J. Chem. Phys. 55, 5393 (1971).

71. D. R. Herschback and V. W. Laurie, J. Chem Phys. 35, 458 (1961).

72. J. L. Franklin, et al., Ionization Potentials, Appearance

Potentials, and Heats of Formation of Gaseous Positive Ions, National Bureau of Standards (NSRDS-NBS-26).

73. A. P. Irsa, and L. Friedman, J. Inorg. Nucl. Chem. 6, 77 (1968).

74. J. Berkowitz, W. A. Chupka, P. M. Guyon, J. H. Holloway, and R. Sporr, J. Phys. Chem., 75, 1461 (1971).

75. A. G. Sharpe,"The Physical Inorganic Chemistry of the Halogens", Chapter in Halogen Chemistry, Vol. 1, Academic Press, London, (1967) p. 1.

76. N. Bartlett and P. L. Robinson, J. Chem. Soc., 3417 (1961).

77. H. Selig and J. Shamir, Inorg. Chem. 3, 294 (1964).

78. A. F. Kapustinskii, Q. Reviews. Chem. Soc. 10, 283 (1956).

79. A. F. Wells, Structural Inorganic Chemistry, Oxford University Press,

80. D. Cubicciotti, J. Chem. Phys. 34, 2189 (1961).

81. A. P. Altshuller, J. Amer. Chem. Soc. 77, 6187 (1955).

82. L. Stein, "Physical and Chemical Properties of Halogen Fluorides", Halogen Chemistry, Vol. 1 (1967) p. 133.

83. A. A. Woolf and G. W. Richards, J. Fluorine Chem. 1, 129 (1971).

84. N. Bartlett and L. E. Levchuck, Proc. Chem. Soc. 342, (1963).

85. W. L. Lockhart, M. M. Jones and D. O. Johnston, J. Inorg. Nucl. Chem 31, 407 (1969).

86. R. Rao, Ph.D. Thesis, University of British Columbia, 1965.

87. R. A. Marcus, and J. M. Fresca, J. Chem. Phys. 27, 546 (1957).

88. N. Bartlett, S. P. Beaton, and N. K. Jha, Chem. Comm. 168, (1966).

89. R. D. W. Kemmitt, D. R. Russell and D. W. A. Sharp, J. Chem. Soc. 4408 (1963).

90. M. A. Hepworth, and G. J. Westland, J. Inorg. and Nucl. Chem. 2, 79 (1956).

91. D. L. Bernitt, R. H. Miller, and J. C. Hisatsune, Spectrochim. Acta 23A, 237 (1967).

92. D. C. Frost, D. Mak, and C. A. McDowell, Can. J. Chem. 40, 1064 (1962).

93. T. Nakayama, M. Kitamura, and K. Watanabe, J. Chem. Phys. 30, 1180 (1959).

94. P. Natalis and J. E. Collin, Chem. Phys. Letts. 2, 79 (1968).

95. O. Glemser, J. Wegener, and R. Mews, Chem. Bev. 100, 2474, (1967).

96. D. T. Cromer and B. Mann, Acta Cryst. A24, 321 (1968).

97. V. Gutmann and H. J. Emeleus, J. Chem. Soc. 1045 (1950).

98. M. A. Hepworth, R. D. Peacock, and P. L. Robinson, J. Chem. Soc. 1197 (1954).

99. M. Schmeisser and E.Pammer, Angew. Chem. 69, 781 (1957).

100. M. A. Hepworth and P. L. Robinson, J. Inorg. and Nucl. Chem. 4, 24 (1957).

101. M. S. Hepworth, P. L. Robinson, and G. Westland, Chem. Ind. (London) 1576 (1955).

102. M. Schmeisser and W. Ludovic, Z. Naturf, 206, 602 (1965).

103a. F. Seel and O. Detmar, Angew. Chem. 70, 163 (1958);

103b. F. Seel and O. Detmar, Z. anorg. allg. Chem. 301, 113 (1959).

104. P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, G. Jones, and D. F. Smith, Science, 139, 942 (1963).

105. N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones, and R. D. Burbank, Chem. Comm. 703 (1969).

106. D. R. Lide, D. E. Mann , and R. M. Fristom, J. Chem. Phys. 26, 734 (1957).

107. R. C. Ferguson, J. Amer. Chem. Soc. 76, 850 (1954).

108. H. Braune and S. Knobe, Zeitschrift fur physikalische Chemie, B21, 297 (1933).

109. R. D. Brown and G. P. Pez, Spectrochim Acta 28A, 1375 (1970).

110. W. M. Kirchoff, and E. B. Wilson, Jr., J. Amer. Chem. Soc.

111. K. H. Hedburg, J. Chem. Phys. 51, 2500 (1969).

112. W. H. Kirchoff, Dissertation, Harvard University, Cambridge, Mass. (1962).

113. Hans Siebert, Anwendung der Schwingungspektroskopie in der Anorganish Chemie, Springer Verlag, Berlin (1966).

114. M. Radhakrishman, J. Mol. Spec. 10, 111 (1963).

115. K. Ramaswamy, K. Sakhiandan, and F. F. Cleveland, J. Mol. Spec. 9, 107 (1962).

116. I. W. Levin, J. Chem. Phys. 55, 5393 (1971).

117. A. J. Edwards and M. A. Mounty, J. Chem. Soc. A, 703 (1969).

118. R. B. Gillespie, R. A. Sparks, and K. N. Trueblood, Acta Crystalographica 12, 867 (195 ).

119. D. R. Johnson and F. X. Powell, Science 164, 950 (1969).

120. S. H. Mastin and R. R. Ryan, Inorg. Chem. 10, 1757 (1971).

121. A. J. Edwards and F. I. Heiwaidy, J. Chem. Soc. A, 2977 (1968).

122. R. Mews and N. Bartlett, to be published in Inorg. Chem., February 1963.

123. I. Groubeau, and W. Bues, Z. Anorg. u algm. Chem. 268, 221 (1952).

VIII. TABLES

TABLE I: Final Positional and Thermal Parameters for $XeF_5^+RuF_6^-$.

TABLE II: Sulfur and Arsenic Positional Parameters for $SF_3^+AsF_6^-$.

TABLE III: Final Positional and Thermal Parameters of $SF_3^+BF_4^-$.

TABLE IV: Final Positional and Thermal Parameters of $IF_4^+SbF_6^-$.

TABLE V: Known Fluoride Donor-Acceptor Complexes.

TABLE VI: Bonding in Some $XeF_2$ Derivatives.

TABLE VII: Interatomic Distances (Å) and Angles (Deg.) for $XeF^+RuF_6^-$.

TABLE VIII: Interatomic Distances (Å)and Angles (Deg.) $IF_4^+SbF_6^-$.

TABLE IX: Interatomic Distances (Å)and Angles (Deg.) $SF_3^+BF_4^-$.

TABLE X: A Comparison of $SF_3^+$ and Some Other $MF_3$ Species.

TABLE XI: Calculated $\Delta H_{diss}$ for Some $F^-$ Donor-Acceptor Complexes.

TABLE XII: Tensimetry of $IrF_6 + NO_2F$.

TABLE XIII: X-Ray Powder Data for $NO_2^+IrF_6^-$.

TABLE XIV: X-Ray Powder Data for $NO_2^+WOF_5^-$.

