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INORGANIC HALOGEN OXIDIZERS

FINAL REPORT

ROCKETDYNE DIVISION
ROCKWELL INTERNATIONAL
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Final Report for Period 1 March 1982 - 31 December 1983

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
A basic research program was carried out in the area of inorganic halogen oxidizers. The main effort was directed towards the synthesis and characteri- zation of ClF ₆ salts. Pure ClF ₆ salts were prepared for the first time and shown to be of excellent kinetic stability. Methods developed for NF ₄ ⁺ chemistry were successfully transferred to ClF ₆ ⁺ chemistry, and ClF ₆ SBF ₆ ⁻ , ClF ₆ AsF ₆ ⁻ and ClF ₆ BF ₄ ⁻ were prepared and characterized. By analogy with NF ₄ ClO ₄ ⁺ ,		

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Fluoro Cations, Dioxygenfluoride Radical, Far-Infrared Laser Magnetic Resonance Spectroscopy, Tungsten Oxide Tetrafluoride, Platinum Hexafluoride, Krypton Difluoride, Cesium Hexafluoromanganate (IV), Chloryl Fluoride, Chlorine Oxyfluorides, Sulfur Tetrafluoride Radical Anion, Sulfur Tetrafluoride Oxide Radical Anion.

20. (Continued)

ClF_6ClO_4 was found to be unstable. The relative oxidizing power of KrF^+ , PtF_6 , and F_2 in the presence of a strong Lewis acid and an activation energy source was studied and found to decrease in this order. Numerous new NF_4^+ salts were prepared and characterized. Attempts to prepare substituted NF_4^+ salts were unsuccessful. The first known example of a metal hypofluorite, TeF_5OF , was prepared and characterized. Attempts conducted on the synthesis of ClF_4OF from ClF_4O^- and FOSO_2F were unsuccessful, but resulted in an unusual oxygen abstraction reaction. The O_2F radical was prepared and subsequently characterized by laser magnetic resonance spectroscopy. The structures of the NF_3^+ radical cation and of the SF_4^- and SF_4O^- radical anions were studied by ESR spectroscopy. The gas phase structure of CF_3N_3^+ was investigated by electron diffraction and microwave spectroscopy. Work on the synthesis of energetic F_2NO -substituted fluorocarbons was completed. Several oxonium and deuterated oxonium salts were prepared and then characterized by x-ray, neutron diffraction and vibrational spectroscopy. Polar covalence theory arguments are presented against the existence of positively polarized fluorine in covalent hypofluorites. A total of 26 papers, manuscripts and patents are included in the Appendix.

PREFACE

The research reported herein was supported by the Mechanics Division of the Office of Naval Research with Dr. R. S. Miller as Scientific Officer and by the Chemistry Division of the Army Research Office with Dr. B. Spielvogel as Scientific Officer. This report covers the period 1 March 1982 through 31 December 1983. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out mainly by Drs. K. O. Christe, W. W. Wilson, C. J. Schack and Mr. R. D. Wilson with contributions from Drs. E. C. Curtis, W. Maya, D. Pilipovich and Mr. M. Warner (all at Rockwell International). Other contributors to these research efforts, at no cost to the contract, were Drs. R. Bougon, P. Charpin, E. Soulie and T. Bui Huy (French Atomic Energy Commission), J. Fawcett (University of Leicester, England), H. Oberhammer and D. Christen (University of Tübingen, Germany) J. Mason (The Open University, Milton Keynes, England), F. Temps and H. G. Wagner (Max Planck Institut, Göttingen, Germany), P. B. Davies and D. P. Stern (University of Cambridge, England) and F. Williams, B. Walther and J. Wang (University of Tennessee). The program was administered by Dr. L. R. Grant.

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INTRODUCTION

This is the final report of a research program carried out at Rocketdyne between 1 March 1982 and 31 December 1983. The purpose of this program was to explore the synthesis and properties of energetic inorganic halogen oxidizers. Although the program was directed toward basic research, applications of the results were continuously considered.

Only completed items of research, which have been summarized in manuscript form, are included in this report. A total of 14 technical papers were published and 9 papers are in press in major scientific journals. In addition, 8 papers were presented at international and national conferences. A further testimony to the creativity of this program is the fact that it resulted in 3 U.S. patents issued and 5 pending. The technical papers and issued patents are reproduced in Appendices A through Z.

PUBLICATIONS AND PATENTS GENERATED UNDER THIS PROGRAM

PUBLICATIONS

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2. "Perfluoroammonium Salts of Metal Heptafluoride Anions," by W. W. Wilson and K. D. Christe, Inorg. Chem., 21, 2091 (1982).
3. "Fluorine Perchlorate. Vibrational Spectra, Force Field, and Thermodynamic Properties," by K. D. Christe and E. C. Curtis, Inorg. Chem., 21, 2938 (1982).
4. "Perfluoroammonium and Alkali-Metal Salts of the Heptafluoroxenon (VI) and Octafluoroxenon (VI) Anions," by K. D. Christe and W. W. Wilson, Inorg. Chem., 21, 4113 (1982).
5. "Synthesis and Characterization of TeF_5OF ," by C. J. Schack, W. W. Wilson and K. D. Christe, Inorg. Chem., 22, 18 (1983).
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9. "Nitrogen-14 and Nitrogen-15 NMR Spectroscopy of Fluoronitrogen Cations: π and σ Fluoro Effects," by J. Mason and K. D. Christe, Inorg. Chem., 22, 1849 (1983).
10. "Synthesis and Properties of ClF_6BF_4 ," by K. D. Christe and W. W. Wilson, Inorg. Chem., 22, 1950 (1983).
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12. "On the Reality of Positive Fluorine," by K. O. Christe, J. Fluorine Chem., 22, 519 (1983).
13. "Thermochemistry of NF_4^+ Salts. On the Enthalpy of Formation of NF_4XeF_7 and the $\text{NF}_4\text{SbF}_6\text{-BrF}_3$ System," by K. O. Christe, W. W. Wilson, R. O. Wilson, R. Bougon, and T. Bui Huy, J. Fluorine Chem., 23, 399 (1983).
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PAPERS IN PRESS

15. "Positive Fluorine - Reality or Misconcept?," by K. O. Christe, J. Fluorine Chem.
16. "Tetrafluoroammonium Salts," by K. O. Christe, W. W. Wilson, C. J. Schack and R. O. Wilson, Inorg. Synth.
17. "Tungsten Oxide Tetrafluoride," by W. W. Wilson and K. O. Christe, Inorg. Synth.
18. "Coordinatively Saturated Fluoro Cations. Oxidative Fluorination Reactions with KrF^+ Salts and PtF_6 ," by K. O. Christe, W. W. Wilson and R. O. Wilson, Inorg. Chem.
19. "Cesium Hexafluoromanganate(IV)," by W. W. Wilson and K. O. Christe, Inorg. Synth.
20. "Chloryl Fluoride," by K. O. Christe, R. O. Wilson and C. J. Schack, Inorg. Synth.
21. "Some Interesting Observations in Chlorine Oxyfluoride Chemistry," by K. O. Christe and W. W. Wilson, J. Fluorine Chem.
22. "Structure and Vibrational Spectra of Oxonium HexafluoroArsenates (V) and -Antimonates (V)," by K. O. Christe, P. Charpin, E. Soulie, R. Bougon and J. Fawcett, Inorg. Chem.
23. "The Gas Phase Structure of CF_3N_3 . An Electron Diffraction, Microwave Spectroscopy and Normal Coordinate Analysis," by K. O. Christe, O. Christen, O. Christen, H. Oberhammer, and C. J. Schack, Inorg. Chem.

PAPERS PRESENTED AT MEETINGS

24. "Structure of Fluorine Containing Radical Anions from ESR Studies of ^{13}C and ^{33}S Hyperfine Interaction," by B. W. Walther, J. T. Wang, F. Williams, K. O. Christe and C. J. Schack, 186th ACS National Meeting, Washington, D.C., August 1983.
25. "Pentafluorotellurium Hypofluorite," by C. J. Schack, W. W. Wilson and K. O. Christe, 183rd National ACS Meeting, Las Vegas, Nevada, April 1982.
26. " ClF_6^+ Chemistry and the Use of KrF_2 for the Synthesis of High Oxidation State Cations," by W. W. Wilson, R. O. Wilson, and K. O. Christe, 10th International Symposium on Fluorine Chemistry, Vancouver, B.C., August 1982.
27. "Perfluoro Ammonium and Alkali Metal Salts of the Heptafluoro Xenon (VI) and Octafluoro Xenon (VI) Anions," by K. O. Christe and W. W. Wilson, 10th International Symposium on Fluorine Chemistry, Vancouver, B.C., August 1982.
28. "Synthesis of N,N-Difluoro-O-Perhaloalkylhydroxylamines," by K. O. Christe, W. Maya, D. Pilipovich, M. Warner and R. Wilson, Sixth Winter Fluorine Conference, Daytona Beach, FLA., February 1983.
29. "Twenty Years of Excitement in High-Energy Halogen Oxidizers," by K. O. Christe, Distinguished Symposium on Chemistry Near the Limits of Oxidation and Bonding, Tarrytown, NY, March 1983.
30. "Synthesis of Coordinatively Saturated Complex Fluoro Cations," by K. O. Christe and W. W. Wilson, 8th European Symposium on Fluorine Chemistry, Jerusalem, Israel, August 1983.
31. Invited seminars on various aspects of our work were given at UC Berkeley and the North Carolina ACS Section.

PATENTS ISSUED

32. "Iodine (VII) Oxytetrafluorohypofluorite and a Process for Preparing Same," by K. O. Christe and R. O. Wilson, U.S. Pat. 4,329,330 (May 1982).
33. "Peroxonium Salts," by K. O. Christe and W. W. Wilson, U.S. Pat. 4,339,423 (July 1982).
34. "Stable NF_4^+ Salt of High Fluorine Content," by K. O. Christe and W. W. Wilson, U.S. Pat. 4,374,112 (February 1983).

PATENTS PENDING

35. "Improved $\text{NF}_3\text{-F}_2$ Gas Generator Composition," by K. O. Christe and W. W. Wilson.
36. "Pentafluorotellurium Hypofluorite," TeF_5OF , by C. J. Schack, W. W. Wilson and K. O. Christe.
37. " NF_4XeF_7 and $(\text{NF}_4)_2\text{XeF}_8$," by K. O. Christe and W. W. Wilson.
38. " NF_4WF_7 and NF_4UF_7 and Methods of Preparation," by W. W. Wilson and K. O. Christe.
39. " $(\text{NF}_4)_2\text{SiF}_6$ and a Method of Preparation," by K. O. Christe and W. W. Wilson.

RESULTS AND DISCUSSION

In view of the large amount of data generated under this program, we will limit ourselves to a highlight of the major areas. For more detail, the interested reader is referred to the manuscripts given in the Appendix.

ClF_6^+ CHEMISTRY

The two most promising energetic oxidizer cations are NF_4^+ and ClF_6^+ . Their central atoms are in their highest oxidation states (+V N and +VII Cl) and they possess a high fluorine content. Whereas the N-F and Cl-F bond energies are relatively low which make them powerful oxidizers, these bond energies are high enough to give them good stability. Furthermore, these two ions possess outstanding kinetic stability due to their energetically favorable structures (tetrahedron for NF_4^+ and octahedron for ClF_6^+). This is also reflected by the fact that NF_4^+ and ClF_6^+ are isoelectronic with CF_4 and SF_6 , respectively, which are the two most thermally stable covalent inorganic fluorides.

Whereas the chemistry of NF_4^+ had been well developed during the past decade, very little work had been done on ClF_6^+ . Although the existence of ClF_6^+ had been firmly established in 1972 (Ref. 1,2), the only known ClF_6^+ salt was $\text{ClF}_6^+\text{PtF}_6^-$ which could be prepared only as an inseparable mixture with ClF_4PtF_6 . Claims by Glemser and coworkers for the synthesis of ClF_6AuF_6 (Ref. 3) and by Batsanov and coworkers for ClF_6CuF_4 (Ref. 4) were shown (Ref. 5) to be invalid. Consequently, it was very desirable to develop methods for the synthesis of pure ClF_6^+ salts and to determine their potential as high energy oxidizers.

Using KrF_2 as the oxidizer, we have succeeded in preparing pure ClF_6AsF_6 and ClF_6SbF_6 (see Appendix A). The salts were thoroughly characterized and exhibited very good thermal stability. In order to increase the energy content of ClF_6^+ salts, the weight of the nonenergetic counterion must be

minimized. This goal was achieved (see Appendix B) by replacing AsF_6^- by BF_4^- using low-temperature metathetical techniques previously developed in our laboratory for NF_4^+ salts. The ClF_6BF_4 also exhibited good thermal stability and is a potentially useful oxidizer. Attempts to replace the nonenergetic anions by the energetic ClO_4^- anion (see Appendix C) were only partially successful. By analogy with NF_4ClO_4 (Ref. 6), ClF_6ClO_4 was found to be thermally unstable. However, as with NF_4ClO_4 , the decomposition of ClF_6ClO_4 provides a new, high yield synthesis of the interesting hypofluorite, FOClO_3 .

Performance calculations were carried out for ClF_6BF_4 with various fuels. It was found that the performance of ClF_6BF_4 is close to but not quite as good as that of NF_4BF_4 . In view of the fact that NF_4BF_4 is thermally more stable and easier to prepare than ClF_6BF_4 , the NF_4^+ cation remains the most promising cationic oxidizer presently known.

NF_4^+ CHEMISTRY

In view of NF_4^+ being theoretically the most powerful cationic oxidizer presently known, we have continued to develop its chemistry. Work on the syntheses of NF_4^+ salts derived from the Lewis acids AlF_3 , BeF_2 , XeF_6 , WF_6 and UF_6 was completed and published in manuscript form (Appendices O through G).

The $(\text{NF}_4)_2\text{XeF}_8$ salt is the most energetic NF_4^+ salt presently known. With 65.6 weight percent of usable fluorine (in the form of F_2 and NF_3) and xenon as the only inert byproduct, $(\text{NF}_4)_2\text{XeF}_8$ is capable of delivering the highest known performance for any $\text{NF}_3\text{-F}_2$ gas generator composition. The difficulty of synthesizing the compound, the high cost of Xe and the shock sensitivity of the XeO_3 hydrolysis product, however, render this compound impractical at the present time.

A summary of the most important synthetic methods for the preparation of NF_4^+ salts was written for publication in *Inorganic Syntheses* and is given in Appendices H through J.

OXIDATIVE FLUORINATIONS WITH KrF^+ SALTS AND PtF_6

KrF^+ salts, PtF_6 and F_2 in the presence of a Lewis acid and an activation energy source appear to be the most powerful fluorinating agents presently known. We therefore have carried out a systematic study of the relative oxidizing power of these three reagents and their usefulness for the preparation of coordinatively saturated fluoro cations (see Appendix K). It was found that KrF^+ was the strongest oxidative fluorinator, capable of fluorinating ClF_5 to ClF_6^+ , BrF_5 to BrF_6^+ , and NF_3 to NF_4^+ . PtF_6 was second strongest, and fluorinated ClF_5 to ClF_6^+ and NF_3 to NF_4^+ , whereas activated F_2 in the presence of a strong Lewis acid oxidized only NF_3 to NF_4^+ . Numerous attempts made to prepare a substituted NF_4^+ cation, such as $CF_3NF_3^+$ or $SF_5NF_3^+$, from KrF^+ salts and either CF_3NF_2 or SF_5NF_2 all failed. Similarly, attempts to prepare OF_3^+ from OF_2 and KrF^+ were unsuccessful.

HYPOFLUORITE CHEMISTRY

Hypofluorites are strong oxidizers and useful fluorinating agents. During our synthesis of NF_4ClO_4 (Ref. 6), a convenient synthesis was discovered for $FOClO_3$ which allowed us to carry out a thorough characterization of this interesting compound (see Appendix L). We have also successfully synthesized and characterized the new hypofluorite TeF_5OF . This compound, which had previously been claimed to be nonexistent (Ref. 7), was shown to be surprisingly stable (see Appendix M). The attempts made to prepare the unknown ClF_4OF molecule from $CsClF_4O$ and $FOSO_2F$ were unsuccessful, but led to an interesting O abstraction reaction from ClF_4O^- (see Appendix C). Numerous attempts to prepare hitherto unknown hypofluorites derived from transition metal fluorides were all unsuccessful. The O_2F radical, prepared by pyrolysis of $O_2^+MF_6^-$ salts, was characterized by far-infrared laser magnetic resonance spectroscopy (see Appendix N).

CHLORINE OXYFLUORIDES

Although the existence of ClF_5O has previously been claimed (Ref. 8), this claim has subsequently been refuted (Ref. 9). Performance calculations carried out at Rocketdyne show that this compound would be the ideal storable liquid oxidizer. Consequently, extensive experimental efforts were conducted on the synthesis of this compound using numerous techniques, such as low-temperature glow discharge in sapphire reactors, UV-photolysis, and fluorination reactions with KrF^+ salts and PtF_6 . So far, all efforts in this direction have been unsuccessful although we firmly believe in the possible existence of this compound. A manuscript on the preparation of FClO_2 was written for Inorganic Synthesis (Appendix O).

ENERGETIC FLUOROCARBONS

Work originally started 10 years ago on the synthesis of $-\text{ONF}_2$ substituted fluorocarbons was completed during this contract. It was summarized in the form of two manuscripts (Appendices P and Q) and describes two different synthetic methods. One involves the reaction of HNF_2 with hypofluorites, while the other one is based on the Lewis acid catalyzed addition of NF_3O to $\text{C}=\text{C}$ double bonds. Numerous new $-\text{ONF}_2$ substituted fluorocarbons were prepared in this manner and were characterized.

The gas phase structure of the most simple fluorocarbon azide, CF_3N_3 , was determined by electron diffraction and microwave spectroscopy (see Appendix R).

STRUCTURAL STUDIES

Under a previous contract (Ref. 10), a series of unusually stable oxonium salts of the composition OH_3MF_6 was discovered. A thorough structural study of these salts was carried out using isotopically substituted salts, X-ray and neutron diffraction and vibrational spectroscopy (see Appendix S).

The structure of the NF_3^+ radical cation, trapped in powdered NF_4AsF_6 , was studied by ESR spectroscopy (Appendix T). The new radical anions SF_4^- and SF_4O^- were prepared by low-temperature γ -irradiation of CsSF_5 and CsSF_5O , respectively, and characterized by ESR spectroscopy. The results of this study will be written up in manuscript form. A number of fluoronitrogen cations was investigated by ^{14}N and ^{15}N NMR spectroscopy and evidence for π and σ fluoro effect was found. The results are summarized in Appendix U.

MISCELLANEOUS

Two brief manuscripts (Appendices V and W) were written to correct a commonly accepted misconception about the existence of positively polarized fluorine in compounds such as hypofluorites.

Three patents issued during this contract are given as Appendices X, Y and Z. They deal with the new iodine hypofluorite OIF_4 , OF , peroxonium salts $\text{H}_3\text{O}_2^+\text{AsF}_6^-$ and $\text{H}_3\text{O}_2^+\text{SbF}_6^-$, and $(\text{NF}_4)_2\text{MnF}_6$.

CONCLUSION

The ClF_6^+ cation is an exceptionally stable, highly energetic ion, comparable to NF_4^+ . Many of the techniques, previously developed for NF_4^+ , can successfully be applied to ClF_6^+ ; however, more convenient routes must be found for the synthesis of ClF_6^+ salts in order to make them competitive with NF_4^+ salts. In addition we have demonstrated again that inorganic halogen oxidizers are a fruitful area of research. There are many potential uses for novel energetic compounds in traditional and new applications, such as rocket propellants, explosives, and chemical lasers, and continuing efforts in this direction are definitely warranted. Furthermore, the productivity of this program proves the feasibility and benefits that can be expected from well-planned, goal-oriented basic research and program continuity.

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Contribution from Rocketdyne, A Division of
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Coordinationally Saturated Complex Fluoro Cations. Synthesis and Characterization of $\text{ClF}_6^+\text{AsF}_6^-$ and $\text{ClF}_6^+\text{SbF}_6^-$

KARL O. CHRISTE,* WILLIAM W. WILSON, and E. C. CURTIS

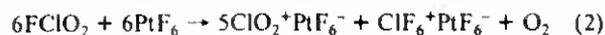
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The reaction of KrF_2 with ClF_3 and AsF_5 in either ClF_3 or anhydrous HF solution produces pure $\text{ClF}_6^+\text{AsF}_6^-$. The white, crystalline solid is stable up to 110 °C under a dynamic vacuum and decomposes at higher temperature to ClF_3 , F_2 , and AsF_5 . X-ray powder diffraction patterns show that $\text{ClF}_6^+\text{AsF}_6^-$ (face-centered cubic; $a = 9.47 \text{ \AA}$) is isotypic with $\text{IF}_6^+\text{AsF}_6^-$. The reaction of KrF_2 with ClF_3 and SbF_5 produces $\text{ClF}_6^+\text{SbF}_6^-$; however, this salt could not be isolated in pure form. ^{19}F NMR and vibrational spectra were recorded for the ClF_6^+ salts, and an anharmonic general valence force field was computed for ClF_6^+ by using the observed frequencies and the ^{35}Cl - ^{37}Cl isotopic shift of ν_3 (F_{10}). General methods for the syntheses of coordinationally saturated complex fluoro cations are compared and discussed.

Introduction

The two kinetically most stable covalent inorganic fluorides are CF_4 and SF_6 . Their exceptional stability is due to the energetically favorable sp^3 and sp^3d^2 hybridization, respectively, of the valence-electron orbitals of the central atoms and their coordinative saturation. Their isoelectronic complex fluoro cations are NF_4^+ and ClF_6^+ , respectively. Recent studies in our and other laboratories have shown that the NF_4^+ cation possesses unusual kinetic stability¹ and forms a surprisingly large number of stable salts.² Consequently, a similar behavior might be predicted for ClF_6^+ , which is isoelectronic with SF_6 .

Although the ClF_6^+ cation has been known for a decade,³⁻⁵ the only salt prepared to date is its PtF_6^- salt



In both reactions the $\text{ClF}_6^+\text{PtF}_6^-$ product could not be sepa-

rated from the other solid byproducts, and to our knowledge the preparation of a pure ClF_6^+ salt has previously not been achieved. Although claims for the syntheses of $\text{ClF}_6^+\text{AuF}_6^-$ and $\text{ClF}_6^+\text{CuF}_4^-$ have previously been made, either these claims have been withdrawn⁶ or, for $\text{ClF}_6^+\text{CuF}_4^-$, the reported properties are incompatible with the presence of a ClF_6^+ salt.⁴² Therefore, the purpose of this study was the preparation of pure ClF_6^+ salts, preferably containing counterions more accessible than the exotic PtF_6^- .

Experimental Section

Caution! The reaction of KrF_2 with AsF_5 can result in a spontaneous exothermic decomposition of KrF_2 accompanied by a bright flash and gas evolution.⁹ Proper safety precautions should be used in working with this system.

Apparatus and Materials. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless-steel-Teflon FEP vacuum system. The reactions between KrF_2 , ClF_3 , and a Lewis acid were carried out in either a 10-mL stainless-steel cylinder (Hoke) or a 30 cm long, 0.5-in. o.d. sapphire tube that was connected to a stainless-steel valve with a Swagelok compression fitting using a Teflon

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front and a stainless-steel backup ferrule. A metal support frame was used to guard against slippage of the sapphire tube out of the compression seal at elevated pressure. To avoid the facile decomposition of KrF_2 during dead-end transfers, the reactors were designed to permit pump-through operation by means of a dip tube. Solid materials were handled in the dry-nitrogen atmosphere of a glovebox.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points.^{10,11} The reported frequencies and isotopic shifts are believed to be accurate to ± 2 and ± 0.3 cm^{-1} , respectively. Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and a Claassen filter¹² for the elimination of plasma lines. Sealed glass or quartz tubes were used as sample containers. The low-temperature spectra were recorded by using a previously described device.¹³

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM390 spectrometer using heat-sealed Teflon FEP sample tubes (Wilma Glass Co.) and $CFCl_3$ as an external standard with positive shifts being downfield from the standard.¹⁴

X-ray powder diffraction patterns were recorded on a General Electric XRD6 diffractometer using Ni-filtered $Cu K\alpha$ radiation. The sample holder was machined out of a solid Teflon block, and the powdered sample was held in place and protected against atmospheric moisture by a 1 mil thick Teflon FEP sheet, which was sealed against the Teflon block with a plastic snap ring. Lines having θ values of less than 10° were difficult to measure by this technique due to interference by Teflon lines. The instrument was calibrated with NaCl and IF_6AsF_6 powder.

Chlorine pentafluoride¹⁵ and KrF_2 ¹⁶⁻¹⁸ were prepared by previously described methods. Hydrogen fluoride (Matheson) was dried by storage over BiF_3 .¹⁹ Arsenic pentafluoride (Ozark Mahoning) and BF_3 (Matheson) were purified by fractional condensation, and SbF_5 (Ozark Mahoning) was purified by distillation.

Synthesis of ClF_6AsF_6 . In a typical experiment, KrF_2 (11.61 mmol) and AsF_5 (11.60 mmol) were combined at $-196^\circ C$ in a 33-mL sapphire reactor. The mixture was allowed to warm slowly to $-78^\circ C$ and then to ambient temperature for 10 min, resulting in the formation of solid $KrFAsF_6$. The sapphire tube was cooled to $-142^\circ C$, and the amount of Kr and F_2 (0.50 mmol) that had formed by decomposition of some KrF_2 during the $KrFAsF_6$ formation was measured. Chlorine pentafluoride (29.6 mmol) was added to the reactor at $-142^\circ C$, and the mixture was gently warmed to ambient temperature for 30 min, resulting in a clear colorless solution containing some white solid. Slow gas evolution was observed and measured by recooling the reactor to $-142^\circ C$. This process was repeated 10 times, and the reactor was finally kept at ambient temperature for 2 days and at $40^\circ C$ for 1 h. A total of about 21 mmol of gas (Kr and F_2), volatile at $-142^\circ C$, was removed in this manner, suggesting that the decomposition of KrF_2 was essentially complete. The unreacted ClF_5 and any ClF_6AsF_6 that has a dissociation pressure of about 1 atm at room temperature²⁰ were pumped off at $25^\circ C$ for 12 h. The white solid residue (428.4 mg = 1.27 mmol) was shown by ^{19}F NMR, infrared, and Raman spectroscopy to consist of pure ClF_6AsF_6 (11.15% yield based on $KrFAsF_6$).

The reaction between $KrFAsF_6$ and ClF_5 was carried out as described above, except for adding about 6 mL of liquid HF to the reactor

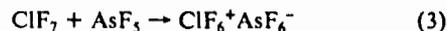
after the KrF_2 addition and before the AsF_5 addition. The Kr and F_2 evolution at ambient temperature was faster than in the absence of HF; however the yield of ClF_6AsF_6 (based on $KrFAsF_6$) was only 3.33%.

When $KrF_2^+AsF_6^-$ was reacted with an excess of ClF_5 in the absence of HF, the best yield of $ClF_6^+AsF_6^-$ obtained was 18.36%, based on AsF_5 , and 9.18%, based on KrF_2 , but on several runs, yields of only about 6% were obtained.

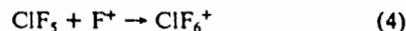
Synthesis of ClF_6SbF_6 . In the drybox SbF_5 (1.67 mmol) was syringed into a passivated sapphire reactor, and KrF_2 (7.19 mmol) was added at $-196^\circ C$ on the vacuum line. The mixture was carefully warmed to room temperature and then re-cooled to $-78^\circ C$. This temperature cycling was repeated several times and a small amount of Kr and F_2 (0.42 mmol) formed by decomposition of some KrF_2 was pumped off at $-78^\circ C$. Chlorine pentafluoride (15.94 mmol) was added to the reactor at $-196^\circ C$, and the resulting mixture was warmed for 30 min to $25^\circ C$. At this temperature slow gas evolution was observed. The reactor was cooled to $-196^\circ C$ and then to $-142^\circ C$ at which temperatures F_2 (1.1 mmol) and Kr (1.2 mmol) were pumped off and measured. This procedure was repeated several times to avoid overpressurization of the reactor by the evolved F_2 and Kr. When the KrF_2 decomposition rate became very slow, the temperature was raised to $35^\circ C$. After most of the KrF_2 had been decomposed and removed in this manner, the excess of ClF_5 was pumped off at $25^\circ C$. The white solid residue (896 mg) was shown by infrared, Raman, and ^{19}F NMR spectroscopy to be a mixture of ClF_6SbF_6 , ClF_5SbF_6 , and $KrF_2 \cdot nSbF_5$. Heating of the solid to $50^\circ C$ for 4 h under a dynamic vacuum resulted in decomposition and removal of all $(KrF_2)_n \cdot SbF_5$, leaving behind a mixture (~ 0.6 g) of ClF_6SbF_6 , ClF_5SbF_6 , and the corresponding polyantimonates, as shown by infrared and Raman spectroscopy.

Results and Discussion

Synthesis of Coordinatively Saturated Complex Fluoro Cations. At present, only three coordinatively saturated complex fluoro cations are known. They are NF_4^+ , ClF_6^+ , and BrF_6^+ .^{21,22} The principal difficulty with their syntheses stems from the fact that the corresponding parent molecules, NF_3 , ClF_7 , and BrF_7 , do not exist.^{1,5,21} Therefore, a simple transfer of a fluoride anion to a strong Lewis acid according to



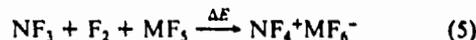
is not possible. Addition of a fluorine cation F^+ to a lower fluoride according to



is preempted by the fact that fluorine is the most electronegative element, and F^+ can therefore not be generated by chemical means.

The following three methods are presently known for the synthesis of these coordinatively saturated complex fluoro cations.

(i) **Reaction of a Lower Fluoride with F_2 and a Lewis Acid in the Presence of an Activation Energy Source,**²³ Such as Heat,²⁴ Glow-Discharge,^{23,25} Bremsstrahlung,²⁶ or UV Photolysis.²⁷ This method is well suited for the synthesis of NF_4^+ salts according to



However, many attempts in our laboratory to apply this me-

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Table I. X-ray Data for ClF_6AsF_6 ^a

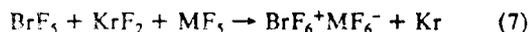
<i>d</i> (obsd), Å	<i>d</i> (calcd), Å	<i>hkl</i> ₀	<i>hkl</i>
3.35	3.35	100	220
2.855	2.858	25	331
2.740	2.737	60	222
2.179	2.175	15	331
2.120	2.120	25	420
1.936	1.935	65	422
1.826	1.824	10	511/333
1.677	1.676	45	440
1.601	1.602	15	531
1.580	1.580	70	600/442
1.498	1.499	20	620
1.428	1.429	25	622
1.367	1.368	10	444
1.313	1.315	25	640
1.265	1.267	25	642

^a Cu K α radiation and Ni filter; space group *Pa*3; face-centered cubic; *a* = 9.47 Å; *Z* = 4; *V* = 849.3 Å³; *d*(calcd) = 2.631 g cm⁻³.

thod to ClF_6^+ were unsuccessful because these activation energy sources decompose ClF_5 to F_2 and ClF_3 with the latter reacting instantaneously with strong Lewis acids to form ClF_2^+ salts.

(ii) **Reaction of PtF_6 with a Lower Fluoride.** As shown in (1) and (2), this method has successfully been applied to the synthesis of ClF_6^+ salts.³⁻⁵ However, attempts to prepare NF_4^+ salts in the same manner have failed. For the preparation of NF_4PtF_6 , elevated temperature and pressure are required,²⁸ i.e. conditions under which PtF_6 decomposes to PtF_5 and F_2 , hereby corresponding to reaction 5 of method i.

(iii) **Reaction of KrF_2 with a Lower Fluoride in the Presence of a Strong Lewis Acid.** This method has successfully been used for the synthesis of BrF_6^+ ²¹ and NF_4^+ ^{29,30} salts



The most promising method for the synthesis of pure ClF_6^+ salts appeared to be method iii, the reaction of ClF_5 with KrF_2 in the presence of a Lewis acid. Indeed, it was found that KrF_2 -Lewis acid adducts are capable of oxidatively fluorinating ClF_5 to ClF_6^+ . It was found advantageous to perform the well-known adducts^{9,21,31,32} between KrF_2 and the Lewis acids, AsF_5 and SbF_5 , before addition of the ClF_5 . The yields of ClF_6^+ salts were as high as 11%, based on the amount of KrF_2 used in the reaction. The reactions proceeded whether KrF^+ or $\text{KrF}^+\cdot n\text{KrF}_2$ salts were used as starting materials, although the ClF_6^+ yields, based on KrF_2 , appeared higher when KrF^+ salts were used. An excess of ClF_5 as a solvent gave the highest yields of ClF_6^+ salts. Addition of anhydrous HF as a diluent significantly reduced the ClF_6^+ yield.

The $\text{ClF}_6^+\text{AsF}_6^-$ salt could readily be prepared in pure form because the byproduct $\text{ClF}_4^+\text{AsF}_6^-$ is unstable at ambient temperature²⁰ and because AsF_6^- does not form stable polyanions with AsF_5 . For $\text{ClF}_6^+\text{SbF}_6^-$, the stability of $\text{ClF}_4^+\text{SbF}_6^-$ ²⁰ and the tendency of SbF_5 to form stable polyanions did not permit isolation of the pure compound.

Properties of $\text{ClF}_6^+\text{AsF}_6^-$ and $\text{ClF}_6^+\text{SbF}_6^-$. Both compounds are white, crystalline, hygroscopic solids that are stable at room temperature. As a result of the above described experimental difficulties, only $\text{ClF}_6^+\text{AsF}_6^-$ could be prepared in a pure state and therefore was characterized more thoroughly than $\text{ClF}_6^+\text{SbF}_6^-$. The $\text{ClF}_6^+\text{AsF}_6^-$ salt is stable up to 110 °C.

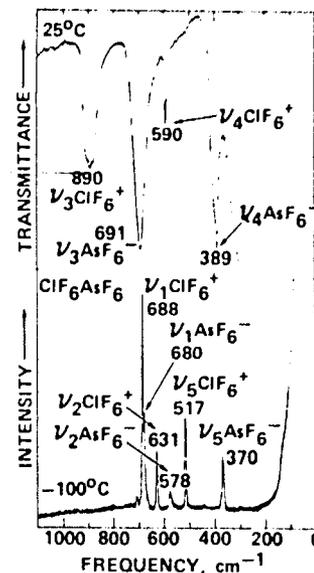
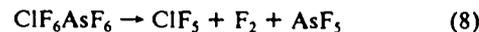


Figure 1. Infrared and Raman spectra of solid ClF_6AsF_6 and assignments to the ions in point group O_h . The broken line is due to absorption by the AgCl window material.

Above this temperature it begins to slowly decompose according to



The infrared spectra of the gaseous decomposition products showed ClF_5 and AsF_5 in a 1:1 mole ratio.

The X-ray powder diffraction data of ClF_6AsF_6 are given in Table I. The lines for *hkl* = 110 and 200 could not be observed by our technique due to an intense broad background peak below a *2θ* value of 20°. The observed data show that ClF_6AsF_6 is isotopic with IF_6AsF_6 ^{33,34} and BrF_6AsF_6 ,¹⁶ although surprisingly the unit cell dimension of ClF_6AsF_6 (9.47 Å) is only slightly smaller than that of IF_6AsF_6 (9.49 Å)^{33,34} and larger than that of BrF_6AsF_6 (9.39 Å).¹⁶ A more detailed study for this series of compounds is needed to verify this effect.

The ¹⁹F NMR spectra of these salts were recorded in anhydrous HF solutions at 29 °C. In addition to a broad unresolved resonance due to rapidly exchanging HF and the anions, a sharp signal was observed at 383.3 ppm downfield from external CFCl_3 . In good agreement with a previous report,³⁵ the signal consisted of two sharp (half-width ~5 Hz) sets of quadruplets of equal intensity due to the ³⁵Cl and ³⁷Cl isotopes (*I* = 3/2) with *J*_{35ClF} = 340 Hz, *J*_{37ClF} = 283 Hz, and *J*_{35ClF}/*J*_{37ClF} = 1.201.

The vibrational spectra of $\text{ClF}_6^+\text{AsF}_6^-$ are shown in Figure 1, together with a listing of the observed frequencies and assignments for the two ions in point group O_h . The only band not marked in Figure 1 is the weak Raman band at 706 cm⁻¹, which can be assigned to $2\nu_6$ ($A_{1g} + E_g + F_{1g} + F_{2g}$) of ClF_6^+ being in Fermi resonance with ν_1 (A_{1g}) at 688 cm⁻¹. The value of 353 cm⁻¹ thus obtained for the infrared and Raman-inactive ν_6 (F_{2u}) mode is in excellent agreement with the value of 347 cm⁻¹ reported for the isoelectronic SF_6 molecule.³⁶ The frequencies for ClF_6^+ in its SbF_6^- salt were within experimental error identical with those of the AsF_6^- salt and therefore are not listed separately. These vibrational spectra confirm our previous assignments⁵ for ClF_6^+ , which had to be made for

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Table II. Symmetry and Valence Force Constants (mdyn/Å) of ClF_6^+ Compared to Those of BrF_6^+ , IF_6^+ , SF_6 , SeF_6 , and TeF_6

assignt (O_h)	$^{35}\text{ClF}_6^+$ freq. cm^{-1}	force constants	ClF_6^+ (AII) ^a	SF_6 (AII) ^b	SF_6 (HF) ^c	BrF_6^+ ^d	SeF_6 ^e	IF_6^+ ^d	TeF_6 ^f	
Symmetry Force Constants										
A_{1g}	ν_1	688	$F_{11} = f_r + 4f_{rr} + f_{rr'}$	5.298	6.70	6.845	4.88	5.61	5.61	5.50
E_g	ν_2	631	$F_{22} = f_r - 2f_{rr} + f_{rr'}$	4.456	4.61	4.715	5.02	4.85	6.00	5.08
T_{1u}	ν_3	894	$F_{33} = f_r - f_{rr'}$	5.200	5.30	5.465	4.82	4.93	5.23	4.98
	ν_4	590	$F_{44} = f_\alpha + 2f_{\alpha\alpha} - 2f_{\alpha\alpha''} - f_{\alpha\alpha'''} - 2(f_{r\alpha} - f_{r\alpha''})$	0.957	1.034	1.051	0.63	0.646	0.45	0.40
			$F_{34} = 2(f_{r\alpha} - f_{r\alpha''})$	0.935	0.90	0.907	0.41	0.46	0.21	0.24
T_{2g}	ν_5	517	$F_{55} = f_\alpha - 2f_{\alpha\alpha'} + f_{\alpha\alpha''}$	0.748	0.765	0.780	0.46	0.453	0.32	0.27
T_{2u}	ν_6	347	$F_{66} = f_\alpha - 2f_{\alpha\alpha} + 2f_{\alpha\alpha''} - f_{\alpha\alpha''}$	0.574	0.670	0.693		0.389		0.22
Valence Force Constants										
			f_r	4.968	5.30	5.445	4.90	5.02	5.42	5.10
			f_{rr} (adjacent bonds)	0.140	0.348	0.355	-0.03	0.13	-0.07	0.07
			$f_{rr'}$ (opposite bonds)	-0.232	0.003	-0.020	0.08	0.09	0.19	0.12
			$f_\alpha - f_{\alpha\alpha'}$ ($\approx f_\alpha$)	0.782	0.809	0.826		0.49		0.30
			$f_\alpha - f_{\alpha\alpha''}$	0.816	0.852	0.872		0.52		0.31
			$f_{r\alpha} - f_{r\alpha''}$	0.468	0.45	0.454	0.21	0.23	0.11	0.12

^a Using observed frequencies and a ^{35}Cl - ^{37}Cl isotopic shift of 13.1 cm^{-1} for ν_3 . PFD for F_{11} , ν_3 , 1.21 (3), 0.24 (4), -0.46 (3, 4); ν_4 , 0.98 (4), 0.02 (3, 4). ^b Using observed frequencies. ^c Using harmonic frequencies. ^d Modified valence force field values from ref. 16, assuming $F_{44} = \text{minimum}$. ^e Data from ref. 37. ^f Data from ref. 38.

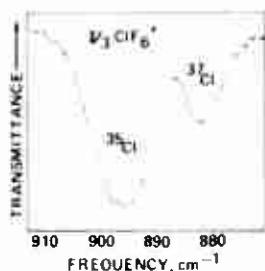


Figure 2. Infrared spectrum of the ν_3 (F_{1u}) band of ClF_6^+ in solid ClF_6SbF_6 recorded with 20-fold scale expansion under higher resolution conditions.

rather complex mixtures and therefore were somewhat tentative. Furthermore, the fact that both ClF_6^+ and AsF_6^- show no detectable deviations from the O_h selection rules suggests little or no ion interaction or distortion in $\text{ClF}_6^+\text{AsF}_6^-$, as expected for these coordinatively saturated ions. The structure of ClF_6AsF_6 can be visualized as a closest fluoride packing with Cl and As occupying some of the interstices in the lattice.

Under higher resolution conditions, the infrared spectra of ClF_6AsF_6 and ClF_6SbF_6 showed a splitting of the ν_3 (F_{1u}) band into two components (see Figure 2). These splittings are due to the ^{35}Cl and ^{37}Cl isotopes, which have a natural abundance of 75.4 and 24.6%, respectively. From a series of measurements the chlorine isotopic shifts for ν_3 (F_{1u}) of ClF_6^+ were found to be $12.8 \pm 0.3 \text{ cm}^{-1}$ for ClF_6AsF_6 and $13.4 \pm 0.3 \text{ cm}^{-1}$ for ClF_6SbF_6 . On the basis of these data, a value of $13.1 \pm 0.3 \text{ cm}^{-1}$ was used for the force field computation of ClF_6^+ .

General Valence Force Field of ClF_6^+ . Modified valence force fields (MVFF) have previously been reported for IF_6^+ ,³³ BrF_6^+ ,¹⁶ and ClF_6^+ ^{5,16} by using for the underdetermined F_{1u} block (two frequencies; three symmetry force constants) the mathematical constraint $F_{44} = \text{minimum}$. A test of this constraint for the isoelectronic series TeF_6 , SeF_6 , and SF_6 for which fully determined general valence force fields (GVFF) are known³⁶⁻³⁸ showed that $F_{44} = \text{minimum}$ is a good approximation for TeF_6 and SeF_6 .¹⁶ However, for the lighter SF_6 , which is isoelectronic with ClF_6^+ , this approximation did not duplicate the GVFF values³⁶ very well. Therefore, for ClF_6^+ a second force field based on a transfer of the f_{rr} value of the GVFF of SF_6 to ClF_6^+ was preferred.⁵ In the resulting force field, however, the value of the Cl-F stretching force

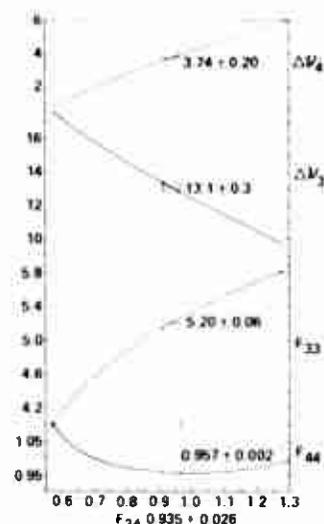


Figure 3. Solution range of the F_{1u} block symmetry force constants (mdyn/Å) of ClF_6^+ with the observed chlorine isotopic shift ($13.1 \pm 0.3 \text{ cm}^{-1}$) as a constraint. The horizontal and the broken vertical lines indicate the preferred values and their uncertainties, respectively.

constant (4.68 mdyn/Å)⁵ was smaller than that found for ClF_2^+ (4.7 mdyn/Å),³⁹ a surprising result in view of the general trends observed for a large number of halogen fluorides.⁴⁰

The observation of the chlorine isotopic shift for ν_3 (F_{1u}) of ClF_6^+ in this study provided the additional data point required for the computation of a GVFF for ClF_6^+ . The force field was computed by a previously described method⁴¹ using the $^{35}\text{ClF}_6^+$ frequencies given in Table II and a ^{35}Cl - ^{37}Cl isotopic shift of $13.1 \pm 0.3 \text{ cm}^{-1}$ for ν_3 (F_{1u}). In the absence of anharmonicity constants, the observed frequencies were used for the calculation of an anharmonic GVFF. On the basis of comparison between the anharmonic and the harmonic GVFF of isoelectronic SF_6 (see Table II),³⁶ the anharmonicity cor-

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(42) The compound claimed to be $\text{ClF}_6^+\text{CuF}_4^-$ has in the meantime been identified as $[\text{Cu}(\text{H}_2\text{O})_6][\text{SiF}_6]$ (von Schnering, H. G.; Vu, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 408).

(37) Königer, F.; Müller, A.; Selig, H. *Mol. Phys.* **1977**, *34*, 1629.

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rections should have only a minor influence on the force field.

To obtain an estimate for the uncertainties of the F_{10} force constants of ClF_6^+ , the relevant parts of the F_{33} and F_{44} ellipses of ClF_6^+ and the corresponding ^{35}Cl - ^{37}Cl isotopic shifts of ν_3 and ν_4 were computed as a function of F_{34} . As can be seen from Figure 3, the resulting uncertainties in the force constants are very small and the force field of ClF_6^+ is rather well determined.

A comparison of the GVFF of ClF_6^+ (see Figure 3 and Table II) with the two previously published modified valence force fields^{5,16} shows that $F_{44} = \text{minimum}$ is a much better constraint than the transfer of the f_{rr} value from SF_6 to ClF_6^+ . Also, the resulting Cl-F stretching force constant value of 4.97 mdyne/Å for ClF_6^+ is, as expected for a perfluoro cation in its highest oxidation state,⁴⁰ the highest value found to date for a Cl-F bond and agrees with the good thermal stability found for these ClF_6^+ salts. A comparison of the ClF_6^+ force field with those of BrF_6^+ ¹⁶ and IF_6^+ ³³ (see Table II) shows the expected trends.⁴⁰ The stretching force constant drops slightly from ClF_6^+ to BrF_6^+ and then markedly increases for IF_6^+ . The deformation constants decrease from ClF_6^+ toward IF_6^+ , as expected from the increase in bond lengths. The stretch-stretch interaction constants f_{rr} and $f_{rr'}$ show smooth trends from ClF_6^+ toward IF_6^+ , similar to those observed for the isoelectronic SF_6 , SeF_6 , TeF_6 series, although the relative contributions from f_{rr} and $f_{rr'}$ are different within each series.

A comparison of the GVFF of ClF_6^+ with that of SF_6 (see Table II)¹⁶ also shows excellent agreement, except for the above noted difference in the relative contribution from f_{rr} and $f_{rr'}$.

Conclusion. The KrF^+ cation is capable of oxidizing ClF_5 to ClF_6^+ and provides a method for the synthesis of pure ClF_6^+ salts. Thus, KrF^+ is the first oxidative fluorinator capable of producing all three of the presently known coordinatively saturated complex fluoro cations, NF_4^+ , BrF_6^+ , and ClF_6^+ . The synthesis of pure $\text{ClF}_6^+\text{AsF}_6^-$ permitted a better characterization of the ClF_6^+ cation and the determination of a general valence force field for ClF_6^+ . The Cl-F bond in ClF_6^+ (4.97 mdyne/Å) is the strongest Cl-F bond presently known, suggesting highly covalent bonds with sp^3d^2 hybridization of the valence electrons of chlorine. By analogy with the known NF_4^+ chemistry, the existence of numerous stable ClF_6^+ salts is predicted.

Acknowledgment. The authors are grateful to Drs. C. J. Schack and L. R. Grant for helpful discussions, to R. D. Wilson for his help with the preparation of KrF_2 , and to the Office of Naval Research and the Army Research Office of financial support.

Registry No. $\text{ClF}_6^+\text{AsF}_6^-$, 86527-33-5; $\text{ClF}_6^+\text{SbF}_6^-$, 86527-34-6; ClF_6^+ , 38217-33-3; KrF_2 , 13773-81-4; AsF_5 , 7784-36-3; ClF_5 , 13637-63-3; SbF_5 , 7783-70-2.

APPENDIX B

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Contribution from Rocketdyne, A Division of
 Rockwell International, Canoga Park, California 91304

Synthesis and Properties of ClF_6BF_4

Karl O. Christie* and William W. Wilson

Received January 11, 1983

The only ClF_6^+ salts presently known are ClF_6PtF_6 ,¹⁻³ ClF_6SbF_6 , and ClF_6AsF_6 .⁴ To improve the energy content of ClF_6^+ salts, replacement of these relatively heavy nonenergetic MF_6^- (M = Pt, Sb, As) anions by a lighter one such as BF_4^- is desirable. Attempts in our laboratory failed to synthesize ClF_6BF_4 by direct methods such as those used for the preparation of ClF_6MF_6 salts.⁴ Consequently, indirect methods were sought to exchange the anion in $\text{ClF}_6^+\text{MF}_6^-$ for BF_4^- . Using low-temperature metathetical techniques, previously developed for NF_4^+ salts,⁵ we have successfully converted ClF_6AsF_6 to ClF_6BF_4 .

Experimental Section

Materials and Apparatus. ClF_6AsF_6 and CsBF_4 were prepared by known methods. The HF (Matheson Co.) was dried by storage over BF_3 . Volatile materials were handled in a Teflon-FEP stainless steel vacuum line that was well passivated with ClF_3 and treated with HF prior to use. Nonvolatile materials were handled in the dry-nitrogen atmosphere of a glovebox. The metathesis was carried out in a previously described double-U-tube filter apparatus.⁷ The thermal decomposition of ClF_6BF_4 was studied in a previously described sapphire apparatus.⁸

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer that was calibrated by comparison with standard gas calibration points.^{9,10} Gas spectra were recorded with a Teflon cell of 5-cm path length equipped with AgCl windows. Spectra of solids were recorded as dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co.). Raman spectra were recorded on a Cary Model 83 spectrophotometer with use of the 4880-Å exciting line of an Ar-ion laser and a Claassen filter¹¹ for the elimination of plasma lines. Sealed glass or quartz tubes were used as sample containers.

Synthesis of ClF_6BF_4 . A mixture of ClF_6AsF_6 (0.5175 mmol) and CsBF_4 (0.5171 mmol) was loaded into the double-U-tube metathesis apparatus in the drybox. Dry HF (42 mmol) was condensed at -196°C into the apparatus on the vacuum line, and the mixture was warmed for 30 min to 25°C with stirring. The apparatus was cooled to -78°C and inverted, and the solid and liquid phases were separated by filtration assisted by 2 atm of dry N_2 gas. The material volatile at 25°C was pumped off for 1.5 h and separated by fractional con-

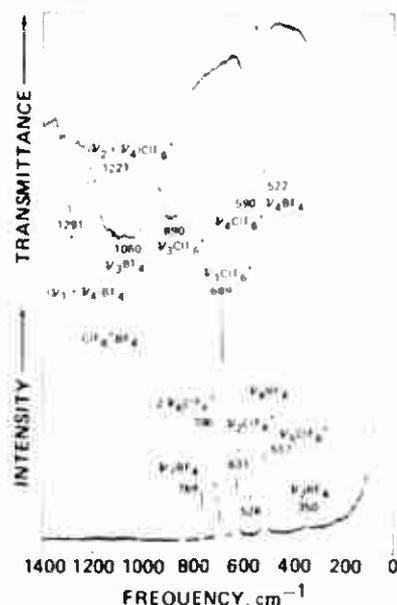
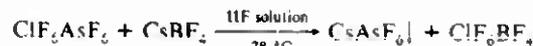


Figure 1. Infrared and Raman spectra of solid ClF_6BF_4 recorded at ambient temperature. The broken line in the infrared spectrum is due to absorption by the AgCl window material. The assignments for ClF_6^+ and BF_4^- are for point groups O_h and T_d , respectively.

densation through a series of traps kept at -112 , -142 , and -196°C . It consisted of BF_3 (~ 0.08 mmol), ClF_5 (~ 0.08 mmol), and the bulk of the HF solvent. The filter cake (199.6 mg, weight calculated for 0.517 mmol of CsAsF_6 166.5 mg) was shown by vibrational spectroscopy to consist of mainly CsAsF_6 containing small amounts of ClF_6^+ and BF_4^- . The filtrate residue (67.4 mg, weight calculated for 0.517 mmol of ClF_6BF_4 122.1 mg, corresponding to a 55% yield) was shown by vibrational spectroscopy to consist mainly of ClF_6BF_4 containing a small amount of AsF_6^- salts as impurities. The losses of ClF_6BF_4 can be attributed to hang-up of ClF_6BF_4 on the filter cake (27%) and some reduction of ClF_6BF_4 (16%).

Results and Discussion

Synthesis and Properties of ClF_6BF_4 . The successful synthesis of ClF_6BF_4 according to



demonstrates that the metathetical process previously developed for the indirect synthesis of NF_4^+ salts⁵ is transferable to ClF_6^+ salts. The yield of only 55% for ClF_6BF_4 can be attributed to the following factors: (i) hang-up of some mother liquor on the filter cake; (ii) possibly, the use of an insufficient amount of solvent causing precipitation of some ClF_6BF_4 ; (iii) reduction of some ClF_6BF_4 to ClF_5 and BF_3 by attack of metal parts of the apparatus by this strongly oxidizing HF solution. No attempts have been made as yet to maximize the yield by varying or eliminating any of these conditions.

ClF_6BF_4 is a white crystalline solid that is highly soluble in anhydrous HF. It is stable at room temperature and starts to slowly decompose under a dynamic vacuum at about 70°C according to



The nature of the decomposition products was established by their infrared spectra, which showed only the absorptions characteristic for BF_3 and ClF_5 . An exhaustive vacuum py-

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rolysis of ClF_6BF_4 was carried out at 110°C and resulted in only a small amount of a solid residue, which was identified by Raman spectroscopy as CsAsF_6 .

The presence of octahedral ClF_6^+ and tetrahedral BF_4^- ions in ClF_6BF_4 was established by infrared and Raman spectroscopy. The spectra together with the observed frequencies and assignments for ClF_6^+ and BF_4^- in point groups O_h and T_d , respectively, are shown in Figure 1. The spectra confirm our previous assignments for ClF_6AsF_6 , where ν_1 of ClF_6^+ and ν_1 of AsF_6^- had almost identical frequencies and had to be assigned on the basis of their relative intensities.⁴ The frequencies and assignments for BF_4^- in ClF_6BF_4 closely correspond to those in NE_4BF_4 .¹²

Conclusion. The successful synthesis of ClF_6BF_4 and its relatively good thermal stability confirm the previous prediction of unusual stability for salts containing coordinatively saturated cations.⁴ However, as expected, the thermal stability of ClF_6^+ salts is inferior to that of NE_4^+ salts.⁸

Acknowledgment. The authors are grateful to C. J. Schack, L. R. Grant, and R. D. Wilson for their help and to the Office of Naval Research and the Army Research Office for financial support.

Registry No. ClF_6BF_4 , 85662-38-0.

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APPENDIX C

SOME INTERESTING OBSERVATIONS IN CHLORINE OXYFLUORIDE CHEMISTRY

KARL O. CHRISTE AND WILLIAM W. WILSON

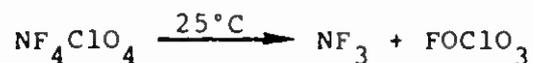
Rocketdyne, A Division of Rockwell International Corporation,
Canoga Park, California 91304 (U.S.A.)

SUMMARY

A new synthesis of FOClO_3 was discovered involving the fluorination of ClO_4^- with ClF_6^+ . An unexpected oxygen abstraction from ClF_4O^- was observed when CsClF_4O was reacted with FOSO_2F .

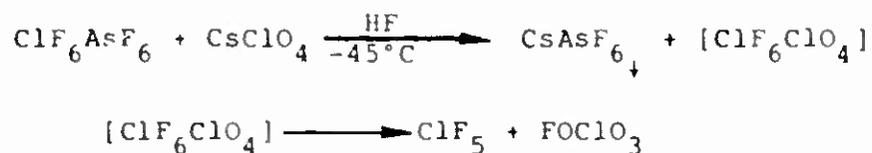
INTRODUCTION

We would like to report two interesting reactions observed during our studies in the area of chlorine oxyfluorides. The first reaction involved the low-temperature metathesis of ClF_6AsF_6 with CsClO_4 in anhydrous HF solution. In view of the known NF_4^+ reaction [1]



it was interesting to study whether ClF_6^+ is also capable of

oxidizing ClO_4^- to FOClO_3 . The thermal stability of ClF_6ClO_4 was found to be lower than that of NF_4ClO_4 [1] and did not permit the isolation of solid ClF_6ClO_4 even at temperatures as low as -45°C . However, the corresponding decomposition products FOClO_3 and ClF_5 , were observed in good yield.



Although this presents an alternative synthetic path to FOClO_3 , the NF_4^+ reaction is preferred from a synthetic point of view since the NF_4SbF_6 starting material is more readily accessible [2].

The second reaction involved CsClF_4O and FOSO_2F . Fluorine fluorosulfate is known to be a useful reagent for the synthesis of hypofluorites [3], such as

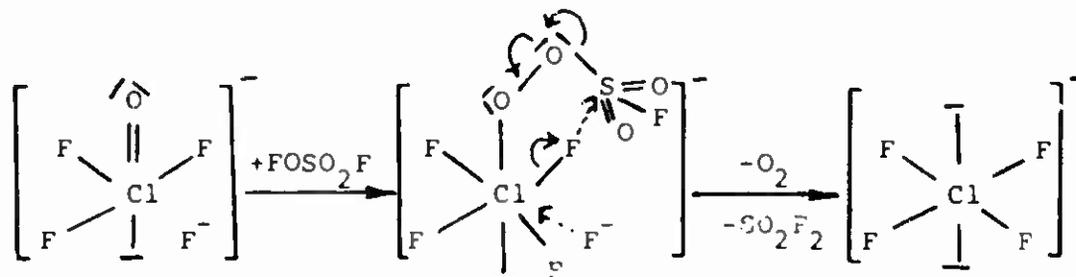


For CsClF_4O , however, the major reaction was not the formation of either the unknown ClF_4OF or its expected decomposition products, but oxygen abstraction accompanied by SO_2F_2 elimination according to the following reaction.



This unexpected reaction path might be rationalized in terms of an addition of FOSO_2F to the $\text{Cl}=\text{O}$ bond in one of the favored resonance structures of ClF_4O^- [4], followed by an intramolecular

nucleophilic substitution (S_N^1) reaction accompanied by O_2 and SO_2F_2 elimination:



To our knowledge, this is the first example of a reaction in which $FOSO_2F$ acts as a deoxygenating agent.

EXPERIMENTAL

Apparatus. Volatile materials were handled in a stainless steel-Teflon FEP vacuum line [5]. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution using a previously described apparatus [6].

Infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer. Spectra of solids were obtained using dry powders pressed between AgCl windows. Spectra of gases were obtained by using a Teflon cell of 5 cm path length equipped with AgCl windows. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar-ion laser.

Materials. Literature methods were used for the syntheses of ClF_6AsF_6 [7], $CsClF_4O$ [8] and $FOSO_2F$ [9] and for the drying of

the HF solvent [10]. The CsClO_4 (ROC/RIC) was used as received.

Reaction of ClF_6AsF_6 with CsClO_4 . In the drybox ClF_6AsF_6 (0.318 mmol) and CsClO_4 (0.304 mmol) were placed into the bottom U-tube of the metathesis apparatus [6]. On the vacuum line, dry HF (1.1 ml of liquid) was added at -78°C . The resulting mixture was agitated at -45°C for 1.5 hr and then filtered at -78°C through a porous Teflon filter while the filtrate was collected at -45°C . All material volatile at -45° was pumped off for 2.5 hr and separated by fractional condensation through a series of traps kept at -126 , -142 and -196°C . The -126° trap contained the HF solvent and a small amount of FCLO_2 , the -142° trap contained a mixture of FOClO_3 and ClF_5 (0.445 mmol), and the -196° trap contained FCLO_3 (0.128 mmol). Essentially no filtrate residue was left behind. The white solid filter cake (106 mg, weight calcd for 0.304 mmol of CsAsF_6 98 mg) was identified by infrared and Raman spectroscopy as CsAsF_6 . The FCLO_3 formed in the above reaction is attributed to decomposition of a small amount of FOClO_3 . For a larger scale reaction, the percentage of FCLO_3 in the product is expected to decrease significantly.

Caution! Fluorine perchlorate is highly shock sensitive [11] and proper safety precautions must be taken when working with this material.

Reaction of CsClF_4O with FOSO_2F . In the dry box CsClF_4O (2.24 mmol) was placed into a 10 ml stainless steel cylinder. On the vacuum line FOSO_2F (4.97 mmol) was added to the cylinder at -196°C . The cylinder was kept at 0°C for 3 days, then cooled

to -196°C . Oxygen (2.23 mmol) was pumped off at -196°C , and all material volatile at ambient temperature was separated by fractional condensation through traps kept at -112 , -142 , and -196°C . The -112° trap contained small amounts of ClF_3O , FClO_2 and ClF_3 . The -142° trap contained FOSO_2F (2.6 mmol) and SO_2F_2 (1.7 mmol), and the -196° trap showed SO_2F_2 (0.52 mmol). The white solid residue showed a weight loss of 39 mg (calcd weight loss for 1.12 mmol of O_2 36 mg) and was identified by infrared and Raman spectroscopy as CsClF_4 [12] containing a small amount of CsSO_3F .

ACKNOWLEDGEMENTS

The authors are grateful to Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson for their help and to the Army Research Office and the Office of Naval Research for financial support.

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SYNTHESES OF NF_4^+ SALTS DERIVED FROM THE LEWIS ACIDS AlF_3 AND BeF_2

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SUMMARY

The new salts $\text{NF}_4\text{Be}_2\text{F}_5$ and NF_4AlF_4 were prepared from concentrated NF_4HF_2 solutions and BeF_2 and AlF_3 respectively.

INTRODUCTION

Salts containing the NF_4^+ cation are of significant practical interest for high detonation pressure explosives [1] or solid-propellant $\text{NF}_3\text{-F}_2$ gas generators for chemical lasers [2]. For these applications, it is desirable to maximize the usable fluorine content, expressed as weight percent of fluorine available as F_2 or NF_3 upon thermal decomposition of the salt. Optimization of the usable fluorine content is best achieved by the selection of an anion which is as light as possible, is multiply charged and, if possible, is itself an oxidizer capable of fluorine evolution. Of the presently known NF_4^+ salts, $(\text{NF}_4)_2\text{NiF}_6$ (64.6%), $(\text{NF}_4)_2\text{MnF}_6$ (59.9%), $(\text{NF}_4)_2\text{SiF}_6$ (59.0%), $(\text{NF}_4)_2\text{TiF}_6$ (55.6%) and NF_4BF_4 (53.7%) have the highest usable fluorine contents. Theoretically, a further increase in the usable fluorine content of NF_4^+ salts should be possible by the use of the very light and multiply charged anions, BeF_4^{2-} and AlF_6^{3-} . Their NF_4^+ salts would have a usable fluorine content of 71.7 and 69.3 percent, respectively. In this paper, we report on the syntheses of NF_4^+ salts containing anions derived from BeF_2 and AlF_3 .

Preparation of $\text{NF}_4\text{Be}_2\text{F}_5$ Dry CsF (30.34 mmol) and NF_4SbF_6 (30.47 mmol) were loaded in the drybox into one half of a prepassivated Teflon double-U metathesis apparatus. Dry HF (20 ml) was added on the vacuum line and the mixture was stirred with a Teflon coated magnetic stirring bar for 15 minutes at 25°C. After cooling the apparatus to -78°C, it was inverted, and the NF_4HF_2 solution was filtered into the other half of the apparatus which contained 12.14 mmol of BeF_2 . The mixture was stirred for 65 hours at 25°C, followed by removal of most of the HF until the onset of NF_4HF_2 decomposition became noticeable. The concentrated mixture was stirred at 25°C for 14 hours and a clear, colorless solution resulted. All volatile materials were pumped off at 55°C for 15 hours, leaving behind a white solid (1.448g, 97% yield based on BeF_2) which, based on its elemental analysis, had the following composition (weight %): $\text{NF}_4\text{BeF}_3 \cdot 1.06\text{BeF}_2$, 84.06; NF_4SbF_6 , 11.23; CsSbF_6 4.71. Anal. Calcd: NF_3 , 31.45; Be, 7.58; Cs, 1.70; Sb, 5.75. Found: NF_3 , 31.43; Be, 7.58; Cs, 1.69; Sb, 5.74.

Preparation of NF_4AlF_4 Freshly prepared AlF_3 (0.469g, 5.58 mmol) was combined with NF_4HF_2 (generated as described above from 33.8 mmol of NF_4SbF_6) in 35 ml of HF. The mixture was stirred at 25°C for 1 hour, then most of the HF solvent was pumped off until incipient decomposition of NF_4HF_2 became noticeable. After stirring for 2 hours at 25°C, this concentrated mixture turned into a clear solution. The remaining HF solvent and the excess of NF_4HF_2 were removed at 55°C for 40 hours in a dynamic vacuum. The weight (1.257g) of the solid white residue agreed with that expected for 5.58 mmol of NF_4AlF_4 (1.077g) containing, as in the case of the analogous $\text{NF}_4\text{Be}_2\text{F}_5$ preparation, about 17 weight % of NF_4SbF_6 and CsSbF_6 . The presence of these ions was confirmed by vibrational spectroscopy which also demonstrated the absence of any unreacted NF_4HF_2 .

RESULTS AND DISCUSSION

The syntheses of $(\text{HF}_4)_2\text{BeF}_4$ and $(\text{NF}_4)_3\text{AlF}_6$ by direct methods involving NF_3 , F_2 and the corresponding Lewis acid in the presence of an activation energy source [9] is not possible because BeF_2 and AlF_3 are nonvolatile polymeric solids. Simple metatheses



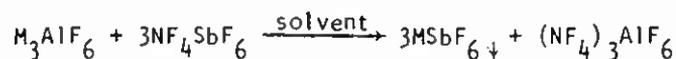
were also investigated where M was either Cs or Na and the solvents were either BrF_5 at 25°C, HF at -78°C or molten NF_4SbF_6 at 275°C under 1000 psi

Preparation of $\text{NF}_4\text{Be}_2\text{F}_5$ Dry CsF (30.34 mmol) and NF_4SbF_6 (30.47 mmol) were loaded in the drybox into one half of a prepassivated Teflon double-U metathesis apparatus. Dry HF (20 ml) was added on the vacuum line and the mixture was stirred with a Teflon coated magnetic stirring bar for 15 minutes at 25°C . After cooling the apparatus to -78°C , it was inverted, and the NF_4HF_2 solution was filtered into the other half of the apparatus which contained 12.14 mmol of BeF_2 . The mixture was stirred for 65 hours at 25°C , followed by removal of most of the HF until the onset of NF_4HF_2 decomposition became noticeable. The concentrated mixture was stirred at 25°C for 14 hours and a clear, colorless solution resulted. All volatile materials were pumped off at 55°C for 15 hours, leaving behind a white solid (1.448g, 97% yield based on BeF_2) which, based on its elemental analysis, had the following composition (weight %): $\text{NF}_4\text{BeF}_3 \cdot 1.06\text{BeF}_2$, 84.06; NF_4SbF_6 , 11.23; CsSbF_6 4.71. Anal. Calcd: NF_3 , 31.45; Be, 7.58; Cs, 1.70; Sb, 5.75. Found: NF_3 , 31.43; Be, 7.58; Cs, 1.69; Sb, 5.74.

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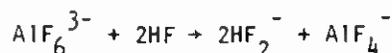
RESULTS AND DISCUSSION

The syntheses of $(\text{NF}_4)_2\text{BeF}_4$ and $(\text{NF}_4)_3\text{AlF}_6$ by direct methods involving NF_3 , F_2 and the corresponding Lewis acid in the presence of an activation energy source [9] is not possible because BeF_2 and AlF_3 are nonvolatile polymeric solids. Simple metatheses



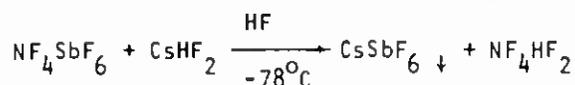
were also investigated where M was either Cs or Na and the solvents were either BrF_5 at 25°C , HF at -78°C or molten NF_4SbF_6 at 275°C under 1000 psi

NF₃ and F₂ pressure. In all cases, no evidence for (NF₄)₃AlF₆ was obtained, probably because the AlF₆³⁻ and BeF₄²⁻ anions are very strong Lewis bases which undergo rapid solvolysis, such as

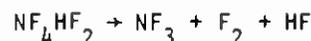


This metathetical approach was further complicated by the fact that the AlF₄⁻ salts appear to be quite insoluble and therefore cannot be separated from the highly insoluble alkali metal SbF₆⁻ salts. Since previous studies in our laboratory had demonstrated that these solubility and separation problems can be overcome by digesting a polymeric insoluble Lewis acid, such as UOF₄ [10] or WOF₄ [11], in a large excess of a highly concentrated NF₄HF₂ solution, this approach was also applied to AlF₃ and BeF₂.

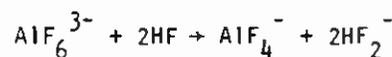
The concentrated solutions of NF₄HF₂ in HF were prepared according to



followed by its addition to either AlF₃ or BeF₂. After digesting these mixtures at 25°C until clear solutions were obtained, the excess of unreacted NF₄HF₂, which in the absence of a solvent is unstable at 25°C, was decomposed at 55°C



and pumped off. Based on the observed material balances and spectroscopic and elemental analyses, the solid residues consisted of mainly NF₄Be₂F₅ and NF₄AlF₄ with some NF₄SbF₆ and CsSbF₆ as the expected impurities. Attempts to purify NF₄AlF₄ by recrystallization or extraction with HF were unsuccessful due to the low solubilities of the salts involved and due to solvolysis. It appears that the presence of a high HF₂⁻ ion concentration is required to diminish the acidity of the HF solvent and to suppress the solvolyses of the strong Lewis bases AlF₆³⁻, AlF₄⁻ or BeF₄²⁻. The fact that at the end of the digestion periods of AlF₃ or BeF₂ in HF solutions of NF₄HF₂ clear solutions were obtained, while NF₄AlF₄ and NF₄Be₂F₅ appear to possess only limited solubilities in HF, suggests the possibility that, in the presence of a large excess of HF₂⁻, either AlF₆³⁻ or BeF₄²⁻ might exist in these solutions. Obviously, an excess of HF₂⁻ should suppress the following solvolysis reactions



Unfortunately the nature of the complex fluoro anions in these solutions could not be established because these anions are inherently poor Raman scatterers. Nor do they result in separate ^{19}F NMR signals due to rapid exchange with the HF solvent.

