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INORGANIC HALOGEN OXIDIZER RESEARCH

FINAL REPORT

ROCKETDYNE DIVISION
ROCKWELL INTERNATIONAL
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Final Report for Period 1 March 1979 - 28 February 1982

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Synthesis, Novel Oxidizers, Solid-Propellant Nitrogen Trifluoride Fluorine Gas Generators, Perfluoroammonium Salts, Fluorine Perchlorate, Fluorocarbon Perchlorates, Polarity of the O-F Bond, Iodine (VII) Oxytetrafluoride Hypo- fluorite, Iodine (VII) Oxytetrafluoride Hypochlorite, Tetrafluoroperiodates, Peroxonium Salts, Formation and Decomposition Mechanism of Perfluoroammonium		
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 program resulted in 27 papers published in major technical journals, 12 papers presented at international and national meetings, and 6 issued and 4 pending U.S. patents. The main effort of this program was in the areas of nitrogen fluoride and halogen fluoride chemistry. Numerous new energetic NF_4 salts were synthesized and characterized, among which was $(\text{NF}_4)_2 \text{XeF}_8$, a compound with the highest known usable fluorine content		

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19. (Continued)

Salts, Sulfur Tetrafluoride, Perfluoroammonium Hexafluoroantimonate Synthesis, Perfluoroammonium Perchlorate, Perfluoroammonium Bifluoride, Perfluoroammonium Hexafluoroarsenate Force Field, Perfluoroammonium Fluorosulfate, Perfluoroammonium Hexafluoromanganate (IV), Repulsion Effects in Trigonal-Bipyramidal Molecules, Chlorine Trifluoride Oxide, Electron Diffraction, Perfluoroammonium Pentafluorooxyuranate (VI), Perfluoroammonium Salt Analysis, Perchloryl Fluoride Force Field, Tetrafluoroorthoperiodic Acid, Azotrifluoromethane, Perfluoroammonium Fluorotungstates, Cesium Fluorotungstates, Perfluoroammonium Hexafluorosilicates, Silicon Tetrafluoride, Perfluoroammonium Salts Thermochemistry, Perfluoroammonium Salts of Aluminum Trifluoride and Beryllium Difluoride, Halogen Oxyfluorides Preparation, Perfluoroammonium Heptafluorotungstate (VI), Perfluoroammonium Heptafluorouranate (VI), Perfluoroammonium Heptafluoroxenate (VI), Perfluoroammonium Octafluoroxenate (VI), Xenon Hexafluoride, Cesium Heptafluoroxenate (VI), Sodium Heptafluoroxenate (VI), Sodium Octafluoroxenate (VI), Tellurium Pentafluoride Hypofluorite, Tellurium Pentafluoride Hypochlorite, Fluorine Perchlorate Force Field, Burning Rate Modifiers, Perfluoroammonium Hexafluorophosphate, High Detonation Pressure Explosives.

20. (Continued)

(71.7 weight %). The formation and decomposition mechanism of NF_4^+ salts was clarified and thermodynamic properties were determined for some of the more important NF_4^+ salts. The reaction chemistry of NF_4^+ salts was studied which resulted in a new general method for the synthesis of hypofluorites. This method was used to synthesize the first known examples of an iodine and a tellurium hypofluorite. The NF_4ClO_4 salt was synthesized and used to prepare pure fluorine perchlorate in high yield and purity. Fluorine perchlorate was thoroughly characterized, and its addition across olefinic double bonds was studied. Other halogen fluorides studied include ClF_3O and FClO_3 . The complete results of the work under this contract were summarized in 33 technical papers and patents, and are reproduced in Appendixes A through GG.

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PREFACE

The research reported herein was supported by the Chemistry Division of the Office of Naval Research, Code 413, 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 1979 through 28 February 1982. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out mainly by Drs. K. O. Christe, C. J. Schack, W. W. Wilson and Mr. R. D. Wilson with contributions from Drs. E. C. Curtis, M. D. Lind, I. B. Goldberg, and R. Rushworth (all at Rockwell International). Other contributors to these research efforts, at no cost to the contract were: W. Sawodny, H. Haertner, K. Birk, and G. Fogarasi (University of Ulm, Germany), R. Bougon and T. Bui Huy (French Atomic Energy Commission), H. Willner (University of Dortmund, Germany), R. Peacock and J. Burgess (University of Leicester, England), and H. Oberhammer (University of Tübingen, Germany). The program was administered by Dr. L. R. Grant.

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CONTENTS

Introduction	3
Publications and Patents Generated Under This Program	4
Publications	4
Papers in Press	6
Papers Presented at Meetings	6
Patents Issued	8
Patents Pending	9
Results and Discussion	10
Nitrogen Fluoride Chemistry	10
Halogen Fluorides and Oxyfluorides	16
Miscellaneous	17
Conclusion	17
References	18
<u>Appendixes A through GG</u>	
Technical Papers and Patents	A-1 thru GG-1
<u>Appendix HH</u>	
Distribution List	HH-1

INTRODUCTION

This is the final report of a research program carried out at Rocketdyne between 1 March 1979 and 28 February 1982. 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 21 technical papers were published and 6 papers are in press in major scientific journals. In addition, 12 papers were presented at international and national conferences. A further testimony to the creativity of this program is the fact that it resulted in 6 U.S. patents issued and 4 pending. The technical papers and issued patents are reproduced in Appendix A through GG.

PUBLICATIONS AND PATENTS GENERATED UNDER THIS PROGRAM

PUBLICATIONS

1. "Reactions of Fluorine Perchlorate with Fluorocarbons and the Polarity of the O-F Bond in Covalent Hypofluorites," by C. J. Schack and K. O. Christe, Inorg. Chem., 18, 2619 (1979).
2. "Cis- and Trans-Iodine (VII) Oxtetrafluoride Hypofluorite, OIF_4OF ," by K. O. Christe and R. D. Wilson, Inorg. Nucl. Chem. Letters, 15, 375 (1979).
3. "Novel Onium Salts. Synthesis and Characterization of the Peroxonium Cation, H_2OOH^+ ," by K. O. Christe, W. W. Wilson, and E. C. Curtis, Inorg. Chem., 18, 2578 (1979).
4. "Formation and Decomposition Mechanism of NF_4^+ Salts," by K. O. Christe, R. D. Wilson and I. B. Goldberg, Inorg. Chem., 18, 2572 (1979).
5. "Sulfur Tetrafluoride. Assignment of Vibrational Spectra and Force Field," by K. O. Christe, H. Willner, and W. Sawodny, Spectrochim. Acta, 35A, 1347 (1979).
6. "Simplified Synthesis of $\text{NF}_4^+\text{SbF}_6^-$," by W. W. Wilson and K. O. Christe, J. Fluor. Chem., 15, 83 (1980).
7. "Synthesis and Properties of $\text{NF}_4^+\text{ClO}_4^-$ and $\text{NF}_4^+\text{HF}_2^- \cdot n\text{HF}$ and Some Reaction Chemistry of NF_4^+ Salts," by K. O. Christe, W. W. Wilson and R. D. Wilson, Inorg. Chem., 19, 1494 (1980).
8. "The Force Field of SF_4 ," by W. Sawodny, K. Birk, G. Fogarasi, and K. O. Christe, Z. Naturforsch., 35B, 1137 (1980).
9. "Vibrational Spectra of $^{15}\text{NF}_4\text{AsF}_6$ and General Valence Force Field of NF_4^+ ," by K. O. Christe, Spectrochim. Acta, 36A, 921 (1980).

10. "Synthesis and Properties of $\text{NF}_4^+\text{SO}_3\text{F}^-$," by K. O. Christe, R. D. Wilson and C. J. Schack, Inorg. Chem., 19, 3046 (1980).
11. "Synthesis and Characterization of $(\text{NF}_4)_2\text{MnF}_6$," by K. O. Christe, W. W. Wilson and R. D. Wilson, Inorg. Chem., 19, 3254 (1980).
12. "Evidence for the Existence of Directional Repulsion Effects by Lone Valence Electron Pairs and π Bonds in Trigonal-Bipyramidal Molecules," by K. O. Christe and H. Oberhammer, Inorg. Chem., 20, 296 (1981).
13. "Synthesis and Properties of $\text{NF}_4^+\text{UF}_5\text{O}^-$," by W. W. Wilson, R. D. Wilson, and K. O. Christe, J. Inorg. Nucl. Chem., 43, 1551 (1981).
14. "Determination of NF_3 in NF_4^+ Containing Complex Fluoro Anion Salts," by R. Rushworth, C. J. Schack, W. W. Wilson, and K. O. Christe, Anal. Chem., 53, 845 (1981).
15. "The General Valence Force Field of Perchloryl Fluoride," by K. O. Christe, E. C. Curtis, W. Sawodny, H. Haertner, and G. Fogarasi, Spectrochim. Acta, 37A, 549 (1981).
16. "Syntheses and Properties of FOIF_4O , ClOIF_4O , HOIF_4O , and Tetrafluoroperiodates," by K. O. Christe, R. D. Wilson and C. J. Schack, Inorg. Chem., 20, 2104 (1981).
17. "Properties of Azidotrifluoromethane," by K. O. Christe and C. J. Schack, Inorg. Chem., 20, 2566 (1981).
18. "Perfluoroammonium and Cesium Fluorotungstates," by W. W. Wilson and K. O. Christe, Inorg. Chem., 20, 4139 (1981).
19. "Synthesis and Properties of $(\text{NF}_4)_2\text{SiF}_6$ and Interaction of SiF_4 with Anhydrous HF and CsHF_2 ," by W. W. Wilson and K. O. Christe, J. Fluor. Chem., 19, 253 (1982).

20. "Thermochemistry of NF_4^+ Salts," by R. Bougon, T. Bui Huy, J. Burgess, K. O. Christe, and R. Peacock, J. Fluor. Chem., 19, 263 (1982).
21. "Gas Phase Structure of ClF_3O ," by H. Oberhammer and K. O. Christe, Inorg. Chem., 21, 273 (1982).

PAPERS IN PRESS

22. "Syntheses of NF_4^+ Salts Derived from the Lewis Acids AlF_3 and BeF_2 ," by K. O. Christe, W. W. Wilson and C. J. Schack, J. Fluor. Chem.
23. "Preparation of Halogen Oxyfluorides," by K. O. Christe, Inorg. Reactions and Methods.
24. "Perfluoro Ammonium Salts of Metal Heptafluoro Anions," by W. W. Wilson and K. O. Christe, Inorg. Chem.
25. "Perfluoro Ammonium and Alkali Metal Salts of the Heptafluoro Xenon (VI) and Octafluoro Xenon (VI) Anions," by K. O. Christe and W. W. Wilson, Inorg. Chem.
26. "Synthesis and Characterization of TeF_5OF ," by C. J. Schack, W. W. Wilson and K. O. Christe, Inorg. Chem.
27. "Fluorine Perchlorate, Vibrational Spectra, Force Field and Thermodynamic Properties," by K. O. Christe and E. C. Curtis, Inorg. Chem.

PAPERS PRESENTED AT MEETINGS

28. "The use of Anhydrous HF as a Solvent for the Synthesis of Novel NF_4^+ and Onium Salts," by K. O. Christe, American Chemical Society - Chemical Society of Japan Congress, Honolulu, Hawaii, (April 1979).

29. "Fluorine Perchlorate, Synthesis, Properties and Reaction Chemistry," by K. O. Christe, C. J. Schack, and E. C. Curtis, American Chemical Society - Chemical Society of Japan Congress, Honolulu, Hawaii, (April 1979).
30. "Handling of Fluorine," by K. O. Christe, Material Research Council Meeting, La Jolla, CA (July 1979).
31. "Synthesis and Characterization of NF_4ClO_4 , $\text{NF}_4\text{HF}_2(\cdot\text{XHF})$ and Cis and Trans OIF_4OF ," by K. O. Christe, W. W. Wilson, and R. D. Wilson, 9th International Symposium on Fluorine Chemistry, Avignon, France (September, 1979).
32. "Recent Results in Nitrogen Fluoride Chemistry," by K. O. Christe, C. J. Schack, W. W. Wilson, and R. D. Wilson, 7th European Symposium on Fluorine Chemistry, Venice, Italy (September, 1980).
33. "Synthesis and Properties of NF_4UOF_5 ," by W. W. Wilson, R. D. Wilson and K. O. Christe, Second Chemical Congress of the North American Continent, Las Vegas, Nev. (August 1980).
34. "On the Syntheses and Properties of FOIF_4O , ClOIF_4O , HOIF_4O and Tetrafluoroperiodates," by K. O. Christe, R. D. Wilson and C. J. Schack, 5th Winter Fluorine Conference, Daytona Beach, Fla. (February 1981).
35. "Perfluoroammonium Chemistry," by K. O. Christe, 1981 Inorganic Gordon Research Conference, New Hampton School, N. H. (August 1981).
36. "Reaction Chemistry of CF_3N_3 ," by C. J. Schack and K. O. Christe, 1981 Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA (October, 1981).
37. "Thermochemistry of NF_4^+ Salts," by R. Bougon, T. Bui Huy, J. Burgess, K. O. Christe and R. D. Peacock, 1981 Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA (October, 1981).