TABLE I

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $XeRuF_7$

| Atom | x | y | z | $B_{11}$[a] | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{23}$ | $B_{13}$ | rmsd[c] |
|---|---|---|---|---|---|---|---|---|---|---|
| Ru | .2493(2)[b] | .0358(1) | .7785(2) | 2.90(5) | 3.39(6) | 6.29(7) | .26(4) | 1.13(4) | .37(5) | .2303 |
| Xe | .2432(1) | .2160(1) | .3294(1) | 3.14(4) | 4.73(6) | 4.75(4) | .26(4) | .77(3) | .36(4) | .2308 |
| $F_1$ | .1952(32) | .3329(25) | .1503(28) | 14.97(1.28) | 15.11(1.73) | 11.31(1.16) | 8.58(1.31) | 5.93(1.04) | 8.11(1.23) | .4173 |
| $F_2$ | .3118(22) | .0787(22) | .5232(22) | 10.08(1.02) | 10.29(1.13) | 8.19(70) | 4.26(84) | 4.19(69) | 3.67(73) | .3466 |
| $F_3$ | .1905(21) | -.0049(24) | .0059(24) | 8.89(1.02) | 12.93(1.26) | 8.85(79) | - .93(94) | 3.09(73) | 1.94(88) | .3595 |
| $F_4$ | .4175(19) | -.0683(14) | .7697(26) | 6.81(80) | 7.52(80) | 13.52(1.03) | 4.97(68) | 1.68(71) | 2.37(75) | .3427 |
| $F_5$ | .0855(20) | .1457(14) | .7677(31) | 7.14(46) | 7.01(84) | 16.51(1.33) | 4.31(69) | 3.55(84) | 1.55(86) | .3593 |
| $F_6$ | .1025(21) | -.0768(17) | .6919(30) | 6.73(82) | 10.44(1.17) | 16.35(1.38) | -4.34(77) | - .92(83) | -5.59(1.12) | .3764 |
| $F_7$ | .3910(16) | .1529(15) | .8676(28) | 5.00(61) | 8.84(1.04) | 14.75(1.19) | -3.25(63) | -1.29(65) | -3.57(94) | .3477 |

[a] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}\underline{h}^2 - \beta_{22}\underline{k}^2 - \beta_{33}\underline{\ell}^2 - 2\beta_{12}\underline{h}\underline{j} - 2\beta_{13}\underline{h}\underline{\ell} - 2\beta_{23}\underline{k}\underline{\ell})$. The $B_{ij}$ in the table = $4\beta_{ij}/\underline{a}_i^*\underline{a}_j^*$, where $\underline{a}_i^*$ and $\underline{a}_j^*$ are the $i^{th}$ and $j^{th}$ reciprocal cell lengths.

[b] Number in parentheses is the estimated standard deviation in the least significant digit.

[c] root-mean square displacement.

TABLE II

Sulfur and Arsenic Positional Parameters

For $[SF_3]^+[AsF_6]^-$ ($\underline{Cm}\underline{C}2_1$) - No. 36)

| Atom | Number | x | y | z |
|---|---|---|---|---|
| As1 | 4 | 0 | -.0177(7) | .0002(3) |
| As2 | 8 | .1632(2) | .4922(7) | .4909* |
| S1 | 4 | 0 | .4091(20) | .3138(15) |
| S2 | 8 | .3346(3) | .4031(10) | .1773(8) |

* fixed value.

TABLE III

Final Positional and Thermal Parameters of $[SF_3]^+[BF_4]^-$

| Atom | x | y | z | $B_{xx}(\AA^2)$ | $B_{yy}(\AA^2)$ | $B_{zz}(\AA^2)$ | $B_{xy}(\AA^2)$ | $B_{xz}(\AA^2)$ | $B_{yz}(\AA^2)$ | rmds[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| S | .28168(8) | 1/4 | .11259(10) | 2.40(3) | 2.80(3) | 2.75(3) | | .44(3) | | .1833 |
| B | .48346(40) | 3/4 | .17658(44) | 2.43(12) | 2.74(13) | 3.09(15) | | .33(11) | | .1867 |
| $F_1$ | .19529(17) | .05453(31) | .05347(21) | 4.35(7) | 4.28(7) | 4.84(8) | -1.43(6) | .46(6) | -0.88(6) | .2385 |
| $F_2$ | .22481(26) | 1/4 | .26822(26) | 4.06(10) | 4.13(10) | 3.17(9) | | 1.31(8) | | .2190 |
| $F_3$ | .628180(23) | 3/4 | .15984(28) | 2.60(8) | 4.53(11) | 4.09(10) | | .35(7) | | .2176 |
| $F_4$ | .42490(30) | 3/4 | .03457(33) | 4.31(12) | 7.81(18) | 4.39(13) | | -0.97(10) | | .2640 |
| $F_5$ | .44087(19) | .55238(33) | .25011(21) | 4.69(8) | 3.78(8) | 5.79(10) | -0.49(7) | .81(7) | 1.16(7) | .2454 |

a) Average root-mean-square displacement along the principle axes of the thermal ellipsoids ($\AA$)

TABLE IV

Final Positional and Thermal Parameters of $IF_4^+SbF_6^-$

| Atom | x | y | z | B |
|---|---|---|---|---|
| Sb | 1/4 | 1/4 | .3294(2) | 1.30(4) |
| I | 1/4 | 1/4 | .8611(2) | 1.76(5) |
| $F_1$ | 1/4 | 1/4 | .1474(17) | 3.99(37) |
| $F_2$ | 1/4 | 1/4 | .4988(22) | 3.68(38) |
| $F_3$ | .0791(41) | -.0208(38) | .3303(18) | 2.18(35) |
| $F_4$ | .0263(36) | .0692(38) | .3313(17) | 1.79(32) |
| $F_5$ | .2545(29) | .0016(28) | .9054(16) | 1.86(25) |
| $F_6$ | .2434(53) | -.0453(1) | .8414(20) | 3.55(49) |

Equiv. Positions: x,y,z; 1/2-x,1/2-y,z; 1/2-y,x,z; y,1/2-x,z; -x,-y,-z; 1/2+x,1/2+y,-z; 1/2+y,-x,-z; -y, 1/2+x,-z.

TABLE V Continued

Known Fluoride Donor Acceptor Complexes

| Fluoride Donor | Cation | Anion: (Known compounds indicated by a reference number) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $RuF_6^-$ | $Ru_2F_{11}^-$ | $OsF_6^-$ | $IrF_6^-$ | $Ir_2F_{11}^-$ | $PtF_6^-$ | $AuF_4^-$ | $BF_4^-$ |
| $KrF_2$ | $KrF^+$ | | | | | | | | |
| $XeF_2$ | $XeF^+$ | 12 | 12 | 12 | 12 | 12 | 12 | | |
| $XeF_2$ | $Xe_2F_3^+$ | 12 | | 12 | 12 | | 12 | | |
| $XeF_4$ | $XeF_3^+$ | | | | | | | | |
| $XeF_6$ | $XeF_5^+$ | | | | 26 | | 28 | | 27 |
| $ClF_3$ | $ClF_2^+$ | | | | | | 5 | | 77 |
| $ClF_5$ | $ClF_4^+$ | | | | | | 37 | | |
| $BrF_3$ | $BrF_2^+$ | 98 | | | | | | | |
| $BrF_5$ | $BrF_4^+$ | 100(?) | | | | | | | |
| $IF_3$ | $IF_2^+$ | | | | | | | | |
| $IF_5$ | $IF_4^+$ | | | | | | | | |
| $IF_7$ | $IF_6^+$ | this work | | | this work | | this work | | |
| $SF_4$ | $SF_3^+$ | 52 | | 53 | 53 | | | | 52 |
| $SeF_4$ | $SeF_3^+$ | | | 101 | 101 | | | 52 | 52 |
| $TeF_4$ | $TeF_3^+$ | | | | | | | | |

TABLE V

Known Fluoride Donor Acceptor Complexes

| Fluoride Donor | Cation | Anion: (Known compounds indicated by a reference number) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $BiF_6^-$ | $SbF_6^-$ | $Sb_2F_{11}^-$ | $TaF_6^-$ | $Ta_2F_{11}^-$ | $NbF_6^-$ | $AsF_6^-$ | $PF_6^-$ |
| $KrF_2$ | $KrF^+$ | | | 9 | | | | | |
| $XeF_2$ | $XeF^+$ | | 14 | 15 | | 15 | | 12 | |
| $XeF_2$ | $Xe_2F_3^+$ | | | | | | | | |
| $XeF_4$ | $XeF_3^+$ | | 24,25 | | | | | | |
| $XeF_6$ | $XeF_5^+$ | | 29 | 29 | | | | 26,27 | |
| $ClF_3$ | $ClF_2^+$ | | 32,45 | | | | | 45 | 33 |
| $ClF_5$ | $ClF_4^+$ | | 38 | | | | | 38 | |
| $BrF_3$ | $BrF_2^+$ | 97 | 39 | | 97 | | 97 | 41 | |
| $BrF_5$ | $BrF_4^+$ | | | 99 | | | | | |
| $IF_3$ | $IF_2^+$ | | 102 | | | | | 102 | |
| $IF_5$ | $IF_4^+$ | | 11 | | | | | | |
| $IF_7$ | $IF_6^+$ | | | | | | | 46,103 | |
| $SF_4$ | $SF_3^+$ | | 52 | | | | | 52 | 54 |
| $SeF_4$ | $SeF_3^+$ | | 52 | | | | 55 | 52 | |
| $TeF_4$ | $TeF_3^+$ | | 52 | | | | | | |