Although the above described experiments did not permit the isolation of either $(\text{NF}_4)_3\text{AlF}_6$ or $(\text{NF}_4)_2\text{BeF}_4$, they resulted in the syntheses of the new salts $\text{NF}_4\text{Be}_2\text{F}_5$ and NF_4AlF_4 . The existence of the Be_2F_5^- anion is well known, and the infrared spectrum observed for $\text{NF}_4\text{Be}_2\text{F}_5$ (see Figure 1) confirms the presence of Be_2F_5^- [12]. Due to the poor scattering by the anion, the Raman spectrum of $\text{NF}_4\text{Be}_2\text{F}_5$ (see Figure 1) is dominated by the NF_4^+ lines. These lines are in excellent agreement with a tetrahedral NF_4^+ cation exhibiting splittings into the degenerate components of each mode due to site symmetry lowering or slight distortion of the cation. The assignments for NF_4^+ agree well with our previous observations [13] and are summarized in Table I.

The results of this study demonstrates that, in principle, the synthesis of NF_4^+ salts containing complex fluoro anions derived from either AlF_3

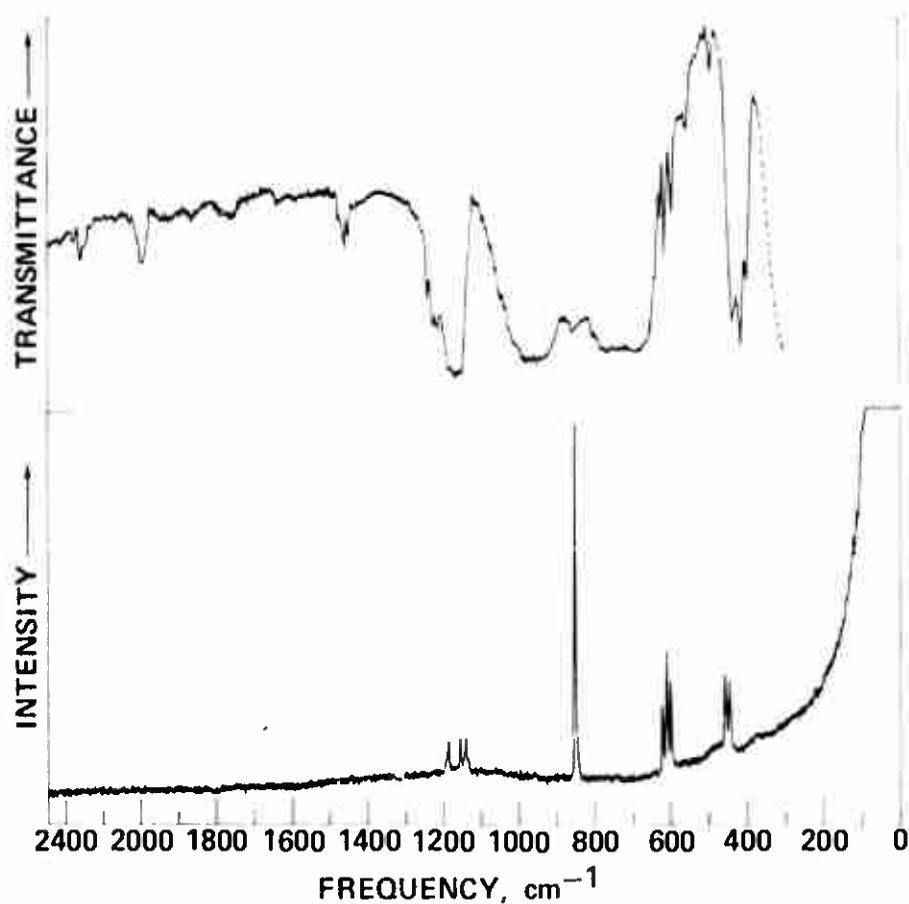


Fig. 1. Infrared and Raman Spectrum of Solid $\text{NF}_4\text{Be}_2\text{F}_5$

or BeF_2 is possible. However, the isolation of NF_4^+ salts containing the strongly basic AlF_6^{3-} or BeF_4^{2-} anions remains a challenge for the synthetic fluorine chemist.

TABLE I

Vibrational Spectra of $\text{NF}_4\text{Be}_2\text{F}_5$

Obsd freq, cm^{-1} and rel. intens.		Assignment for NF_4^+ in point group T_d
IR	Ra	
2310 vw		$2\nu_3 (A_1 + E + F_2)$
1995 w		$\nu_1 + \nu_3 (F_2)$
1455 } w		$\nu_1 + \nu_4 (F_2)$
1444 }		
1234 } mw		$2\nu_4 (A_1 + E + F_2)$
1220 }		
1210 }		
1185 sh } 1189 (1.0) }		$\nu_3 (F_2)$
1160 vs } 1158 (1.0) }		
1145 sh } 1141 (1.0) }		
955 s, br	851 (10)	Be_2F_5^- $\nu_1 (A_1)$
765 ms, br } 690 ms, br }		Be_2F_5^-
623 mw } 621 (1.9) }		$\nu_4 (F_2)$
611 m } 610 (3.3) }		
597 mw } 599 (2.4) }		
558 vw		
498 vw	458 (2.2) }	$\nu_2 (E)$
	447 (2.1) }	
436 m } 416 ms }		Be_2F_5^-
400 mw }		

ACKNOWLEDGEMENTS

The authors are grateful to Mr. R. D. Wilson and Dr. L. R. Grant for their help and to the Office of Naval Research and the Army Research Office for financial support.

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APPENDIX E

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Perfluoroammonium Salts of Metal Heptafluoride Anions

William W. Wilson and Karl O. Christe*

Received October 21, 1981

Due to its high-energy content and unusual kinetic stability, the NF_4^+ cation is a unique oxidizer. Its salts have found numerous applications such as solid propellant $\text{NF}_3\text{-F}_2$ gas generators for chemical HF-DF lasers,¹ ingredients in high detonation pressure explosives,² and fluorinating agents for aromatic compounds.³ Although the NF_4^+ cation has successfully been combined with a large number of different anions in the form of stable salts, all these anions were derived from relatively strong Lewis acids, and their number of ligands did not exceed six. It was therefore of interest to explore whether NF_4^+ salts containing metal heptafluoride anions can exist.

Experimental Section

Apparatus. Volatile materials used in this work were handled in a stainless-steel-Teflon PTFE vacuum line. The line and other hardware

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used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry-nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution with an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.⁴ Thermal decomposition measurements were carried out in a previously described⁵ sapphire reactor.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows in an Econo press (Barnes Engineering Co). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of an Ar ion laser and Claassen filter⁶ for the elimination of plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

Elemental analyses were carried out as previously described.⁷

Materials. Literature methods were used for the syntheses of NF_4SbF_6 ⁸ and NF_4HF_2 solutions in HF.⁹ Hydrogen fluoride (Matheson) was dried by storage over BiF_3 to remove the H_2O ¹⁰ Tungsten hexafluoride (high purity, Alfa) and UF_6 (Allied) were used as received. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox.

Preparation of NF_4WF_7 . Dry CsF (15.0 mmol) and NF_4SbF_6 (15.0 mmol) were loaded in the drybox into half of a prepassivated Teflon double U metathesis apparatus. Dry HF (15 mL of liquid) was added on the vacuum line, and the mixture was stirred with a Teflon-coated magnetic stirring bar for 15 min at 25 °C. After the apparatus was cooled to -78 °C, it was inverted and the NF_4HF_2 solution was filtered into the other half of the apparatus. Tungsten hexafluoride (22.5 mmol) was condensed at -196 °C onto the NF_4HF_2 . The mixture was warmed to ambient temperature, and two immiscible liquid phases were observed. After 30 min of vigorous stirring at 25 °C, the lower WF_6 layer dissolved in the upper HF phase. Most of the volatile products were pumped off at ambient temperature until the onset of NF_4HF_2 decomposition became noticeable (NF_3 evolution). An additional 8.0 mmol of WF_6 was added at -196 °C to the residue. When the mixture was warmed to ambient temperature, a white solid product appeared in the form of a slurry. All material volatile at -31 °C was pumped off for 1 h and consisted of HF and some NF_3 . An additional 14.5 mmol of WF_6 was added to the residue, and the resulting mixture was kept at 25 °C for 14 h. All material volatile at -13 °C was pumped off for 2 h and consisted of HF and WF_6 . The residue was kept at 22 °C for 2.5 days, and pumping was resumed at -13 °C for 2.5 h and at 22 °C for 4 h. The volatiles, collected at -210 °C, consisted of some HF and small amounts of NF_3 and WF_6 . The white solid residue (5.138 g, 84% yield) was shown by vibrational and ¹⁹F NMR spectroscopy to consist mainly of NF_4WF_7 with small amounts of SbF_6^- as the only detectable impurity. On the basis of its elemental analysis, the product had the following composition (weight %): NF_4WF_7 , 98.39; CsSbF_6 , 1.61. Anal. Calcd: NF_3 , 17.17; W, 44.46; Cs, 0.58; Sb, 0.53. Found: NF_3 , 17.13; W, 44.49; Cs, 0.54; Sb, 0.55.

Preparation of NF_4UF_7 . A solution of NF_4HF_2 in anhydrous HF was prepared from CsF (14.12 mmol) and NF_4SbF_6 (14.19 mmol) in the same manner as described for NF_4WF_7 . Most of the HF solvent was pumped off on warmup from -78 °C toward ambient temperature until the onset of NF_4HF_2 decomposition became noticeable. Uranium hexafluoride (14.59 mmol) was condensed at -196 °C into the reactor, and the mixture was stirred at 25 °C for 20 h. The material volatile at 25 °C was briefly pumped off and separated by fractional con-

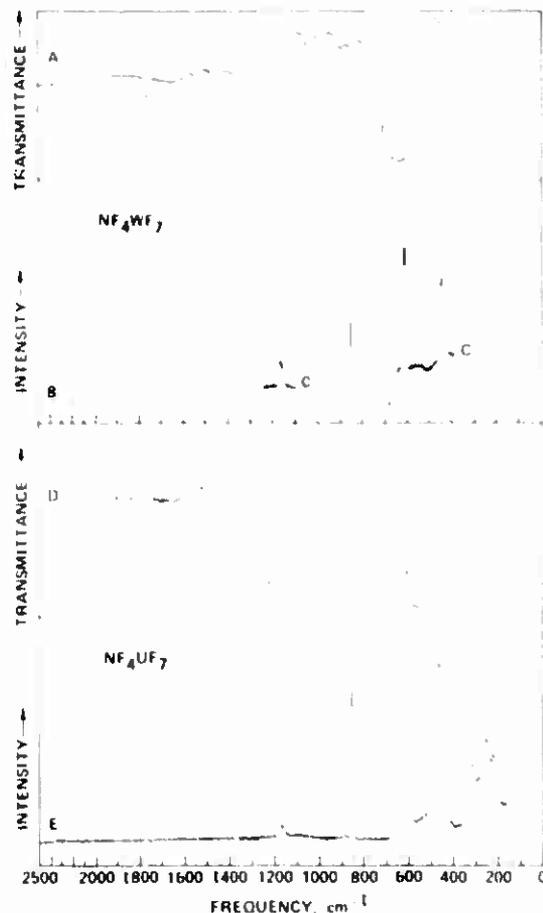


Figure 1. Vibrational spectra of solid NF_4WF_7 and NF_4UF_7 ; traces A and D, infrared spectra of the dry powders pressed between AgCl disks (the broken lines indicate absorption due to the AgCl window material); traces B, C, and E, Raman spectra recorded at different sensitivities and resolution.

densation through traps kept at -78, -126, and -210 °C. It consisted of HF (6.3 mmol), UF_6 (9.58 mmol), and a trace of NF_3 . Since the NF_4HF_2 solution had taken up only about one-third of the stoichiometric amount of UF_6 , the recovered UF_6 was condensed back into the reactor. The mixture was stirred at 25 °C for 12 h, and the volatile material was pumped off again and separated. It consisted of HF (12.8 mmol), UF_6 (1.7 mmol), and a trace of NF_3 . Continued pumping resulted in the evolution of only a small amount of UF_6 , but no NF_3 or HF, thus indicating the absence of any unreacted NF_4HF_2 . The pale yellow solid residue (5.711 g, 88% yield) was shown by vibrational and ¹⁹F NMR spectroscopy and elemental analysis to have the following composition (weight %): NF_4UF_7 , 97.47; NF_4SbF_6 , 1.50; CsSbF_6 , 1.03. Anal. Calcd: NF_3 , 15.34; U, 50.32; Sb, 0.90; Cs, 0.37. Found: NF_3 , 15.31; U, 50.2; Sb, 0.90; Cs, 0.37.

Results and Discussion

Synthesis of NF_4XF_7 Salts. The synthesis of NF_4XF_7 salts proved rather difficult because metal hexafluorides are weak Lewis acids and exhibit only a moderate tendency to form the energetically relatively unfavorable heptafluoro anions. Consequently, neither direct synthetic methods, based on the reaction of NF_3 with F_2 and a Lewis acid in the presence of an activation energy source,¹¹ nor indirect methods such as displacement reactions¹² or metathesis in anhydrous HF solution¹⁰ could be used. For example, anhydrous HF displaces UF_6 from NOUF_7 or CsUF_7 .¹³ However, in the course of

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Table 1. Vibrational Spectra of Solid NF_4WF_7 and NF_4UF_7

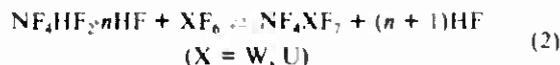
obsd freq, cm^{-1} (rel intens) ^a		obsd freq, cm^{-1} (rel intens) ^a		assign point group ^b	
NF_4WF_7		NF_4UF_7		NF_4^+ (T_d)	WF_6^- (D_{3h}) ^c
IR	Raman	IR	Raman		
2315 vw		2315 vw		$2\nu_1(A_1 + E + T_2)$	
2000 w		2001 w		$\nu_2 + \nu_3(T_2)$	
1760 vw		1760 vw		$\nu_4 + \nu_5(A_1 + E + T_2)$	
1456 w		1458 w		$\nu_6 + \nu_7(T_2)$	
1220 mw		1222 mw		$2\nu_8(A_1 + E + T_2)$	
1165 vs	1165 (0.3)	1165 vs	1164 (0.1)	$\nu_9(T_2)$	
	1155 sh			$\nu_{10} + \nu_{11}(E_1 + E_2)$	
1055 vw		1052 vw		$2\nu_{12}(A_1 + A_2 + E)$	
895 vw	890 (10+)	898 vw	885 (10+)	$\nu_{13}(A_1)$	
851 vw	849 (5.0)		851 (1.1)		
711 w	711 (10)	626 w	628 (10)		$\nu_{14}(A_1)$
630 vs, br		530 vs, br			$\nu_{15}(A_1), \nu_{16}(E_1)$
610 sh	614 (1.3)	610 m	613 (1.0) sh	$\nu_{17}(E_1)$	
	609 (2.0)			$\nu_{18}(E_1)$	
	446 (10.9)		457 (1.0)		
	441 (1.1)				
436 w	435 sh	460 sh	457 (1.0)		$\nu_{19}(E_1)$
	328 (0.3) br		311 (0.4)		$\nu_{20}(E_1)$
	285 sh		283 (0+)		$\nu_{21}(A_1)$
			249 (0.5)		
			225 (0+)		
			214 (0.3)		

^a Uncorrected Raman intensities. ^b Based on the splitting of the bands and the violations of the selection rules observed for some of the modes, the actual site symmetries of these ions are expected to be lower than T_d and D_{3h} . ^c Assignments used on ref 16.

a recent study in our laboratory a method for the preparation of $(\text{NF}_4)_2\text{SiF}_6$ was discovered¹⁴ in which equilibrium 1 was

$$2\text{NF}_4\text{HF}_2 + n\text{HF} + \text{SiF}_4 \rightleftharpoons (\text{NF}_4)_2\text{SiF}_6 + 2(n+1)\text{HF} \quad (1)$$

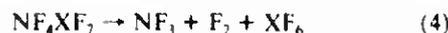
successfully shifted to the right by repeatedly treating a highly concentrated NF_4HF_2 -HF solution⁹ with an excess of SiF_4 while periodically stripping off the HF. This method has now been extended to the synthesis of NF_4WF_7 and NF_4UF_7 according to (2) and provided the first known examples of NF_4^+ salts containing complex anions with more than six ligands about their central atom.



The purity of the NF_4XF_7 salts prepared in this manner was about 98 weight % with CsSbF_6 and NF_4SbF_6 as the principal impurities. Product purification by recrystallization from HF solution was not possible due to equilibrium 2, which in the presence of a large excess of HF is shifted to the left. The yields of NF_4XF_7 were about 86%, on the basis of NF_4HF_2 , with most of the NF_4HF_2 values lost being due to hang up of some mother liquor on the CsSbF_6 filter cake during the metathetical preparation of NF_4HF_2 according to (3).



Physical Properties. NF_4WF_7 and NF_4UF_7 are white and pale yellow, respectively, and are moderately soluble in BrF_3 . They are crystalline, hygroscopic solids that are stable in a dynamic vacuum at 125 °C. At higher temperatures, both salts decompose according to (4), with no evidence for the

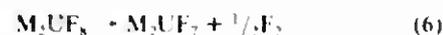


formation of stable, volatile, higher valence state fluorides. The ratio of NF_3 to XF_6 in the decomposition products was shown to be 1:1, and the vibrational spectra of the solid residues

showed no evidence for doubly charged anions. These observations indicate that neither the stepwise (eq 5) nor re-



ductive (eq 6) decomposition, previously observed for the



alkali-metal salts,¹⁵ are significant for the NF_4^+ salts. Based on the observed decomposition rates in a dynamic vacuum at 145 °C (NF_4UF_7 , 25% decomposition/h; NF_4WF_7 , 1.4% decomposition/h), NF_4WF_7 is thermally somewhat more stable than NF_4UF_7 .

Vibrational Spectra. The infrared and Raman spectra of NF_4WF_7 and NF_4UF_7 are shown in Figure 1, and the observed frequencies and their assignments are summarized in Table 1. These spectra establish beyond doubt the presence of NF_4^+ cations¹⁵ and WF_6^- ¹⁶ and UF_6^- ¹⁷ anions¹³ and also demonstrate that, under the given reaction conditions, no significant amounts of XF_6^{2-} salts are formed.

¹⁹F NMR Spectra. The ionic nature of the NF_4XF_7 salts in BrF_3 solution was established by ¹⁹F NMR spectroscopy. For NF_4WF_7 at -60 °C two signals, a triplet of equal intensity at $\phi = 222.7$ with $J_{\text{NF}} = 232.7$ Hz and a half-line width of 2 Hz and a singlet at $\phi = 142.2$ with a half-line width of 2.8 Hz and missing ¹⁸³W satellites were observed which are characteristic for NF_4^+ ¹⁸ and WF_6^- ^{13,17} respectively. An area integration of the two signals showed a ratio of 4:6.99, in excellent agreement with the expected ratio of 4:7. These two signals changed very little when the sample was warmed to ambient temperature; however, the solvent signals which at -60 °C were well resolved collapsed at 25 °C to a single peak. For NF_4UF_7 at -60 °C, again, well-resolved signals for the BrF_3 solvent and NF_4^+ were observed, but the UF_6^- signal could not be detected. These observations rule out a rapid

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exchange between UF_6^- and either the BrF_3 solvent or NF_4^+ , but can be explained by the relatively large (400–600 Hz) half-line width previously reported¹³ for UF_6^- .

Conclusion. The successful synthesis of NF_4WF_6^- and NF_4UF_6^- shows that even very weak Lewis acids such as metal hexafluorides are capable of forming stable NF_4^+ salts. This surprising result is a further manifestation of the unique properties of the NF_4^+ cation.

Acknowledgment. The authors gratefully acknowledge helpful discussions with Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson and financial support from the Office of Naval Research and the Army Research Office.

Registry No. NF_4WF_6^- , 80735-93-9; NF_4UF_6^- , 80735-09-7; WF_6 , 7783-82-6; UF_6 , 7783-81-5; $\text{NF}_4\text{SbF}_6^-$, 16871-76-4.

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Perfluoroammonium and Alkali-Metal Salts of the Heptafluoroxenon(VI) and Octafluoroxenon(VI) Anions

KARL O. CHRISTE* and WILLIAM W. WILSON

Received February 2, 1982

The NF_4XeF_7 salt was prepared from XeF_6 and NF_4HF_2 and was converted to $(\text{NF}_4)_2\text{XeF}_8$ by selective laser photolysis. These new salts and the known CsXeF_7 and Cs_2XeF_8 were characterized, and their vibrational spectra are reported. Evidence is presented for the existence of a stable NaXeF_7 salt. The presence of different phases in solid XeF_6 was confirmed by Raman spectroscopy.

Introduction

Perfluoroammonium salts are the major ingredient in solid-propellant $\text{NF}_3\text{-F}_2$ gas generator compositions for chemical lasers.¹ For these applications, the active fluorine content should be high, and the evolved gases should contain, besides F_2 and NF_3 , only inert gases to avoid deactivation of the laser. Removal of undesired gases such as the parent Lewis acids of the salts' anions can be accomplished by the addition of a suitable alkali-metal fluoride which forms a nonvolatile clinker with the Lewis acids.² However, the additional weight of the clinking agents lowers the effective fluorine yields of these compositions and renders them less desirable. This problem might be circumvented by the use of NF_4^+ salts containing noble-gas fluoride anions which, on decomposition, would yield additional fluorine values and inert noble-gas diluent as the only byproduct. In this paper we report the successful synthesis of the first known examples of NF_4^+ salts containing noble-gas fluoride anions and the characterization of the XeF_7^- and XeF_8^{2-} anions.

Experimental Section

Caution! Hydrolysis of XeF_6 and of its NF_4^+ salts produces highly sensitive xenon oxides and results in violent explosions. These compounds must therefore be handled with the necessary safety precautions and in the complete absence of moisture.

Materials and Apparatus. The apparatus, handling procedures, analytical methods, and spectroscopic techniques used in this study have previously been described.³ Literature methods were used for the preparation of XeF_6 ,⁴ CsXeF_7 , Cs_2XeF_8 ,⁵ and the NF_4HF_2 solution in anhydrous HF .⁶ Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox.

Preparation of NF_4XeF_7 . Dry CsF (15.54 mmol) and NF_4SbF_6 (15.65 mmol) were loaded in the drybox into half of a prepassivated Teflon U metathesis apparatus. Dry HF (9 mL of liquid) was added

on the vacuum line, and the mixture was stirred with a Teflon-coated magnetic stirring bar for 45 min at 25 °C. After the apparatus was cooled to -78 °C, it was inverted and the NF_4HF_2 solution was filtered into the other half of the apparatus. Most of the HF solvent was pumped off during warm-up from -78 °C toward room temperature until the first signs of NF_4HF_2 decomposition became noticeable. At this point the solution was cooled to -196 °C and XeF_6 (17.87 mmol) was added. The mixture was warmed to 25 °C and stirred for 12 h. Although most of the XeF_6 dissolved in the liquid phase, there was some evidence for undissolved XeF_6 . Material volatile at 25 °C was removed under a static vacuum and separated by fractional condensation through traps kept at -64 and -196 °C. Immediately, a white copious precipitate formed in the reactor but disappeared after about 10 min, resulting in a clear colorless solution. As soon as the first signs of NF_4HF_2 decomposition were noted, removal of volatiles was stopped and the reactor was cooled to -196 °C. The HF collected in the -196 °C trap was discarded, but the XeF_6 collected in the -64 °C trap was recycled into the reactor, resulting in a yellow solution at room temperature. This mixture was stirred at 25 °C for several hours, followed by removal of the material volatile at 25 °C under a dynamic vacuum. The volatiles were separated by fractional condensation through traps kept at -210, -126, and -64 °C and consisted of NF_3 (~0.3 mmol), HF (~11 mmol), and XeF_6 , respectively. The reactor was taken to the drybox, and the solid products were weighed. The yellow filtrate residue (5.149 g; weight calculated for 15.54 mmol of NF_4XeF_7 , 5.506 g, corresponding to a yield of 93.5%) consisted of NF_4XeF_7 , and the white filter cake (5.78 g; weight calculated for 15.54 mmol of CsSbF_6 , 5.72 g) consisted of CsSbF_6 . The composition of these solids was confirmed by vibrational and ¹⁹F NMR spectroscopy, pyrolysis, and analysis of the pyrolysis residue for NF_4^+ , Cs^+ , and SbF_6^- . On the basis of these results, the reaction product had the following composition (wt %): NF_4XeF_7 (98.01), NF_4SbF_6 (0.88), and CsSbF_6 (1.11).

Results and Discussion

The XeF_7^- and XeF_8^{2-} anions are thermally quite stable⁵ and, therefore, were a logical choice for the synthesis of the corresponding NF_4^+ salts. Although the syntheses of MXeF_7 ($\text{M} = \text{Cs, Rb, NO}_2$)^{5,7} and M_2XeF_8 ($\text{M} = \text{Cs, Rb, K, Na, NO}$)^{5,8} salts have been reported, these salts have not been well characterized, except for a crystal structure determination of

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F-1

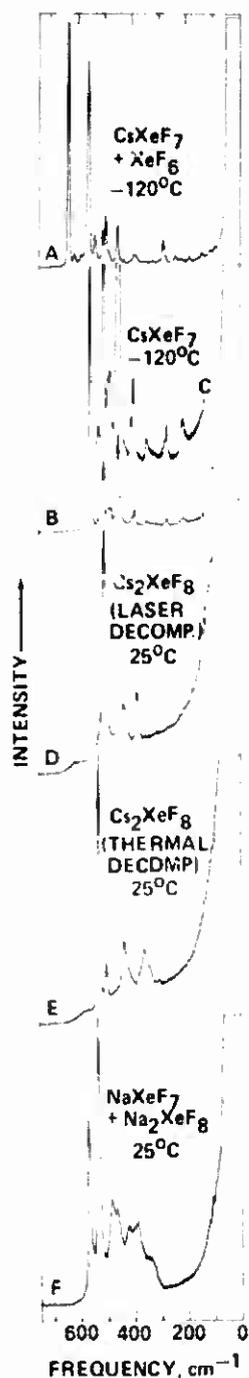


Figure 1. Raman spectra of CsXeF_7 containing excess XeF_6 (trace A), CsXeF_7 recorded at two different sensitivity levels (traces B and C), Cs_2XeF_8 generated by decomposition of CsXeF_7 at 25 °C in the 4880-Å laser beam (trace D), Cs_2XeF_8 generated by vacuum pyrolysis of CsXeF_7 at 160 °C (trace E), and a mixture of NaXeF_7 and Na_2XeF_8 (trace F).

$(\text{NO})_2\text{XeF}_8$.⁹ Therefore, a better characterization of the XeF_7^- and the XeF_8^{2-} anion was necessary to allow proper identification of their NF_4^+ salts.

Synthesis and Characterization of CsXeF_7 , Cs_2XeF_8 , and XeF_6 . In agreement with a previous report⁵ it was found that CsF reacts with XeF_6 at 60 °C to form CsXeF_7 . However, the following observations deviate from the previous report.⁵

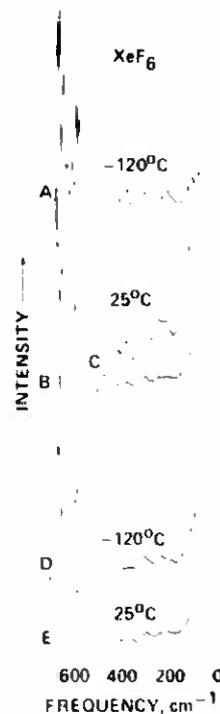


Figure 2. Raman spectra of XeF_6 recorded at -120 and 25 °C and at different sensitivity levels. The differences between traces A-C and D, E are attributed to different phases (see text).

(i) It was not necessary to carefully add the XeF_6 in small increments to the CsF . No evidence for decomposition or explosions was noted, as long as the CsF was carefully dried. (ii) We could not obtain complete conversion of CsF to CsXeF_7 . Even with a 13-fold excess of XeF_6 and 3-week reaction time at 60 °C, followed by 1 week at ambient temperature, the XeF_6 uptake by the CsF was less than expected for a 1:1 stoichiometry. When the removal of the excess of XeF_6 from the sapphire reactor was stopped at a weight corresponding approximately to a 1:1 adduct, the Raman spectrum of the product showed, in addition to CsXeF_7 , the presence of either free or very weakly associated XeF_6 , and the product evolved XeF_6 on standing. Even after removal of additional XeF_6 (weight corresponding to the composition of $\text{CsXeF}_7 \cdot 0.19\text{CsF}$) the Raman spectrum still showed the presence of free XeF_6 (see trace A of Figure 1). A pumping time of about 8 h at ambient temperature was required to obtain a constant weight and to completely remove free XeF_6 (see trace B of Figure 1). At this point the composition of the product had dropped to $\text{CsXeF}_7 \cdot 0.89\text{CsF}$. (iii) The Cs_2XeF_8 salt, prepared by vacuum pyrolysis of CsXeF_7 at 160 °C, was white and not cream colored.

Since xenon fluorides are excellent Raman scatterers, Raman spectroscopy was used to distinguish XeF_6 , XeF_7^- , and XeF_8^{2-} from each other. Previous work on similar MF_6 , MF_7^- , MF_8^{2-} ($\text{M} = \text{Mo}, \text{W}, \text{Re}$)¹⁰ systems has shown that the addition of F^- to a MF_6 molecule or MF_7^- anion increases the polarity of the M-F bonds and therefore progressively lowers the frequencies of the MF_n stretching modes. Since XeF_7^- salts are yellow, they strongly absorbed the blue 4880-Å exciting line of our laser. To avoid decomposition of the samples in the laser beam, we recorded the Raman spectra of XeF_7^- salts at low temperature. Although the Raman spectrum of solid

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Table I. Raman Spectra of Solid XeF₆^a

	A		B	
	25 °C	120 °C	25 °C	120 °C
656 (10)	658 (10)	649 (9.7)	652 sh	658 (5)
636 (6)	633 (7.1)	646 (10)	649 (10)	
			620 sh	
			613 sh	
			589 sh	
582 (4.2)	576 (5.0)	579 (4.1)	579 (4.3)	
	564 (4.5)		564 sh	
404 (0.1)	396 (0.4)	398 (0.3)	396 (0.2)	
365 (0.2)	365 (1.0)	362 (0.4)	365 (0+) br	
	346 (0+)			
294 (0.3)	296 (0.4)	291 (0.6)	296 (0.4) br	
	284 (0.5)			
236	232 (0.4)	235-180 (0+) br	235-180 (0.4) br	
220	205 sh			
204	195 (0.3)			
	179 sh			
	142 (0+)		140 (0+)	
105 (0+)	110 (0.2)		107 (0+)	
	93 (0.3)		86 (0+)	
	64 sh			

^a The observed differences in the A and B type spectra are attributed to the presence of more than one phase in different ratios. Observed frequencies are given in cm⁻¹, with relative intensities in parentheses (uncorrected Raman intensities).

XeF₆ has previously been recorded at 40 °C,¹¹ its low-temperature spectrum was required to allow its comparison with those of XeF₇⁻ and XeF₈²⁻. The spectrum observed for XeF₆ at -120 °C (trace A of Figure 2) shows splittings for most of the bands observed in the room-temperature spectrum (trace B of Figure 2). The latter agrees well with that previously reported.¹¹ However, depending on temperature cycling and exposure time to the laser beam, a second type of spectrum could reversibly be generated from the same sample and was recorded at both -120 °C (trace D of Figure 2) and 25 °C (trace E of Figure 2). Since XeF₆ is known to exist in at least four different crystalline modifications,¹² the different spectra are attributed to the presence of more than one XeF₆ phase. The observed frequencies are summarized in Table I.

As expected from the previously known MF₆, MF₇⁻, MF₈²⁻ series spectra,¹⁰ the strongest Raman line in the spectra of XeF₆ and XeF₇⁻ and XeF₈²⁻ shows a frequency decrease with increasing negative charge (see Figure 1). For Cs₂XeF₈, two different spectra were observed, depending on its method of preparation. When the sample was prepared by laser photolysis at ambient temperature (XeF₇⁻ is yellow and strongly absorbs the blue 4880-Å line of the Ar ion laser, whereas XeF₈²⁻ is white and does not decompose in the laser beam), the spectrum shown by trace D of Figure 1 was observed. When the Cs₂XeF₈ sample was prepared by vacuum pyrolysis of CsXeF₇ at 160 °C,⁵ the spectrum shown by trace E of Figure 1 was obtained. The general appearance of the spectra is quite similar, but some of the bands exhibit significant frequency shifts (see Table II). These shifts might be caused by solid-state effects.

On the Existence of NaXeF₇. On the basis of a previous report⁵, only CsF and RbF form 1:1 adducts with XeF₆, while for NaF only a 2:1 adduct can be isolated. However, the experimental evidence given by the same authors⁵ (combining ratios of NaF:XeF₆ were as low as 1.73) suggested that NaXeF₇ might exist in addition to Na₂XeF₈. This was now verified by Raman spectroscopy. As can be seen from Table II and trace F of Figure 1, the product obtained by reacting

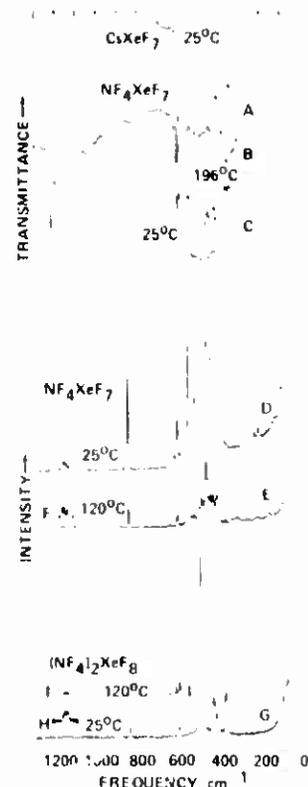


Figure 3. Infrared spectra of CsXeF₇ recorded at 25 °C between AgCl windows (trace A) and of NF₄XeF₇ recorded at -196 °C between CsI windows (trace B) and 25 °C between AgCl windows (trace C) and Raman spectra of NF₄XeF₇ and (NF₄)₂XeF₈ recorded at different temperatures and sensitivities (traces D-I). The broken lines in the infrared spectra indicate absorption due to the AgCl windows.

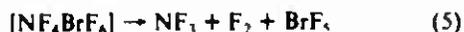
Xe with a large excess of F₂ and NaF at 250 °C, followed by removal of all material volatile at 55 °C in vacuo,⁴ clearly contains XeF₇⁻ in addition to XeF₈²⁻. Consequently, NaF can form a 1:1 adduct with XeF₆ that is stable up to at least 55 °C. Since KF generally forms more stable adducts than NaF, it appears safe to predict that KXeF₇ should also exist. The difficulty in obtaining 1:1 combining ratios for MF (M = Na or K) with XeF₆ might therefore be attributed to difficulties in achieving a high conversion of the starting materials and not to the nonexistence of the 1:1 adducts.

On the Structure of XeF₇⁻ and XeF₈²⁻. From a crystal structure determination of (NO)₂XeF₈,⁹ the XeF₈²⁻ anion is known to possess a square-antiprismatic structure. The observed Raman spectra of Cs₂XeF₈ are in excellent agreement with such a structure of symmetry D_{4d}. Three Raman-active stretching modes should be observed, one each in species A₁, E₂, and E₃. Of these, the A₁ mode is assigned to the most intense and single band at about 510-530 cm⁻¹, while the two doubly degenerate E modes are assigned to the two doublets at about 430 and 370 cm⁻¹ (see Table II). The observed frequencies agree well with those reported for TaF₈³⁻ (622, 426, and 377 cm⁻¹),¹⁰ which is also known from X-ray data¹³ to be a square antiprism. The fact that XeF₈²⁻ has a square-antiprismatic structure suggests that the free valence electron pair on xenon is sterically inactive. This is analogous to the observations previously made for BrF₆⁻, which due to its smaller central atom can accommodate only a maximum of six ligands, thus forcing the free valence electron pair on bromine to become sterically inactive.¹⁴

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with $J_{\text{NF}} = 232 \text{ Hz}$,¹⁶ which was slowly replaced by the signal of NF_3 (triplet of equal intensity at 145 ppm below CFCl_3 with $J_{\text{NF}} = 290 \text{ Hz}$),¹⁹ suggesting again solvolysis of NF_4XeF_7 , followed by decomposition of the unstable NF_4BrF_6 intermediate:



When a sample of NF_4XeF_7 was exposed at room temperature for prolonged time to blue 4880-Å laser light, photolytic decomposition of NF_4XeF_7 occurred, resulting in $(\text{NF}_4)_2\text{XeF}_8$ formation:



Attempts were unsuccessful to duplicate this reaction by carefully controlled thermal decomposition of NF_4XeF_7 . The only products obtained were NF_3 , F_2 , XeF_6 , and unreacted NF_4XeF_7 . The selective decomposition of NF_4XeF_7 and stability of $(\text{NF}_4)_2\text{XeF}_8$ in the laser beam can be explained by the different color of the two compounds. The yellow NF_4XeF_7 strongly absorbs the blue 4880-Å light, whereas the white $(\text{NF}_4)_2\text{XeF}_8$ does not. Since the output of the available laser was just 75 mW, only very small amounts of $(\text{NF}_4)_2\text{XeF}_8$

could be produced in this manner, and identification of the product was limited to Raman spectroscopy. As can be seen from traces G-I of Figure 3 and Table II, the spectra clearly show the presence of the NF_4^+ ¹⁸ and XeF_6^{2-} ions (see above). The observed splittings are due to lifting of the degeneracies for the E and F modes in the solid state.¹⁸

Conclusion. The present study further demonstrates the unique ability of the NF_4^+ cation to form a host of stable salts. The successful synthesis of NF_4XeF_7 and $(\text{NF}_4)_2\text{XeF}_8$ provided the first known examples not only of NF_4^+ salts containing noble-gas fluoride anions but also of an NF_4^+ salt containing an octafluoro anion. These salts are very powerful oxidizers and on thermal decomposition generate NF_3 , F_2 , and only inert gases. The formation of $(\text{NF}_4)_2\text{XeF}_8$ is an interesting example of a selective laser-induced reaction. The XeF_7^- and XeF_6^{2-} anions were characterized by vibrational spectroscopy. Raman spectroscopic evidence was obtained for the existence of a stable NaXeF_7 salt, and the presence of different phases in solid XeF_6 was confirmed.

Acknowledgment. The authors gratefully acknowledge helpful discussions with Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson and financial support from the Office of Naval Research and the Army Research Office.

Registry No. $(\text{NF}_4)(\text{XeF}_7)$, 82963-12-0; CsF , 13400-13-0; $(\text{NF}_4)\text{SbF}_6$, 16871-76-4; $\text{Cs}(\text{XeF}_7)$, 19033-04-6; $\text{Cs}_2(\text{XeF}_6)$, 17501-71-2; XeF_6 , 13693-09-9; $\text{Na}(\text{XeF}_7)$, 82963-13-1; Xe , 7440-63-3; F_2 , 7782-41-4; NaF , 7681-49-4; $(\text{NF}_4)_2\text{XeF}_8$, 82963-15-3; $\text{Na}_2(\text{XeF}_6)$, 17501-70-1.

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THERMOCHEMISTRY OF NF_4^+ SALTS. ON THE ENTHALPY OF FORMATION OF NF_4XeF_7 AND THE $\text{NF}_4\text{SbF}_6\text{-BrF}_3$ SYSTEMK.O. CHRISTE^a, W.W. WILSON^a, R.D. WILSON^a, R. BOUGON^b and T. BUI HUY^b^aRocketdyne Division of Rockwell International, Canoga Park, CA 91304 (USA)^bCentre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette Cedex (France)

SUMMARY

The thermal decomposition of NF_4XeF_7 was studied by differential scanning calorimetry. From the observed enthalpy of decomposition, a value of -491 kJ mol^{-1} was calculated for $\Delta H_f^\circ(\text{NF}_4\text{XeF}_7(\text{s}))$. The reaction of NF_4^+ salts with BrF_3 , previously suggested [1] for the determination of more precise thermochemical values for NF_4^+ salts by solution calorimetry, was shown to be infeasible.

INTRODUCTION

In a previous paper [2] thermochemical data were summarized for NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4SbF_6 , NF_4GeF_5 and $(\text{NF}_4)_2\text{GeF}_6$. In this paper we would like to report thermochemical data for the recently synthesized [3] NF_4XeF_7 which is of particular interest due to its exceptionally high energy content. Furthermore, we would like to comment on several suggestions, recently made by Woolf [1], concerning the thermochemistry of NF_4^+ salts.

EXPERIMENTAL

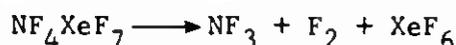
The synthesis of NF_4XeF_7 [3] and the DSC method [2] have previously been described. Based on its elemental analysis [3] the purity of the NF_4XeF_7 sample used in this study was 98.0 weight percent with a total of two percent of NF_4SbF_6 and CsSbF_6

being present as impurities. Since these impurities are thermally much more stable [4] than NF_4XeF_7 [3], they did not interfere with the DSC measurements, and a simple 2 percent correction of the starting weights was made.

The reaction of NF_4SbF_6 [5] with BrF_3 (The Matheson Company) was carried out in a well-passivated (with ClF_3) Teflon FEP ampule connected to a 314-stainless steel Teflon FEP vacuum system. The NF_4SbF_6 was treated with a tenfold excess of BrF_3 at 25°C for 2 hours. The volatile products were separated by fractional condensation and consisted of mainly unreacted BrF_3 and a small amount of HF and NF_3 . No evidence for the formation of either BrF_5 or F_2 was observed. The solid residue had changed only little in weight and based on its Raman spectrum consisted mainly of NF_4SbF_6 , a small amount of Br_2^+ and possibly some BrF_2^+ salts.

RESULTS AND DISCUSSION

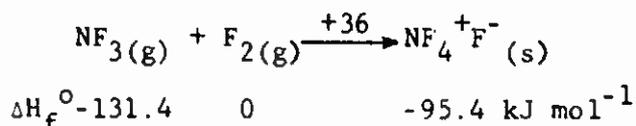
Enthalpies of Decomposition and Formation of NF_4XeF_7 In a previous study [3] it was shown that the thermal decomposition of NF_4XeF_7 proceeds according to



Although $(\text{NF}_4)_2\text{XeF}_8$ is the logical intermediate in this decomposition, this compound could only be isolated by selective laser photolysis [3]. The observation of a shoulder at 107°C on the main decomposition endotherm of NF_4XeF_7 (onset at 80°C) supports a two step decomposition mechanism for NF_4XeF_7 and suggests the formation of $(\text{NF}_4)_2\text{XeF}_8$ as an intermediate. Unfortunately, a large enough sample of pure $(\text{NF}_4)_2\text{XeF}_8$ was not available to measure the decomposition enthalpy of the second step separately. For the overall decomposition enthalpy of NF_4XeF_7 a value $\Delta H_{\text{dec}} = 64.6 \pm 5 \text{ kJ mol}^{-1}$ (10) was found. From the known enthalpies of formation of NF_3 [6] and XeF_6 [7] the enthalpy of formation of NF_4XeF_7 is calculated as $\Delta H_{\text{f}}^\circ(\text{NF}_4\text{XeF}_7(\text{s})) = -490.7 \text{ kJ mol}^{-1}$. A comparison of this value with those previously found [2] for a series of NF_4^+ salts containing other complex fluoro anions clearly demonstrates that NF_4XeF_7 is by far the most energetic of these salts.

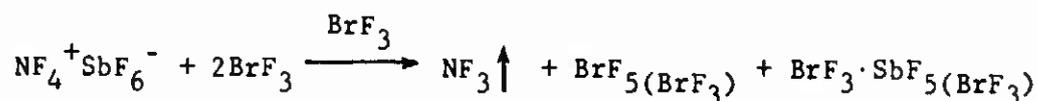
Comments on the Paper by Woolf In a recent paper by Woolf [1] the interesting observation was made that the experimentally determined enthalpies of formation of several NF_4^+ salts [2] closely correspond to those estimated for the corresponding NO_2^+ salts [1]. Furthermore, it was extrapolated that this relationship for salts with anion dominated lattices should also hold for the cation dominated lattice salts NF_4^+F^- and NO_2^+F^- , deriving the enthalpy of formation of NF_4^+F^- from an estimate for NO_2^+F^- [1]. Criticizing the admittedly substantial uncertainties in the known experimental data [2], Woolf preferred his values derived from the same data, but extended by estimates and extrapolations. In our opinion, this is unwarranted.

In spite of the above criticism, it is most gratifying that Woolf's estimated value of -91 kJ mol^{-1} for the enthalpy of formation of solid NF_4^+F^- [1] is almost identical to that (-95 kJ mol^{-1}) derived from our previous data [2]



Unfortunately, the commentary in [1] could easily be misinterpreted. After listing an exothermic value of -91 kJ mol^{-1} for the enthalpy of formation of NF_4^+F^- , reference is made [1] to "the previous prediction of instability" of this compound. Obviously, in both papers [1,2] almost identical exothermic values are obtained for the enthalpy of formation of solid NF_4^+F^- . However, as stressed in [2], solid NF_4^+F^- is unstable with respect to decomposition to NF_3 and F_2 by about 36 kJ mol^{-1} .

In [1], solvolysis of NF_4^+ salts in BrF_3 according to



was suggested as a method of obtaining more precise thermochemical values for NF_4^+ salts, and a heat of reaction of about 70 kJ mol^{-1} was anticipated for this reaction. A study of the $\text{NF}_4\text{SbF}_6\text{-BrF}_3$ system carried out in our laboratory shows that this reaction does not proceed as postulated and therefore is of no practical

usefulness. No BrF_5 formation was observed, and the evolution of some NF_3 , accompanied by some Br_2^+ and HF formation, is indicative of experimental difficulties with undesired side reactions, even in well-passivated Teflon-stainless steel equipment. The discrepancy between the predicted [1] 70 kJ mol^{-1} exothermicity and the observed unreactivity of the above system might be attributed to the previous neglect of taking the strong association of liquid BrF_3 into account. If the left side of the equation is corrected for ΔH_{vap} of BrF_3 ($42.84 \text{ kJ mol}^{-1}$) [8], the heat of reaction becomes endothermic by about 15 kJ mol^{-1} and agrees with the observed lack of reactivity.

ACKNOWLEDGEMENTS

The authors are indebted to the Office of Naval Research, the Army Research Office and la Direction des Recherches Etudes et Techniques for financial support, and to Drs. C. J. Schack and L. R. Grant for helpful discussions.

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APPENDIX H

TETRAFLUOROAMMONIUM SALTS

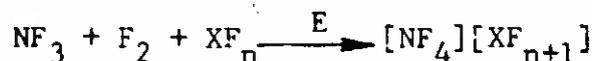
Submitted by KARL O. CHRISTE,^{*} WILLIAM W. WILSON,^{*}
 CARL J. SCHACK,^{*} and RICHARD D. WILSON^{*}
 Checked by R. BOUGON[†]

Since $[\text{NF}_4]^+$ is a coordinatively saturated complex fluoro cation, the synthesis of its salts is generally difficult.¹ A limited number of salts can be prepared directly from NF_3 , and these salts can then be converted by indirect methods into other $[\text{NF}_4]^+$ salts which are important for solid propellant $\text{NF}_3\text{-F}_2$ gas generators or reagents for the electrophilic fluorination of aromatic compounds.

The two direct methods for the synthesis of $[\text{NF}_4]^+$ salts are based on the reaction of NF_3 with either $[\text{KrF}]^+$ salts².



or F_2 and a strong Lewis acid in the presence of an activation energy source E.³



For the chemist interested in synthesis, the second method³ is clearly superior due to its high yields, relative simplicity and scalability.

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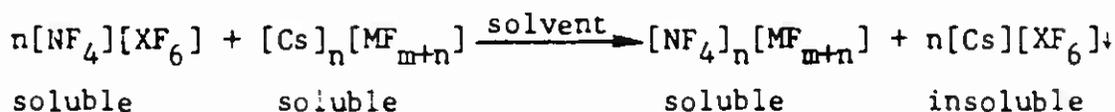
Four different activation energy sources have been used for the direct syntheses of the following $[\text{NF}_4]^+$ salts:

- (i) Heat: ⁴⁻⁷ $[\text{NF}_4][\text{BiF}_6]$, $[\text{NF}_4][\text{SbF}_6]$, $[\text{NF}_4][\text{AsF}_6]$,
 $[\text{NF}_4]_2[\text{TiF}_6 \cdot n\text{TiF}_4]$
- (ii) Glow discharge: ^{8,9} $[\text{NF}_4][\text{AsF}_6]$, $[\text{NF}_4][\text{BF}_4]$
- (iii) UV-photolysis: ^{10,11} $[\text{NF}_4][\text{SbF}_6]$, $[\text{NF}_4][\text{AsF}_6]$, $[\text{NF}_4][\text{PF}_6]$,
 $[\text{NF}_4][\text{GeF}_5]$, $[\text{NF}_4][\text{BF}_4]$
- (iv) Bremsstrahlung: ¹² $[\text{NF}_4][\text{BF}_4]$

Of these, the thermal synthesis of $[\text{NF}_4][\text{SbF}_6]^{4-7}$ is most convenient (Method A) and provides the starting material required for the syntheses of other $[\text{NF}_4]^+$ salts by indirect methods. For the syntheses of pure $[\text{NF}_4]^+$ salts on a small scale, low-temperature UV-photolysis is preferred (Method B).¹¹

The following indirect methods for the interconversion of $[\text{NF}_4]^+$ salts are known:

- (i) Metathesis reaction:



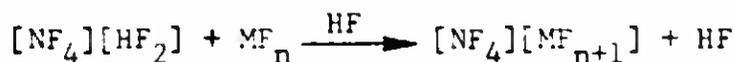
where typically X = Sb and solvent = anhydrous HF or BrF₅. This method is limited to anions which are stable in the given solvent and results in an impure product. Typical compounds prepared in this manner include: $[\text{NF}_4][\text{BF}_4]$,^{6,13,14} $[\text{NF}_4][\text{HF}_2]$ ¹⁵ (Method C), $[\text{NF}_4][\text{SO}_3\text{F}]$,¹⁶ $[\text{NF}_4][\text{ClO}_4]$,¹⁵ and $[\text{NF}_4]_2[\text{MF}_6][\text{M}=\text{Sn},^{17} \text{Ti},^{18} \text{Ni},^{19} \text{Mn}^{20}]$ (Method D).

(ii) Reaction of solid $[\text{NF}_4][\text{HF}_2 \cdot x\text{HF}]$ with a weak Lewis acid: When the MF_{m+n}^{n-} anion is unstable in a solvent, such as HF, and the Lewis acid MF_m is volatile, the equilibrium



can be shifted to the right by the use of an excess of MF_m and continuous removal of HF with the excess of MF_m . Typical salts prepared in this manner include: $[\text{NF}_4]_2[\text{SiF}_6]^{21}$ (Method E) and $[\text{NF}_4][\text{MF}_7]$ ($M=\text{U}, \text{W}^{22}, \text{Xe}^{23}$).

(iii) Reaction of $[\text{NF}_4][\text{HF}_2]$ with a nonvolatile polymeric Lewis acid: When in the metathesis (i) all the materials except $[\text{NF}_4][\text{XF}_6]$ are insoluble, product separation becomes impossible. This problem is avoided by digesting the Lewis acid in a large excess of $[\text{NF}_4][\text{HF}_2]$ in HF solution, followed by thermal decomposition of the excess $[\text{NF}_4][\text{HF}_2]$ at room temperature.

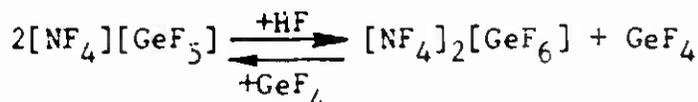


Salts prepared in this manner include $[\text{NF}_4][\text{MOF}_5]$ ($M=\text{U}, \text{W}^{24,25}$) (Method F), $[\text{NF}_4][\text{AlF}_4]$ and $[\text{NF}_4][\text{Be}_2\text{F}_5]$.²⁶

(iv) Displacement reaction: Displacement of a weaker Lewis acid by a stronger Lewis acid can be carried out easily, as demonstrated for $[\text{NF}_4][\text{PF}_6]$.¹¹

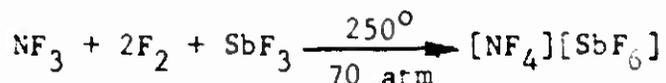


(v) Rearrangement reaction: When $[\text{NF}_4][\text{GeF}_5]$ is treated with anhydrous HF, the following equilibrium is observed.



This equilibrium can be shifted to the right by repeated treatments of $[\text{NF}_4][\text{GeF}_5]$ with HF and GeF_4 removal, and to the left by treatment of $[\text{NF}_4]_2[\text{GeF}_6]$ with GeF_4 .¹¹

A. TETRAFLUOROAMMONIUM HEXAFLUOROANTIMONATE (V)



Procedure

■ Caution. High pressure fluorine reactions should only be carried out behind barricades or in a high pressure bay using appropriately pressure-temperature rated nickel or Monel reactors which have been well passivated with several atmospheres of F_2 at the described reaction temperature. Stainless steel reactors should be avoided due to the potential of metal fires. All $[\text{NF}_4]^+$ salts are moisture sensitive and must be handled in a dry atmosphere. They are strong oxidizers and contact with organic materials and fuels must be avoided.

A prepassivated (with ClF_3), single-ended, 95-mL-Monel cylinder (Hoke,^{*} rated for 5000 psi working pressure), equipped with a Monel valve (Hoke^{*} 3232 M4M or equivalent), is loaded in the dry nitrogen atmosphere of a glove box with SbF_3^+ (31 mmole). The cylinder is connected to a metal vacuum system,²⁷ evacuated, vacuum leak tested, and charged with NF_3^{\S} (65 mmole) and F_2^{\S} (98 mmole) by condensation at -196° . The barricaded cylinder is heated for five days to 250° . The cylinder is allowed to cool by itself to ambient temperature and is then cooled to -196° . The unreacted F_2 and NF_3 are pumped off at

* Available from Hoke Inc., One Tenakill Park, Creskill, NJ 07626

† Available from Ozark-Mahoning, 1870 South Boulder, Tulsa, OK 74119

§ Available from Air Products and Chemicals Inc., Specialty Gas Dept., Hometown Facility, P.O. Box 351, Tamaqua, PA 18252

-196° (the pump must be protected by a fluorine scrubber²⁸), and during the subsequent warm-up of the cylinder to ambient temperature, $[\text{NF}_4][\text{SbF}_6]$ (10.1g, 31 mmole, 100% yield based on SbF_3) is left behind as a solid residue. The product is either scraped out of the cylinder in the dry box or, more conveniently, dissolved in anhydrous HF which has been dried over BiF_5 .¹³ Small amounts of $\text{Ni}[\text{SbF}_6]_2$ and $\text{Cu}[\text{SbF}_6]_2$, formed as impurities by attack of the Monel reactor by F_2 and SbF_5 , are only sparingly soluble in HF and are removed from the $[\text{NF}_4][\text{SbF}_6]$ solution by filtration using a porous Teflon filter*. If desired, the SbF_3 starting material can be replaced by SbF_5^\dagger without changing the remaining procedure. Anal.²⁹ Calcd. for $[\text{NF}_4][\text{SbF}_6] \cdot \text{NF}_3$, 21.80; Sb, 37.38. Found: NF_3 , 21.73; Sb, 37.41.

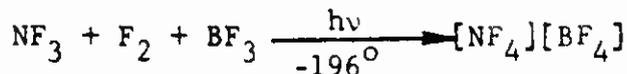
Properties

Tetrafluoroammonium hexafluoroantimonate (V) is a hygroscopic, white, crystalline solid which is stable up to about 270°.^{4,5,30} It is highly soluble in anhydrous HF (259 mg per g of HF at -78°)¹³ and moderately soluble in BrF_5 . Its ^{19}F NMR spectrum⁴ in anhydrous HF solution consists of a triplet of equal intensity at 214.7 ppm downfield from CFCl_3 ($J_{\text{NF}}=231\text{Hz}$) for $[\text{NF}_4]^\dagger$. The vibrational spectra⁵ of the solid exhibit the following major bands (cm^{-1}): IR(pressed AgCl disk), 1227(mw), 1162(vs), 675(vs), 665(vs), 609(m); R_a, 1160(0.6), 1150(0.2), 843(7.0), 665(1), 648(10), 604(3.9), 569(0.9), 437(1.5), 275(3.8).

* Available from Pallflex Products Corp., Kennedy Drive, Putnam, Conn 06260

† Available from Ozark-Mahoning, 1870 South Boulder, Tulsa, OK 74119

B. TETRAFLUOROAMMONIUM TETRAFLUOROBORATE (III)



Procedure

■ Caution. Ultraviolet goggles should be worn for eye protection when working with higher power UV-lamps, and the work should be carried out in a fume hood. NF_4BF_4 is a strong oxidizer and contact with organic materials, fuels and moisture must be avoided.

The low-temperature UV-photolysis reaction is carried out in a quartz reactor with a pan-shaped bottom and a flat top consisting of a 7.5-cm diameter optical grade quartz window (see Figure 1). The vessel has a side arm connected by a Teflon O ring joint to a Fischer-Porter Teflon valve* to facilitate removal of solid reaction products. The depth of the reactor is about 4 cm, and its volume is about 140 mL. The UV source consists of a 900-W, air-cooled, high-pressure mercury arc (General Electric Model B-H6) which is positioned 4 cm above the flat reactor surface. The bottom of the reactor is kept cold by immersion in liquid N_2 . Dry, gaseous N_2 is used as a purge gas to prevent condensation of atmospheric moisture on the flat top of the reactor. As a heat shield, a 6-mm thick quartz plate is positioned between the UV source and the top of the reactor.

Premixed NF_3^\dagger and BF_3^\S (27 mmole of each) are condensed into the cold bottom of the quartz reactor. Fluorine[†] (9 mmole) is added, and the mixture is photolyzed at -196° for 1 hour. After termi-

* Available from Fischer & Porter Co., 51 Warminster Rd, Warminster, PA 18974

† Available from Air Products and Chemicals, Inc., Specialty Gas Dept., Hometown Facility, P.O. Box 351, Tamaqua, PA 18252

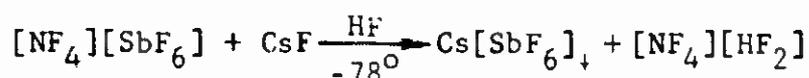
§ Available from Matheson, P.O. Box 85, 932 Paterson Plank Rd., East Rutherford, NJ 07073

nation of the photolysis, volatile material is pumped out of the reactor (through a scrubber²⁸) during its warm-up to room temperature. The nonvolatile white solid residue (1.0g) is pure $[\text{NF}_4][\text{BF}_4]$. Instead of the pan-shaped reactor a simple round quartz bulb can be used with a $[\text{NF}_4][\text{BF}_4]$ yield of about 0.3g/hr. Anal.²⁹ Calcd. for $[\text{NF}_4][\text{BF}_4]$: NF₃, 40.16; B, 6.11. Found: NF₃, 40.28; B, 6.1.

Properties

Tetrafluoroammonium tetrafluoroborate (III) is a hygroscopic, white, crystalline solid which is stable up to about 150°. ^{9,11,12,30} It is highly soluble in anhydrous HF and moderately soluble in BrF₅. Its ¹⁹F NMR spectrum in anhydrous HF solution consists of a sharp triplet of equal intensity at 220 ppm downfield from CFC₃ ($J_{\text{NF}}=230\text{Hz}$) for $[\text{NF}_4]^+$ and an exchange broadened singlet at 158 ppm upfield from CFC₃ for $[\text{BF}_4]^-$. The vibrational spectra of the solid exhibit the following major bands (cm^{-1}): IR(pressed AgCl disk), 1298(ms), 1222(mw), 1162(vs), 1057(vs), 609(s), 522(s); Ra, 1179(0.6), 1148(0.6), 1130(0+), 1055(0.2), 884(0+), 844(10), 772(3.2), 609(6.3), 524(0.4), 443(2.6), 350(0.9).

C. TETRAFLUOROAMMONIUM (HYDROGEN DIFLUORIDE)



Procedure

■ Caution. Anhydrous HF causes severe burns and protective clothing should be worn when working with this material. The HF solutions of NF_4^+ salts are strongly oxidizing and contact with fuels must be avoided.

A mixture of dry CsF^* (2.361g = 15.54 mmole) and $[\text{NF}_4][\text{SbF}_6]$ (5.096g = 15.64 mmole) is placed inside the drybox into trap I of the leak-checked and passivated (with ClF_3 and dry HF^{13}) Teflon FEP-Monel metathesis apparatus shown in Figure 2. The CsF is dried by fusion in a platinum crucible, immediately transferred to the drybox, cooled and finely ground. The apparatus is attached to a metal-Teflon vacuum system²⁷ by two flexible, corrugated Teflon tubes[†] and the connections are vacuum leak-checked and passivated. The system is repeatedly exposed to anhydrous HF^{\S} , until the HF is colorless when frozen out at -196° in a Teflon U-trap of the vacuum system to avoid contamination of the product with any chlorine-fluorides which may be adsorbed onto the walls of the metal vacuum system. Anhydrous HF^{13} (16.2g = 810 mmole) is added to trap I and the mixture is magnetically stirred for 1 hour at room temperature. The metathesis apparatus is cooled with powdered dry ice to -78° for 1 hour, and then inverted. The HF solution which contains the $[\text{NF}_4][\text{HF}_2]$ is separated from the $\text{Cs}[\text{SbF}_6]$ precipitate by filtration. To facilitate the filtration step, trap I is pressurized with 2 atm of dry N_2 after inversion. A pressure drop in trap I indicates the completion of the filtration step. If desired, repressurization of trap I may be repeated to minimize the amount of mother liquor held up in the filter cake. The desired HF solution of $[\text{NF}_4][\text{HF}_2]$ is collected in trap II. It contains about 94% of the original $[\text{NF}_4]^+$ values, with the remainder being adsorbed on the $\text{Cs}[\text{SbF}_6]$ filter cake. The $[\text{NF}_4][\text{HF}_2]$

* Available from Kawecki Berylco Industries, Inc., 220 E. 42nd Street, New York, NY 10017

† Available from Penntube Plastics Co., Madison Ave and Holley St., Clifton Heights, PA 19018

§ Available from Matheson, P.O. Box 85, 932 Paterson Plank Road, East Rutherford, NJ 07073

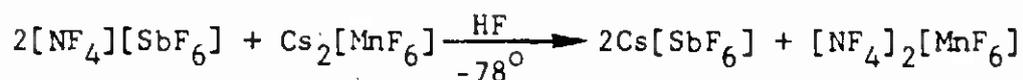
solution has a purity of about 97 mole % and contains small amounts of $\text{Cs}[\text{SbF}_6]$ (solubility of $\text{Cs}[\text{SbF}_6]$ in HF at -78° is 1.8 mg/gHF)¹³ and $[\text{NF}_4][\text{SbF}_6]$ (if a slight excess of $[\text{NF}_4][\text{SbF}_6]$ has been used in the reaction to suppress, by the common ion effect, the amount of dissolved $\text{Cs}[\text{SbF}_6]$).

An unstable solid having the composition $[\text{NF}_4][\text{HF}_2 \cdot n\text{HF}]$ ($n=2-10$) can be prepared by pumping off as much HF as possible below 0° .

Properties

Tetrafluoroammonium (hydrogen difluoride) is stable in HF solution at room temperature, but decomposes to NF_3 , F_2 and HF on complete removal of the solvent.¹⁵ The ^{19}F NMR spectrum of the solution shows a triplet of equal intensity of 216.2 ppm downfield from CFCl_3 with $J_{\text{NF}}=230\text{Hz}$. The Raman spectrum of the HF solution shows bands at 1170(w), 854(vs), 612(m) and 448(mw) cm^{-1} .

D. BIS(TETRAFLUOROAMMONIUM) HEXAFLUOROMANGANATE(IV)



Procedure

■ Caution. Anhydrous HF can cause severe burns and protective clothing should be worn when working with this solvent. $[\text{NF}_4]_2[\text{MnF}_6]$ is a strong oxidizer and contact with water and fuels must be avoided.

The same apparatus is used as for procedure C. In the dry N_2 atmosphere of a glovebox, a mixture of $[\text{NF}_4][\text{SbF}_6]$ (37.29 mmole)

and $\text{Cs}_2[\text{MnF}_6]^{20}$ (18.53 mmole) is placed in the bottom of a pre-passivated (with ClF_3) Teflon FEP (fluoro-ethylene-propylene copolymer) double U-tube metathesis apparatus. Dry HF^{13} (20 mL of liquid) is added at -78° on the vacuum line,²⁷ and the mixture is warmed to 25° for 30 minutes with stirring. The mixture is cooled to -78° and pressure filtered at this temperature. The HF solvent is pumped off at 30° for 12 hours resulting in 14g of a white filter cake (mainly $\text{Cs}[\text{SbF}_6]$) and 6.1g of a yellow filtrate residue having the approximate composition (weight %): $[\text{NF}_4]_2[\text{MnF}_6]$, 92; $[\text{NF}_4][\text{SbF}_6]$, 4; $\text{Cs}[\text{SbF}_6]$, 4. Yield of $[\text{NF}_4]_2[\text{MnF}_6]$ = 87% based on $\text{Cs}_2[\text{MnF}_6]$.

Properties

Bis(tetrafluoroammonium) hexafluoromanganate(IV) is a yellow, crystalline solid which is stable at 65° , but slowly decomposes at 100° to NF_3 , F_2 and MnF_3 .²⁰ It is highly soluble in anhydrous HF and reacts violently with water. Its ^{19}F NMR spectrum in anhydrous HF solution shows a broad resonance at 218 ppm below CFCl_3 due to $[\text{NF}_4]^+$. The vibrational spectra of the solid show the following major bands (cm^{-1}): IR(pressed AgCl disk), 1221(mw), 1160(vs), 620(vs), 338(s); Ra, 855(m), 593(vs), 505(m), 450(w), 304(s).

E. BIS(TETRAFLUOROAMMONIUM) HEXAFLUROSILICATE(IV)



Procedure

■ Caution. Anhydrous HF can cause severe burns and protective clothing should be worn when working with liquid HF. All $[\text{NF}_4]^+$

salts are strong oxidizers and contact with fuels and water must be avoided.

A solution of $[\text{NF}_4][\text{HF}_2]$ (27 mmole) in anhydrous HF^{13} is prepared at -78° by procedure C. Most of the HF solvent is pumped off during warm-up towards 0° until the first signs of decomposition of $[\text{NF}_4][\text{HF}_2]$ are noted from the onset of gas evolution. The resulting residue is cooled to -196° and SiF_4^* (35 mmole) is added. The mixture is allowed to warm to ambient temperature while providing a volume of about 1L in the vacuum line for expansion. During warm-up of the apparatus, the SiF_4 evaporates first and, upon melting of the $[\text{NF}_4][\text{HF}_2 \cdot n\text{HF}]$ phase, a significant reduction in the SiF_4 pressure is noted, resulting in a final pressure of about 400 torr. A clear colorless solution is obtained without any sign of solid formation. The material volatile at 0° is pumped off, and separated by fractional condensation through -126° and -196° traps. The SiF_4 portion (about 22 mmole), trapped at -196° , is condensed back into the reactor which contains a white fluffy solid. After this mixture has been kept at 25° for 24 hours, all volatile material is pumped off at 25° and the SiF_4 is separated again from the HF. The solid residue is treated again with the unreacted SiF_4 at 25° for 14 hours. The materials volatile at 25° are pumped off again. They contain at this point less than 1 mmole of HF. The solid residue is heated in a dynamic vacuum to 50° for 28 hours until no further HF evolution is noticeable. The white solid residue (about 3.8g = 80% yield) has the approximate composition (weight %): $[\text{NF}_4]_2[\text{SiF}_6]$ (95.0), $\text{Cs}[\text{SbF}_6]$ (2.2), $[\text{NF}_4][\text{SbF}_6]$ (2.3).

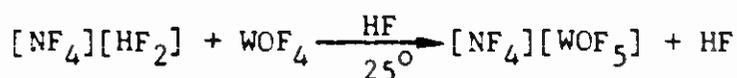
Properties

Bis(tetrafluoroammonium) hexafluorosilicate(IV) is a white

* Available from Matheson, P.O. Box 85, 932 Paterson Plank Road, East Rutherford, NJ 07073

crystalline solid which is stable at 25°, but slowly decomposes at 90° to NF₃, F₂ and SiF₄.²¹ The vibrational spectra of the solid show the following major bands (cm⁻¹): IR(pressed AgCl disk), 1223(mw), 1165(vs), 735(vs,br), 614(m), 609(mw), 478(s), 448(w); Ra, 1164(1.5), 895(0+), 885(0+), 859(10), 649(3.2), 611(5.8), 447,441(3.8), 398(1).

F. TETRAFLUROAMMONIUM PENTAFLUROOXOTUNGSTATE (VI)



Procedure

■ Caution. Anhydrous HF can cause severe burns and protective clothing should be worn when working with liquid HF. All [NF₄]⁺ salts are strong oxidizers and contact with fuels and water should be avoided.

A solution of 20 mmole of [NF₄][HF₂] in 16 mL of dry HF¹³ is prepared at -78° by procedure C and pressure filtered into the second half of the metathesis double U-tube containing 14.6 mmole of WOF₄.³¹ The mixture is stirred with a magnetic stirring bar for 30 min at 25°. The volatile material is pumped off at 25° for 12 hours. The solid residue (about 5g = 86% yield based on WOF₄) has the approximate composition (weight %): [NF₄][WOF₅](96), Cs[SbF₆](2), [NF₄][SbF₆](2).

Properties

Tetrafluoroammonium pentafluoroxotungstate (VI) is a white, crystalline solid which is stable at 55°, but slowly decomposes at 85° to yield

NF_3 , OF_2 , WF_6 and $[\text{NF}_4][\text{W}_2\text{O}_2\text{F}_9]$.²⁵ The vibrational spectra of the solid show the following major bands (cm^{-1}): IR (pressed AgCl disk), 1221(mw), 1160(vs), 991(vs), 688(vs), 620(vs,br), 515(vs); Ra, 1165(0.7), 996(10), 852(8.4), 690(5.4), 613(4.9), 446(1.6), 329(6.8), 285(0.5).