38. " NF_4^+ Salts of Heptafluoro Anions," by W. W. Wilson and K. O. Christe, 1981 Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA (October, 1981).
39. "Pentafluorotellurium Hypofluorite," by C. J. Schack, W. W. Wilson and K. O. Christe, 183rd National ACS Meeting, Las Vegas, Nev. (April 1982).
40. Invited seminars on various aspects of our work were given at different universities.

PATENTS ISSUED

41. "Self-Clinkering NF_4^+ Compositions for $\text{NF}_3\text{-F}_2$ Gas Generators and Methods of Producing Same," by K. O. Christe, C. J. Schack, R. D. Wilson, U.S. Pat. 4,152,406.
42. "Self-Clinkering Burning Rate Modifier for Solid Propellant $\text{NF}_3\text{-F}_2$ Gas Generators for Chemical HF-DF lasers," by K. O. Christe and C. J. Schack, U.S. Pat. 4,163,773.
43. " $\text{N}_2\text{F}_3\text{SbF}_6$ and its Preparation," by C. J. Schack and K. O. Christe, U.S. Pat. 4,163,774.
44. "Displacement Reaction for Producing NF_4PF_6 ," by K. O. Christe and C. J. Schack, U.S. Pat. 4,172,881.
45. "Self-Clinkering NF_4^+ Compositions for $\text{NF}_3\text{-F}_2$ Gas Generators and Method of Producing Same," by K. O. Christe, C. J. Schack and R. D. Wilson, U.S. Pat. 4,172,884.
46. "High Detonation Pressure Explosives," by K. O. Christe, U.S. Pat. 4,207,124.

PATENTS PENDING

47. "Iodine (VII) Oxytetrafluorohypofluorite and a Process for Preparing Same," by K. O. Christe and R. D. Wilson.
48. "Peroxonium Salts," by K. O. Christe and W. W. Wilson.
49. "Stable NF_4^+ Salt of High Fluorine Content," by K. O. Christe and W. W. Wilson.
50. "Improved $\text{NF}_3\text{-F}_2$ Gas Generator Composition," by K. O. Christe and W. W. Wilson.

RESULTS AND DISCUSSION

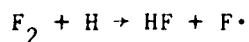
In view of the very large amount of data generated under this program and their highly diversified nature, we will restrict ourselves to highlight only those areas that are most important and in which our efforts were most heavily concentrated.

NITROGEN FLUORIDE CHEMISTRY

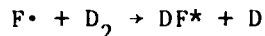
For a long time, nitrogen fluorides have been of great interest as advanced oxidizers for rocket propulsion. Of these, nitrogen trifluoride is the most important compound because it combines a high fluorine and energy content with a remarkable inertness. Its only major drawback is its low boiling point of -129°C . Therefore, the conversion of NF_3 into stable storable solids without significant loss in energy was highly desirable. The first step in this direction was undertaken in 1965 when one of us, under ONR sponsorship at Stauffer Chemical (Ref. 1), discovered the existence of the stable $\text{NF}_4^+\text{AsF}_6^-$ salt. However, it was not until 1971 when, with the advent of chemical HF-DF lasers, the interest in storable $\text{NF}_3\text{-F}_2$ sources was renewed.

It became rapidly obvious that NF_4^+ salts were the most promising oxidizers for solid propellant $\text{NF}_3\text{-F}_2$ gas generators. The concept of such a gas generator was conceived (Ref. 2) and, to a large extent (Ref. 3 through 9), developed at Rocketdyne. It offers significant logistics and safety advantages over cryogenic or storable liquid oxidizers.

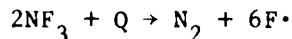
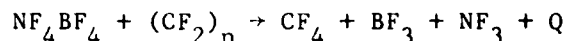
In a chemical HF-DF laser, F atoms are generated by burning F_2 in a precombustor with a fuel, such as hydrogen:



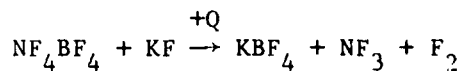
The F atoms are subsequently reacted with a cavity fuel, such as D₂, to produce vibrationally excited DF as the active lasing species:



In the original solid F atom generator concept (Ref. 2), the F atoms were directly generated by burning the solid propellant grain, thus eliminating the need of a precombustor. This concept is demonstrated for NF₄BF₄ with a small percentage of Teflon serving both as a fuel and a binder. The heat of reaction (Q) is sufficient to dissociate most of the NF₃ and F₂ to F atoms and N₂:



From a practical point of view, however, such a direct generation of F atoms is not desirable, since it does not allow the necessary flow controls and flexibility required for operation. Consequently, the concept was modified to that of an NF₃-F₂ molecule generator, using a gas catch tank. Further modification of this concept became necessary, when system analysis data revealed that gaseous by-products of high molecular weight and low C_p/C_v significantly degrade the performance of a laser. Consequently, an NF₃-F₂ gas generator was desired that would produce no gases other than NF₃ and F₂. The latter objective can be achieved by a so-called clinker system in which the BF₃ byproduct is converted by an alkali metal fluoride to a nonvolatile BF₄⁻ salt:



Whereas the feasibility of such a clinker system approach has been well demonstrated, the addition of KF lowers the NF₃-F₂ yield per pound of solid propellant and the possibility always exists of having incomplete clinkering.

Realizing these limitations, we have developed "self-clinkering" NF₄⁺ salts (Patents 41 and 45). These are salts derived from anions that will yield

nonvolatile fluorides, such as SnF_4 or TiF_4 , after thermal decomposition. Test firings of these salts in formulations, however, revealed problems. The "non-volatile" fluorides were found to be not so nonvolatile after all, and either sublimed or were blown as fine dust throughout the system. Furthermore, very high fuel levels were required to burn these formulations. To be able to fire these formulations, it was necessary to add some alkali metal fluorides as burning aids and to develop burning rate modifiers (Patents 42 and 43). It was found possible to increase the fluorine yields by using the lighter LiF instead of KF in some of these formulations and to use less than the stoichiometric amount (Patent 50).

As reported in the preceding final report under this program (Ref. 10), the NF_4^+ salt with the highest theoretical fluorine yield (64.6 weight % before burning) was $(\text{NF}_4)_2\text{NiF}_6$. However, this salt had the disadvantage of being of limited thermal stability and did not completely meet our long-term storability requirements. We therefore searched for other high fluorine yield NF_4^+ salts and found with $(\text{NF}_4)_2\text{MnF}_6$ a compound which approaches the fluorine yield of the nickel salt, but is thermally more stable (Paper 11, Patent 49).

Since $(\text{NF}_4)_2\text{BeF}_4$ and $(\text{NF}_4)_3\text{AlF}_6$ have very high theoretical fluorine yields, (see Table I), we have pursued the syntheses of these two compounds. Although our efforts to prepare these two compositions were unsuccessful, we succeeded partially in that NF_4AlF_4 and $\text{NF}_4\text{Be}_2\text{F}_5$ (paper 22) were prepared.

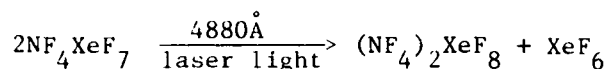
We have continued our search for highly energetic NF_4^+ salts which are useful for applications such as high detonation pressure explosives (Patent 46). For example, we have prepared and characterized NF_4ClO_4 (paper 7); however, the compound is too unstable thermally to be of practical use. The attempts made to prepare NF_4^+ salts having NO_3^- or halogen fluoride based anions were also unsuccessful, but resulted in extremely interesting reaction chemistry (see below).

In our search for novel energetic NF_4^+ salts, we prepared and characterized NF_4HF_2 . Although this salt is thermally unstable and cannot be isolated

TABLE 1. THEORETICAL FLUORINE YIELDS OF
 $\text{NF}_3\text{-F}_2$ GAS GENERATOR COMPOSITIONS

SYSTEM	USABLE F CONTENT (WT%) BEFORE BURNING	COMMENTS
$(\text{NF}_4)_2\text{XeF}_8$	71.7	REQUIRES NO CLINKERING. AGENT DIFFICULT TO SYNTHESIZE. HYDROLYZES TO SHOCK-SENSITIVE XeO_3 . EXPENSIVE.
$(\text{NF}_4)_2\text{BeF}_4$	71.7	UNKNOWN
$(\text{NF}_4)_3\text{AlF}_6$	69.3	UNKNOWN
$(\text{NF}_4)_2\text{NiF}_6$	64.6	MARGINAL LONG-TERM STORABILITY
NF_4XeF_7	62.9	SAME AS FOR $(\text{NF}_4)_2\text{XeF}_8$
$(\text{NF}_4)_2\text{MnF}_6$	59.9	REQUIRES BURNING AID
$(\text{NF}_4)_2\text{SiF}_6$	59.0	REQUIRES CLINKERING AGENT
$(\text{NF}_4)_2\text{TiF}_6$	55.6	REQUIRES BURNING AID
NF_4BF_4	54.0	REQUIRES KF AS CLINKERING AGENT
$(\text{NF}_4)_2\text{GeF}_6$	51.8	REQUIRES CLINKERING AGENT
NF_4AlF_4	49.2	REQUIRES BURNING AID
$\text{NF}_4\text{Be}_2\text{F}_5$	46.8	VERY TOXIC. REQUIRES BURNING AID
$(\text{NF}_4)_2\text{SnF}_6$	46.0	REQUIRES BURNING AID
NF_4PF_6	40.4	REQUIRES CLINKERING AGENT
NF_4GeF_5	36.9	REQUIRES CLINKERING AGENT
NF_4AlF_6	34.1	REQUIRES CLINKERING AGENT. TOXIC.
NF_4SnF_5	31.3	REQUIRES BURNING AID
NF_4SbF_6	29.2	REQUIRES CLINKERING AGENT
NF_4BiF_6	23.0	REQUIRES CLINKERING AGENT

completely free of some solvated HF, this compound turned out to be an extremely useful intermediate. It was found that, by the repeated reaction of this salt with a large excess of a Lewis acid, new NF_4^+ salts could be prepared which are derived from Lewis acids that are weaker than HF. Synthesis of these salts by the standard technique, i.e., metathesis in anhydrous HF or BrF_5 solutions, had proven impossible due to displacement of the Lewis acid by the solvent. Using solid $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$ as a starting material, we have successfully prepared and characterized the following new NF_4^+ salts: $\text{NF}_4\text{UF}_5\text{O}$ (paper 13), NF_4WOF_5 (paper 18), NF_4WF_7 and NF_4UF_7 (paper 24), $(\text{NF}_4)_2\text{SiF}_6$ (paper 19), and NF_4XeF_7 (paper 25). The last compound was successfully converted to $(\text{NF}_4)_2\text{XeF}_8$ by a photoselective laser-induced reaction:

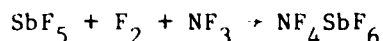
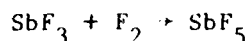


The NF_4XeF_7 starting material is yellow and strongly absorbs the blue laser line; whereas, $(\text{NF}_4)_2\text{XeF}_8$ is white and therefore does not absorb the light. Attempts undertaken to convert NF_4XeF_7 into $(\text{NF}_4)_2\text{XeF}_8$ by simple heating were unsuccessful since both compounds decomposed at comparable rates.

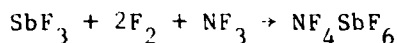
The NF_4^+ xenon fluoride salts are the first known examples of a NF_4^+ noble gas compound and also are the most energetic NF_4^+ salts presently known. $(\text{NF}_4)_2\text{XeF}_8$ has the highest theoretical fluorine yield (see Table 1) and with TATB gives a theoretical detonation pressure of 498 kbars. The drawbacks of these compounds are (1) the high cost of xenon, (2) the hydrolysis of XeF_6 to XeO_3 , which is extremely shock sensitive, and (3) the difficulty encountered with a scaleup of the laser-induced photo synthesis. The advantage of the compound is that no clinker-forming agent is required because Xe, the only gaseous byproduct, does not deactivate an HF-DF laser. Also, the ratio of $\text{F}_2:\text{NF}_3$ (1:2) is higher than for any other known NF_4^+ salt.