TABLE VI

Bonding in Some $XeF_2$ Derivatives

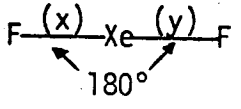
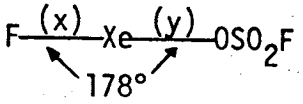
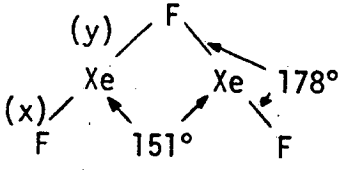
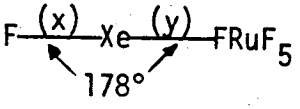
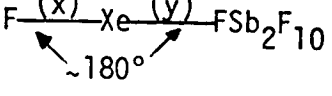
| Molecule | (x),Å | (y),Å | $\nu(Xe\overset{(x)}{-}F)cm^{-1}$ | Bond Order $(Xe\overset{(x)}{-}F)$ | Ref. |
|---|---|---|---|---|---|
|  | 2.01(1) | 2.01(1) | 496 | .5 | 67,104 |
|  | 1.94(1) | 2.16(1) | 531,536 | $.6_3$ | 105 |
|  | 1.90(2) | 2.14(1) | 600,588 | $.7_6$ | 13,12 |
|  | 1.87(2) | 2.18(2) | 604,598 | $.8_3$ | This work,12 |
|  | 1.84(2) | 2.35(2) | 621 | $.9_6$ | 11,2 |

TABLE VII

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG.)

FOR $XeF^{+}RuF_6^{-}$

(All F-F contacts > 2.5Å)

| | | | |
|---|---|---|---|
| $Ru-F_2$ | 1.919(13)[a] | $F_2-Ru-F_4$ | 85.65(76) |
| $Ru-F_3$ | 1.778(16) | $F_2-Ru-F_5$ | 89.36(98) |
| $Ru-F_4$ | 1.781(12) | $F_2-Ru-F_6$ | 91.30(1 |
| $Ru-F_5$ | 1.789(13) | $F_2-Ru-F_7$ | 89.21(98) |
| $Ru-F_6$ | 1.820(14) | $F_3-Ru-F_4$ | 94.27(121) |
| $Ru-F_7$ | 1.835(13) | $F_3-Ru-F_5$ | 90.73(93) |
| | | $F_3-Ru-F_6$ | 88.22(109) |
| $Xe-F_1$ | 1.872(17) | $F_3-Ru-F_7$ | 91.28(113) |
| $Xe-F_2$ | 2.182(15) | $F_4-Ru-F_6$ | 91.25(104) |
| $Xe-F_5$ | 3.163(13) | $F_4-Ru-F_7$ | 90.77(82) |
| $Xe-F_6$ | 3.171(15) | $F_5-Ru-F_6$ | 89.08(123) |
| $Xe-F_7$ | 3.172(13) | $F_5-Ru-F_7$ | 88.93(86) |
| $Xe-F_4$ | 3.256(12) | | |
| $Xe-F_3$ | 3.483(29) | $F_1-Xe-F_2$ | 177.08(123) |
| $Xe-F_5$ | 3.506(20) | | |
| $Xe-F_7$ | 3.625(21) | $Xe-F_2-Ru$ | 137.19(46) |

[a] Estimated Standard deviations in parentheses.

TABLE VIII

Interatomic Distances (Å) and Angles (Deg) $IF_4^+SbF_6^-$

| Atom 1 | Atom 2 | Distance | Angles | |
|---|---|---|---|---|
| Sb | F1 | 1.856(.018) | F5-I-F5 | 153.27(?) |
| Sb | F2 | 1.801(.023) | F6-I-F6 | 107.04(?) |
| Sb | F3 | 1.878(.023) | | |
| Sb | F4 | 1.923(.022) | F1-Sb-F3 | 90.18(.56) |
| I | F5 | 1.811(.017) | F1-Sb-F4 | 90.42(.52) |
| I | F6 | 1.792(.025) | F2-Sb-F3 | 89.82(.56) |
| I | F4 | 2.674(.021) | F2-Sb-F4 | 89.58(.52) |
| I | F3 | 2.709(.022) | | |
| I | F1 | 3.603(.018) | Sb-F3-I | 143.66(.99) |
| I | F2 | 3.072(.023) | Sb-F4-I | 143.05(.92) |

TABLE IX

Interatomic Distances[(a)] (Å) and Angles (Deg) $[SF_3]^+[BF_4]^-$

| | | | |
|---|---|---|---|
| S-2F1 | 1.495(2),[1.518] | F3...2F5 | 2.277(3) |
| 2-F2 | 1.499(2),[1.514] | F4...2F5 | 2.249(3) |
| S...Fe | 2.593(3) | F5...F5 | 2.275(4) |
| S...2F5 | 2.624(2) | B...2F1 | 3.456(4) |
| S...B | 3.438(4) | F1-S-F1 | 97.62(7) |
| S...F4 | 3.111(3) | F1-S-F2 | 97.39(12) |
| S...2F4 | 3.265(2) | F3-B-F4 | 107.63(25) |
| B-F3 | 1.397(4),[1.410] | F3-B-F5 | 110.29(16) |
| B-F4 | 1.393(5),[1.438] | F4-B-F5 | 108.58(17) |
| B-2F5 | 1.377(3),[1.404] | F5-B-F5 | 111.37(14) |
| F2...2F1 | 2.249(3) | S...F3-B | 115.66(17) |
| F1...F1 | 2.250(4) | S...F5-B | 119.69(17) |
| F3...F4 | 2.252(4) | | |

(a) Values in square brackets are thermally corrected distances based on in phase motion of the atoms.

TABLE X

A Comparison of $SF_3^+$ and Some Other $MF_3$ Species

| | $SF_3^+$ | $PF_3$ (67) |
|---|---|---|
| M-F(Å) | 2 at 1.495(2)<br>1 at 1.499(2) | 3 at 1.5700 ± 0.0012 |
| F-M-F(°) | 2 at 97.39(12)<br>1 at 97.62(07) | 3 at 97.8 ± 0.2 |

| | $SeF_3^+$ (59a) | $AsF_3$ (60) |
|---|---|---|
| M-F(Å) | 1.67(2)<br>1.64(2)<br>1.66(2) | 3 at 1.7063 ± 0.0006 |
| F-M-F(°) | 94.9(1.7)<br>93.9(1.7)<br>94.6(1.7) | 3 at 96.1 ± 0.05 |