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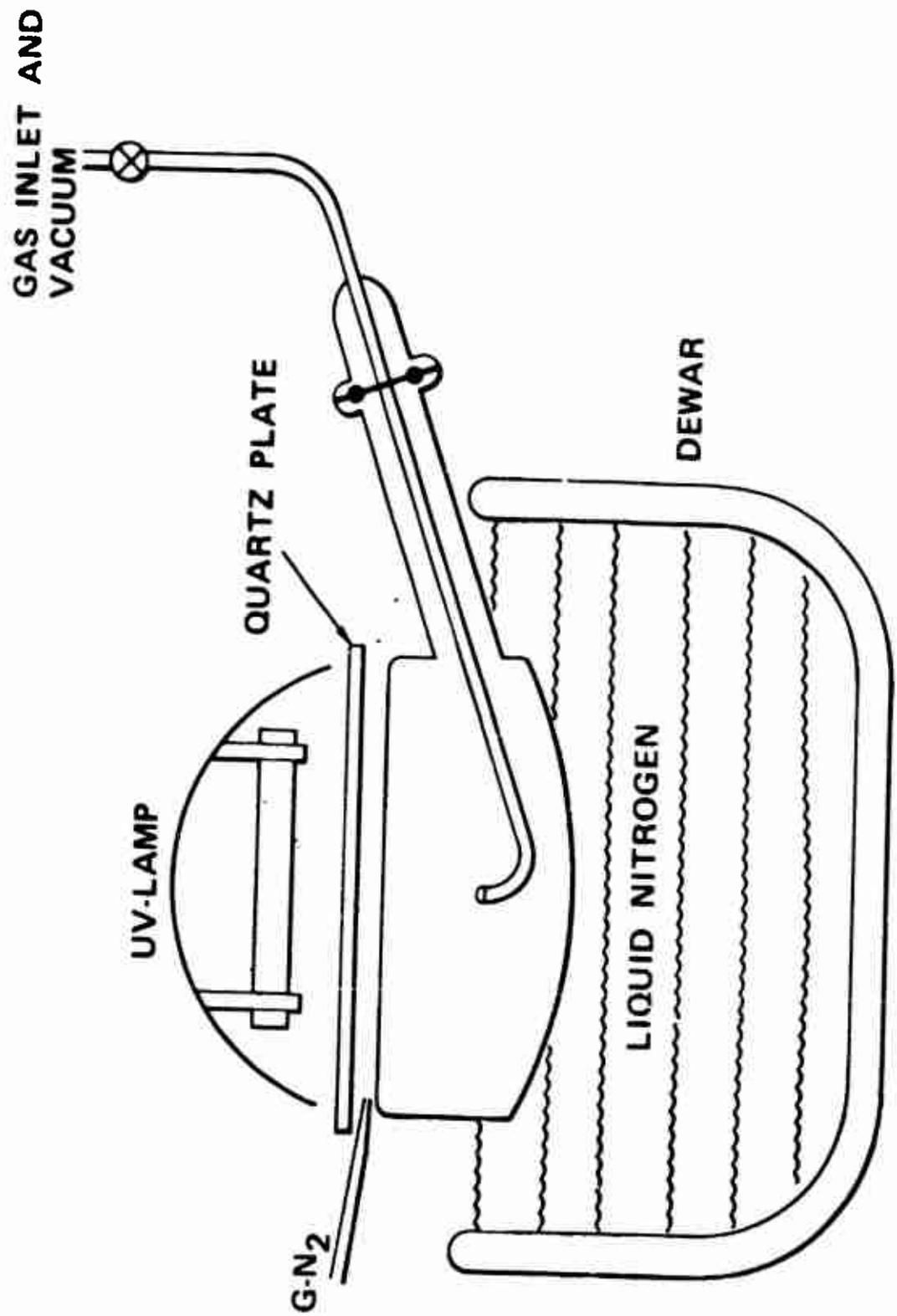


FIGURE 1.

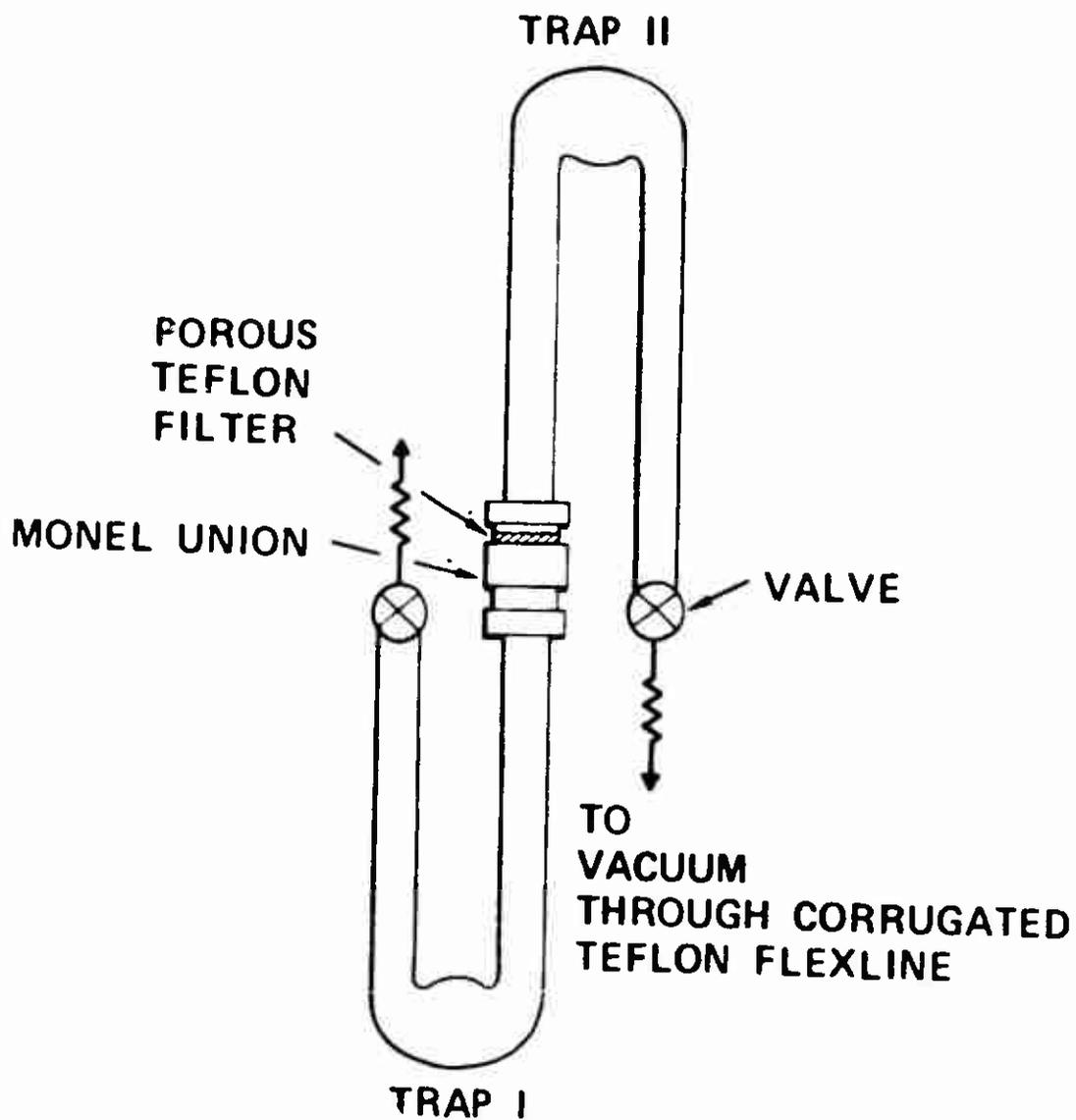


FIGURE 2.

APPENDIX I

CESIUM HEXAFLUOROMANGANATE (IV)

Submitted by WILLIAM W. WILSON* and KARL O. CHRIS^TE*

Checked by

Several methods have been described in the literature for the syntheses of alkali metal hexafluoromanganates (IV). The reactions of K_2MnO_4 ¹, MnO_2 and KF mixtures, or KMnO_4 and 30% H_2O_2 ² with aqueous HF produce K_2MnF_6 , however, the yields and product purities are low. Pure alkali metal hexafluoromanganates (IV) were obtained in high yield by the fluorination with F_2 in a flow system of either $\text{MnCl}_2 + 2\text{MCl}$ at 375 to 400°C,^{3,4} $\text{MnF}_3 + 2\text{KF}$ in a rotating Al_2O_3 tube at 600°C,⁵ or $\text{MnCl}_2 + 2\text{KCl}$ at 280°C,⁶ or by the fluorination of a KMnO_4 - KCl mixture with BrF_3 .⁷ The method described below is based on the fluorination of a stoichiometric mixture of CsF and MnCl_2 in a static system at 400°C.⁸ Hexafluoromanganate (IV) salts have interesting spectroscopic properties,^{9,10} and Cs_2MnF_6 is a starting material for the metathetical synthesis of $(\text{NF}_4)_2\text{MnF}_6$.¹¹

Procedure

■ Caution. Safety barricades must be used for carrying out high pressure fluorination reactions. The ClF_5 - ClF_3 byproducts are strong oxidizers and contact with fuel, water or reducing agents must be avoided.

*Rocketdyne, A Division of Rockwell International Corp.,
Canoga Park, CA 91304

Commercially available $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}^*$ is dehydrated by heating in a Pyrex flask to 255°C in vacuo (10^{-4} torr) for 24 hours. Commercially available CsF^\dagger is dried by fusion in a platinum crucible and immediately transferred to the drybox.

A mixture of finely ground dry CsF (7.717g, 50.80 mmol) and MnCl_2 (3.150g, 25.40 mmol) is placed inside the drybox into a pre-passivated (with ClF_3) 95mL high pressure Monel cylinder (Hoke Model 4HSM, rated for 5000 psi working pressure) equipped with a Monel valve (Hoke, Model 3212M4M). The cylinder is attached to a metal-Teflon vacuum system,¹² evacuated, and cooled to -196°C with liquid N_2 . Fluorine[§] (262 mmol) is condensed into the cylinder. The cylinder is disconnected from the vacuum line, heated in an oven to 400°C for 36 hours, and then cooled again to -196°C on the vacuum line. Unreacted F_2 is pumped off at -196°C through a fluorine scrubber,¹² and the ClF_5 - ClF_3 by-products are pumped off during the warm-up of the cylinder towards room temperature. The yellow solid residue (11.045g, 100% yield) is pure Cs_2MnF_6 . Anal. Calcd. for Cs_2MnF_6 : Cs, 61.14; Mn, 12.63. Found: Cs, 61.2; Mn, 12.5.

Properties

Cesium hexafluoromanganate (IV) is a stable yellow solid which decomposes only slowly in moist air. The infrared spectrum of the solid as a dry powder pressed between AgCl plates shows the following major absorptions: 620, vs (antisymmetric stretch); 338 cm^{-1} , s (antisymmetric deformation). The Raman spectrum of the solid shows bands at 590 vs (symmetric in phase stretch), 502 m (symmetric out of phase stretch), and 304 cm^{-1} , s (symmetric deformation).⁸ According to ref. 4, Cs_2MnF_6 crystallizes at room temperature in the cubic K_2PtCl_6 system with $a = 8.92\text{A}$.

* Available from Alfa Products, Thiokol/Ventron Divn., P.O. Box 299, 152 Andover Street, Danvers, MA 01923

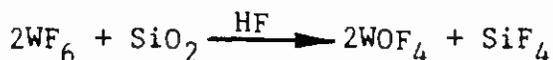
† Available from Kawecki Berylco Industries, Inc., 220 E. 42nd Street, New York, NY 10017

§ Available from Air Products and Chemicals Inc., Specialty Gas Dept., Hometown Facility, P.O. Box 351, Tamaqua, PA 18252

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APPENDIX J
TUNGSTEN OXIDE TETRAFLUORIDE



Submitted by WILLIAM W. WILSON* and KARL O. CHRIS^TE*

Checked by

Tungsten oxide tetrafluoride can be prepared by numerous methods, such as the fluorination of WO_3 at 300°C ,¹ slow hydrolysis of WF_6 ,² the direct fluorination of W in the presence of O_2 at 300°C ,³ the reaction of WF_6 with WO_3 at 400°C ,⁴ the reaction of WOCl_4 with HF ,^{5,6} or by oxygen-fluorine exchange between WF_6 and B_2O_3 .⁶ The method given below is a modification of the method of Paine and McDowell which uses stoichiometric amounts of SiO_2 and WF_6 in anhydrous HF for the controlled hydrolysis of WF_6 .² In our experience,⁷ the use of stoichiometric amounts of SiO_2 and WF_6 leads to the formation of some $\text{H}_3\text{O}^+\text{WOF}_5^-$ and $\text{H}_3\text{O}^+\text{W}_2\text{O}_2\text{F}_9^-$ as by-products which are difficult to separate from WOF_4 . This problem can however be avoided by the use of an excess of WF_6 . Tungsten oxide tetrafluoride is a starting material for the syntheses of numerous WOF_5^- salts.

Procedure

■ Caution. Anhydrous HF causes severe burns and protective clothing and safety glasses should be worn when working with liquid HF.

Quartz wool[†] (1.0482g, 17.445mmol) is placed into a 3/4 inch o.d. Teflon FEP (fluoro-ethylene-propylene copolymer) ampule equipped

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† Available from Preiser Scientific, 1500 Algonquin Parkway,
Louisville, KY 40201

with a Teflon coated magnetic stirring bar and a stainless steel valve. The ampule is connected to a metal-Teflon vacuum system,⁸ evacuated, and dry⁹ HF* (19g) and WF₆[†] (22.102g, 74.207 mmol) are condensed into the ampule at -196°C. The contents of the ampule are allowed to warm to room temperature and are kept at this temperature for 15 hours with stirring. All material volatile at room temperature is pumped off (vacuum of 10⁻⁴ torr) for 12 hours leaving behind 9.7226g of a white solid (weight calcd for 34.89 mmol WOF₄ 9.6244g). This crude product usually still contains some H₃O⁺W₂O₂F₉⁻ (infrared spectrum of the solid pressed as a AgCl disk 3340, 3100, 1625, 1040, 1030, 908 cm⁻¹) and can be purified by vacuum (10⁻⁴ torr) sublimation in an ice water cooled Pyrex sublimator at 55°C resulting in 4.245g of sublimate. The purity of the sublimate is verified by vibrational spectroscopy of the solid (infrared spectrum as a AgCl disk: 1054vs, 733s, 666vs, 550vs, cm⁻¹. Raman: 1058(10), 740(1.9), 727(6.3), 704(0+), 668(0+), 661(0.9), 559(0+), 518(0.7), 325sh, 315sh, 311(5), 260(0+), 238(0.7), 212(0.5), 185(0+) cm⁻¹.¹⁰

Anal. Calcd. for WOF₄: W, 66.65; F, 27.55. Found: W, 66.5; F, 27.7.

Properties

Tungsten oxide tetrafluoride is a white hygroscopic solid (mp 104.7 at 33 mbar, bp 185.9°C) which can readily be sublimed. It is soluble in HF, propylene carbonate, CHCl₃, and absolute alcohol. The ¹⁹F NMR spectrum in propylene carbonate solution consists of a singlet at 65.2 ppm downfield from external CFC1₃ with two satellites with J_{WF} = 69 Hz.¹¹

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† Available from Alfa Products, Thiokol/Ventron Divn., P.O. Box 299, 152 Andover Street, Danvers, MA 01923

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APPENDIX K

Contribution from Rocketdyne, A Division of
Rockwell International, Canoga Park, California 91304

Coordinatively Saturated Fluoro Cations. Oxidative Fluorination Reactions with KrF^+ Salts and PtF_6

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Abstract

The usefulness of KrF^+ salts and PtF_6 as oxidative fluorinators for the syntheses of the coordinatively saturated complex fluoro cations NF_4^+ , ClF_6^+ , and BrF_6^+ was studied. The syntheses of NF_4SbF_6 , NF_4AsF_6 , NF_4BF_4 , and $NF_4TiF_5 \cdot nTiF_4$ from KrF_2 ·Lewis acid adducts and NF_3 were investigated under different reaction conditions. The fluorination of NF_3 by $KrF^+SbF_6^-$ in HF solution was found to proceed quantitatively at temperatures as low as $-31^\circ C$, indicating an ionic two electron oxidation mechanism. An improved synthesis of $KrF^+MF_6^-$ ($M=As, Sb$), Raman data and solubilities in HF, and the existence of a $Kr_2F_3^+ \cdot nKrF_2BF_4^-$ adduct in HF at $-40^\circ C$ are reported. Attempts to fluorinate OF_2 , CF_3NF_2 , and ClF_4O^- with KrF^+ salts were unsuccessful. Whereas KrF^+ is capable of oxidizing NF_3 , ClF_5 , and BrF_5 to the corresponding complex fluoro cations, PtF_6 was shown to be capable of oxidizing only NF_3 and ClF_5 . Since the yield and purity of the NF_4^+ fluoroplatinate salts obtained in this manner was low, NF_4PtF_6 was also prepared from NF_3 , F_2 and PtF_6 at elevated temperature and pressure. General aspects of the formation mechanisms of coordinatively saturated complex fluorocations are discussed briefly.

Introduction

The preparation of coordinatively saturated complex fluoro cations presents a great challenge to the synthetic chemist. The

nonexistence of the corresponding parent molecules preempts the normally facile cation formation by a simple F^- abstraction from a parent molecule, and an F^+ addition to a lower fluoride is ruled out by the fact that fluorine is the most electronegative element and therefore F^+ cannot be generated by chemical means.¹ In view of these difficulties it is not surprising that at the present time only three coordinatively saturated fluoro cations, NF_4^+ ,^{2,3} ClF_6^+ ,^{4,5} and BrF_6^+ ,⁶ are known to exist. In addition to their challenge to the synthetic chemist, the formation mechanism of these cations represents an intriguing and yet unsolved puzzle.⁷

These problems were complicated by the facts that each of the three known coordinatively saturated fluoro cations had been prepared by a different method,²⁻⁶ and that these methods could not readily be transferred from one cation to another. The purpose of this study was to examine whether the synthesis of each coordinatively saturated fluoro cation is indeed limited to a specific method and whether these methods possess any commonalties.

Experimental

Apparatus. Volatile materials used in this work were handled in a stainless steel-Teflon FEP vacuum line. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions and solubility measurements were carried out in HF solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.⁸

Infrared spectra were recorded in the range $4000-200\text{ cm}^{-1}$ on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl windows

in an Econo press (Barnes Engineering Company). Spectra of gases were obtained by using a Teflon cell of 5 cm path length equipped with AgCl windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-A exciting line of an Ar-ion laser and Claassen filter⁹ for the elimination of plasma lines. Sealed glass, Teflon FEP, or Kel-F tubes were used as sample containers in the transverse-viewing transverse-excitation mode. Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

Materials. Literature methods were used for the preparation of PtF_6 ,¹⁰ KrF_2 ,¹¹ CF_3NF_2 ,¹² ClF_3O ,¹³ ClF_5 ,¹⁴ and FNO ¹⁵ and for the drying of HF.¹⁶ Nitrogen trifluoride (Rocketdyne), F_2 (Air Products), OF_2 (Allied Chemical), BrF_5 and BF_3 (Matheson), and AsF_5 , SbF_5 and TiF_4 (Ozark Mahoning) were commercially available. Their purity was checked by vibrational spectroscopy prior to use, and where necessary, improved by fractional condensation or distillation.

Preparation of KrFSbF_6 . Antimony pentafluoride (21.7 mmol) was syringed in the drybox into a prepassivated Teflon-FEP U-tube equipped with two stainless steel valves. The tube was connected to the vacuum line and dry HF (5 ml of liquid) was distilled into the tube. The HF and SbF_5 were allowed to homogenize at ambient temperature, and a preweighed amount of KrF_2 (22.9 mmol) was transferred in a dynamic vacuum into the U-tube at -196°C . The mixture was warmed towards room temperature until a slight effervescence was noted. At this point the tube was cooled again, and the warm up procedure was repeated. After a total of three warm up cycles, all volatile material was pumped off at -22°C leaving behind pure KrFSbF_6 (21.5 mmol = 99% yield based on SbF_5).

KrFAsF_6 was prepared in an analogous manner, except for loading the AsF_5 into the tube on the vacuum line.

Reaction of NF_3 with KrF_2 and AsF_5 . A prepassivated (with ClF_3) 10 ml stainless steel Hoke cylinder equipped with a 1/8" Whitey stainless steel valve was loaded on the vacuum line at -196°C with KrF_2 (6.15 mmol), AsF_5 (3.07 mmol) and NF_3 (21.9 mmol). The cylinder was placed in a liquid N_2 -dry ice slush bath and allowed to warm slowly to room temperature over a 30 hr time period and then was kept in an oven at 53°C for 4 days. The cylinder was cooled to -210°C (N_2 slush bath, prepared by pumping on liquid N_2) and the volatile products were separated during warm up of the cylinder by fractional condensation through traps kept at -156°C (nothing) and -210°C (24.9 mmol of NF_3 and Kr). The white solid residue (827.6 mg = 2.97 mmol) was identified by infrared and Raman spectroscopy as pure NF_4AsF_6 ¹⁷ (96.7% yield based on AsF_5).

Reaction of NF_3 with KrF_2 and BF_3 . The reaction was carried out as described above for the corresponding AsF_5 system, except for a 40% reduction in the amount of starting materials used. The yield of solid NF_4BF_4 was 30.6% based on BF_3 .

Reaction of Solid KrFSbF_6 with NF_3 . KrFSbF_6 (2.42 mmol) was added in the drybox to a prepassivated Teflon PFA U-tube (59 ml volume) equipped with Teflon PFA valve(s). The tube was connected to the vacuum line and NF_3 (2.43 mmol) was added at -196°C . After 3 hr at 22°C , the volatile products were removed. Analyses of the volatile material and of the solid residue showed that 12.7 percent of the KrFSbF_6 had been converted to an NF_4^+ salt.

When the reaction was repeated with 2.32 mmol of KrFSbF_6 and 6.84 mmol of NF_3 at 30°C for 3.5 hr, the conversion of KrFSbF_6 to NF_4^+

salts was 43.8 percent. An additional treatment of the solid mixture of NF_4^+ salts and unreacted KrFSbF_6 with more NF_3 for 4 hr at 30°C resulted in little further conversion to NF_4^+ salts. Vibrational spectra of the white solid product showed the presence of the NF_4^+ , $^{17}\text{KrF}^+$, $^{18}\text{SbF}_6^-$, 19 and $\text{Sb}_2\text{F}_{11}^-$, 17 ions.

Reactions of KrFSbF_6 with NF_3 in HF Solution. General procedure: KrFSbF_6 (~ 3 mmol) was weighed in the drybox into a prepassivated 0.5 in o.d. Teflon PFA U-tube (58 ml volume) equipped with two Teflon PFA valves. The tube was connected to the vacuum line, and anhydrous HF ($\sim 1.25\text{g}$) and NF_3 were added at -196°C . The contents of the tube were warmed for a specified time period to the desired reaction temperature. The reaction was stopped by quickly pumping off the NF_3 , followed by removal of the HF solvent. The material balances were obtained by separating the volatile products via fractional condensation through traps kept at -126° and -210°C , PVT measurements and infrared analysis of each fraction, and by the weight change of the solid phase and its Raman and infrared spectra which were compared against mixtures of known composition. When stoichiometric amounts of KrFSbF_6 and NF_3 were used, the NF_3 was condensed into the U-tube and the valves were closed. When a large excess of NF_3 was used, the NF_3 pressure was kept constant at 1000 mm by the use of a large ballast volume and a pressure regulator. The results of these reactions are summarized in Table 1.

Reaction of PtF_6 with NF_3 in HF. A prepassivated Teflon FEP U-trap (119 ml volume) was loaded at -196°C with HF (5 ml liquid) and equimolar amounts (4.88 mmol each) of PtF_6 , NF_3 and F_2 . The contents of the trap were kept at 25°C for 14 hr. All volatile material was pumped off at 25°C leaving behind 828 mg of a dark

red tacky solid which based on its infrared spectrum was an NF_4^+ salt (1158 cm^{-1} , vs, $\nu_3(\text{F}_2)$) of PtF_6^- and/or a fluoroplatinate polyanion ($665\text{vs}, 625\text{s}, 560\text{vs}$). Attempts were unsuccessful to purify the sample by extraction with anhydrous HF.

UV-Photolysis of $\text{NF}_3\text{-PtF}_6$. A prepassivated 0.5 in o.d. sapphire reactor¹ (26 ml volume) was loaded at -196°C with PtF_6 (1.22 mmol) and NF_3 (1.31 mmol). The mixture was irradiated for 2 days at ambient temperature with a Hanovia Model 616A high-pressure quartz mercury vapor arc lamp. All volatile material was pumped off at 25°C , leaving behind a red-brown solid (116 mg) which based on its infrared spectrum contained the NF_4^+ cation ($2000\text{w}, \nu_1 + \nu_3(\text{F}_2)$; $1218\text{mw}, 2\nu_4(\text{A}_1 + \text{E} + \text{F}_2)$; $1159\text{vs}, \nu_3(\text{F}_2)$; $607\text{m}, \nu_4(\text{F}_2)$)¹⁷ and a fluoroplatinate polyanion (690vs ; 659vs ; 630s ; $535\text{vs}, \text{br}$).

Synthesis of NF_4PtF_6 . Into a prepassivated Monel cylinder (100 ml volume) PtF_6 (2.22 mmol), NF_3 (211.8 mmol), and F_2 (216.7 mmol) were loaded at -196°C . The cylinder was heated to 125°C for 7 days, followed by removal of all material volatile at 25°C . The residue consisted of 802 mg of a dark red solid (weight calcd for 2.22 mmol of $\text{NF}_4\text{PtF}_6 = 884\text{ mg}$) which based on its infrared and Raman spectra consisted mainly of NF_4PtF_6 .^{15, 17, 20} IR: NF_4^+ , $2305\text{vw}, 2\nu_3$; $1995\text{w}, \nu_1 + \nu_3$; $1758\text{vw}, \nu_3 + \nu_4$; $1452\text{w}, \nu_1 + \nu_4$; $1220\text{mw}, 2\nu_4$; $1180\text{sh}, 1158\text{vs}, 1145\text{sh}, \nu_3$; $1049\text{w}, \nu_2 + \nu_4$; $606\text{m}, \nu_4$; PtF_6^- , $1320, 1300$, $1280\text{w}, \nu_1 + \nu_3$; $1220\nu_2 + \nu_3$; $675\text{sh}, 650\text{vs}, 625\text{sh}, \nu_3$; $570\text{s}, \text{tr}, \nu_2$; Ra: NF_4^+ , $850\text{mw}, \nu_1$; PtF_6^- , $641\text{vs}, \nu_1$; $580\text{mw}, \nu_2$; $239\text{m}, \nu_5$; $194\text{w}, \nu_6$.

Reaction of PtF_6 with ClF_5 in HF. A prepassivated 0.75 in o.d. Teflon FEP ampule (49 ml volume) was loaded at -196°C with PtF_6 (2.10 mmol), HF (2 ml liquid), and ClF_5 (4.20 mmol). The mixture was allowed to slowly warm to ambient temperature in an empty

cold dewar. After keeping the ampule for 2 days at ambient temperature, the brown PtF_6 color had disappeared. The volatile material was removed in vacuo at room temperature and separated by fractional condensation. It consisted of the HF solvent and ClF_5 (2.1 mmol). The orange-yellow solid residue (0.91g) was shown by infrared and Raman spectroscopy to be an about equimolar mixture of ClF_4PtF_6 and ClF_6PtF_6 ¹⁵ (weight calcd for a mixture of 1.05 mmol ClF_4PtF_6 and 1.05 mmol ClF_6PtF_6 = 0.923g).

When the reaction was repeated under the same conditions, except for using BrF_5 in place of ClF_5 , no evidence for the formation of a stable BrF_6^+ salt was obtained.

Results

Syntheses and Some Properties of KrF_2 ·Lewis Acid Adducts. Although the synthesis of $\text{KrF}^+\text{MF}_6^-$ (M=As,Sb) salts is well known,^{6,18,21,22} the reported direct combination of KrF_2 with the Lewis acids can result in a spontaneous exothermic decomposition of KrF_2 accompanied by a bright flash and gas evolution.¹⁸ In this study this problem was avoided by dissolving the Lewis acid in a large excess of anhydrous HF, before adding a stoichiometric amount of KrF_2 . This procedure resulted in an easily controllable, scalable and quantitative synthesis of the desired KrF_2 ·Lewis acid adducts.

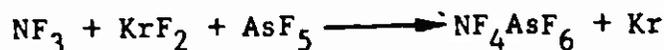
Since the Raman spectra of solid $\text{KrF}^+\text{MF}_6^-$ salts show many more bands than expected for an isolated diatomic cation and an octahedral anion,¹⁸ we have recorded the Raman spectrum of $\text{KrF}^+\text{SbF}_6^-$ in HF solution at -5°C . The total number of bands was reduced to four, as expected for a diatomic KrF^+ (610 cm^{-1}) and octahedral SbF_6^- ($\nu_1(\text{A}_{1g})=656, \nu_2(\text{E}_g)=576, \nu_5(\text{F}_{2g})=278\text{ cm}^{-1}$), thus confirming that the additional bands observed for solid $\text{KrF}^+\text{SbF}_6^-$ ¹⁸ are indeed due to

solid state effects. The solubility of $\text{KrF}^+\text{SbF}_6^-$ in anhydrous HF at -31°C was also measured as 43.9 mg/g HF by the use of a previously described method¹⁶.

Since mixtures of KrF_2 and BF_3 in anhydrous HF are capable of oxidizing NF_3 to NF_4^+ (see below), it was interesting to establish whether BF_3 forms an adduct with KrF_2 under these conditions. Raman spectra of an equimolar mixture of KrF_2 and BF_3 in anhydrous HF at -40°C showed bands (597(10), 561(2), 462(7.5), 334(1), 179(1.7)) characteristic for $\text{Kr}_2\text{F}_3^+ \cdot x\text{KrF}_2$ ¹⁸ and a weak band at 879 cm^{-1} due to $\nu_1(\text{A}_1)$ of BF_3 .²³ The bands expected for BF_4^- were difficult to observe under the given conditions due to their low relative intensity and the low signal to noise ratio. Removal of volatile material in a dynamic vacuum at -78°C resulted in a white solid residue which, based on its Raman spectrum (461 cm^{-1}) at -110°C , consisted of KrF_2 .²⁴ These results clearly show that KrF_2 does not form a stable solid adduct with BF_3 at temperatures as low as -78°C , but that in HF solution, even at temperatures as high as -40°C , ionization to $[\text{Kr}_2\text{F}_3^+ \cdot x\text{KrF}_2][\text{BF}_4^-]$ occurs. The observation of free BF_3 is readily accounted for by the formation of krypton fluoride polycations which leaves most of the BF_3 uncomplexed. Whether any free KrF_2 is also present in the HF solution is difficult to say because the KrF_2 band coincides with the 462 cm^{-1} band of $\text{Kr}_2\text{F}_3^+ \cdot x\text{KrF}_2$.¹⁸

Fluorination Reactions with KrF^+ Salts. The oxidative fluorination of NF_3 to NF_4^+ by KrF^+ salts was first discovered²⁵ by Artyukhov and Khoroshev and independently rediscovered in our laboratory. In our study, mixtures of NF_3 , KrF_2 and either AsF_5 or BF_3 in mole ratios of 7:2:1 were allowed to warm in stainless steel cylinders from -196 to 50°C under autogenous pressures of about 75 atm. In two

days NF_4AsF_6 and NF_4BF_4 had formed in 97 and 30% yield, respectively, based on the limiting reagents AsF_5 and BF_3 , in agreement with the following equations



and



In the Russian study the reactions were carried out at room temperature with either solid $\text{KrF}^+\text{SbF}_6^-$ and one atm of NF_3 , or in HF solution with stoichiometric amounts of KrF_2 , NF_3 and the following Lewis acids, SbF_5 , NbF_5 , PF_5 , TiF_4 or BF_3 at total pressures of 3-4 atm and with reaction times of 1-3 hr. Based on elemental analyses and vibrational spectra their products were assigned to NF_4^+ salts of SbF_6^- , NbF_6^- , PF_6^- , TiF_6^{2-} and BF_4^- , respectively.²⁵ We have repeated some of these reactions in our laboratory because for $(\text{NF}_4)_2\text{TiF}_6$ and NF_4SbF_6 the reported vibrational spectra were those of poly-anions,^{17,19,26} and no yields and concentration or temperature dependences were given which would help to shed some light on the possible mechanism of these reactions.

Our results for the reaction of solid KrFSbF_6 with NF_3 showed that indeed the NF_4^+ cation is formed, but that under the reported conditions²⁵ the reaction is incomplete and that the NF_4^+ salt is mainly $\text{NF}_4\text{Sb}_2\text{F}_{11}$ and not NF_4SbF_6 .

When the reaction of KrF_2 - SbF_5 mixtures or of preformed KrFSbF_6 with stoichiometric amounts of NF_3 was carried out, as previously reported,²⁵ in HF solution at ambient temperature, the reaction was complete in less than three hours. However, contrary to the previously reported elemental analysis but in agreement with the listed vibrational spectra,²⁵ the solid product consisted mainly of $\text{NF}_4\text{Sb}_2\text{F}_{11}$ (~90%) and not NF_4SbF_6 . The formation of mainly $\text{NF}_4\text{Sb}_2\text{F}_{11}$ suggests that under these conditions the oxidation of

NF₃ by KrFSbF₆ is not quantitative and that some KrFSbF₆ decomposes to Kr, F₂ and SbF₅ with the latter combining with NF₄SbF₆ to form NF₄Sb₂F₁₁. By lowering the reaction temperature, we succeeded in completely suppressing the formation of NF₄Sb₂F₁₁, and NF₄SbF₆ was obtained as the only product, contaminated by large amounts of unreacted KrFSbF₆. However a quantitative oxidation of NF₃ by KrFSbF₆ according to



was accomplished by the use of a sufficient excess of NF₃. Since the concentration of NF₃ in the HF solution is proportional to the NF₃ pressure above the solution,²⁷ the excess of NF₃ required for a complete reaction can be minimized by using a small ullage in the reactor. This results in a high NF₃ pressure and consequently in a high concentration of NF₃ in the HF solution. The results of a series of runs are summarized in Table 1 and demonstrate that, for example at -31°C in HF solution at an NF₃ pressure of 1000 mm, NF₃ can quantitatively be oxidized by KrFSbF₆ to NF₄SbF₆ in less than one hour.

In the absence of yield data in the previous report,²⁵ it was of interest to examine whether NF₄BF₄ can also be formed quantitatively under similar conditions. We found that an equimolar mixture of KrF₂, NF₃ and BF₃ in anhydrous HF, when allowed to warm slowly from -196 to 25°C and kept at 25°C for 3 hr, resulted in only a 28.1% yield of pure NF₄BF₄. When the reaction was carried out at -78°C for 3 hr, the yield of NF₄BF₄ (7.1%) was, contrary to the NF₃-KrFSbF₆ system, still appreciable. Without the use of HF as a solvent and at ambient pressure, no detectable amounts of NF₄BF₄ were obtained after 3 hr at 25°C. However, as stated above, the use of a sevenfold excess of NF₃ at 45 atm pressure and gentle

Table 1. Oxidative Fluorination of NF_3 to NF_4SbF_6 by KrFSbF_6 in HF Solution

Reaction Temperature [°C]	Ratio of Start. Mat. $\text{KrFSbF}_6:\text{NF}_3$	Reaction time [hr]	Conversion of KrFSbF_6 (%)	Product Composition (%)
25	1:1	3	100	$\text{NF}_4\text{Sb}_2\text{F}_{11}$ (91), NF_4SbF_6 (9)
-31	1:1	3	37	NF_4SbF_6 (37), KrFSbF_6 (63)
-31	large excess of NF_3 $P_{\text{NF}_3} = 1000 \text{ mm}$	1	100	NF_4SbF_6 (100)
-45	1:1	3	23	NF_4SbF_6 (23), KrFSbF_6 (77)
-78	1:1	3	0	KrFSbF_6 (100)

heating to 53°C for 4 days resulted in a 31% yield of NF_4BF_4 .

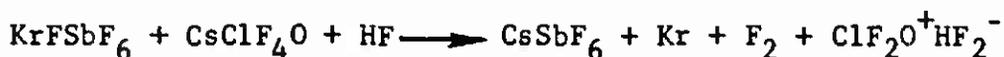
In view of the known tendency of TiF_4 to form polyanion salts with $(\text{NF}_4)_2\text{TiF}_6^{26}$ and the fact that the vibrational bands attributed in the Russian study²⁵ to TiF_6^{2-} resemble those of a polyanion,²⁶ we have also repeated the reaction of NF_3 with KrF_2 and TiF_4 in the same 2:2:1 mole ratio in HF solution at room temperature for 3 hr. Based on the observed material balance, our solid product had the average composition $\text{NF}_4\text{TiF}_5 \cdot 2.25\text{TiF}_4$. The presence of only polytitanate anions and of no TiF_6^{2-} was confirmed by vibrational spectroscopy (strongest Raman bands at 795 and 755 cm^{-1}). Based on our above results for NF_4SbF_6 , it appears safe to predict that the use of a large excess of NF_3 and particularly of an increase in the NF_3 pressure and concentration should also decrease the extent of polyanion formation in the NF_3 - KrF_2 - TiF_4 system.

Attempts to prepare the unknown $\text{OF}_3^+\text{AsF}_6^-$ and $\text{OF}_3^+\text{SbF}_6^-$ salts by the above methods (reaction of OF_2 with KrFMF_6 in either HF solution at temperatures as low as -31°C or neat in a nickel cylinder under 25 atm of OF_2 pressure) produced no evidence for the existence of these salts.

We have also attempted to oxidatively fluorinate CF_3NF_2 with KrF^+ salts to CF_3NF_3^+ salts. A mixture of KrF_2 , AsF_5 and CF_3NF_2 in a mol ratio of 1.86:1:5.62, when slowly warmed in a nickel reactor from -196 to 50°C produced NF_3 and CF_4 as the main products, with the excess of CF_3NF_2 being decomposed to give CF_4 and cis- and trans- N_2F_2 . The cis- N_2F_2 reacted with AsF_5 to form solid $\text{N}_2\text{F}^+\text{AsF}_6^-$.²⁸ Attempts to moderate this reaction

by using preformed KrFSbF_6 and HF as a solvent resulted again in an oxidative fluorination of the C-N bond with CF_4 , and NF_3 and some trans- N_2F_2 as the main products. However in this case the white solid product consisted mainly of $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$.

An attempt was also made to oxidize the ClF_4O^- anion^{29,30} with preformed KrFSbF_6 in anhydrous HF solution at -78°C . The following reaction was observed.



This result is not surprising since CsClF_4O was shown to readily undergo solvolysis in HF,

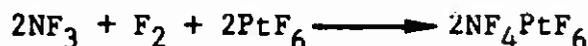


and because the ClF_2O^+ cation is difficult to oxidize.¹⁵ Reaction of solid KrFSbF_6 with CsClF_4O and of liquid ClF_3O with KrF_2 also did not result in oxidation of the ClF_4O^- anion.

Fluorination Reactions with PtF_6 . Since gaseous PtF_6 does not react with gaseous NF_3 at ambient temperature to any significant extent,²⁰ we have studied this reaction in HF solution without irradiation and in the gas phase under the influence of unfiltered uv-irradiation. In both cases, the vibrational spectra of the solid reaction products demonstrated the formation of some NF_4^+ salts. The anions in these salts were not very well defined due to the simultaneous formation of PtF_5 and possibly lower platinum fluorides and their interaction with PtF_6^- to form polyanions. Attempts to purify the products by extraction with anhydrous HF were unsuccessful.

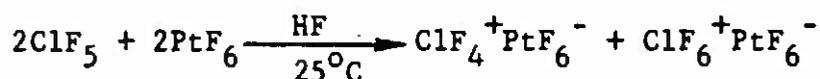
To obtain a better defined sample of an NF_4^+ fluoroplatinate salt for comparison, we have prepared NF_4PtF_6 by a known, but unpublished

method.²⁰ Using a large excess of F_2 and NF_3 and carrying out the reaction at $125^\circ C$ under an autogenous pressure of about 140 atm, NF_4PtF_6 was obtained in high yield according to



The NF_4PtF_6 salt is a stable solid which shows spectra characteristic for tetrahedral NF_4^{+17} and octahedral PtF_6^{-15} .

It was shown that the known oxidative fluorination of ClF_5 to ClF_6^+ with $PtF_6^{4,5,15}$ can also be carried out at room temperature in HF solution without requiring uv-irradiation.



However, attempts to prepare $BrF_6^+PtF_6^-$ in an analogous manner from BrF_5 and PtF_6 were unsuccessful.

Discussion

Syntheses of Coordinatively Saturated Fluoro Cations. At present, only three coordinatively saturated fluoro cations, i.e. NF_4^+ , ClF_6^+ and BrF_6^+ are known to exist. They can be prepared from the corresponding lower fluorides by one or more of the following three methods: (1) oxidation by KrF^+ salts; (2) oxidation by PtF_6 ; and (3) oxidation by F_2 in the presence of a strong Lewis acid and an activation energy source.

One of the goals of this study was to examine the scope of these methods. A priori one would expect that the ease of preparing a

given coordinatively saturated fluoro cation should increase with increasing oxidizing power of the fluorinating agent and with decreasing oxidation potential of the desired coordinatively saturated fluoro cation. Although the oxidation potentials of the three coordinatively saturated fluoro cations are unknown, a comparison with those of either the isoelectronic fluorides CF_4 , SF_6 and SeF_6 or the corresponding oxo anions in the same oxidation states, i.e. NO_3^- , ClO_4^- and BrO_4^- , suggests that the oxidation potentials should increase in the following order $\text{NF}_4^+ < \text{ClF}_6^+ < \text{BrF}_6^+$. As far as the order of oxidizing power of KrF^+ , PtF_6 and F_2 -Lewis acid combinations is concerned, Sokolov et al. have shown that KrF^+ can oxidize PtF_6^- to PtF_6 ,³¹ and both, KrF^+ and PtF_6 , are expected to be stronger oxidizers than mixtures of F_2 with Lewis acids. Therefore, the oxidizer strength should increase in order: F_2 -Lewis acid $< \text{PtF}_6 < \text{KrF}^+$.

The results of this study are in accord with these predictions. Thus, KrF^+ , the most powerful oxidizer, is capable of oxidizing all three substrates, NF_3 , ClF_5 and BrF_5 . The second strongest oxidizer, PtF_6 , can still fluorinate NF_3 and ClF_5 , whereas the weakest oxidizer, the Lewis acid- F_2 mixtures, can oxidize only NF_3 . These results show that the preparative methods are transferable from one coordinatively saturated fluoro cation to another, provided that the oxidant is powerful enough to oxidize the substrate. Obviously, secondary effects, such as the possibility of high activation energy barriers and competitive side reactions might also be important. For example, the activation energy sources used in the F_2 -Lewis acid method can cause breakdown of ClF_5 and BrF_5 to F_2 and lower fluorides with the latter being continuously removed from the equilibrium by rapid complexing with the Lewis acid. For NF_3 , such a side reaction is not effective, and the F_2 -Lewis acid method is therefore well suited for the preparation of NF_4^+ salts.

Formation Mechanisms of Coordinatively Saturated Fluoro Cations.

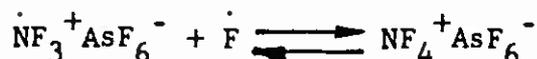
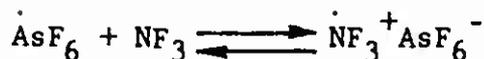
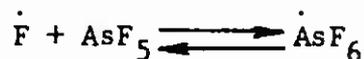
Previous reports⁷ have been concerned almost exclusively with the formation and decomposition mechanisms of NF_4^+ salts, and several different mechanisms have been proposed. These include the heterolytic fission of fluorine,^{2,32}



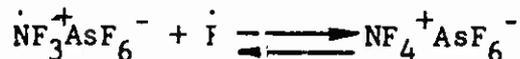
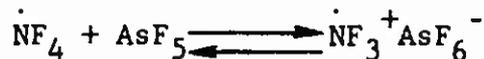
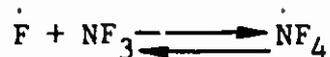
the dissociation of NF_4AsF_6 to yield unstable NF_5 ,³³



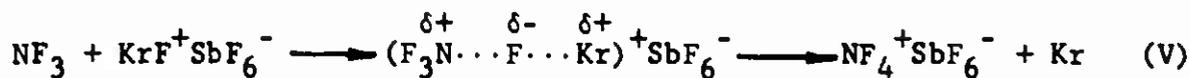
the formation of an intermediate strongly oxidizing Lewis acid·F radical,³⁴



the formation of an intermediate NF_4 radical,⁷



and the absorption and ionization of NF_3 on a $\text{KrF}^+\text{MF}_6^-$ surface.²⁵



For the formation of NF_4^+ salts from NF_3 , F_2 and Lewis acids, the importance of the F_2 dissociation step and of NF_3^+ formation has previously been experimentally confirmed,^{34,35} thus rendering mechanisms (III) and IV) most likely. Of these two mechanisms (IV) has previously been preferred by us because the formation and decomposition of NF_4^+ salts were assumed to follow the same mechanism and the decomposition of NF_4AsF_6 is suppressed more strongly by AsF_5 than by NF_3 .⁷ However recent ab initio molecular orbital calculations³⁶ have provided evidence for NF_4 being energetically unfavorable, and the formation and decomposition of NF_4^+ salts do not necessarily proceed by the same mechanism. These considerations prompted us to reconsider our previous preference.

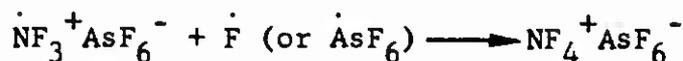
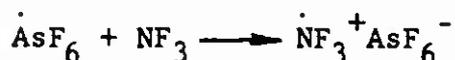
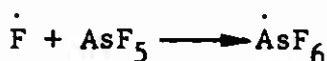
The results of the present study confirm that NF_4^+ salts can be formed from NF_3 and either F_2 -Lewis acid mixtures, KrF^+ salts or PtF_6 . Furthermore, the fact that the reaction of KrF^+ with NF_3 proceeds not only quantitatively, but also at temperatures (-31 to -45°C) at which $\text{KrF}^+\text{SbF}_6^-$ is completely stable, rules out a free radical mechanism based on the decomposition of KrF_2 to Kr and F atoms and supports an ionic mechanism for the KrF^+-NF_3 reaction. In such an ionic mechanism, NF_3 is oxidized either to an intermediate NF_3^+ radical cation or directly to NF_4^+ . In view of the quantitative yields of NF_4^+ salts and our failure to obtain evidence for an intermediate NF_3^+ radical cation in these KrF^+ reactions by ESR spectroscopy, the direct fluorination to NF_4^+ is preferred. One can easily envision an intermediate activated complex between the electrophilic KrF^+ cation and the, albeit weak, electron donor NF_3 which could readily decompose to NF_4^+ with Kr elimination.

For the reactions of NF_3 with F_2 -Lewis acid mixtures the requirement for an activation energy source capable of dissociating F_2 ,³⁴ the ESR evidence for the intermediate formation of the NF_3^+ radical cation,³⁵ and the unlikely formation of an NF_4 radical³⁶ favor the free radical mechanism III. For the thermal decomposition of NF_4^+ salts which are derived from stable Lewis acids, mechanism II is preferred because it best explains the observed strong rate suppression by the Lewis acids.⁷

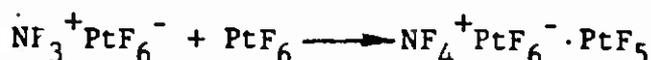
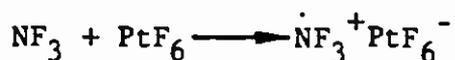
Even in the absence of experimental data it appears rather safe to propose for the PtF_6 oxidation reactions a one electron transfer leading to $\text{NF}_3^+\text{PtF}_6^-$ as an intermediate which is then further fluorinated by a second PtF_6 molecule to NF_4^+ . Such a mechanism is in accord with the rather low yields of NF_4^+ salts obtained for the NF_3 - PtF_6 system, and has previously also been proposed for the ClF_5 - PtF_6 system.¹⁵

Considering all the experimental evidence presently available for the formation mechanisms of coordinatively saturated complex fluoro cations, it appears that all reactions exhibit a certain commonality. The crucial step in all systems appears to be the reaction of a powerful one electron (PtF_6 or Lewis acid·F) or two electron (KrF^+) oxidizer with the substrate (NF_3 , ClF_5 , or BrF_5) resulting in an electron transfer from the substrate to the oxidant, with a simultaneous (in the case of KrF^+) or subsequent (in the case of PtF_6 and Lewis acid·F) fluorination of the intermediate radical cation (NF_3^+ , ClF_5^+ , BrF_5^+) to give the final product (NF_4^+ , ClF_6^+ , BrF_6^+). Thus, the mechanisms of the three presently known methods for the syntheses of NF_4^+ salts might be written in the following manner.

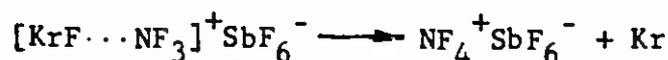
Lewis acid -F₂ system:



PtF₆ system:



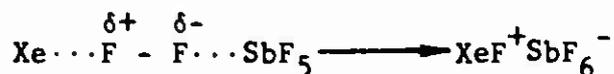
and KrF⁺ system:



As can be seen from these equations, an ionic oxidant (KrF⁺) results in an ionic mechanism and a radical oxidant (LAF or PtF₆) in a radical mechanism.

If in the Lewis acid -F₂ reactions the hard base NF₃ is replaced by a soft base, such as Xe, the reaction can proceed even in the absence of an activation energy source, as was demonstrated by Stein for the Xe-F₂-SbF₅ system.³⁷ Although XeF⁺ is not a coordinatively saturated cation, this reaction is most interesting. Contrary to the NF₃-F₂-Lewis acid reactions, it probably proceeds as a two electron oxidation reaction by F₂ and therefore might be

considered as the only presently known example of an actual heterolytic fission of fluorine by a Lewis acid and a Lewis base.³²



The lower activation energy required for fluorinating Xe, compared to NF_3 , is attributed mainly to its increased polarizability, i.e. it is a softer base, and to a lesser degree to the difference in their ionization potentials ($\text{IP}_{\text{NF}_3} = 13.0$, $\text{IP}_{\text{Xe}} = 12.13\text{eV}$), because the hard base O_2 has an even lower IP of 12.06eV , but does not react with fluorine and a Lewis acid in the absence of an activation energy source.

Conclusion. Although the present study has provided us with more insight into the formation reactions of coordinatively saturated complex fluoro cations, and particularly into those involving the use of KrF^+ salts as an oxidant, there is a definite need for more experimental and theoretical work in this field to further establish the mechanisms of these interesting reactions.

Acknowledgement. We are indebted to Drs. C. J. Schack and L. R. Grant for helpful discussions, to Drs. I. B. Goldberg and T. McKinney for ESR measurements, and to the Army Research Office and the Office of Naval Research for financial support of this work.

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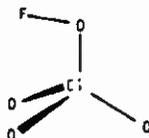
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Fluorine Perchlorate. Vibrational Spectra, Force Field, and Thermodynamic Properties

KARL O. CHRISTE* and E. C. CURTIS

Received December 15, 1981

Infrared spectra of gaseous, solid, and matrix-isolated ClO_3OF and Raman spectra of liquid ClO_3OF are reported. All 12 fundamental vibrations expected for the covalent perchlorate structure



of symmetry C_2 , were observed and assigned. A modified valence force field was computed for ClO_3OF by using the observed ^{35}Cl - ^{37}Cl isotopic shifts, symmetry relations between the A' and the A'' block, and the off-diagonal symmetry force constants of the closely related FCIO_3 molecule as constraints. Previous assignments for ClO_3OCl , ClO_3OBr , ClO_3OCF_3 , Cl_2O_7 , and Cl_2O_8 are revised. The ^{19}F NMR spectrum of ClO_3OF was recorded, and thermodynamic properties were computed in the range 0–2000 K.

Introduction

Fluorine perchlorate (or perchloryl hypofluorite) was probably first prepared¹ in 1929 by Fichter and Brunner by the fluorination of dilute HClO_4 with F_2 but was incorrectly identified. The first positive identification of ClO_3OF was reported² in 1947 by Rohrback and Cady, who obtained the compound from the reaction of F_2 with concentrated perchloric acid. They reported that ClO_3OF consistently exploded when frozen.

In view of its explosive nature, it is not surprising that very few papers dealing with ClO_3OF have been published since then. In 1962, Agahigian and coworkers reported³ the ^{19}F NMR spectrum of ClO_3OF in CFCl_3 and four infrared absorptions of the gas. The same four infrared bands have also been observed in a study⁴ at United Technology Corp. in which the heat of hydrolysis was measured for ClO_3OF . Macheteau and Gillardeau studied⁵ the thermal decomposition of ClO_3OF

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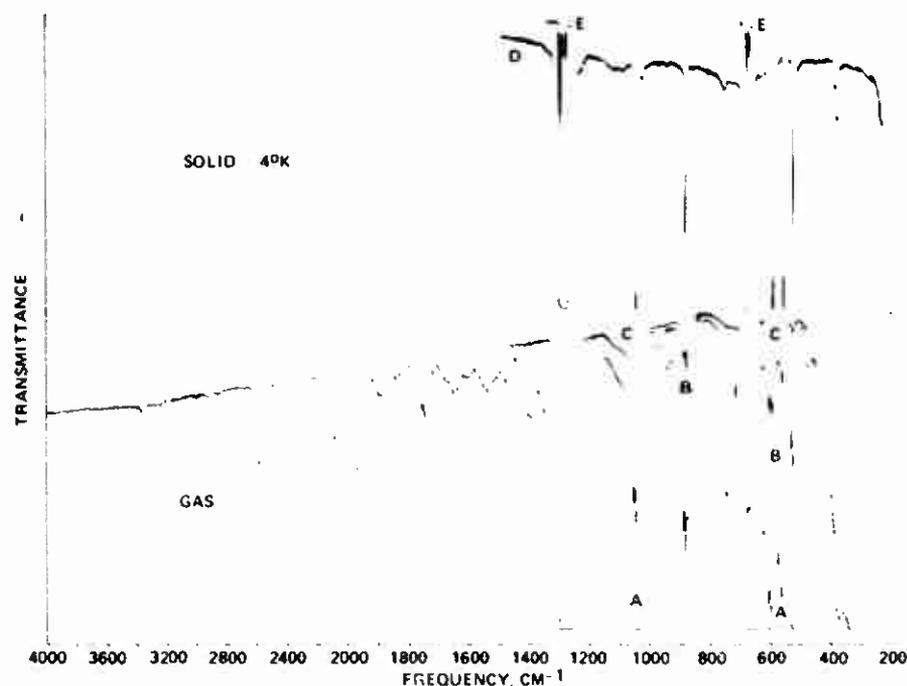


Figure 1. Traces A, B, and C: infrared spectra of gaseous ClO_3OF recorded in a 5-cm path length cell at pressures of 1000, 100, and 10 torr, respectively. The broken line indicates background absorption by the AgCl windows. Traces D and E: infrared spectra of neat and Ne matrix-isolated ClO_3OF , respectively, recorded at 4 K with CsI windows.

and confirmed the four infrared bands previously reported.^{3,4} Small amounts of ClO_3OF have been reported to form as byproducts in the reactions of F_2 with metal perchlorates^{4,6,7} and Cl_2O_6 .⁸ Force constants have been predicted⁹ for ClO_3OF by Witt and Hammaker using the four published infrared frequencies, estimating the missing frequencies from the known ClO_3OCl data¹⁰ and transferring five internal force constants from ClO_3OCl to ClO_3OF . It was recently found that very pure ClO_3OF could be obtained in high yield by the thermal decomposition of NF_4ClO_4 .¹¹ The ClO_3OF , prepared in this manner, could be manipulated and repeatedly frozen without explosions.¹² In view of this improved synthesis and the paucity of previous data on ClO_3OF , a better characterization of this compound was undertaken.

Experimental Section

Caution! Although no explosions were incurred during the present study, the original reports² of Rohrback and Cady indicate that ClO_3OF is a highly sensitive and powerful explosive. It should be handled only in small quantities and with proper safety precautions.

Fluorine perchlorate was prepared by thermal decomposition of NF_4ClO_4 ^{11,13} at ambient temperature and was purified by fractional condensation in a well-passivated (with ClF_3) stainless steel-Teflon FEP vacuum system. Fluorine perchlorate was found to pass slowly through a -126°C trap but to stop in a colder trap. The only impurity detectable in the infrared spectrum of the gas at 1000 mm pressure was a trace of FClO_2 .

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points.^{14,15} The reported frequencies and isotopic shifts

are believed to be accurate to ± 2 and $\pm 0.1\text{ cm}^{-1}$, respectively. Gas spectra were recorded with use of a Teflon cell of 5-cm path length equipped with a Teflon PFA valve (Fluoroware Inc.) and AgCl windows. The spectra of neat and matrix-isolated ClO_3OF were recorded at 4 K with use of an Air Products Model ACL3 helium refrigerator equipped with CsI windows. Research grade N_2 or Ne (Matheson) was used as the matrix in a mole ratio of 1000:1.

The Raman spectra were recorded on a Cary Model 83 spectrometer using the 4880-Å exciting line with a Claassen filter for the elimination of plasma lines.¹⁶ Polarization measurements were carried out by method VIII, as described¹⁶ by Claassen et al. A flamed-out 4-mm o.d. quartz tube was used as a sample container in the transverse excitation-transverse viewing mode. It was cooled to -100°C in an apparatus similar to that¹⁷ described by Miller and Harney.

The ^{19}F NMR spectrum of ClO_3OF in HF solution was recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external CFCl_3 with positive shifts being downfield from CFCl_3 .

Results and Discussion

Properties of ClO_3OF . Fluorine perchlorate is colorless as a gas and a liquid and white as a solid. It was found to be stable at room temperature in either Teflon or passivated steel containers and to be the most stable member of the series ClO_3OF , ClO_3OCl , ClO_3OBr . Contrary to the original report of Rohrback and Cady,² explosions were not incurred on either freezing or melting ClO_3OF . Since Rohrback and Cady had prepared their sample of ClO_3OF by fluorination of HClO_4 , a small amount of the latter could have caused their samples to be more sensitive.¹⁸

The ^{19}F NMR chemical shift of ClO_3OF has been reported³ to be 225.9 ppm downfield from CFCl_3 . However, since the

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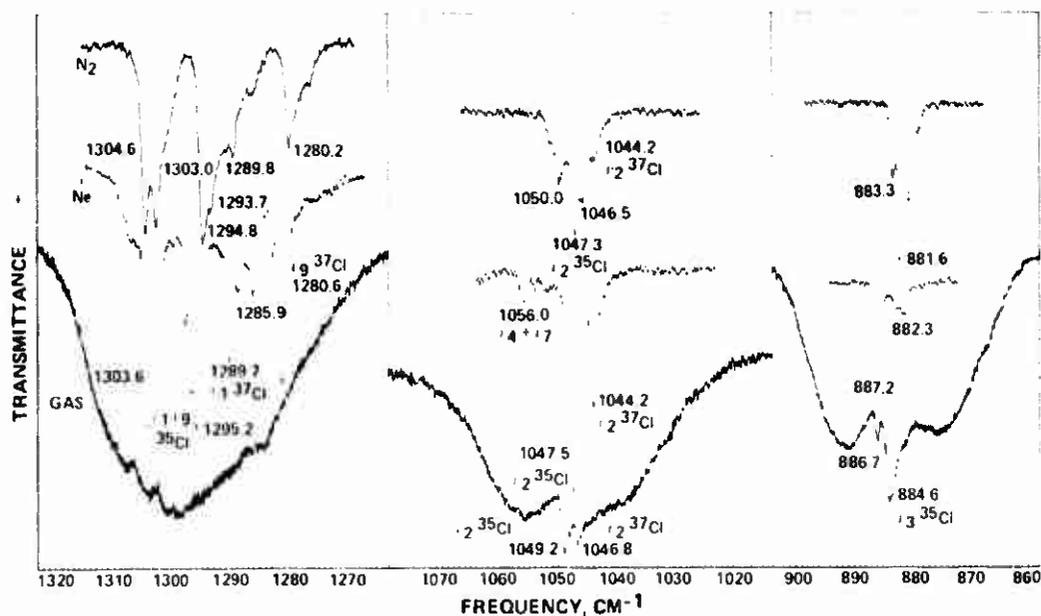


Figure 2. Infrared spectra of N₂ and Ne matrix-isolated and of gaseous ClO₃OF recorded with 20-fold scale expansion under higher resolution conditions.

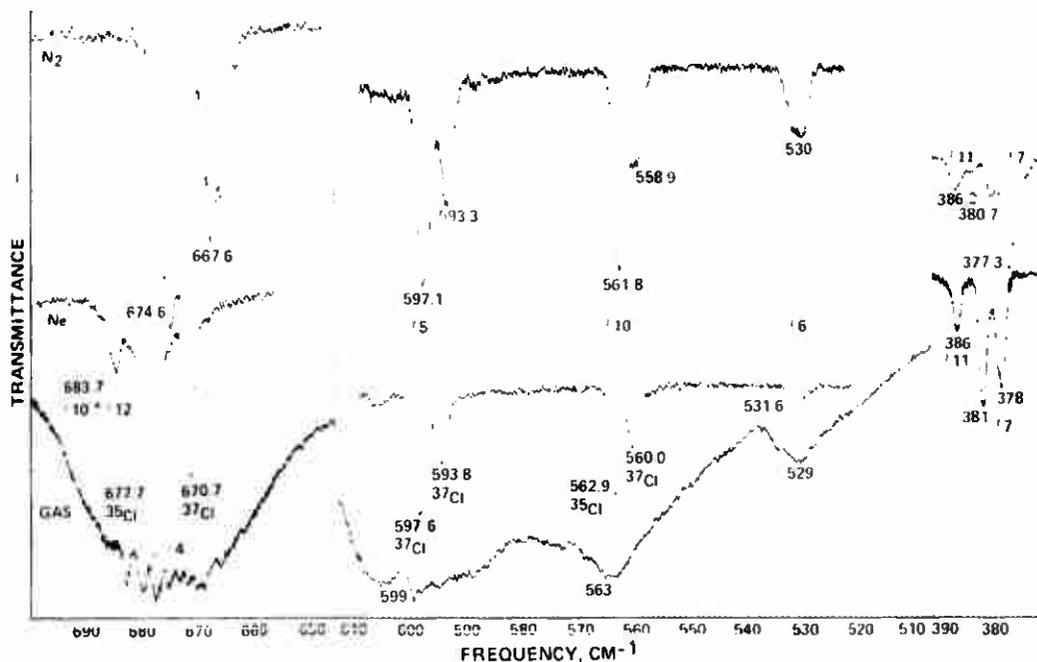
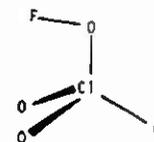


Figure 3. See caption of Figure 2.

shift for FClO₃, reported in the same paper, is in error by about 35 ppm,¹⁹ we have redetermined the shift for ClO₃OF. In HF solution, a single line, 219.4 ppm downfield from external CFCl₃, was observed, in fair agreement with the previously reported³ value of 225.9 ppm.

Vibrational Spectra. The infrared spectra of ClO₃OF were recorded for the gas, and for the neat and the neon- and nitrogen-matrix-isolated solid (see Figures 1-3). The Raman spectra of liquid ClO₃OF, recorded at -100 °C, are given in Figure 4. The observed frequencies and their assignments are summarized in Table I. The four infrared bands previously reported³⁻⁵ for gaseous ClO₃OF agree well with our results.

Assignments. By analogy with closely related molecules, such as CF₃OF,^{20,21} fluorine perchlorate should possess a staggered structure of symmetry C_{3v}.



The 12 fundamental vibrations expected for ClO₃OF of symmetry C_{3v} can be classified as 8 A₁' and 4 A₂'', where all modes are allowed in both the infrared and the Raman spectra. In

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Table I. Vibrational Spectra of ClO₃OF

obsd freq, cm ⁻¹ , and intens						assign in point group C _{2v}	
gas	infrared			Raman			
	N ₂ matrix	Ne matrix	solid	liquid	III' soln		
2588 vw						{1302 + 1295 = 2597 2 × 1295 = 2590	ν ₁ + ν ₆ (A'') 2ν ₆ (A'')
2335 w						1295 + 1049 = 2344	ν ₉ + ν ₂ (A'')
2183 vvw						{1302 + 885 = 2187 1295 + 885 = 2180	ν ₁ + ν ₅ (A') ν ₆ + ν ₄ (A'')
2092 vw						2 × 1049 = 2098	2ν ₂ (A')
1968 vw						1295 + 677 = 1972	ν ₉ + ν ₄ (A'')
1891 vvw						1295 + 599 = 1894	ν ₉ + ν ₅ (A'')
1749 vw						2 × 885 = 1770	2ν ₃ (A')
1670 vvw, sh						1295 + 379 = 1674	ν ₉ + ν ₇ (A'')
1645 vvw						1049 + 599 = 1648	ν ₂ + ν ₅ (A')
1610 vvw, sh						1049 + 563 = 1612	ν ₂ + ν ₁₀ (A'')
1555 vvw, sh						885 + 677 = 1562	ν ₃ + ν ₈ (A')
1538 vvw						1302 + 230 = 1532	ν ₁ + ν ₈ (A')
1480 vvw						885 + 599 = 1484	ν ₃ + ν ₄ (A')
1394 vvw						563 + 559 + 230 = 1392	ν ₁ + ν ₁₁ + ν ₆ (A'')
1345 vvw, sh						2 × 677 = 1354	2ν ₄ (A')
		1307 sh					
	1304.6 vs	{1303.6 vw	1284 vs	1289 (0.3) br	1289 (0.3)		ν ₁ (A') ³⁵ Cl
	1303.0 vs	{1302 sh				2 × 386 + 529 = 1301	2ν ₁₁ + ν ₆ (A')
	1301.8 sh	{1297.4 mw					
	1294.8 vs	{1296.1 mw	1284 vs	1289 (0.3) br	1289 (0.3)		ν ₉ (A'') ³⁵ Cl
	1293.7 sh	{1295.2 vs					
129 ⁺ vs	1289.8 m	{1289.7 m					ν ₁ (A') ³⁷ Cl
		{1288.4 mw				2 × 378 + 529 = 1285	2ν ₇ + ν ₆ (A')
	1286.4 m	{1285.9 mw					ν ₆ (A'') ³⁷ Cl
		{1281.6 w					
	1280.2 ms	{1280.6 ms					
	1276 sh						
1195 vs		1063 w				2 × 599 = 1198	2ν ₅ (A')
		1056.0 w				2 × 529 = 1058	2ν ₆ (A')
	1055 vw					678 + 379 = 1057	ν ₆ + ν ₇ (A') ³⁵ Cl
	{1051.2 sh					671 + 379 = 1050	ν ₄ + ν ₇ (A') ³⁷ Cl
	{1050.0 mw						
1049.2 s	1047.3 ms	1047.5 ms	1042 ms	1044 (10) p	1045 (10)		ν ₂ (A') ³⁵ Cl
	1046.5 mw						
1046.8 ms	1044.2 mw	1044.2 m					ν ₂ (A') ³⁷ Cl
975 vvw						599 + 379 = 978	ν ₂ + ν ₇ (A')
943 vvw						563 + 379 = 942	ν ₁₀ + ν ₇ (A'')
886.7 w	883.3 mw	882.3 mw				2 × 379 + 127 = 885	2ν ₇ + ν ₁₂ (A'')
884.6 mw	881.6 m	887.2 m	879 m	882 (4.3) p	882 (1.9)		ν ₃ (A')
751 w			750 w			2 × 379 = 758	2ν ₇ (A')
		683.7 mw				563 + 127 = 690	ν ₁₀ + ν ₁₂ (A')
682.1							
679.2							
676.8							
674.6	674.6	677.7 s	669 s	670 (2.8) p	670 (1.5)		ν ₄ (A') ³⁵ Cl
672.3	667.6 ms	670.7 ms					ν ₄ (A') ³⁷ Cl
671.0							
668							
599 mw	597.1 ms	597.6 ms	595 ms	596 (0.8) dp			ν ₅ (A') ³⁵ Cl
	593.3 m	593.8 m					ν ₅ (A') ³⁷ Cl
563 mw	561.8 ms	562.9 ms	558 ms	559 (0.8) dp			ν ₁₀ (A'') ³⁵ Cl
	558.9 m	560.0 m					ν ₁₀ (A'') ³⁷ Cl
529 w	530 m	531.6 m	529 m	528 (4.4) p	528 (1.8)		ν ₆ (A')
	{386.9 w	386 w					
378 w	{380.7 w	381 mw	383 sh	382 sh, dp	382 sh	3 × 127 = 381	ν ₁₁ (A') and 3ν ₁₃ (A'')
	{377.3 mw	378 mw	377 mw	377 (8.7) p	377 (4.7)		ν ₇ (A')
				230 (1.4) p	232 (0.8)		ν ₄ (A')
				127 (0.6) dp			ν ₁₂ (A')

The Raman spectrum, the A' modes can be either polarized or depolarized, while the A'' modes should all be depolarized. An approximate description of all 12 modes is given in Table II.

By comparison with the known spectra of the related molecules ClO₃OCl,¹⁰ ClO₃OBr,¹⁰ ClO₃OH,²² ClO₃OD,²² O₃ClOClO₃,^{9,23,24} CF₃OClO₃,²⁵ FClO₃,²⁶⁻³⁰ FOSO₂F,³¹⁻³³ and

CF₃OF,³⁴⁻³⁹ the assignments for most fundamental vibrations of ClO₃OF (see Table II) are straightforward. Additional

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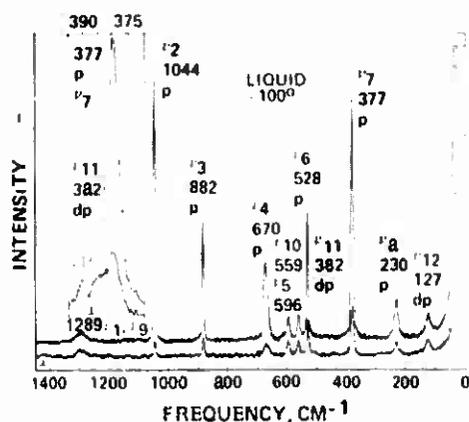


Figure 4. Raman spectra of liquid ClO_3OF in a 4-mm quartz tube recorded at -100°C with parallel and perpendicular polarization. The insert shows the 377-cm^{-1} band recorded with scale expansion.

support for these assignments comes from the observed ^{35}Cl - ^{37}Cl isotopic shifts (chlorine has two naturally occurring isotopes, ^{35}Cl and ^{37}Cl , with an abundance ratio of 3:1), from the normal-coordinate analysis (see below), and from the Raman polarization data. Consequently, only the less straightforward assignments will be discussed.