As can be seen from Table 1, most of the new NF_4^+ salts synthesized during this contract rank at or near the top of the performance list and, therefore, significantly contribute to the choice of materials available for $\text{NF}_3\text{-F}_2$ gas generators.

Since most of the advanced NF_4^+ salts are prepared from NF_4SbF_6 as a starting material, it was also important to simplify its synthesis as much as possible. The previous best synthesis involved the following two steps:

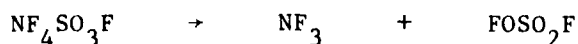
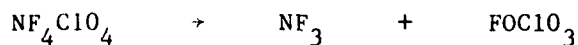


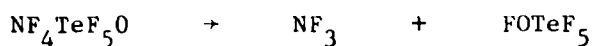
This synthesis was simplified to a one-step process (paper 6) according to:



Excellent progress was made in the general characterization of NF_4^+ salts. Thus, the formation and decomposition mechanism of these salts was studied and classified (paper 4), thermodynamic properties were experimentally measured (paper 20), the general valence force field was determined from $^{14}\text{N} - ^{15}\text{N}$ isotopic data (paper 9), and analytical procedures for NF_4^+ salts were worked out (paper 14). Considerable efforts were made to obtain a crystal structure for one of the NF_4^+ salts. Single crystals of NF_4SbF_6 , $\text{NF}_4\text{Sb}_2\text{F}_{11}$, and NF_4BF_4 were successfully grown and X-ray diffraction data were collected at the Rockwell Science Center, USC, and the University of Leicester, England. However, in all cases we were unable to sufficiently refine the data. At this point it is not entirely clear whether these difficulties are due to ion rotation and disorder phenomena or are caused by poor starting solutions used for the refinement.

The reaction chemistry of NF_4^+ salts also was studied. The most important reaction discovered was the general ability of NF_4^+ salts of oxyanions to thermally decompose to give the corresponding hypofluorites in high yields and purities. The following systems were successfully demonstrated (papers 2, 7, 10, 16, 26):





and led to the syntheses of the first known examples of iodine and tellurium hypofluorites.

In addition to the above-described NF_4^+ work, we have also undertaken extensive efforts to prepare novel energetic anions which we hoped would be stable and compatible with NF_4^+ salts to make solid "super oxidizers." Target ions included $-\text{NF}_2$ substituted anions, such as $\text{I}(\text{NF}_2)_4^-$ and $\text{B}(\text{NF}_2)_4^-$. There is a definite need for such energetic anions, because the conventional ClO_4^- and NO_3^- anions were shown by this study to form only unstable NF_4^+ salts. So far, however, all our efforts in this direction have been unsuccessful.

Studies also were carried out on the preparation of the unknown H_2NF molecule and $-\text{NF}_2$ substituted halogen fluorides, such as IF_4NF_2 . So far, however, these experiments have been unsuccessful.

HALOGEN FLUORIDES AND OXYFLUORIDES

In the area of halogen fluorides, the improved synthesis of fluorine perchlorate from NF_4ClO_4 (paper 7) allowed us to better characterize FOClO_3 (paper 27) and to study its addition reaction across olefinic double bonds (paper 1). For the determination of a reliable force field of FOClO_3 , it became necessary to determine a general valence force field for the closely related FClO_3 molecule. This was achieved by the use of ^{35}Cl - ^{37}Cl isotopic data and ab initio calculations (paper 15). The gas-phase structure of ClF_3O was determined by electron diffraction (paper 21) and revealed the existence of directional repulsion effects by lone valence electron pairs and π bonds in trigonal bipyramidal molecules (paper 12).

Since SF_4 is isoelectronic with ClF_4^+ and since the vibrational spectra of the latter are still in question, a reliable general valence force of SF_4 was

determined from ^{32}S - ^{34}S isotopic data (paper 5) and ab initio calculations (paper 8).

MISCELLANEOUS

The protonation studies, which during the previous contract (Ref. 10) led to the discovery of novel OH_3^+ , SH_3^+ , and NH_2F_2^+ salts, were extended to hydrogen peroxide. The novel peroxonium cation, H_3O_2^+ , was prepared and characterized in the form of several salts (paper 3, patent 48). These salts were of particular interest as a potential source for a solid-propellant singlet delta oxygen gas generator for a continuous-wave, oxygen-iodine laser.

In the area of azide chemistry, CF_3N_3 was synthesized and thoroughly characterized (paper 17).

The TeF_5OF molecule, prepared from the corresponding NF_4^+ salt (see above), was also thoroughly characterized, and the results were summarized in paper 26.

CONCLUSION

The results from this contract have again demonstrated that the field of inorganic halogen oxidizers is an extremely promising and rewarding 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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APPENDIX A

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

Reactions of Fluorine Perchlorate with Fluorocarbons and the Polarity of the O-F Bond in Covalent Hypofluorites

Carl J. Schack* and Karl O. Christe

Received March 9, 1979

Although FOClO_3 has been known for decades,^{1,2} its reaction chemistry has remained virtually unexplored and is limited to references to unpublished work, cited in a review.³ This lack of data is attributed to the previous report² that FOClO_3 consistently exploded during attempted freezing. During a study⁴ of NF_4ClO_4 , it was found that very pure FOClO_3 could be obtained in high yield by the thermal decomposition of NF_4ClO_4 . The FOClO_3 , prepared in this manner, could be manipulated and repeatedly frozen without explosions, thus allowing us to study some of its properties⁵ and reaction chemistry.

Of particular interest to us were the reactions of FOClO_3 with fluorocarbons. Previous work⁶ in our laboratory had demonstrated that ClOClO_3 and BrOClO_3 add readily to fluorocarbon double bonds, resulting in covalent fluorocarbon perchlorates. Consequently, one would expect fluorine perchlorate to undergo a similar reaction. However, a literature citation³ suggested that FOClO_3 does not add across the double bond in $\text{Cl}_3\text{C}=\text{CF}_2$. Furthermore, reactions of covalent hypofluorites, such as CF_3OF , are commonly interpreted in terms of a highly unusual $\text{CF}_3\text{O}^+-\text{F}^{\delta-}$ type polarization of the O-F bond ("positive fluorine"). If the O-F bond in FOClO_3 is indeed polarized in this direction, the fluorine in FOClO_3 should be even more positive because of the higher electronegativity of the perchlorato group. Since the direction of the addition of a hypohalite across an unsymmetrical olefinic double bond strongly depends on the direction and the degree of polarization of the O-Hal bond,⁷ a study of the $\text{O}_3\text{ClOF}/\text{CF}_3\text{CF}=\text{CF}_2$ reaction system offered an ideal opportunity to experimentally test the validity of the "positive fluorine" concept.

Experimental Section

Caution! Although no explosions were encountered in the present study, FOClO_3 must be considered a highly sensitive material and should be manipulated only in small quantities with appropriate safety precautions.

Apparatus and Materials. Volatile materials were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon-FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gage (0-1500 mm, $\pm 0.1\%$). Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (CS Laboratory Supplies) and CFCl_3 as an internal standard. Hexafluoropropylene and CF_3I were purchased while $\text{CF}_2=\text{CF}_2$ was prepared by pyrolyzing Teflon. Fluorine perchlorate was obtained from the decomposition of NF_4ClO_4 .^{4,5}

Reaction with Hexafluoropropylene. A 30-mL stainless steel cylinder was loaded at -196°C with FOClO_3 (1.59 mmol) and C_3F_6 (2.05 mmol). The closed cylinder was warmed to -45°C and kept at that temperature overnight. Separation of the products was achieved by vacuum fractionation in U-traps cooled at -78 , -95 , and -196°C . The coldest trap contained unreacted C_3F_6 together with FOClO_3 , $\text{C}_3\text{F}_7\text{ClFO}$, and a small amount of $(\text{CF}_3)_2\text{CO}$. In the other traps only the colorless liquid $\text{C}_3\text{F}_5\text{OCIO}_3$ was found (1.18 mmol, 74% yield based

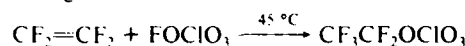
on FOClO_3). The following temperature-vapor pressure data were measured ($^\circ\text{C}$, mm): 46.6, 4; 22.7, 17; -9.3, 36; 0.0, 59; 10.6, 99; 22.0, 161. The vapor pressure-temperature relation is described by the equation $\log P = 7.5257 - (1571.94/T)$ (pressure in mmHg and temperature in K) with a calculated normal boiling point of 65.2°C and a heat of vaporization of 7.19 kcal/mol. A vapor density of 265 g/mol was measured compared to a calculated value of 268.5 g/mol for $\text{C}_3\text{F}_5\text{OCIO}_3$. Strong mass spectral peaks were found for the ions $\text{C}_3\text{F}_4\text{ClO}_4^+$, C_3F_7^+ , $\text{CF}_3\text{ClO}_4^+$, $\text{C}_3\text{F}_6\text{O}^+$, C_3F_5^+ , $\text{C}_3\text{F}_4\text{O}^+$, C_3F_4^+ , $\text{C}_2\text{F}_3\text{O}^+$, ClO_3^+ , $\text{C}_2\text{F}_2\text{O}^+$, CF_3^+ (base peak), ClO_2^+ , COF_2^+ , ClO^+ , CF_2^+ , and COF^+ . The following infrared bands were observed (cm^{-1} , intensity): 1340 (sh), 1325 (sh), 1290 (vs), 1250 (sh), 1235 (vs), 1200 (m), 1171 (w), 1153 (m), 1119 (ms), 1088 (m), 1026 (s), 988 (s), 968 (m), 784 (w), 746 (m), 723 (w), 676 (m), 641 (m-s), 614 (s), 530 (w).

Reaction with Tetrafluoroethylene. Fluorine perchlorate (0.61 mmol) and C_2F_4 (0.62 mmol) were combined at -196°C in a 10-mL stainless steel cylinder. By evaporation of the liquid nitrogen from a liquid nitrogen-dry ice slush used to cool the reaction cylinder, the temperature was allowed to slowly rise to -78°C and finally over several days by loss of solid CO_2 to about -45°C . Fractional condensation of the products at -112 and -196°C permitted the isolation of $\text{C}_2\text{F}_3\text{OCIO}_3$ (0.42 mmol, 68% yield) which was identified by its known vibrational, NMR, and mass spectra.⁸ Smaller amounts of CF_3CFO , C_2F_6 , Cl_2 , and O_2 were observed as byproducts.

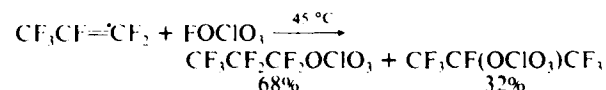
Reaction with Trifluoromethyl Iodide. Into a cold (-196°C) 30-mL stainless steel cylinder CF_3I (0.66 mmol) and then FOClO_3 (1.40 mmol) were condensed. Warm-up to about -45°C was accomplished slowly as noted in the preceding example. After several days at -45°C the reactor was recooled to -196°C , and the presence of a considerable amount of noncondensable gas (oxygen) was noted. Fractionation of the condensable products showed a mixture of COF_2 , CF_4 , Cl_2 , I_2 , IF_3 , and a solid iodine oxide to be the principal species present. However, a small amount of CF_3OCIO_3 (0.05 mmol, 8% yield) was also found and identified by comparison with reported data.⁸

Results and Discussion

Under carefully controlled reaction conditions, similar to those previously used for the polar additions of ClOClO_3 and BrOClO_3 ,⁶ fluorine perchlorate was found to add across olefinic double bonds in high yield. With tetrafluoroethylene the following reaction occurred:



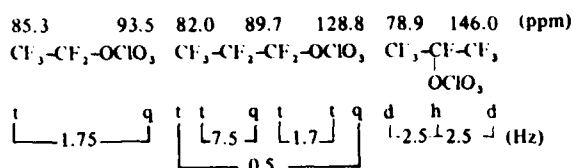
With the unsymmetrical olefin perfluoropropylene a mixture of two isomers was found



These two perfluoropropyl perchlorates are novel compounds which were identified by vapor density measurements and spectroscopic data. The presence of the covalent $-\text{OCIO}_3$ group was demonstrated by infrared spectroscopy which showed the intense bands typical of this group⁸ at 1290 ($\nu_s(\text{ClO}_3)$), 1026 ($\nu_s(\text{ClO}_3)$), and 614 cm^{-1} ($\nu(\text{Cl-O})$). Additional support for the covalent perchlorate structure was obtained from the mass spectrum which showed strong peaks for the ions, ClO_3^+ , ClO_2^+ , and ClO^+ but not for ClO_4^+ , as is generally the case for fluorocarbon perchlorates. A parent ion was not observed, and the highest m/e was $\text{C}_2\text{F}_4\text{ClO}_4^+$, i.e., the parent minus a CF_3 group.