TABLE XI

Calculated $\Delta H_{dis}$ for Some $F^-$ Donor-Acceptor Complexes

(A (✓) indicates a known compound and a (#) indicates an unknown compound)

| Compound | $\Delta H_{diss}$ | ✓/# | Compound | $\Delta H_{diss}$ | ✓/# |
|---|---|---|---|---|---|
| $BrF_4^+PF_6^-$ | +24 | # | $SF_3^+SbF_6^-$ | -55 | ✓ |
| $BrF_4^+BF_4^-$ | 18 | # | $ClF_2^+SbF_6^-$ | -51 | ✓ |
| $IF_4^+BF_4^-$ | 15 | # | $ClF_4^+SbF_6^-$ | -49 | ✓ |
| $BMF_4^+AsF_6^-$ | 13 | # | $BrF_2^+SbF_6^-$ | -45 | ✓ |
| $IF_4^+BF_4^-$ | 9 | # | $XeF^+SbF_6^-$ | -44 | ✓ |
| $IF_4^+AsF_6^-$ | 4 | # | $IF_6^+SbF_6^-$ | -44 | ✓ |
| $BrF_2^+PF_6^-$ | 0 | # | $XeF_5^+SbF_6^-$ | -41 | ✓ |
| $XeF_3^+PF_6^-$ | - 1 | # | $XeF_3^+SbF_6^-$ | -36 | ✓ |
| $XeF_3^+BF_4^-$ | - 6 | # | $SF_3^+AsF_6^-$ | -31 | ✓ |
| $XeF_3^+PF_6$ | - 6 | # | $ClF_2^+AsF_6^-$ | -27 | ✓ |
| $BrF_2^+BF_4^-$ | - 8 | # | $SF_3^+BF_4^-$ | -25 | ✓ |
| $IF_6^+PF_6^-$ | - 9 | # | $ClF_4^+AsF_6^-$ | -25 | ✓ |
| $XeF^+BF_4^-$ | - 9 | # | $ClF_2^+BF_4^-$ | -24 | ✓ |
| $XeF_5^+BF_4^-$ | -11 | # | $ClF_2^+PF_6^-$ | -22 | ✓ |
| $BrF_2^+AsF_6^-$ | -11 | ✓ | $IF_4^+SbF_6^-$ | -20 | ✓ |
| $BrF_4^+SbF_6^-$ | -11 | $BrF_4^+Sb_2F_{11}^-$ | $XeF^+AsF_6^-$ | -20 | ✓ |
| $IF_6^+BF_4^-$ | -12 | ✓ | $SF_3^+PF_6^-$ | -20 | ✓ |
| $XeF_3^+AsF_6^-$ | -12 | # | $ClF_4^+BF_4^-$ | -20 | # |
| $XeF^+BF_4^-$ | -14 | # | $IF_6^+AsF_6^-$ | -20 | ✓ |
| $ClF_4^+PF_6^-$ | -14 | # | $XeF_5^+AsF_6^-$ | -17 | ✓ |

TABLE XII

Tensimetry of $IrF_6 + NO_2F$

| $IrF_6$(torr) | $NO_2F$(torr) | Residual Gas [$F_2$] |
|---|---|---|
| 105 | 110 | 45 |
| 110 | 105 | 45 |
| 40 | 70 | 50 |
| 55 | 55 | 20 |
| 320 | 320 | 140 |
| 240 | 260 | 140 |

TABLE XIII

Powder Data $NO_2^+IrF_6^-$

| d(Å) | $I/I_1$ | h k ℓ | d(Å) | $I/I_1$ | h k ℓ |
|---|---|---|---|---|---|
| 5.541 | 50 | 001 | 1.531 | 1 | 421 |
| 4.983 | 70 | 110 | 1.499 | 6 | 241 |
| 4.253 | --- | --- | 1.483 | 2 | 223 |
| 3.693 | 100 | 111 | 1.467 | 5 | 042 |
| 3.576 | 50 | 200 | 1.425 | 4 | 313 |
| 3.456 | 50 | 020 | 1.424 | 4 | 332 |
| 3.003 | 30 | 201 | 1.413 | 4 | 510,133 |
| 2.930 | 30 | 021 | 1.380 | 4 | 422,004 |
| 2.773 | 60 | 002 | 1.359 | 3 | 150,242 |
| 2.486 | 60 | 220 | 1.335 | 5 | 114 |
| 2.419 | 50 | 112 | 1.319 | 5 | 151 |
| 2.262 | 40 | 221,310 | 1.288 | 4 | 403,204 |
| 2.195 | 40 | 202,130 | 1.235 | 4 | 333 |
| 2.160 | 60 | 022 | 1.215 | 6 | 530 |
| 2.092 | 70 | 211 | 1.206 | 3 | 423 |
| 2.039 | 10 | 121 | 1.199 | 3 | 600 |
| 1.852 | 90 | 222 | 1.190 | 3 | 243 |
| 1.696 | 70 | 400 | 1.182 | 3 | 314 |
| 1.752 | 70 | 313 | 1.170 | 3 | 135 |
| 1.731 | 70 | 113 | 1.136 | 3 | 442 |
| 1.725 | 50 | 040 | 1.116 | 3 | 513 |
| 1.648 | 50 | 041,203 | 1.097 | 4 | 404 |
| 1.630 | 70 | 023 | 1.082 | 1 | 044 |
| 1.592 | 70 | 420,311 | 1.064 | 3 | 334 |
| 1.558 | 10 | 240 | | | |

TABLE XIV

X-Ray Powder Data for $NO_2^+WOF_5^-$

| d(Å) | Intensity | d(Å) | Intensity |
|---|---|---|---|
| 5.78 | s* | 2.75 | w |
| 5.06 | w | 2.63 | w |
| 4.56 | s | 2.42 | w |
| 4.11 | s | 2.38 | w |
| 3.77 | s | 2.29 | 2 |
| 3.90 | m | 2.26 | w |
| 3.67 | m | 2.19 | 2 |
| 3.61 | vw | 2.23 | w |
| 3.52 | m | 2.13 | w |
| 3.46 | m | 2.06 | w |
| 3.13 | ms | 2.00 | m |
| 2.93 | w | 1.97 | w |
| 2.81 | w | 1.94 | vw |
| | | 1.90 | w |
| | | 1.87 | w |
| | | 1.77 | w |

*s = strong, m = medium, w = weak, v = very.

## IX. ILLUSTRATIONS

Figure 1: The $XeF^{+}RuF_6^{-}$ Structural Unit (Distances in Ångstroms and Standard Deviations in Parentheses).

Figure 2: Stereoscopic View to Show Packing of the XeF $RuF_6$ Units in the Crystal Lattice.

Figure 3a: The $XeF_5^{+}$ and $RuF_6^{-}$ Structural Units and the Coordination of $XeF_5^{+}$ (Distances in Ångstroms and Standard Deviations in Parentheses).

Figure 3b: The Molecular Structure of $XeF_5^{+}[AsF_6]^{-}$.

Figure 4: Molecular Geometries of $XeF_5^{+}$, $IF_5$, $TeF_5^{-}$.

Figure 5: Molecular Geometries of $ClF_2^{+}$, $SF_2^{+}$, $ClO_2^{-}$.

Figure 6: Molecular Geometries of $BrF_4^{+}$, $SeF_4$.

Figure 7: Molecular Geometries of $IF_4^{+}$, $TeF_4$, $SbF_4^{-}$.

Figure 8: Packing Diagram of $SF_3^{+}BF_4^{-}$.

Figure 9: The $SF_3$ Cation.

Figure 10: Plot of Bond Length -vs- the Logarithm of the Stretching Force Constant for Some S-F Bonds.

Figure 11: Comparison of Raman Spectra of $SF_3^{+}BF_4^{-}$.