The two antisymmetric ClO_3 stretching modes, $\nu_1(\text{A}')$ and $\nu_9(\text{A}'')$, are almost degenerate and therefore could be observed as separate bands only in the matrix spectra at about 1303 and 1295 cm^{-1} . In the Ne matrix, the ^{37}Cl satellite of the 1303.6-cm^{-1} fundamental at 1289.7 cm^{-1} appears to be in Fermi resonance with the A' combination band ($2\nu_7 + \nu_6$) at 1285.9 cm^{-1} . Because Fermi resonance is possible only between vibrations belonging to the same symmetry species, the 1303.6-cm^{-1} band is tentatively assigned to the A' mode. The additional smaller splittings observed for the 1295-cm^{-1} band in the Ne matrix and for the other bands in the N_2 matrix are attributed to matrix site effects. The Raman polarization data for the 1289-cm^{-1} band were inconclusive due to the great line width, low intensity, and low degree of polarization and therefore were not useful for distinguishing between the A' and the A'' fundamental.

The frequencies of the two ClO_3 rocking modes, $\nu_7(\text{A}')$ and $\nu_{11}(\text{A}'')$, almost coincide and are readily assigned on the basis of their Raman polarization ratios (see Figure 4). The splitting of $\nu_{11}(\text{A}'')$ (see Figure 3) into two components in the matrix-isolated infrared spectra is attributed to Fermi resonance with $3\nu_{12}(\text{A}'')$.

The symmetric (umbrella) ClO_3 deformation mode, $\nu_5(\text{A}')$, and the two antisymmetric ClO_3 deformation modes, $\nu_{10}(\text{A}'')$ and $\nu_6(\text{A}')$, are assigned to the three fundamentals observed at about 599, 563, and 529 cm^{-1} , respectively. The assignment of the 599-cm^{-1} fundamental to $\nu_5(\text{A}')$ is established by the

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Table II. Vibrational Spectra of ClO_3OF Compared to Those of Closely Related Molecules

assign for ClO_3OF in point group C_3	approx description of mode for ClO_3OF	obsd freq, cm^{-1}									
		FCIO_3^a	ClO_3OH^b	ClO_3OD^b	ClO_3OF	ClO_3OCF	$\text{O}_3\text{ClOClO}_3^d$	ClO_3OBF^e	CF_3OF^e		
A'	ν_1	1314 (15.8) ^f	1326	1282	1302 (14.5) ^g	1287 (15) ^h	1300	1279	1222		
	ν_2	1062 (3.05)	1048	1050	1049 (3.3)	1040	1060, 1025	1039	1294		
	ν_3	717 (10.0)	3553	2624	885 (~0)	749 (3.8)	704, 698	683	882		
	ν_4	549 (0.89)	726	725	677 (7.0)	646 (8.5)	600	648	947		
	ν_5	589 (3.1)	582	587	599 (3.8)	580 (2.5)	521, 512	572	678		
	ν_6	405 (0.2)	555	555	529 (~1)	511 (<1.5)	430, 283	509	585		
	ν_7		421	420	379 (<1)	355	154	387	429		
	ν_8		1326	930	230	198			278		
A''	ν_9	1314 (15.8)	1263	1282	1295 (14.6)	1271 (15)	1300	1262	1261		
	ν_{10}	589 (3.1)	582	577	563 (2.9)	561 (2.5)	571, 567	566	607		
	ν_{11}	405 (0.2)	421	420	385 (<1)	382 (<1)	490, 272	387	431		
	ν_{12}		306		127	92			127		

^a References 28-30. ^b Reference 22: ν_1 and ν_8 of ClO_3OH are strongly coupled and best described as antisymmetric (1326) and symmetric (1200) combination of the corresponding symmetry coordinates. ^c Reference 10. ^d Reference 9, but with revised assignment for ν_5 , ν_6 , and ν_7 . ^e References 34-38; it should be noted that for the A' block of CF_3OF the mode description is inaccurate due to strong mixing. ^f ^{35}Cl - ^{37}Cl isotopic shifts.

Table III. Symmetry Force Constants,^a Observed and Calculated Frequencies, and ³⁵Cl-³⁷Cl Shifts and Potential Energy Distribution^b of ClO₃OF

assign	freq, cm ⁻¹		Cl isotopic shift, cm ⁻¹		symmetry force constants	potential energy distribution		
	obsd	calcd	obsd	calcd				
A'	ν_1	1302	1303	14.5	15.7	$F_{11} = f_r - f_{rr}$	9.53	97 (1)
	ν_2	1049	1049	3.3	3.3	$F_{22} = f_r + 2f_{rr}$	9.49	97 (2)
	ν_3	885	885	<1	0.1	$F_{33} = f_D$	3.51	84 (3) + 10 (7)
	ν_4	677	677	7.0	7.0	$F_{44} = f_R$	2.38	52 (4) + 41 (5) + 9 (8) + 6 (6) - 20 (45)
	ν_5	599	599	3.8	3.8	$F_{55} = 0.65f_\beta + 0.35f_\alpha + 1.30f_{\beta\beta} + 0.70f_{\alpha\alpha} - 1.91f_{\alpha\beta} - 0.95f_{\alpha\beta}$	2.38	54 (5) + 20 (6) + 8 (8)
A'	ν_6	529	529	~1	1.2	$F_{66} = f_\alpha - f_{\alpha\alpha}$	1.62	63 (6) + 28 (4) + 7 (8) + 4 (5) - 9 (46) - 5 (45)
	ν_7	379	379	<1	0.7	$F_{77} = f_\beta - f_{\beta\beta}$	1.54	69 (7) + 13 (3) + 10 (6) + 7 (4) + 5 (8) - 6 (67)
	ν_8	230	230		0.3	$F_{88} = f_\gamma$	0.99	66 (8) + 18 (7) + 15 (4)
A''	ν_9	1295	1295	14.6	15.1	$F_{99} = f_r - f_{rr}$	9.53	99 (9)
	ν_{10}	563	563	2.9	2.9	$F_{10,10} = f_\alpha - f_{\alpha\alpha}$	1.55	80 (10) + 8 (11) + 7 (10,11)
	ν_{11}	385	385		0.3	$F_{11,11} = f_\beta - f_{\beta\beta}$	1.21	94 (11) + 18 (10) - 12 (10,11)
	ν_{12}	127				$F_{12,12} = f_\gamma$		
						$F_{16} = -F_{9,10} = f_{r\alpha'} \cdot f_{r\alpha}$	0.27	
						$F_{17} = F_{9,11} = f_{r\beta} \cdot f_{r\beta'}$	0.35	
						$F_{24} = 3^{1/2} f_{rR}$	0.16	
						$F_{33} = 0.81f_{r\beta} - 1.18f_{r\alpha} + 1.61f_{r\beta'} - 0.59f_{r\alpha'}$	0	
						$F_{43} = 1.39f_{R\beta} - 1.02f_{R\alpha}$	0.51	
						$F_{46} = f_{R\alpha}$	0.218	
						$F_{67} = -F_{10,11} = f_{\alpha\beta'} - f_{\alpha\beta}$	-0.2	

^a Stretching constants in mdyn/A, deformation constants in mdyn A/rad², and stretch-bend interaction constants in mdyn/rad. Although identical explicit F terms are given for F_{11} , F_{66} , F_{77} and F_{99} , $F_{10,10}$, $F_{11,11}$, respectively, it must be kept in mind that the corresponding A' and A'' force constants are similar, but not identical (see text for explanation). ^b Contributions of less than 5% to the PED are not listed.

observed PQR band contour in the infrared spectrum of the gas, by its large ³⁵Cl-³⁷Cl isotopic shift, and, in particular, by the results from the normal-coordinate analysis (see below). By analogy with CF₃OF,³⁵ ClO₃OF is an accidental symmetric top with Cl and F lying on the axis of the smallest moment of inertia (I_A) and rotational constants of $A = 0.181$, $B = 0.0932$, and $C = 0.0931$ cm⁻¹. Therefore, the band contours for ClO₃OF are expected to be analogous of those of CF₃OF for which the PQR band contour of the umbrella deformation mode is well established. By analogy with FClO₃³⁰ and ClO₃OCl,¹⁰ the Cl-O single bond stretching and the ClO₃ umbrella deformation mode in ClO₃OF are expected to exhibit a total of about 11 cm⁻¹ in ³⁵Cl-³⁷Cl isotopic shift whose distribution between the two modes is governed by their degree of coupling. The assumption of a total isotopic shift of about 11 cm⁻¹ for these two modes was supported by a large number of different force fields. As long as plausible interaction terms were used, this total isotopic shift remained close to 11 cm⁻¹. In ClO₃OF, the Cl isotopic shift of the Cl-O stretching mode is only 7.0 cm⁻¹, thus requiring a Cl shift of about 4 cm⁻¹ for the ClO₃ umbrella deformation mode. This condition is met by the 599-cm⁻¹ fundamental ($\Delta\nu = 3.8$ cm⁻¹) but not by that at 529 cm⁻¹ ($\Delta\nu \approx 1$ cm⁻¹). Furthermore, the normal-coordinate analysis strongly preferred a Cl isotopic shift of about 3.0 cm⁻¹ for ν_{10} (A'') and could accommodate a 3.8- or 1-cm⁻¹ shift only with unreasonable off-diagonal symmetry force constants. Also, the potential energy distributions of all physically meaningful force fields, obtained with the different possible assignments, insisted on 599 cm⁻¹ belonging to the A' block and being the umbrella deformation mode. With the 599-cm⁻¹ fundamental being firmly assigned to the umbrella deformation mode, assignments for ν_6 (A') and ν_{10} (A'') are unambiguous on the basis of the Raman polarization data.

The frequency of 127 cm⁻¹ for the Cl-OF torsional mode in ClO₃OF is in excellent agreement with that^{36,39} found for the closely related CF₃OF molecule and confirmed by microwave spectroscopy.²¹ Since the reduced moment of inertia for internal rotation (I_A), of CF₃OF and ClO₃OF should be comparable, the potential barrier to internal rotation in ClO₃OF is expected to be similar to that of CF₃OF (about 4 kcal

mol⁻¹).^{20,39} The remaining assignments for ClO₃OF are all unambiguous and require no further comment.

Only minor frequency shifts were observed for ClO₃OF when going from the gas to the liquid and the solid. This indicates little or no association in the condensed phases.

Comparison of the ClO₃OF Assignments with Those of Similar Molecules. In Table II, the assignments for ClO₃OF are compared to those of similar molecules. The general agreement between the different compounds is excellent and permitted improvement of some of the previous assignments. For example, the assignments previously proposed for the antisymmetric (A') and the symmetric ClO₃ deformation modes of ClO₃OCl,¹⁰ ClO₃OBr,¹⁰ and Cl₂O₇⁹ should be reversed and the assignments for ClO₃OCF₃ should be revised to conform with those of ClO₃OF.

For CF₃OF, we propose to exchange the previous assignments³⁸ for the symmetric and antisymmetric CF₃ stretching modes in species A'. The CF₃ modes in CF₃OF are almost identical with those in CF₃ONF₂. Raman polarization data recently obtained in our laboratory for CF₃ONF₂ established beyond doubt that the highest CF₃ fundamental represents the symmetric stretching mode.

Chlorine Isotopic Shifts. The ³⁵Cl-³⁷Cl isotopic shifts observed for ClO₃OF are summarized in Table III. In view of the importance of these shifts for the force field computation, factors influencing some of these shifts will be briefly discussed. Whereas ν_5 , ν_9 , and ν_{10} are essentially undisturbed, some of the other bands appear to be influenced by effects such as Fermi resonance with combination bands.

For ν_1 , resonance between ($2\nu_7 + \nu_8$) ³⁷Cl and ν_1 ³⁷Cl most likely shifts the latter to higher frequency and decreases its relative intensity and the apparent ³⁵Cl-³⁷Cl separation of ν_1 's. Using a weighted average of the 1285.9- and 1289.7-cm⁻¹ bands for the frequency of ν_1 ³⁷Cl results in a Cl isotopic shift of about 14.5 cm⁻¹, similar to that (14.6 cm⁻¹) observed for the almost degenerate ν_9 (A'') fundamental.

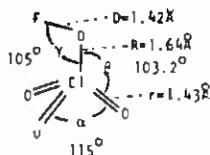
For ν_2 a discrepancy exists between the matrix isolation and the gas-phase data. Whereas two Q branches with a frequency separation of 2.4 cm⁻¹ were observed in the gas-phase spectrum, the matrix isolation data show that in the Ne and N₂

matrices the isotopic shifts are 3.3 cm^{-1} . Two combination bands, $(\nu_4 + \nu_7)$ and $2\nu_6$, occur in this region and were indeed observed in the matrix spectra. However, since in the Ne matrix they occur on the high-frequency side of ν_2 and are of low relative intensity, the larger isotopic shift in the matrix spectrum cannot be attributed to Fermi resonance effects. Since in the closely related FCIO_3 molecule the Cl isotopic shift of this highly characteristic symmetric ClO_3 stretching mode is 3.05 cm^{-1} ,³⁰ we prefer the matrix shift value for ν_2 of ClO_3OF . The second Q branch, observed in the infrared spectrum of the gas, might be due to other effects such as hot bands.

The O-F stretching mode, $\nu_3(\text{A}')$, shows a splitting of about 5 cm^{-1} in the Ne-matrix spectrum, but in the N_2 -matrix and gas-phase spectra the satellite band is shifted to the high-frequency side of ν_3 and therefore is attributed to the combination band $(2\nu_7 + \nu_{12})$.

Normal-Coordinate Analysis. The normal-coordinate analysis of ClO_3OF presented a particular challenge because previous force field computations for the closely related ClO_3OX ($\text{X} = \text{Cl}, \text{Br}, \text{ClO}_3$),^{9,10} CF_3OX ($\text{X} = \text{F}, \text{Cl}$),^{34,35,41} and FSO_2OF ³³ molecules revealed difficulties in reproducing the experimental frequencies and resulted in extensive mixing of symmetry coordinates for many of the A' modes. Because of the highly underdetermined nature of these force fields, the mere reproduction of the observed frequencies does not necessarily result in a meaningful force field or even support a certain assignment. In order to avoid most of these drawbacks, we have used for our normal-coordinate analysis of ClO_3OF the following additional constraints: (i) ^{35}Cl - ^{37}Cl isotopic shifts, (ii) symmetry relations between the A' and A'' block, and (iii) transfer of many force constants, particularly off-diagonal symmetry force constants from the closely related FCIO_3 molecule to ClO_3OF . For this purpose, it became necessary to determine first a reliable general valence force field for FCIO_3 from a combination of Cl isotopic shifts, Coriolis constants, and ab initio force constant calculations.³⁰ Using this well-established FCIO_3 force field both as a starting point for the ClO_3OF computations and as a criterion for judging the plausibility of the resulting force field, we determined a force field that met all our criteria.

For the computation of the ClO_3OF force field, the vibrational frequencies, Cl isotopic shifts, and assignments of Tables II and III were used. The required potential and kinetic energy metrics were computed by a machine method⁴² using the following geometry, estimated from a comparison with the related molecules FCIO_3 ,⁴³ ClO_3OH ,⁴⁴ and CF_3OF .^{20,21}



The symmetry coordinates used were the same as those given in ref 38, except that the numbering is different and the redundant coordinate was made exactly orthogonal to the other coordinates by the Gram-Schmidt process. Analytical expressions for the symmetry force constants are given in Table III. The off-diagonal symmetry force constants were adjusted by trial and error and then kept fixed during adjustment of the diagonal symmetry force constants by a least-squares

Table IV. Comparison of Internal Force Constants^a of ClO_3OF with Those of FCIO_3

	ClO_3OF	FCIO_3		ClO_3OF	FCIO_3
f_r	9.52	9.76	$f_\beta - f_{\beta\beta}$	1.54 (A')	1.49
f_{rr}	-0.01	0.07		1.21 (A'')	
f_{rR}	0.09	0.08	$f_{r\alpha} - f_{r\alpha'}$	0.27	-0.29 ^b
$f_{\alpha} - f_{\alpha\alpha}$	1.62 (A')	1.53	$f_{r\beta} - f_{r\beta'}$	0.35	-0.33 ^b
	1.55 (A'')		$f_{\alpha\beta} - f_{\alpha\beta'}$	0.2	0.26

^a For dimensions of force constants see footnote a of Table III.

^b The different signs in these force constants are caused by the different signs in the symmetry coordinates used for the two computations and therefore have no physical meaning.

method to reproduce the observed frequencies and isotopic shifts. Due to the symmetry relations between the A' and the A'' block ($F_{11} = F_{99}$, $F_{66} = F_{10,10}$, $F_{77} = F_{11,11}$, $F_{16} = -F_{9,10}$, $F_{17} = F_{9,11}$, and $F_{67} = -F_{10,11}$), both blocks were refined simultaneously. Due to its low frequency and weak coupling with other modes, the torsional mode ν_{12} was omitted for the analysis.

With use of this method and the FCIO_3 force field as a starting solution (supplemented by appropriate estimates for the O-F group), the A' - A'' symmetry constraint was at first fully enforced. Although a close duplication of the observed frequencies and isotopic shifts was possible, the resulting force field and potential energy distribution were unsatisfactory. For satisfactory force field solutions, the computed frequency of ν_7 was always too low and that of ν_{11} too high. This suggested that the two ClO_3 rocking modes, $\nu_7(\text{A}')$ and $\nu_{11}(\text{A}'')$, are not completely degenerate, and therefore the $F_{77} = F_{11,11}$ constraint was removed. Removal of this constraint significantly improved that force field, but again the results suggested that removal of the $F_{66} = F_{10,10}$ constraint would significantly benefit the force field. In this manner, a very satisfactory force field (see Table III) was obtained that exactly duplicated the observed frequencies and isotopic shifts and contained force constants for the ClO_3 part of the molecule, which are very similar to those of FCIO_3 ³⁰ (see Table IV). Removal of the $F_{11} = F_{99}$ constraints was shown to be unnecessary since it did not change the values of F_{11} and F_{99} . The only minor deviation between observed and computed isotopic shifts exists for ν_1 and ν_6 ; however, it must be kept in mind (i) that the shift of ν_1 is disturbed by Fermi resonance effects (see above) and (ii) that anharmonicity corrections⁴⁵ for these large shifts would be of the same magnitude as the observed deviations.

The force field of ClO_3OF , given in Table III, contains, in addition to the interaction terms transferred from FCIO_3 , only one relatively small ($F_{46} = 0.22 \text{ mdyne rad}^{-1}$) off-diagonal symmetry force constant. This is not surprising in view of the near degeneracy of the $-\text{OCIO}_3$ modes. If these modes were completely degenerate, ν_1 , ν_6 , and ν_7 would belong to species E and ν_2 , ν_4 , and ν_5 to species A_1 of the corresponding C_{3v} symmetry molecule and, therefore, no interaction force constants between the two species would be allowed. In the case of near degeneracy of these modes, as in ClO_3OF , the interaction force constants between the two groups can be nonzero because they both belong now to species A' . However, their numerical values should be very small or zero, as can be shown by semiquantitative arguments.

The fact that the symmetry constraints between the A' and the A'' block are not strictly valid is not surprising. As expected, the two ClO_3 rocking modes are the least degenerate (22% difference). Because the O-F group is situated in the symmetry plane of the molecule, the in-plane rocking motion requires a significantly higher force than the corresponding out-of-plane motion. For the antisymmetric ClO_3 deformation

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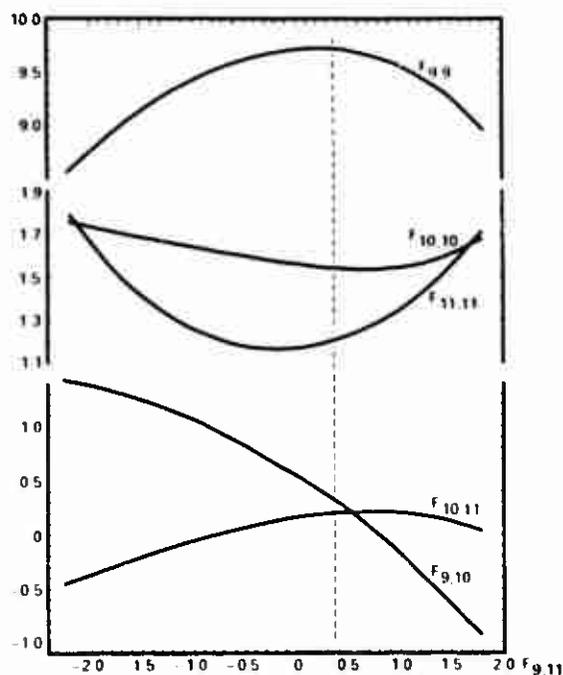


Figure 5. Solution range of the A'' block symmetry force constants of ClO_3OF computed from the chlorine isotopic data and plotted as a function of $F_{9,11}$. The units are identical with those given in Table III. The broken line indicates the preferred force field.

constants the difference between A' and A'' values amounts to only 4% and for the antisymmetric ClO_3 stretching modes it is zero. In view of the very near degeneracy of the antisymmetric ClO_3 stretching and deformation modes, it is not surprising the symmetry constraint imposed on the corresponding off-diagonal symmetry force constants worked well for our force field. In this connection, it should be pointed out that the expected, albeit small, tilt angle of the Cl-O bond away from the threefold axis of the ClO_3 group should cause a small difference between the A' and A'' force constants. However, in the absence of exact structural data for ClO_3OF , the tilt angle was assumed to be zero in this study.

To obtain a better feel for the possible variation in the force constant values of ClO_3OF , we calculated the range of possible solutions for the A'' block which is shown in Figure 5. Since five independent frequency values were available from the isotopic data for the computation of six symmetry force constants, five force constants were calculated as a function of the sixth one, in this case $F_{9,11}$. As can be seen from Figure 5, limitation of the off-diagonal force constants to reasonable values places rather narrow limits on the more important diagonal terms. The force field selected from the simultaneous $A'-A''$ refinement is given by the broken line and is analogous to the FCIO_3 E block force field.³⁰ The differences in the signs of some of the off-diagonal force constants between FCIO_3 and ClO_3OF are caused by the different signs in the symmetry coordinates used for the two computations and therefore have no physical meaning.

The potential energy distribution for ClO_3OF is given in Table III. It shows that the approximate mode descriptions used in Table II are appropriate. The largest amount of mixing was observed for ν_4 , which, by analogy with ν_2 of FCIO_3 ,³⁰ is an antisymmetric combination of S_4 (Cl-O stretch) and S_5 ($\delta_2(\text{ClO}_3)$).

In order to test the possibility of interchanging the assignments of ν_5 , ν_6 , and ν_{10} , we computed force fields for all possible

Table V. Thermodynamic Properties of ClO_3OF

T , K	C_p° , cal/(mol deg)	$(H^\circ_T - H^\circ_0)$, kcal/mol	$-(F^\circ_T - F^\circ_0)/T$, cal/(mol deg)	S°_T , eu
0	0	0	0	0
100	9.438	0.841	50.106	58.411
200	14.097	2.003	56.234	66.347
298.15	18.311	3.592	60.712	72.761
300	18.176	3.626	60.187	72.873
400	21.166	5.601	64.532	78.535
500	23.289	7.830	67.840	83.500
600	24.789	10.238	70.823	87.886
700	25.861	12.774	73.545	91.793
800	26.641	15.401	76.049	95.299
900	27.221	18.095	78.367	98.472
1000	27.660	20.840	80.524	101.364
1100	28.000	23.624	82.541	104.017
1200	28.266	26.438	84.434	106.465
1300	28.480	29.275	86.217	108.736
1400	28.652	32.132	87.902	110.854
1500	28.794	35.005	89.499	112.835
1600	28.911	37.890	91.016	114.697
1700	29.010	40.786	92.461	116.453
1800	29.093	43.692	93.841	118.114
1900	29.164	46.605	95.160	119.689
2000	29.225	49.524	96.424	121.186

assignments, which led to the conclusions stated in the discussion of the assignments.

Thermodynamic Properties. The thermodynamic properties of ClO_3OF were computed with the molecular geometry given above and the vibrational frequencies of Table II, with the assumption of an ideal gas at 1 atm pressure and use of the harmonic-oscillator, rigid-rotor approximation.⁴⁶ These properties for the range 0–2000 K are given in Table V.

Conclusions. The observed spectra of ClO_3OF agree well with a covalent perchlorate structure of symmetry C_1 . All 12 fundamental vibrations were observed and assigned. The assignments were confirmed by a normal-coordinate analysis using Cl isotopic shifts, symmetry relations between the A' and A'' block, and force constants transferred from FCIO_3 , as constraints. The resulting force field exactly duplicates the experimental data, retains the most important force constant features of FCIO_3 , and results in a characteristic potential energy distribution, thus demonstrating the usefulness of these constraints for the determination of a reliable force field. A comparison of the A' and A'' block force constants shows that the two ClO_3 rocking modes significantly differ, whereas the two antisymmetric ClO_3 deformation modes are almost degenerate and the two antisymmetric ClO_3 stretching modes are completely degenerate. This is not obvious from the observed frequencies, which due to a different degree of mixing in A' and A'' are very similar for the two rocking modes but are significantly different for the two antisymmetric ClO_3 deformations. The force constants of the ClO_3 group of ClO_3OF are very similar to those of FCIO_3 but, as expected from the replacement of F by the somewhat less electronegative $-\text{OF}$ group, are slightly lowered.

Acknowledgment. The authors are indebted to Mr. R. D. Wilson for help in the sample preparation, to the Office of Naval Research and the Army Research Office for financial support, and to Dr. E. Appelman for making a preprint of his paper on the vibrational spectra of SO_3OF^- and ClO_3OF available to us.

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Synthesis and Characterization of TeF_3OF

APPENDIX M

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A new method for the synthesis of hypofluorites was discovered utilizing fluorine fluorosulfate as the fluorinating agent. The method was successfully applied to the high-yield synthesis of the new hypofluorite TeF_3OF . The compound was also prepared in lower yield by the fluorination of TeF_3OH with a concentrated NF_3HF_2 solution. The physical properties and infrared, Raman, ^{19}F NMR and mass spectra of TeF_3OF are reported. The vibrational spectra of TeF_3OCl were redetermined, and complete vibrational assignments are given for TeF_3OF and TeF_3OCl .

Introduction

The number of elements known to form hypofluorites is small and until recently was limited to the following nonmetal main-group elements: H, C, N, O, S, Se, F, and Cl.¹ The synthetic method used for the syntheses of these hypofluorites involved the fluorination of the corresponding hydroxyl compounds of their metal salts with elemental fluorine. An unsuccessful attempt² was made to apply this method to the synthesis of the hitherto unknown TeF_3OF . This failure to prepare TeF_3OF , but the success in the synthesis of TeF_3OCl by an analogous method,³ led to the conclusion³ that TeF_3OF is unstable or actually nonexistent.

Our recent success⁴ in preparing a stable iodine hypofluorite and the observation that hypofluorites are generally more stable than the other hypohalites suggested that TeF_3OF should not only exist but should also be stable. In this paper we present data that show that TeF_3OF indeed exists and is stable.

Experimental Section

Materials and Apparatus. Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U-Traps, 316 stainless steel bellows-seal valves, and a Heise Bourdon tube-type pressure gauge. Telluric acid was prepared by a literature method⁵ and also purchased from Cerac, Inc., and from Pfaltz and Bauer. Fluorosulfuric acid (Allied) was used both as it was received (light brown color) and after it was distilled to obtain the clear colorless material. Fluorine fluorosulfate was synthesized as described.⁶ The reaction of TeF_3OH with either ClOSO_2F or ClF was used to prepare TeF_3OCl .⁷ Cesium and potassium chloride were oven-dried and then cooled and powdered under the dry N_2 atmosphere of a glovebox.

Infrared spectra were recorded in the range $4000\text{--}200\text{ cm}^{-1}$ on a Perkin-Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points,^{8,9} and the reported frequencies are believed to be accurate to $\pm 2\text{ cm}^{-1}$. The spectra of gases were obtained with use of either a Teflon cell of 5-cm path length equipped with AgCl windows or a 10-cm stainless steel cell equipped with polyethylene windows that were seasoned with ClF_3 . The spectra of matrix-isolated TeF_3OF and TeF_3OCl were obtained at 6 K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research grade Ne (Matheson) was used as a matrix material in a mole ratio of 400:1.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer with use of the 488-nm exciting line of an Ar ion laser

and a Claassen filter¹⁰ for the elimination of plasma lines. Quartz tubes (3 mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A previously described¹¹ device was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al.¹⁰

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer. Chemical shifts were determined relative to the CFCl_3 solvent with positive shifts being downfield from CFCl_3 .¹² Second-order spectra were analyzed by using the programs NMRIT and NMREN by Swalen.¹³

The mass spectra were recorded with an EAI Quad 300 quadrupole spectrometer at an ionization potential of 40 eV.

Synthesis of TeF_3OH . Telluric acid, $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ or $\text{Te}(\text{OH})_6$, was fluorinated to give TeF_3OH by the method of Seppelt and Nothe² with use of HSO_3F as the fluorinating agent. This technique calls for the use of distilled HSO_3F , and initially we encountered difficulty in producing TeF_3OH . Subsequently, it was discovered that adding a few milliliters of H_2O to the reaction mixture and heating the reaction mixture at $160\text{--}170\text{ }^\circ\text{C}$ for 5–6 h resulted in continuous evolution of TeF_3OH at a slow to moderate rate. Finally, undistilled HSO_3F was employed which furnished TeF_3OH in 70% purified yield; 93.9 mmol of TeF_3OH from 135 mmol of $\text{Te}(\text{OH})_6$ and 1.75 mol of HSO_3F . Fractional condensation was used for the final product purification.

Fluorination of $\text{M}^+\text{TeF}_5\text{O}^-$. The salts $\text{CsTeF}_5\text{O}^{14}$ and $\text{KTeF}_5\text{O}^{15}$ were treated with F_2 in stainless steel cylinders at low temperature. Thus CsTeF_5O (1.43 mmol) and F_2 (4.46 mmol) were allowed to react for 8 days at $-45\text{ }^\circ\text{C}$. The only volatile product condensable at $-196\text{ }^\circ\text{C}$ was TeF_6 (0.38 mmol, 26%). Similarly at $-10\text{ }^\circ\text{C}$ for 2 weeks a 48% yield of TeF_6 was obtained from the cesium salt. When the potassium salt (2.92 mmol) and F_2 (4.46 mmol) were kept at $-45\text{ }^\circ\text{C}$ for 6 weeks, again TeF_6 (2.35 mmol, 80%) was the only volatile tellurium compound observed.

Synthesis of TeF_3OF from CsTeF_5O and FOSO_2F . A 30-mL stainless steel Hoke cylinder was loaded with CsTeF_5O (3.42 mmol) in the glovebox. After evacuation and cooling of the cylinder to $-196\text{ }^\circ\text{C}$, FOSO_2F (2.79 mmol) was added from the vacuum line. The closed cylinder was slowly warmed to $-78\text{ }^\circ\text{C}$ in a liquid-nitrogen- CO_2 slush bath and finally kept at $-45\text{ }^\circ\text{C}$ for 9 days. When the cylinder was recooled to $-196\text{ }^\circ\text{C}$, about $4\text{--}5\text{ cm}^3$ of noncondensable gas was observed to be present. This was pumped away, and the condensable products were separated by fractional condensation in a series of U-traps cooled at -78 , -126 , and $-196\text{ }^\circ\text{C}$. The $-78\text{ }^\circ\text{C}$ fraction was TeF_3OH (0.19 mmol) while the $-196\text{ }^\circ\text{C}$ fraction was TeF_6 (0.49 mmol). A white solid was retained at $-126\text{ }^\circ\text{C}$, which changed to a colorless glass and melted, over a range of a few degrees, near $-80\text{ }^\circ\text{C}$ to a clear, colorless liquid. This material was identified as TeF_3OF (1.91 mmol, 68% yield) on the basis of its vapor density molecular weight: found, 256.2; calculated, 257.6. Further identification was based on its spectroscopic properties (see below) and on the preparation of derivatives.¹⁶ The observed weight loss of the solid (0.375 g) agreed

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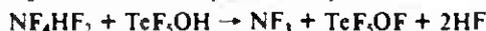
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well with that calculated (0.389 g) for the conversion of 2.79 mmol of CsTeF₅O to CsSO₃F. The following vapor pressure-temperature data of TeF₅OF were measured (*T* in °C, *P* in mm): -79.3, 16; -64.2, 45; -57.6, 63; -46.9, 108; -32.5, 210; -23.0, 312.

Synthesis of TeF₅OF from TeF₅OH and NF₄HF₂. A sample of NF₄HF₂·*n*HF (10.5 mmol) was prepared and concentrated in a Teflon double-U metathesis apparatus, as previously described.¹⁷ To this reactor was added TeF₅OH (10.5 mmol) on the vacuum line at -196 °C. The mixture was allowed to warm slowly to -23 °C and was kept at this temperature for 8 h under a dynamic vacuum. The volatile products were separated by fractional condensation through traps kept at -95, -126, -142, and -210 °C. On the basis of their infrared and ¹⁹F NMR spectra the following products were collected in these traps: -210 °C, NF₃ and a trace of TeF₆; -142 °C, TeF₆ and TeF₅OF in a mole ratio of about 3:1; -126 °C, HF and some TeF₅OF; -95 °C, TeF₅OH and some HF. The white solid residue (0.57 g) decomposed during an attempt to transfer it at ambient temperature to a drybox for further characterization. The overall yield of TeF₅OF was estimated to be about 10–20% with TeF₆ and unreacted TeF₅OH being the principal products.

Results and Discussion

Synthesis of TeF₅OF. By analogy to previous attempts^{2,18} to synthesize TeF₅OF from either Hg(TeF₅O)₂ or CsTeF₅O and F₂, the fluorination of either CsTeF₅O or KTeF₅O with F₂ at -45 to -10 °C was unsuccessful and resulted only in TeF₆ formation. Since the decomposition of NF₄XO salts had recently been shown to provide new high-yield syntheses for hypofluorites such as FOClO₃,¹⁹ FOSO₂F,²⁰ and FOIF₄O,⁴ the synthesis of NF₄TeF₅O by metathesis of NF₄SbF₆ and CsTeF₅O in anhydrous HF was attempted. This attempt, however, was preempted by the fact that CsTeF₅O was found to react with anhydrous HF, undergoing a displacement reaction. Recent work¹⁷ in our laboratory had shown that even in cases of Lewis acids that are weaker than HF their NF₄⁺ salts can be prepared by treating NF₄HF₂·*n*HF with this acid. Therefore, this approach was studied for NF₄TeF₅O. Although the NF₄TeF₅O salt itself could not be isolated, it was found that TeF₅OH (which is equivalent to an equimolar mixture of the Lewis acid TeF₅O and HF) reacted with NF₄HF₂·*n*HF at -23 °C to produce TeF₅OF in moderate yield:



Since TeF₆ was the major product, we prefer to interpret this reaction in terms of a fluorination of TeF₅OH by nascent fluorine formed in the decomposition of NF₄HF₂, rather than in terms of a decomposition of an unstable NF₄TeF₅O intermediate. In the latter case, we would expect a near-quantitative yield of TeF₅OF.

A more facile high-yield synthesis of TeF₅OF was discovered by reacting CsTeF₅O with FOSO₂F at -45 °C:



This reaction represents a new synthetic route to hypofluorites. On the basis of the general usefulness of the analogous ClO₂F reagent for the syntheses of hypochlorites,²¹ FOSO₂F may be similarly useful for the synthesis of hypofluorites.

When the synthesis of TeF₅OF from CsTeF₅O and FOSO₂F was carried out above -45 °C, the amount of TeF₆ byproduct sharply increased. For example, at -10 °C and with a reaction time of 7 days, the TeF₆ to TeF₅OF ratio in the product increased to 1:1. The use of an excess of CsTeF₅O in this reaction was found advantageous for the product purification since it eliminates the need for separating TeF₅OF from FOSO₂F.

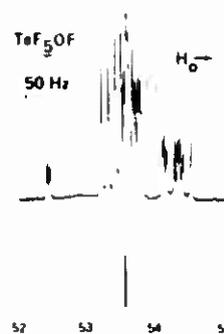


Figure 1. Observed and calculated ¹⁹F NMR spectra of the AB₄ part of TeF₅OF.

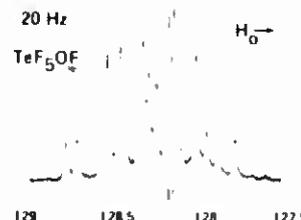


Figure 2. Observed and calculated ¹⁹F NMR spectra of the X part of TeF₅OF.

Table I. Mass Spectrum of TeF₅OF Compared to Those of TeF₅OCl and TeF₅OH

TeF ₅ OF		TeF ₅ OCl		TeF ₅ OH	
assignt	intens	assignt	intens	assignt	intens
TeF ₅ OF ⁺	vw	TeF ₅ OCl ⁺	vw	TeF ₅ OH ⁺	w
TeF ₄ OI ⁺	vw	TeF ₄ OCl ⁺	vw	TeF ₄ OH ⁺	vw
TeF ₃ O ⁺					
TeF ₄ ⁺	s	TeF ₄ ⁺	s	TeF ₄ ⁺	vs
TeF ₃ ⁺	w	TeF ₃ ⁺	vw	TeF ₃ ⁺	w
TeF ₃ O ⁺	m	TeF ₃ O ⁺	ms	TeF ₃ O ⁺	s
TeF ₂ ⁺	vs	TeF ₂ ⁺	vs	TeF ₂ ⁺	vs
TeF ₂ ⁺	m	TeF ₂ ⁺	m	TeF ₂ ⁺	m
TeF ₁ O ⁺	vw	TeF ₁ O ⁺	w	TeF ₁ O ⁺	w
TeF ⁺	w	TeF ⁺	w	TeF ⁺	w
Te ⁺	w	Te ⁺	w	Te ⁺	w

Properties of TeF₅OF. This compound is colorless as a gas and liquid. Its vapor pressure-temperature relationship for the range -79 to -23 °C is given by the equation

$$\log\{P(\text{mm})\} = 6.9022 - 1101.2/[T(\text{K})]$$

The extrapolated boiling point is 0.6 °C. The derived heat of vaporization is $\Delta H_{\text{vap}} = 5039 \text{ cal mol}^{-1}$ and the Trouton constant is 18.4, indicating little or no association in the liquid phase. Vapor density measurements showed that in the gas phase the compound is also not associated. We were not able to observe a sharp melting point for TeF₅OF because our samples showed a tendency to form a glass near -80 °C. The compound appears to be completely stable at ambient temperature and has been stored in stainless steel cylinders for more than 4 months without any sign of decomposition.

¹⁹F NMR Spectrum. The ¹⁹F NMR spectrum of TeF₅OF in CFCl₃ solution at 28 °C is shown in Figures 1 and 2 and is characteristic for a second-order AB₄X spin system. A computer-aided analysis of the spectrum resulted in the following parameters: $\phi^*(A) = -52.5$, $\phi^*(B_4) = -54.0$, $\phi^*(X) = 128.3$, $J_{AB} = 180 \text{ Hz}$, $J_{AX} = 4.9 \text{ Hz}$, $J_{BX} = 19.0 \text{ Hz}$, $R = 1.20$, $J_{113}\text{Te}^{19}\text{F} = 3800 \text{ Hz}$. These values are in excellent agreement with those found for numerous other covalent TeF₅O-type compounds.²²

(17) Wilson, W. W.; Christie, K. O. *J. Fluorine Chem.* **1982**, *19*, 253.

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(19) Christie, K. O.; Wilson, W. W.; Wilson, R. D. *Inorg. Chem.* **1980**, *19*, 1494.

(20) Christie, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1980**, *19*, 3046.

(21) Schack, C. J.; Christie, K. O. *Isr. J. Chem.* **1978**, *17*, 20.

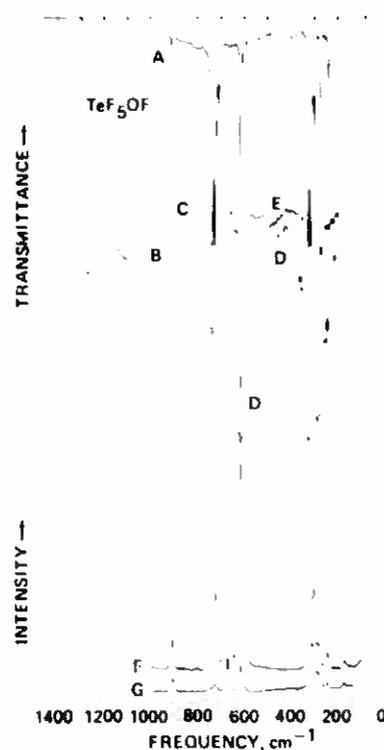


Figure 3. Vibrational spectra of TeF_5OF : trace A, infrared spectrum of TeF_5OF isolated in a neon matrix (mole ratio 400:1) and recorded at 6 K; traces B and C, infrared spectra of the gas, recorded at pressures of 74 and 3 mm, respectively, in a 5-cm path length cell equipped with AgCl windows (the very weak bands at 1272, 1105, 640, and 548 cm^{-1} in spectrum B are due to a trace of FCIO_2 resulting from the ClF_3 used for passivation); traces D and E, infrared spectra of the gas, recorded at pressures of 86 and 8 mm, respectively, in a 10-cm path length cell equipped with polyethylene windows and with polyethylene windows in the reference beam; traces F and G, Raman spectra of the liquid, recorded in 3 mm o.d. quartz tubes at -55°C with the incident polarization parallel and perpendicular, respectively.

Table II. Vibrational Spectra of TeF_5OF

obsd freq, cm^{-1} (rel intens ^a)				
IR		Raman		assign ^b
gas	Ne matrix	liquid, -55°C	solid, -110°C	
1800 vw				$2\nu_{12}$
1449 vw				$2\nu_1$
1403 w				$\nu_2 + \nu_8$
908 vw		905 (0.4) p	904 (0.8)	ν_{12}
738 vs ^c	738 ^c vs	738 sh, dp	735 sh	ν_2
	727 vs	721 (1.1) p	721 (1.3)	ν_1
718 vw				} impurity?
709 vw				
668 vw		669 (10) p	670 (10)	ν_2
		660 (0.3) dp	662 sh	ν_5
616 m	618 m	613 (3.8) p	613 (4)	ν_3
324 vs ^c	327 vs	325 sh, dp	325 sh	ν_9
	318 vs		319 sh	ν_{10}
	308 vw	309 (1.0) dp	309 (1.6)	ν_7
300 sh	302 m	301 (0.5) p	301 sh	ν_4
280 mw	278 m	279 (0.2) dp	279 (0.2)	ν_{11}
241 mw	239 mw	240 (0.2) p	240 (0.2)	ν_{13}
		166 (0.1) dp	167 (0.1)	ν_{14}

^a Uncorrected Raman intensities (peak heights). ^b For mode description see Table IV. ^c Band shows tellurium isotope fine structure with splittings of about 1.30 cm^{-1}

Mass Spectrum. The mass spectrum of TeF_5OF is listed in Table I together with the spectra of TeF_5OCl and TeF_5OH , which were measured for comparison. All of the listed frag-

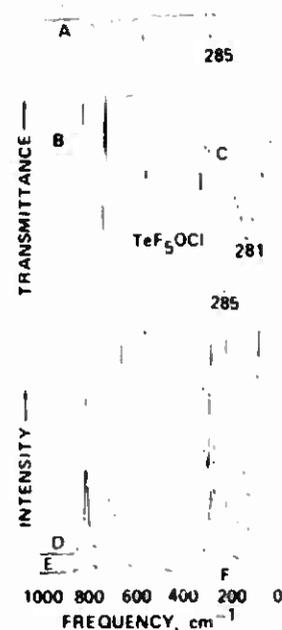


Figure 4. Vibrational spectra of TeF_5OCl : traces A and C, infrared spectra of TeF_5OCl isolated in a neon matrix (mole ratio 400:1) at 6 K; trace B, infrared spectrum of the gas, recorded at a pressure of 27 mm in a 5-cm path length cell equipped with AgCl windows; traces D and E, Raman spectra of the liquid, recorded in 3 mm o.d. quartz tubes at -80°C with the incident polarization parallel and perpendicular, respectively; trace F, spectrum recorded under the same conditions as for trace D, except for a narrower slit width.

Table III. Vibrational Spectra of TeF_5OCl

obsd freq, cm^{-1} (rel intens ^a)				
IR		Raman liquid, -80°C		assign ^b
gas	Ne matrix			
1365 vw				$\nu_3 + \nu_{12}$
812 s	814 s	809 (0.9) p		ν_{12}
732 vs	732 vs ^c	730 sh, dp		ν_8
	718 s	713 (1.6) p		ν_1
		663 (10) p		ν_2
551 m		655 sh, dp		ν_5
	558 m	554 (6.5) p		ν_3
	327 vs	328 sh, dp		ν_9
	322 vs	316 (0.8) dp		ν_{10}
		308 (0.8) dp		ν_7
	285 m			ν_{11}
	281 m	281 (2.8) p		ν_4
		218 (1.1) p		ν_{13}
		141 (0.3) dp		ν_{14}

^a Uncorrected Raman intensities. ^b I or mode description see Table IV. ^c Band shows fine structure with splittings of about 1.30 cm^{-1} due to tellurium isotopes.

ments showed the characteristic tellurium isotope pattern, and therefore the individual m/e listings were omitted for simplicity. The spectra of all three compounds show weak parent ions and TeF_3^+ as the base peak.

Vibrational Spectra of TeF_5OF and TeF_5OCl . The infrared spectra of gaseous and of neon-matrix-isolated TeF_5OF and the Raman spectra of liquid and solid TeF_5OF were recorded (see Figure 3), and the observed frequencies are summarized in Table II. Since the assignments previously reported²³ for TeF_5OCl could not be reconciled with our results for TeF_5OF , the vibrational spectra of TeF_5OCl were also recorded (see Figure 4 and Table III). The following deviations from the

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Table IV. Vibrational Spectra of TeF₅OF and TeF₅OCl and Their Assignment Compared to Those of TeF₅Cl

assign	approx description of mode ^a	obsd freq, cm ⁻¹ (rel intens ^b)						
		TeF ₅ Cl ^b		TeF ₅ OCl		TeF ₅ OF		
		IR (gas)	Raman (liquid)	IR (gas, matrix)	Raman (liquid)	IR (gas, matrix)	Raman (liquid)	
C _{4v}	A ₁ ν ₁	711 sh, m	708 (3.1) p	718 s	713 (1.6) p	727 vs	721 (1.1) p	
	ν ₂	662 vw	659 (1.0) p		663 (1.0) p		669 (1.0) p	
	ν ₃	411 ms	413 (7.7) p	551 m	554 (6.5) p	616 m	613 (3.8) p	
	ν ₄	317 s	312 (0.8) p	381 m	281 (2.8) p	301 m	301 (0.5) p	
	B ₁ ν ₅		651 (0.8) dp		655 sh, dp		660 (0.3) dp	
	ν ₆							
	B ₂ ν ₇		302 (0.5) dp		308 (0.8) dp	308 vw	309 (1.0) dp	
	ν ₈		726 vs	726 (0.6) dp	732 vs	730 sh, dp	738 vs	738 sh, dp
	ν ₉		325 ms	327 (0.9) dp	327 vs	328 sh, dp	327 vs	325 sh, dp
	ν ₁₀			167 (1.8) dp	322 vs	316 (0.8) dp	318 vs	(309-325)
	ν ₁₁		259 m	259 (1.7) dp	285 m		280 mw	279 (0.2) dp
C _s	A ν ₁₂			812 s	809 (0.9) p	908 vw	905 (0.4) p	
	A ν ₁₃				248 (1.1) p	240 mw	240 (0.2) p	
	ν ₁₄				141 (0.5) dp		166 (0.1) dp	

^a Uncorrected Raman intensities (peak heights). ^b Data from ref. 24.

previous literature data²¹ were observed. (i) The infrared spectrum of the gas does not exhibit a very strong band at 708 cm⁻¹. Although our Ne-matrix spectra show the presence of two intense bands at 732 and 718 cm⁻¹, respectively, their frequencies are too close to result in two separate bands in the gas-phase spectrum. (ii) In the Raman spectrum of the liquid the 141-cm⁻¹ band is depolarized and the 809-cm⁻¹ band is polarized. (iii) The infrared spectrum of the neon-matrix sample shows the presence of two fundamental vibrations in the 280-cm⁻¹ region (see trace C of Figure 4).

Using the well-established²⁴ assignments of TeF₅Cl and the revised experimental data of TeF₅OCl for comparison, we can readily assign the vibrational spectra of TeF₅OF (see Table IV), assuming a model with C_{4v} symmetry for the TeF₅O part and C_s symmetry for the TeOF part of the molecule:



Except for the symmetric out of phase, out of plane TeF₅ deformation mode in species B₁, which is usually not observed for pseudooctahedral molecules and is inactive under O_h symmetry, all fundamentals expected for the above C_{4v}-C_s model were observed. The assignments (see Table IV) are straightforward and show for the three molecules almost identical frequencies for the TeF₅ part of the molecules. The modes involving the XY group of this TeF₅XY molecule show the expected mass effects for different X and Y groups. Since

the Te-O stretching mode is expected to couple strongly with the O-Hal stretch and to couple moderately with δ₂(TeF₅) (A₁),²⁵ these modes also exhibit a mass effect.

Comparison of the assignments of Table IV with those previously given²³ for TeF₅OCl shows that with the exception of ν₇ (B₂) and ν₁₃ all the previously given assignments for the deformation modes should be revised. Since a thorough normal-coordinate analysis has previously been carried out²⁴ for TeF₅Cl and since the TeF₅Cl and TeF₅XY spectra are similar, a normal-coordinate analysis of the latter molecules appears unwarranted.

Conclusion. The results of this study show that FOSO₂F is a useful reagent for the synthesis of hypofluorites.²⁶ Furthermore, it is shown that TeF₅OF, as expected from comparison with TeF₅OCl, TeF₅OBr, and FOIF₂O, indeed exists and is a stable molecule. The TeF₅OF molecule was characterized, and the vibrational assignments were made for TeF₅OF and TeF₅OCl.

Acknowledgment. The authors are grateful to R. D. Wilson for his help in some of the experiments, to L. R. Grant for helpful discussions, and to K. Seppelt for a sample of TeF₅OH used in the initial part of this work. This work was financially supported by the Air Force Office of Scientific Research, the Office of Naval Research, and the Army Research Office.

Registry No. TeF₅OH, 57458-27-2; CsTeF₅O, 19610-48-1; KTeF₅O, 19610-51-6; TeF₅OF, 83314-21-0; FOSO₂F, 13536-85-1; NF₄HF₂, 71485-49-9; TeF₅OCl, 41524-13-4.

(25) Christie, K. O.; Curtis, E. C. *Inorg. Chem.* **1982**, *21*, 2938.

(26) After completion of this work, D. D. DesMariseau has informed us in a private communication that he has also used FOSO₂F for the preparation of CF₃C(O)OF from the corresponding alkali-metal salt.

(24) Brooks, W. V. F.; Eshaque, M.; Lau, C.; Passmore, J. *Can. J. Chem.* **1976**, *54*, 817.

In conclusion, we have identified three crystalline forms of N_2O_4 . We believe that α - N_2O_4 is identical with the low-temperature crystal already reported. The β - N_2O_4 form is new, and we are currently working to obtain its crystal structure. We know, however, that this form is not cubic, that it has a significant N-N bond alignment lacking in a α - N_2O_4 , and that it converts readily to the ionic structure. The third form of N_2O_4 is the ionic $NO^+NO_3^-$, which is apparently the thermodynamically favored structure at high density. It is obtained upon either rapidly increasing the pressure of fluid N_2O_4 or increasing the pressure of β - N_2O_4 above 20 kbar. Indeed, it is the only well-formed single α - N_2O_4 crystals that can survive at

higher than 20 kbar. Work is now in progress to identify the crystal structures of these various solids by X-ray diffraction.

Note Added in Proof. We have recently become aware of work by Boldman and Jodl¹⁰ also concerning the production of $NO^+NO_3^-$ from N_2O_4 . In this work the metastable ionic solid was trapped in a low-temperature neon matrix.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy.

Registry No. N_2O_4 , 10544-72-6.

APPENDIX N

Far-Infrared Laser Magnetic Resonance Detection of FO_2

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New far-infrared laser magnetic resonance (LMR) spectra have been detected in the reactions of fluorine atoms with O_2 and O_3 . These are assigned to the FO_2 radical based on chemical and kinetic results and on a qualitative spectroscopic investigation. Thermal decomposition of O_2SbF_6 , a known source of FO_2 , also yielded the same spectra.

Introduction

The FO radical has not been as extensively studied as the other diatomic halogen oxides. The first structural parameters for the radical¹ in the gas phase were determined only recently from the 10- μ m laser magnetic resonance spectrum of the $^2\Pi$ ground state.¹ Subsequent photoelectron spectroscopy yielded ionization potentials,² and improved vibrational and rotational parameters have been determined from infrared diode laser spectroscopy by McKellar et al.³

Prior to these investigations the microwave spectrum had been searched for unsuccessfully by gas-phase electron paramagnetic resonance spectroscopy.⁴ The relatively high concentrations of FO measured mass spectrometrically⁵ and the much enhanced sensitivity of far-infrared laser magnetic resonance over microwave spectroscopy led to the present search for FO spectra by LMR. During this investigation strong, previously unreported spectra were detected at many laser frequencies. Based on chemical and qualitative spectroscopic evidence the carrier of these

TABLE I: Source Reactions and Far-IR Laser Lines Used to Detect FO_2 Spectra^a

wavelength, μ m	laser gas	source reaction	
		F + O ₂	F + O ₃ + M
119	CH ₃ OH		X
170	CH ₃ OH		X
354	CD ₃ OD	X	X
383	CH ₃ F	X	X
419	HCOOH		X
433	HCOOH		X
502	C ₂ H ₂ F	X	X
513	HCOOH		X
634	C ₂ H ₂ Cl	X	X
635	C ₂ H ₂ Br	X	X
742	HCOOH	X	

^a X indicates spectra observed.

spectra is identified as the FO_2 radical.

LMR Spectra and Assignment

The LMR spectrometers operated on a large number of far-infrared molecular laser lines excited by optical pumping with flowing gas CO_2 lasers. Further details of these instruments have been published elsewhere.^{6,7} With

- (1) A. R. W. McKellar, *Can. J. Phys.*, **57**, 2106 (1979).
- (2) J. M. Dyke, N. Jonathan, J. D. Mills, and A. Morris, *Mol. Phys.*, **46**, 1177 (1980).
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- (7) D. P. Stern, Ph.D. Thesis, University of Cambridge, 1983.

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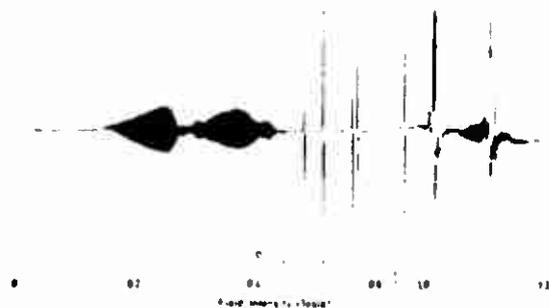


Figure 1. LMR spectrum in parallel polarization recorded with the 354- μm CO_2/CO laser line by using the reaction of F atoms with ozone as source.

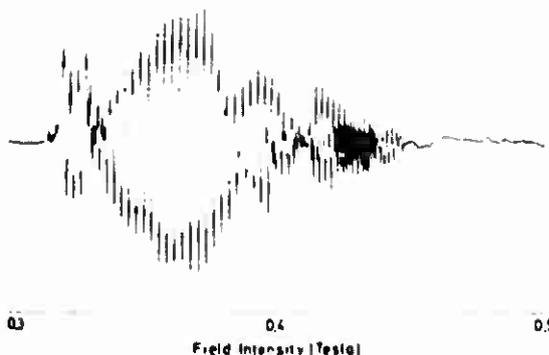


Figure 2. Part of the LMR spectrum at 634 μm in perpendicular polarization between 0.3 and 0.5 T. Identical spectra were recorded in both $\text{F} + \text{O}_3$ and $\text{F} + \text{O}_2 + \text{M}$ sources.

He-cooled bolometer detectors, 1-2-kHz Zeeman modulation, and phase-sensitive detection, the sensitivity for OH was $\sim 2 \times 10^6/\text{cm}^3$.

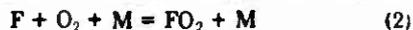
Initially the reaction of F atoms with ozone was selected for generating high concentrations of FO^5



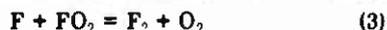
Mixing occurred within a few nanoseconds of the center of the LMR sampling region, which was part of a fast flow system inside the far-IR laser cavity. Under these conditions the concentration of FO is known⁵ to be $> 2 \times 10^{13}/\text{cm}^3$.

Suitable laser lines for FO in both $v = 0$ and 1 levels were selected for rotational transition frequencies calculated from the 10- μm data.^{1,3} Spectra were detected at 11 wavelengths between 119 and 742 μm (Table I). They usually consisted of complicated patterns (Figures 1 and 2) with occasional doublet splittings of ~ 50 G (Figures 3 and 4). All the spectra behaved identically with respect to reactant concentrations, pressure, etc. indicating that a single carrier was responsible.

The complexity and extent of these spectra suggested that FO was not the carrier and an alternative source, reaction 2, was tried. This reaction gave identical but



more intense spectra. Zetzsch⁶ has reported a kinetic study of (2) using mass spectroscopy and shown that (2) is followed by reaction 3 which partly removes FO_2 . It was also



found⁶ that FO_2 formed in (2) increased steadily with reaction time and identical behavior was observed with the

(8) C. Zetzsch, "European Symposium on Combustion", 1973, p 35.

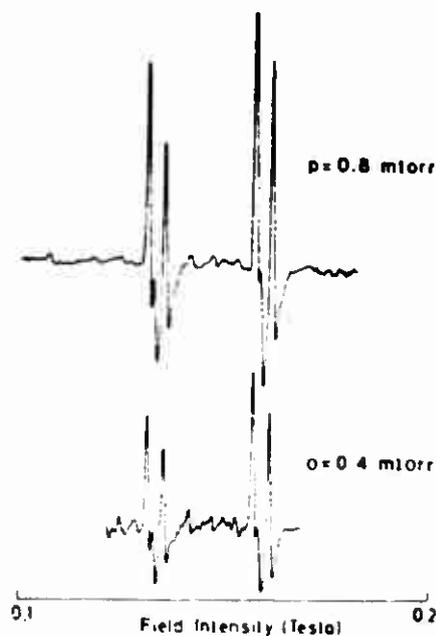


Figure 3. Part of the 382.6- μm spectrum showing the effect of increasing pressure for the $\text{F} + \text{O}_2 + \text{M}$ source.

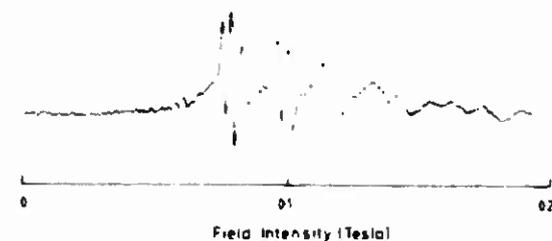
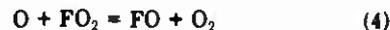


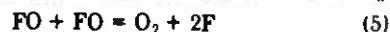
Figure 4. Part of the LMR spectrum at 513 μm in perpendicular polarization showing a doublet splitting of the lines.

spectra reported here. If the LMR spectra arise from FO_2 formed in the three-body reaction 2 their intensity should also increase linearly with pressure and with O_2 . Both effects were qualitatively observed, for example, in the spectra at 382.6 μm (Figure 3) recorded at two different pressures.

In addition to FO_2 small concentrations of FO were detected in the mass spectrometric study.⁸ These were thought to arise from reaction with an O-atom impurity in the rapid interaction



This reaction was also used to test the assignment. When oxygen atoms were added through a second discharge the new spectra disappeared and the O_2 LMR signals increased in intensity. The presence of the same but weaker spectra in the $\text{F} + \text{O}_3$ system is accounted for by the known^{9,10} bimolecular reaction of FO with itself (reaction 5), followed by reaction 2, and also by the reaction of FO with O_3 .



Supplementary evidence was provided by using a quite different source of the radical. It has been shown^{11,12} that

(9) Hg. Gg wagner, J. Warnatz, and C. Zetzsch, *Angew. Chem., Int. Ed. Engl.*, **10**, 564 (1971).

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(11) R. D. Coombe, D. Pilipovich, and R. K. Horne, *J. Phys. Chem.*, **82**, 2484 (1978).

thermal decomposition of O_2AsF_6 and O_2SbF_6 is a source of FO_2 . A weak spectrum identical with that in Figure 3 was obtained when a sample of O_2SbF_6 was heated to about 200 °C and the products pumped rapidly into the spectrometer sample region.

Supporting spectroscopic evidence comes from the doublet splittings observed in a small number of spectra indicating the presence of a single $I = 1/2$ nucleus. These splittings are about 50 G (Figure 4) and much smaller than expected for FO. ESR spectra of FO_2 in an inert matrix and in the liquid phase yield values¹³ of $|A| = 36$ MHz (12.83 G¹⁴) and $B_1 = \pm 252$, $B_2 = \mp 177$, and $B_3 = \mp 75$ MHz for the fluorine hyperfine splittings. Gas-phase hyperfine splittings cannot be calculated from this data without an exact rotational assignment but the relative magnitude of isotropic and anisotropic components accounts qualitatively for observed splittings several times larger than A itself. Assuming the same geometry suggested by Adrian¹³ we have calculated the rotational levels and transitions of FO_2 . Both a- and b-type transitions are allowed and for each laser frequency several possible candidates exist. However, these predictions are strongly dependent on the assumed geometry and not surprisingly transitions occur in high rotational levels accounting, in part, for the complexity of the spectra.

Discussion

The discovery of strong LMR spectra in the gas phase attributable to FO_2 rather than FO is not surprising considering the ubiquitous presence of FO_2 in the condensed and liquid phases.^{13-16,18} Recently, McKellar¹⁹ has

measured the electric dipole moment of FO using 10- μ m LMR. In the $v = 0$ level it is 0.0043 D which explains the elusive nature of its rotational spectra. Following the initial experiments²⁰ on FO_2 the far-infrared LMR spectra of ClSO and FSO have been reported.²¹ FSO has also been investigated by microwave spectroscopy²² which has enabled an assignment of its 513- μ m LMR spectrum to be made. Some of the FO_2 spectra are strikingly similar to both FSO and ClSO spectra, i.e., many sharp resonances varying steadily in intensity (Figures 1 and 2). The complexity of these Zeeman patterns suggests that the best approach initially for structure determination will be microwave spectroscopy or tunable laser spectroscopy in the mid-infrared, and results have recently been reported on two of the fundamentals of FO_2 using diode laser spectroscopy.²³ The discovery of these quite intense far-infrared LMR spectra of FO_2 may well explain the origin of many unassigned LMR spectra at 5^{24,25} and 10 μ m¹ in systems containing fluorine atoms.

Acknowledgment. We thank the Max-Planck-Gesellschaft and the Science and Engineering Research Council for financial support. We are grateful to Prof. E. Hirota for communicating his results to us before publication and Prof. B. A. Thrush for helpful comments on the work. K.O.C. thanks the Office of Naval Research and the US Army Office for financial support and Dr. C. J. Schack and Mr. R. D. Wilson for help with the preparation of the O_2^+ salts.

Registry No. FO_2 , 15499-23-7.

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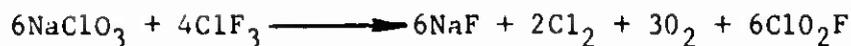
(23) E. Hirota, unpublished results.

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(25) W. Urban, private communication.

APPENDIX O

CHLORYL FLUORIDE



Submitted by KARL O. CHRISTE*, RICHARD D. WILSON*,
and CARL J. SCHACK*

Checked by D. D. DESMARTEAU†

Chloryl fluoride is the most common chlorine oxyfluoride. It is always encountered in reactions of chlorine mono-, tri-, or pentafluorides with oxides, hydroxides or poorly passivated surfaces. It was first obtained¹ in 1942 by Schmitz and Schumacher by the reaction of ClO_2 with F_2 . Other methods involve the reaction of KClO_3 with either BrF_3 or ClF_3 ^{3,4}. The simplest method⁵ involves the reaction of NaClO_3 with ClF_3 , resulting in the highest yields and products which can readily be separated.

Procedure

■ Caution. The hydrolysis of ClO_2F can produce shock sensitive ClO_2 .⁶ Therefore, the use of a slight excess of ClF_3 is recommended for the synthesis to suppress any ClO_2 formation. Chlorine trifluoride is a powerful oxidizer and ignites most organic substances on contact. The use of protective face shields and gloves is recommended when working with these materials.

Dry sodium chlorate (30 mmol 3.193g) is loaded in the dry box into a 30-mL high-pressure stainless steel Hoke cylinder equipped with

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a stainless steel Hoke valve. The cylinder is connected to a stainless steel Teflon FEP vacuum manifold (Fig. X) which has been well passivated with ClF_3 until the ClF_3 , when condensed at -196° , shows no color. The cylinder is then evacuated and ClF_3^* (21.5 mmol) is condensed into the cylinder at -196° . Next, the cylinder is allowed to warm to room temperature and is kept at this temperature for one day. The cylinder is then cooled back to -196° and during subsequent warm-up of the cylinder the volatile products are separated by fractional condensation in a dynamic vacuum through a series of U-traps kept by liquid N_2 slush baths at -95° (toluene), -112° , (CS_2), and -126° (methylcyclohexane). The trap at -95° contains only a trace of chlorine oxides, the trap at -112° contains most of the ClO_2F (29 mmol) and the trap at -126° (7 mmol) contains mainly Cl_2 and some ClO_2F . The yield of ClO_2F is almost quantitative (29.4 mmol, 98%) based on the limiting reagent NaClO_3 .[†] The purity of the material is checked by infrared spectroscopy in a well passivated Teflon or metal cell equipped with AgCl windows and should not show any impurities. A small amount of chlorine oxides which can readily be detected by their intense color if present or formed during handling of ClO_2F , can readily be removed by either conversion to ClO_2F with elemental F_2 or by allowing them to decompose to Cl_2 and O_2 during storage at ambient temperature. Chloryl fluoride can be stored in a metal vessel at room temperature for long time periods without significant decomposition.

Properties⁶

Chloryl fluoride is a colorless liquid boiling at -6° . The infrared spectrum of the gas⁴ shows the following major bands (cm^{-1}): 1271(vs),

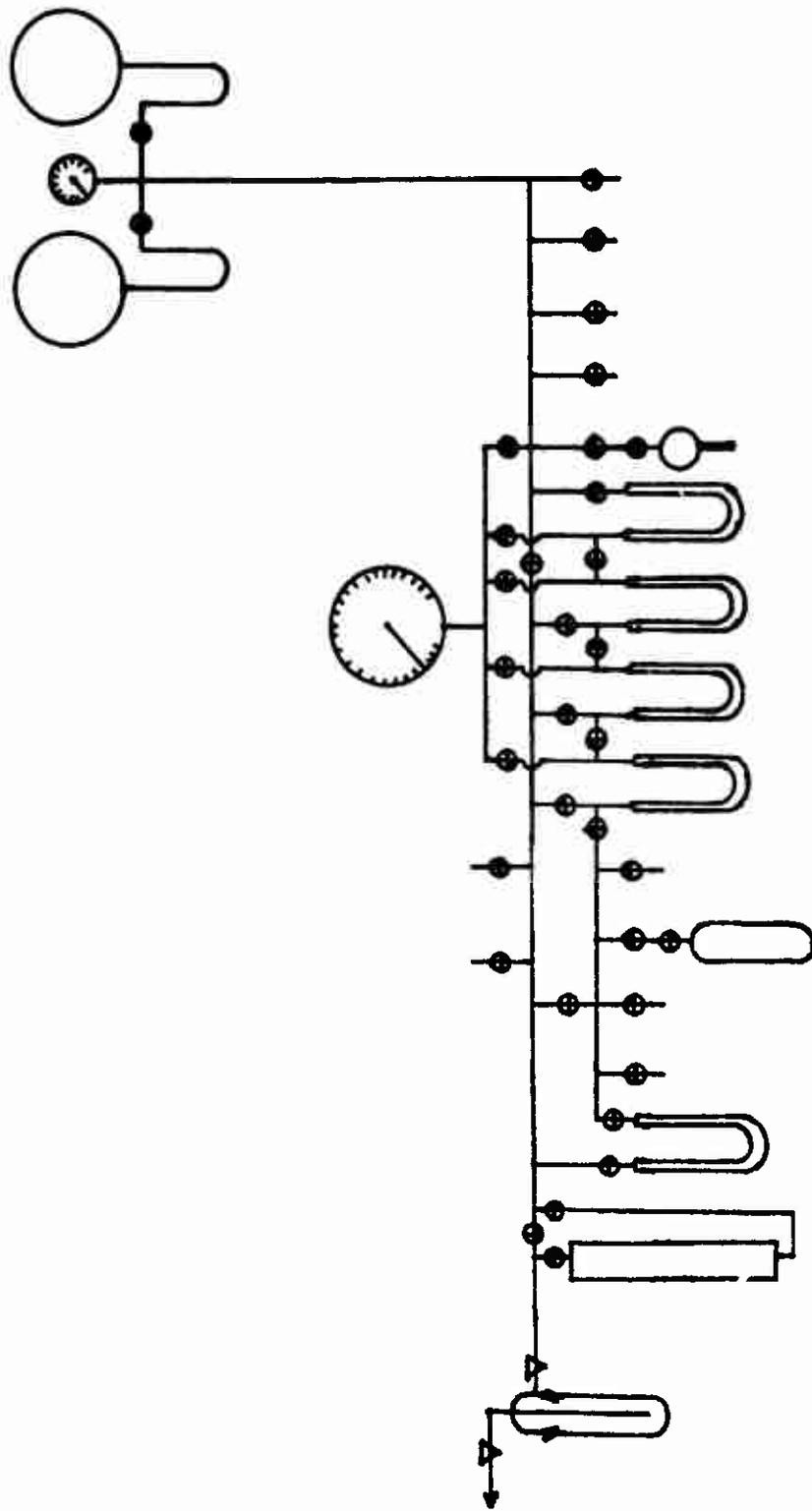
* Available from Ozark Mahoning Co., 1870 So. Boulder, Tulsa, OK 74119

† The checker used one-third of the stated scale and obtained ClO_2F in a yield of 95%.