Gas chromatography of the product revealed a slight asymmetry for the $\text{C}_3\text{F}_5\text{ClO}_4$ peak, thereby indicating the presence of isomers. This was confirmed by ^{19}F NMR spectroscopy, showing that both possible adducts were formed. The observed chemical shifts and coupling constants, together

Chart 1



with higher resolution data than previously reported⁸ for $C_2F_5OCIO_3$, are summarized in Chart 1 (d = doublet, t = triplet, q = quartet, h = heptet). The resonances of fluorines geminal to a perchlorato group were broadened due to chlorine quadrupole relaxation. On the basis of their relative peak areas, the ratio of the two isomers was *n* 68% and iso 32%.

The fact that in the reaction of $FOClO_3$ with $CF_3CF=CF_2$ both isomers are formed significantly differs from the previously reported⁶ $ClOCIO_3$ and $BrOCIO_3$ reactions where exclusive Markownikoff type additions occurred. The latter produced 100% of $CF_3CFXCF_2OCIO_3$, as expected for a polar addition of the positively polarized terminal halogen to the carbon with the highest electron density.⁷



The formation of both isomers (*n* and iso) in the corresponding $FOClO_3$ reaction suggests that the F-O bond in $FOClO_3$ is not strongly polarized in either direction. This is not surprising in view of the known very small dipole moment (0.023 D) of the closely related $FCIO_3$ molecule⁹ and the expected similar electronegativities of a $-ClO_3$ and an $-OCIO_3$ group. The fact that the percentage of *n* isomer was somewhat higher than that of the iso isomer can be explained by steric effects (bulky CF_3 group) and is insufficient reason to postulate a strongly positive fluorine in $FOClO_3$. The occurrence of a free-radical mechanism is unlikely in view of the high yield of the products (74%), the mild ($-45^\circ C$) and well-controlled reaction conditions, and the absence of detectable amounts of C_3F_8 and $C_3F_6(OCIO_3)_2$ in the reaction products.

In contrast to the olefin addition reactions, the reaction of $FOClO_3$ with CF_3I was more difficult to control. The primary reaction path appears to have involved oxidation of the iodine followed by degradation to oxygenated and fluorinated species. Nevertheless, a modest yield (8%) of the desired perchlorate, CF_3OCIO_3 , was realized. By comparison, the $ClOCIO_3-CF_3I$ reaction is also vigorous but can be controlled to give a nearly quantitative yield of CF_3OCIO_3 .⁸

In summary, it has been shown that $FOClO_3$ can add to carbon-carbon double bonds to produce alkyl perchlorates in good yield. The formation of two isomers with the unsymmetrical olefin $CF_3CF=CF_2$ indicates that the O-F bond in $FOClO_3$ is of low polarity and does not justify the assumption of significant positive character for fluorine. Since a CF_3O -group is considerably less electronegative than a O_3ClO -group, the above results imply that, contrary to general acceptance, covalent hypofluorites, such as CF_3OF , do not contain a positive fluorine. Indeed, it would be most difficult to rationalize how the addition of fluorine to a less electronegative element, such as carbon, would render the latter more electronegative than fluorine itself.

Acknowledgment. We gratefully acknowledge helpful discussion with Dr. L. R. Grant and financial support of this work by the Office of Naval Research, Power Branch.

Registry No. $FOClO_3$, 10049-03-3; $CF_3CF_2CF_2OCIO_3$, 70749-47-2; $CF_3CF(OCIO_3)CF_3$, 70749-48-3; $C_2F_5OCIO_3$, 22675-67-8; CF_3OCIO_3 , 52003-45-9; C_3F_8 , 116-15-4; C_2F_4 , 116-14-3; CF_3I , 359-37-5.

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APPENDIX B

INORG. NUCL. CHEM. LETTERS Vol.15, pp. 375-376
Pergamon Press Ltd. 1979. Printed in Great Britain

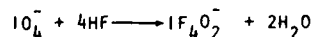
Cis- and Trans- IODINE (VII) OXYTETRAFLUORIDE HYPOFLUORITE, OIF_4OF

Karl O. Christe and R. D. Wilson
Rocketdyne Division of Rockwell International
Corporation, Canoga Park, CA 91304

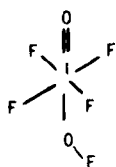
(Received 22 June 1979)

To our knowledge, only two examples of a halogen hypofluorite are presently known. These are FOF (1) and O_3ClOF (2). Compounds containing an $-\text{OF}$ group attached to either bromine or iodine have previously not been reported. Since the thermal decomposition of NF_4ClO_4 produces O_3ClOF in high yield (3,4), it appeared interesting to study the interaction of NF_4^+ salts with other perchlorate anions.

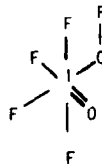
Metathetical reactions between NF_4SbF_6 and CsXO_4 were carried out in anhydrous HF solution as previously described (5). The solutions were cooled to -78°C and the insoluble CsSbF_6 precipitate was separated from the solution by filtration. The HF solvent was pumped off at -30°C and the residue was allowed to undergo thermal decomposition during warm up. Although for CsBrO_4 the desired O_3BrOF could not be isolated, its expected (6) decomposition products, FBrO_2 and O_2 , were observed. Since CsIO_4 undergoes (7) fluorination in anhydrous HF solution according to



the CsIO_4 was first converted to CsIF_4O_2 which was then used for the metathesis. The thermal decomposition of the resulting metathetical product generated two novel iodine (VII) compounds which were identified by chemical analysis, molecular weight (clcd 253.9, found 254.5), infrared (cm^{-1} , int, 918 ms, 688 vs, 655 m, 584 mw), Raman ($\nu_1=925$ and 914, ν_{OF} 890, ν_{IF} and ν_{O} 679, 651, 630, 622, 584), ^{19}F NMR ($-\text{OF}$ of trans isomer: quintet at $\delta=202$ with $J_{\text{FF}} = 36$ Hz, $-\text{OF}$ of cis isomer: multiplet



trans



cis

at $\phi = 176^\circ$), and mass spectroscopy as an approximately 2:1 mixture of the two stereo isomers cis- OIF_4OF and trans- OIF_4OF .

These two isomers possess very similar volatility and could not be separated even by gas-chromatography. The isomer mixture is white as a solid (mp = -33°C), pale yellow as a liquid and colorless as a gas. It is stable at ambient temperature and can be manipulated in well passivated stainless steel and Teflon equipment without appreciable decomposition.

Acknowledgement

The authors are indebted to Drs. C. J. Schack, W. W. Wilson and L. R. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

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

Novel Onium Salts. Synthesis and Characterization of the Peroxonium Cation, H_2OOH^+

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

Received March 5, 1979

The synthesis and properties of $\text{H}_2\text{O}_2^+\text{SbF}_6^-$, $\text{H}_2\text{O}_2^+\text{SbF}_4^-$, and $\text{H}_2\text{O}_2^+\text{AsF}_6^-$, the first known examples of peroxonium salts, are reported. These salts were prepared by protonation of H_2O_2 in anhydrous HF solutions of the corresponding Lewis acids. They were isolated as metastable solids which underwent decomposition to the corresponding H_3O^+ salts and O_2 in the temperature range 20–50 °C. The H_2O_2^+ salts were characterized by vibrational and NMR spectroscopy. Modified valence force fields were computed for the isoelectronic series H_2OOH^+ , H_2NOH^+ , and H_2NNH^+ . The similarity of their observed spectra and computed force fields suggests that the ions are isostructural with H_2NOH^+ which possesses C_s symmetry with the unique hydrogen being trans to the other two hydrogens. The influence of protonation on the stretching frequency of the two central atoms is discussed for the series HOO^+ , HOOH^+ , H_2OOH^+ , H_2NNH^+ , H_2NNH_2^+ , H_3NNH_2^+ , and $\text{H}_3\text{NNH}_3^{2+}$. Attempts to protonate both oxygen atoms in H_2O_2 to form $\text{H}_2\text{O}_2^{2+}(\text{SbF}_6^-)_2$ resulted in $\text{H}_2\text{O}_2^+\text{SbF}_6^-$ as the only product. The strongly oxidizing Lewis acid BiF_3 underwent a redox reaction with H_2O_2 in HF, resulting in quantitative reduction of BiF_3 to BiF_2 , accompanied by O_2 evolution. When a 2:1 excess of BiF_3 was used, an adduct formed having the approximate composition $\text{BiF}_2\cdot\text{BiF}_3$. Heating a mixture of solid $\text{H}_2\text{O}_2^+\text{SbF}_6^-$ with a strongly fluorinating agent, such as BiF_3 or Cs_2NiF_6 , resulted in a green chemiluminescence band centered at 5150 Å.

Introduction

Anhydrous HF Lewis acid solutions are ideally suited to protonate less acidic substrates. This technique has successfully been applied to the isolation of novel salts containing the H_3O^+ ,^{1–4} H_3S^+ ,^{5,6} NH_3F_2^+ ,⁷ and AsH_4^+ cations. Since all these cations contain a single central atom, it appeared interesting to extend this method to a substrate containing two central atoms, such as H_2O_2 . In such a case, both single and double protonation are possible, and the influence of protonation on the strength of the bond between the two central atoms can be studied. Such effects are well-known⁸ for the related hydrazine molecule. Although the HO_2^- anion is known,^{9,10} to our knowledge the corresponding cations derived from H_2O_2 have only been postulated,¹¹ but not characterized or isolated as salts.

Further interest was added to this study by the fact that H_2O_2 is a starting material for the generation of excited molecular oxygen which in turn is of great interest for a near resonant energy-transfer iodine laser. Therefore, the combination of an H_2O_2^+ cation with a strongly oxidizing anion in the form of a stable salt could provide a suitable solid-propellant gas generator for excited oxygen.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in well-passivated (with ClF_3 and HF) vacuum lines constructed either entirely from Monel-Teflon-FEP or entirely from Teflon-PFA with injection-molded fittings and valves (Fluoroware Inc.). Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Hydrogen fluoride was dried by treatment with F_2 , followed by storage over BiF_3 to remove last traces of H_2O .¹ Antimony pentafluoride and AsF_5 (Ozark Mahoning Co.) were purified by distillation and fractional condensation, respectively. Bismuth pentafluoride (Ozark Mahoning Co.) was used as received. Hydrogen peroxide (90%, FMC Corp.) was purified by repeated fractional crystallization,¹² and material of 99.95% purity, as analyzed by titration with KMnO_4 solution, was obtainable by this method. All equipment, used for handling H_2O_2 , was washed with 12 N H_2SO_4 , thoroughly rinsed with distilled H_2O and dried in an oven prior to use. For the hazards and necessary precautions of handling concentrated H_2O_2 see ref. 12. The synthesis of Cs_2NiF_6 has previously been described.¹³

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of dry powders at room temperature were obtained by using pressed (Wilks mimpellet press) disks between AgCl windows. Low-temperature spectra were obtained as dry powders between CsI plates with a technique similar to one previously reported.¹⁴

The 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 or Teflon-FEP tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded with a previously described¹⁷ device. Polarization measurements were carried out according to method VIII listed by Claassen et al.¹⁵

Debye-Scherrer powder patterns were taken with a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries ($\sim 0.5\text{-mm}$ o.d.).

The ^{19}F and ^1H NMR spectra were recorded at 84.6 and 90 MHz, respectively, on a Varian Model EM-390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external CFCl_3 and Me_4Si , respectively.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1B, was used for the determination of the thermal stability of the compounds. The samples were sealed in aluminum pans, and heating rates of 2.5 and $10^\circ/\text{min}$ were used.

For the chemiluminescence experiments, $\text{H}_2\text{O}_2\text{SbF}_6$ was mixed with either solid BiF_3 or Cs_2NiF_6 and placed into the bottom of a Pyrex glass tube which was equipped with a stopcock. The tube was connected to a vacuum manifold and heated in a dynamic vacuum by a stream of hot air until gas evolution and chemiluminescence were observed. The emitted light was analyzed with a 0.5-m McKee-Pederson monochromator over the range 2000–10000 Å using a spectral slit width of 25 Å.