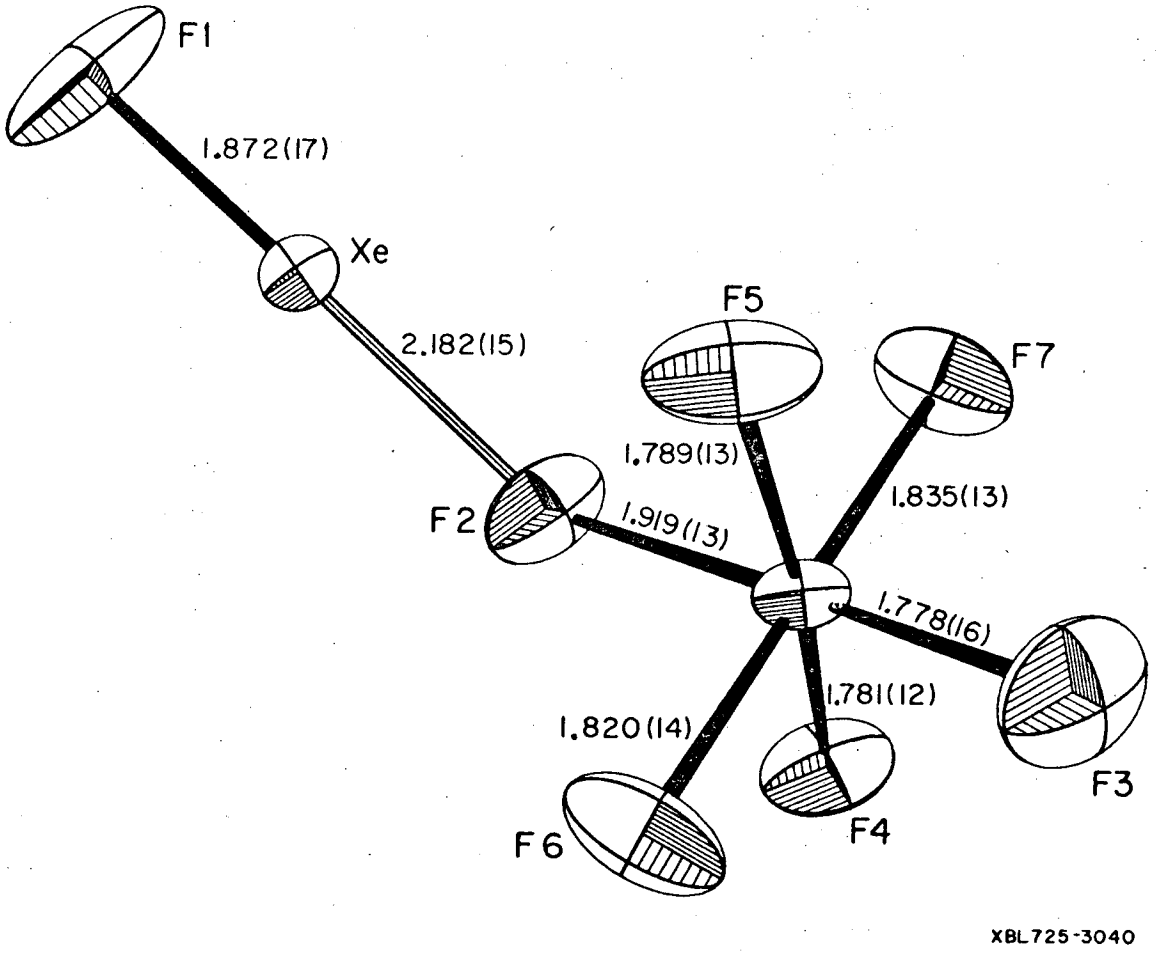

F1
1.872(17)
Xe
2.182(15)
F5
F7
1.789(13)
1.835(13)
F2
1.919(13)
1.778(16)
1.781(12)
1.820(14)
F3
F4
F6
XBL725-3040

FIGURE 1

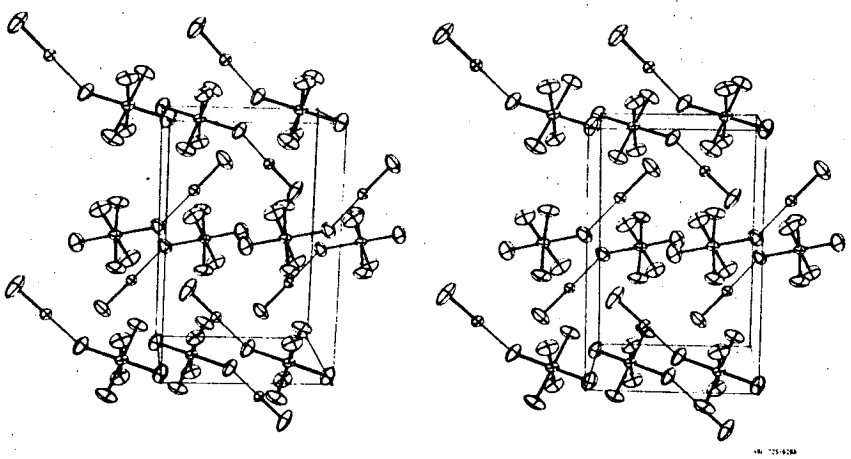


FIGURE 2

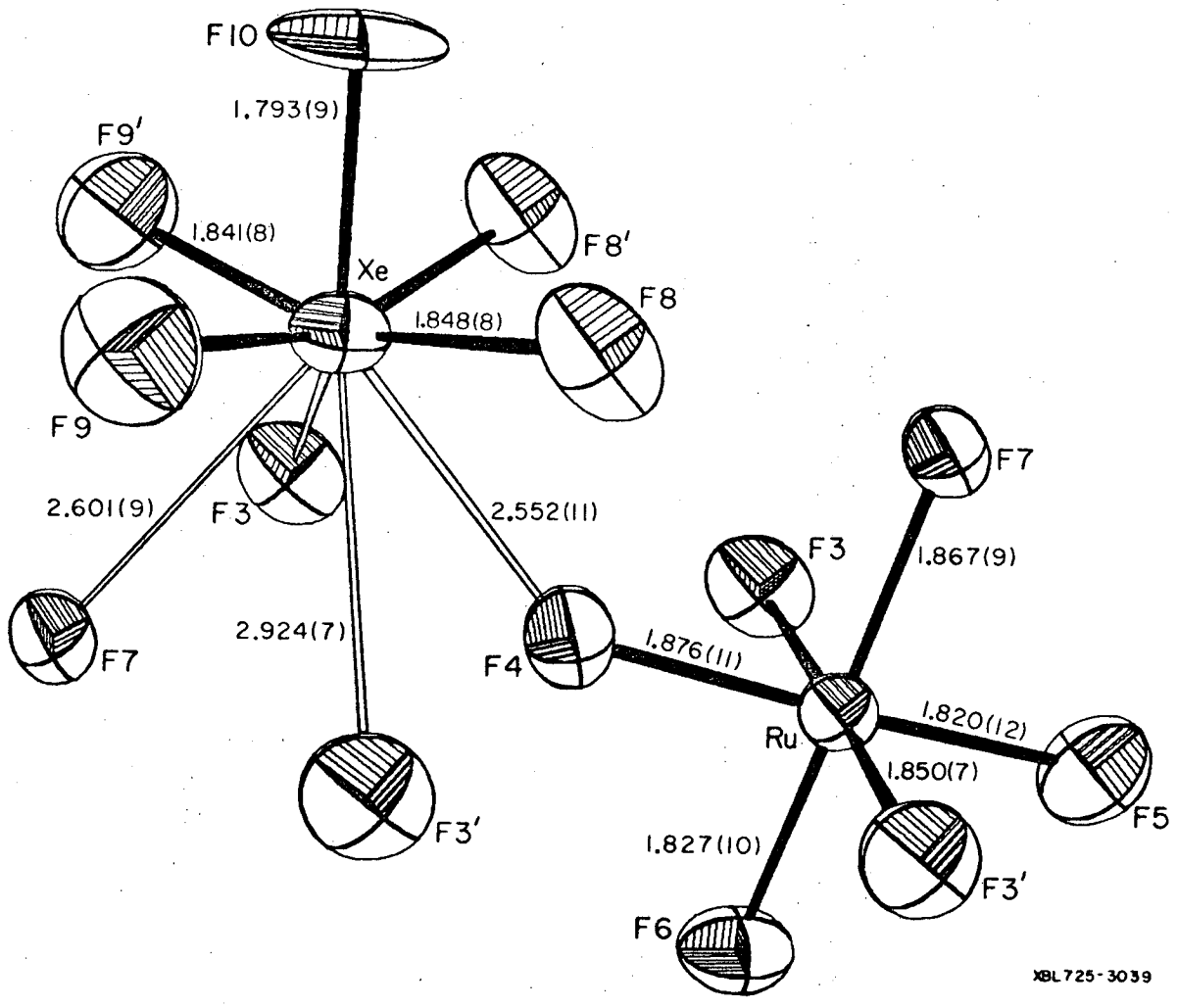

F10
1.793(9)
F9'
1.841(8)
Xe
F8'
F8
1.848(8)
F9
2.601(9)
F3
2.552(11)
F7
2.924(7)
F4
1.876(11)
F3'
F3
F7
1.867(9)
Ru
1.820(12)
1.850(7)
F5
1.827(10)
F3'
F6
XBL725-3039