1106(ms), 630(s) and 547(ms). The ^{19}F NMR spectrum⁷ of the liquid at -80°C consists of a singlet at 315 ppm downfield from external CFCl_3 .

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0-4

Fig. X. Typical metal-Teflon vacuum system used for handling strongly oxidizing or corrosive fluorine compounds. As the vacuum source A, a good mechanical pump (10^{-4} torr or better) is normally sufficient. The use of a fluorocarbon oil, such as Fomblin (Montedison), Krytox (Du Pont), or Halocarbon (Halocarbon Products Corp.) as a pump oil is strongly recommended for safety reasons. B, glass waste trap with glass or Teflon stopcocks and a detachable bottom; only fluorocarbon grease should be used for the stopcocks and joint; the trap is kept cold by a dewar with liquid nitrogen; great care must be taken and a face shield and heavy leather gloves must be worn when pulling off the cold lower half of the waste trap for disposal of the trapped material by evaporation in a fume hood. The glass waste trap can be connected to the metal line by either a glass-metal joint, a graded glass-metal seal, or most conveniently by a quick coupling compression fitting with Viton O-ring seals; C, scrubber for removal of fluorine; the scrubber consists of a glass tower packed with alternating layers of NaCl and soda lime which are held in place by plugs of glass wool at either end; the valves E are arranged in such a manner that the scrubber can be by-passed during routine operation; D, Teflon FEP (fluoro-ethylene-propylene-copolymer) or PFA (polyperfluoroether) U-traps made from 1/2 or 3/4 inch o.d. commercially available heavy wall tubing,; all metal lines are made from either 316 or 321 3/8 inch o.d. stainless steel or Monel tubing, except for the lines from the U-traps to the Heise gage J for which 1/4 inch o.d. tubing is preferred; stainless steel bellows valves E, such as Hoke Model 4200 series, are used throughout the

whole line; metal-metal or metal-Teflon connections are all made with either flare or compression (Swagelok or Gyrolok) compression fittings; F, lecture bottle of ClF_3 (Air Products) used for passivation of the vacuum line; G, He gas inlet; H, F_2 gas inlet; I, connectors for attaching reaction vessels, reagent containers, etc.; J, Heise Bourdon tube pressure gage (0-1000mm \pm 0.1%); K, crude pressure gage (0-5 atm); L, 2 liter steel bulbs used for either measuring or storing larger amounts of gases; M, 3/8 inch o.d. metal U-tubes to permit condensation of gases into the storage bulbs L; N, infrared cell for gases, Teflon body with condensing tip, 5 cm pathlength, AgCl windows. The four U-traps D, connected in series constitute the fractionation train used routinely for the separation of volatile materials by fractional condensation employing slush baths of different temperatures. The volumes of each section of the vacuum line are carefully calibrated by PVT measurements using a known standard volume.

Synthesis of *N,N*-Difluoro-*O*-perfluoroalkylhydroxylamines. 1. Reaction of Perfluoroalkyl Hypofluorites with Difluoramine

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Perfluoroalkyl hypofluorites react with difluoramine in the presence of alkali-metal fluorides to produce the corresponding -ONF₂-substituted perfluoroalkanes. This method was used to prepare the prototype compounds CF₃ONF₂, (CF₃)₂CFOF₂, CF₂(ONF₂)₂, and FOCHF₂ONF₂. Physical and spectroscopic properties are reported for these compounds including vibrational assignments for CF₃ONF₂, the simplest member of this class of compounds.

Introduction

Although the existence of NF₃O has been known for more than 20 years,² only a few R(ONF₂)₂ compounds have been reported, e.g. CF₃ONF₂, FC(O)ONF₂, SF₆ONF₂, and FS-O₂ONF₂, usually prepared by the combination of NF₂ and RO radicals generated from N₂F₄ and the corresponding peroxides or hypohalites, respectively.³ In 1964 studies at Rocketdyne showed that the low-temperature reaction of alkali-metal fluoride-difluoramine adducts with fluorocarbon hypofluorites provides a new synthetic route to -ONF₂-substituted fluorocarbons. However, except for a brief and incomplete description of some of the results in a U.S. patent,⁴ these data remained unpublished. In this paper, we present a full account of this and some subsequent work in our laboratory.

Experimental Section

Caution: Difluoramine is highly explosive,⁵ and protective shielding should be used during handling operations. The compound was always condensed at -142 °C, and the use of a -196 °C bath for condensing HNF₂ should be avoided.⁶ Furthermore, the CsF·HNF₂ adduct invariably explodes before reaching 0 °C.⁷

Materials and Apparatus. Volatile materials, except for HNF₂, were manipulated in a passivated (with ClF₃) stainless-steel vacuum line equipped with Teflon FEP U-traps and 316 stainless-steel bellows-seal valves and a Heise Bourdon tube-type pressure gauge. Difluoramine was handled in either a Pyrex glass or an all-Teflon PFA vacuum system. The hypofluorites CF₃OF, (CF₃)₂CFOF, and CF₂(OF)₂,^{8,9} and difluoramine⁶ were prepared by literature methods. The alkali-metal fluorides were dried by fusion in a platinum crucible and then cooled and powdered in the dry N₂ atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000–200 cm⁻¹ on a Perkin-Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points,^{10,11} and the reported frequencies

Table I. Reaction of Perfluoroalkyl Hypofluorites with HNF₂ in the Presence of KF^a

starting materials (mole ratio)	product	yield, %
CF ₃ OF, HNF ₂ (1:1)	CF ₃ ONF ₂	10
(CF ₃) ₂ CFOF, HNF ₂ (1:1)	(CF ₃) ₂ CFOF ₂	10
CF ₂ (OF) ₂ , HNF ₂ (1:2)	CF ₂ (ONF ₂) ₂	10–20
	CF ₂ (OF)ONF ₂	5–10
CF ₂ (OF)ONF ₂ , HNF ₂ (1:2.5)	CF ₂ (ONF ₂) ₂	20–100 ^b

^a In all reactions, except for that indicated in footnote b, HNF₂·KF was performed at -78 °C with use of using a large excess of KF; the perfluoroalkyl hypofluorites were added at -126 or -142 °C, and the mixtures were allowed to warm slowly to -80 °C over a period of several hours. ^b The quantitative yield of CF₂(ONF₂)₂ was achieved by cocondensation of the starting materials over KF (see text).

are believed to be accurate to ±2 cm⁻¹. The spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The spectra of matrix-isolated CF₃ONF₂ were obtained at 6 K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research grade Ar (Matheson) was used as a matrix material in a mole ratio of 300:1.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488-nm exciting line of an Ar ion laser and a Claassen filter¹² for the elimination of plasma lines. Quartz tubes (3-mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A previously described¹³ device was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al.¹²

The ¹⁹F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer. Chemical shifts were determined relative to the CFCl₃ solvent with positive shifts being downfield from CFCl₃.¹⁴

Mass spectra were recorded with a CEC21-103C mass spectrometer modified with a metal inlet system, CEC Part No. 285400.

Syntheses of R₂ONF₂ Compounds. Most reactions between the perfluoroalkyl hypofluorites and HNF₂ were carried out according to the following general procedure. Finely powdered dry KF (2 g) was loaded in the drybox into a 300-mL Pyrex reactor. Difluoramine (4 mmol) was added from the glass or Teflon line to the reactor at -142 °C. The mixture was warmed briefly to -78 °C and then recooled to -142 °C. The reactor was transferred to the metal line, and a slightly less than stoichiometric amount of perfluoroalkyl hypofluorite was added at -142 °C. The mixture was allowed to warm slowly over several hours to -78 °C. The volatile products were separated by fractional condensation through a series of cold traps kept at appropriate temperatures. The amounts of material were determined by PVT measurements and identified by spectroscopic techniques. Typical reaction conditions and yields are summarized in Table I.

Synthesis of F₂C(ONF₂)₂ in a Flow System. In a vacuum line, a U-trap filled with glass beads coated with KF was kept at -112 °C;

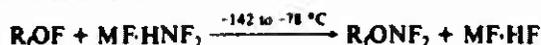
- (1) Present addresses: (a) Department of Chemistry, California State Polytechnic University, Pomona, CA 91768; (b) MVT, Microcomputer Systems, Inc., Westlake Village, CA 91361; (c) Jacobs Engineering Group, Inc., Pasadena, CA 91101.
- (2) NF₃O was independently discovered in 1961 at Rocketdyne (Mays, W. U.S. Patent 3320147, 1962) and Allied Chemical (Fox, W. B.; MacKenzie, J. S.; Vaanderkooi, N.; Sukornick, B.; Warner, C. A.; Holmes, J. R.; Eibeck, R. E.; Stewart, B. B. *J. Am. Chem. Soc.* 1966, 88, 2604) and in 1965 at the University of British Columbia, Vancouver (Bartlett, N.; Passmore, J.; Wells, E. J. *Chem. Commun.* 1966, 213).
- (3) For a review of these reactions see: Schmutzler, R. *Angew. Chem., Int. Ed. Engl.* 1968, 7, 440.
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- (5) Lawless, E. W.; Smith, I. C. "Inorganic High Energy Oxidizers"; Marcel Dekker: New York, 1968; p 69.
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- (7) Lawton, E. A.; Pilipovich, D.; Wilson, R. D. *Inorg. Chem.* 1965, 4, 118.
- (8) Ruff, J. K.; Pitochelli, A.; Lustig, M. *J. Am. Chem. Soc.* 1966, 88, 4531.
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on either side, U-traps were kept at -142 °C to condense products. A mixture of F₂C(OF)₂ (6.70 mmol) and HNF₂ (6.70 mmol) was passed through the system. The reactants were condensed at -142 °C allowed to pass through the cold traps and KF trap by warming, and recondensed at -142 °C. The operation was repeated several times. The products were separated by fractional condensation through traps kept at -142 and -196 °C. The -142 °C trap contained 0.45 mmol of a mixture of F₂C(ONF₂)₂ and FOCF₂ONF₂. In the -196 °C trap, there was left 6.52 mmol of a mixture of F₂C(OF)₂, N₂F₄, and NF₃.

Results and Discussion

Syntheses of R₂ONF₂ Compounds. Perfluoroalkyl hypofluorites react with alkali-metal fluoride-HNF₂ adducts at low temperatures to produce the corresponding -ONF₂-substituted perfluoroalkanes:



The generality of this reaction was demonstrated by the synthesis of a primary (CF₃ONF₂), a secondary [(CF₂)₂CFONF₂], a geminal bis-substituted [CF₂(ONF₂)₂], and a geminal -OF-substituted (FOCF₂ONF) *N,N*-difluoro-*O*-perfluoroalkylhydroxylamine. It was found important to preform the alkali-metal fluoride-difluoramine adduct because in the absence of alkali-metal fluorides most of these hypofluorites react uncontrollably and sometimes explosively with HNF₂ to give zero yields of the desired -ONF₂-substituted products. A study of the effect of different alkali-metal fluorides showed that KF-, RbF-, and KF-NaF mixtures were all equivalent; CsF afforded only traces of the desired compounds and is also less desirable because of the tendency of its HNF₂ adduct to explode before reaching 0 °C.⁷ Sodium fluoride alone and LiF were not examined because they do not form an adduct with HNF₂.⁷

The yields of R₂ONF₂ in these reactions were generally low and were in the 10-20% range, except for the reaction of CF₂(OF)ONF₂ with HNF₂. When this reaction was carried out with preformed KF·HNF₂, the yield of CF₂(ONF₂)₂ was low, but it was found that CF₂(OF)ONF₂ and HNF₂ could be premixed without reaction and after cocondensation over KF at -142 °C and slow warm-up to -78 °C produced CF₂(ONF₂)₂ in quantitative yield. The generally low yields and the nature of the main products (COF₂, CF₃CFO, CF₃COCF₃, CF₄, N₂F₄, NF₃, etc.) suggest a free-radical mechanism for these reactions. For CF₂(OF)₂ and HNF₂ a flow reaction was also studied by repeatedly passing an equimolar mixture of the starting materials over KF at -112 °C. Although CF₂(ONF₂)₂ and CF₂(OF)ONF₂ were formed, their yields were considerably lower than those obtained in a static system.

Since for CF₃ONF₂ the synthesis from CF₃OF and N₂F₄ under the influence of UV radiation^{15,16} is clearly superior to the method reported here, we examined the analogous reaction between CF₂(OF)₂ and N₂F₄ under the influence of water-filtered UV radiation. However, no evidence could be obtained for the formation of either CF₂(OF)ONF₂ or CF₂(ONF₂)₂. The only -ONF₂ compound formed was a small amount of CF₃ONF₂, with COF₂ and FNO being the major products. Therefore, the KF-catalyzed reaction of HNF₂ with CF₂(OF)₂ represents, presently, the only known method for the syntheses of CF₂(OF)ONF₂ and CF₂(ONF₂)₂.

Properties of CF₃ONF₂. This compound is well-known and has been well characterized,^{15,16} and the properties observed in this study were in good agreement with the literature data. However, since CF₃ONF₂ is the simplest member of the class of *N,N*-difluoro-*O*-perfluoroalkylhydroxylamines and since

Table II. Vibrational Spectra of CF₃ONF₂

Wave No., cm ⁻¹ , and Assign ^a		Assign ^a to point group C _s
Infrared (KBr Pellets)	Raman (Liquid)	
2605 vs		2 ₁
2530 vs		1 ⁺ 2
2485 vs		2 _{1,2}
2433 vs		2 ₂
2340 vs		1 ⁺ 1 ₂
2280 vs		1 ⁺ 1 ₂
2245 vs		2 ⁺ 3
2180 sh		1 ⁺ 1 ₂
2151 w		2 ⁺ 4
2020 vs		2 ⁺ 5
1975 sh		1 ⁺ 6 ⁺ 6 ⁻ 7 ⁺ 7 ⁻
1936 w		1 ⁺ 7 ⁺ 7 ⁻ 2 ⁺ 1 ⁺ 6 ⁺ 6 ⁻ 1 ⁺ 1 ₂
1901 sh		1 ⁺ 7 ⁻
1862 vs		2 ⁺ 7 ₃
1809 vs		2 ⁺ 1 ⁺ 6 ⁺ 4 ⁺ 5
1792 sh		1 ⁺ 7 ₅
1739 vs		2 ⁺ 5 ⁺ 1 ⁺ 7 ⁺ 8
1661 vs		1 ⁺ 7 ⁺ 7 ⁻ 1 ⁺ 5 ⁺ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻
1564 vs		2 ⁺ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻
1562 vs		1 ⁺ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻
1420 vs		2 ⁺ 7 ⁺ 7 ⁻
1340 sh	1361 vs	1 ⁺ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻ 7 ⁺ 7 ⁻
1303 vs	1302 vs	130A (0 2)g
	1282 vs	7 ⁺
	1264 w	4 ⁺ 7 ⁺ 6 ⁺ 7 ⁺ 7 ⁻
	1251 w	7 ⁺ 7 ⁻
1247 vs	1242 vs	124B (0 1)
	1230 w	7 ⁺
1221 vs	1218 vs	122A (0 1)
	1216 sh	7 ⁺ 7 ⁻
	1207 sh	7 ⁺ 7 ⁻
	1196 w	7 ⁺ 7 ⁻
1076 vs		1060 sh
		5 ⁺ 7 ⁺ 7 ⁻ 5 ⁺ 7 ⁻
1034 vs	1035 w	1032 (10)g
		7 ⁺
942 vs	942 vs	938 (1 4)g
		7 ⁺
901 s	901 vs	906 (1 2)g
		7 ⁺
870 vs	866 vs	860 (1 2)g
		7 ⁺
	853 vs	85 ⁺ 7 ⁺
718 w	722 s	718 (9 8)g
		7 ⁺
	710 vs	708 (0 7)g
		7 ⁺ 7 ⁻
628 vs	629 vs	625 (1 3) 6g
		7 ⁺
579 w	568 w	566 (4 2)g
		7 ⁺
578 vs	514 w	510 (0 1)g
		7 ⁺
480 w	480 vs	476 (0 2)g
		7 ⁺ 7 ⁻
		368 (2 1)g
		16
		151 (7 3)g
		110
		201 (1 8)g
		111
		75 (0 1)
		137 718

(a) Uncorrected Raman Intensities representing relative peak height.

only a partial infrared spectrum had previously been reported,^{15,16} it was desirable to obtain complete vibrational spectra (see Figure 1 and Table II). Assignments were made for CF₃ONF₂ by assuming symmetry C_s with the F-C-O-N part of the molecule being located in the symmetry plane. These assignments are summarized in Table III and were made by comparison with the spectra of similar molecules such as CF₃OF,¹⁷ CF₃NO,¹⁸ CF₃N₃,¹⁹ CF₃NF₂,²⁰ SF₃ONF₂,¹⁶ and

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(17) Kuo, J. C.; DesMarteau, D. D.; Fately, W. G.; Hammaker, R. M.; Marsden, C. J.; Witt, J. D. *J. Raman Spectrosc.* 1980, 9, 230.

Table III Vibrational Assignments of $\text{CF}_2(\text{ONF}_2)_2$ Compared to Those of Similar Molecules

assign in point group C_s	approx descripn of mode for $\text{CF}_2(\text{ONF}_2)_2$	obsd freq, cm^{-1}								
		$\text{CF}_2(\text{ONF}_2)_2$	CF_2N_2 ^a	CF_2OI ^b	CF_2NO ^c	CF_2NF_2 ^d	NF_3 ^e	HNF_2 ^f	$\text{SF}_2(\text{ONF}_2)_2$ ^g	
j	$\nu_1(\text{CF}_2)$ ^h	1303	1284	1294	1291	1290				
	$\nu_{as}(\text{CF}_2)$ ^h	1218	1168	1222	1175	1221				
	$\nu_2(\text{NF}_2)$	1034				1018	1070	972	1029	
	$\nu_3(\text{C-O})$	942		947						
	$\nu_4(\text{O-N})$	866								858
	$\nu_5(\text{CF}_2)$	720	730	678	730	721				
	$\nu_6(\text{CF}_2)$	567	513	585	533	576				
	$\nu_7(\text{NF}_2)$	512				525	573	500		
	$\nu_8(\text{CF}_2)$	478	402	429	428					
	$\nu_9(\text{NF}_2)$	351								
	$\nu_{10}(\text{CON})$	205	179	278						
a''	$\nu_{as}(\text{CF}_2)$ ^h	1245	1254	1261	1230	1240				
	$\nu_{as}(\text{NF}_2)$	907				951	931	888	928	
	$\nu_{14}(\text{CF}_2)$	627	556	607	551	600				
	$\nu_{15}(\text{CF}_2)$	478	450	431	428					
	$\nu_{16}(\text{NF}_2)$	368								
	$\nu_{17}(\text{C-O})$	75		127	[50]					
	$\nu_{18}(\text{O-N})$									

^a Reference 19. ^b Reference 17. ^c Reference 18. ^d Reference 20; the potential energy distribution of the fundamentals assigned to the CF_2 , NF_2 , and CN stretching modes indicates strong mixing of the corresponding symmetry coordinates. ^e Harmony, M. D.; Myers, R. J. *J. Chem. Phys.* 1962, 37, 636. ^f Comford, J. J.; Mann, D. E.; Schoen, L. J.; Lide, D. R. *ibid.* 1963, 38, 461. ^g Reference 16. ^h The assignments given in this table for the CF_2 stretching modes are tentative.

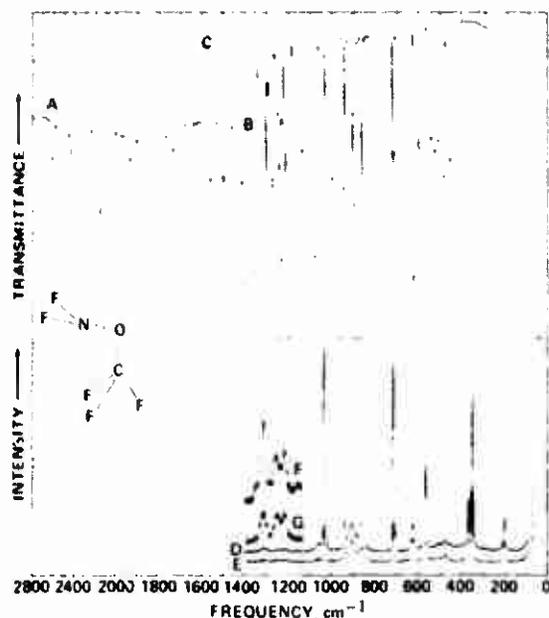


Figure 1. Vibrational spectra of $\text{CF}_2(\text{ONF}_2)_2$: traces A and B, infrared spectra of the gas recorded in a 5-cm path length cell with AgCl windows at pressures of 300 and 8 torr, respectively; trace C, infrared spectrum of Ar-matrix-isolated $\text{CF}_2(\text{ONF}_2)_2$ (mole ratio 300) at 6 K; traces D, E, and F, G, Raman spectra of the liquid in a quartz tube at -80°C recorded at two different sensitivities with incident polarization parallel and perpendicular.

other $-\text{ONF}_2$ -substituted perfluoroalkanes.²¹ Most stretching modes and the ν_6 , ν_7 , and ν_{14} deformation modes can be assigned with confidence. The assignment for the remaining six deformation modes and for the CF_2 stretching modes are more

or less tentative. In all the >CONF_2 compounds studied in this laboratory, the >CONF_2 group exhibits a very characteristic band pattern at about 860, 910, 940, and 1030 cm^{-1} of almost constant frequencies and intensities and therefore is well suited for the identification of a >CONF_2 group. In particular, the symmetric NF_2 stretching mode at about 1030 cm^{-1} is very useful for diagnostic purposes due to its high Raman intensity and the absence of other bands in this frequency region.

Properties of $(\text{CF}_3)_2\text{CFONF}_2$. This compound had previously been prepared by the reaction of $(\text{CF}_3)_2\text{CO}$ with N_2F_4 and N_2F_2 in a platinum tube at 100°C and 1000 atm external pressure and identified by its infrared and mass spectrum.²² The infrared spectrum of our product (frequency (cm^{-1}), intensity: 1327, s; 1264, vs; 1215, w; 1176 s; 1121, s; 1064, ms; 985, s; 910, ms; 849, s; 804, vw; 740, m; 725, m) was identical with that previously reported.²² The identity of the compound was confirmed by its ^{19}F NMR spectrum, which showed the following shifts, multiplicities, coupling constants, and area ratios:

$(\text{CF}_3)_2$		CF	ONF_2
2.2 Hz		1.91 Hz	
doublet of triplets		septet	binomial triplet with partially resolved NF spin-spin coupling
δ	-79	-140	+131
area	6	1	2

Properties of $\text{CF}_2(\text{ONF}_2)_2$. $\text{CF}_2(\text{ONF}_2)_2$ is the first known example of geminal $(\text{ONF}_2)_2$ -substituted compound. It is colorless as a solid, liquid, and gas. A sharp melting point was not observed for $\text{CF}_2(\text{ONF}_2)_2$ due to its tendency to form a glass at low temperature. The liquid boils at -9°C . The vapor slowly passes through a -112°C trap but stops at -126°C . Vapor density measurements (M_r found 187, calcd 186) showed that in the gas phase the compound is not associated. The compound is completely stable at ambient temperature. Drop-weight tests performed on the liquid at about 0°C were

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Table IV. Vibrational Spectra of CF₂(ONF₂)₂

obsd freq, cm ⁻¹ , and intens			assignt
IR gas	Raman liquid, -80 °C		
1306 m	1310 (0+)	ν _{as} (CF ₂) and combination bands in Fermi resonance	
1274 s	1274 (0+)		
1250 s	1248 (0+)		
1226 ms	1223 (0+)		
1189 vs	1185 (0+)	ν _s (CF ₂)	
	1042 sh p	ν _s (NF ₂)	
1038 ms	1035 (10) p		
949 mw	949 (10.4) p	ν(C-O)	
916 s	909 (1) dp	ν _{as} (NF ₂)	
877 s	870 (1) p	ν(N-O)	
849 vs	835 (1)		
752 mw	749 (0.7)		
729 mw			
669 w	670 (7) p		
624 w	621 (0.5)		
571 vw	570 (7) p		
517 vw			
	458 (0.4)		
	391 (2.5) p		
	358 (2.2) p		
	341 (1.9) p		
	317 (2.5) p		
	270 (0.6) p		
	260 (3.2) p		
	241 (1.6) dp		
	217 (2) p		
	166 (0.6) dp		

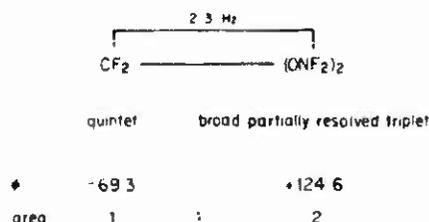
Table V. Mass Spectrum^a of CF₂(ONF₂)₂

m/e	abund	ion	m/e	abund	ion
118	21.5	CF ₂ ONF ₂ ⁺	50	2.2	CF ₂ ⁺
99	1	CF ₂ ONF ₂ ⁺ and CFONF ₂ ⁺	47	44.3	CFO ⁺
69	0.64	CF ₂ ⁺	33	14.7	NF ⁺
68	1	NF ₂ O ⁺	31	<0.5	CF ⁺
66	<0.5	CF ₂ O ⁺	30	70.5	NO ⁺
52	100	NF ₂ ⁺	28	<0.5	CO ⁺

^a Recorded at 70 eV.

all negative at the 115 cm kg level, compared to a 50% point at 6.1 cm kg for ethyl nitrate. These tests indicate that CF₂(ONF₂)₂ is surprisingly stable and is much less sensitive than the analogous CNF₂ derivative, CF₂(NF₂)₂, which under the same conditions gave a positive test at 23 cm kg.

The structure of CF₂(ONF₂)₂ was established by its vibrational (see Figure 2, Table IV), mass (see Table V), and ¹⁹F NMR spectra. The latter showed the following parameters:



As expected, CF₂(ONF₂)₂ is an oxidizer liberating iodine from a KI solution. Unlike fluorocarbon ethers, CF₂(ONF₂)₂ does not readily hydrolyze in concentrated H₂SO₄ at 25 °C. After a 40-h contact time with agitation, 95% of the CF₂(ONF₂)₂ was recovered unchanged. In CH₃OH after 40 h at 25 °C, 90% of CF₂(ONF₂)₂ was recovered; however, in 1 M sodium metboxide in methanol, slow reaction was observed. Similarly, it slowly reacted with acetic acid. The nature of the reaction products was not investigated.

Properties of CF₂(OF)ONF₂. Like CF₂(ONF₂)₂, this compound had not been prepared previously. It is colorless as a

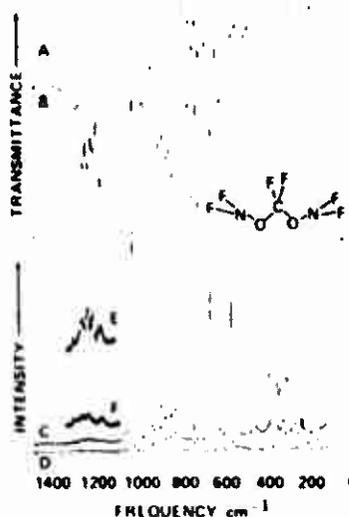


Figure 2. Vibrational spectra of CF₂(ONF₂)₂; traces A and B, infrared spectra of the gas in a 5-cm path length cell at 60 and 7 torr, respectively; traces C, E and D, F, Raman spectra of the liquid at -80 °C at two different sensitivities with incident polarization parallel and perpendicular.

Table VI. Vibrational Spectra of CF₂(OF)ONF₂

obsd freq, cm ⁻¹ , and intens			assignt
IR gas	Raman liquid, -100 °C		
1305 m	1305 (0.2)	ν _{as} (CF ₂) and combination bands in Fermi resonance	
1279 s	1279 (0.3) p		
1251 s	1249 (0+)		
1220 s	1216 (0.3) p		
1182 vs	1184 sh	ν _s (CF ₂)	
	1171 (1.1) p		
1050 sh	1045 sh	ν _s (NF ₂)	
1031 ms	1031 (10) p		
944 m	950 (3) p	ν(C-OF)	
	939 (7.2) p		
914 s	917 (3) dp	ν(C-ONF ₂)	
895 sh	891 (7.5) p		
854 vs	855 sh	ν(OF)	
	845 (3.5) p		
753 m	751 (2.5) p	δ(CF ₂)	
689 mw	690 (8.2) p		
668 vw	667 (4.4) p		
601 w	601 (4.2) p		
563 vw	561 (6.8) p		
	520 (0.6) dp		
	463 (0.5) dp		
	450 (1.2) p		
	371 (3.3) dp		
	359 (7.3) p		
	348 (8.8) p		
	296 (2.8) p		
	258 (3.2) p		
	199 (3.1) p		
	146 (2) dp		
	131 (2.2) dp		

solid, liquid, and gas and also shows a tendency to form a glass at low temperature. From experimental data (temperature (°C), vapor pressure (mm): -94.8, 11; -78.4, 41; -64, 101; -57.5, 141; -47, 228), the vapor pressure-temperature relationship was found to be

$$\log [P (\text{mm})] = 7.31997 - 1116.029/[T (\text{K})]$$

with an index of correlation of 0.9997. During fractional condensation, the compound slowly passes through a -126 °C trap but stops at -142 °C. The extrapolated boiling point is -21.8 °C, and the derived heat of vaporization is ΔH_{vap} = 5105

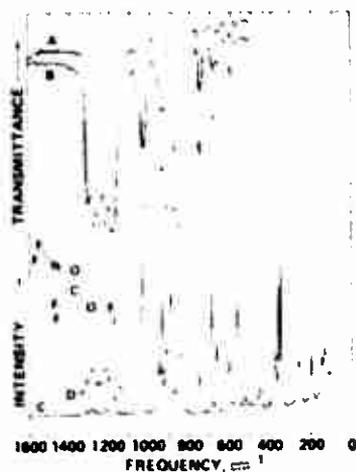
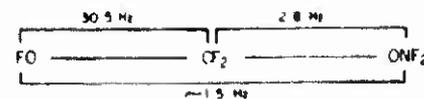


Figure 3. Vibrational spectra of $\text{CF}_2(\text{OH})\text{ONF}_2$; traces A and B, infrared spectra of the gas recorded in a 5-cm path length cell with AgCl windows at pressures of 42 and 15 torr, respectively; traces C and D, Raman spectra of liquid $\text{CF}_2(\text{OH})\text{ONF}_2$ at -100°C recorded at two different sensitivities.

cal mol^{-1} . The Trouton constant (20.3) and the molecular weight of the gas M , found 153, calcd 153) indicate little or no association in both the liquid and the gas phases.

The structure of the compound was established by vibrational (see Figure 3, Table VI) and ^{19}F NMR spectroscopy:



triplet of triplets doublet of triplets broad triplet
 $J_{\text{C-N}} = 19.1 \text{ Hz}$

♦	+156.6	-79	+125
area	1	2	2

The compound is stable at ambient temperature and liberates iodine from KI solution.

Conclusion. Complexing of HNF_2 with alkali-metal fluoride has successfully been used to moderate the otherwise explosive reaction of HNF_2 with hypofluorites. The general applicability of this method for the syntheses of *N,N*-difluoro-*O*-perfluoroalkylhydroxylamines has been demonstrated, and $\text{CF}_2(\text{ONF}_2)_2$, the first known example of a geminal-disubstituted $-\text{ONF}_2$ compound, has been prepared by this method.

Acknowledgment. The authors are grateful to Dr. C. J. Schack for helpful discussions and to the Air Force Rocket Propulsion Laboratory, the Office of Naval Research, and the Army Research Office for financial support of this work.

Registry No. CF_2OF , 373-91-1; $(\text{CF}_3)\text{CFOF}$, 3848-93-9; $\text{CF}_2(\text{OF})_2$, 16282-67-0; $\text{CF}_2(\text{OH})\text{ONF}_2$, 36781-60-9; HNF_2 , 10405-27-3; CF_3ONF_2 , 4217-93-0; $(\text{CF}_3)_2\text{CFONF}_2$, 84194-25-2; $\text{CF}_2(\text{ONF}_2)_2$, 36781-59-6; KF, 7789-23-3.

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Synthesis of *N,N*-Difluoro-*O*-perhaloalkylhydroxylamines. 2. Lewis Acid Catalyzed Addition of NF_3O to Olefins

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N,N-Difluoro-*O*-perhaloalkylhydroxylamines, R_2ONF_2 , were successfully prepared by the Lewis acid catalyzed addition of NF_3O to olefins. The new compounds $\text{XC}_2\text{F}_4\text{ONF}_2$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) were obtained and characterized. The unexpected direction of the NF_3O addition, resulting exclusively in the anti-Markownikoff-type isomer $\text{XCF}_2\text{CF}_2\text{ONF}_2$, was elucidated by model reactions involving the stepwise addition of BF_3 and NF_3O to $\text{CF}_2=\text{C}=\text{CF}_2$. It is shown that all reactions can be rationalized in terms of an R_2BF_2 intermediate produced by the normal polar addition of BF_3 to the olefin. In the case of $\text{CF}_2=\text{C}=\text{CF}_2$, the new vinyldifluoroborane $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_2$ was isolated and characterized. Attempts to isolate $-\text{ONF}_2$ -substituted vinyl compounds by reaction of NF_3O with vinyldifluoroboranes led to difluoramino ketones formed via a keto-enol-type tautomerism.

Introduction

Following the discovery of NF_3O in 1961 by Rocketdyne² and Allied Chemical,³ studies were carried out in these two laboratories to add NF_3O to olefinic double bonds. Except for an incomplete description of some of the Rocketdyne results in a patent⁴ and a one-sentence statement in a paper on NF_3O by the Allied group,⁵ these data have not been published, partially due to their incompleteness and the lack of a plausible mechanism to explain the observed direction of the NF_3O addition. The previous Rocketdyne studies have now been complemented and are summarized in this paper.

Experimental Section

Caution! The addition reactions of NF_3O to olefins, particularly hydrogen-containing compounds, can proceed explosively. Appropriate safety precautions must be taken when these reactions are carried out.

Materials and Apparatus. The apparatus, handling techniques, and instrumental conditions used in this study have been described in part I of this series.⁵ Literature methods were used for the syntheses of NF_3O ,⁶ $\text{CF}_2=\text{C}=\text{CF}_2$,⁷ and $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_2$.⁸ Monomeric C_2F_4 was prepared by vacuum pyrolysis of poly(tetrafluoroethylene); $\text{C}_2\text{F}_3\text{Cl}$ and BF_3 (The Matheson Co.) and $\text{C}_2\text{F}_3\text{Br}$ (Ozark Mahoning Co.) were purified by fractional condensation prior to their use.

Syntheses of $\text{XCF}_2\text{CF}_2\text{ONF}_2$. Most reactions of NF_3O in the presence of BF_3 with C_2F_4 , $\text{C}_2\text{F}_3\text{Cl}$, or $\text{C}_2\text{F}_3\text{Br}$ were carried out according to the following general procedure. Equimolar amounts (3 mmol each) of $\text{C}_2\text{F}_3\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$) and BF_3 were condensed at -196°C into the tip of a 250-ml Pyrex reactor. The mixture was warmed for 2 h to -78°C and then recooled to -196°C . An equimolar

amount of NF_3O (3 mmol) was condensed at -196°C above the $\text{C}_2\text{F}_3\text{X}-\text{BF}_3$ mixture. The reactor was allowed to warm slowly to -78°C and was kept at this temperature for several hours before being allowed to warm to ambient temperature. The volatile materials were separated by fractional condensation through a series of traps at -78°C , at -95°C (for $\text{C}_2\text{F}_3\text{Br}$ reaction), or -112°C (for $\text{C}_2\text{F}_3\text{Cl}$ reaction), or -142°C (for C_2F_4 reaction), and at -196°C . The -78°C trap contained small amounts of unidentified material. The -196°C trap contained mainly unreacted BF_3 , $\text{C}_2\text{F}_3\text{X}$, C_2F_4 , and sometimes small amounts of NF_3O . The -95 , -112 , or -142°C trap contained the desired $\text{XCF}_2\text{CF}_2\text{ONF}_2$ product. The reactor generally contained some white solid residue, which according to its spectra consisted of NOBF_2 . The yields of $\text{C}_2\text{F}_3\text{ONF}_2$, $\text{CF}_2\text{ClCF}_2\text{ONF}_2$, and $\text{CF}_2\text{BrCF}_2\text{ONF}_2$ were about 60, 18, and 10%, respectively. Whereas $\text{C}_2\text{F}_3\text{ONF}_2$ could be obtained in high purity by the above described simple fractionation, $\text{ClCF}_2\text{CF}_2\text{ONF}_2$ and $\text{BrCF}_2\text{CF}_2\text{ONF}_2$ contained about 10% of an unidentified halocarbon impurity whose removal required either repeated careful fractionations or gas chromatographic techniques.

$\text{CF}_3\text{CF}_2\text{ONF}_2$: bp -24.9°C ; mp -146.5°C ; mol wt found 185; mol wt calcd 187; $\log [P (\text{mm})] = 8.0222 - 1271/[T (\text{K})]$; $\Delta H_{\text{vap}} = 5.8 \text{ kcal/mol}$; Trouton constant 23.5; mass spectrum (70 eV) [m/e (intensity) ion], 119 (69) C_2F_3^+ , 100 (3.4) C_2F_4^+ , 69 (100) CF_3^+ , 66 (2.1) CF_2O^+ , 52 (29) NF_2^+ , 50 (10) CF_2^+ , 47 (7.1) CFO^+ , 33 (7.7) NF^+ , 31 (12) CF^+ , 30 (24) NO^+ , 19 (1.1) F^+ , 16 (0.3) O^+ ; ^{19}F NMR (positive shifts are low field from CFCl_3) neat ϕ_A (tr tr = sept) $-\delta 9.0$, ϕ_B (quat tr) $-\delta 9.9$, ϕ_C (br tr) 124.9, CFCl_3 solvent ϕ_A $-\delta 85.9$, ϕ_B $-\delta 93.0$, ϕ_C 128.1 ($J_{AB} = 2.02$, $J_{AC} = 1.01$, $J_{BC} = 3.0$, $J_{SC} = 110 \text{ Hz}$); IR 2640 (vw), 2600 (vww), 2478 (vw), 2408 (vw), 2350 (vww), 2317 sh, 2235 (vw), 2090 (vww), 2050 (vw), 1984 (vw), 1931 (vw), 1867 (vw), 1815 sh, 1791 (vw), 1775 sh, 1679 (vw), 1594 (vw), 1510 (vw), 1471 (vww), 1401 (mw), 1300 sh, 1247 (vs), 1206 (vs), 1114 (vw), 1028 (vs), 903 (s), 850 (vs), 741 (m, PQR), 730 sh, 660 (w), 621 (vw), 569 (vw), 531 (mw), 474 (vww), 462 (vww), 444 (vww) cm^{-1} ; Raman (liquid -90°C) 1402 (0.7), 1240 (0.1), 1205 (0.1), 1111 (1.2) p, 1025 (6.6) p, 903 (0.7) dp, 849 (2.4) p, 835 (1.2) p, 741 (10) p, 659 (2.8) p, 619 (0.7) dp, 570 (3.1) p, 559 (0.2) dp, 529 (0.2) dp, 466 (0.2) dp, 442 (0.1) dp, 358 (1.7) p, 342 (1.9) dp, 303 (6.2) p, 244 (4.1) p, 121 (0.6) dp cm^{-1} . Anal. Calcd for $\text{C}_2\text{F}_3\text{NO}$: N, 7.48. Found: N, 7.21 (N₂ by evolution by Na reduction).

$\text{ClCF}_2\text{CF}_2\text{ONF}_2$: bp 13.8°C ; mol wt found 204.6; mol wt calcd 203.5; $\log [P (\text{mm})] = 7.6002 - 1355/[T (\text{K})]$; $\Delta H_{\text{vap}} = 6.2 \text{ kcal/mol}$; Trouton constant 21.6; mass spectrum (70 eV) [m/e (intensity) ion] 137 (16.2) $\text{C}_2\text{F}_4^{37}\text{Cl}^+$, 135 (52.3) $\text{C}_2\text{F}_4^{35}\text{Cl}^+$, 119 (20.7) C_2F_3^+ , 118 (0.6) $\text{C}_2\text{F}_3^{37}\text{Cl}^+$, 116 (1.9) $\text{C}_2\text{F}_3^{35}\text{Cl}^+$, 100 (9) C_2F_4^+ , 87 (32) $\text{CF}_2^{37}\text{Cl}^+$.

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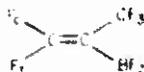
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85 (100) $\text{CF}_2^{13}\text{Cl}^+$, 69 (20) CF_3^+ , 68 (2.4) $\text{CF}^{37}\text{Cl}^+$, 66 (5.3) $\text{CF}^{35}\text{Cl}^+$, 52 (28) NF_2^+ , 50 (23) CF_2^+ , 49 (1.3) $\text{CCl}^{37}\text{Cl}^+$, 47 (4.2) $\text{CCl}^{35}\text{Cl}^+$, 47 (18.9) CFO^+ , 37 (1.1) $^{13}\text{Cl}^+$, 35 (3.4) $^{35}\text{Cl}^+$, 33 (7.7) NF^+ , 31 (21.2) CF^+ , 30 (23) NO^+ , 19 (1.2) F^+ , 16 (0.5) O^+ ; ^{19}F NMR (neat) (liquid 29 °C) ϕ_A (tr tr) -75.2, ϕ_B (tr tr) -93.7, ϕ_C (br tr) 126.0 ($J_{AB} = 2.3$, $J_{AC} = 0.95$, $J_{BC} = 3.15$, $J_{BC} \sim 100$ Hz); IR 1339 (m), 1286 (vw), 1241 (m), 1200 (vs), 1185 (vs), 1179 (vs), 1160 (sh), 1058 (vw), 1033 (m), 975 (vs), 909 (m), 898 (sh), 845 (vs), 802 (w), 784 (vw), 768 (vw), 720 (vw), 702 (vw), 680 (vw), 656 (w), 615 (vw), 558 (vw), 480 (vww) cm^{-1} .

$\text{BrCF}_2\text{C}(\text{CF}_2)_2\text{ONF}_2$: mol wt found 245; mol wt calcd 248; mass spectrum (70 eV) [m/e (intensity)] 197 (4.6) $\text{C}_2\text{F}_5^{81}\text{BrO}^+$, 195 (4.6) $\text{C}_2\text{F}_5^{79}\text{BrO}^+$, 181 (66) $\text{C}_2\text{F}_5^{81}\text{Br}^+$, 179 (66) $\text{C}_2\text{F}_5^{79}\text{Br}^+$, 162 (2.4) $\text{C}_2\text{F}_5^{81}\text{Br}^+$, 160 (2.4) $\text{C}_2\text{F}_5^{79}\text{Br}^+$, 131 (100) $\text{CF}_2^{81}\text{Br}^+$, 129 (100) $\text{CF}_2^{79}\text{Br}^+$, 119 (83) C_2F_3^+ , 112 (7.8) C^{81}Br^+ , 110 (7.8) $\text{CF}^{79}\text{Br}^+$, 100 (28) C_2F_2^+ , 93 (4.2) C^{81}Br^+ , 91 (4.2) C^{79}Br^+ , 81 (38) $^{81}\text{Br}^+$, 79 (38) $^{79}\text{Br}^+$, 69 (59) CF_3^+ , 66 (1.5) CF_2O^+ , 52 (25) NF_2^+ , 50 (46) CF_2^+ , 47 (18) CFO^+ , 33 (10) NF^+ , 31 (60) CF^+ , 30 (47) NO^+ , 19 (2.4) F^+ , 16 (8.0) O^+ ; ^{19}F NMR (neat liquid, -20 °C, trans rotamer) ϕ_A (tr tr) -70.5, ϕ_B (quint) -91.9, ϕ_C (br tr) 126 ($J_{AB} = 3.2$, $J_{AC} = 1.0$, $J_{BC} = 3.2$ Hz); IR 1330 (m), 1249 (m), 1208 (vs), 1183 (vs), 1126 (s), 1032 (m), 948 (vs), 908 (mw), 882 (w), 848 (s), 825 (sh), 782 (mw), 777 (mw), 751 (w), 672 (w), 650 (w), 635 (vw), 602 (vw), 550 (vw), 477 (vww) cm^{-1} .

Synthesis of $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$. Tetrafluoroallene (5.1 mmol) and BF_3 (5.1 mmol) were combined at -196 °C in a Pyrex ampule. The mixture was allowed to warm slowly to ambient temperature, then cooled again to -196 °C, and warmed as before. The volatile products were separated by fractional condensation with $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ (3.6 mmol) stopping in a -112 °C trap. The other reaction products were a trace of SiF_4 , oily tetrafluoroallene polymer, and unreacted BF_3 .

$\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$: colorless liquid and gas; mol wt found 179; mol wt calcd 179.8; approximate bp 12 °C; ^{19}F NMR (neat liquid, 25 °C) $\phi(\text{CF}_2)$ (broad unresolved multiplet) -47.6, $\phi(\text{CF}_3)$ (d quart)



-57.3, $\phi(\text{CF}_3)$ (d d) -59.9, $\phi(\text{BF}_2)$ (br s) -82.2; area ratios t:1:3:2 ($J_{\text{CF}_2\text{CF}_2} = 22.6$, $J_{\text{CF}_2\text{CF}_3} = 12.0$, $J_{\text{CF}_2\text{BF}_2} = 39.0$ Hz). Vibration spectra: IR (gas) 1769 (mw), 1714 (vs), 1689 (sh), 1469 (m), 1426 (vs), 1392 (vs), 1323 (m), 1290 (mw), 1260 (sh), 1170 (vs), 1129 (mw), 1081 (vw), 1043 (s), 998 (ms), 969 (mw), 875 (vw), 744 (mw), 736 (m), 708 (vw), 650 (vw), 642 (mw), 608 (m), 581 (w), 539 (mw), 434 (w), 392 (w) cm^{-1} ; Raman (liquid, -80 °C) 1770 (0.3) p, 1713 (1.6) p, 1689 (sh), 1465 (0+), 1415 (0.1), 1382 (0.1), 1323 (0.7) p, 1298 (0.4), 1175 (0.1), 1135 (0.1), 992 (0.3) p, 964 (0.2) p, 873 (1.5) p, 742 (10) p, 730 (1.8) dp, 708 (0.5) p, 650 (2.4) p, 637 (1.7) dp, 608 (0.8) p, 580 (0.2) dp, 538 (0.6) p, 434 (0.2) dp, 399 (2.1), 376 (4.5) p, 331 (1.4) p, 193 (0.2) dp, 169 (1.5) dp, 150 (0.2) dp, 129 (0.2) cm^{-1} . The mass spectrum showed parent at m/e 180 ($\text{C}_2^{11}\text{BF}_2^+$) and 179 ($\text{C}_2^{10}\text{BF}_2^+$) and parent minus F at m/e 161 and 160. Hydrolysis of $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ gave $\text{CF}_2=\text{CHCF}_3 + (\text{HOBF}_2)$.

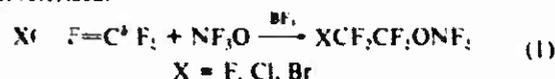
Reaction of $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ with NF_3O . Trifluoramine oxide (1.8 mmol) and $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ (0.45 mmol) were combined at -196 °C in a Pyrex reactor and allowed to warm slowly to room temp. This cooling-warming was repeated several times. The volatile materials were separated by fractional condensation and consisted of BF_3 (0.45 mmol), unreacted NF_3O (1.3 mmol), and $\text{CF}_3\text{COCF}_2\text{NF}_2$ (0.45 mmol). This ketone stopped in a -112 °C trap and was identified by its infrared, mass, and ^{19}F NMR spectra,⁹ molecular weight, and its hydrolysis reaction, which yielded the hydrate $\text{CF}_3\text{C}(\text{OH})(\text{CF}_2)\text{NF}_2$.

The compound $\text{CF}_3\text{COCF}_2\text{NF}_2$ was also directly obtained by co-condensing equimolar amounts of NF_3O , BF_3 , and $\text{CF}_2=\text{C}=\text{CF}_2$ at -196 °C in a Pyrex ampule and allowing the mixture to warm up slowly to ambient temperature. This warm-up procedure was repeated twice to ensure complete reaction. The reaction products were separated by fractional condensation with the -112 °C trap containing $\text{CF}_3\text{COCF}_2\text{NF}_2$ in 25% yield. $\text{CF}_3\text{COCF}_2\text{NF}_2$: ^{19}F NMR (CFCl₃, -55 °C) ϕ_A (tr tr) -76.2, ϕ_B (quart tr) -109.9, ϕ_C (br s) 18.0 ($J_{AB} = 6.4$, $J_{AC} = 2.0$, $J_{BC} = 3.1$ Hz), area ratios A:B:C = 3:2:2.

Results and Discussion

Syntheses of -ONF₂-Substituted Perhalocarbons and Mechanism of the NF_3O Addition. Shortly after the discovery

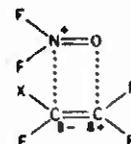
of NF_3O in 1961,^{2,3} studies were begun at Rocketdyne to add NF_3O across olefinic double bonds. At ambient temperature neat NF_3O was unreactive toward olefins such as $\text{CF}_2=\text{CF}_2$ or $\text{CH}_2=\text{CH}_2$. Furthermore, UV irradiation of mixtures of NF_3O with either $\text{CF}_2=\text{CF}_2$ or $\text{CF}_2=\text{CFCl}$ in Pyrex did not result in any appreciable reaction. Although heating of NF_3O with C_2F_4 or $\text{C}_2\text{F}_3\text{Cl}$ to 150 °C resulted in reaction, the principal products (C_2F_6 , C_4F_{10} , CF_3COF , $\text{C}_2\text{F}_3\text{Cl}$, etc.) arose from fluorination of the olefins and were not the desired RONF_2 addition compounds. However, Lewis acids catalyzed the addition of NF_3O to olefinic double bonds. The most effective Lewis acid was BF_3 , but the reaction was generally limited to perhalogenated olefins. Low temperatures were necessary with NF_3O being added at -196 °C to a mixture of BF_3 and the olefin, which had been premixed at -78 °C. The ternary mixture was allowed to warm slowly from -196 to -78 °C and sometimes to ambient temperature. Although other Lewis acids such as PF_5 , AsF_5 , or SbF_5 in the presence or absence of solvents such as anhydrous HF or CF_3COCF_3 were also used, the above described low-temperature BF_3 -catalyzed reaction gave generally the best and most reproducible results. With use of this method, the following reactions were carried out and their reaction products well characterized.



For X = F the yields of the -ONF₂ adduct were as high as 70% but decreased with increasing atomic weight of X, with the competitive fluorination reaction to $\text{C}_2\text{F}_5\text{X}$ becoming dominant. For X being iodine, the yield of $\text{ICF}_2\text{CF}_2\text{ONF}_2$ became almost zero.

Only one isomer was obtained for all reactions and, surprisingly, corresponded to an anti-Markownikoff-type addition; i.e., the ONF_2 group was added to the positively polarized carbon atom of the substrate. The observation of only one isomer and the fact that free-radical conditions such as UV irradiation and heat did not produce significant amounts of RONF_2 adducts suggest a polar mechanism.

Since NF_3O is known¹⁰ to form with Lewis acids such as BF_3 ionic adducts containing the NF_3O^+ cation and since the positive charge in NF_3O^+ resides on the nitrogen atom, the simplest polar mechanism would involve a π - π bond interaction between the N=O bond of NF_3O^+ and the C=C bond of the olefin:



Although such an intermediate could conveniently account for an attack of the positively polarized carbon by oxygen, the following arguments can be raised against this mechanism: (i) the above π - π mechanism is analogous to the reaction of two ground-state ethylene molecules to ground-state cyclobutane, which is symmetry forbidden;¹¹ (ii) also, the π - π mechanism cannot account for the products observed in the reaction of $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ with NF_3O (see below); (iii) the Lewis acid catalyzed addition of NF_3O to the olefin appears to require reaction temperatures at which the NF_3O^+ salt has some, albeit small, dissociation pressure. If a preformed stable NF_3O^+ salt is used, fluorination is obtained instead of sub-

(9) Lustig, M.; Ruff, J. K. *Inorg. Chem.* 1965, 4, 1441.

(10) Christie, K. O.; Mays, W. *Inorg. Chem.* 1969, 8, 1253. Wamser, C. A.; Fox, W. B.; Sukornick, B.; Holmes, J. R.; Stewart, B. B.; Juurik, R.; Vanderkooi, N.; Gould, D. *Ibid.* 1969, 8, 1249.

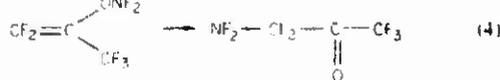
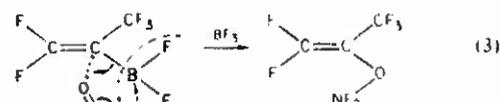
(11) Woodward, R. B.; Hoffmann, R. In "The Conservation of Orbital Symmetry"; Verlag Chemie, GmbH: Weinheim/Bergstrasse, West Germany, 1971.

stitution; (iv) premixing of the Lewis acid with the olefin enhances the yield of RONF_2 . Most of these arguments suggest that the first step in the NF_3O addition to olefins is the interaction of the olefin with the Lewis acid. Examination of the $\text{BF}_3\text{-C}_2\text{F}_4$ system at -112°C showed a positive interaction between the two compounds; i.e., the vapor pressure was significantly lower than that expected from Raoult's law, but no stable adduct was formed. The lack of a stable $\text{C}_2\text{F}_4\cdot\text{BF}_3$ adduct is not surprising since $-\text{BF}_2$ -substituted saturated fluorocarbons are very unstable due to the great facility for intramolecular migration of a fluorine atom from an α - or β -carbon atom to boron followed by BF_3 elimination.¹² This facility of BF_3 elimination can be strongly decreased by incorporation of an α -perfluorovinyl group. Thus $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_2$ is known⁸ to be stable, and another stable compound $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ was prepared for the first time during this study from tetrafluoroallene and BF_3 (eq 2). The direction of this



addition agrees with that expected from the known¹³ polarity of the bonds in tetrafluoroallene and a normal polar addition of BF_3 . The observation of only the BF_3 monoadduct is not surprising, since the addition of a second BF_3 molecule would result in a saturated $-\text{BF}_2$ -substituted fluorocarbon, which would be prone to undergo the above mentioned BF_3 elimination¹² with re-formation of $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$.

The availability of $\text{CF}_2=\text{C}=\text{CF}_2$ and of its BF_3 adduct allowed us to test the hypothesis that a BF_3 adduct is an intermediate in the BF_3 -catalyzed addition reaction of NF_3O to $\text{CF}_2=\text{C}=\text{CF}_2$, the intermediate is $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$, then the reaction of $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ with NF_3O should result in the same final product. Indeed this was found to be the case. In both reactions, $\text{CF}_3\text{COCF}_2\text{NF}_2$ was the only $-\text{NF}_2$ -containing product. For the $\text{CF}_2=\text{C}=\text{CF}_2 + \text{BF}_3 + \text{NF}_3\text{O}$ reaction its yield was 25%, whereas for the $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3 + \text{NF}_3\text{O}$ reaction its yield was essentially quantitative. The fact that $\text{CF}_3\text{COCF}_2\text{NF}_2$ was the only product and that no evidence for an $-\text{ONF}_2$ -substituted compound was observed can be readily rationalized by the following sequence. Reaction 2 is followed by a Lewis acid-Lewis base interaction between $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3$ and NF_3O . The formed adduct can then undergo BF_3 elimination (eq 3) to form the vinyl- ONF_2 compound, followed by a quasi keto-enol tautomeric rearrangement (eq 4) to give the observed final product, a difluoroamino ketone. The fact that in the BF_3 -catalyzed ad-

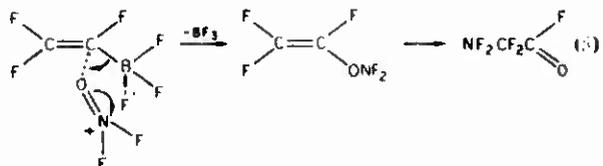


dition of NF_3O to $\text{CF}_2=\text{C}=\text{CF}_2$ the yield of $\text{NF}_2\text{CF}_2\text{C}(\text{O})\text{CF}_3$ was only 25% compared to 100% for the $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3 + \text{NF}_3\text{O}$ reaction can be ascribed to the low (60%) yield observed for reaction 2 and the ease of polymerization of tetrafluoroallene.⁷

(12) Lappert, M. F. In "The Chemistry of Boron and its Compounds"; Muehler, E. L., Ed.; Wiley: New York, 1967; p 461.

(13) Banks, R. E.; Hazeldine, R. N.; Taylor, D. R. *Proc. Chem. Soc., London* 1964, 121.

The above reactions of tetrafluoroallene lead to a better understanding of the observed reactions between $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_2$ and NF_3O . Two $-\text{NF}_2$ -containing products, $\text{CF}_3\text{CF}_2\text{ONF}_2$ and $\text{NF}_2\text{CF}_2\text{C}(\text{O})\text{CF}_3$, were observed for this reaction. The formation of the latter compound is analogous to the tetrafluoroallene reactions

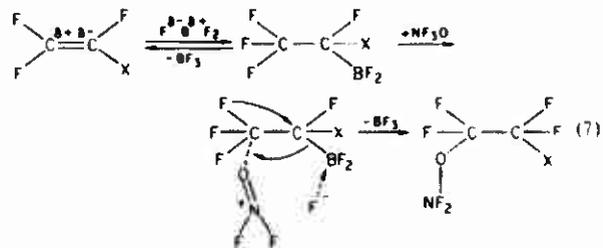


The formation of $\text{CF}_3\text{CF}_2\text{ONF}_2$ is ascribed to the competitive fluorination reaction (6), followed by reaction 1, the BF_3 -



catalyzed addition of NF_3O to CF_2CF_2 .

The formation of an intermediate α -halo difluoroborane can also explain the unexpected "anti-Markownikoff-type" addition of NF_3O to the unsymmetric perhalogenated ethylene (eq 1). The observed reaction products can be rationalized by a mechanism assuming the normal polar addition of BF_3 to the double bond, followed by the interaction of the Lewis base NF_3O with the Lewis acid $\text{R}-\text{BF}_2$, followed by BF_3 elimination, a fluoride migration from the β - to the α -carbon atom, and formation of the $\text{C}-\text{ONF}_2$ bond (eq 7). This



mechanism is analogous to that (eq 3 and 5) outlined for the perfluorovinylboranes, except for the $-\text{ONF}_2$ substitution occurring on the β -carbon due to the facile migration of fluorine from the β -carbon to the α -carbon in these saturated fluoroalkylboranes. The $-\text{ONF}_2$ substitution on the β -carbon in saturated fluoroalkylboranes vs. α -carbon substitution in vinylboranes may also be favored by the decrease in the $\text{C}-\text{C}-\text{B}$ bond angle upon going from an sp^2 -hybridized vinylborane to an sp^3 -hybridized alkylborane.

Attempts to extend the BF_3 -catalyzed NF_3O addition to hydrogen-containing olefins such as $\text{CH}=\text{CH}_2$, $\text{CF}_2=\text{CHF}_2$, and $\text{CF}_2=\text{CFH}$ were unsuccessful due to both fluorination and polymerization of the substrate. Fluorination of the double bond was also the only reaction observed for $\text{CFCl}=\text{CFCl}$ and $\text{CF}_2=\text{CClCF}_2\text{Cl}$. Similarly, attempts to replace the BF_2 group in CH_2FBF_2 by an ONF_2 group by low-temperature treatment with NF_3O were unsuccessful, resulting in the quantitative fluorination (8).



The low-temperature BF_3 -catalyzed addition of NF_3O to the perfluorinated acetylene $\text{CF}_3\text{C}=\text{CCF}_3$ was also studied, but no reaction was observed under the given conditions. With perfluorobutadiene a smooth reaction occurred, but resulted only in fluorination to perfluorobutene-2.

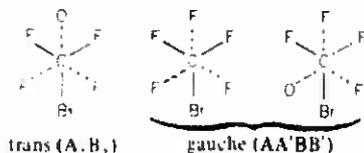
Attempts were unsuccessful to verify the intermediates postulated in eq 3-5 and 7 by low-temperature ^{19}F NMR spectroscopy. For the $\text{CF}_2=\text{C}(\text{BF}_2)\text{CF}_3-\text{NF}_3\text{O}$ system, when kept at -80°C or below, only the final products $\text{NF}_2\text{CF}_2\text{C}-$

(O)CF₃ and BF₃ were observed. For CF₂=CF₂ and BF₃ in CFC₁₂ solution, no interaction was observable at temperatures as low as -120 °C.

Properties of the *N,N*-Difluoro-*O*-perhaloalkylhydroxylamines. All the XCF₂CF₂ONF₂-type (X = F, Cl, Br) compounds prepared in this study are colorless gases or liquids, which are stable at ambient temperature. The thermal stability of the compounds is surprisingly high. For example, C₂F₅O-NF₂, when heated over CsF in a Pyrex ampoule to 93 °C for 17 h, showed no decomposition. In stainless steel, heating to 325 °C for several hours was required to observe degradation to C₂F₆ and NO. In their chemical properties these R-ONF₂ compounds are similar to NF₃. Thus, C₂F₅ONF₂ is not reduced by HI and is not hydrolyzed by concentrated aqueous alkali solutions at 50 °C. Fluorination of C₂F₅ONF₂ with F₂ at 150 °C produced C₂F₆, but no evidence for NF₃O or the unknown and probably unstable FONF₂ was obtained.

The lack of NF₃O formation in this fluorination reaction supports the spectroscopic evidence that the ONF₂ group in these RONF₂ compounds is bonded to the carbon atom through an oxygen and not a nitrogen atom.

The new RONF₂ compounds prepared in this study were thoroughly characterized by spectroscopic techniques, and the observed data are listed in the Experimental Section. ¹⁹F NMR data were particularly useful to demonstrate the presence of the -ONF₂ group and to show that, for the unsymmetric perhaloethylenes, XCF₂CF₂ONF₂ was the only isomer formed. It should be mentioned that for BrCF₂CF₂ONF₂, the ¹⁹F NMR spectra were strongly temperature dependent, indicating the presence of different rotamers due to hindered rotation caused by the bulky bromine ligand. The BrCF₂CF₂ONF₂ molecule is expected to exist as three different rotamers, one trans and two equally probable gauche forms, which could be sterically less favored.



At 30 °C, the two CF₂ group signals consisted of broad (~15-Hz half-width) unresolved lines. At 20 °C, the two lines separated into two signals each, a resolved lower field signal for the trans isomer and a poorly resolved signal of similar intensity at slightly higher field attributed to the two gauche isomers. At -20 °C the relative intensity and resolution of the trans signals were significantly increased. At -50 °C, the resolution of the trans signal decreased again and the frequency separation between the trans and the gauche signals increased.

Although only the XCF₂CF₂ONF₂ isomers were present, the mass spectra generally exhibited CF₃⁺ ions of medium intensity. This is not unusual for compounds of this type and is readily explainable by ion recombination in the mass spectrometer.

The vibrational spectra are listed in the Experimental Section. The assignments for the CONF₂ group are straightforward and can be made by comparison with those previously discussed for CF₃ONF₂.⁵ In addition to the characteristic⁵ CONF₂ stretching modes in the 1050-850-cm⁻¹ region and the CF₂ stretching modes in the 1300-1100-cm⁻¹ region, the spectra exhibit a medium intense infrared and weak Raman band at about 1400 cm⁻¹, characteristic for the C-C stretching mode.

Properties of CF₂=C(BF₂)CF₃. This new vinyldifluoroborane is a colorless liquid and gas and is stable at ambient temperature. In addition to its spectroscopic identification (see Experimental Section), the compound was identified by its hydrolysis reaction (9), yielding CF₂=CHCF₃.¹⁴ The vibrational spectra of CF₂=C(BF₂)CF₃ show bands in the regions expected for the stretching modes of the C=C (~1710 cm⁻¹), BF₂ (~1450 and 1290 cm⁻¹),¹⁵ and F₂C=CF (~1390, 1177, and 1040 cm⁻¹)¹⁶ groups. However, these assignments are tentative, and a definitive assignment will require a more detailed study.

Conclusion. The Lewis acid catalyzed addition of NF₃O to olefins provides a useful method for the synthesis of -ONF₂-substituted halocarbons, provided the substrates do not contain hydrogen and are highly fluorinated. Heavy halogens such as iodine or bromine also appear to be detrimental to the yield of R₂ONF₂. The only isomer observed for the addition of NF₃O to XCF=CF₂ is XCF₂CF₂ONF₂. This apparent anti-Markownikoff-type addition is explainable by the normal polar addition of the Lewis acid to the olefins followed by appropriate substitution and elimination reactions. The intermediate formation of the Lewis acid-olefin adduct was demonstrated for CF₂=C=CF₂. The reactions of NF₃O with vinyldifluoroboranes such as CF₂=CFBF₂ and CF₂=C(BF₂)CF₃ indicate that -ONF₂-substituted vinyl compounds are unstable and easily undergo a keto-enol-type tautomeric rearrangement to the corresponding difluoramino ketones.

Acknowledgment. The authors are grateful to M. Warner for his help with some of the experiments and to Drs. C. J. Schack, W. W. Wilson, and L. R. Grant for helpful discussions. This work was financially supported by the Air Force, the Office of Naval Research, and the Army Research Office.

Registry No. NF₃O, 13847-65-9; C₂F₄, 116-14-3; C₂F₂Cl₂, 79-38-9; C₂F₃Br, 598-73-2; CF₃CF₂ONF₂, 24687-10-3; ClCF₂CF₂ONF₂, 24684-27-3; BrCF₂CF₂ONF₂, 24684-28-4; CF₂=C(BF₂)CF₃, 84238-04-0; CF₃COCF₂NF₂, 4188-38-9; CF₃C(OH)CF₂NF₂, 84238-05-1; BF₃, 7637-07-2; tetrafluoroallene, 461-68-7

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 (15) Parsons, T. D.; Self, J. M.; Schaad, L. H. *J. Am. Chem. Soc.* **1967**, *89*, 3446.
 (16) Shimanouchi, T. *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)* **1972**, NSRDS-NBS 39, 75-83.

APPENDIX R

Contribution from the Institut für Physikalische und Theoretische
Chemie der Universität Tübingen, 7400 Tübingen, West Germany,
and Rocketdyne, A Division of Rockwell International
Corporation, Canoga Park, California 91304

THE GAS PHASE STRUCTURE OF AZIDOTRIFLUOROMETHANE. AN ELECTRON DIFFRACTION, MICROWAVE SPECTROSCOPY AND NORMAL COORDINATE ANALYSIS

Karl O. Christe,^{1a} Dines Christen,^{1b} Heinz Oberhammer,^{*1b}
and Carl J. Schack^{1a}

ABSTRACT

The geometric structure of azidotrifluoromethane has been obtained by a combined analysis of electron diffraction intensities and ground state rotational constants derived from the microwave spectrum.

The following parameters were obtained (r_{av} -values in Å and deg. with 2σ uncertainties in units of the last decimal): C-F = 1.328(2), C-N_α = 1.425(5), N_α-N_β = 1.252(5), N_β-N_ω = 1.118(3), ∠CN_αN_β = 112.4(2), ∠N_αN_βN_ω = 169.6(34) and ∠FCF = 108.7(2). The CF₃ group is in the staggered position with respect to the N₃ group and tilted away from it by 5.8(4)°.

INTRODUCTION

Structural data on covalent azides are rare due to the explosive nature^(2,3) and handling difficulties encountered with these compounds. One of the more stable covalent azides is CF₃N₃, a

compound originally prepared by Makarov and coworkers^(4,5) and recently studied in more detail by two of us⁽⁶⁾. Although the closely related CH_3N_3 molecule has previously been studied by both electron diffraction⁽⁷⁾ and microwave spectroscopy⁽⁸⁾, the available data were insufficient to determine whether the N_3 group is linear, and to obtain a reliable value for the tilt angle of the methyl group. Furthermore, a comparison of the structures of CH_3N_3 and CF_3N_3 was expected to contribute to our knowledge of how the substitution of a CH_3 group by a CF_3 group influences the structure of the rest of the molecule⁽⁹⁾.

EXPERIMENTAL SECTION

Synthesis and Handling of CF_3N_3 : The sample of CF_3N_3 was prepared as previously described⁽⁶⁾. Prior to the electron diffraction experiments, a small amount of N_2 formed by decomposition of some CF_3N_3 was pumped off at -196°C . The only other decomposition products were nonvolatile and therefore did not interfere with the measurements.

Electron Diffraction. The scattering intensities were recorded with the Balzers gas diffractograph at two camera distances (25 and 50 cm) on Kodak electron image plates (13 x 18 cm). The accelerating voltage was about 60 kV. The sample was cooled to -80°C and the nozzle temperature was 15°C . The camera pressure never exceeded 2.10^{-5} torr during the experiment. Exposure time was 6-9 sec for the long, and 15-25 sec for the short camera distance. The electron wavelength was calibrated with ZnO diffraction patterns. Two plates for each camera distance were analyzed by the usual procedures. Background scattering recorded without gas was subtracted from the 25 cm data. Averaged molecular intensities for both camera distances

($s = 1.4 - 17$ and $8 - 35\text{\AA}^{-1}$) are presented in Fig. 1 and numerical values for the total scattering intensities are available as supplementary data⁽¹⁰⁾.

Microwave Spectroscopy. The microwave spectrum was recorded at temperatures between -70° and -40°C at pressures around 10 mtorr, and at frequencies between 7 and 25 GHz (X- and K-Band) using a standard 100 kHz Stark spectrometer.

CF_3N_3 was initially flowed through the cell, but since the sample proved to be very stable, it was only changed at hours' intervals.