Preparation of $\text{H}_2\text{O}_2^+\text{AsF}_6^-$. In a typical experiment, AsF_5 (15.39 mmol) and anhydrous HF (50.76 mmol) were combined at -196°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 the drybox, and H_2O_2 of 99.95% purity (15.29 mmol) was syringed in at -196°C . The ampule was transferred back to the vacuum line and evacuated at -196°C ; it was then kept at -78°C for 2 days to allow reaction. After this period, no evidence was found for material noncondensable at -196°C , i.e., no O_2 evolution. The mixture was warmed to -45°C , and a clear solution resulted. Material volatile at -45°C was removed by pumping for 10 h and was collected at -196°C . A white solid residue resulted which was of marginal stability at ambient temperature. On the basis of the observed material balance (weight of 15.29 mmol $\text{H}_2\text{O}_2\text{AsF}_6$ calculated, 3.423 g; found, 3.47 g), the conversion of H_2O_2 to $\text{H}_2\text{O}_2^+\text{AsF}_6^-$ was complete within experimental error. The compound was shown by infrared and Raman spectroscopy to contain the H_2O_2^+ cation and AsF_6^- anion.^{12,17,20}

Thermal Decomposition of $\text{H}_2\text{O}_2^+\text{AsF}_6^-$. A sample of $\text{H}_2\text{O}_2\text{AsF}_6$ (28.93 mmol) was allowed to decompose at ambient temperature. An exothermic reaction occurred, generating 14.6 mmol of O_2 and a white solid residue which was identified by vibrational spectroscopy as $\text{H}_2\text{O}^+\text{AsF}_6^-$.

Preparation of $\text{H}_2\text{O}_2^+\text{SbF}_6^-$. Antimony pentafluoride (27.96 mmol) was added in the 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°C , and the mixture was homogenized by stirring at 20°C . In the drybox hydrogen peroxide (27.97 mmol) was syringed into the U-tube at -196°C .

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°C. The cold tube was transferred back to the vacuum line and was evacuated. The tube was warmed from -196 to 78 °C for 1 h 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 °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 °C. The HF solvent was pumped off at -22 °C for 3 h resulting in 7.566 g of a white solid (weight calculated for 27.96 mmol of $\text{H}_3\text{O}_2^+\text{SbF}_6^-$ = 7.570 g), stable at 20 °C. The compound was shown by vibrational spectroscopy to be composed of H_3O_2^+ cations and SbF_6^- anions.^{1,5,7,18,19} Additional support for the composition of the product was obtained by allowing a sample of $\text{H}_3\text{O}_2^+\text{SbF}_6^-$ to thermally decompose at about 45 °C. This decomposition produced O_2 and the known H_3OSbF_6 salt¹ in almost quantitative yield.

Preparation of $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$. The synthesis of this compound was carried out in a manner identical with that described above for the preparation of $\text{H}_3\text{O}_2^+\text{SbF}_6^-$, 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 $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^- \cdot 1.17\text{SbF}_5$ = 3.581 g), stable up to about 50 °C. The compound was shown by vibrational and NMR spectroscopy to contain the H_3O_2^+ cation and $\text{Sb}_2\text{F}_{11}^-$ as the principal anion.

The H_3O_2^+ HF BiF_4 System. Bismuth pentafluoride (10.68 mmol), HF (394 mmol), and H_2O_2 (10.15 mmol) were combined in a passivated Teflon ampule in a manner analogous to that described for the preparation of $\text{H}_3\text{O}_2^+\text{SbF}_6^-$. The mixture was warmed from -196 °C to ambient temperature. During the warm-up operation gas evolution was observed which was accompanied by the formation of a copious white precipitate which showed little solubility in HF at ambient temperature. Bands due to either BiF_6^- or BiF_4 ^{21,22} (both are strong Raman scatterers) could not be detected in the Raman spectra of either the liquid or the solid phase. The evolved gas was removed from the ampule at -196 °C and consisted of 10.1 mmol of O_2 . The material volatile at 20 °C was pumped off, leaving behind 2.897 g of a white solid which was identified by vibrational spectroscopy as BiF_3 ²³ (weight calculated for 10.68 mmol BiF_3 = 2.841 g).

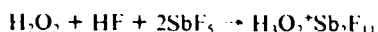
When BiF_3 and H_2O_2 in a mole ratio of 2:1 were combined in a similar manner in anhydrous HF solution, the weight of the resulting white stable solid product closely corresponded to that expected for $\text{BiF}_3 \cdot \text{BiF}_4$. The product was characterized by vibrational spectroscopy which showed it to be an adduct and not a simple physical mixture of BiF_3 and BiF_4 .

Results and Discussion

Synthesis. On the basis of the observed material balances, H_3O_2^+ is protonated in $\text{HF} \cdot \text{MF}_x$ ($\text{M} = \text{As}, \text{Sb}$) solutions according to



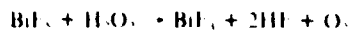
No evidence was found for double protonation, i.e., $\text{H}_3\text{O}_2^{2+}$ formation, even when SbF_5 was used in a twofold excess. Instead, the polyanion $\text{Sb}_2\text{F}_{11}^-$ was formed according to



It is interesting to compare these results with those previously reported²⁴ for the $\text{N}_2\text{H}_4 \cdot \text{HF} \cdot \text{TaF}_5$ system for which double protonation, i.e., $\text{N}_2\text{H}_6^{2+}(\text{TaF}_6)_2$ and $\text{N}_2\text{H}_6^{2+}\text{TaF}_7^{2-}$ formation, has been observed. Although other effects, such as the relative solubilities of the possible products, are certainly important, the predominant reason for the exclusive single protonation of H_2O_2 appears to be its decreased basicity. Whereas N_2H_4 is a weak base in aqueous solution ($\text{p}K_b = 5.77$), H_2O_2 is a weak acid ($\text{p}K_a = 11.6$). With increasing protonation, the basicity of the resulting cations further decreases, and N_2H_5^+ ($\text{p}K_a = 6.1$) becomes a weak and $\text{N}_2\text{H}_6^{2+}$ ($\text{p}K_a = -1$) a strong acid.^{24,25} Whereas N_2H_5^+ has an acidity comparable to that of H_2S ($\text{p}K_a = 7$) which is known²⁶ to form stable H_3S^+ salts, H_3O_2^+ is too acidic to undergo further protonation to $\text{H}_4\text{O}_2^{2+}$.

Attempts to prepare H_3O_2^+ salts derived from BiF_4 were unsuccessful. The latter is a relatively strong oxidizer and is

readily reduced by H_2O_2 in HF solution according to



When a twofold excess of BiF_3 was used, the following reaction was observed:



The resulting $\text{BiF}_3 \cdot \text{BiF}_4$ product was shown by vibrational spectroscopy [Raman: 591 (10), 583 (4.6), 538 (1.5), 521 (0.1), 496 (0.6), 475 (sh), 232 (0.5, br), 120 (0.2, br) cm^{-1} ; IR: 708 (w), 615 (s), 606 (sh), 575 (s), 550 (sh), 535 (vs), 400–500 (m, vbr) cm^{-1}] not to be a physical mixture of BiF_3 ²³ and BiF_4 ^{21,22}. By analogy with the known $\text{BiF}_3 \cdot \text{SbF}_5$ and $\text{SbF}_3 \cdot \text{SbF}_5$ systems,^{26,28} a $\text{BiF}_3 \cdot \text{BiF}_4$ -type adduct appears most plausible. However, in view of the complexity of the products formed in the $\text{SbF}_3 \cdot \text{SbF}_5$ system,^{27,28} a detailed characterization of this $\text{BiF}_3 \cdot \text{BiF}_4$ adduct was beyond the scope of this study.

Properties. The $\text{H}_3\text{O}_2^+\text{SbF}_6^-$, $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$, and $\text{H}_3\text{O}_2^+\text{AsF}_6^-$ salts are white crystalline solids. X-ray powder patterns were taken for $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$ but contained too many lines to allow indexing. All these H_3O_2^+ salts are of marginal thermal stability and were shown to undergo exothermic decomposition to the well-known¹ H_3O^+ salts according to



Of the above H_3O_2^+ salts, the AsF_6^- salt is the least stable and easily decomposes at room temperature. The $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$ salt was found to be most stable. On the basis of DSC data, its decomposition starts with a small endotherm at 51 °C, followed by a large exotherm. In a sealed melting point capillary, decomposition accompanied by foaming was observed at about 65 °C. The thermal stability of $\text{H}_3\text{O}_2^+\text{SbF}_6^-$ is intermediate between those of $\text{H}_3\text{O}_2^+\text{AsF}_6^-$ and $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$. It should be pointed out that the thermal stability of these H_3O_2^+ salts appears to decrease in the presence of free H_2O_2 . Probably, the highly acidic H_3O_2^+ salt catalyzes the exothermic decomposition of H_2O_2 , with the evolved heat promoting the decomposition of the H_3O_2^+ salt itself.

The reaction of H_3O_2^+ salts with fluorinating agents appeared interesting as a potential method for the generation of excited molecular oxygen (O_2^*). Antimony pentafluoride or SbF_5 were not strong enough oxidizers to fluorinate H_3O_2^+ , and BiF_4 reacted at too low a temperature with H_2O_2 to permit isolation of the desired $\text{H}_3\text{O}_2^+\text{BiF}_4$ salt. Therefore, the concept could not be directly tested to produce O_2^* by the simple thermal decomposition of a salt composed of H_3O_2^+ and an oxidizing anion. However, when solid $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$ was mixed at room temperature with a solid oxidizer, such as BiF_4 or Cs_2NiF_6 , and when this mixture was heated to about 80 °C, a reaction occurred which was accompanied by green (5150-Å) chemiluminescence. This 5150-Å band did not exhibit detectable fine structure, and no additional bands were observed over the range 2000–10000 Å. Consequently, the 5150-Å emission is not attributed to either vibrationally excited HF^{29} or O_2 .³⁰

Nuclear Magnetic Resonance Spectra. The ^{19}F NMR spectrum of $\text{H}_3\text{O}_2^+\text{SbF}_6^- \cdot 1.17\text{SbF}_5$ was recorded for a SO_2 solution at -90 °C. It showed resonances (ϕ 91, multiplet: 111, doublet of doublets; 133, quintet) characteristic³¹ for $\text{Sb}_2\text{F}_{11}^-$. In addition, a weaker doublet at ϕ 102 was observed which is characteristic^{31,32} for $\text{SbF}_4 \cdot \text{SO}_2$. The quintet part of this species could not be directly observed since it exhibits a chemical shift similar to that of the quintet of $\text{Sb}_2\text{F}_{11}^-$. The observation of some $\text{SbF}_4 \cdot \text{SO}_2$ is in excellent agreement with a previous report³¹ that the highest polyanion observed for $\text{SbF}_4 \cdot n\text{SbF}_5$ in SO_2 solution is $\text{Sb}_2\text{F}_{11}^-$, with any remaining SbF_4 being converted to $\text{SbF}_4 \cdot \text{SO}_2$. In addition to the signals due to $\text{Sb}_2\text{F}_{11}^-$ and $\text{SbF}_4 \cdot \text{SO}_2$, a weak unresolved signal was

Table I. Vibrational Spectra of $\text{H}_3\text{O}_2\text{AsF}_6$, $\text{H}_3\text{O}_2\text{SbF}_6$, and $\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$ and Their Assignments

obsd freq. cm^{-1} (rel intens) ^a							
$\text{H}_3\text{O}_2\text{AsF}_6$		$\text{H}_3\text{O}_2\text{SbF}_6$		$\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$		assign (pt group)	
IR (-196 °C)	Raman (-100 °C)	IR (-196 °C)	Raman (-110 °C)	Raman (25 °C)	IR (25 °C)	Raman (25 °C)	HOOH_2^+ (C_2) SbF_6^- (O_h) ^b
3440 sh	3440 (0.8)	3440 sh		3440 (0+)	3447 s	3435 (0+)	ν_1 (A')
3400-3150 vs		3400-3150 vs			3400 } vs, vbr		ν_2 (A'')
3228 vs	3230 (0+) br	3230 vs			2600 }		ν_3 (A')
					2178 w		
1535 w	1547 (0.4)			1539 (0+)	1531 m	1530 (0+)	ν_4 (A')
1425 mw	1417 (1)	1421 mw		1426 (0+)	1420 ms	1419 (0+)	ν_5 (A')
		1280 w					
					1228 mw	1227 (0+)	ν_6 (A')
1115 m		1126 mw		1130 (0+) br	1137 s	1135 (0+)	ν_7 (A')
1100 } m, vbr		1065 sh					
900 }		965 sh					
		915 w					
870 m	873 (10)	876 mw	879 (8.6)	880 (5.4)		878 (1.5) }	ν_8 (A')
					869 m	868 (3) }	
728 vs	734 (39)		689 (5)		730 }	771 (0.2) }	
	711 (1.5)		677 (10)	667 (10)	640 } vs, br	688 (10) }	ν_9 (A_{1g})
665 vs	673 (9.5)	666 vs	642 (7)			664 (0.5) }	
635 sh		615 s				649 (5.4) }	
585 m		571 ms			594 mw		
	559 (2.4)		560 (2)				
550 ms		514 m		555 (0.7) br	565 m	576 (0.7)	ν_{10} (A_g)
	528 (1.4)		530 (0.5)				
470 m		375 mw			508 m		
	400 (0+)		326 (1)			301 (2.5)	
388 vs		309 ms					
	370 (5.0)		283 (5)	282 (4)		280 (1)	ν_{11} (A_{2g})
348 ms			263 (0.9)				
	316 (1.2)		226 (0.5)	226 (0+)		236 (2)	
	202 (2.5)		200 (1.5)				
	189 sh		174 (3.2)	167 (0+)		167 sh	
	149 sh		126 (2.4)	122 (0+)		144 (0.6)	
	129 (3.2)					112 sh	