FIGURE 3a

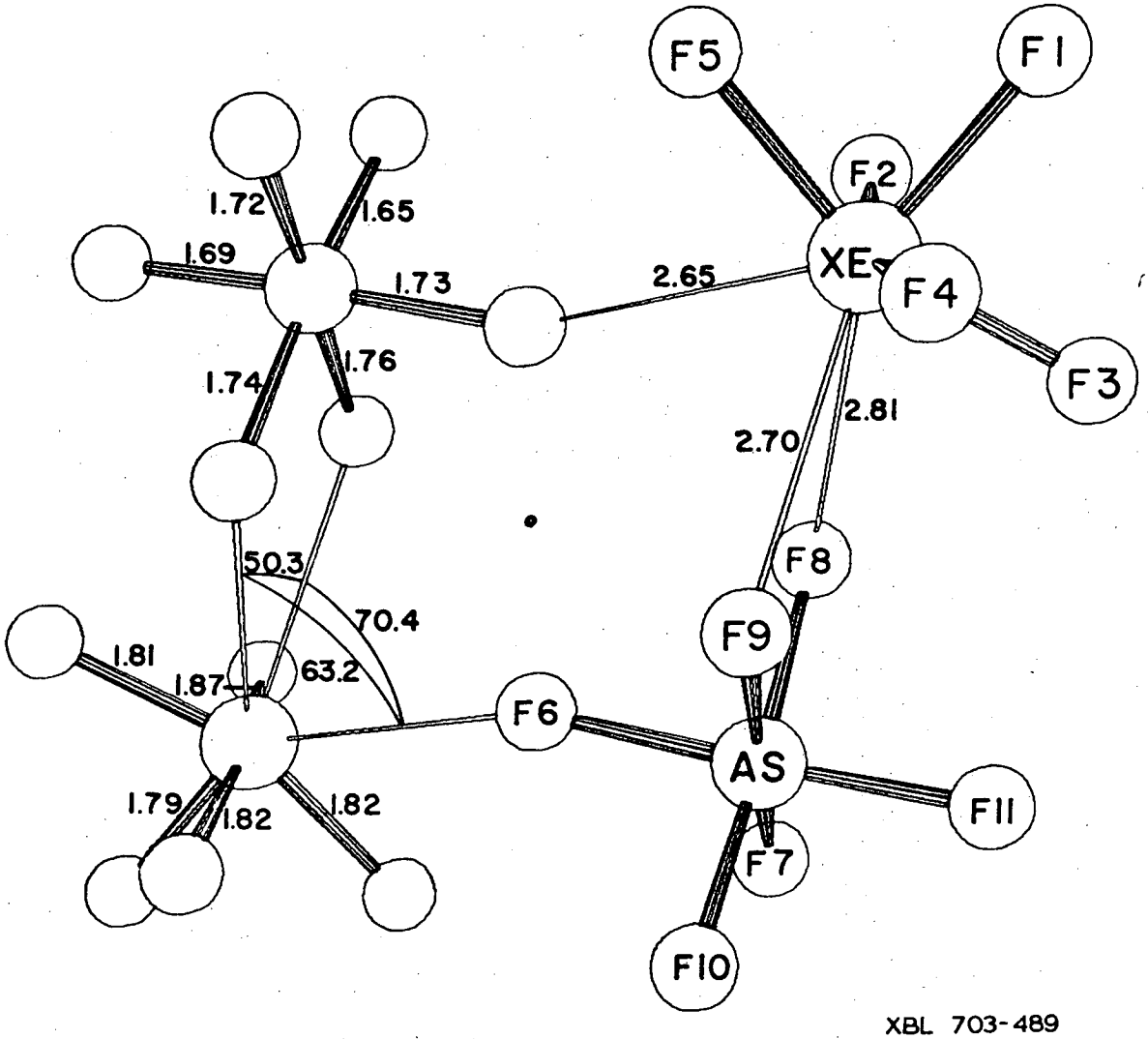
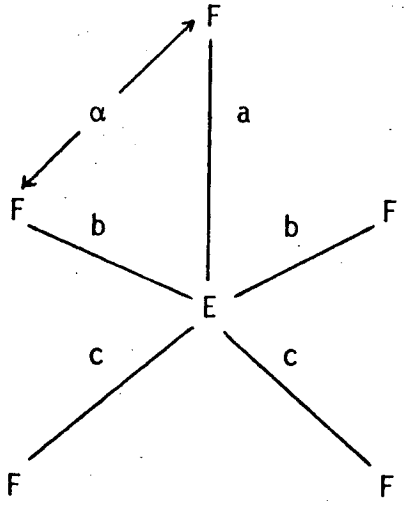

F5
F1
F2
XE
F4
F3
1.72
1.65
1.69
1.73
2.65
1.74
1.76
2.81
2.70
F8
50.3
70.4
F9
1.81
1.87
63.2
F6
AS
F11
1.79
1.82
1.82
F7
F10
XBL 703-489