An initial broad band sweep in K-band, applying a 0-20 V ramp voltage at the external sweep connector of the Marconi sweeper, immediately revealed the μ_a R-branch heads typical of a near prolate rotor, and thus restricted the ranges to be searched.

STRUCTURE ANALYSIS

A preliminary analysis of the radial distribution function (Fig. 2) clearly demonstrates that the CF_3 group is staggered with respect to the N_3 chain. Model calculations for the eclipsed configuration result in very bad agreement with the experimental data in the range $r > 2.5\text{\AA}$ (see Fig. 2). The radial distribution function for the eclipsed configuration was calculated with the final geometric parameters derived for the staggered conformation. Increase of the $\text{CN}_\alpha\text{N}_\beta$ angle to about 130° improved the fit for the peak at 3.3\AA but the disagreement for the peaks around 2.7 and 4.5\AA remained. Therefore, in the following analysis the CF_3 group was constrained to the staggered position. However, small torsional deviations ($<10^\circ$) from this position cannot definitely be excluded.

In the least squares analysis a diagonal weight matrix was applied to the intensities and scattering amplitudes, and the phases of J. Haase⁽¹¹⁾ were used. The spectroscopic corrections, Δr (Table 1), were incorporated in the refinement. For torsional vibrations, the concept of perpendicular (rectilinear) amplitudes results in unrealistically large contributions to these corrections for torsion independent distances (C-F, F..F and N..F). Therefore, contributions from the CF_3 torsion, which is a large amplitude vibration, were neglected for torsion independent distances⁽¹²⁾. Assuming local C_{3v} symmetry for the CF_3 group with a possible tilt angle between the C_3 axis and the C-N bond, eight geometric parameters (including the $N_\alpha N_\beta N_\omega$ angle) are required for the determination of the structure of CF_3N_3 . These parameters were refined simultaneously with six vibrational amplitudes (see Table 1). The remaining vibrational amplitudes which either cause high correlations or are badly determined in the electron diffraction experiment, were constrained to the spectroscopic values, calculated from the force field. This is justified, since the refined amplitudes agree very well with the spectroscopic values. The results from the electron diffraction analysis is included in Tables 1 and 2.

In the final stage of the analysis, structural parameters were fitted to electron diffraction intensities as well as rotational constants⁽¹³⁾. The relative weight between electron diffraction and microwave data was adjusted until all rotational constants were reproduced within their estimated uncertainties. The geometric parameters derived from the combined analysis agree within their error limits with the results derived using the electron diffraction intensities alone.

The results demonstrate the usefulness of the rotational constants for the reduction of the uncertainties in the $CN_{\alpha}N_{\beta}$ and the CF_3 tilt angle, which are very sensitive to the asymmetry or, in other words, to B_2-C_2 .

NORMAL COORDINATE ANALYSIS

A force field, required for the joint analysis of microwave and electron diffraction data, was derived from the 14 fundamental frequencies determined in a previous study⁽⁶⁾, the torsional frequency, derived from relative intensity measurements of rotational transitions of the excited torsional states, and the centrifugal distortion constant D_{JK} , determined from the rotational spectrum of the ground state.

Valence force constants were refined with the program NCA⁽¹⁴⁾ based on mass weighted cartesian coordinates. The modified harmonic force field (Table 3) looks reasonable, but is, of course, underdetermined.

The mean deviation between measured and calculated frequencies is $\overline{\Delta\nu} = 4 \text{ cm}^{-1}$.

ROTATIONAL SPECTRUM

The assignment of the band heads in the K-band region to the J: 4+5 (19.62 GHz) and J: 5+6 (23.54 GHz) transitions was straightforward since these band heads appeared very close to the frequencies predicted by the preliminary electron diffraction model ($B+C = 3.94$ GHz), but the high resolution recordings do not openly display the characteristic pattern of a near prolate ($K = -0.989$) rotor (see

Fig. 3). The deviations arise from excited vibrational states - especially the low lying torsional states - as will be discussed below. The frequencies of all measured transitions and the ensuing rotational constants have been collected in Table 4. The $K_{-1} = 1$ lines stand out quite clearly, though, and recording at different Stark fields permitted the identification of $K_{-1} = 0$ lines which appear only at high fields. Subsequently higher K_{-1} lines were identified, but because many of them are subject to heavy overlapping, some of them could only be measured using a radio frequency/microwave double resonance technique (RFMWDR) as described below.

The lowest J-lines show signs of quadrupole hyperfine structure, but no attempt was made to resolve and analyze these splittings. Stark measurements on different M-components of the transitions $4_{14} \rightarrow 5_{15}$, $4_{13} \rightarrow 5_{14} \rightarrow 5_{15} \rightarrow 6_{16}$ and $5_{14} \rightarrow 6_{15}$ (calibrating the field against the OCS shifts and using Muentzer's value for its dipole moment⁽¹⁵⁾) yielded a dipole moment in the a-direction of $\mu_a = 1.15(10)$ D.

To understand the microwave spectrum in detail, especially the many lines between the two $K_{-1} = 1$ transitions, it is necessary to consider the possible molecular vibrations. In an earlier study⁽⁶⁾, the vibrational spectra were investigated and 14 of the 15 fundamentals identified. The missing one, the torsion of the CF_3 group, was predicted to lie below 90 cm^{-1} , but could not experimentally be observed.

Fig. 4 shows the $5_{15} \rightarrow 6_{16}$ transition in a highly amplified recording. From the characteristic Stark patterns it is possible to identify all of the obvious lines with the same transition, only in different vibrational states. The very intense progression to higher frequency must be assigned to the torsion, and relative intensity

measurements using the Wilson-Nesbitt method⁽¹⁶⁾ yield an energy above the ground state of $47(3) \text{ cm}^{-1}$ for the first excited torsional state and thus for the torsional frequency.

To test the reliability of this method, the energy of excited states of other vibrations were determined and compared to the fundamental frequency determined from the IR and Raman spectra (in parenthesis): ν_{10} : 177 (179), ν_9 : 409 (402). ν_{14} : 459 (450), $\nu_{10} + \nu_{15}$: 221 cm^{-1} comprised of ν_{10} : 174 and ν_{15} : 47 cm^{-1} .

The reliability of the method obviously decreases with increasing frequency (decreasing intensity) and the method fails for transitions falling between the two $K_{-1} = 1$ lines because of serious overlapping of lines and Stark components.

Examination of the $5_{14} + 6_{15}$ transitions to determine their relative intensities revealed that the ν_{15} progression extends toward lower frequencies, and thus the frequency difference between the $K_{-1} = 1$ lines decreases with increasing excitation of ν_{15} . This effect is not observed with the other excited states (notably ν_{10}). The frequency difference between the $K_{-1} = 1$ lines directly determines B-C, and thus the observed trend indicates an increase in symmetry in the ν_{15} progression.

In order to explain this trend, it must be noted that a structural model having the C_3 axis of the CF_3 group colinear with the C-N bond, only produces a B-C value of 1-2 MHz. To reproduce the observed B-C value for the ground state (20.5 MHz) it is necessary to assume a tilt angle of $\sim 5^\circ$.

Consequently, one could propose that the effect of higher torsional excitation is the removal of the tilt of the CF_3 group. In that case one would expect higher torsional states to have B-C values between 1 and 2 MHz.

On the other hand, if one realizes that most of the molecular mass is concentrated in the trifluoro methyl group, it is possible to visualize the light "frame" rotating about the heavy "top" and higher excitation would lead to an effective symmetric top molecule with the excited energy levels lying well above the barrier to the torsional motion. In that case, however, as the energy levels approach the top of the barrier, tunnelling through the threefold barrier would cause the rotational lines to split into nondegenerate A and doubly degenerate E components.

Unfortunately, this splitting is expected to take place at the frequency where the center of the rotational transitions of the excited torsional states have "turned back" (see Fig. 3) into the upper $K_{-1} = 1$ lines of the lower torsional states, and thus it is impossible to clearly distinguish the weaker lines of the higher excited states.

It was hoped that double resonance experiments (RFMWDR) could circumvent this problem⁽¹⁷⁾ RFMWDR techniques were used to identify and measure the $J: 5 \rightarrow 6$, $K_{-1} = 2$ transitions of the molecule in its ground as well as first excited torsional state, using a pump frequency of 3.1 MHz, which happens to be the asymmetry splitting of the $J=5$ levels for the ground state and the splitting of the $J=6$ levels of the first excited torsional state. Using a pump frequency of 6.15 MHz (the ground state splitting of the $J=6$ levels) only the ground state transitions are observed.

It was also possible to observe the $K_{-1} = 1$ lines in RFMWDR ($J: 5+6$) for the ground ($\nu_p = 307.0$ MHz), the 1st excited torsional ($\nu_p = 218.4$ MHz), the 2nd ($\nu_p = 128.7$ MHz) and barely the 3rd excited torsional state ($\nu_p = 36.1$ MHz).

The weakness of the 3rd excited torsional state transitions extinguished the hope of finding the $\nu_{15} = 4$ lines using the DR-technique, which would otherwise have overcome the problem of overlapping.

Fortunately, however, the $J: 1+2$ transitions around 7.9 GHz (Fig. 5), modulated at a Stark field of 800 V/cm only show the $K_{-1} = 0$ transitions, and thus provide a somewhat clearer picture. It looks like the $\nu_{15} = 3$ transition is somewhat broadened compared to the $\nu_{15} = 0, 1$ and 2 transitions, and the $\nu_{15} = 4$ transition is possibly split into two components, indicating a torsional level approaching the top of the barrier.

The assumption of a purely sinusoidal potential allows a determination of the barrier heights from the torsional force constant, known from the normal coordinate analysis

$$\text{f.c.} = \frac{\partial^2 V}{\partial \alpha^2} = \frac{\partial^2}{\partial \alpha^2} \left(\frac{V_3}{2} (1 - \cos 3\alpha) \right) \text{ at } \alpha = 0 = \frac{9V_3}{2}$$

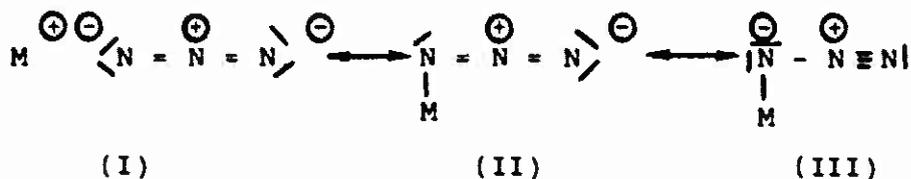
$$\text{or: } 0.03 \text{ m dyn } \text{\AA}^2 = 4.35 \text{ kcal/mol} = \frac{9V_3}{2}; V_3 = 0.97 \text{ kcal/mol.}$$

Thus, the $\nu_{15} = 4$ state with an energy of .675 kcal is in fact quite close to the top of the barrier, especially since the addition of a few per cent V_6 potential would somewhat lower the value of V_3 . It seems, although the evidence is sparse, that the decrease in B-C on excitation of ν_{15} is due to the hindered internal rotation of the trifluoro methyl group.

DISCUSSION

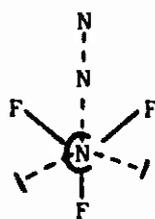
The most significant features of the CF_3N_3 structure are the bond lengths, the nonlinearity of the N_3 group, and the torsion and tilt angle of the CF_3 group with respect to the N_3 group. These features are discussed in the following paragraphs.

Bond Lengths. The above results clearly demonstrate that in CF_3N_3 the $N_\beta-N_w$ bond is significantly shorter than the $N_\beta-N_\alpha$ bond. This can be attributed to the electron withdrawing effect of the CF_3 group. A comparison of the MN_3 series ($M =$ alkali metal, $(CH_3)_3Si$, H , Cl , CF_3) shows that if M is of very low electronegativity, as for example in the alkali metals, we have an ionic $M^+N_3^-$ structure (I) with two degenerate N-N bonds of $1.16\overset{\circ}{\text{A}}$ each. With increasing electronegativity of M , the M-N bond becomes more covalent and the contribution from the resonance structure (III) increases, due to the electron withdrawing effect of M . This causes an increase in the bond length difference between $N_\beta-N_w$ and $N_\beta-N_o$ (see Table 5).

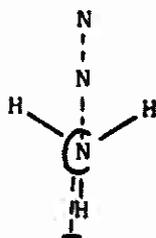


A comparison of the C-N bond lengths in CH_3N_3 and CF_3N_3 also shows the expected effect⁽⁹⁾. Replacement of the CH_3 by the CF_3 group results in bond shortening if the groups are bonded to electronegative atoms or groups. Hence the C-N bond in CF_3N_3 ($1.425\overset{\circ}{\text{A}}$) is significantly shorter than that in CH_3N_3 ($1.468\overset{\circ}{\text{A}}$).

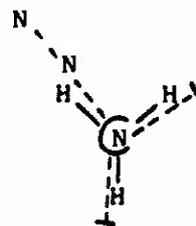
Torsional Angle of the CX₃ Group. In general methyl or trifluoro methyl groups prefer the staggered position with respect to single bonds, but prefer an eclipsed position with respect to double bonds. Representative examples i. the case of C=C double bonds are: CX₃CH=CH₂⁽¹⁸⁾ and trans CX₃CH=CHCX₃^(19,20). Only strong steric repulsions can force CF₃ groups to abandon the eclipsed position, such as in cis CF₃CH=CHCF₃⁽²⁰⁾. Only one example is known for N=N double bonds: trans CX₃N=NCX₃^(20,21,22), where the CX₃ groups again eclipse the N=N double bond and stagger the N lone pair. In CF₃N₃ the CF₃ group occupies a staggered position with respect to the N₃ group as shown by (IV), and this indicates



(IV)



(V)



(VI)

a significant contribution from resonance structure (III). For this structure configuration (IV) minimizes the repulsion between the fluorine free valence electrons and the two sterically active free electron pairs on the N_α atom (indicated by broken lines in (IV)). In contrast to CF₃N₃, the CH₃ group in CH₃N₃ appears to be in an intermediate position between eclipsed and staggered⁽²³⁾, (25±7° from the eclipsed position) which may be explained in the following manner: resonance structure (II) should result in a staggered (V) and resonance structure (III) in an eclipsed (VI) configuration. Since, as discussed above, the bond lengths indicate that structure (II) contributes more strongly to the structure of CH₃N₃ than to that of CF₃N₃, the observation of an

Intermediate torsional angle is not surprising.

Linearity of the N_3 Group and CF_3 Tilt Angle. In CF_3N_3 the N_3 group is slightly (10°) bent away from the CF_3 group, and the CF_3 group is tilted away from the N_3 group by 5.8° . This is readily explained by the repulsion between the fluorine free valence electron pairs and the π bond electron system of the N_3 group. A comparison of these values with those in CH_3N_3 would be most interesting, but unfortunately no experimental values are presently available for CH_3N_3 . It is interesting to note that the angles of the N_3 group found for HN_3 , ClN_3 , NCN_3 , and CF_3N_3 are all very similar. However, it should be kept in mind that most of these values carry rather large uncertainties.

Torsional Effects on the Structure. The present data for the excited torsional states do not allow a determination of the structural changes upon excitation of ν_{15} . It is clear from model calculations, however, that several parameters must change their value in order to reproduce the rotational constants of the excited states. Thus heavy relaxation, not only in the trifluoro methyl group, but also in the tilt and the $CN_\alpha N_\beta$ angle, is assumed to take place.

ACKNOWLEDGEMENT

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Table 1. Interatomic distances, vibrational amplitudes from spectroscopic and electron diffraction data (error limits are 3σ values) and vibrational corrections Δ (in \AA).

atom pair	r_{ij}	vibrational amplitudes		$\Delta = r_a - r_z$
		spectr.	e.d.	
$N_\beta - N_\omega$	1.12	0.034	0.034 ^a	0.0060
$N_\alpha - N_\beta$	1.25	0.042	0.042 (4) ^b	0.0004
C - F	1.33	0.045	0.045 (4) ^b	0.0013
C - N_α	1.43	0.053	0.053 (4) ^b	-0.0001
F..F	2.16	0.054	0.056 (3) ^c	0.0009
N_α ..F _t	2.18	0.061	0.063 (3) ^c	0.0004
N_α ..F _g	2.30	0.063		0.0001
C.. N_β	2.23	0.067	0.067 ^a	-0.0006
N_α .. N_ω	2.36	0.046	0.046 ^a	0.0028
N_β ..F _g	2.71	0.169	0.174 (26)	-0.0072
C.. N_ω	3.27	0.085	0.095 (40)	-0.0003
N_β ..F _t	3.31	0.092	0.092 ^a	0.0021
N_ω ..F _g	3.56	0.229	0.250 (33)	-0.0096
N_ω ..F _t	4.42	0.141	0.096 (57)	0.0130

^aNot refined, ^{b,c}Ratio constrained to spectroscopic ratio.

Table 2. Geometric parameters (\AA and degrees) for CF_3N_3 from electron diffraction and combined electron diffraction - microwave analysis.

	e.d. ^a <u>r_{α}°</u>	e.d. + m.w. ^b <u>r_{av}</u>
C-F	1.329 (3)	1.328 (2)
C-N _{α}	1.427 (5)	1.425 (5)
N _{α} -N _{β}	1.250 (7)	1.252 (5)
N _{β} -N _{ω}	1.117 (4)	1.118 (3)
CN _{α} N _{β}	111.8 (1.1)	112.4 (0.2)
N _{α} N _{β} N _{ω} ^c	175.3 (4.3)	169.6 (3.4)
FCF	108.4 (0.4)	108.7 (0.2)
tilt ^d	4.4 (1.2)	5.8 (0.4)

^aResults from electron diffraction analysis; error limits are 2σ values and include a possible scale error of 0.1% for bond lengths.

^bResults from combined electron diffraction - microwave analysis; error limits are 2σ values.

^cBend away from CF_3 group.

^dTilt of CF_3 group away from N_3 group.

Table 3. Force Field^a for CF₃N₃

CF	6.69	CF/CF	1.06
CN	4.84	CF/CN	0.46
N _α N _β	7.75	CF/FCF (adj)	0.51
N _β N _ω	16.88	CF/FCF (opp)	-0.33
FCF	1.82	CN/FCF	-1.00
NCF	1.20	CN/NCF (adj)	0.42
CNN	1.49	CN/NNN	-0.54
NNN	0.67	FCF/FCF	0.23
tors	0.03	FCF/NNN	-0.18
		NNN/tors	-0.07

^aStretch in m dyn/Å, stretch/bend in m dyn/rad,
bend in m dynÅ/rad²

Table 4. Measured rotational transitions and derived rotational constants (MHz).

	$v = 0$	$v_{15} = 1$	$v_{15} = 2$	$v_{15} = 3$	$v_{15} = 4^a$	$v_{10} = 1$	$v_{10} = 2$	$v_{15} = 1, v_{10} = 1, v_9 = 1$
101 ² 02	7845.90	7848.36	7851.39	7854.87	7858.13	7851.84	7857.67	7853.68
212 ³ 13	11738.22	11750.70	11764.13	11778.62		11743.79	11749.23	11755.80
202 ³ 03	11768.73	11772.52	11777.05	11782.32	11787.38	11777.53		11780.40
221 ³ 22	11768.72	11772.33	11776.69	11781.82		11777.72		11780.28
220 ³ 21	11768.93	11772.49	11776.69	11781.82		11778.00		11780.51
211 ³ 12	11799.67	11794.40	11789.80	11785.77				11805.19
414 ⁵ 15	19563.32	19584.34	19606.66	19630.92		19572.60	19581.52	19592.76
441 ⁵ 42	19612.98	19618.70	19625.77	19633.66		19627.90		19632.07
440 ⁵ 41								
404 ⁵ 05	19613.36	19620.17	19627.90	19637.11	19646.89	19627.75	19641.95	19633.17
432 ⁵ 33	19614.09	19619.84	19626.93	19635.37		19629.06	19643.67	19633.17
431 ⁵ 32								
423 ⁵ 24	19614.28	19620.17	19627.75	19636.38		19629.06	19643.67	19633.58
422 ⁵ 23	19615.96	19621.02	19627.90	19636.38			19646.29	19634.74
413 ⁵ 14	19665.79	19657.02	19649.58	19642.92		19686.00	19706.00	19675.23
515 ⁶ 16	23475.69	23500.96	23527.92	23557.02		23486.68	23497.42	23510.98
551 ⁶ 52	23534.01	23540.81	23549.30			23551.87		
550 ⁶ 51	23534.97	23543.71	23553.54	23564.72		23552.18	23568.80	
505 ⁶ 06								23560.39
542 ⁶ 43	23535.65	23542.48	23551.08	23560.39		23553.51		
541 ⁶ 42								
524 ⁶ 25	23536.98	23544.36	23553.06	23563.73		23554.88		
533 ⁶ 34	23537.01	23543.71	23552.40	23562.22		23554.88		
532 ⁶ 33								
523 ⁶ 24	23540.01	23545.76	23553.54	23563.73		23558.48	23562.22	
514 ⁶ 15	23598.62	23588.29	23579.39	23571.50		23662.84	23646.77	23609.94
554 ⁶	5544.	5631.5	5722.4	5817.2	5880.5	5517.5	5490.	5600.
A ^b	1971.750(4)	1969.374(6)	1967.121(6)	1964.924(7)	1971.679(6)	1974.335(6)	1976.896(5)	1971.679(6)
B	1951.260(4)	1954.825(6)	1958.544(6)	1962.519(7)	3929.1 ^c	1951.648(6)	1952.002(5)	1955.188(6)
C	0.0142(1)	0.0150(2)	0.0158(2)	0.0220(31)		0.0143(2)	0.0141(5)	0.0148(3)
D ^c								0.
J ^c								
K								

^aA species, ^bfixed to value determined from structural model and harmonic effects. ^cB + C. ^dkHz. ^eassumed.

Table 5. Principal geometric parameters of some azides, XN_3 , studied in the gas phase.

	HN_3^b	CH_3N_3^c	$\text{Me}_3\text{SiN}_3^d$	ClN_3^e	NCN_3^f	CF_3N_3^g
X-N $_{\alpha}$	1.015 (15)	1.468 (5)	1.734 (7)	1.745 (5)	1.355 (2)	1.425 (5)
N $_{\alpha}$ -N $_{\beta}$	1.243 (5)	1.216 (4)	1.198 (8)	1.252 (10)	1.261 (2)	1.252 (5)
N $_{\beta}$ -N $_{\omega}$	1.134 (2)	1.130 (5)	1.150 (11)	1.133 (10)	1.121 (2)	1.118 (3)
XN $_{\alpha}$ N $_{\beta}$	108.8 (4.0)	116.8 (0.3)	128.0 (1.6)	108.7 (0.5)	114.5 (0.2)	112.4 (0.2)
N $_{\alpha}$ N $_{\beta}$ N $_{\omega}$	171.3 (5.0)	180 ^h	180 ^h	171.9 (0.5)	169.2 (1.6)	169.6 (3.4)
τ^a	---	35.0 (7.0)	24.0 (5.0)	---	---	0.0

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^aTorsional angle of group X around X-N bond. $\tau = 0$ corresponds to staggered position.

^b r_s values, Ref. ^c r_a values, Ref. 7,8. ^d r_a values, Ref. ^e r_s/r_o values, Ref. 24.

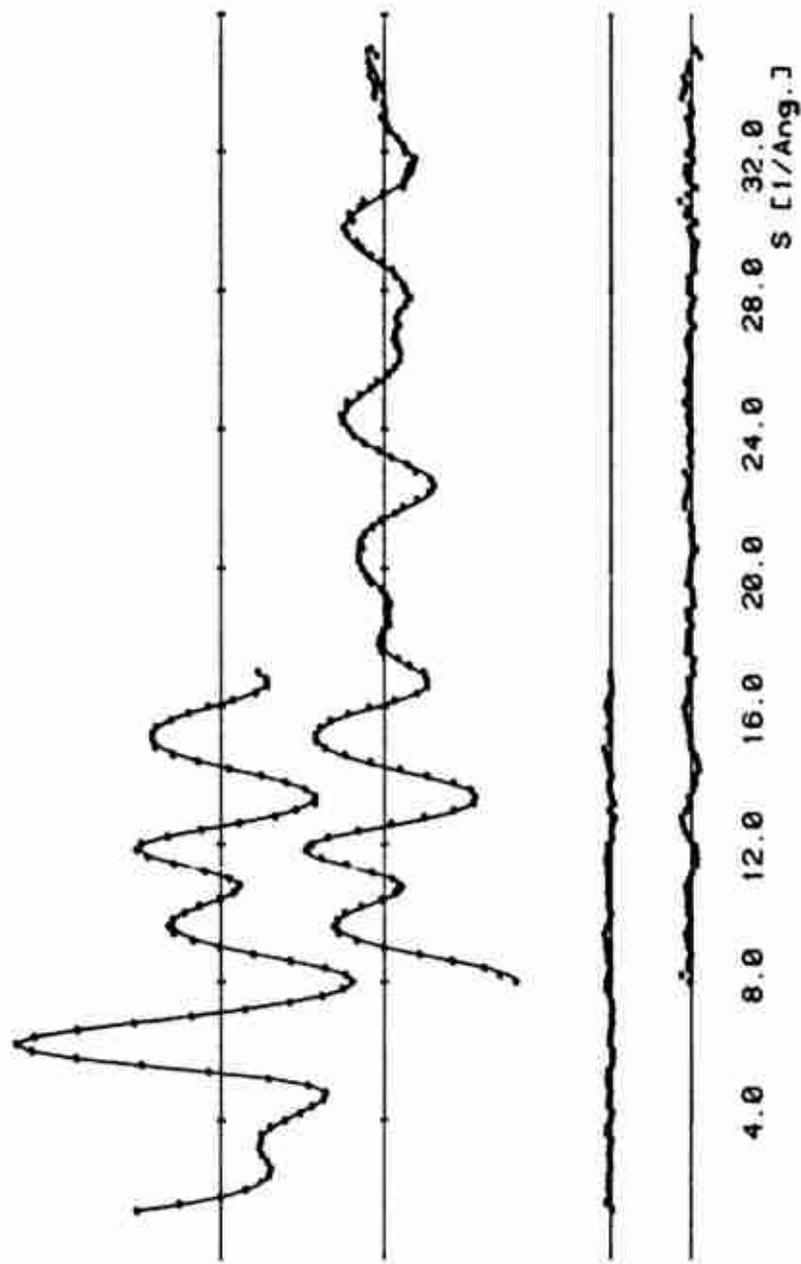
^f r_o values, Ref. ^g r_{av} values, this study. ^hestimated value.

Figure Captions

1. Experimental (.....) and calculated (——) molecular intensities and differences.
2. Experimental radial distribution function, theoretical functions for staggered and eclipsed conformations and difference curve between experimental and theoretical staggered conformation.
3. The J: 4+5 rotational transitions. Stark field: 200 V/cm. Arrows indicate frequencies at which $K_{-1} = 0$ lines appear at higher Stark fields.

$\nu_T = \nu_{15}$. $\nu_T = 4$ indicates the center of the A components of the torsionally split $\nu_T = 4$ state. The $K_{-1} = 1$ lines have not definitively been assigned.

4. The J: $5_{15}+6_{16}$ transitions showing several vibrationally excited states at a Stark field of 800 V/cm. $\nu_T = \nu_{15}$.
5. The J: $1_{01}+2_{02}$ transitions at a Stark field of 800 V/cm. Marker spacing is 0.8 MHz. The assignment of $\nu_T = 4$ is speculative, although other J candidates for the A components have been located.



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FIGURE 1.

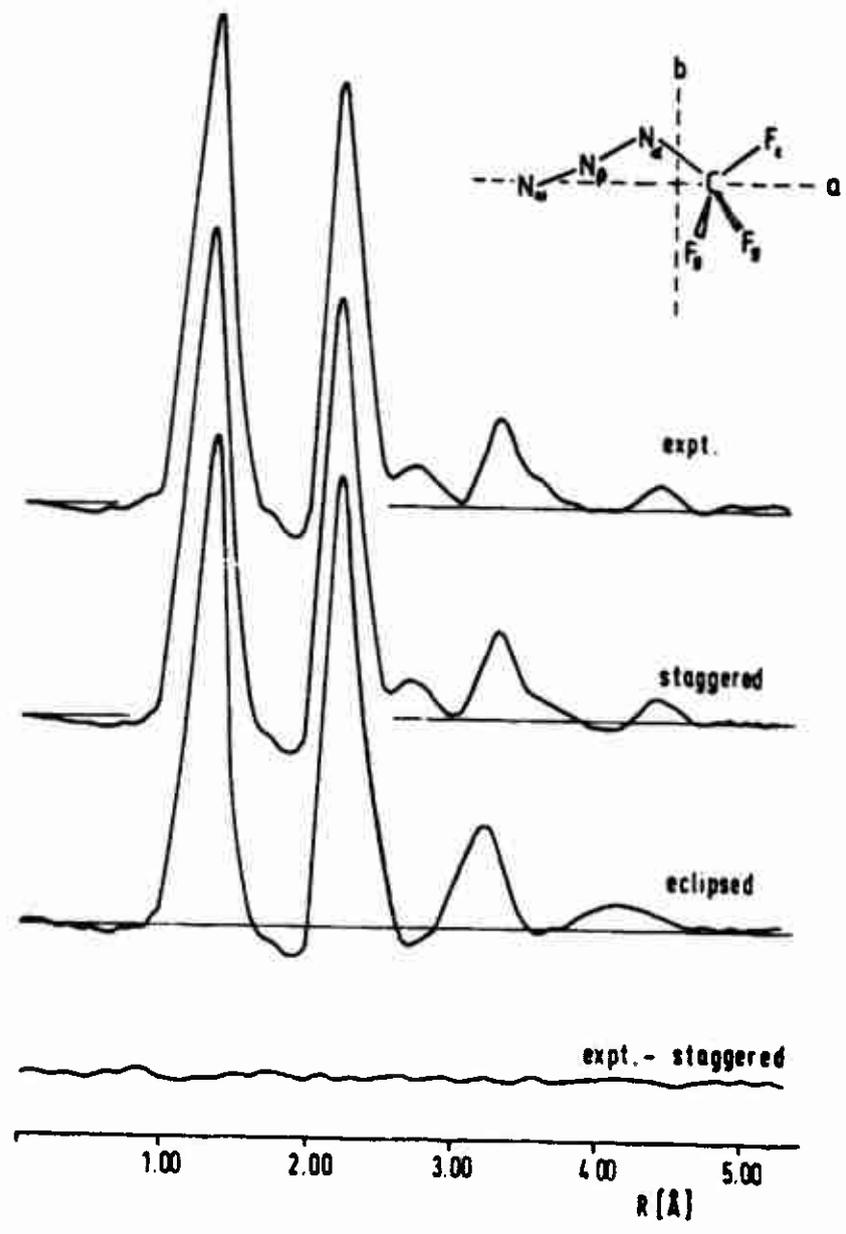


FIGURE 2.



FIGURE 3.

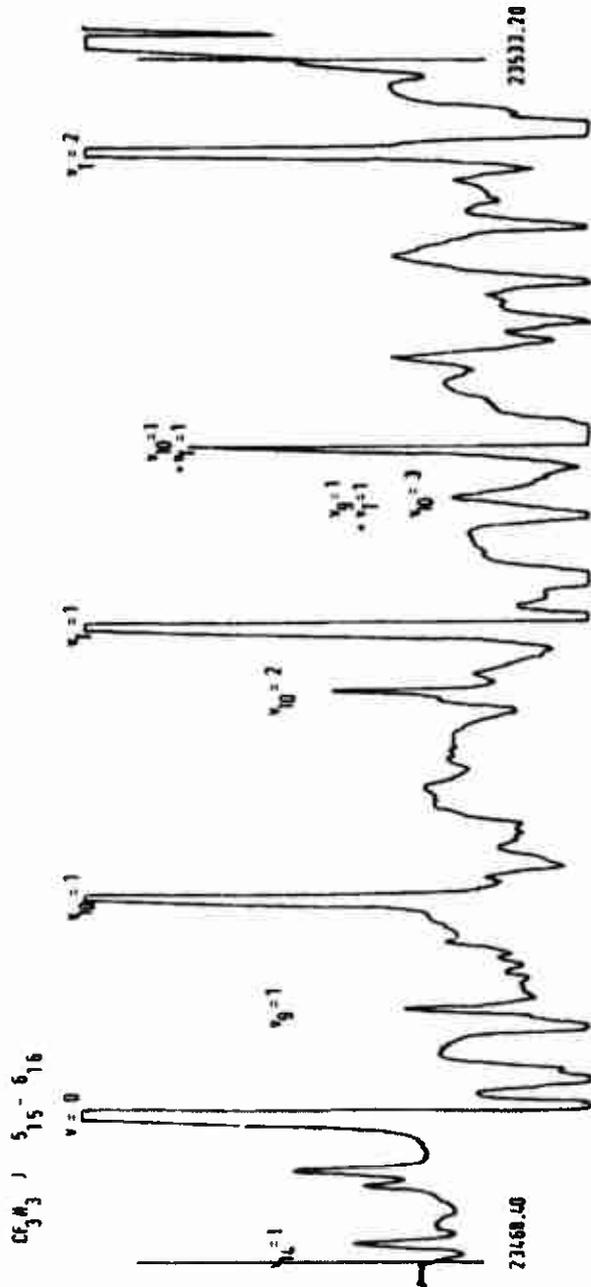


FIGURE 4.

APPENDIX S

Contribution from Rocketdyne, A Division of
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Structure and Vibrational Spectra of Oxonium Hexafluoro-Arsenates (V) and-Antimonates (V)

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Abstract

The salts $\text{OO}_3^+\text{AsF}_6^-$, $\text{OO}_3^+\text{SbF}_6^-$ and partially deuterated $\text{OH}_3^+\text{SbF}_6^-$ were prepared and characterized by X-ray and neutron diffraction techniques, OSC measurements, and vibrational spectroscopy. At room temperature, $\text{OH}_3^+\text{AsF}_6^-$ exists in a plastic phase where ions, centered on the atomic positions of the NaCl structure, are in motion or oscillation. No valuable information on atomic distances or angles in $\text{OH}_3^+\text{AsF}_6^-$ could be obtained due to these dynamic structural disorder problems. For $\text{OH}_3^+\text{SbF}_6^-$ the phase transition from an ordered to a disordered phase was shown to occur above room temperature. The room temperature phase can be described by an ordered hydrogen bonded model based on a CsCl type structure. Vibrational spectra were recorded for these oxonium salts and confirm the presence of the different phases and phase transitions. Improved assignments are given for the OH_3^+ and OD_3^+ cations, and the OH...FM bridge stretching mode and some of the bands characteristic for OD_2H^+ and ODH_2^+ were identified. A modified valence force field was calculated for OH_3^+ which is in good agreement with the known general valence force field of isoelectronic NH_3 and values obtained by ab initio calculations.

Introduction

Although the existence of oxonium salts at low temperature had been well known for many years, the synthesis of surprisingly stable OH_3^+ salts containing the AsF_6^- and SbF_6^- anions has been reported⁴ only in 1975. Since then numerous papers have been published on other OH_3^+ salts containing complex fluoro anions, such as UF_6^- ,⁵ BiF_6^- ,⁶ IrF_6^- , PtF_6^- , RuF_6^- ,^{7,8} TiF_5^- ,⁹ or BF_4^- .¹⁰ In these oxonium salts the cations and anions are strongly hydrogen bonded, as shown by the short O-F distances of 2.51 to 2.61 Å found by X-ray diffraction studies.^{9,10} Since the nature of these hydrogen bridges is strongly temperature dependent, these oxonium salts show phase transitions and present interesting structural problems. In this paper we report unpublished results accumulated during the past eight years in our laboratories for these oxonium salts.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3 and HF or DF) Monel-Teflon FEP vacuum system.¹¹ Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Hydrogen fluoride (The Matheson Co.) was dried by storage over BiF_5 .⁶ SbF_5 and AsF_5 (Ozark Mahoning Co.) were purified by distillation and fractional condensation, respectively, and DF (Ozark Mahoning Co.) and O_2O (99.6%, Volk) were used as received. Literature methods were used for the preparation of O_2AsF_6 ¹² and OH_3SbF_6 and OH_3AsF_6 .⁴

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, which was calibrated by comparison with standard gas calibration points.^{13,14} Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). For low-temperature spectra, the pressed silver halide disks were placed in a copper block cooled to -196°C with liquid N_2 and mounted in an evacuated 10 cm path length cell equipped with CsI windows.

Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter¹⁵ for the elimination of plasma lines. Sealed quartz tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded using a previously described¹⁶ device.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, equipped with a liquid N₂ cooled low-temperature assembly, was used to measure phase transitions above -90°C. The samples were crimp sealed in aluminum pans, and a heating rate of 5°/min in N₂ was used. The instrument was calibrated with the known mp of n-octane, water, and indium.

The neutron powder diffraction patterns of OH₃⁺AsF₆⁻, OD₃⁺AsF₆⁻, and D₂O⁺AsF₆⁻ were measured at Saclay using the research reactor EL3 with λ = 1.140 Å for 2θ ranging from 6 to 44°. The data for OD₃⁺SbF₆⁻ were recorded at ILL Grenoble with λ = 1.2778 Å for 2θ ranging from 12 to 92° with 400 measured values of intensity separated by 0.10°.

The X-ray powder diffraction patterns were obtained from samples sealed in 0.3mm Lindemann capillaries with a 114.6mm diameter Philips camera using Ni-filtered Cu Kα radiation. Low-temperature diagrams were measured using a jet of cold N₂ to cool the sample and a Meric MV3D00 regulator.

The single crystal of OH₃⁺SbF₆⁻ was isolated as a side product from the reaction of MoF₄O and SbF₅ in a thin walled Teflon FEP reactor with H₂O slowly diffusing through the reactor wall.

Preparation of OD₃⁺AsF₆⁻. A sample of D₂O (987.5mg, 49.30mmol) was syringed in the drybox into a 3/4 inch Teflon FEP ampule equipped with a Teflon coated magnetic stirring bar and a stainless steel valve. The ampule was connected to a Monel-Teflon vacuum line, cooled to -196°C, evacuated, and DF (10g) was added. The mixture was homogenized at room temperature, and AsF₅ (57.7mmol) was added at -196°C. The mixture was warmed to -78°C and then to ambient

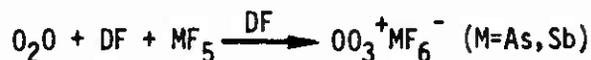
temperature for 1 hr with agitation. All material volatile at ambient temperature was pumped off for 2 hr, leaving behind a white solid residue (10.408g, weight calcd for 49.30mmol of $\text{OO}_3^+\text{AsF}_6^-$ 10.402g) identified by IR spectroscopy as mainly $\text{OD}_3^+\text{AsF}_6^-$ containing a small amount of $\text{OD}_2\text{H}^+\text{AsF}_6^-$ as impurity.

Preparation of $\text{OD}_3^+\text{SbF}_6^-$. Antimony pentafluoride (18.448g, 85.11mmol) was added in the drybox to a 3/4 inch Teflon FEP ampule equipped with a Teflon coated magnetic stirring bar and a stainless steel valve. The ampule was connected to the vacuum line, cooled to -78°C , evacuated and DF (23.1g) was added. The mixture was homogenized at room temperature. The ampule was cooled inside the drybox to -196°C , and D_2O (1.6951g, 84.63mmol) was added with a syringe. The mixture was agitated for several hours, and all material volatile at 45°C was pumped off for 14 hr. The white solid residue (21.987g, weight calcd for 84.63mmol of $\text{OD}_3^+\text{SbF}_6^-$ 21.813g) was identified by spectroscopic methods as mainly $\text{OD}_3^+\text{SbF}_6^-$ containing small amounts of $\text{OD}_2\text{H}^+\text{SbF}_6^-$.

Preparation of Partially Deuterated $\text{OH}_3^+\text{SbF}_6^-$. A sample of $\text{OH}_3^+\text{SbF}_6^-$ (2.0016g, 7.857mmol) was dissolved in liquid DF (2.012g, 95.81mmol) in a Teflon ampule for 1 hr. All volatile material was pumped off at 45°C for 3 hr leaving behind a white solid residue (2.020g, weight calcd for 7.857mmol of $\text{OD}_3^+\text{SbF}_6^-$ 2.0252g) which based on its vibrational spectra showed about equimolar amounts of OD_3^+ and OD_2H^+ , and smaller amounts of $\text{ODH}_2^+\text{SbF}_6^-$ (calcd statistical product distribution for 19.74%H and 3D.26%D: OD_3^+ 51.68, OD_2H^+ 38.16, OOH_2^+ 9.33, and OH_3^+ 0.77 mol%).

Results and Discussion

Syntheses and Properties of Deuterated Oxonium Salts. The OD_3^+ salts were prepared by the same method as previously reported⁴ for the corresponding OH_3^+ salts, except for replacing H_2O and HF by D_2O and OF, respectively.



The yields are quantitative and the samples were almost completely deuterated. The small amounts of DD_2H^+ observed in the infrared spectra and to a lesser degree in the Raman spectra of the products (see below), are attributed to small amounts (0.6%) of H_2D in the D_2D starting material and to exchange with traces of moisture during the preparation of the IR samples. A partially deuterated sample of $DH_3^+SbF_6^-$ was prepared by treating solid $DH_3^+SbF_6^-$ with an excess of DF.



The exchange appeared to be fast, and the product exhibited the correct statistical DD_3^+ , DD_2H^+ , DDH_2^+ , DH_3^+ distribution based on the H:D ratio of the starting materials. As expected, the physical properties of the deuterated oxonium salts were practically identical to those⁴ of the corresponding OH_3^+ salts.

DSC Data. Since the neutron and X-ray diffraction data suggested (see below) that at room temperature DH_3SbF_6 is ordered whereas OH_3AsF_6 exists in a plastic phase, low-temperature DSC data were recorded to locate the corresponding phase changes for each compound.

The OD_3AsF_6 salt exhibited on warm up from $-9D^{\circ}C$ a large endothermic phase change at 2.5° which was shown to be reversible, occurring at -7.5° on cooling. For DH_3AsF_6 this phase change was observed at practically the same temperatures. No other endotherms or exotherms were observed between $-9D^{\circ}C$ and the onset of irreversible decomposition. The observed phase change temperatures are in excellent agreement with those found by low-temperature Raman spectroscopy (see below).

For DH_3SbF_6 three small endotherms at 2D, 49, and $81^{\circ}C$ and a large endothermic phase change at $100^{\circ}C$ were observed on warming. All of these were reversible occurring at 19, 42, 77 and $96^{\circ}C$, respectively, on cooling. For OD_3SbF_6 the

corresponding changes were observed at 20, 48, 82, and 100°C on warming and 20, 43, 74, and 76°C on cooling. Again no other heat effects were observed in this temperature range. The temperature differences observed for phase changes between the heating and cooling data is attributed to hysteresis which normally is a problem in salts of this type.¹⁷ The smaller heat effects observed for OH_3SbF_6 below the major order-disorder phase transition may be attributed to damping of rotational motions of the ions, similar to those found for O_2AsF_6 .¹⁷

For OH_3BiF_6 no phase transitions were observed between -90°C and the onset of decomposition.

Structural Studies

OH_3AsF_6 . As previously reported,⁴ this compound is cubic at room temperature, and a cell parameter of 8.043(8)Å was found in this study from X-ray powder data. It exhibits only one phase transition at $-2 \pm 5^\circ\text{C}$ (based on DSC and Raman data) in the temperature range from -90°C to its decomposition point. The X-ray powder pattern at -153°C is given in Table I and indicates a lowering of the symmetry in agreement with the low-temperature vibrational spectra (see below). Attempts to index the pattern were unsuccessful.

It is interesting to compare the X-ray powder diffraction patterns of OH_3AsF_6 and O_2AsF_6 . Whereas their room temperature patterns^{4,12,18} and cell parameters are for practical purposes identical, their low-temperature patterns (Table I and ref. 19) are very distinct due to different ion motion freezing. Since OH_3^+ , OD_3^+ , and O_2^+ are weak X-ray scatterers, but contribute strongly to the neutron scattering, neutron diffraction powder patterns were also recorded at room temperature for their AsF_6^- salts (see Table II). As expected, the cell dimensions were for practical purposes identical, but the observed relative intensities were very different.

Attempts were made to obtain structural information from the room-temperature neutron diffraction powder patterns of OH_3AsF_6 and OD_3AsF_6 . It was shown that the unit cell is indeed face-centered cubic and that an alternate solution,⁴ a primitive cubic CsPF_6 structure, can be ruled out for both compounds. The number of observed peaks is rather small, but the respective intensities due to the substitution of hydrogen by deuterium (scattering lengths $b_{\text{H}} = -0.374$, $b_{\text{D}} = 0.667$) are very different (Table II). The rapid vanishing of intensities at large diffraction angles and the presence of a bump in the background level implying a short distance order, are characteristic of plastic phases with ions in motion. The only models which could be tested to describe such a motion have been tried successively.

The first one is a disordered model with statistical occupancy factors for fluorine atoms and hydrogen atoms in the $\text{Fm}\bar{3}$ symmetry group. This corresponds to four equivalent positions of the octahedra around the fourfold axes, and to eight positions for the OH_3^+ ion. Using the intensities observed for OH_3AsF_6 , the solution refines to $R = 0.047$, but is not considered acceptable because the resulting distances $\text{As-F} = 1.58\text{\AA}$ and $\text{O-H} = 0.82\text{\AA}$ are too short when compared to $\text{As-F} = 1.719(3)\text{\AA}$ in KAsF_6 ²⁰ and $\text{O-H} = 1.011(8)\text{\AA}$ in $\text{OH}_3^+ \text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$.²¹

The second one is a rotating model which places As at the 000 position connected to fluorines by a complex term

$$b_{\text{As}} + 6b_{\text{F}} \frac{\sin x}{x} \quad \text{with } x = 4 \pi r_{\text{F}} \sin \theta / \lambda$$

and O at the $1/2 \ 1/2 \ 1/2$ position connected to H atoms by

$$b_{\text{O}} + 3b_{\text{H}} \frac{\sin x}{x} \quad \text{with } x = 4 \pi r_{\text{H}} \sin \theta / \lambda$$

where b_{As} , b_{F} , b_{O} and b_{H} are the scattering lengths of As, F, O, and H, respectively. The As-F distance, r_{F} , and the O-H distance, r_{H} , are the only unknowns with the scale factor of the structure.²² The best results

($R = 0.059$) are obtained with the combination $\text{As-F} = 1.59\text{\AA}$ and $\text{O-H} = 0.81\text{\AA}$, not so different indeed from the first model.

For O_3AsF_6 , the second model gives more plausible distances, $\text{As-F} = 1.65\text{\AA}$ and $\text{O-O} = 1.01\text{\AA}$ with $R = 0.054$, if the intensity of the 200 reflexion is arbitrarily lowered by 20% assuming the excessive intensity being due to preferential orientation.

Based on the short distances found for OH_3AsF_6 , we can consider that the real structure is probably not properly accounted for by either one of the models, due to the motion of the ions which is not correctly simulated as for other plastic phases.

OH_3SbF_6 . Based on the DSC data (see above) the transition from an ordered to a disordered phase occurs at $88 \pm 12^\circ\text{C}$. The existence of an ordered phase at room temperature for OH_3SbF_6 and its deuterated analogues was confirmed by the diffraction studies. The X-ray powder diffraction pattern, which originally had been read backwards due to very intense back reflections and indexed incorrectly as tetragonal,⁴ is listed in Table III. By analogy with a large class of other MF_6^- compounds, such as O_2PtF_6 ²³ and O_2SbF_6 ,²⁴ the OH_3SbF_6 pattern can be indexed for a cubic unit cell with $a = 10.143(3)\text{\AA}$ (CEN data) or 10.090\AA (Rocketdyne data). The cell dimensions were confirmed by a single crystal X-ray study at Leicester (see below) which resulted in $a = 10.130(8)\text{\AA}$. Although all of the observed X-ray reflections obey the conditions ($h+k+l=2n$ and $0kl$ where $kl=2$) for space $Ia3$, the neutron diffraction data (see below) suggest a lower symmetry subgroup, such as I_23 . In the following paragraphs the results obtained for the ordered cubic, room temperature phase of OH_3SbF_6 are discussed in more detail.

Single Crystal X-ray Study. The OH_3SbF_6 single crystal had the approximate dimensions $0.46 \times 0.35 \times 0.22\text{mm}$ and was sealed in a Pyrex capillary. Preliminary cell dimensions were obtained from Weissenberg and precession

photographs. The final value for the unit cell parameter was determined from the optimized counter angles for zero layer reflections on a Stoe Weissenberg diffractometer. The data were collected for layers 0kl to 6kl of the aligned pseudotetragonal cell, using the Stoe Stadi-2 diffractometer, in the four quadrants $h \pm k \pm l$ and an ω -scan technique with Zr filtered Mo K α radiation. The intensities of reflections with $0.171 \leq \text{Sine}/\lambda \leq 1.22\text{\AA}^{-1}$ were collected, and a total of 719 reflections obtained with $I/OI \geq 3$. Check reflections were monitored during the data collection of each layer and no deterioration of the crystal was indicated. Lorentz and polarisation corrections were made to the data set.

The program system Shelx²⁵ was used to solve the structure. Neutral scattering factors were used with anomalous dispersion coefficient. Three cycles of least squares refinement with antimony on the Wyckoff position, 8a ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) of the space group Ia3 gave an R factor of 0.27. The Fourier difference map located a 9 electron peak, assumed to be oxygen, on the 8b position ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) with two sets of possible fluorine octahedra each at 1.90 \AA from Sb. Three cycles of refinement with the oxygen atom included, reduced the R factor to 0.22. The inclusion of either of the peaks on the general positions about Sb, as F atoms, with all atoms refining isotropically resulted in a reduced R_0 factor of 0.13; however, the refinement cycles moved the F atoms to $> 2.0\text{\AA}$ from Sb. The inclusion of fluorine atoms also resulted in a more complex difference Fourier map, with several peaks ≤ 3 electrons appearing. The alternate fluorine atom positions indicated were refined as disordered, initially refining the site occupation factors and then the temperature factors. The resultant R factor of 0.12 was not significantly less than with an ordered structure; one of the fluorine atoms refined to a position 2.2 \AA from Sb, and further possible fluorine sites appeared in the Fourier map. Refinement of various models with either ordered fluorine atoms or disordered atoms constrained to be 1.86(3) \AA from antimony, did not improve the R factor or the residual Fourier map. For final cycles of least-squares refinement, the atomic positional and thermal parameters of that fluorine atom which remained at the expected distance from antimony in the disordered model, were refined. This

represents an incomplete solution, as the fluorine atom parameters reported appear representative of disorder. This is reflected in the structure factors, where agreement between $|F_o|$ and $|F_c|$ is good for even, even, even reflections with dominant contribution by the antimony and oxygen atoms but poor for odd, odd, even reflections which are dependent only upon the fluorine (and hydrogen) atom parameters. The final atomic positional and thermal parameters are given in Table IV, with some atomic distances and angles. Final residual indices for 155 unique reflections is $R = 0.119$.

Neutron Powder Diffraction Study. For 00_3SbF_6 46 reflexions were observed (see Figure 1) out of which 4 could not be indexed on the basis of the cubic cell and are attributed to an unidentified impurity (mainly lines at 3.269, 2.235 and 2.225Å). The list of observed reflexions is given in Table V in comparison with X-ray data. The cell parameter is 10.116(6)Å.

The Rietveld program for profile refinement²⁶ was used to solve the structure. The first refinement was attempted in the Ia3 space group starting from the X-ray values for Sb, O and F and adding approximate values for O with the 00_3^+ ion being disordered on two equivalent positions (occupancy factor = $\frac{1}{2}$ of general positions xyz). The system refined to $R = 0.135$ with the following parameters:

Atom	x	y	z	$B \text{ (Å}^2\text{)}$
Sb	0.5	0.5	0.5	0.94(25)
Ox	0.25	0.25	0.25	4.87(41)
F	0.441(6)	0.604(6)	0.641(7)	2.88(13)
O	0.300(1)	0.317(1)	0.204(1)	2.98(27)

The y and z coordinates of fluorine atom have been permuted, probably due to the choice of the coordinates of deuterium. The atomic distances and angles

are then

Sb-F	1.87 ⁰ A	
O-F	2.67 ⁰ A	
O-D	0.96 ⁰ A	
D-D	1.56 ⁰ A	000: 108 ⁰

which compare relatively well with the X-ray values of Table IV. At this stage, our attention was drawn to the presence of a weak but well isolated line at an angle θ high enough not to be attributed to the impurity. This line corresponded to a 730 reflexion, a forbidden reflexion in the space group Ia3 (hko, $hk = 2n$). In view of a similar observation for the cubic phase of KSbF_6 (II) (in this case the 310 reflexion),²⁷ the trouble with locating the fluorine atoms by difference X-ray syntheses, and mainly the incompatibility of the group Ia3 with the observed Raman and IR spectra (see below), we considered the possibility of an ordered structure in a subgroup of the Ia3 space group, first the noncentrosymmetric $I2_13$ space group (No. 199).

Since the symmetry center does not exist anymore, the local symmetry of the Sb and O atoms is then only a threefold axis. The structure has to be described with two sets of fluorine atoms F_1 and F_2 , and the oxonium ion is ordered with a full occupation of deuterium atoms on the general positions. The Sb and O atoms are also allowed to move along the threefold axes from their ideal positions (000, 1/2, 1/2, 1/2).

This hypothesis was tested and led to a better R factor (0.106) with the following parameters:

Atom	x	y	z	$B(\text{Å}^2)$
Sb	-0.012(1)	-0.012(1)	-0.012(1)	0.13(0.38)
O	0.238(3)	0.238(3)	0.238(3)	3.50(0.75)
F1	0.044(1)	-0.118(1)	-0.143(2)	1.26(0.42)
F2	-0.75(2)	0.091(1)	0.137(2)	1.89(0.45)
O	0.199(2)	0.184(1)	0.299(1)	3.40(0.30)

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Figure 1 gives the resulting profile of observed and calculated neutron diffraction diagrams and shows satisfactory agreement.

The Sb and O atoms are displaced from their ideal positions by 0.21Å, and the environment of the Sb atom has 3 F₁ atoms at 1.80Å and 3F₂ atoms at 1.94Å, which seems to be compatible with the Raman and IR spectra.

The F₂ atoms are closer to the oxygen atom of the oxonium group than the F₁ atoms with F₂-O = 2.60Å and F₁-O = 2.79Å. The F₂-O distance is within the correct range for a strong OO...F hydrogen bridge bond (2.51-2.56Å in OH₃TiF₅⁸ and 2.58-2.61Å in OH₃BF₄⁹).

The deuterium atoms are located at 0.91Å from the oxygen atom, (with a D-O distance of 1.54Å and a DOD angle of 116°) on the line O-F₂ (OD + OF₂ = 0.91 + 1.69 = 2.60Å). This confirms, in the precision of our results, the quasi linearity of the O-O...F bond in this compound. The geometry of the OO₃⁺ cation itself is a flat pyramid with C₃ symmetry. The oxygen atom lies 0.18Å out of the plane of the 3 deuterium atoms.

Figure 2 illustrates the environment around the oxonium ion, with the F₂ atoms being differentiated from the F₁ atoms by traces of the ellipses. The two SbF₆⁻ octahedra fully represented are approximately located at 000 and 1/2 1/2 1/2 along the [111] direction and bring the environment to an icosahedron. The distinction between F₁ and F₂ implies a small displacement of the fluorine atoms from their average positions obtained in the Ia3 space group (F-F₁ or F-F₂ distances are about 0.20Å) but the angular distortion of the octahedron is small, one side being flattened (F₁ 53°9) and the other one being elongated (F₂ 55°5). To obtain a refinement in the I2₁3 symmetry group, we had to allow the existence of antiphase domains without local symmetry centers, but which are images of each other.

The interesting point of this structure is the existence of an ordered solution for all atoms with a scheme of hydrogen bonding which prevents at room temperature the existence of a plastic phase. Such a phase may however exist at higher temperatures and explains the phase changes observed before the decomposition point. To obtain more information on the motions of the ions in the different phases, additional experimental data, such as second moment and relaxation time NMR measurements, are required.

As far as the exact geometry of the OD_3^+ cation is concerned, it must be pointed out that the precision of the results obtained from the powder diffraction data is not very high and that the final values depend on the starting points used for the different refinements. Thus the O-D distance was found to vary from 0.91 to 1.05Å with the ODO angle varying from 116° to 92° . The correct values certainly lie between these extreme values. This is also reflected by the higher thermal parameters found for the deuterium and oxygen positions (see above) indicating high thermal motion of the OD_3^+ cation itself. For the O-H bond length in OH_3^+ , a lower limit of 0.97Å appears more realistic for the following reasons. The bond length in free OH_2 is already 0.96Å and both the hydrogen-fluorine bridging and the increased $\delta^-\delta^+$ polarity of the O-H bond in OH_3SbF_6 are expected to increase the O-H bond length. This bond weakening in OH_3^+ when compared to free OH_2 is also supported by the force constant calculations given below. The most likely range of the O-H bond length in these OH_3MF_6 salts is therefore 0.98-1.05Å which is in excellent agreement with the values of 1.013(8), 1.020(3), and 0.994(5)Å previously found for $\text{OH}_3^+\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$,²⁰ $\text{OD}_3^+\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$,²⁸ and $\text{OH}_3^+\text{CF}_3\text{SO}_3^-$,²⁹ respectively, by neutron diffraction, and values of 1.01 to 1.04Å for $\text{OH}_3^+\text{NO}_3^-$ and $\text{OH}_3^+\text{ClO}_4^-$, derived from wide line NMR measurements.³⁰

The value of 1.19Å, previously reported⁹ for the O-H bond length in $\text{OH}_3^+\text{BF}_4^-$, is based on X-ray data and therefore is deemed unreliable. It should be pointed out that the OH...F distances in $\text{OH}_3^+\text{BF}_4^-$ and $\text{OD}_3^+\text{AsF}_6^-$ are practically

identical (2.60Å). This suggests that r_{O-H} and r_{O-D} in these two compounds should also be similar.

Vibrational Spectra. Although many papers have been published on the vibrational spectra and force field of the oxonium ion,^{4-9,31-45} many discrepancies exist among these data. Frequently, the infrared bands observed for the stretching modes are very broad, overlap and are complicated by Fermi resonance with combination bands. Also, the smooth transition from highly ionic OH_3^+ salts to proton transfer complexes and the interpretation of some of the more weakly ionized proton transfer complexes in terms of discrete OH_3^+ salts may have significantly contributed to the general confusion. As a consequence there is still considerable ambiguity⁴ whether the antisymmetric or the symmetric OH_3^+ stretching mode has the higher frequency. Furthermore, the symmetric OH_3^+ deformation mode is generally very difficult to locate due to the great line width of the band.⁴⁶ Although vibrational spectra have previously been reported for OD_3^+ ,^{32,34,38} they have been of little help to strengthen the vibrational assignments for the oxonium cation. Consequently, it was interesting to record the vibrational spectra of deuterated and partially deuterated OH_3^+ in salts containing well defined discrete oxonium cations. We hoped to verify the above described phase changes and to compare the experimentally observed spectra with the results from recent theoretical calculations⁴⁷⁻⁴⁹ and with those of the isoelectronic ammonia analogues.⁵⁰⁻⁵⁴

The observed infrared and Raman spectra and the more important frequencies are given in Figures 3-7 and Table VI.

Room Temperature Spectra of OD_3AsF_6 . Figure 3 shows the room temperature spectra of solid OD_3AsF_6 . As can be seen, the bands are broad and show no splittings or asymmetry as expected for ions undergoing rapid motion in a plastic phase.^{4,17,19} Based on their relative infrared and Raman intensities, the band at about 2450 cm^{-1} can be assigned with confidence to the

antisymmetric OD_3^+ stretching mode $\nu_3(\text{E})$ and the band at about 2300 cm^{-1} to the symmetric OD_3^+ stretching mode $\nu_1(\text{A}_1)$. This assignment of $\nu_3 > \nu_1$ is further supported by all the other spectra recorded in this study (see below). Also, their frequency separation of about 150 cm^{-1} is very similar to that of 144 cm^{-1} found for isoelectronic ND_3 .⁵⁰ Furthermore, a recent ab initio calculation for OD_3^+ also arrived (after applying the suggested -12.3% correction to all frequencies) at ν_3 being 165 cm^{-1} higher than ν_1 (see Table VII).⁴⁹ This finding that in a strongly hydrogen bridged oxonium salt ν_3 is higher than ν_1 disagrees with the previous suggestion that the order of the OH_3^+ stretching frequencies should invert when $r_{\text{X-Y}}$ in $\text{X-H}\dots\text{Y}$ becomes shorter than the van der Waals radius sum.³⁸

The assignment of the 1192 cm^{-1} infrared and the 1178 cm^{-1} Raman band to the antisymmetric OD_3^+ deformation $\nu_4(\text{E})$ is straight forward and again is in excellent agreement with the frequency values of 1191 and 1161 cm^{-1} , found for isoelectronic ND_3 ⁵⁰ and calculated for OD_3^+ by ab initio methods,⁴⁹ respectively (see Table VII).

The assignment of the last yet unassigned fundamental of OD_3^+ , the symmetric deformation mode $\nu_2(\text{A}_1)$ is more difficult. Based on analogy with ND_3 , this mode should occur at about 750 cm^{-1} and indeed the Raman spectrum of OD_3AsF_6 exhibits a band at 770 cm^{-1} of about the right intensity. The failure to observe a well defined infrared counterpart could possibly be due to its great linewidth. The ab initio calculations for $\nu_2(\text{A}_1)$ of OD_3^+ predict an intense infrared band at 549 cm^{-1} . Indeed the infrared spectrum of OD_3AsF_6 (trace A, Figure 3) shows a medium strong band at 580 cm^{-1} . However, we prefer to assign this band to $\nu_2(\text{E}_g)$ of AsF_6^- for the following reasons. This mode frequently becomes infrared active in many AsF_6^- salts. Furthermore, it has also been observed in OH_3AsF_6 ⁴ if it were due to OD_3^+ , it would have been shifted in OH_3AsF_6 to a significantly higher frequency. This

assignment to ν_2 of AsF_6^- is also supported by the low-temperature infrared spectra of $\text{OH}_3\text{AsF}_6^+$ and $\text{OD}_3\text{AsF}_6^-$ (Figure 4) both of which show two sharp bands of almost identical intensities and frequencies at about 580 and 560 cm^{-1} .

The remaining bands due to AsF_6^- in $\text{OD}_3\text{AsF}_6^-$ are in excellent agreement with those previously observed for $\text{OH}_3\text{AsF}_6^+$ and can be assigned accordingly.⁴ IR: $\nu_3(\text{F}_{1u})$, 700; $\nu_4(\text{F}_{1u})$, 389 cm^{-1} . RA: $\nu_1(\text{A}_{1g})$, 682; $\nu_2(\text{E}_g)$, 560; $\nu_5(\text{F}_{2g})$, 363 cm^{-1} . Several weak bands in the spectrum of $\text{OD}_3\text{AsF}_6^-$ are marked by an asterisk. These are due to a small amount of OD_2H^+ and will be discussed below.

Low-Temperature Spectra of $\text{OD}_3\text{AsF}_6^-$ Figure 4 shows the low-temperature spectra of $\text{OD}_3\text{AsF}_6^-$. The most prominent changes from the room temperature spectra are the pronounced sharpening of all bands accompanied by splittings. As discussed above, these changes are caused by freezing of the ion motions. The change from a plastic phase to an ordered one, occurring based on the DSC measurements in the -7 to +2°C temperature range was confirmed by Raman spectroscopy. As can be seen from Figure 5, the freezing out of the ion motion occurs indeed within the very narrow temperature range.

Compared to the room temperature spectra, the low-temperature spectra do not provide much additional information on the fundamental vibrations of OD_3^+ . The $\nu_1(\text{A}_1)$ fundamental is shown to occur at a lower frequency than $\nu_3(\text{E})$, and $\nu_4(\text{E})$ shows a splitting into two components in the infrared spectrum. The $\nu_2(\text{A}_1)$ deformation mode is again difficult to locate but clearly cannot be attributed to the 582 cm^{-1} infrared band for the above given reasons.

From the AsF_6^- part of the spectra some conclusions concerning the possible site symmetry of AsF_6^- might be reached. All degeneracies appear to be lifted for the fundamentals and the bands are not mutually exclusive. This eliminates all centrosymmetric space groups and site symmetries, such as C_h , T_h or C_{3i} . The highest possible site symmetry appears to be C_3 , in

agreement with our triply hydrogen bonded model possessing AsF_6^- ions with three shorter and three longer As-F bonds. Since the unit cell contains more than one molecule, additional splittings are possible due to in-phase out-of-phase coupling effects within the unit cell.

The low-temperature spectra of OO_3AsF_6 show a medium strong IR band at 341 cm^{-1} and a Raman band at 329 cm^{-1} . These bands are of too low a frequency to be assignable to AsF_6^- and also were not observed in the low-temperature spectra of OH_3AsF_6 .⁴ In OH_3AsF_6 , however, two corresponding bands were observed at 467 cm^{-1} (IR) and 480 cm^{-1} (RA).⁴ Since their average frequency values, 335 and 474 cm^{-1} , respectively, are exactly in a ratio of 1:2, these bands must involve the hydrogen atoms and therefore are assigned to the O...F and H...F stretching modes, respectively. As expected, these bands due to H...F stretching are not observed in the plastic phase, room temperature spectra due to rapid motion of the ions.

Spectra of OO_3SbF_6 , OH_3SbF_6 and Partially Deuterated OH_3SbF_6 . Figure 6 shows the room temperature vibrational spectra of OO_3SbF_6 , OH_3SbF_6 and partially deuterated OH_3SbF_6 . Although the Raman lines due to SbF_6^- (670 , 590 , 555 and 282 cm^{-1} in trace E) are broadened, the 670 cm^{-1} line has a pronounced shoulder at 644 cm^{-1} , the $\nu_2(E_g)$ mode is split into its two degenerate components (see Figure 5), and the D...F stretching mode at 355 cm^{-1} (trace E of Figure 6) and H...F stretching mode at 487 cm^{-1} (trace A of Figure 6) are observed. All these features clearly indicate that OO_3SbF_6 and OH_3SbF_6 are ordered at room temperature, thus confirming the above given DSC and diffraction data.

The assignments for OO_3^+ in its SbF_6^- salt can be made by complete analogy to those given above for OD_3AsF_6 . The increased splitting of the 2430 and 2330 cm^{-1} bands and their relative infrared intensities⁴⁹ (trace D of Figure 6) lend further support to the $\nu_3 > \nu_1$ assignment for the oxonium salts. On cooling (see Figure 7) all the important spectral features are retained,

but become more evident due to better resolution caused by the narrower linewidths. Thus the D...F stretching vibrations at 380 cm^{-1} become very prominent in the infrared spectra.

An analysis of the bands attributable to SbF_6^- (IR: 668, 645, 590, 554, 548, 285sh, 270sh, 261; RA: 680sh, 673, 650sh, 640, 586, 554, 291sh, 287sh, 281, 265sh) shows again that a centrosymmetric space group, such as Ia3 must be ruled out and that the site symmetry can be at best C_3 . Thus the vibrational spectra appear to be compatible with a space group, such as $I2_13$ which was chosen for the above given neutron diffraction structure analysis.

Assignments for OD_2H^+ and ODH_2^+ . The vibrational spectra of the OD_3^+ salts showed bands at about 3160, 2920 and 1470 cm^{-1} , marked by an asterisk in Figure 3, which could not readily be attributed to combination bands of OD_3^+ . Assignment of the 1470 cm^{-1} infrared band to the antisymmetric stretching mode of HF_2^- is also unsatisfactory, because the band was also observed in the Raman spectrum which in turn did not show the expected symmetric HF_2^- stretching mode at 600 cm^{-1} . Furthermore, $\text{OD}_3^+\text{SbF}_6^-$ should result in the formation of OF_2^- and not of HF_2^- . Consequently, we have examined the possibility of these bands being due to small amounts of incompletely deuterated oxonium ions by recording the spectra of partially deuterated OH_3SbF_6 . As can be seen from trace B of Figure 6, the intensity of the band at about 3160, 2920 and 1470 cm^{-1} has increased strongly for the partially deuterated sample and therefore these bands are assigned to the OD_2H^+ cation. The observed frequencies closely correspond to those of isoelectronic NO_2H ⁵¹⁻⁵⁴ and the ab-initio calculated OD_2H^+ values⁴⁹ (see Table VIII). Consequently the 3160 and 1470 cm^{-1} bands are assigned to the OH stretching mode and the antisymmetric (A') OD_2H deformation mode, respectively of OD_2H^+ . The 2920 cm^{-1} band can readily be assigned to the first overtone of the 1470 cm^{-1} band being in Fermi resonance with the OH stretching mode. The antisymmetric and symmetric OD_2 stretching modes of

OO_2H^+ are expected to have frequencies of about 2400 and 2300 cm^{-1} ,^{49,51-54} respectively, and therefore are hidden underneath the intense OO_3^+ stretching modes. The antisymmetric (A'') OO_2H^+ deformation mode is expected^{49,51-54} to have a frequency between 1190 and 1250 cm^{-1} and therefore can be assigned to the infrared band at 1220 cm^{-1} observed in Trace B of Figure 6.

In addition to the bands attributed to OO_3^+ and OO_2H^+ , the infrared spectrum of the partially deuterated OH_3SbF_6 sample (calcd. product distribution: OO_3^+ 51.68, OD_2H^+ 38.16, OOH_2^+ 9.33, and OH_3^+ 0.77mol%) exhibits two bands at 1601 and 1388 cm^{-1} (see trace 8 of Figure 6). These bands are in excellent agreement with our expectations^{49,51-54} (see Table VIII) for $\delta_{as}(A'')$ and $\delta_{as}(A')$, respectively, of ODH_2^+ and are assigned accordingly. The OD and OH_2 stretching modes of OOH_2^+ are again buried in the broad intense bands centered at about 2400 and 3300 cm^{-1} and therefore cannot be located with any reliability. The symmetric deformation modes of OO_2H^+ and OOH_2^+ are probably giving rise to the strong shoulder in the 800-900 cm^{-1} range (trace 8 of Figure 6), but cannot be located precisely due to their broadness.

The above assignments for OD_2H^+ and ODH_2^+ are further substantiated by the low-temperature spectra shown in Figures 4 and 7, with the decreased line widths allowing a more precise location of the individual frequencies. Most of the infrared bands observed in the 320-510 cm^{-1} region for the low-temperature spectra of the different oxonium SbF_6^- salts are attributed to the O...F and H...F stretching modes of the hydrogen bridges.