^a Uncorrected Raman intensities. ^b The assignments given for SbF_6^- are for the room-temperature Raman spectrum of $\text{H}_3\text{O}_2\text{SbF}_6$ in which SbF_6^- appears to be octahedral due to rotational averaging. In the low-temperature spectra the symmetry of the MF_6^- anion is much lower than O_h (see text).

observed at δ 106, in agreement with previous observations³¹ on the $t\text{-BuF}_3\cdot 3.8\text{SbF}_5$ system. This signal is tentatively assigned to some $\text{SbF}_5\cdot\text{H}_2\text{O}$ - or $\text{SbF}_5\cdot\text{H}_2\text{O}\cdot\text{SbF}_5$ -type species.³³

Attempts to observe the characteristic SbF_6^- signal in the ^{19}F NMR spectra of $\text{H}_3\text{O}_2\text{SbF}_6$ in different solvents were unsuccessful. In SO_2ClF the compound was insoluble. In either HF or HF acidified with AsF_5 only a single peak was observed due to rapid exchange between all fluorine-containing species. In SO_2 at -85°C only two unresolved signals were observed at δ 107 and 127 with an area ratio of 4:1 indicating the possible presence of some $(\text{SbF}_6)_2\cdot\text{H}_2\text{O}$ -type species.³³ The failure to observe SbF_6^- for $\text{H}_3\text{O}_2\text{SbF}_6$ in SO_2 parallels the previous report³¹ by Bacon and co-workers who found that, unlike $\text{CsSb}_2\text{F}_{11}$, the CsSbF_6 salt is rather insoluble in SO_2 and $\text{Sb}_2\text{F}_{11}^-$ is the only observable anion in this solvent.

The ^1H NMR spectrum of $\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$ in CH_3SOCH_3 solution showed a single broad asymmetric peak. Its line width and chemical shift were temperature dependent. At 20°C its line width at half-height was 81 Hz, and δ was 11.80 relative to external Me_4Si with a shoulder on the upfield side. At 0°C the line narrowed to 36 Hz and broadened again at 60°C to 72 Hz. With decreasing temperature the line became more symmetric and shifted downfield (δ 12.20 at -60°C). The failure to observe two different types of protons and the variation of the observed line widths indicate rapid proton exchange for H_3O_2^+ . The assignment of the observed signal to H_3O_2^+ is supported by its large downfield shift. For comparison, 99% pure H_2O_2 exhibits between 20 and 30°C a chemical shift of δ 10.3 relative to external Me_4Si . On protonation, this signal is expected to be shifted further

downfield, as has previously been demonstrated³⁴ for numerous other species. The signal assigned to H_3O_2^+ also occurs significantly downfield from those previously reported for H_3O^+ ^{1,34,35} and $\text{SbF}_5\cdot\text{H}_2\text{O}$ ³³ and therefore cannot be due mainly to these species.

In $\text{HF}\cdot\text{AsF}_5$ solution at -80°C , only a single broad signal at δ 11.06 was observed for $\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$ indicating rapid proton exchange between H_3O_2^+ and the HF solvent. In SO_2 solutions of $\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$, two lines at δ 9.94 and 11.84, respectively, were observed at -80°C . The relative intensity of the δ 9.94 signal varied from sample to sample and also as a function of temperature. With decreasing temperature the peak area of the δ 9.94 signal decreased more rapidly than that of the δ 11.84 signal. These observations suggest that the two signals cannot belong to the same species. By comparison with previous reports,^{1,34,35} the δ 9.94 signal is assigned to H_3O^+ , and the more intense δ 11.84 signal is attributed to H_3O_2^+ , in good agreement with our observations for the CH_3SOCH_3 solution. The line width of the δ 11.84 signal was temperature dependent and showed a minimum (~ 7 Hz) at about -60°C , but no splittings could be observed. With increasing temperature, the δ 9.94 and 11.84 signals moved closer together, indicating the onset of chemical exchange between the two species.

The observations of H_3O^+ in the proton spectrum and possibly of a small amount of an $(\text{SbF}_6)_2\cdot\text{H}_2\text{O}$ adduct in the fluorine spectrum suggest that $\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$ may undergo either a redox reaction or decomposition in SO_2 solution.

Vibrational Spectra. The infrared and Raman spectra of $\text{H}_3\text{O}_2\text{AsF}_6$, $\text{H}_3\text{O}_2\text{SbF}_6$, and $\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$ are shown in Figures

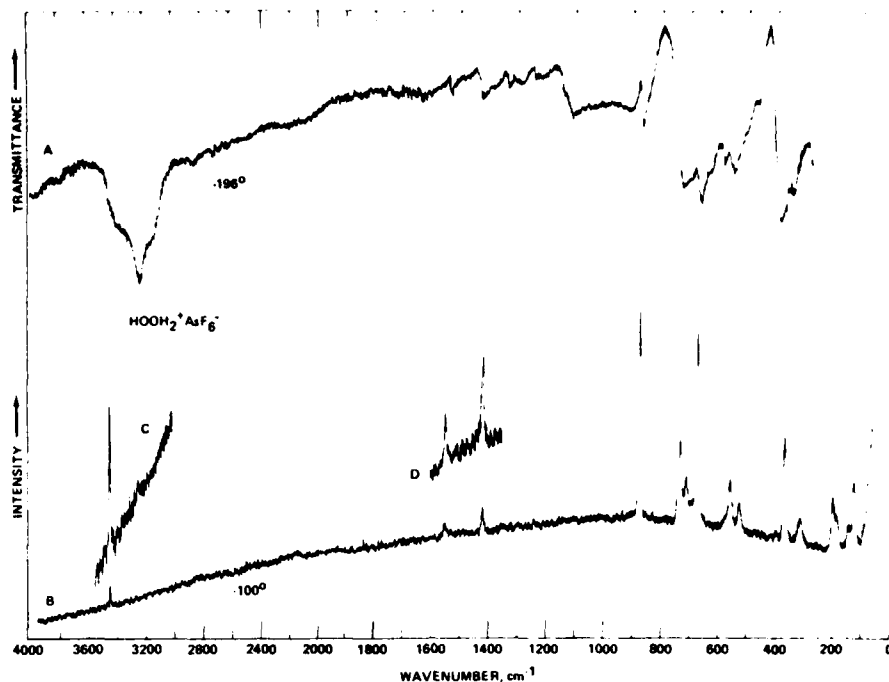


Figure 1. Vibrational spectra of $\text{H}_3\text{O}_2^+\text{AsF}_6^-$: trace A, infrared spectrum of the solid as a dry powder between CsI disks recorded at -196°C ; trace B, Raman spectrum of the solid in a glass tube recorded at -100°C with a spectral slit width of 8 cm^{-1} and a sensitivity of 100 000; inserts C and D were recorded with a spectral slit width of 10 cm^{-1} at sensitivities of 380 000 and 250 000, respectively.

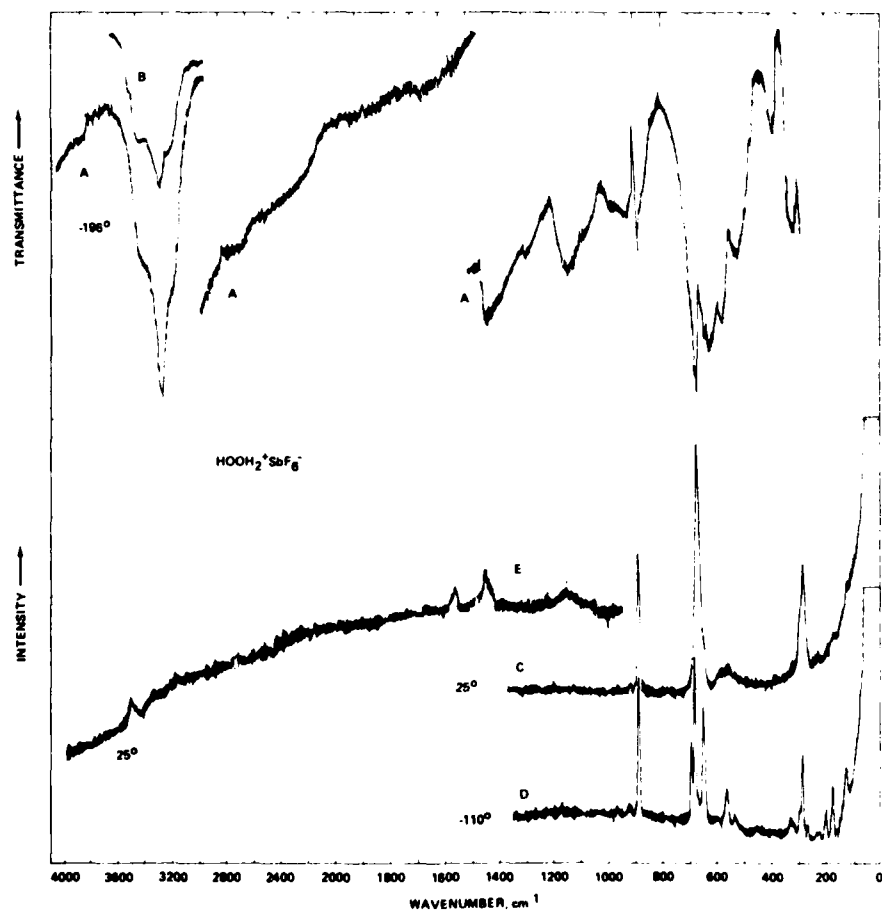


Figure 2. Vibrational spectra of $\text{H}_3\text{O}_2^+\text{SbF}_6^-$: traces A and B, infrared spectra of the solid recorded at -196°C at two different sample concentrations; traces C and E, Raman spectra of the solid recorded at 25°C with spectral slit widths of 5 and 10 cm^{-1} , respectively; trace D, Raman spectrum of the solid recorded at -110°C .

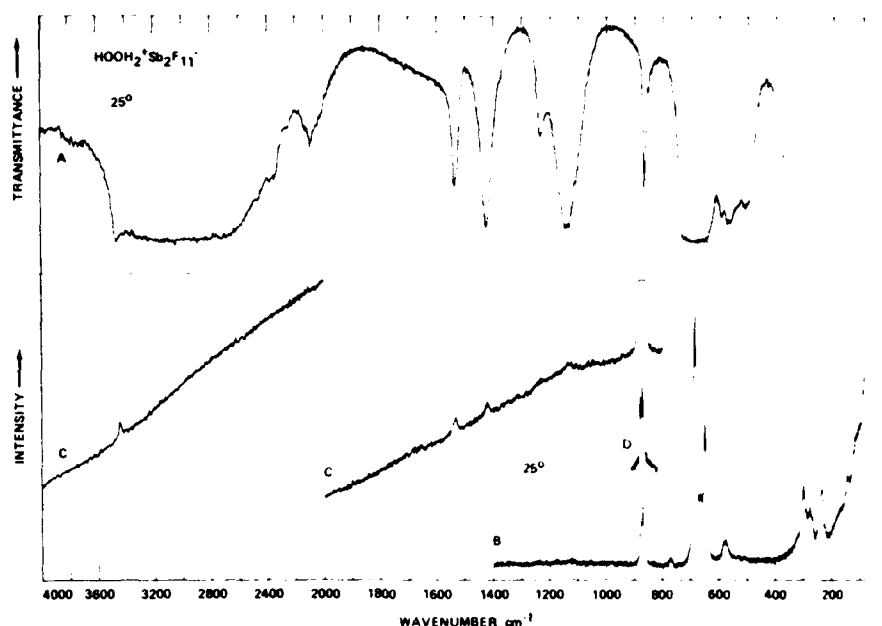


Figure 3. Vibrational spectra of $\text{H}_3\text{O}_2^+\text{Sb}_2\text{F}_{11}^-$: trace A, infrared spectrum of the solid as a dry powder between pressed AgCl disks; traces B, C, and D, Raman spectra of the solid recorded at 25 °C with spectral slit widths of 5, 10, and 2.5 cm^{-1} , respectively.