FIGURE 3b




$XeF_5^+$

a = 1.793(8) Å

b = 1.848(8) Å

c = 1.841(8) Å

α = 78.59(43)°

Ref. 31

$IF_5$

a = 1.817(10) Å

b = c = 1.873(5) Å

α = 80.9(2)°

Ref. 50

$TeF_5^-$

a = 1.84(2) Å

b = c = 1.96(2) Å

α = 78.9(1.6)°

Ref. 117

XBL-7211-7149

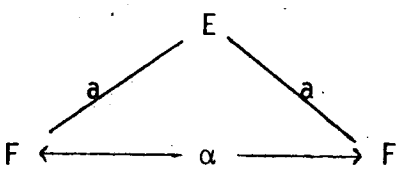
FIGURE 4

$ClF_2^+$

a = 1.58 Å

α = 96°

Ref. 36




$SF_2^+$

a = 1.589 Å

α = 98.16°

Ref. 119

$ClO_2^-$

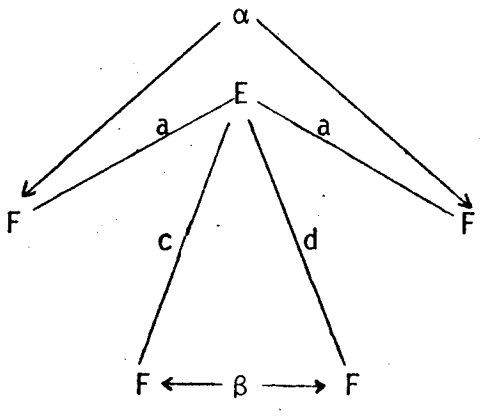
a = 1.57 Å

α = 110.5°

Ref. 118

XBL-7211-7150

FIGURE 5




$BrF_4^+$

a = 1.80 ± .12 Å

b = 1.91 ± .13 Å

c = 1.98 ± .09 Å

d = 1.76 ± .12 Å

α = 186.5 ± 6.1°

β = 95.5 ± 5.5°

Ref. 42

$SeF_4$

a = b = 1.771 Å

c = d = 1.682 Å

α = 190.80°

β = 100.55°

Ref. 43

XBL-7211-7151

FIGURE 6

$IF_4^+$

a = b = 1.811(17) Å

c = d = 1.792(25) Å

α = 206.73°

β = 107.04°

Ref. This work

$TeF_4$

a = 1.92(3) Å

b = 2.08(3) Å

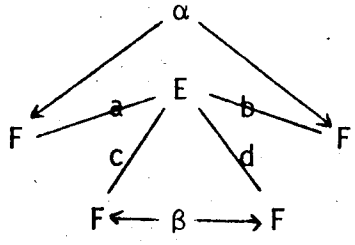
c = 1.87(3) Å

d = 1.80(2) Å

α = 198.9(2.7)°

β = 88.5(2.3)°

Ref. 121




$SbF_4^-$

a = 2.082(3) Å

b = 2.051(3) Å

c - 1.908(3) Å

d = 1.933(3) Å

α = 204.8(2)°

β = 90.4(2)°

Ref. 120

XBL-7211-7152

FIGURE 7

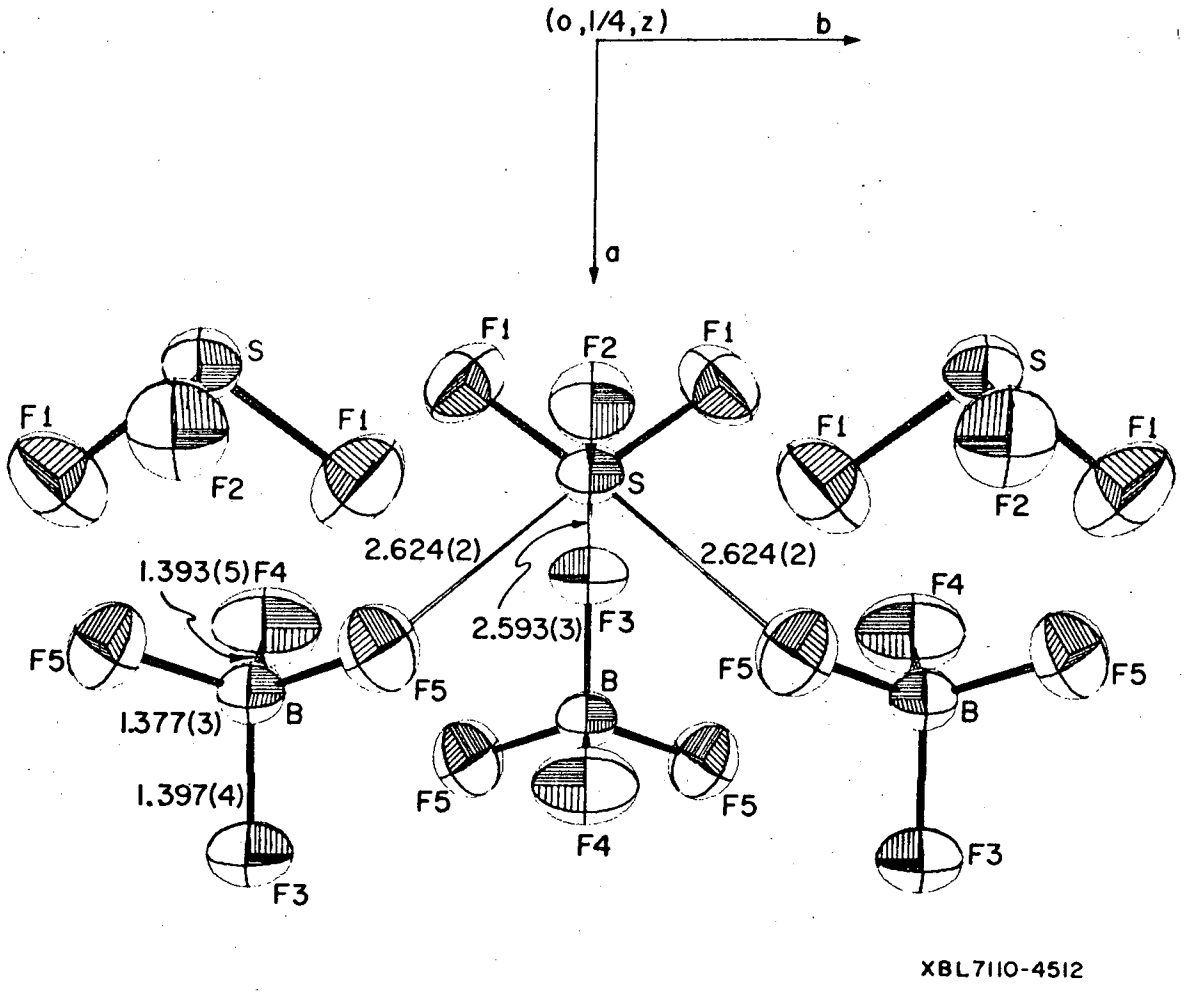

(o,1/4,z)
b
a
S
F1
F2
F1
F1
F2
F1
S
F1
F1
F2
S
2.624(2)
2.624(2)
1.393(5)F4
2.593(3)
F3
F5
F5
B
1.377(3)
B
1.397(4)
F5
F5
F4
F4
F5
F5
B
F3
F3
XBL7110-4512