In summary, most of the features observed for the vibrational spectra of the oxonium salts can satisfactorily be accounted for by the assumption of disordered higher-temperature and ordered, strongly hydrogen bridged, lower-temperature phases. Reasonable assignments can be made for the series OH_3^+ , ODH_2^+ , OD_2H^+ , OO_3^+ (see Table VI) which are in excellent agreement with

those of the corresponding isoelectronic ammonia molecules⁵¹⁻⁵⁴ and the results of recent ab-initio calculations⁴⁹ (see Tables VII and VIII). The only discrepancy between the ab-initio calculations and the experimental data exists in the area of the symmetric deformation modes. This could be caused by the low barrier to inversion in OH_3^+ ⁴⁹.

Force Constants. In view of our improved assignments for the oxonium cation, it was interesting to redetermine its force field. The frequencies and assignments given in Table VIII, a bond length of 1.01 Å and a bond angle of 110° were used to calculate a valence force field of OD_3^+ using a previously described method⁴ to obtain an exact fit between calculated and observed frequencies. The results of these computations are summarized in Table IX.

Since isotopic shifts obtained by light atom substitution, such as H-D, are virtually useless for the determination of a general valence force field⁵⁶, approximating methods were used. Three different force fields were computed for OD_3^+ to demonstrate that for a vibrationally weakly coupled system, such as OD_3^+ , the choice of the force field has little influence on its values. Our preferred force field is that assuming F_{22} and F_{44} being a minimum. This type of force field has previously been shown⁵⁷ to be a good approximation to a general valence force field for vibrationally weakly coupled systems. As can be seen from Table IX, the force field obtained in this manner is indeed very similar to the general force field previously reported⁵⁵ for ND_3 and NH_3 . The fact that the force constants of OD_3^+ deviate somewhat from those of OH_3^+ is mainly due to the broadness of the OH_3^+ vibrational bands and the associated uncertainties in their frequencies. Since the stretching frequencies of OD_3^+ are more precisely known than those of OH_3^+ , the OD_3^+ force field should be the more reliable one. The fact that F_{12} in NH_3 and ND_3 is somewhat larger than the value obtained for F_{12} in our $F_{22}=\text{Min}$ force field is insignificant because in the published⁵⁵ NH_3 force field F_{12} was not well determined and was con-

sequently assumed to equal $-2F_{34}$. The fact that the stretching force constant f_r in OD_3^+ is slightly lower and the deformation constant f_a in OD_3^+ is slightly higher than those in ND_3 is not unexpected. The ND_3 frequencies were those of the free molecule, whereas the OD_3^+ values are taken from the ionic solid $OD_3^+AsF_6^-$. In this solid, D-F bridging occurs (see above), hereby lowering the OD stretching and increasing the deformation frequencies. As secondary effects, the higher electronegativity of oxygen and the positive charge in OD_3^+ are expected to increase the polarity of the O-D bonds, thereby somewhat decreasing all the frequencies. These explanations can well account for the observed differences.

For the bending force constant f_a values of 0.576 and D.552 mdyn $\text{\AA}^0/\text{radian}^2$ were obtained for OD_3^+ and OH_3^+ , respectively. These values are in excellent agreement with the value of D.55 mdyn $\text{\AA}^0/\text{radian}^2$ obtained for OH_3^+ by an ab-initio calculation.⁴⁷

In summary, the results from our normal coordinate analysis lend strong support to our analysis of the vibrational spectra. They clearly demonstrate the existence of discrete OH_3^+ ions which in character closely resemble the free NH_3 molecule, except for some secondary effects caused by hydrogen-fluorine bridging.

Conclusion. The results of this study show that OD_3AsF_6 exists at room temperature in a plastic phase, whereas OD_3SbF_6 has an ordered structure. Based on diffraction data and vibrational spectra, a structural model is proposed for the ordered phase of OD_3SbF_6 . More experimental data are needed to define the exact nature of the ion motions and the associated phase changes in these salts. Many of the observations made in this study are in poor agreement with previous reports for other oxonium salts and cast some doubt on the general validity of some of the previous conclusions.

Due to their strong hydrogen-fluorine bridges and good thermal stability, oxonium salts of complex fluoro cations are well suited for further experimental studies.

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Table I. X-ray Diffraction Powder Pattern of OH_3AsF_6 at -153°C^a

d obs ($\overset{\circ}{\text{A}}$)	int	d obs ($\overset{\circ}{\text{A}}$)	int
6.35	vw	2.024	ms
4.95	s	2.010	m
4.72	s	1.942	m
4.12	w	1.913	vvw
3.87	w	1.877	ms
3.749 }	ms	1.871	w
3.730 }		1.802	vw
3.473	m	1.775	vw
3.225	m	1.769	vw
3.163	m	1.739	vw
3.029	mw	1.712	w
2.845 }	m	1.695	w
2.837 }		1.659	vw
2.596	w	1.648	mw
2.530	vw	1.612	w
2.362	vvw	1.585	mw
2.139	w	1.581	vw
2.061 }	m		
2.055 }			

^aCuK α radiation and Ni filter

Table II. Neutron Diffraction Powder Patterns of the Face Centered Cubic, Room Temperature Phases of OH_3AsF_6 , OD_3AsF_6 and O_2AsF_6 ^a

h k l	OH_3AsF_6		OD_3AsF_6	O_2AsF_6
	int calc	int obs	int obs	int obs
111	1100	1127	12	200
200	177	174	1033	1000
220	11	-	177	215
311	5	-	137	210
222	0	-	19	45
400	2	-	12	20
331	5	-	-	-
420	66	71	38	90
422	100	92	26	100
511/333	5	-	16	35

^a Intensities in arbitrary units

Table III. Room-Temperature X-ray Powder Data for OH_3SbF_6

$d_{\text{obsd}}, \overset{\circ}{\text{A}}$	$d_{\text{clcd}}, \overset{\circ}{\text{A}}$	Intens	h	k	l
5.04	5.04	vs	2	0	0
3.56	3.57	vs	2	2	0
2.909	2.912	mw	2	2	2
2.691	2.696	w	3	2	1
2.519	2.522	mw	4	0	0
2.374	2.378	w	4	1	1
2.254	2.256	m	4	2	0
2.149	2.151	mw	3	3	2
2.060	2.059	s	4	2	2
1.979	1.978	w	4	3	1
1.784	1.783	ms	4	4	0
1.682	1.681	ms	6	0	0, 4 4 2
1.637	1.636	vw	5	3	2
1.596	1.595	ms	6	2	0
1.519	1.521	ms	6	2	2
1.456	1.456	w	4	4	4
1.398	1.399	ms	6	4	0
1.372	1.373	vw	6	3	3
1.349	1.348	ms	6	4	2
1.282	1.281	vw	7	3	2, 6 5 1
1.262	1.261	vw	8	0	0
1.225	1.223	m	8	2	0, 6 4 4
1.189	1.189	m	8	2	2, 6 6 0
1.159	1.157	w	6	6	2
1.129	1.128	m	8	4	0
1.103	1.101	m	8	4	2

cubic, $a = 10.09\text{\AA}$, $V = 1027.2\text{\AA}^3$, $Z = 8$, $\rho_{\text{calc}} = 3.296 \text{ g cm}^{-3}$, CuK_α radiation, Ni filter

Table IV. Final Atomic Positional and Thermal Parameters
(with e.s.d. in parentheses) for OH_3SbF_6 from X-ray Data

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}
Sb	0.5	0.5	0.5	0.0205(18)		
O	0.25	0.25	0.25	0.043(17)		
F	0.4334(33)	0.6444(34)	0.6021(22)	0.059(20)	0.158(35)	0.003(12)
H	Not located					

Atomic Distances and Angles

Sb-F	1.891(19) $\overset{\circ}{\text{A}}$	F-Sb-F	180 $^\circ$
Sb-O	4.386 $\overset{\circ}{\text{A}}$	F-Sb-F	89.5 $^\circ$ (1.0)
O-F	2.63 $\overset{\circ}{\text{A}}$	F-Sb-F	90.5 $^\circ$ (1.0)
F-F	2.68/2.71 $\overset{\circ}{\text{A}}$		

Table V. X-ray and Neutron Powder Patterns of OD_3SbF_6 at Room Temperature

h k l	X-ray	Neutron	h k l	X-ray	Neutron
200	100	6	710/550/543	-	1
211	-	2	640	11	8
220	70	100	721/633/552	1	8
222	13	8	642	21	9
321	3	30	730	-	3
400	7	2	732/651	2	18
411/330	6	13	800	4	-
420	17	17	811/741/554	-	7
332	4	22	820/644	11	9
422	36	18	653	-	3
431/510	3	13	822/660	10	2
440	19	14	831/750/743	-	4
433/530	21	3	662	4	-
442/600	2	7	752	-	3
611/532	2	9	840	6	2
620	21	3			
541	1	14			
622	12	5			
631	-	2			
444	4	4			

Table VII. Frequencies (cm^{-1}), Frequency Shifts on Deuteration, and Relative Infrared Intensities of OO_3^+ and OH_3^+ Compared to Those of Gaseous NO_3 and NH_3^a and to the Results from Ab-Initio Calculations^b

Assignment for point group C_{3v}	Approximate description of mode	OO_3^+ obsd	OH_3^+ obsd	$\nu_{\text{OH}_3^+} \cdot \nu_{\text{OO}_3^+}$	NO_3	NH_3	$\nu_{\text{NH}_3} \cdot \nu_{\text{NO}_3}$	OO_3^+ calcd	OH_3^+ calcd	$\nu_{\text{OH}_3^+} \cdot \nu_{\text{OO}_3^+}$
A_1 ν_1	$\nu_{\text{sym}} \text{XY}_3$	2300(m)	3150(m)	1.37	2420	3336	1.38	2424(0.6)	3411(1.0)	1.41
ν_2	$\delta_{\text{sym}} \text{XY}_3$	715	900(m.br)	1.26	748	950	1.27	549(6.6)	725(13.9)	1.32
E ν_3	$\nu_{\text{asym}} \text{XY}_3$	2450(vs)	3300(vs)	1.35	2564	3444	1.34	2589(7.0)	3516(13.5)	1.36
ν_4	$\delta_{\text{asym}} \text{XY}_3$	1182(ms)	1620(ms)	1.37	1191	1626	1.37	1161(1.3)	1598(3.2)	1.38

(a) Data from ref 50. (b) Data from ref 49 after application of the suggested -12.3% frequency correction.

Table VIII. Frequencies (cm^{-1}) and Relative Infrared Intensities of OO_2H^+ and OOH_2^+ Compared to Those of Solid NO_2H and NHO_2^a and to the Results of Ab-Initio Calculations^b

Assignment for point group C_s	Approximate description of mode for XY_2Z	OO_2H^+		OO_2H^{+c}		NO_2H		OOH_2^+		NOH_2	
		clcd	obsd	obsd	clcd	obsd	obsd	clcd	obsd	obsd	obsd
A' ν_1	XZ stretch	3484(9.9)	3150(vs)	3329(s)	2532(4.4)						2447(s)
ν_2	sym XY_2 stretch	2476(2.1)		2392(m)	3450(5.8)						3300(m)
ν_3	asym deformation	1447(2.7)	1481(mw)	1476(mw)	1344(1.7)			1398(w)			1393(w)
ν_4	sym deformation	611(9.0)		905(vs)	671(11.5)						992(vs)
A'' ν_5	asym XY_2 stretch	2589(7.2)		2501(vs)	3516(13.5)						3359(vs)
ν_6	asym deformation	1186(1.2)	1229(w)	1254(w)	1580(3.4)			1613(mw)			1602(mw)

(a) Data from ref 52. (b) Data from ref 49 after application of the suggested -12.3% frequency correction. (c) Frequency values taken from the low-temperature IR spectra of the SbF_6^- salts.

Table IX. Symmetry and Internal Force Constants^a of OD₃⁺ Compared to Those of OH₃⁺, NH₃ and NO₃^b

Forcefield ^c	OD ₃ ⁺		OH ₃ ⁺		NH ₃ -NO ₃
	OFF	F ₂₂ and F ₄₄ ≡ Min	NH ₃ TR	F ₂₂ and F ₄₄ ≡ Min	
A ₁					GVFF
F ₁₁ = f _r + 2f _{rr}	6.030	6.0440	6.085	5.7783	6.4540
F ₂₂ = f _α + 2f _{αα}	0.4966	0.4964	0.5097	0.4470	0.4130
F ₁₂ = 2f _{rα} + f _{rα'}	0	0.0532	0.3276	0.0244	0.3276
F ₃₃ = f _r - f _{rr}	6.0595	6.1194	6.133	5.9696	6.4732
F ₄₄ = f _α - f _{αα}	0.6162	0.6131	0.6132	0.6053	0.6285
F ₃₄ = -f _{rα} + f _{rα'}	0	-0.1240	-0.1638	-0.0661	-0.1638
f _r	6.0497	6.0943	6.117	5.9058	6.4668
f _{rr}	-0.0098	-0.0251	-0.016	-0.0638	-0.0064
f _α	0.5763	0.5762	0.5787	0.5525	0.5567
f _{αα}	-0.0399	-0.0369	-0.0345	-0.0528	-0.0718
f _{rα}	0	0.0591	0.1638	0.0359	0.1638
f _{rα'}	0	-0.0649	0	-0.0302	0

(a) Stretching constants in mdyn/Å, deformation constants in mdyn/Å/radian², and stretch-bend interaction constants in mdyn/radian. The following bond angles and lengths were used, OD₃⁺ and OH₃⁺, 110° and 1.01Å, NH₃, 107° and 1.01Å, and the bending coordinates were weighted by unit (1Å) distance. Frequency values used: OD₃⁺, ν₁=2300, ν₂=715, ν₃=2450, ν₄=1182; OH₃⁺, ν₁=3150, ν₂=900, ν₃=3300, ν₄=1620cm⁻¹. (b) Values from ref 55 assuming F₁₂ = -2F₃₄. (c) The potential energy distribution for OD₃⁺ showed all fundamentals to be close to or 100% characteristic with the largest amount of mixing being observed for ν₄ in the NH₃ transfer force field of OH₃⁺.

Diagram Captions

Figure 1. - Neutron powder diffraction diagram of OD_3SbF_6 at ambient temperature, traces A and B, observed and calculated profiles, respectively.

Figure 2. - ORTEP stereoview of the structure of OD_3SbF_6 . The bridging F_2 atoms are differentiated from the non-bridging F_1 atoms by smaller circles marked by traces.

Figure 3. - Vibrational spectra of solid OD_3AsF_6 at room temperature. Trace A, infrared spectrum of the solid pressed between AgCl disks. The broken line indicates absorption due to the window material. The bands marked by an asterisk are due to OO_2H^+ mainly formed during sample handling. Traces B and C, Raman spectra recorded at two different sensitivities with a spectral slit width of 3 and 8 cm^{-1} , respectively.

Figure 4. - Vibrational spectra of solid OD_3AsF_6 at low-temperature. Trace A, infrared spectrum of the solid pressed between AgCl disks and recorded at -196°C . Traces B and C, Raman spectra recorded at -100°C at two different sensitivities.

Figure 5. - Raman spectra of OD_3SbF_6 and OD_3AsF_6 at different temperature contrasting the slow gradual temperature induced line broadening for the ordered OD_3SbF_6 phase against the abrupt change within a narrow temperature range for OD_3AsF_6 caused by the transition from an ordered to a plastic phase.

Figure 6. - Vibrational spectra of solid OD_3SbF_6 , OH_3SbF_6 and partially deuterated OH_3SbF_6 at room temperature. Trace A, IR spectrum of OH_3SbF_6 ; trace B, IR spectrum of partially deuterated OH_3SbF_6 containing about equimolar amounts of OD_3SbF_6 , and OD_2HSbF_6 and smaller amounts of ODH_2SbF_6 ; trace C, IR spectrum of OD_3SbF_6 containing a significant amount of OD_2HSbF_6 formed during sample handling; trace D, IR spectrum of OO_3SbF_6 containing only a small amount of OO_2HSbF_6 ; traces E and F, RA spectra of OD_3SbF_6 recorded at two different sensitivities.

Figure 7. - Vibrational spectra of solid OD_3SbF_6 and partially deuterated OH_3SbF_6 at low temperature. Traces A and B, infrared spectra of partially deuterated OH_3SbF_6 and of OD_3SbF_6 , respectively, between AgBr windows; traces C and C, Raman spectra recorded at two different sensitivities.

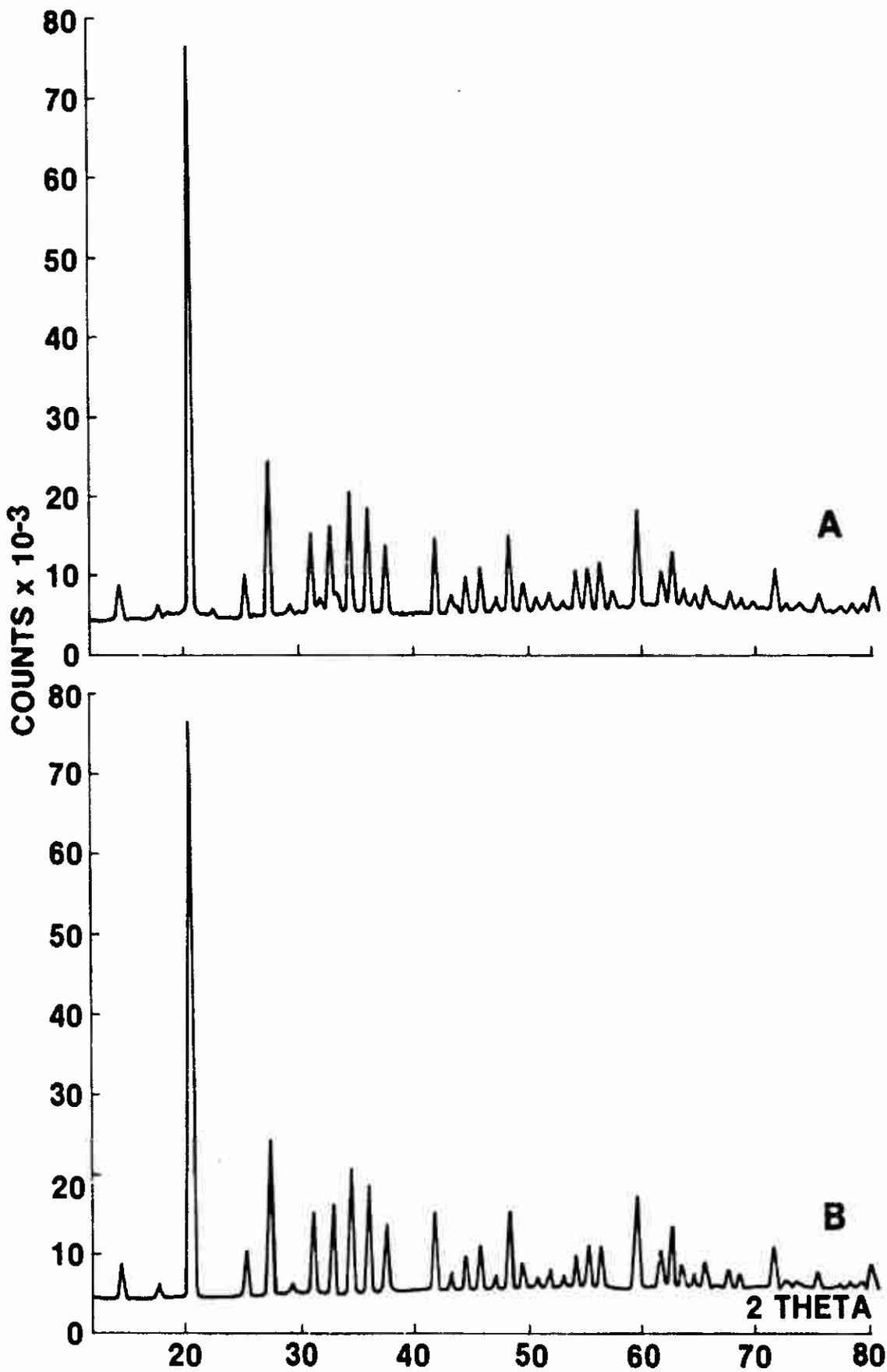


FIGURE 1. S-38

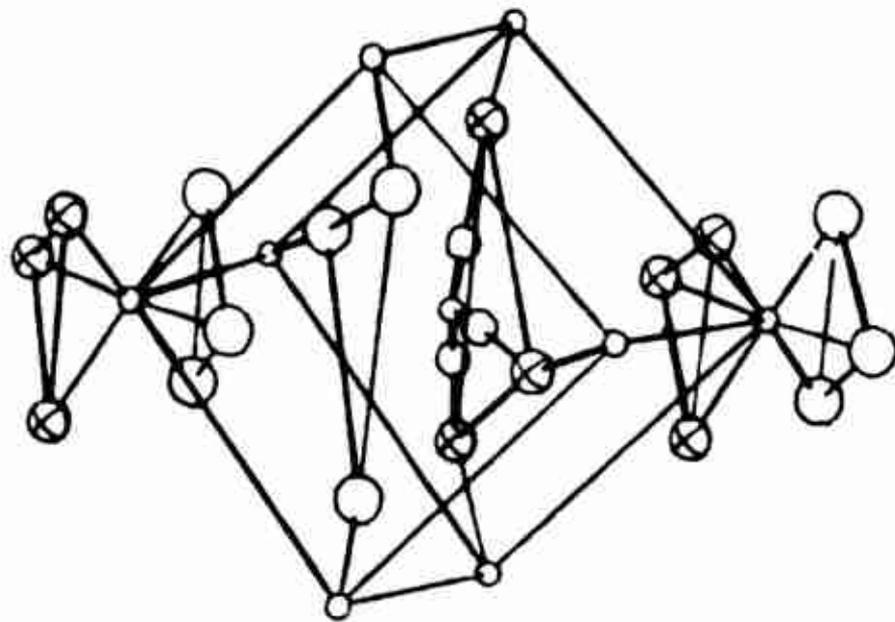
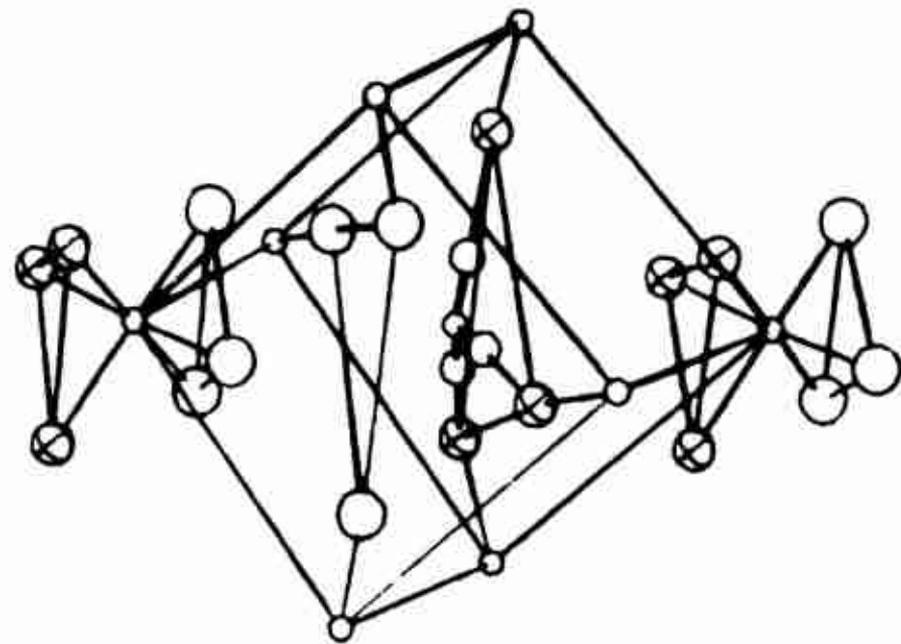


FIGURE 2.

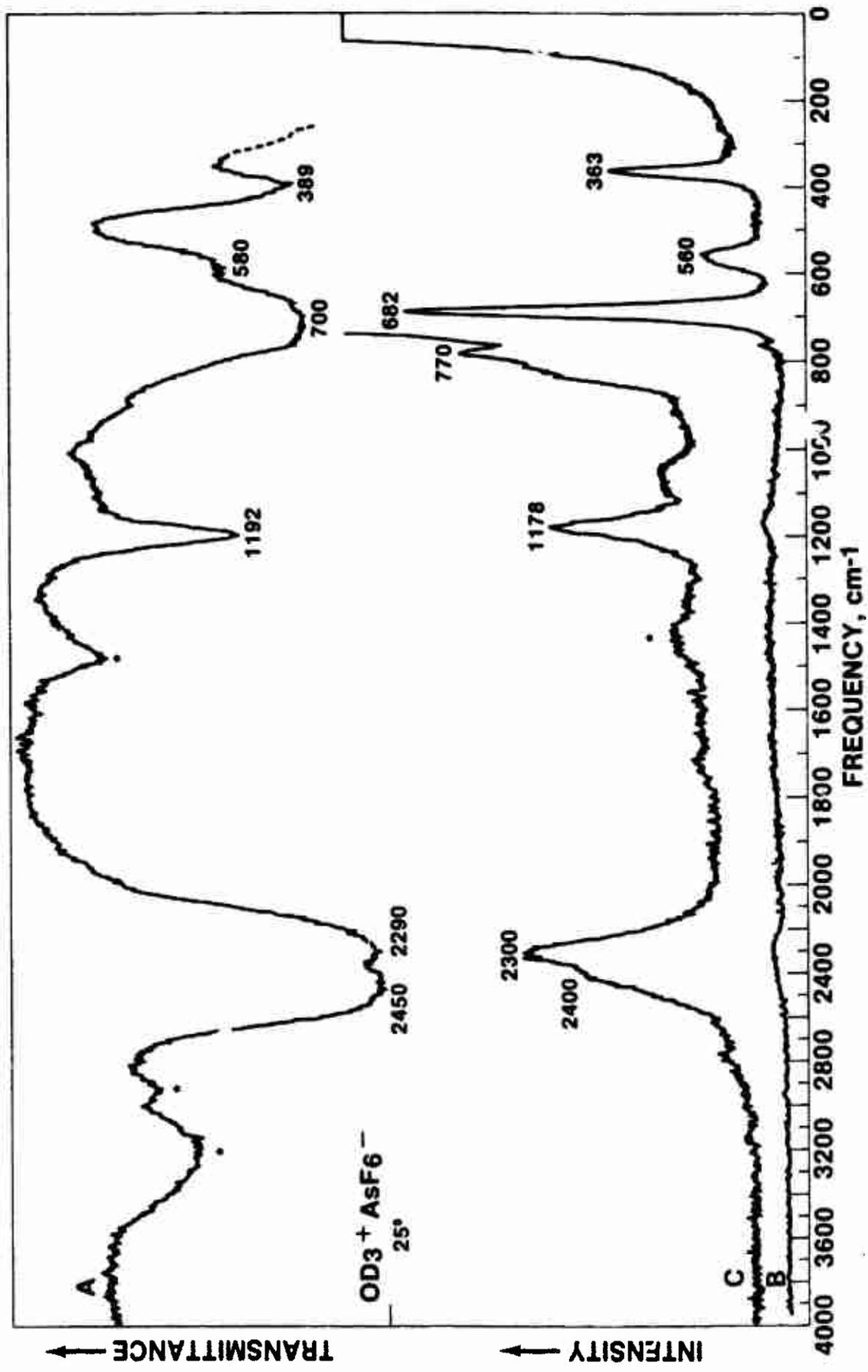
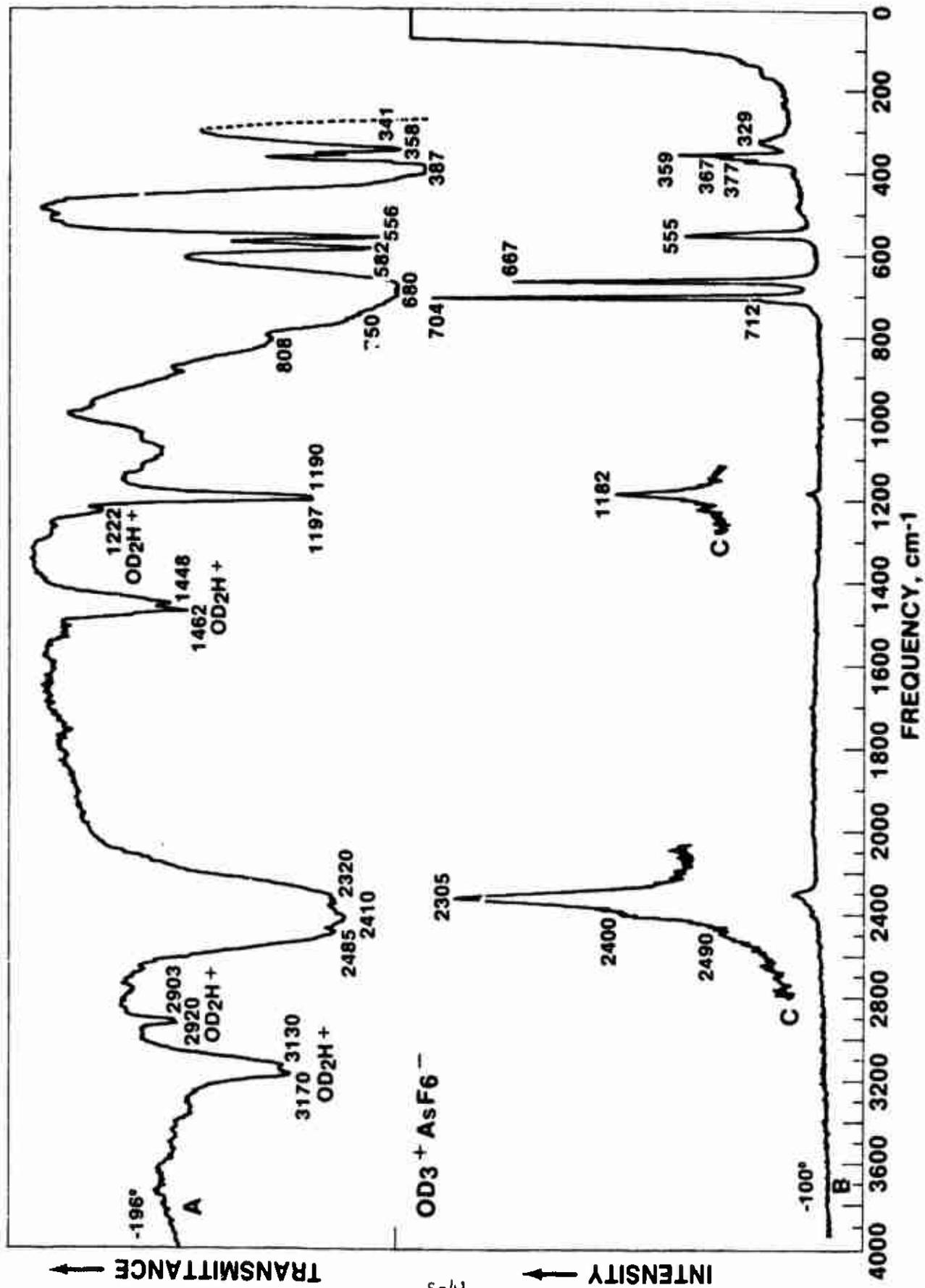


FIGURE 3.



14-5

FIGURE 4.

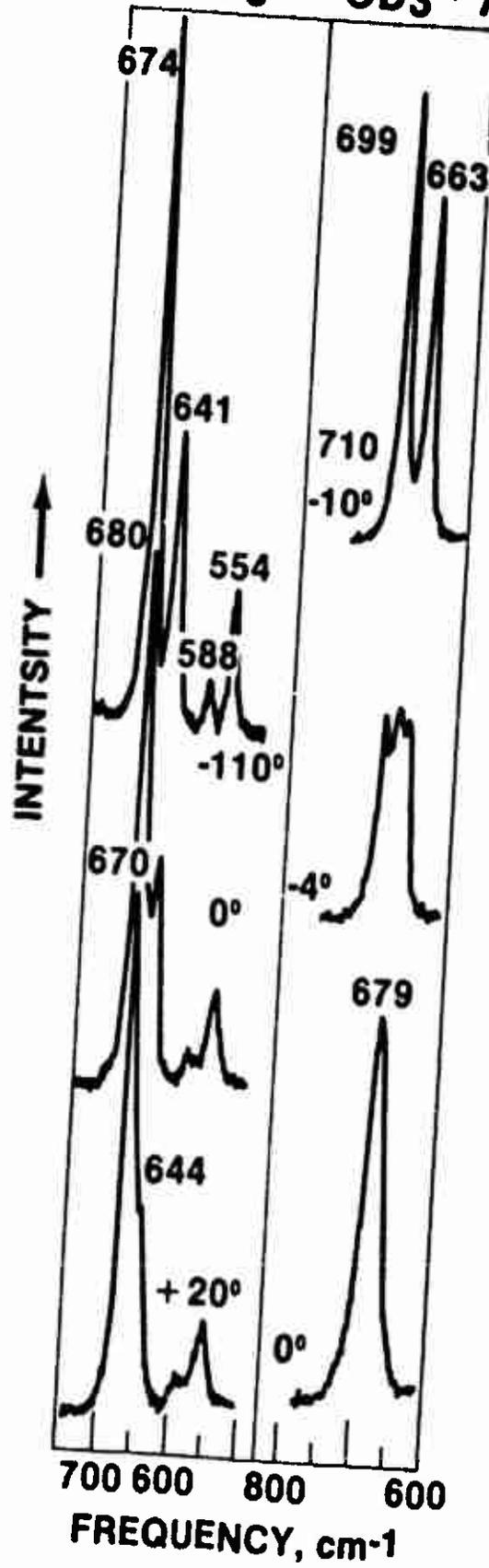
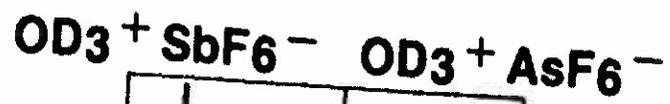


FIGURE 5.

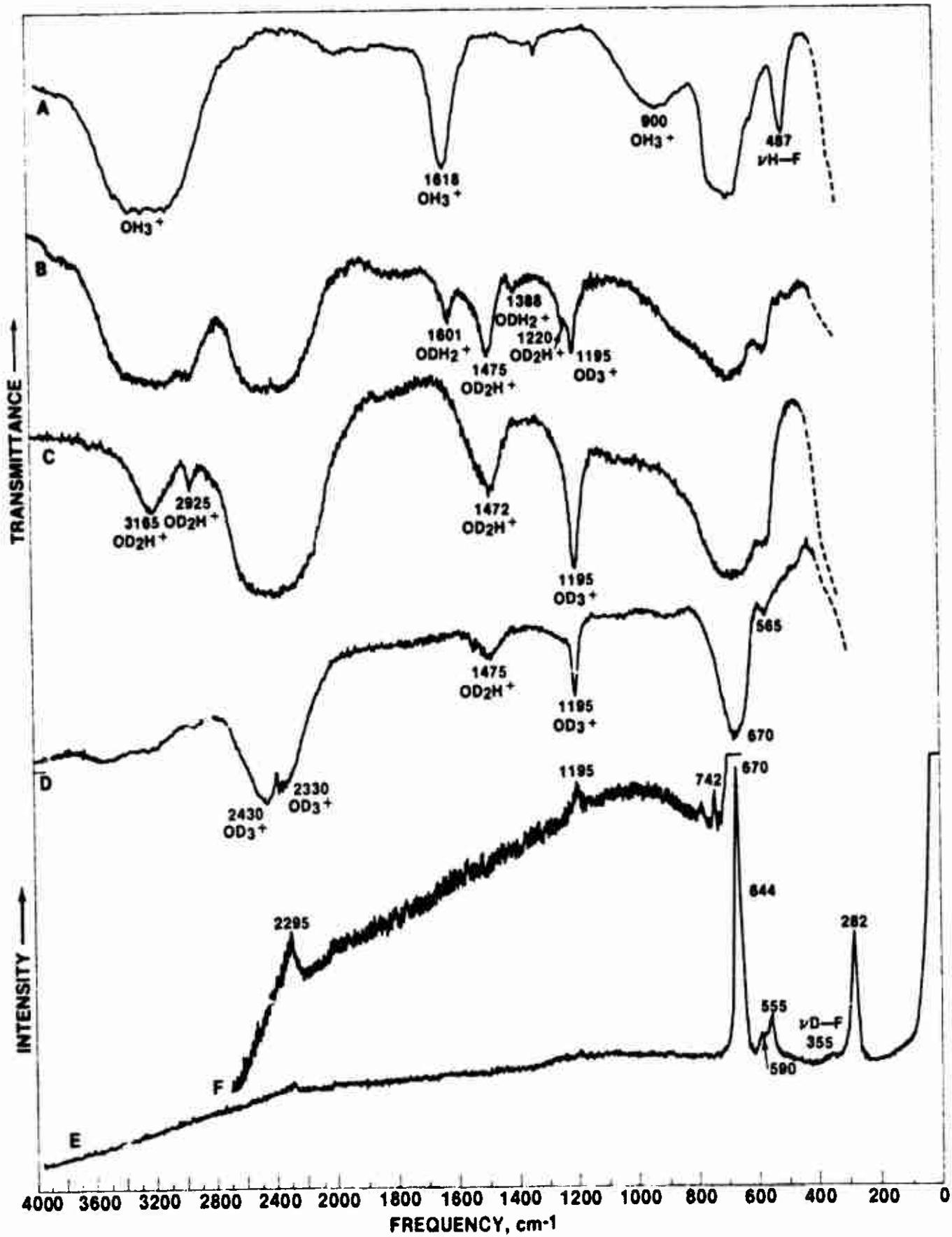


FIGURE 6.

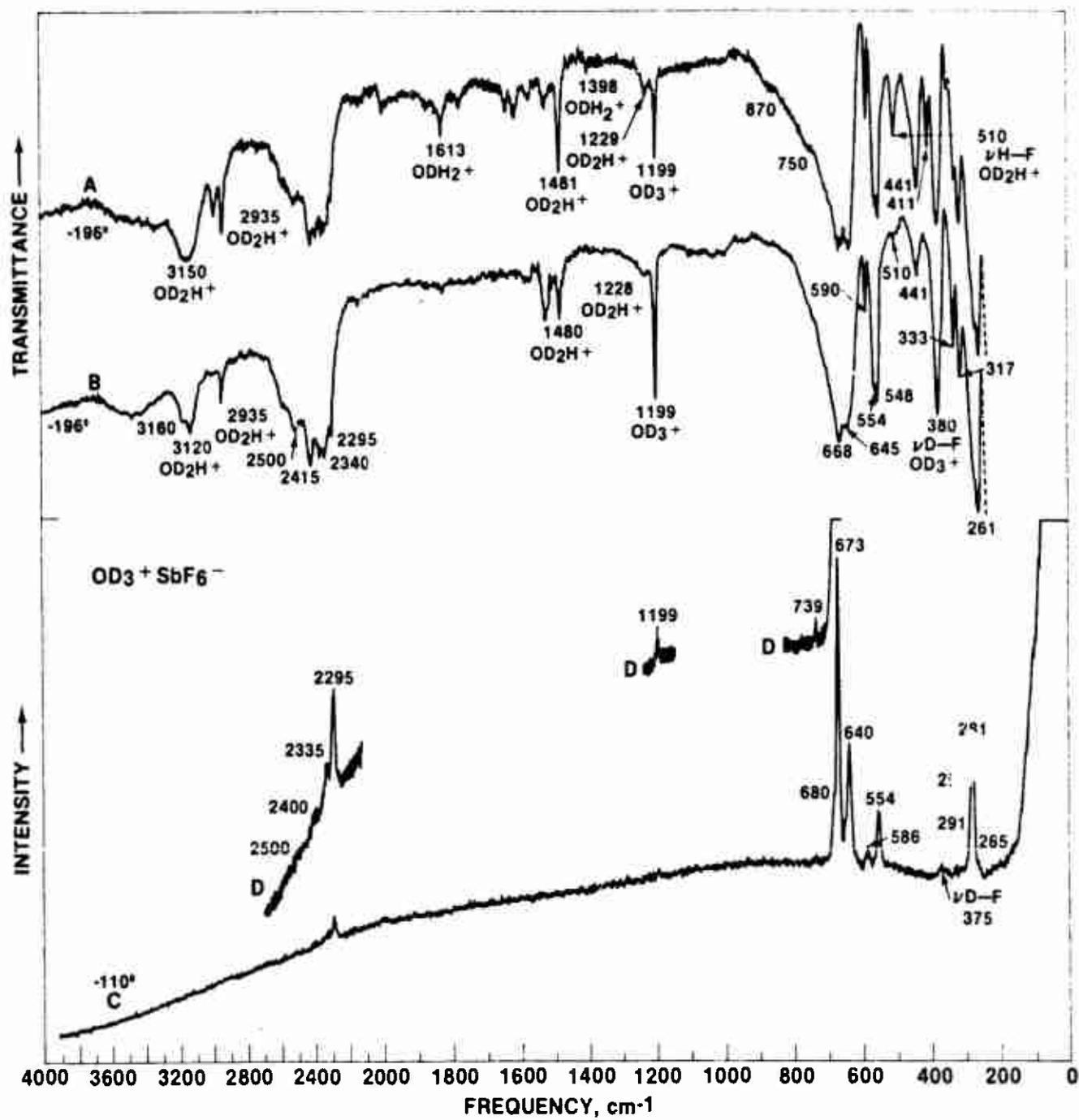
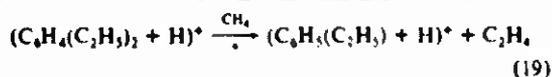
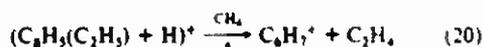


FIGURE 7.

The Cl ion chromatogram contains the usual CH_4 Cl ions: predominantly protonated diethylbenzene and smaller amounts of $(\text{M} - \text{H})^+$, $(\text{M} + \text{C}_2\text{H}_5)^+$, and $(\text{M} + \text{C}_3\text{H}_7)^+$. The HPCA spectra contain several fragment ions diagnostic of the structure of the sample with the major dissociation pathways being



and



HPCA mass spectra acquired at a fixed extent of dissociation cannot provide the detailed structural information obtained from a breakdown curve. However, when combined with the Cl mass spectra and GC retention times, the HPCA data provide a potentially powerful additional dimension in sample characterization.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. CH_4 , 74-82-8; C_2H_4 , 74-84-0; ethyl acetate, 141-78-6; 3-heptanone, 106-35-4; o-dichlorobenzene, 95-50-1; m-dichlorobenzene, 541-73-1; ethylbenzene, 100-41-4; m-xylene, 108-38-3; p-xylene, 106-42-3.

APPENDIX T

EPR Evidence on Molecular and Electronic Structure of Nitrogen Trifluoride Radical Cation

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Abstract: Computer simulations of the EPR spectra of rigid $^{14}\text{NF}_3^+$ and $^{15}\text{NF}_3^+$, trapped in powdered NF_4AsF_6 at 25 K show characteristics of a trigonal pyramid with the following principal values for the coupling matrices: $|g(\parallel, \perp)| = 2.003$, $|A_{\text{N}}(\parallel, \perp)| = 324, 187$ MHz; $A_{\text{F}}(\parallel, \perp) = 451, 260$ MHz; $A_{\text{HF}}(\sigma, \pi, \rho) = 880, 340, 360$ MHz; α , the angle between parallel axes for A_{F} and $A_{\text{N}} = 15^\circ$. The nitrogen p:s spin-density ratio (computed from the nitrogen hyperfine splittings) is consistent with $\text{sp}^{2.5}$ nitrogen hybrids in the NF bonds and with a pyramid angle of about 105° . Although the same pyramid angle appears to agree with the orientation of the principal axis of the fluorine hyperfine coupling matrix ($|\alpha| = 15^\circ$, pyramid angle = $90^\circ + |\alpha|$), electronic structure computations imply that α is negative and that the agreement is fortuitous. Some comparisons are made with isoelectronic radicals BF_3^- and CF_3^- —the latter being essentially tetrahedral with sp^3 hybridization.

Goldberg, Crowe, and Christe have presented high- and low-temperature EPR spectra of the radical cations $^{14}\text{NF}_3^+$ and $^{15}\text{NF}_3^+$, produced by γ -irradiation of NF_4AsF_6 .¹ Their analyses properly accounted for the high-temperature (~ 240 K) spectra, but computational limitations prevented a complete analysis of the low-temperature (~ 25 K) EPR spectra, which are drastically different. At the high temperature, the molecule is axially symmetric, apparently spinning freely, probably both about its threefold axis and about an axis nearer to the F_3 plane. In contrast, at the low temperature, each molecule appears to be locked into a fixed orientation and the EPR spectra are, as expected, much more complex. Now, with an appropriately modified computer simulation program, we are able to interpret these low-temperature spectra.

Several studies providing information on hyperfine coupling, spin density, and geometry of the isoelectronic species BF_3^- and CF_3^- have been published.²⁻⁷ The opportunity to compare those bonding features that can be deduced from hyperfine matrices of the isoelectronic series provides one of the motivations for the study of NF_3^+ . Here we describe our interpretation of the low-temperature EPR spectra and draw conclusions regarding geometry and bonding in the nitrogen trifluoride radical cation.

Experiment and Computation

Low-temperature EPR spectra of $^{14}\text{NF}_3^+$ and $^{15}\text{NF}_3^+$ have been described¹ as have the synthesis, experimental conditions, and the spectrometer used in this work. The spectra chosen for the current analysis are reproduced in the figures.

Simulated EPR spectra are generated by means of the program "POWD" running on the VAX 11/780 computer connected to a Houston Instruments HILOT digital plotter. Program POWD has its origins in an EPR powder simulation program, kindly provided by Dr. J. R. Pilbrow of Monash University, which employs second-order perturbation theory for the first nucleus and first-order approximations for superhyperfine terms. It was revised by White and Belford^{8,9} and Chasteen et al.¹⁰ into EPRPOW. Nilges and Belford^{11,12} rewrote this program as POW to employ more efficient angular sampling (to minimize the unevenness of point density on the sphere) and integration technique (four-point Gauss quadrature).¹³ The version of POWD that we have created for the current work is a substantially modified POW that uses a perturbation method accurate to second order in all hyperfine terms (including internuclear cross-terms)¹⁴ to calculate a powder spectrum for a spin $S = 1/2$ system with up to four hyperfine nuclei. Program POWD permits principal axes of all four hyperfine nuclei interaction matrices as well as those of the

(1) I. B. Goldberg, H. R. Crowe, and K. O. Christe, *Inorg. Chem.*, **17**, 3189 (1978).

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(11) M. J. Nilges and R. L. Belford, *J. Magn. Reson.*, **35**, 259 (1975).

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(13) R. L. Belford and M. J. Nilges, "Computer Simulation of EPR Powder Spectra", Symposium on Electron Paramagnetic Resonance Spectroscopy, Rocky Mountain Conference on Analytical Chemistry, Denver, August 1979.

(14) J. A. Weil, *J. Magn. Reson.*, **18**, 113 (1975).

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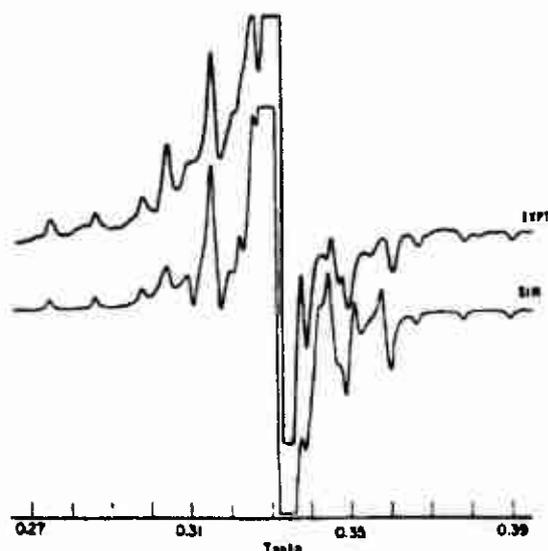


Figure 1. (EXPT) EPR spectrum of $^{14}\text{NF}_3^+$ at 26 K in NF_4F_6 γ -irradiation at 77 K after annealing at 195 K. (SIM) $^{14}\text{NF}_3^+$ computer simulation with the parameters listed in Table I.

g tensor to be noncoincident. For this computation, all nuclear Zeeman and quadrupole terms are deemed insignificant and are ignored.

Theory

The Hamiltonian is

$$\mathcal{H}_1 = \beta \vec{S} \cdot \vec{g} \cdot \vec{B} + \sum_r \vec{I}_r \cdot \vec{A}_r \cdot \vec{S}$$

which generates the following energy terms, correct to the second order of perturbation:⁴

$$E(M, m_1, m_2, m_3, m_4) =$$

$$g\beta B M_S + \left[K_1 M_1 m_1 + \frac{M_1}{2g\beta B} \left\{ \frac{1}{2} (\text{tr}(\vec{A}_1 \cdot \vec{A}_1) - k_1^2) \left(\frac{1}{2} \right) (I_1(I_1 + 1) - m_1^2) \right\} \right] + \left[K_2 M_1 m_2 + \frac{M_2}{2g\beta B} \left\{ \frac{1}{2} (\text{tr}(\vec{A}_2 \cdot \vec{A}_2) - k_2^2) \left(\frac{1}{2} \right) \times (I_2(I_2 + 1) - m_2^2) \right\} \right] + \dots + \frac{1}{2g\beta B} \left[\left\{ -\frac{\text{Det}(A_1)}{K_1} \left(\frac{1}{2} \right) m_1 + (k_1^2 - K_1^2) M_1 m_1^2 \right\} + \left\{ -\frac{\text{Det}(A_2)}{K_2} \left(\frac{1}{2} \right) m_2 + (k_2^2 - K_2^2) M_2 m_2^2 \right\} + \dots \right] + \frac{M_1}{2g\beta B} [(L_{12} - K_1 K_2) m_1 m_2 + (L_{13} - K_1 K_3) m_1 m_3 + (L_{14} - K_1 K_4) m_1 m_4 + (L_{23} - K_2 K_3) m_2 m_3 + (L_{24} - K_2 K_4) m_2 m_4 + (L_{34} - K_3 K_4) m_3 m_4]$$

where

$$\begin{aligned} g^2 &= \vec{g} \cdot \vec{g} \cdot \vec{g} \\ g^2 K_1^2 &= \vec{g} \cdot \vec{g} \cdot \vec{A}_1 \cdot \vec{A}_1 \cdot \vec{g} \cdot \vec{g} \\ g^2 K_1^2 k_1^2 &= \vec{g} \cdot \vec{g} \cdot \vec{A}_1 \cdot \vec{A}_1 \cdot \vec{A}_1 \cdot \vec{A}_1 \cdot \vec{g} \cdot \vec{g} \\ g^2 K_1 K_2 L_{12} &= \vec{g} \cdot \vec{g} \cdot \frac{1}{2} (\vec{A}_1 \cdot \vec{A}_1 \cdot \vec{A}_2 \cdot \vec{A}_2 + \vec{A}_2 \cdot \vec{A}_2 \cdot \vec{A}_1 \cdot \vec{A}_1) \cdot \vec{g} \cdot \vec{g} \end{aligned}$$

These terms are used in POWD to construct transition energies from which transition fields are computed by an approximation to the

Table I. Hyperfine Matrices^a and g Values of $^{14}\text{NF}_3^+$ and $^{15}\text{NF}_3^+$.

	$^{14}\text{NF}_3^+$	$^{15}\text{NF}_3^+$
$A_N(\parallel)$	(+) 187.1 \pm 5.0 ^b	(-) 259.5 \pm 7
$A_N(\perp)$	(+) 324.3 \pm 1.4	(-) 450.8 \pm 2
$A_F(x)$	(+) 340.0 \pm 20	(+) 340.0 \pm 20
$A_F(y)$	(-) 360.0 \pm 20	(+) 360.0 \pm 20
$A_F(z)$	(+) 880.0 \pm 1	(+) 880.0 \pm 1
$g(\parallel)$	2.002	2.002
$g(\perp)$	2.001	2.001
α	15.0 \pm 1 ^c	15.0 \pm 1 ^c

^a Hyperfine splittings are in MHz. ^b Uncertainties were estimated by comparing numerous simulations to the experimental spectra. The estimates given are ranges outside which, in our subjective judgment, a satisfactory fit to the spectra could not be achieved.

first-order frequency shift perturbation formula.¹⁵

Low-Temperature Spectrum of $^{14}\text{NF}_3^+$. The overall shape of the experimental EPR spectrum (see Figure 1) does not match our preliminary computer simulations. The comparisons suggest that the experimental spectrum contains a spurious component—a broad background. The EPR spectra of BF_3^{-2} exhibited a similar background, which was attributed to a matrix radical ($-\text{CH}_2\text{SiMe}_3$). Accordingly, a background curve consisting of a single, broad peak was included for all simulations of NF_3^+ . A word of caution is in order. Even though we had to include an extra background peak to accomplish the analysis, we cannot prove that it is not part of the spectrum of the species under study. To avoid any further arbitrariness, we allowed this background to have no structure. The necessity for including a superimposed background spectrum introduces extra uncertainty in the parameters, especially the perpendicular peaks that are located where the background is most intense. Because the hyperfine splitting is larger for parallel peaks, these peaks are masked to a lesser degree.

The additional uncertainty introduced by the background spectrum is somewhat compensated for by the availability of spectra for two different nitrogen isotopes. The ground rules for simulation of the two isotopic species are as follows. Both spectra should be defined by identical g matrices and fluorine hyperfine matrices and angle α . (Note: α is the angle between the principal axes of the ^{19}F and N hyperfine matrices; it may be close to the angle between the $\text{N}-\text{F}$ bond and the plane of the three fluorines (see Figure 3 and Discussion).) The nitrogen hyperfine matrix elements should be related by a factor of -1.4029 , which is the ratio of their nuclear moments (i.e., $A_{\perp}(^{15}\text{N})/A_{\perp}(^{14}\text{N}) = A_{\parallel}(^{15}\text{N})/A_{\parallel}(^{14}\text{N}) = -1.4029$). Fitting two isotopic spectra with the same parameters in this way increases our confidence in the resulting values.

Low-Temperature Spectrum of $^{15}\text{NF}_3^+$. Similarly, the $^{15}\text{NF}_3^+$ experimental spectrum (see Figure 2) also suggests a broad background resonance, which was included in the simulations.

Discussion

The principal values of the hyperfine and g matrices for both isotopes are listed in Table I. One can estimate the spin density of the free electron from the nitrogen hyperfine parameters obtained from the $^{14}\text{NF}_3^+$ simulation and the equations in the article by Goldberg et al.¹

$$\rho_N^s = a_N(\text{iso})/a_N^0 \quad \rho_N^p = (A_N(\parallel) - a_N(\text{iso}))/2h^0_N$$

In these equations ρ_N^s and ρ_N^p are integrated spin densities of the s and p orbitals; a_N^0 and h^0_N are the reference atomic isotropic and anisotropic hyperfine couplings,¹⁶ respectively. The calculated ratio of ρ_N^p to ρ_N^s , 6.37, suggests the unpaired electron to be largely in the following hybrid orbitals:

$$\psi_1 = 0.9293\psi_N(2p_z) + 0.3694\psi_N(2s)$$

(15) R. L. Belford, P. H. Davis, G. G. Belford, T. M. Lenhart, *ACS Symp. Ser.*, No. 5 (1974).

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Table II. Comparison of Hyperfine Couplings^a and Spin Densities^b of M^+ Radicals

	$A_M(x)$	$A_M(y)$	$A_M(z)$	$a_M(\text{iso})$	$A_F(x)$	$A_F(y)$	$A_F(z)$	$a_F(\text{iso})$	ρ_M^s	ρ_M^p	ρ_F^s	ρ_F^p	hybridization of M-F bond	
BF_3^+				428.7 ^c				498.8 ^c	0.211		0.0104			
CF_3^+	667.7 ^d	720.8 ^d	891.2 ^d	759.9 ^d	258.1 ^d	246.8 ^d	709.1 ^d	404.7 ^d	0.244	0.723	0.0084	0.1113	$sp^{3.01}$	
CF_3^+					244.1 ^e	224.4 ^e	738.5 ^e	402.3 ^d						
NF_3^+	187.1 ^f	187.1 ^f	324.3 ^f	232.8 ^f	340.0 ^f	360.0 ^f	880.0 ^f	526.7 ^f	0.151 (0.129)	0.957 (0.824)	0.0110	0.1166	$sp^{3.47}$	

^a Hyperfine splittings are in MHz. ^b Spin densities are calculated from hyperfine values as in ref 1 and 16; those in parentheses are calculated from the newer compilation by J. R. Morton and K. F. Preston, *J. Magn. Reson.* 30, 577 (1978). ^c See ref 2. ^d See ref 5. ^e See ref 6 and 7. ^f This work.

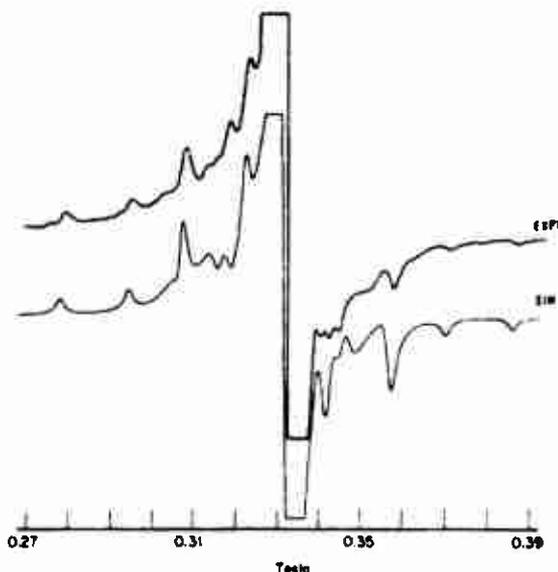


Figure 2. (EXPT) EPR spectrum at $^{15}\text{NF}_3^+$ at 24 K in $^{15}\text{NF}_3\text{A}_3\text{F}_6$, γ -irradiated at 77 K after annealing at 195 K. (SIM) $^{15}\text{NF}_3^+$, computer simulation generated by the program POWD with the variables listed in Table I. See text.

having about 13.6% s and 86.4% p character. A simplified hybrid orbital picture of the bonding in NF_3^+ can then be constructed in the following way. Starting with an isolated $^{15}\text{N}^+$ ion (prepared for bonding with four valence electrons in four orbitals—one s and three p ($2s^1, 2p^3 \uparrow \uparrow \uparrow$)) and eliminating the singly occupied nonbonding $s^{0.136}p^{0.864}$ orbital from the s and 3p's leaves 0.8635 s and 2.1365 p—that is, three N-F bonds, each using a nitrogen hybrid $s^{0.2878}p^{0.7122}$ or ca. $sp^{2.5}$. Now it is interesting to predict the angle, α' , between $sp^{2.5}$ orbitals and the plane of the 3 F atoms¹⁷ and compare it with the angle α , which characterizes the ^{19}F hyperfine interaction anisotropy.

The four N^+ bonding electrons must be placed in four orthogonal orbitals, the nonbonding one directed along the z axis (ψ_1) and three equivalent ones (ψ_2, ψ_3, ψ_4) directed along the N-F bonds. It is sufficient to consider any one of the bonding orbitals, ψ_2 , chosen to be directed somewhere in the xz plane (Figure 3). Orthonormality requires $\langle \psi_1, \psi_2 \rangle = 0$ and

$$\psi_1 = (1 - 3f)^{1/2}\psi_N(2s) + (3f)^{1/2}\psi_N(2p_z)$$

$$\psi_2 = f^{1/2}\psi_N(2s) + (1 - f)^{1/2}\psi_N(2p_x) + f^{1/2}\psi_N(2s) + (1 - f)^{1/2}[-\cos \lambda \psi_N(2p_y) + \sin \lambda \psi_N(2p_z)]$$

where the f is the fraction of s character in the nitrogen bonding orbital ψ_2 . With $3f^{1/2} = 0.9293$ as previously estimated, we find $\cos \lambda = 0.2527$, or $\lambda = 75.4^\circ$, $\alpha' = 14.6^\circ$. The angle between

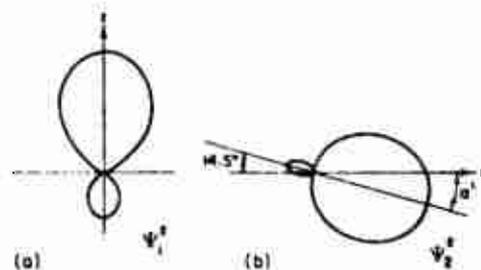


Figure 3. (a) Nonbonding orbital directed along the z axis, ψ_1 . This orbital is a linear combination of a nitrogen 2s and 2p_z orbital. (b) One of the three nitrogen bonding orbitals. This orbital is in the xz plane and is directed along the N-F bond.

any NF bond and the threefold axis might be expected to be about 104.6° , a little under the tetrahedral angle (109.5°).

It is interesting that the magnitude of α' agrees with the value of $|\alpha| = 15 \pm 1^\circ$ (Table I). The consistency in magnitude between the isotropic and dipolar nitrogen hyperfine matrix and the dipolar fluorine hyperfine matrix within a simple hybrid-orbital picture of bonding is remarkable. However, since the experiment and simulations provide only the magnitude of α and not its sign, the agreement could be illusory. A similar, generally consistent picture can be constructed for -CF_3 , which was previously analyzed. For this radical, the magnitude of α was 17.8° , and judging from the ^{13}C hyperfine matrices, it has a consistent hybridization of $\sim sp^2$; more specifically, $\alpha' = 19.6^\circ$; Edlund et al.¹⁶ propose, on the basis of INDO calculations, that the measured value of α is actually -17.8° . That is, they assert that, fortuitously, the spin-density distribution is such that α and α' are approximately equal in magnitude but opposite in sign, making a large angle ($\sim 37^\circ$) between the principal axis of the fluorine hyperfine matrix and the normal to the C-F bond. With no more information, it is difficult to judge the validity of their conclusion, particularly as INDO methods are grounded in a great many formidable approximations. However, since Edlund et al. supplemented their INDO work with a few ab initio computations, with similar results, one must suspect that α really is negative for -CF_3 and possibly for -NF_3^+ and/or -BF_3^- as well. Therefore, Benzal et al.¹⁹ have carried out full ab initio computations, with geometric variation to establish the potential minima, on the isoelectronic series -NF_3^+ , -CF_3 , and -BF_3^- . The results, presented in the following paper, generally confirm the proposition of Edlund et al.¹⁶ They support the idea that the main fluorine contribution to the singly occupied molecular orbital (HOMO) is a p orbital that is directed along the principal axis of the ^{19}F hyperfine coupling matrix but that is neither coincident with nor orthogonal to any of the bonds or molecular symmetry axes. The anisotropic part of the fluorine hyperfine coupling apparently can indicate the spin density and orientation of this participating p orbital but cannot be used to establish the molecular geometry.

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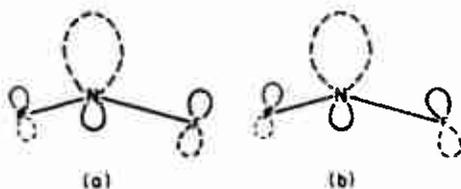


Figure 4. Schematic representation of the two possible local orbital schemes for the highest (singly) occupied molecular orbital in $\text{NF}_3^{\bullet+}$: (a) F orbital essentially orthogonal to bond direction, $\alpha = +15^\circ$; (b) F orbital tilted toward bond direction, $\alpha = -15^\circ$.

Conclusions

Despite an apparently large, diffuse background, it has been possible to obtain satisfactory Zeeman, nitrogen hyperfine, and fluorine hyperfine matrices for the rigid trigonal-pyramidal $\text{NF}_3^{\bullet+}$ radical cation by computer simulation of the EPR spectra of λ -irradiated NF_3AsF_6 and $^{15}\text{NF}_3\text{AsF}_6$, annealed and then cooled to ~ 25 K.

All the data can be rationalized in terms of a hybrid-orbital bonding scheme with (1) the unpaired electron in mainly a non-bonding $\text{N}(sp^{3.3})$ orbital (which also to some extent involves fluorine p orbitals in an antibonding interaction), (2) $sp^{2.5}$ nitrogen hybrid bonding orbitals, (3) 105° angles between the threefold

axis and the N-F bonds, and (4) the fluorine part of the HOMO being mainly p_z -like, with its z axis tilted plus or minus 15° from the threefold axis (see Figure 4).

The isoelectronic radical CF_3^{\bullet} is similar, the corresponding angle being 108° and the carbon bonding hybrids about sp^3 (see Table II). Unfortunately, no anisotropic data are available for $\text{BF}_3^{\bullet-}$, the next member of the isoelectronic series; isotropic parameters are compared in Table II.

The structural angles between the C_3 axis and normals to the bonds for $\text{NF}_3^{\bullet+}$ and CF_3^{\bullet} are $\sim 14.6^\circ$ and 19.6° , respectively. The principal axes of the fluorine hyperfine matrices deviate from the C_3 axes by $\sim 15^\circ$ and 18° , respectively. Depending on the sign of this deviation, these fluorine A axes could be either essentially perpendicular to or tilted, by $\sim 30^\circ$ or 37° , respectively, from the N-F or C-F bonds. The latter interpretation (schematically indicated in Figure 4b) is supported by electronic structure calculations.

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Registry No. $^{14}\text{NF}_3^{\bullet+}$, 54384-83-7; $^{15}\text{NF}_3^{\bullet+}$, 67745-75-9; NF_3AsF_6 , 16871-75-3.

Ab Initio SCF Study of Hyperfine Couplings, Geometries, and Inversion Barriers in the Isoelectronic Radicals $\text{NF}_3^{\bullet+}$, CF_3^{\bullet} , and $\text{BF}_3^{\bullet-}$

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Abstract: Ab initio SCF molecular orbital calculations with double- ζ and polarized double- ζ bases are reported for the isoelectronic series of C_{3v} radicals $\text{NF}_3^{\bullet+}$, CF_3^{\bullet} , and $\text{BF}_3^{\bullet-}$. At the potential minima, the bond lengths are 1.314 Å for $\text{NF}_3^{\bullet+}$, 1.341 Å for CF_3^{\bullet} , and 1.442 Å for $\text{BF}_3^{\bullet-}$; the complements of the umbrella angles are $+12.1^\circ$ for $\text{NF}_3^{\bullet+}$, $+17.1^\circ$ for CF_3^{\bullet} , and $+19.6^\circ$ for $\text{BF}_3^{\bullet-}$. Calculated inversion barriers are about 11, 33, and 28 kcal/mol for $\text{NF}_3^{\bullet+}$, CF_3^{\bullet} , and $\text{BF}_3^{\bullet-}$, respectively. Bonding and the predicted dependence of EPR parameters upon radical geometry are discussed. With respect to the spin-density distribution and the radical geometry, these calculations confirm the general inferences drawn from the previous EPR analysis—in particular, the hyperfine interaction of the central atom. However, an experimental ambiguity in orientation of the principal axis of the fluorine hyperfine coupling matrix is resolved in favor of the nonintuitive alternative. It is concluded that quantitative information about the geometry of such radicals cannot be inferred from the orientation of the halogen hyperfine axes.

The trigonal-pyramidal fluorocarbon CF_3^{\bullet} and its isoelectronic neighbors $\text{NF}_3^{\bullet+}$ and $\text{BF}_3^{\bullet-}$ are archetypal fluoro radicals. However, there have been no direct determinations of the molecular structure of any of these species, and experimental information bearing on their electronic structure is still being accumulated.¹ The most detailed experimental clues available on these species are to be found in the anisotropic electron paramagnetic resonance spectra of YM_3 ($Y = \text{C}, \text{N}^+, \text{B}^-$) as impurity sites in solids at low temperature. An intriguing feature of both CF_3^{\bullet} , whose EPR parameters are fairly well-known, and $\text{NF}_3^{\bullet+}$, for which anisotropic EPR results are just now being reported,² is that the angle α between the trigonal axis and the principal axis of the ^{19}F hyperfine coupling tensor is about the same as the structural angle α' by the pyramid is expected to deviate from a planar structure. The obvious interpretation is that the part

of the spin density localized on the fluorine center occupies a pn orbital oriented perpendicular to the bond. However, since the experiments were done on isotropic (polycrystalline) samples, the relative signs of α and α' are indeterminable. If they are of opposite sign, the obvious interpretation is invalid. In that event, it would seem that the fluorine p orbital involved in the highest (singly occupied) molecular orbital would be poised for bonding by being strongly skewed with respect to the Y-F ($Y = \text{C}, \text{B}^-$, or N^+) bond. In the case of CF_3^{\bullet} , INDO calculations and limited ab initio calculations² have supported this second interpretation. Here we report ab initio self-consistent-field (SCF) calculations with large basis sets, carried out to determine not only the equilibrium structures of the three radicals but also their inversion barriers. These calculations provide detailed information on the electron-spin distributions leading to an elucidation of the rela-

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Nitrogen-14 and Nitrogen-15 NMR Spectroscopy of Fluoronitrogen Cations: π and σ Fluoro Effects

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APPENDIX U

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High-resolution spectra have been obtained for (anhydrous HF) solutions of NOF_2^+ , NF_4^+ , NH_4^+ , NO_2^+ , and NO^+ in ^{14}N resonance and for NH_3F^+ (in $\text{CF}_3\text{SO}_3\text{H}$) in ^{15}N resonance. Broader ^{14}N lines were obtained for N_2F^+ (although the one-bond NF coupling was resolved), N_2F_2^+ , and NH_3F^+ . For $\text{F}_2\text{N}=\text{NF}^+$ and NH_3F^+ the reduced electronic symmetry promotes quadrupolar broadening of the ^{14}N line; for N_2F^+ and $\text{F}_2\text{N}=\text{NF}^+$ exchange processes may contribute also. The nitrogen lines in the linear or planar species $\text{N}=\text{NF}^+$, NOF_2^+ , and $\text{F}_2\text{N}=\text{NF}^+$ show π fluoro effects, being shifted upfield relative to those in corresponding species with hydrogen, alkyl, or aryl groups instead of fluorine, despite the reduction in electron density on nitrogen. The higher shielding is related to increase in energy of $n_{\text{N}} \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ paramagnetic circulations and so corresponds to perfluoro effects which are well-known in electronic and photoelectron spectroscopy. In planar systems, fluorination stabilizes σ relative to π orbitals, since interaction with the filled F_p orbitals counteracts the inductive stabilization of the π orbitals. In the nonplanar species, however, the nitrogen line moves strongly downfield with fluorination, as from NH_4^+ to NH_3F^+ to NF_4^+ . These shifts are described as σ fluoro effects and are explained, at least in part, by the decrease in electron density on nitrogen. The higher shielding of nitrogen in NH_4^+ in anhydrous HF relative to that in aqueous solutions can be attributed to N-H...F hydrogen bonding.