1, 2, and 3, respectively, and the observed frequencies are summarized in Table I. For the thermally more stable antimonate salts, spectra could be obtained at ambient temperature without the samples undergoing significant decomposition to the corresponding H_3O^+ salts. For $\text{H}_3\text{O}_2^+\text{AsF}_6^-$, only low-temperature spectra could be obtained.

The vibrational spectra of $\text{H}_3\text{O}_2^+\text{SbF}_6^-$ (see Figure 2) showed a pronounced temperature dependence. At room temperature, the Raman spectrum (traces C and E) exhibited three bands at 667, 555, and 282 cm^{-1} , respectively, characteristic for octahedral SbF_6^- .^{15,17,18,19} When the sample temperature was lowered, the number of bands due to SbF_6^- significantly increased, indicating that the symmetry of SbF_6^- became lower than O_h . This transition was found to be reversible and to occur close to room temperature. Similar transitions have previously been observed for the corresponding H_3O^+ ,¹ D_3O^+ ,³⁶ and O_2^{+37} salts. They can be attributed to rapid motions of the ions in the crystal lattice at room temperature, causing rotational averaging. With decreasing temperature, these motions are frozen out, causing the observed effects of symmetry lowering of the anions. Since the symmetry of the corresponding cations is low (no degeneracies), their vibrational spectra are much less affected.

Assignments for the H_3O_2^+ Cation. The assignments for H_3O_2^+ were made on the basis of the following arguments. With the exception of the O—O torsional mode, which by comparison with the known frequency³⁸ of the corresponding N—O torsion in the isoelectronic H_2NOH molecule is expected to occur below 400 cm^{-1} , all of the fundamental vibrations of H_3O_2^+ should have frequencies higher than those of the anions. The bands due to the anions can be further identified by comparison with the ambient and low-temperature spectra previously reported for the corresponding H_3O^+ and NH_2F_2^+ salts. In view of the complexity of the low-temperature anion spectra, in Table I only the room-temperature Raman spectrum of rotationally averaged SbF_6^- has been assigned. Keeping in mind that $\text{Sb}_2\text{F}_{11}^-$ spectra strongly depend on the nature of the counterion, the room-temperature spectrum of $\text{Sb}_2\text{F}_{11}^-$ in $\text{H}_3\text{O}_2\text{Sb}_2\text{F}_{11}$ is in fair agreement with those previously observed for this anion in numerous other salts.^{39–43}

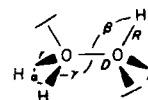
Thus, the intense bands occurring above 800 cm^{-1} should belong to H_3O_2^+ . By comparison with the known trans

Table II. Comparison of the Vibrational Spectrum of H_3O_2^+ with Those of Isoelectronic H_2NOH and H_2N_2

assign for H_2XYH in pt group C_s	approx descript of mode	obsd freq, cm^{-1}			
		H_2O_2^+ OOH^a	H_2O_2^+ NOH^b	H_2O_2^+ NNH^c	
A'	ν_1	$\nu(\text{YH})$	3440	3656	3202
	ν_2	$\nu_{\text{sym}}(\text{XH}_2)$	3229	3297	3100
	ν_3	$\delta_{\text{sciss}}(\text{XH}_2)$	1536	1605	1599
	ν_4	$\delta(\text{XYH})$ in plane	1421	1357	1330
	ν_5	$\delta_{\text{wag}}(\text{XH}_2)$	1136	1115	1103
	ν_6	$\nu(\text{XY})$	875	895	847
A''	ν_7	$\nu_{\text{asym}}(\text{XH}_2)$	3275	3350	3155
	ν_8	$\tau(\text{XH}_2)$	1228	1297	1232
	ν_9	$\tau(\text{XY})$	[386] ^a	386	[386] ^a

^a Estimated frequency values. ^b Data from ref 46, but revised according to ref 38. ^c Data from ref 48, but with revised assignments for ν_4 and ν_5 .

structure of isoelectronic H_2NOH ,⁴⁴ this cation should have the following structure of symmetry C_s .



Consequently, nine fundamentals ($6 \text{ A}' + 3 \text{ A}''$) are expected for H_3O_2^+ . These fundamentals should all be active in both the infrared and the Raman spectra. Of these, eight should occur above 800 cm^{-1} (see above). As can be seen from Figures 1–3 and Table I, indeed eight bands were observed in this frequency region. An approximate description of the H_3O_2^+ fundamental vibrations is given in Table II. There should be four stretching modes. Three of these should involve hydrogen ligands, while the fourth one is the oxygen–oxygen stretching mode.

The three hydrogen–oxygen stretching modes should occur above 2500 cm^{-1} . Their assignment, however, is somewhat complicated. By comparison with the known spectra of related molecules, such as CH_3NH_2 ,⁴⁵ H_2NOH ,^{38,46} H_2O , CH_3OH , and $>\text{CH}_2$ group containing molecules,⁴⁷ we would expect the H_2O -group to exhibit two intense infrared bands in the OH stretching region. Of these two, the antisymmetric stretching

mode should have a frequency 50–100 cm^{-1} higher than that of the symmetric stretching mode. In the Raman spectrum the symmetric stretching mode should be much more intense than the antisymmetric one. The unique –OH stretching mode should be of considerably lower infrared intensity than the two –OH₂ stretching modes.

Inspection of the Raman spectrum of $\text{H}_3\text{O}_2\text{AsF}_6$ shows a very narrow Raman line at 3440 cm^{-1} and a barely detectable broad line at 3230 cm^{-1} . Since the 3440- cm^{-1} Raman line shows only a rather weak infrared counterpart while the 3230- cm^{-1} one exhibits a very intense infrared counterpart and since no intense infrared band occurs above 3440 cm^{-1} , the 3440- cm^{-1} band is assigned to the unique –OH stretch and the 3230- cm^{-1} band to the symmetric –OH₂ stretch of H_2OOH^+ . The 3228- cm^{-1} infrared band exhibits a shoulder on both its high- and its low-frequency side. Instead of assigning these two shoulders to two separate bands, one might equally well attribute them to a single broad band onto which the sharper 3228- cm^{-1} band is superimposed. Such a broad band might be expected for the antisymmetric –OH₂ stretching mode, and its center (3275 cm^{-1}) results in a frequency value which agrees well with the above predicted frequency difference between the symmetric and the antisymmetric –OH₂ stretching mode. In the spectrum of $\text{H}_3\text{O}_2\text{SbF}_6$ the situation is almost identical. For $\text{H}_3\text{O}_2\text{SbF}_6 \cdot 1.17\text{SbF}_5$ ("H₃O₂Sb₂F₁₁") the 3435- cm^{-1} Raman band is also rather narrow and occurs at the very edge of the intense and extremely broad infrared band. These observations seem to support our assignments, although it is not obvious why the Raman line for the unique –OH stretch should be so much sharper than that for the symmetric –OH₂ stretch. If the –OH stretch and the symmetric –OH₂ stretch would have comparable Raman line widths, the latter should have a greater peak height than the –OH stretch and should be easily observed.

Whereas the modes involving mainly O–H bonds should be of low Raman and of high infrared intensity, the O–O stretching mode should be quite intense in the Raman spectrum and occur in the frequency range 800–1000 cm^{-1} . It is therefore assigned to the strong Raman line occurring in all samples between 868 and 880 cm^{-1} . As expected, this band shows a counterpart of medium intensity in the infrared spectra. In the spectra of $\text{H}_3\text{O}_2\text{SbF}_6 \cdot 1.17\text{SbF}_5$ ("H₃O₂Sb₂F₁₁") this band shows a splitting into two components, separated by about 10 cm^{-1} . This splitting might be due to the sample not having an exact 1:2 stoichiometry and therefore containing a mixture of different polyanionates. For the two well-defined 1:1 adducts $\text{H}_3\text{O}_2\text{AsF}_6$ and $\text{H}_3\text{O}_2\text{SbF}_6$, no splittings of this band could be detected.

Of the five deformation modes expected for H_3O_2^+ of symmetry C_{2v} , four involve the O–H bonds and should occur in the frequency range 1000–1700 cm^{-1} . Indeed, four infrared bands were observed in this frequency range for $\text{H}_3\text{O}_2\text{SbF}_6$ with counterparts in the Raman spectrum. Their assignment to the individual modes (see Table II) was made by analogy to those known⁴⁷ for related molecules, such as H_2O , CH_3OH , CH_3NH_2 , and CH_2X_2 .

The –OH₂ scissoring mode should have the highest frequency and occur between 1500 and 1600 cm^{-1} . It is therefore assigned to the band observed in most spectra at about 1535 cm^{-1} . The –XH₂ in-plane deformation mode is usually very intense in the infrared spectrum and occurs for H_2NOCH_3 ³⁸ and H_2NOH ^{38,46} at 1150 and 1115 cm^{-1} , respectively. For H_2OOH^+ it is therefore assigned to the strong infrared band at about 1130 cm^{-1} . The –XH₂ twisting mode is usually very weak and occurs in H_2NNH_2 , H_2NOH ,³⁸ and H_2NNH^- ⁴⁸ at 1260, 1297, and 1232 cm^{-1} , respectively. It is therefore assigned to the medium weak band observed for $\text{H}_3\text{O}_2\text{SbF}_6$ at 1228 cm^{-1} . There is only one frequency (~1420 cm^{-1}) left

Table III. Geometries^a Used for the Normal-Coordinate Analyses of the Isoelectronic H_2XYH Molecules and Ions

	H_2OOH^+	H_2NOH	H_2NNH^-
r (XH)	0.98	1.016	1.03
R (YH)	0.99	0.962	1.03
D (XY)	1.475	1.453	1.47
α (HXH)	107.06	107.06	107.06
β (HXYH)	101.22	101.22	101.22
γ (HXY)	103.15	103.15	103.15

^a Bond distances in Å and angles in degrees.

for assignment to the –OOH in-plane deformation mode. This assignment is in fair agreement with the value of 1345 cm^{-1} attributed to the corresponding COH deformation in CH_3OH .⁴⁷

The fifth deformation mode, the O–O torsion, is expected to occur in the 300–400- cm^{-1} frequency region. Since numerous bands due to either the anion or anion-cation interactions occur in this region, no assignments are proposed at this time for this mode.

In summary, with the exception of the O–O torsional mode, all fundamentals of H_2OOH^+ have been observed and assigned. The assignments are summarized in Table III and are compared to those of isoelectronic H_2NOH ^{38,46} and H_2NNH^- .⁴⁸ The similarity of the vibrational spectra of H_2OOH^+ , H_2NOH , and H_2NNH^- suggests that the two ions are isostructural with NH_2OH for which a trans structure of symmetry C_s was established⁴⁴ by microwave spectroscopy and confirmed⁴⁹ by ab initio molecular orbital theory. As expected for salts containing cations with hydrogen ligands and anions with fluorine ligands, strong cation-anion interactions were observed. These result in a lowering of the oxygen-hydrogen stretching frequencies and cause splittings of the anion bands in the spectra at low temperature at which rotational-averaging processes are frozen out.

Normal-Coordinate Analyses. Normal-coordinate analyses were carried out for H_2OOH^+ and the isoelectronic H_2NOH molecule and H_2NNH^- anion to support the above assignments and the contention that the three isoelectronic species are isostructural. Furthermore, it was important to establish whether the fundamental vibration assigned to the stretching mode of the two central atoms is highly characteristic and therefore can be taken as a direct measure for their bond strength.

For the computation of the force fields, the vibrational frequencies and assignments of Table II were used. The required potential and kinetic energy metrics were computed by a machine method⁵⁰ using the geometries given in Table III. Since the frequency of the X–Y torsion mode ν_9 (A'') is unknown for both H_2OOH^+ and H_2NNH^- and since, on the basis of its expected low frequency, coupling with other modes should be negligible, this fundamental was omitted from the normal-coordinate analyses. For H_2OOH^+ and H_2NNH^- , the bond angles were assumed to be identical with those known⁴⁴ for H_2NOH , and the bond lengths were estimated by comparison with those known for the similar H_2O_2 and N_2H_4 molecules. The bending coordinates were weighted by unit (1 Å) distance.