FIGURE 8

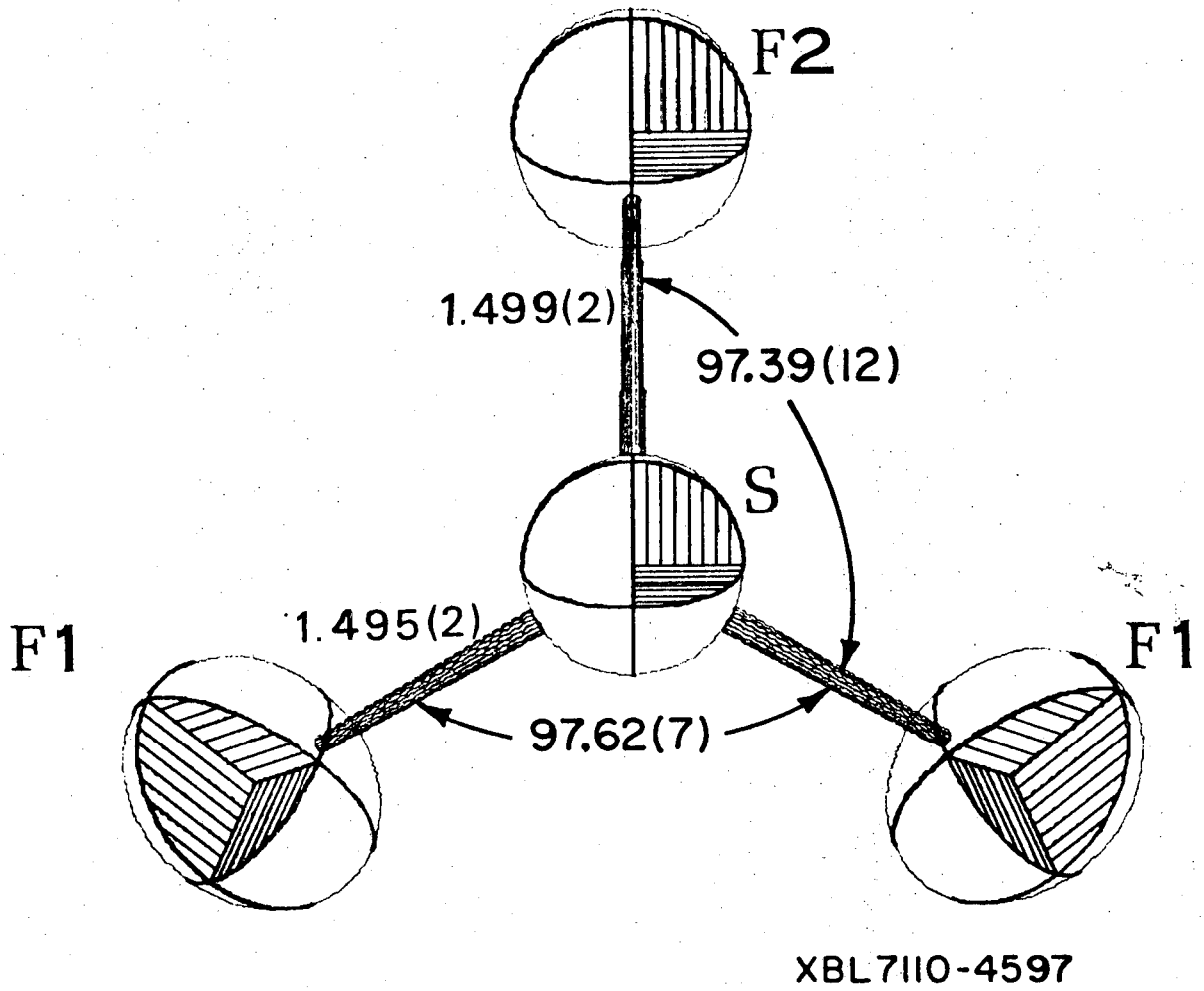



FIGURE 9

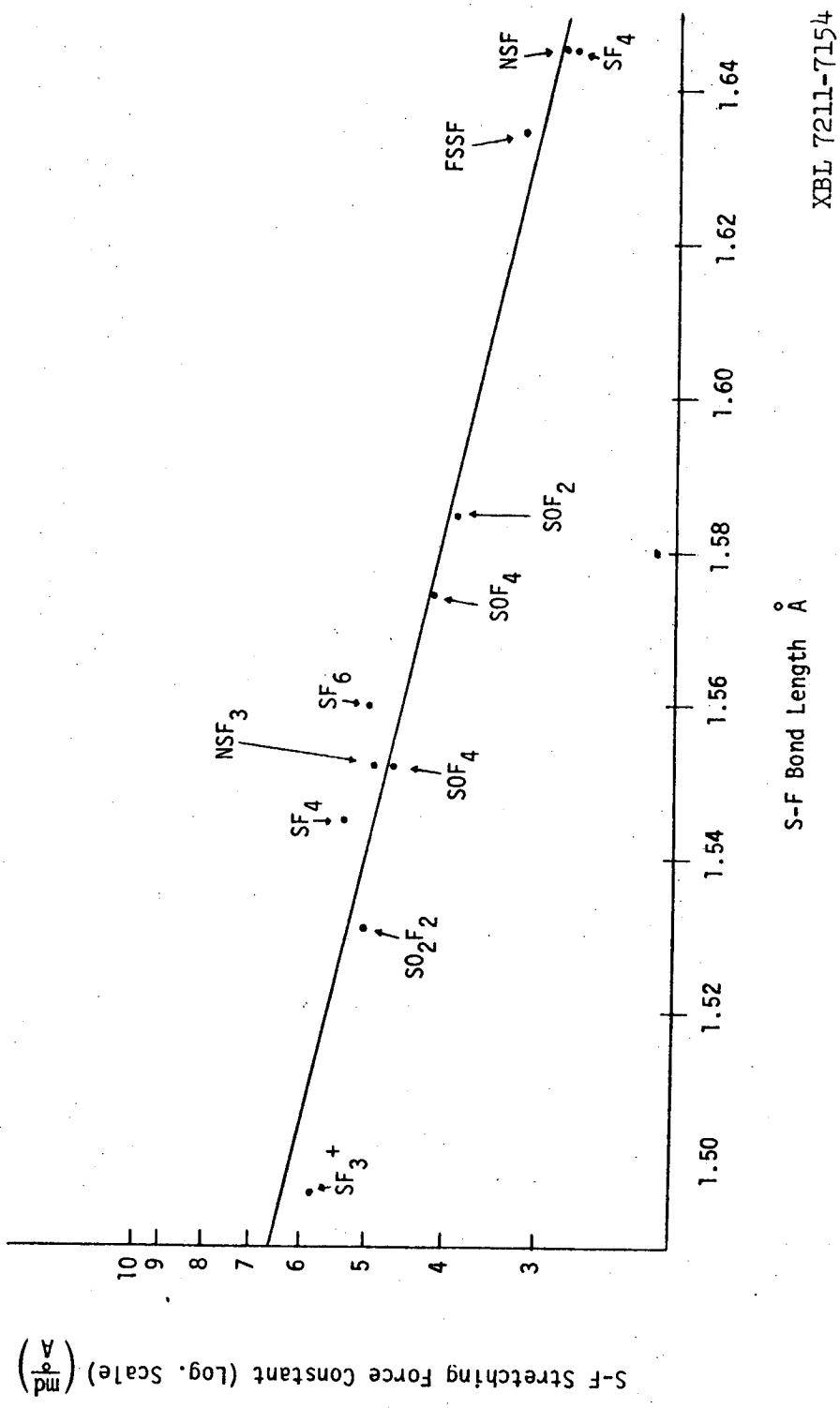
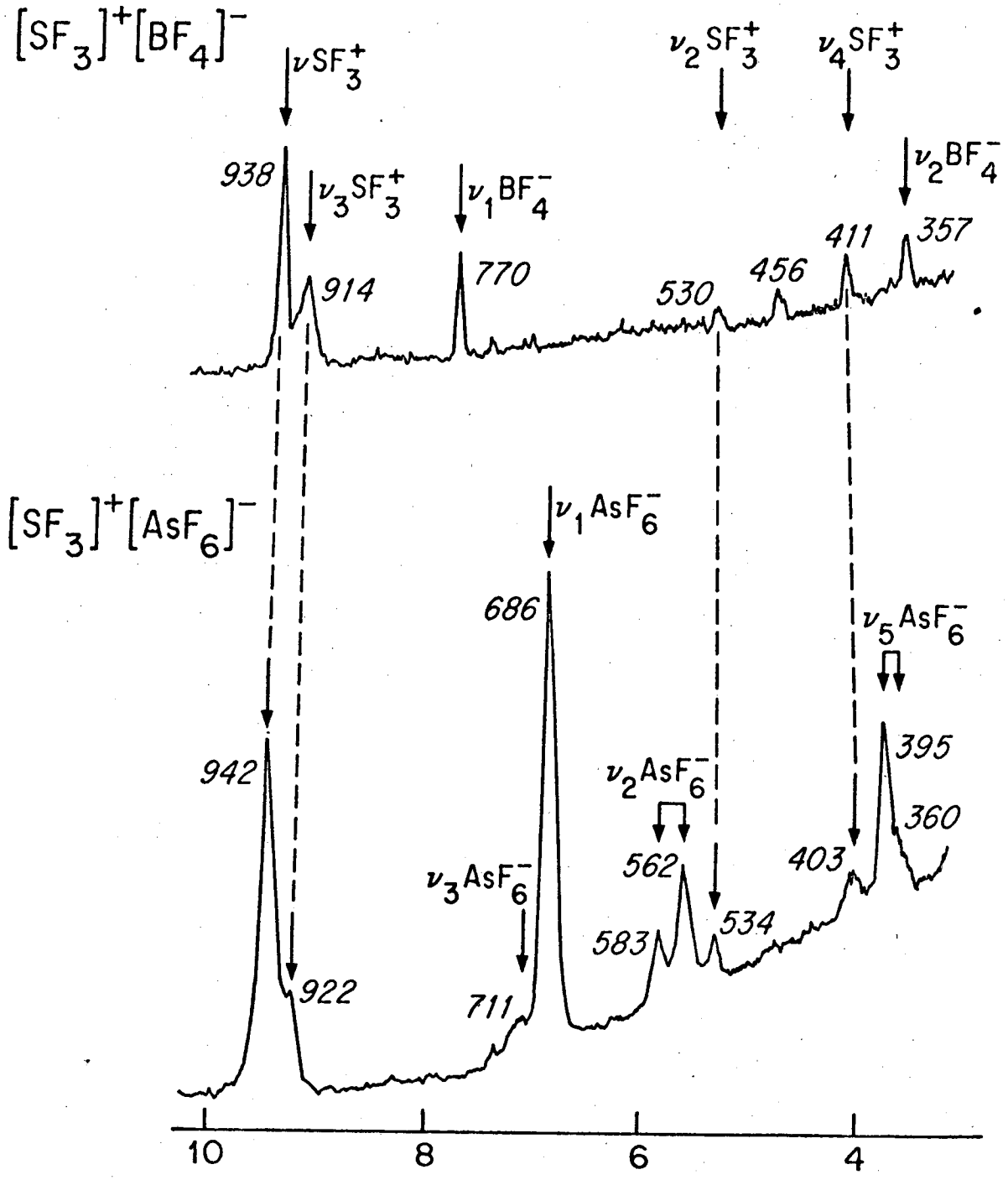

S-F Stretching Force Constant (Log. Scale) $\left(\frac{md}{A^{\circ}}\right)$
10
9
8
7
6
5
4
3
$SF_3^+$
$SO_2F_2$
$SF_4$
$NSF_3$
$SF_6$
$SOF_4$
$SOF_4$
$SOF_2$
FSSF
NSF
$SF_4$
1.50
1.52
1.54
1.56
1.58
1.60
1.62
1.64
S-F Bond Length Å
XBL 7211-7154

FIGURE 10

References for Figure 10

Bond Lengths: $SO_2F_2$, 106; $SOF_2$, 107; $SF_6$, 108; FSSF, 109; NSF, 110; $SOF_4$, 111; $NSF_3$, 112; $SF_4$, 68.

Force Constants: $SO_2F_2$, $SOF_2$, $SF_6$, FSSF, NSF, as compiled in Reference 113; $SOF_4$, 114; $NSF_3$, 115; $SF_4$, 116.




XBL-7211-7153

FIGURE 11

LEGAL NOTICE

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

*TECHNICAL INFORMATION DIVISION*
*LAWRENCE BERKELEY LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*