Introduction

Because of the extreme position of fluorine in the periodic table, effects that occur to a lesser degree with other substituents can be "tested" in fluorine chemistry; indeed some are then so marked as to be called "(per)fluoro effects". An example is the perfluoro effect in planar systems which is used to distinguish σ from π orbitals in photoelectron spectroscopy and to characterize $n \rightarrow \pi^*$ (or $\sigma \rightarrow \pi^*$) excitations in electronic spectroscopy.¹⁻³ It results from the marked stabilization of the σ -orbital manifold relative to the π when hydrogens or alkyl groups are replaced by fluorine. Although the (-) inductive effect of fluorine stabilizes the σ and the π orbitals, the effect on the π orbitals is offset by the repulsion of the fluorine nonbonding electrons (+I_r).

Corresponding effects can be discerned in ^{13}C and ^{15}N NMR shifts.⁴ In the azabenzene,⁵ for example, $n_{\text{N}} \rightarrow \pi^*$ bands are strongly blue shifted and nitrogen resonances shifted upfield, since (planar) nitrogen carrying a lone pair is deshielded by $n_{\text{N}} \rightarrow \pi^*$ electronic circulations in the magnetic field, and an increase in the excitation energy $\Delta E(n_{\text{N}} \rightarrow \pi^*)$ acts to reduce the circulation and the deshielding. Such "perfluoro" effects are usefully (following Liebman⁶) termed π fluoro effects, as they are evident also on partial fluorination, with some additivity. The term " σ fluoro effects" can then be applied to nonplanar systems (in which dramatic downfield shifts may be observed for atoms directly bonded to fluorine) and also in contributory influences of fluorine attached to a resonant atom in a π -bonded system. These effects reflect changes in electron density and orbital coefficients as well as in excitation energies, as discussed below.

We now report a nitrogen NMR spectroscopic study of the cations NF_4^+ ,⁷ NH_3F^+ ,⁸ $\text{F}_2\text{N}=\text{NF}^+$,⁹ NOF_2^+ ,¹⁰ $\text{FN}=\text{N}^+$,^{11,12} NH_4^+ , NO^+ , and NO_2^+ , in anhydrous HF (or $\text{CF}_3\text{SO}_3\text{H}$) solution, to throw light on the effects of fluorination in these ions.

^{14}N vs. ^{15}N NMR Spectroscopy

Nitrogen NMR spectroscopy in high resolution normally requires the ^{15}N nucleus, but the low abundance (0.365%) has severely restricted its application to fluoronitrogen chemistry. Sharp lines can, however, be obtained for the abundant but quadrupolar ^{14}N nucleus in mobile solutions of NH_4^+ , $\text{CH}_3\text{N}=\text{C}$, or NO_2^+ , since the high local symmetry (small electric

field gradient) allows the nuclear electric quadrupole and therefore the nuclear spin to relax sufficiently slowly.³ Thus high-resolution ^{14}N NMR spectroscopy should in principle be possible for the NF_4^+ , $\text{FN}=\text{N}^+$, and $\text{F}_2\text{N}=\text{NF}^+$ ions, but greater quadrupolar broadening is expected for the $\text{F}_2\text{N}=\text{NF}^+$ nitrogen, which carries a lone pair of electrons, although $^1J_{\text{NF}}$ and $^2J_{\text{NF}}$ were resolved in $^{19}\text{F}\{^{14}\text{N}\}$ double resonance studies of *cis*- and *trans*- $\text{FN}=\text{NF}$.¹³ ($^{14}\text{N}\{^{14}\text{N}\}$ coupling constants are expected to be small, 5 Hz or less, since $^1J_{^{14}\text{N}\{^{14}\text{N}\}}$ is about 6 Hz for the dinitrogen ligand $\text{M}-\text{N}=\text{N}^{14a}$ or 10 Hz for the hydrazido(2-) ligand $\text{M}=\text{N}-\text{NH}_2$.^{14b})

The low viscosity of fluoro compounds and liquid HF as solvent is advantageous for ^{14}N work since the quadrupolar relaxation rate is proportional to the molecular reorientation time and therefore to the viscosity. Pure liquid HF has a viscosity of 0.26 cP at 0 °C and 0.45 cP at -45 °C (cf. 1 cP at 20 °C for water). Unfortunately this solvent is (understandably) unpopular with operators of widebore spectrometers for

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Table I. π -Bonded Fluoronitrogen and Related Compounds^a

compd	solvent	$T/^\circ\text{C}^a$	$\delta(\text{N})^b$	$^1J_{\text{NF}}/\text{Hz}^c$	$^2J_{\text{NF}}/\text{Hz}^c$	$W_{1/2}/\text{Hz}^d$	T_Q/ms^e	ref (^{19}F) ^f	ref (^{14}N) ^g
$\text{F}^-\text{N}^+\text{AsF}_6^-$ 1 2	N-1	HF	-191.2	339 (14) [328]	nr	120 (12)		11	
			-50			400			
PhN=N ⁺ BF ₄ ⁻ 1 2	N-1		-156.4						19 (^{14}N)
	N-2		-63.4			205 (14) 600			
$\text{NOF}_2^+\text{AsF}_6^-$	III ^f		-99.0	254 (3) [250]	...	18 (3)	18 (6)	10	
NO_2^+F^-	neat liq		-87.6	109 (5) [112.5]	...				24
$\text{F}_2\text{N}=\text{NF}^+\text{AsF}_6^-$ 1 2	N-1	HF	-75.9	nr	nr	870 (50) 2200			
	N-2		-50			280 (20) 950			
<i>cis</i> -F ₂ N=NF <i>trans</i> -F ₂ N=NF	CCl ₃ F		4	± 145	± 37				13
				66	± 136	± 73			13
NO ⁺	neat liq		-80	104	...	245			21
			-78	110					24
$\text{CF}_3\text{N}(\text{O})=\text{NF}^-$ 1 2	N-1		-123						h
	N-2		-58						

^a Other than ambient temperature. ^b ^{14}N shift relative to neat liquid CD_3NO_2 , with low field positive. The new measurements were made at 28.9 MHz (400 MHz for protons) except for $\text{NOF}_2^+\text{AsF}_6^-$, which was measured at 4.33 MHz (60 MHz for protons). The reference for shifts measured at 4.33 MHz is 5 M NH_4NO_3 in 2 M HNO_3 , for which $\text{NH}_4^+(\text{aq})$ has $\delta = -360.0$ relative to neat liquid CH_3NO_2 . ^c $J_{\text{NF}}/J_{\text{NF}}$ = -1.403. nr means "not resolved". The spin-spin coupling unresolved in ^{14}N resonance has not been resolved in ^{19}F resonance. Coupling constants shown in brackets were measured in ^{19}F resonance. ^d Line width at half-height. ^e Quadrupolar relaxation time, given by $T_Q = 1/\pi W_{1/2}$ when the line is not broadened significantly by unresolved coupling of exchange. ^f Reference to ^{19}F measurement of J_{NF} . ^g Reference to nitrogen NMR measurement. ^h Frazer, J. W.; Holder, B. E.; Worden, E. F. *J. Inorg. Nucl. Chem.* 1962, 24, 45. ⁱ Uncertainties are given in parentheses in units of the last digits.

Table II. Nitrogen Oxide Ions

compd	solvent	$T/^\circ\text{C}^a$	$\delta(\text{N})^b$	$W_{1/2}/\text{Hz}$	T_Q/ms	ref
$\text{NO}_2^+\text{AsF}_6^-$	HF	-70	-136.3	5 (1)	65 (30)	
$\text{NO}_2^+\text{BF}_4^-$ (FSO_3^-)	SO_2	-60	-131.5			34 (^{14}N)
$\text{NO}_2^+\text{HSO}_4^-$	4:1 H_2SO_4 - HNO_3		-132 (1)	29	11	c
$^-\text{O}_2\text{N}=\text{NO}^-\text{Na}_2^{2+}$	aq		-43.4			16
			-27.9			
$\text{NO}^+\text{AsF}_6^-$	HF		-7.5	95 (14)	3 (0.3)	
$\text{NO}^+\text{HSO}_4^-$	H_2SO_4		-5 (10)	broad		21
NO^+BF_4^- (PF_6^-)	SO_2	-60	-3.2			34 (^{14}N)
$\text{NH}_4^+\text{NO}_3^-$ (5 M)	$\text{HNO}_3(\text{aq})$ (2 M)		-4.5			
Na^+NO_2^-	(satd, aq)		229			

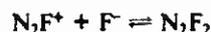
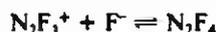
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the study of ^{15}N in natural abundance when the sample volume is 12 cm³ or more, particularly if the solute is under pressure. Triflic acid ($\text{CF}_3\text{SO}_3\text{H}$) is more acceptable, and we used this for the ^{15}N spectrum of NH_3F^+ .

Results and Discussion

As recorded in Tables I-III, the ^{14}N lines are very sharp for NF_4^+ and NH_4^+ , quite sharp for NOF_2^+ and NO_2^+ , but rather broad for NO^+ , and broader still for $\text{N}=\text{NF}^+$, $\text{FN}=\text{NF}_2^+$, and NH_3F^+ . For solutions of similar viscosity, the quadrupolar broadening should perhaps increase as $\text{NF}_4^+ < \text{F}_2\text{NO}^+ < \text{F}_2\text{N}=\text{NF}^+ \leq \text{N}=\text{NF}^+ < \text{N}=\text{NF}^+ \ll \text{F}_2\text{N}=\text{NF}^+$, and also $\text{NF}_4^+ < \text{NH}_3\text{F}^+$. Thus some of the lines are broader than might be expected from the electronic asymmetry near nitrogen and the resolution of $^1J_{\text{NF}}$ and $^2J_{\text{NF}}$ in NF_3 and $\text{FN}=\text{NF}$.¹³

Another possible mechanism for line broadening is exchange of F^- or H^+ with the solvent, e.g.



Such exchange is evident in the ^{19}F spectrum of N_2F_3^+ in liquid HF, the line sharpening with decrease in temperature, or

addition of a Lewis acid such as AsF_5 to slow down exchange by withdrawing F^- as AsF_6^- .⁹ The three FF couplings were resolved but NF coupling was not. In the ^{14}N spectra, unexpectedly, $^1J_{\text{NF}}$ could be observed for the less symmetrical nitrogen (carrying a lone pair) but not for the other (Table I). Both resonances are broad and broaden further with decrease in temperature because of the increase in viscosity.⁵ For N_2F^+ the one-bond NF coupling was resolvable in ^{14}N and in ^{19}F resonance, but no two-bond coupling was resolved, and these ^{14}N lines, also, broaden with decrease in temperature (Table I). Clearly there is a conflict between the temperature conditions needed for the reduction of quadrupolar broadening and of exchange broadening.

In ^{19}F resonances of $(^{14}\text{NH}_3\text{F})(\text{CF}_3\text{SO}_3)$ in concentrated H_2SO_4 no coupling was resolved at 30 $^\circ\text{C}$. An optimum spectrum was obtained at -40 $^\circ\text{C}$, a quartet with $^2J_{\text{HF}} = 4.3$ Hz and $W_{1/2} = 5.6$ Hz, but no ^{14}NF coupling was resolved. No NH or NF coupling in NH_3F^+ in HF solution could be resolved in ^{14}N resonance under the various conditions given in Table III. Addition of AsF_5 increased the line width, indicating that any decrease in exchange broadening is outweighed by effects of increased viscosity. ⁷⁵As observations of KAsF_6 in acetone showed^{15a} that doubling the concentration (from 1 to 2 M) increased the viscosity by a factor of about 1.7 and roughly halved the spin-lattice relaxation time, cor-

Table III. Nonplanar Fluoronitrogen and Related Compounds^a

compd	solvent	T/°C ^b	$\delta(N)^b$	$^1J_{NF}^c$ /Hz	$^1J_{NH}^c$ /Hz	$W_{1/2}/\text{Hz}^d$	T_Q/ms^e	ref (¹⁵ N) ^f	ref (¹⁴ N) ^g
NH ₃	neat liq		-380.0						
NH ₃ ⁺ AsF ₆ ⁻	HF		-369.6	...	54.3 (1.7)	2 (1)	160		
NH ₃ ⁺ NO ₃ ⁻ (5 M)	HNO ₃ (aq) (2 M)		-360.0	...	52				
N ₂ H ₄	neat liq		-335						25 (¹⁴ N)
NH ₃ I ⁺ O ₃ SCF ₃	CF ₃ SO ₃ H	+20	-252.1 ^b	33.9 (3.0) ^b	30.8 (3.0) ^b	3			
	HF	+10	-259.6	nr	nr	350 ^c	1		
		-40	-257.6			600 ^c	0.6		
	III/AsI ₆ ⁺	+10	-260.0	nr	nr	420			
		-40	-256			730			
NOF ₂	neat liq	-120	-147			208			23a
		-110	-137	134					24
NF ₂ ⁺ BF ₄ ⁻	HF		-92.3	[135.5] 230.5	...	2 (1)	160	23b	
NF ₂ ⁺ AsF ₆ ⁻	HF		-92.2	[231] 230.5	...	3 (1)	100		
				[234] [231]				7b 7c	
N ₂ F ₄	neat liq		-49	nr					13
			-41	nr					24
				[160]				d	
NF ₃	neat liq	-130	-9	nr	...	225			23
		-152	-14.3	158					24
				[155]					13

^a Terms in the column heads are defined in footnotes a-g of Table I. ^b ¹⁵N measurements at 18.24 MHz giving $^1J_{NF}^c = 47.6$ (3.0) Hz with proton decoupling and $^1J_{NH}^c = 43.2$ (3.0) Hz. ^c Broad-band proton decoupling reduced these line widths by about 50 Hz. ^d Ettinger, R.; Colburn, C. B. *Inorg. Chem.* 1963, 2, 1311.

responding to a doubling of the line width. We obtained a septet for the ⁷⁵As line for AsF₆⁻ in the (NH₃F)(CF₃SO₃)₂ solution in HF, with $^1J_{AsF} = 933$ Hz as obtained previously,¹⁵ but with a greater line width ($W_{1/2} = 800$ Hz at 25 °C) than those reported for aqueous solutions (94 Hz)^{15b} or in organic solvents (150–450 Hz)^{15a} despite the lower viscosity of liquid HF. This indicates exchange broadening as well as quadrupolar broadening of the ⁷⁵As line. (In highly symmetric environments, as in AsF₆⁻, quadrupolar relaxation is mediated by transient electric field gradients at the nucleus during Brownian motions.)

Fortunately we could measure the natural-abundance ¹⁵N spectrum of NH₃F⁺ in solution in triflic acid, CF₃SO₃H. Proton decoupling gave a doublet with negative intensity corresponding to the maximal NOE factor for ¹⁵N ($\eta = -4.93$) and an ¹⁵NF coupling constant of 48 Hz, equivalent to 34 Hz for ¹⁴N. The fully coupled spectrum gave an ¹⁵NH coupling constant of 43 Hz, equivalent to 31 Hz for ¹⁴N.

π Fluoro Effects. Table I gives the nitrogen NMR parameters for linear or planar fluoronitrogen ions and molecules, with some related compounds for comparison. Some interesting correspondences can be observed in the chemical shifts. The F₂N⁺ nitrogen has similar shifts in F₂N=O⁺ and in F₂N=NF⁺, and the mean of the two nitrogen shifts in F₂N=NF⁺ resembles that for the isoelectronic nitrohydroxamate ion (O₂N=NO)²⁻.¹⁶ The resonance of the =NF nitrogen in F₂N=NF⁺, which has fluorine cis and trans, lies between the resonances for cis- and trans-FN=NF.¹³

A π fluoro effect is evident in the upfield shift of up to 100 ppm on replacement of R or Ar by fluorine in diazenes (azo compounds) RN=NR,¹⁷ and similarly for the diazenium nitrogen =NF₂⁺ compared with protonated diazenes¹⁸ and for terminal nitrogen in the diazonium ions FN≡N⁺ compared with PhN≡N⁺.¹⁹ Interestingly the upfield shift is smaller,

30 ppm, for the two-coordinate diazonium nitrogen FN≡N⁺, and this illustrates the multiplicity of factors when fluorine is directly attached to the resonant atom. As well as the π fluoro effect, tending to increase the shielding by increasing $\Delta E(\text{HOMO-LUMO})$, the fluoro substitution tends to increase the shielding by removing electron density from the paramagnetic circulations on nitrogen; but the increase in positive charge on nitrogen reduces the radius of the paramagnetic circulations, increasing their effect. These factors are represented (respectively) by the three terms ΔE , $\sum Q$, and $\langle r^{-3} \rangle_{2p}$ in the approximate formulation of the local paramagnetic term, restricted to electronic circulations on the observed atom A bonded to other atoms B²⁰

$$\sigma_p^{AA} = \frac{-\mu_0 \mu_B \langle r^{-3} \rangle_{2p}}{2\pi(\Delta E)} (Q_{AA} + \sum_{A \neq B} Q_{AB}) \quad (1)$$

where μ_0 is the permeability of free space, μ_B the Bohr magneton, and r_{2p} the radius of the valence p electrons, and the downfield shift increases with the absolute magnitude of σ_p^{AA} . The $\sum Q$ term expresses the imbalance of electronic charge that allows the paramagnetic circulation in the magnetic field. The Q_{AA} part depends on the 2p orbital populations on the atom A, whereas $\sum Q_{AB}$ is a multiple-bond term that (with the energy term) is responsible for the large differences in chemical shift for the different bond orders. Loss of electron density (or reduction of orbital coefficients) with substitution by electronegative ligands such as oxygen or fluorine may increase the shielding, by reducing $\sum Q$. On the other hand, the radial term $\langle r^{-3} \rangle_{2p}$ and therefore the deshielding increase in proportion to the increase in (positive) atomic charge. Thus the π fluoro (ΔE) effects tend to increase the shielding, whereas the σ fluoro effects, decrease in $\sum Q$ and increase in radial terms $\langle r^{-3} \rangle_{2p}$, tend to cancel. Substituent effects are particularly influential for the lower field resonances such as those of the diazene or nitroso compounds: there is an upfield shift of 450 ppm from alkyl or aryl nitroso compounds to NOF,

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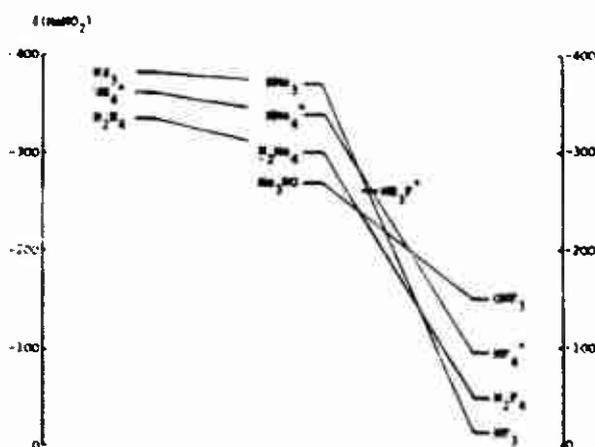


Figure 1. σ fluoro effects in nonplanar systems.

paralleled by a blue shift in $n_N \rightarrow \pi^*$ absorption from 760 to 311 nm (corresponding to an increase in ΔE from 1.6 to 4 eV, for this contribution to the appropriate component of the shielding tensor).²¹

Replacement of O^- by fluorine results in upfield nitrogen shifts, of 120 ppm for NOF compared with NO_2^- and 80 ppm for NO_2F (95 ppm for NOF_2^+) compared with NO_2^- (Tables I and II); cf. the blue shift in the $n_N \rightarrow \pi^*$ absorption from 357 nm for NO_2^- to 311 nm for NOF. Again, there are σ fluoro effects of the reduction in electron density on nitrogen which tend to cancel: a CNDO/S estimate indicates a 5% increase in $(r^{-3})_{2p}$ from NO_2^- to NOF, corresponding to deshielding by 30 ppm or so, counteracted by effects of decrease in the constitutive terms.

σ Fluoro Effects in Nonplanar Groups. Table III and Figure 1 show the strong deshielding of nitrogen in nonplanar groups when directly bonded hydrogen or alkyl (or aryl) substituents are replaced by fluorine. The deshielding is particularly large from NH_3 to NF_3 ,^{23a,24} and N_2H_4 ²⁵ to N_2F_4 ,¹³ and is smaller for nitrogen bearing a positive charge (NH_4^+ to NF_4^+) or an oxygen substituent (Me_3NO ²² to NOF_3 ^{23b}). The increase in the radial factor with fluorination now acts in the same direction as the observed shifts, on the whole; $(r^{-3})_{2p}$ increases by 17% from NH_3 to NF_3 and by 20% from NH_4^+ to NF_4^+ . However, the line shifts upfield from NF_3 to NF_4^+ or NOF_3 , despite sizable increase in the radial term. The upfield shift from NF_3 to NOF_3 has been attributed in part to the increase in the electronic symmetry around nitrogen, approaching the spherically symmetric distribution of an inert gas,²⁶ but nitrogen in NF_4^+ is significantly deshielded compared to NOF_3 (despite similar values of the radial term). Indeed, the deshielding in NF_4^+ compared with NH_4^+ or NOF_3 illustrates the subtlety of the concept of "imbalance of electronic charge" as it contributes to nuclear magnetic deshielding.

As to the energy terms, the electronic circulations deshielding nitrogen in these molecules are all of $\sigma \rightarrow \sigma^*$ type, including the $n_N \rightarrow \sigma^*$ circulations in NH_3 , NF_3 , N_2H_4 , and N_2F_4 , since the nitrogen lone-pair orbitals are strongly linked to the σ framework. The higher shielding of nitrogen in NOF_3 or NF_4^+ compared with NF_3 follows the normal pattern on replacement of a lone pair on nitrogen by a strong σ bond,

removing the lower energy $n_N \rightarrow \sigma^*$ circulation.³ The strong deshielding of nitrogen with fluorination of NH_3 or NH_4^+ is paralleled by that of phosphorus²⁷ in phosphines or phosphonium ions, carbon in alkanes, silicon in silanes,²⁸ and so on. It is part of a periodic trend, of increased deshielding in saturated compounds as the ligand moves across the row of the periodic table,²⁹ so that it might be expected to be an inductive effect influencing the energy terms, since these are usually involved when substituent effects are large. On the other hand, the evidence¹⁻³ from photoelectron, optical, and electron impact energy loss spectroscopy suggests that the relevant excitation energies are significantly higher overall in the fluorinated than in the unfluorinated molecules. The $n_N \rightarrow \sigma^*$ excitation energy increases from about 6.5 to 8.7 eV from NH_3 to NF_3 ,²⁶ and there are similar increases in excitation energies with fluorination in the series of the fluoromethanes,^{2c} which are iso-electronic with the fluoroammonium ions, although the CH σ orbitals are destabilized in CH_3F and CH_2F_2 (but not CH_3F_2) compared with CH_4 . The high ionization energy of fluorine, compared with that of the other halogens, makes for better matching, and therefore mixing, of the 2p orbitals with carbon and nitrogen bonding orbitals. Whereas the halogen lone-pair orbitals are highest lying in the other halogenomethanes, the CH σ orbitals are highest lying in the fluoromethanes, and the fluorine "lone pair" and CF σ orbitals are comparable in energy. The fluorine "lone pair" electrons are extensively delocalized, and it may be that their circulations in the magnetic field help to deshield nitrogen or carbon (etc.) as well as fluorine in these molecules, reinforcing the effects of increase in the radial term.

Patterns of chemical shifts can be described in broad terms by eq 1, which is a very approximate version (with an average energy denominator) of the local term approximation, which restricts calculation to electronic circulations on the observed atom A.²⁰ Our use of this equation is intended to give a "chemical" picture of nuclear magnetic shielding, in terms of orbitals and bonds. More accurate calculations sum over all the excited states (or else treat the magnetic field as a perturbation on the orbital manifold) and reckon the shielding contribution from circulations on neighboring atoms by means of a dipolar (neighbor anisotropy) approximation, although this gives an underestimate, as is evident from the magnitudes of observed substituent effects.²⁹ The deshielding of carbon from CH_4 to CH_3F is matched quite well (slightly underestimated) by ab initio SCF methods with some extension of the basis set,³⁰ but further fluoro substitution would make large demands on computer time. The semiempirical methods can deal with larger molecules but cannot usually match experimental shifts without ad hoc parameterization. This has been demonstrated for the INDO method with the specific example of the deshielding of carbon from CH_4 to CH_3F .³¹ The standard parameterization greatly underestimates the deshielding, but the estimate can be increased by a (drastic) reduction in the absolute value of the resonance integral β_{CF}^0 , which corresponds to the splitting of CF σ and σ^* orbitals. This reduction corresponds to an increase in ionicity of the CF bond; but the fault may be with the local term approximation, which cannot take full account of the deshielding of the central atom in these nonplanar molecules by circulations of the fluorine "lone pair" electrons.

Effects of the HF Medium on the Nitrogen Shifts. The nitrogen shift of -369.9 ppm for NH_4^+ in anhydrous HF effectively doubles the range that has now been observed for

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this ion. The range previously extended from -359 or -360 ppm for the nitrate in water or aqueous nitric acid to -350 ppm for the chloride in concentrated HCl, with the bromide and iodide slightly downfield of this. Briggs and Randall³² found that the nitrogen shifts in aqueous acid solutions of $^{15}\text{NH}_4^+$ are independent of pH and concentration of NH_4^+ but are sensitive to the nature of the counterion, depending in linear fashion on its concentration. The nitrogen shielding increases in the sequence $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{SCN}^- < \text{SO}_4^{2-} < \text{NO}_3^-$, which differs from that of the efficiency of the anion in disrupting the hydrogen bonding of water. It is the order of increasing strength of hydrogen bonding of NH_4^+ to the anion,³² and corresponding results were subsequently found for chlorides, iodides, etc., of protonated (saturated) amines.³³ Similarly, for a given anion, the nitrogen line moves upfield with change from a chlorinated solvent to methanol or water.³³ It is pleasing to find that the HF solutions of fluoro anions lie to the extreme of the NH_4^+ series, with maximal nitrogen shielding for the strongest hydrogen bond, $\text{N}-\text{H}\cdots\text{F}$. There appears to be a significant upfield shift also of the nitrogen lines in NO^+ and NO_2^+ from liquid SO_2 ³⁴ to HF as medium, with fluoro anions in each case (Table II). Hydrogen bonding to a lone pair on nitrogen in ammonia or alkylamines normally deshields the nitrogen,³³ with a sizable deshielding from gaseous to liquid NH_3 and from NH_3 to NH_4^+ .³⁵

Spin-Spin Coupling Constants. The NF coupling constants measured in nitrogen resonance agree with those observed in ^{19}F resonance, as shown in the tables. The $^1J_{\text{NF}}$ value of 339 Hz for $\text{FN}=\text{N}^+$ is the largest known, correlating with the high s character in the nitrogen bonding orbitals, analogous to the maximal $^1J_{\text{NH}}$ value of 96 Hz (120 Hz for ^{15}N) measured for $\text{HC}=\text{NH}^+$.³⁶ The new $^1J_{\text{NF}}$ value of 195 Hz for the diazene nitrogen $\text{F}_2\text{N}=\text{NF}^+$ is larger than those observed for *cis*- or *trans*- $\text{FN}=\text{NF}$. If the qualitative correlation with s character holds (the quantitative relation frequently fails when nitrogen bears a lone pair with s character, as here³⁷), it would suggest that this diazene NNF angle is larger than in *cis*- $\text{FN}=\text{NF}$ (114.4°, ³⁸ $^1J_{\text{NF}} = 145$), which is larger than in *trans*- $\text{FN}=\text{NF}$ (105.5°, ³⁸ $^1J_{\text{NF}} = 136$ Hz).

The NF coupling constant is much smaller in NH_3F^+ than in NF_4^+ , the disparity being greater than in the fluoro-

methanes: $^1J_{\text{CF}}$ is 158 Hz in CH_3F compared with 259 Hz for CF_4 . But the factors involved are not simple, for the fluoromethane values peak at 274 Hz for CHF_3 . $^1J_{\text{NH}}$ in NH_3F^+ is unexpectedly small (31 Hz, cf. 54 Hz for NH_4^+) since an electronegative substituent usually increases the magnitude of a coupling constant, regardless of sign.

Our discussion so far has been of absolute magnitudes of J_{NF} . One-bond $^{14}\text{N}\text{F}$ coupling constants are expected to be negative³⁹ (and the $^{15}\text{N}\text{F}$ values positive because of the negative magnetogyric ratio of ^{15}N), so that the two-bond coupling constants in the diazenes are positive.¹³

It seems that the NH coupling constants increase with the strength of hydrogen bonding in the medium, as does the nitrogen shielding. For NH_4^+ , $^1J_{\text{NH}}$ increases from (+)50 Hz for chlorides in aqueous HCl to 52 Hz for nitrates in aqueous HNO_3 , and this trend is continued by the value of 54 Hz that we observe for $[\text{NH}_4][\text{AsF}_6]$ in anhydrous HF (Table III). This increase is consistent with contraction of the valence s orbitals increasing the Fermi contact term, with increase in effective nuclear charge as electron density is withdrawn in hydrogen bonding.

Experimental Section

The compounds were made by published methods.⁷⁻¹² The ^{14}N spectra were measured with a Bruker WH 400 spectrometer operating at 28.9 MHz. The solution in anhydrous HF was contained in a sealed 4-mm FEP Teflon tube, which was placed within coaxial 5- and 10-mm glass tubes with CD_3NO_2 between them to serve as reference and deuterium field-frequency lock. Susceptibility effects are small, since the volume susceptibility of liquid HF is close to that of MeNO_2 . The $[\text{NOF}_2][\text{AsF}_6]$ measurements were made with a Bruker WP 60 spectrometer at 4.33 MHz. The natural-abundance $^{15}\text{NH}_3\text{F}^+$ spectra were measured on a Bruker WH 180 widebore spectrometer operating at 18.24 MHz, with a sealed tube containing the $\text{CF}_3\text{SO}_3\text{H}$ solution and a coaxial 5-mm tube containing CD_3NO_2 .

Acknowledgment. We thank Gordon Howell for spectra run on the WP 60 spectrometer at The Open University, Drs. Oliver Howarth and Eirian Curzon for the many spectra run on the WH 400 spectrometer at the University of Warwick, Maurice Cooper for the $^{15}\text{NH}_3\text{F}^+$ spectra run on the 180-MHz widebore spectrometer at PCMU, Harwell, and the Science and Engineering Research Council for the provision of high-field spectrometers. K.O.C. is indebted to the U.S. Army Research Office and the Office of Naval Research for financial support.

Registry No. NOF_2^+ , 43575-45-7; NF_4^+ , 30494-78-1; NH_4^+ , 14798-03-9; NO_2^+ , 14522-82-8; NO^+ , 14452-93-8; NH_3F^+ , 53768-39-1; N_2F^+ , 33687-51-3; N_2F_3^+ , 39448-70-9; nitrogen, 7727-37-9; nitrogen-15, 14390-96-6

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APPENDIX V

ON THE REALITY OF POSITIVE FLUORINE

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SUMMARY

Recent experimental data are not consistent with the postulate of a positively polarized fluorine for compounds such as hypofluorites.

INTRODUCTION

In their recent paper on fluorination with positive fluorine, Cartwright and Woolf commented [1] on the marked reluctance by fluorine chemists to accept the "reality" of positive fluorine. They cite as evidence for this reality the weakening of aromatic carboxylic acids by o- and p- fluorine substitution and the $\delta^- \delta^+$ CF₃O-F polarity required to explain fluorination reactions. Whereas their first argument is not convincing experimental proof for positively polarized fluorine due to the complexity of the system and the different possible electronic effects, recent experimental studies show that in covalent hypofluorites fluorine is not positively polarized.

RESULTS and DISCUSSION

For example, the addition of ClO₃OF to the unsymmetrical olefin CF₃CF=CF₂ produces 68% of CF₃CF₂CF₂OCLO₃ and 32% of CF₃CF(OCLO₃)CF₃. The direction and the nature of these addition products suggest that the O-F bond in ClO₃OF is not strongly polarized in either direction, and that the direction of the addition is probably governed by steric effects with the bulkier CF₃ group repelling the larger OCLO₃ group [2]. Similar results were found for the addition of CF₃OF to olefins. By analogy with ClO₃OF, low stereospecificity was observed, and the direction of the addition was again governed mainly by steric effects [3].

Extreme electronegativities, *i.e.*, electronegativities larger than that of fluorine, have previously been postulated not only for the $\text{CF}_3\text{O-}$ and $\text{ClO}_3\text{O-}$ groups, but also for the $\text{TeF}_5\text{O-}$ and $\text{SeF}_5\text{O-}$ groups [4-6]. However recent multinuclear nmr and Mossbauer measurements have shown that fluorine is more electronegative than the $\text{TeF}_5\text{O-}$ group with the latter having a value of 3.87 on the Pauling scale [7]. This is also supported by the results from the addition of TeF_5OF to olefins [8], which are analogous to those obtained for ClO_3OF and CF_3OF .

Since fluorine is the most electronegative element it appears logical that the addition of fluorine to a central atom of lower electronegativity cannot result in a group which has a group electronegativity higher than that of fluorine itself. In the extreme case, the addition of an infinite number of fluorines to a highly electronegative element might produce a group with an electronegativity asymptotically approaching that of fluorine. In the absence of convincing experimental data in favor of a positively polarized fluorine and in view of the existing experimental data to the contrary [2,3,7,8], the postulate of a positively polarized fluorine should be labeled 'misconception' rather than 'reality'.

ACKNOWLEDGEMENT

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APPENDIX W

POSITIVE FLUORINE-REALITY OR MISCONCEPTION?

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SUMMARY

Polar covalence theory arguments are presented against the existence of a permanent positive polarization of fluorine in heteronuclear X-F molecules and against the existence of X groups having a higher electronegativity than fluorine itself. The heterolytic fission of fluorine and the possibility of inducing a positive fluorine dipole in X-F molecules with highly electronegative X groups are briefly discussed.

INTRODUCTION

Fluorination reactions with highly electronegative compounds are frequently explained by invoking a positive fluorine. In a recent note [1], this author took exception to the postulate of positive fluorine by criticizing a recent paper of Cartwright and Woolf on this subject [2]. In the preceding paper [3], the same authors (C+W) summarized some arguments in favor of positive fluorine. Since the issue of a positive fluorine is largely a conceptual problem and is not readily accessible to direct experimental measurements, a speculative interpretation of the mechanism of poorly studied complex organic reactions has little merit. A systematic analysis of this problem therefore appeared more rewarding and is given below.

DISCUSSION

Definition of a Positive Fluorine.

A positive fluorine is the direct result of a transfer of electron density in a covalent X-F bond from F to X resulting in the following polar covalence $\overset{\delta^-}{\text{X}}-\overset{\delta^+}{\text{F}}$, where XF can be either heteronuclear (X is different from F) or homonuclear (X equals F). If XF is homonuclear, i.e. F₂, one cannot have a permanent but only an induced dipole. If XF is heteronuclear, one can have both a permanent and an induced dipole. It should be noted that this dipole is not identical with the experimentally measurable overall dipole moment of the XF molecule due to other factors such as lone valence electron pair effects.

Definition of the Problem.

The issue raised by us in our previous critique [1] was that there is no experimental and theoretical justification for the assumption of a permanent $\overset{\delta^-}{\text{X}}-\overset{\delta^+}{\text{F}}$ polarity in a heteronuclear XF molecule. Therefore, unless stated otherwise, the following arguments will be referring to this issue.

Theoretical Arguments.

The assumption of a permanent positive fluorine dipole in a heteronuclear XF atom violates the principle of electronegativity equalization which was first published in 1951 by Sanderson [4] and proven correct by quantum mechanics in 1978 by Parr and coworkers [5] and in 1979 by Politzer and Weinstein [6]. This principle states that when two or more atoms unite to form a compound, their electronegativities become adjusted to the same intermediate value within the compound. In other words, the

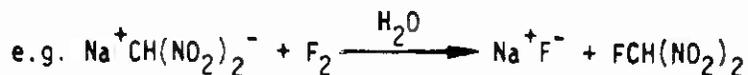
different kinds of atoms become equal in electronegativity by unequal sharing of the bonding electrons. This means that the more electronegative atom must acquire a negative charge and the less electronegative atom a positive charge. Since fluorine is without doubt the most electronegative element, a heteroatomic X-F bond can be permanently polarized in only one direction, i.e. X-F. This principle also rules out the possibility that X groups, such as $\overset{\delta+}{\text{C}}\overset{\delta-}{\text{F}}_3\text{O}-$, $\text{SeF}_5\text{O}-$, or $\text{TeF}_5\text{O}-$, which consist of fluorine substituted heteroatoms of lower electronegativity can become more electronegative than fluorine itself [1,7-10].

Experimental Arguments.

Electrophilic substitution reactions are not a convincing argument in favor of a positive fluorine. First of all, the mechanisms of most of these complex reactions have not been established. Secondly, in these reactions a strong electrophile attacks an electron rich center, and the polarity of the bonds within the electrophile is of lesser importance than other factors. In NF_4^+ , for example, the nitrogen atom is coordinatively saturated. Consequently, NF_4^+ can attack an electron rich center only through one of its fluorine ligands but not through its nitrogen atom. The fact that NF_4^+ can undergo electrophilic substitution reactions is therefore no indication for a positively polarized fluorine.

On the other hand, addition reactions in which a polar X-F molecule is added across a polar double bond, are capable of yielding information about the polarity of the X-F bond. Several such studies have recently been carried out using ClO_3OF [11], TeF_5OF , and CF_3OF [12] and did not provide any evidence for a positive fluorine in these hypofluorites.

One piece of experimental evidence for positive fluorine, cited by (C+W) is the selective substitution at acidic hydrogens,

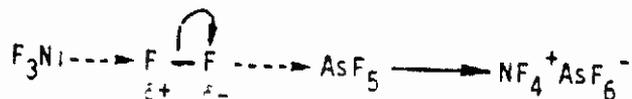


(C+W) concluded that, if half the fluorine becomes fluoride, by a simple charge-balance the other half must be positive fluorine. The shallowness of this conclusion can easily be demonstrated by the following analogous equation which would prove that the fluorine in HF must be positive.

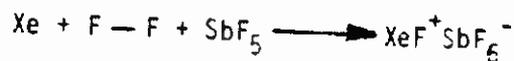


Induced Polarization and Heterolytic Fission of Fluorine.

Although our original critique of the paper by (C+W) was only concerned with the permanent dipole of a heteronuclear XF molecule, the preceding paper [3] requires some comment on the heterolytic fission of fluorine. If in XF molecules X becomes more and more electronegative and eventually becomes F, the energy required to induce a dipole moment decreases and the possibility of forming an induced positive fluorine dipole increases. Although the formation of NF_4AsF_6 was originally postulated [13] to involve the heterolytic fission of F_2 ,



subsequent studies [14-16] have shown that the mechanism of this reaction is more complicated, requires predissociation of F_2 , and involves the formation of the NF_3^+ radical cation as an intermediate. However, if the hard Lewis base NF_3 is replaced by the soft base Xe, the following reaction proceeds spontaneously even in the dark [17].



It is likely that this reaction is a rare example of an actual heterolytic fission of fluorine and therefore involves a Lewis acid - Lewis base induced polarization of fluorine. However, the possible existence of such

a reaction for homonuclear difluorine has no bearing on the formation of a permanent positive fluorine in the heteronuclear XF molecules discussed above.

ACKNOWLEDGEMENT

The author wishes to thank Ors. C. J. Schack and W. W. Wilson for helpful discussions and the Army Research Office and the Office of Naval Research for financial support.

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[54] IODINE (VII)
OXYTETRAFLUOROHYPOFLUORITE AND
A PROCESS FOR PREPARING THE SAME

[75] Inventors: Karl O. Christe, Calabasas, Richard
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[73] Assignee: Rockwell International Corporation,
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[21] Appl No. 176,314

[22] Filed: Aug. 8, 1980

[51] Int. Cl. C01B 7/24

[52] U.S. Cl. 423/473; 423/466,

423/472, 149/119

[58] Field of Search 423/462, 466, 472, 473

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Primary Examiner—Brian E. Hearn

Attorney, Agent, or Firm—H. F. Hamann, Harry B.

Field

[57] ABSTRACT

A fluorinating agent having an empirical formula which
comprises FOIF₄O whereby said fluorinating agent is
prepared by a metathetical reaction of solutions of
NF₄SbF₆ and CsIF₄O₂ in anhydrous HF, removing the
precipitated CsSbF₆ and HF solvent, followed by ther-
mal decomposition of the filtrate residue

5 Claims, No Drawings

IODINE (VII) OXYTETRAFLUOROHYPOFLUORITE AND A PROCESS FOR PREPARING THE SAME

The Government has rights in this invention pursuant to Contract (or grant) NO0014-79-C-0176 awarded by the U.S. Department of the Navy.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to fluorinating agents and, more specifically, to iodine (VII) oxytetrafluorohypo-fluorite and the process for its preparation

2. Description of the Prior Art

The number of elements known to form stable hypo-fluorites is very limited. They are known only for carbon, nitrogen, sulfur, selenium, fluorine, and chlorine containing compounds. In addition, the unstable hypo-fluorous acid, HOF, has been prepared. However, no iodine hypo-fluorites had been known prior to this invention.

Inorganic hypo-fluorites are generally prepared by the alkali metal fluoride catalyzed fluorination of the corresponding oxyfluorides by elemental fluorine (Lustig and Shreeve, *Advances in Fluorine Chemistry*, Vol. 7, pages 175-198, 1973). In the case of iodine compounds, this method does not lead to the formation of iodine hypo-fluorites, as demonstrated by extensive experiments in the inventors' laboratory.

Recent work in the inventors' laboratory has resulted in an alternate synthetic method for the hypo-fluorites FOIClO_2 and FOSO_2F . It was found that the $\text{NF}_4^+\text{ClO}_4^-$ and $\text{NF}_4^+\text{SO}_3\text{F}^-$ salts, which were isolated from a metathetical reaction of NF_4SbF_6 with CaClO_4 or CsSO_3F in anhydrous HF solution, on thermal decomposition yield the corresponding hypo-fluorites FOIClO_2 and FOSO_2F . However, application of this approach to CsIO_4 failed because CsIO_4 interacts with HF to give fluorinated products, as demonstrated by Selig and coworkers (*Journal Inorganic Nuclear Chemistry*, Supplement, 91, 1976). Furthermore, it was shown by the inventors that $\text{Cs}^+\text{IF}_4\text{O}_2^-$, when dissolved in anhydrous HF undergoes solvolysis to produce Cs^+HF_2^- and HOIF_4O .

SUMMARY OF THE INVENTION

Accordingly, there is provided by the present invention iodine (VII) oxytetrafluorohypo-fluorite (FOIF_4O) and a process for preparing the same. The interaction of CsIF_4O_2 with NF_4SbF_6 in anhydrous HF results in solutions containing NF_4^+ , HF_2^- , and HOIF_4O . On standing or when pumped to dryness, these mixtures decompose to yield NF_3 and the new compound FOIF_4O in high yield. The latter compound is the first known example of an iodine hypo-fluorite.

OBJECTS OF THE INVENTION

Therefore, it is an object of the invention to provide a fluorinating agent.

Another object of the invention is to provide a high-density oxidizer for pyrotechnics.

Yet another object of the present invention is to provide a compound capable of introducing fluorine into drugs.

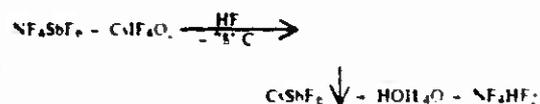
A further object of the present invention is to provide a process for preparing iodine hypo-fluorites.

Other objects, advantages, and novel features of the present invention will become apparent from the following detailed description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In view of the previous art, it appeared very unlikely that any iodine hypo-fluorites could be prepared. Direct fluorinations with elemental fluorine do not produce hypo-fluorites, metathetical reactions of IO_4^- in anhydrous HF are impossible because IO_4^- chemically reacts with HF to give other products, and the synthesis of an $\text{NF}_4^+\text{IF}_4\text{O}_2^-$ salt was not possible due to the solvolysis of IF_4O_2^- to give HOIF_4O .

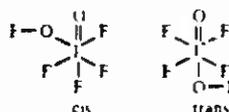
Surprisingly, it was now found that the product from a low-temperature metathetical reaction between NF_4SbF_6 and CsIF_4O_2 in anhydrous HF solution, when warmed to ambient temperature, produces an iodine hypo-fluorite in high yield. The first step of this reaction involved the following reaction:



The CsSbF_6 precipitate could be easily filtered off at -30°C and Raman and F NMR spectroscopy of the filtrate showed the presence of NF_4^+ and HOIF_4O with no evidence for the IF_4O_2^- anion. This is in agreement with the above results for CsIF_4O_2 which demonstrated that MIF_4O_2 salts undergo solvolysis in anhydrous HF according to:



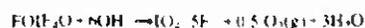
Raman and F NMR spectra showed that these NF_4HF_2 · HOIF_4O containing HF solutions are unstable at room temperature and slowly decompose to NF_3 and a new compound identified as a mixture of cis and trans FOIF_4O .



At the same time, the relative intensities of the NF_4^+ and HOIF_4O signals decreased accordingly. When the HF solvent was pumped off at -30°C from a freshly-prepared NF_4HF_2 · HOIF_4O solution, a white solid residue was obtained. The low-temperature Raman spectrum of this solid showed the presence of the NF_4^+ cation, but the remaining bands were too broad to permit a positive distinction between IF_4O_2^- , HOIF_4O and possibly some HF_2 · $n\text{HF}$. The new compound FOIF_4O was obtained in high yield by decomposing at room temperature this thermally unstable solid, with the by-product being NF_3 . Since the same products were obtained from HF solutions which, based on their F NMR and Raman spectra, contained only HOIF_4O but not IF_4O_2^- , it appears that FOIF_4O is formed by fluorination of HOIF_4O by either NF_4^+ or nascent fluorine formed during the thermal decomposition of the marginally stable $\text{NF}_4^+\text{HF}_2^-$ · $n\text{HF}$.

By way of example and not limitation, the following synthesis of FOIF₄O is given. In a typical experiment, CsIF₄O₂ (5.0 mmol) and NF₄SbF₆ (5.0 mmol) were placed in a Teflon-FEP metathesis apparatus and anhydrous HF (5 ml liquid) was condensed in at -78° C. The mixture was stirred for one hour at room temperature. The apparatus was cooled to -78° C., inverted and the white precipitate was separated from the solution by pressure filtration. Most of the HF solvent was pumped off over several hours at temperatures ranging from -64° to -30° C. The resulting white solid residue was allowed to decompose during slow warm-up from -30° C. to ambient. The volatile products were passed through a Teflon U-trap containing passivated NaF pellets, followed by a series of cold traps kept at -78°, -95°, -112° and -210° C. The -89° C trap contained a small amount of unidentified material which was discarded, the -95° C fraction consisted of pure FOIF₄O (2.36 mmol), the -112° C. trap had 1.69 mmol of FOIF₄O containing a small amount of IF₃O as impurity, and the contents of the -210° C. trap consisted of NF₃ (4.0 mmol). A small amount of white solid residue, which was left behind after the thermal decomposition of the filtrate was shown by vibrational spectroscopy to consist mainly of trans-CsIF₄O₂. The filter cake (1.8 g) was identified by Raman spectroscopy as CsSbF₆. The -95° C fraction was used for the characterization of HOIF₄O and was shown by vibrational and F NMR analysis to be free of IF₃O.

For the elemental analysis, 278.7 mg of the material was condensed at -196° C. into an ampule containing 12 ml of frozen 1 N NaOH. The mixture was warmed to ambient temperature for twelve hours and then analyzed for total iodine by energy dispersive X-ray fluorescence spectrometry, for IO₄⁻ by iodometric titration, for base consumption by back titration with 0.1 N HCl using a pH electrode and for fluoride by titration using La(NO₃)₃ and an anion specific ion electrode. Anal. calcd for FOIF₄O 1, 49.98; F, 37.42, OH⁻ consumed, 6.0 equiv/mol, iodometric titration, 8.0 equiv/mol, assuming the following hydrolysis reaction:



Found: I, 50.0, F, 36.0, OH⁻ consumed, 6.1 equiv/mol, iodometric titration, 7.8 equiv/mol

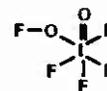
Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that, within

the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

What is claimed and desired to be secured by Letters Patent of the United States is:

1. A compound having an empirical formula which consists essentially of FOIF₄O.

2. A compound having an empirical formula of FOIF₄O which comprises a stereo-isomer selected from the group consisting of



cis

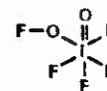
and



trans

and mixtures thereof.

3. The compound of claim 2 wherein one stereo-isomer has the cis structural formula comprising



4. The compound of claim 2 wherein a second stereo-isomer has the trans structural formula comprising



5. A process for preparing FOIF₄O, comprising the steps of:

metathetically reacting solutions of NF₄SbF₆ and CsIF₄O₂ in anhydrous HF; removing the CsSbF₆ precipitate and HF solvent, and thermally decomposing the filtrate residue.

United States Patent [19]

[11] 4,339,423

Christe et al.

[45] Jul. 13, 1982

[54] PEROXONIUM SALTS

[75] Inventors: Karl O. Christe, Calabasas, William W. Wilson, Canoga Park, both of Calif.

[73] Assignee: The United States of America as represented by the Secretary of the Navy, Washington, D.C.

[21] Appl. No.: 115,306

[22] Filed: Jan. 25, 1980

[51] Int. Cl.³ C01B 15/00

[52] U.S. Cl. 423/462

[58] Field of Search 423/462

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Primary Examiner—Brian E. Hearn
 Attorney, Agent, or Firm—Robert F. Beers; W. Thom Skeer; Lloyd E. K. Pohl

[57] ABSTRACT

The peroxonium salts, $H_3O_2^+Sb_2F_{11}^-$, $H_3O_2^+SbF_6^-$ and $H_3O_2^+AsF_6^-$, are prepared by protonation of H_2O_2 in anhydrous HF solutions of the corresponding Lewis acids. The salts decompose producing the corresponding H_3O^+ salts and O_2 in the temperature range of from 20° to 50° C. and thus are useful as oxidizers in situations where the production of oxygen in the 20°-50° C. temperature range is desirable. The salts also provide a convenient means for storing H_2O_2 in a solid form.

3 Claims, No Drawings

PEROXONIUM SALTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to peroxonium salts and to method for their preparation.

2. Description of the Prior Art

Materials which will produce O_2 at relatively low temperatures are in demand. For example, such a material could be used to produce oxygen for use in manned space vehicles and the like simply by placing a quantity of the material in a heatable container and heating the material when oxygen production was desired.

H_2O_2 is a very useful producer of molecular oxygen. For example, it is used to generate excited oxygen for use in chemical lasers. Also, it is used as a monopropellant in liquid rocket engines. However, it has a drawback in that it is difficult to handle. It readily undergoes autocatalytic decomposition. Accordingly, it would be convenient if this material could be stored in a stable salt form.

SUMMARY OF THE INVENTION

According to this invention, the first known peroxonium salts are prepared. The salts are $H_3O_2^+ \cdot SbF_{11}^-$, $H_3O_2^+ \cdot SbF_6^-$ and $H_3O_2^+ \cdot AsF_6^-$. The salts are prepared by protonation of H_2O_2 in anhydrous HF solutions of the corresponding Lewis acids. The salts may be used to produce oxygen by heating them to a temperature in the range of from 20° to 50° C. whereupon they decompose producing the corresponding H_3O^+ salts and O_2 . The salts also provide a convenient means for storing H_2O_2 in a solid form.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following specific examples describe the preparation of the three peroxonium salts of this invention.

EXAMPLE I

PREPARATION OF $H_3O_2^+ \cdot AsF_6^-$

The Lewis acid, AsF_5 (15.39 mmol) and anhydrous HF (50.76 mmol) were combined at $-196^\circ C.$ in a passivated Teflon-FEP ampule equipped with a valve. The mixture was allowed to melt and homogenize. The ampule was then taken to a drybox and H_2O_2 of 99.95% purity (15.29 mmol) was syringed in at $-196^\circ C.$ The ampule was then transferred back to the vacuum line and evacuated at $-196^\circ C.$ It was then kept at $-78^\circ C.$ for 2 days to allow reaction. After this period, no evidence was found for material noncondensable at $-196^\circ C.$, i.e., there was no evidence of O_2 evolution. The mixture was then (after 2 days) warmed to $-45^\circ C.$ and a clear solution resulted. Material volatile at $-45^\circ C.$ was removed by pumping for 10 hours and was collected at $-196^\circ C.$ A white solid residue resulted which was marginal stability at ambient temperature. On the basis of the observed material balance (weight of 15.29 mmol $H_3O_2^+ \cdot AsF_6^-$ calculated; 3.423 g; found; 3.47 g) the conversion of H_2O_2 to $H_3O_2^+ \cdot AsF_6^-$ was complete within experimental error. The compound was shown by infrared and Raman spectroscopy to contain the $H_3O_2^+$ cation and the AsF_6^- anion.

EXAMPLE II

PREPARATION OF $H_3O_2^+ \cdot SbF_6^-$

Antimony pentafluoride (27.96 mmol) was added in a drybox to a passivated Teflon FEP U-tube equipped with two valves and a Teflon-coated magnetic stirring bar. Anhydrous HF (522.9 mmol) was added on the

vacuum line at $-196^\circ C.$ and the mixture was homogenized by stirring at $20^\circ C.$ In the drybox, hydrogen peroxide (27.97 mmol) was syringed into the U-tube at $-196^\circ C.$ The cold tube was transferred back to the vacuum line and was evacuated. The tube was warmed from $-196^\circ C.$ to $-78^\circ C.$ for 1 hour with agitation which resulted in the formation of a finely divided white solid, suspended in the liquid HF. When the mixture was warmed to $20^\circ C.$ the white solid completely dissolved. No gas evolution was observed during the entire warm-up operation, and no noncondensable material could be detected when the mixture was cooled again to $-196^\circ C.$ The HF solvent was pumped off at $-22^\circ C.$ for 3 hours resulting in 7.566 g of a white solid (weight calculated for 27.96 mmol of $H_3O_2^+ \cdot SbF_6^-$ = 7.570 g), stable at $20^\circ C.$ The compound was shown by vibrational spectroscopy to be composed of $H_3O_2^+$ cations and SbF_6^- anions. Additional support for the composition of the product was obtained by allowing a sample of $H_3O_2^+ \cdot SbF_6^-$ to thermally decompose at about $45^\circ C.$ This decomposition produced O_2 and the known H_3OSbF_6 salt in almost quantitative yield.

EXAMPLE III

PREPARATION OF $H_3O_2^+ \cdot Sb_2F_{11}^-$

The synthesis of this compound was carried out in a manner identical with that described above for the preparation of $H_3O_2^+ \cdot SbF_6^-$, except for using an excess of SbF_5 . Thus, the combination of SbF_5 (14.83 mmol), HF (407 mmol), and H_2O_2 (6.83 mmol) produced 3.581 g of a white solid (weight calculated for 6.83 mmol of $H_3O_2^+ \cdot Sb_2F_{11}^-$ = 3.581 g), stable up to about $50^\circ C.$ The compound was shown by vibrational and NMR spectroscopy to contain the $H_3O_2^+$ cation and $Sb_2F_{11}^-$ as the principal anion.

All of the above peroxonium salts decompose to form O_2 and the corresponding H_3O^+ salts at temperatures in the range of from 20° to 50° C. Thus, to use the salts of this invention to produce O_2 one may heat them to a temperature within the stated range.

As has been indicated above, the salts of this invention also provide a means for storing H_2O_2 in a solid form.

What is claimed is:

1. A peroxonium salt having the formula $H_3O_2^+ \cdot X^-$ wherein X^- is selected from the group of anions having the formulas SbF_6^- and AsF_6^- .

2. A method for preparing a solid salt having the formula $H_3O_2^+ \cdot X^-$ wherein X^- is selected from the group consisting of SbF_6^- , said method comprising the steps of:

A. dissolving a Lewis acid selected from the group consisting of AsF_5 and SbF_5 in anhydrous HF to form a solution;

B. adding H_2O_2 in an amount equimolar to that of said Lewis acid to the solution to form a reaction mixture; and

C. allowing the mixture to react to form a solid salt.

3. A method for preparing a salt containing $H_3O_2^+$ cations and $Sb_2F_{11}^-$ anions, said method comprising the steps of:

A. dissolving SbF_5 in anhydrous HF to form a solution;

B. adding H_2O_2 to said solution to form a reaction mixture, said H_2O_2 being added in an amount calculated to provide an excess of SbF_5 in said reaction mixture; and

C. allowing the mixture to react.

United States Patent [19]
Christe et al.

[11] 4,374,112
[45] Feb. 15, 1983

- [54] STABLE NF_4^+ SALT OF HIGH FLUORINE CONTENT
- [75] Inventors: Karl O. Christe, Calabasas; William W. Wilson, Canoga Park, both of Calif.
- [73] Assignor: The United States of America as represented by the Secretary of the Army, Washington, D.C.
- [21] Appl. No.: 219,056
- [22] Filed: Dec. 22, 1980
- [51] Int. Cl. _____ C01B 21/00; C01G 45/00
- [52] U.S. Cl. _____ 423/351; 423/472; 149/119
- [58] Field of Search _____ 423/351, 472
- [56] **References Cited**

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4,172,884	10/1979	Christe et al.	_____	423/351

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 Karl O. Christe, *Inorg. Chem.*, 16, 2238-2241 (1977).
Primary Examiner—Brian E. Hears
Attorney, Agent, or Firm—Nathan Edelberg, Robert P. Gibson, Jack W. Voight

[57] ABSTRACT

An improved NF_4^+ composition for solid propellant NF_3-F_2 gas generators and high detonation pressure explosives is described which combines high oxidizer content with good thermal stability. The novel composition has the formula $(NF_4)_xMnF_6$, and a process for its production is disclosed.

1 Claim, No Drawings

STABLE NF_4^+ SALT OF HIGH FLUORINE CONTENT

DEDICATORY CLAUSE

The invention described herein was made in the course of or under a contract or subcontract thereunder with the Government, therefore, the invention described herein may be manufactured, used, or licensed by or for the Government for governmental purposes without the payment to us of any royalties thereon.

BACKGROUND OF THE INVENTION

1 Field of the Invention

This invention relates to a composition of matter and a method of producing the same and is particularly directed to improved solid propellant NF_3 - F_2 gas generators and high detonation pressure explosives.

2 Description of Prior Art

NF_4^+ salts are the key ingredients for solid propellant NF_3 - F_2 gas generators, as shown by D. Filipovich in U.S. Pat. No. 3,963,542. These propellants consist of a highly over-oxidized grain using NF_4^+ salts as the oxidizer. Burning these propellants with a small amount of fuel, such as aluminum, powder, generates sufficient heat to thermally dissociate the bulk of the oxidizer. This is shown in NF_4BF_4 in the following equation:



As can be seen from the equation the gaseous combustion products contain the volatile Lewis acid BF_3 . This disadvantage of a volatile Lewis acid by-product is shared by many of the previously known NF_4^+ compositions. These volatile Lewis acids possess a relatively high-molecular weight and a low γ value ($\gamma = C_p/C_v$) relative to the preferred diluent helium and frequently act as a deactivator for the chemical HF-DF laser. Consequently, these volatile Lewis acids must be removed from the generated gas prior to its use in an efficient chemical laser. Based on the state of the art, this is achieved by adding a clinker forming agent, such as KF, to the solid propellant formulation. The function of this additive serves to convert the volatile Lewis acid, such as BF_3 , to a non-volatile salt as shown by the following equation:



In addition, several NF_4^+ compositions are known which are based on self-clinkering NF_4^+ salts, as shown by K. O. Christe et al in U.S. Pat. No. 4,172,884. The theoretical fluorine yields achievable with the presently known NF_4^+ salts are summarized in Table I.

TABLE I

Theoretical Fluorine Yields (in the form of NF_3 and F_2) of Presently Known NF_4^+ Salts Before Burning		
RANK	SYSTEM	THEORETICAL F, WT PERCENT
1	$(NF_4)_2NiF_6$	64.6
2	$(NF_4)_2SnF_6$	46.0
3	$(NF_4)_2TiF_6 \cdot 1.4KF$	39.5
4	$NF_4BF_4 \cdot 1.2KF$	34.6
5	$(NF_4)_2GeF_6 \cdot 1.4KF$	37.6
6	NF_4SbF_6	31.3
7	$NF_4PF_6 \cdot 1.2KF$	31.2
8	$NF_4GeF_5 \cdot 1.2KF$	29.0
9	$NF_4AsF_6 \cdot 1.2KF$	27.3
10	$NF_4SbF_5 \cdot 1.2KF$	24.0

TABLE I-continued

Theoretical Fluorine Yields (in the form of NF_3 and F_2) of Presently Known NF_4^+ Salts Before Burning		
RANK	SYSTEM	THEORETICAL F, WT PERCENT
11	$NF_4BF_4 \cdot 1.2KF$	19.7

As can be seen from Table I, the self-clinkering $(NF_4)_2NiF_6$ salt gives by far the highest fluorine yield. Unfortunately, the thermal stability of $(NF_4)_2NiF_6$ (See: K. O. Christe, Inorg. Chem. 16, 2236, 1977) is insufficient to pass the requirements of long term stability tests.

Another potential application for energetic NF_4^+ salts is their use in high detonation pressure explosives as disclosed in a recently issued patent titled "High Detonation Pressure Explosives", (for additional information see U.S. Pat. No. 4,207,124 dated June 10, 1980, by Karl O. Christe, one of the co-inventors of the instant invention).

Again, the most energetic NF_4^+ salt, i.e. $(NF_4)_2NiF_6$, has the major drawback of insufficient thermal stability to meet long term storability requirements.

The above discussion demonstrates that the prior art provided either a high performing NF_4^+ salt of insufficient thermal stability or low performing NF_4^+ salts of sufficient thermal stability. However, an NF_4^+ salt combining both high energy and good thermal stability has previously been unknown.

Accordingly, it is an object of the present invention to provide a high performing NF_4^+ salt of a thermal stability sufficient to meet long term stability requirements.

Another object of the present invention is to provide a process for the production of such a high performing stable NF_4^+ salt.

These and other objects and features of the present invention will be apparent from the examples set forth hereinafter. It is understood, however, that these examples are merely illustrative of the invention and should not be considered as limiting the invention in any sense.

BRIEF SUMMARY OF THE INVENTION

The above described problem of obtaining an NF_4^+ salt which combines both high energy and good thermal stability is overcome by the present invention. We have found that the new composition $(NF_4)_2MnF_6$ not only has a high theoretical fluorine content of 59.9 weight percent, but also possesses the thermal stability required for long term storability. This salt is prepared by the metathetical reaction of Ca_2MnF_6 with NF_4SbF_6 in anhydrous HF as a solvent.

DETAILED DESCRIPTION OF THE INVENTION

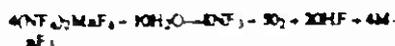
Preparation and Purification

In the N_2 atmosphere of a dry box a mixture of NF_4SbF_6 (37.29 mmol) and Ca_2MnF_6 (18.53 mmol) was placed into the bottom a prepassivated Teflon FEP double U-tube metathesis apparatus. Dry HF (20 ml liquid) was added at $-78^\circ C$. on the vacuum line, and the mixture was warmed to $25^\circ C$. for 30 min with stirring. The mixture was cooled to $-78^\circ C$. and pressure filtered at this temperature. The HF solvent was pumped off at $30^\circ C$. for 12 hours. The white filter-cake (14 g. weight) dried for 37.1 mmol of $Ca_2SbF_6 = 13.7 g$.

was shown by Raman spectroscopy to consist mainly of CaSbF_6 . The yellow filtrate residue (6.1 g. weight) dried for 18.5 mmol of $(\text{NF}_4)_2\text{MnF}_6 = 6.46 \text{ g}$ was shown by elemental analysis to have the following composition (weight %): $(\text{NF}_4)_2\text{MnF}_6$, 91.27; NF_4SbF_6 , 4.27; CaSbF_6 , 4.46. For the elemental analysis, a sample of $(\text{NF}_4)_2\text{MnF}_6$ was hydrolyzed in H_2O , and NF_3 and O_2 evolution was measured by PVT and gas chromatography, and Ca, Sb, and Mn in the hydrolysate were determined by atomic absorption spectroscopy. Anal. Calcd for $(\text{NF}_4)_2\text{MnF}_6$, 91.27, NF_4SbF_6 , 4.27, CaSbF_6 , 4.46; NF_3 , 38.07, Mn, 14.37, Sb, 3.07, Ca, 1.61. Found NF_3 , 37.8, Mn, 14.5, Sb, 3.10, Ca, 1.62. Purification of the sample is accomplished by using well established recrystallization techniques.

Solubility and Reactivity Properties

The $(\text{NF}_4)_2\text{MnF}_6$ salt is a yellow, crystalline solid which is highly soluble in anhydrous HF. At 24° C., its solubility exceeds 1.30 g per g HF. It is stable at room temperature and, in the absence of fuels, it is not shock sensitive. With water a violent reaction occurs. By analogy with the other known NF_4^+ salts, the hydrolysis was found to result in quantitative NF_3 evolution and therefore, is a useful analytical method. The hydrolysis also produced oxygen in a $\text{NF}_3:\text{O}_2$ mole ratio of 8.5 in excellent agreement with the following equation



Stability and Thermal Decomposition Rate

At 65° C., $(\text{NF}_4)_2\text{MnF}_6$ appears to be stable, but at about 100° it starts to slowly decompose. Its decomposition rate in a sapphire reactor was monitored by total pressure measurements over the temperature range 100° to 130° C. Except for a slightly faster rate during the first 20 minutes, the decomposition pressures increased approximately linearly with time at 100° C. At 130° C. the rates slightly accelerated with increasing time, however, this rate increase was quite small. At 100° C. 0.17% of the sample decomposed in 17 hours, whereas, at 130° C. 0.66% of the sample decomposed in the same time. The gaseous decomposition products consisted of NF_3 and F_2 in a mole ratio of about 1 to 1.2. For identification of the solid residue a sample of $(\text{NF}_4)_2\text{MnF}_6$ was completely decomposed in a dynamic vacuum at 240° C. Based on its weight, X-ray powder diffraction pattern and mauve color, this residue was identified as MnF_3 . Consequently, $(\text{NF}_4)_2\text{MnF}_6$ decomposes according to



A comparison with the decomposition data previously published for $(\text{NF}_4)_2\text{NiF}_6$ shows that the thermal stability of $(\text{NF}_4)_2\text{MnF}_6$ is significantly higher than that of $(\text{NF}_4)_2\text{NiF}_6$ which in 6 hours at 100° C. exhibited 9% decomposition.

Crystallographic Data

The X-ray powder diffraction pattern of $(\text{NF}_4)_2\text{MnF}_6$ is listed in Table 2. It was indexed for a tetragonal unit

cell with $a = 6.90 \text{ \AA}$, $c = 9.23 \text{ \AA}$, $Z = 2$, space group $I4/m$, and a calculated density of 2.64 g cm^{-3} .

Ionic Nature By NMR Spectrum

The ionic nature of $(\text{NF}_4)_2\text{MnF}_6$ in HF solution was established by its ^{19}F NMR spectrum which was recorded over the temperature range +20° to -75° C. It showed at all temperatures a broad resonance at $\delta = 218$ (downfield from external CFCl_3), characteristic of NF_4^+ . The lack of observable NF spin-spin coupling, generally seen for tetrahedral NF_4^+ is attributed to the influence of the paramagnetic MnF_6^{2-} anion which can provide rapid relaxation.

TABLE 2

X-Ray Powder Diffraction Data of $(\text{NF}_4)_2\text{MnF}_6$

d calcd	int	d calcd	d obsd	int	d calcd
3.75	vs	3.53	1.875	ms	1.874
3.45	s	3.45			
3.35	s	3.35	1.794	w	1.793
2.93	ms	2.93	1.726	vw	1.725
2.81	ms	2.81	1.677	vw	1.676
2.64	m	2.64	1.647	mw	1.647
2.307	mw	2.307	1.627	mw	1.627
2.183	s	2.182	1.585	w	1.585
		2.179			
2.085	mw	2.086	1.534	mw	1.534
1.975	vw	1.973	1.466	mw	1.467

^{19}F NMR solution and 76 liter

The ionic nature of $(\text{NF}_4)_2\text{MnF}_6$ in the solid state was established by its vibrational spectra which exhibit the bands characteristic of NF_4^+ and MnF_6^{2-} . The observed vibrational frequencies and their assignments are summarized in Table 3

TABLE 3

VIBRATIONAL SPECTRA OF SOLID $(\text{NF}_4)_2\text{MnF}_6$

IR	Obsd freq, cm^{-1} , and rel. intens.	Assignment (point group)	
		NF_4^+ (T_d)	MnF_6^{2-} (O_h)
40	2310vw	$2\nu_3(A + E + F_2)$	
	2000w	$\nu_1 + \nu_2(F_2)$	
	1799vw	$\nu_2 + \nu_6(A_1 + E + F_2)$	
	1666s	$\nu_1 + \nu_6(F_2)$	
	1221mw	$2\nu_6(A_1 + E + F_2)$	$\nu_1 + \nu_2(F_{1g})$
45	1160vs	$\nu_3(F_2)$	$\nu_2 + \nu_3(F_{1g} + F_{2g})$
	1110sh		$\nu_2 + \nu_3(F_{1g} + F_{2g})$
	1061vw	$\nu_2 + \nu_6(F_1 + F_2)$	$\nu_1 + \nu_6(F_{1g})$
	913vw		$\nu_1 + \nu_6(F_{1g})$
	846vw	$\nu_4(A_1)$	
	760sh		$\nu_2 + \nu_6(F_{1g} + F_{2g})$
	735sh		$\nu_3(F_{1g})$
50	620vs	$\nu_6(F_2)$	$\nu_1(A_{1g})$
	593s		$\nu_2(E_g)$
	500vw		$\nu_6(F_{1g})$
	450vw		$\nu_3(F_{2g})$
	336s		
55	304s		

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

We claim:

1. The salt having the formula: $(\text{NF}_4)_2\text{MnF}_6$, and characterized by having good thermal stability in storage.

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APPENDIX AA

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