The force constants of these H_2XYH -type species were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. Since in the A' block the X–Y stretching force constant F_{66} was found to strongly depend on the values of the stretch-bend interaction constants F_{46} and F_{56} , the diagonal-symmetry force constants were computed as a function of F_{46} and F_{56} . As can be seen from Figures 4 and 5, the values of YH (F_{11}) and XH₂ (F_{22}) stretching force constants are unaffected by the choice of F_{46} and F_{56} , but the X–Y stretch (F_{66}) depends strongly on the choice of F_{46} and F_{56} . In the absence of additional ex-

Table IV. Anharmonic Symmetry Force Constants^a and Potential Energy Distribution^b of H₂OOH⁺, H₂NOH, and H₂NNH⁻ ^c

symmetry force constants					PED			
		H ₂ OOH*	H ₂ NOH	H ₂ NNH				
		H ₂ OOH*	H ₂ NOH	H ₂ NNH				
A'	$F_{11} = f_R$	6.607	7.46	5.675	F_{11}	100	100	100
	$F_{22} = f_r + f_{rr}$	5.92	6.13	5.42	F_{22}	100	100	100
	$F_{33} = f_\alpha$	0.628	0.733	0.748	F_{33}	95	99	99
	$F_{44} = f_\beta$	1.054	0.902	0.977	F_{44}	94	98	98
	$F_{55} = f_\gamma + f_{\gamma\gamma}$	0.715	0.72	0.728	F_{55}	95	97	96
	$F_{66} = f_D$	3.93	3.87	3.15	F_{66}	101	99	103
	$F_{35} = 2^{1/2} f_{\alpha\gamma}$	0.1	0.1	0.1				
	$F_{46} = f_{D\beta}$	0.2	0.2	0.2				
	$F_{56} = 2^{1/2} f_{D\gamma}$	0.3	0.3	0.3				
	A''	$F_{77} = f_r f_{rr}$	5.884	6.089	5.401	F_{77}	100	100
$F_{88} = f_\gamma - f_{\gamma\gamma}$		0.782	0.922	0.850	F_{88}	100	100	100

^a Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad², and stretch-bend interaction constants in mdyn/rad. ^b Percent contributions. Contributions of less than 9% to the PED are not listed. ^c Computed with the frequencies and assignments of Table III; all interaction constants except for F_{35} , F_{46} , and F_{56} were assumed to be zero.

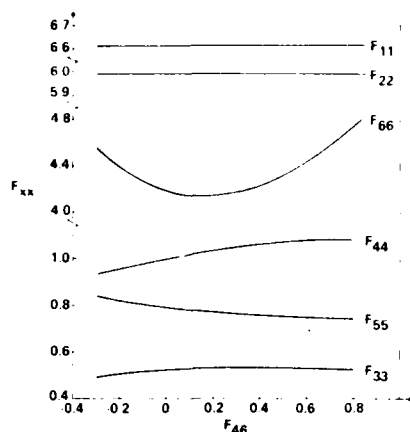


Figure 4. Diagonal symmetry force constants (stretching constants F_{11} , F_{22} , and F_{66} in mdyn/Å and deformation constants F_{33} , F_{44} , and F_{55} in mdyn Å/rad²) of the A' block of H₂OOH⁺ as a function of the stretch-bend interaction constant F_{46} (in mdyn/rad). All the remaining off-diagonal symmetry force constants were assumed to be zero.

perimental data, such as oxygen isotopic shifts, the uncertainty in the value of F_{66} obtained by underdetermined force fields must therefore be considered to be substantial. In the absence of such additional data, we have chosen for the isoelectronic H₂XYH series a force field which resulted in a highly characteristic potential energy distribution (PED) for all fundamentals (see Table IV). The X-Y stretching force constants obtained in such a manner represent minimal values but could be higher by as much as 0.4 mdyn/Å if larger positive values are assumed for F_{46} and F_{56} . A moderate size value was found necessary for F_{35} to obtain a characteristic PED for ν_3 and ν_5 .

In a recent paper, Botschwina and co-workers have reported⁵¹ a partial ab initio harmonic force field for H₂NOH. Since this type of computation can yield valuable information about the off-diagonal force constants, a comparison with the results of Table IV appeared interesting. Botschwina et al. report a value of 0.629 mdyn/rad for F_{46} (using the force constant designation of Table IV of our work) and predict values of 8.1 ± 0.1 mdyn/Å and 0.9 ± 0.05 mdyn Å/rad² for F_{11} and F_{33} , respectively. The latter two values and the positive sign of F_{46} are in fair agreement with the anharmonic force field of Table IV, although the value computed⁵¹ for F_{46} appears to be high. A calculation of a force field with $F_{46} = 0.63$ and $F_{56} = 0$ resulted in ν_5 and ν_6 becoming almost equal mixtures of F_{55} and F_{66} and an unacceptably high value of about 5 mdyn/Å for F_{66} . Assuming a positive value for F_{56} resulted in even less acceptable force constants.

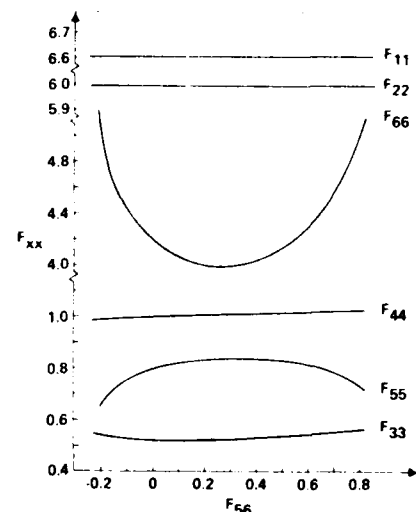
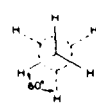
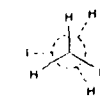
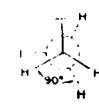
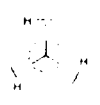
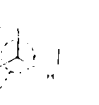


Figure 5. Diagonal symmetry force constants of the A' block of H₂OOH⁺ as a function of F_{56} .

A comparison of the results of Table IV shows that the force fields of isoelectronic H₂OOH⁺, H₂NOH, and H₂NNH⁻ are indeed very similar and suggests that all members of this series are isostructural. The small deviations observed within the series (higher values of F_{11} , F_{22} , and F_{77} for H₂NOH) can be readily explained. For H₂NOH, gas-phase frequencies of the isolated molecule were used, whereas in the H₂OOH⁺ and H₂NNH⁻ salts the anion-cation interactions lower the stretching frequencies somewhat (see above).

The question whether ν_6 , the fundamental vibration assigned to the stretching mode of the two central atoms, is highly characteristic or not also needed to be answered. The fact that ν_6 is of very high Raman intensity, whereas ν_5 is barely observable, and the known high polarizabilities of the central atoms relative to those of the hydrogen ligands argue strongly in favor of ν_6 being predominately the O-O stretching mode. Furthermore, the value of the O-O stretching force constant F_{66} (3.93 mdyn/Å) and the highly characteristic nature of ν_6 (101% F_{66}) of H₂OOH⁺ are in excellent agreement with the previously reported⁵² findings for gaseous HOOH ($F_{O-O} = 3.776$ mdyn/Å; $\nu_{O-O} = 105\%$ of F_{O-O}). For solid HOOH, a value ($F_{O-O} = 3.999$ mdyn/Å) was found⁵³ which is slightly higher than that in H₂OOH⁺. A further argument in favor of highly characteristic X-Y stretching frequencies in these and closely related molecules is based on the vibrational spectra observed for deuterated molecules, such as DOOD.^{52,53} If the fundamental assigned to the O-O stretch in HOOH would contain strong contributions from X-H bending modes, its frequency should significantly decrease on deuteration.

Table V. Preferred Rotational Isomers, Number of Vicinal Ligand Repulsions (R), and Attractions (A), and Frequencies (cm^{-1}) of the Stretching Mode of the Two Central Atoms of $\text{H}_3\text{NNH}_3^{2+}$,^a H_3NNH_2^+ ,^b H_2NNH_2 ,^c H_2NNH^+ ,^d H_2OOH^+ ,^e HOOH ,^e and HOO^- ^f

					
3R $\text{H}_3\text{NNH}_3^{2+}$ 1048 ^g	2R-1A H_3NNH_2^+ 949 ^h -968 ⁱ	1R-2A H_2NNH_2 850-938 ^j	3A H_2NNH^+ 847 ^k H_2OOH^+ 875 ^l	2A-1R HOOH 864-881 ^m	1A-2R HOO^- 836 ⁿ

^a Geometry of preferred rotational isomer is based on that of isoelectronic C_2H_6 .⁵⁵ ^b Geometry assumed to be analogous to that of isoelectronic CH_3NH_2 .⁵⁶ ^c Reference 57. ^d Geometry is based on that of isoelectronic H_2NOH .⁴⁴ ^e Reference 58. ^f For HOO^- , a preferred rotational isomer does not exist. The structure is given exclusively for didactic purposes. ^g From Raman spectrum of $\text{N}_2\text{H}_4\text{F}_2$ in anhydrous HF solution (B. Fricke and H. H. Hyman, *Inorg. Chem.*, **6**, 2233 (1967)). ^h From infrared spectrum of solid $(\text{N}_2\text{H}_5)_3\text{TaF}_7$.⁵⁴ ⁱ From Raman spectrum of $\text{N}_2\text{H}_4\text{Cl}$ in aqueous HCl solution (J. T. Edsall, *J. Chem. Phys.*, **5**, 225 (1937)); see also J. C. Decius and D. P. Pearson, *J. Am. Chem. Soc.*, **75**, 2436 (1953). ^j The assignments for the N-N stretching mode in N_2H_4 are not well established and significantly differ for the gas and condensed phases (see example ref 48 and J. R. Durig, S. F. Bush, and F. E. Mercer, *J. Chem. Phys.*, **44**, 4238 (1966)). The latter authors assigned the N-N stretch in N_2H_4 to bands in the 1087-1126- cm^{-1} frequency region which does not fit the general trends listed in this table. ^k From infrared spectrum of solid NaNH_2H_2 .⁵⁸ ^l This work. ^m Reference 12. ⁿ Reference 10.

In summary, it appears justified to assume that the fundamentals, assigned to the stretching modes of the two central atoms in these molecules and ions, are highly characteristic and that a highly characteristic PED might be a good criterion for selecting a plausible force field.

Influence of Progressive Protonation on the Bond Strength of the Two Central Atoms. It seemed interesting to examine how in an H_mXYH_n -type species the replacement of a free valence electron pair of a central atom by a hydrogen ligand influences the strength of the X-Y bond. Further interest was added to this problem by the fact that these X-Y bonds are single bonds, thus resulting in hindered rotation and rotational conformers. In the literature,^{8,54} the concept has been advanced that in a singly bonded X-Y system the replacement of a free valence electron pair on X or Y by a bonded ligand will diminish the overall ligand or electron-pair repulsions, thereby strengthening the X-Y bond. The results of the present study combined with previous literature data offered an excellent opportunity to examine the validity of this simple repulsion concept for the progressively protonated series HOO^- , HOOH , and H_2OOH^+ , which is isoelectronic with H_2NNH^+ , followed by H_2NNH_2 , H_3NNH_2^+ , and $\text{H}_3\text{NNH}_3^{2+}$.

For this series the energetically most favored rotational isomers and the stretching frequencies of the two central atoms are summarized in Table V. Stretching frequencies are preferred over force constants because for HOOH ,⁵³ H_2OOH^+ , and H_2NNH^+ these frequencies are highly characteristic and because of the lack of reliable fully determined force fields for most of these species. In Table V, frequency ranges are given for HOOH , H_3NNH_2^+ , and N_2H_4 . For the first two, these ranges are caused by the fact that the frequencies vary somewhat for different phases. For N_2H_4 , the large given range is mainly due to the uncertainty in the assignment of the N-N stretching mode (see footnote k of Table V). In spite of these limitations, inspection of the listed frequencies reveals not only that there is a definite X-Y stretching frequency increase with progressive protonation but also that the increase of the O-O stretching frequency from HOO^- to H_2OOH^+ (30 cm^{-1}) is much smaller than that (201 cm^{-1}) encountered for the H_2NNH^+ to $\text{H}_3\text{NNH}_3^{2+}$ part of the series.

This marked difference is difficult to explain by the simple free valence electron pair repulsion concept^{8,54} which should result in a more uniform trend and cannot account for the eclipsed structure of H_2NOH . A better explanation for the observed trends can be given on the basis of the following considerations. (i) The preferred rotational isomers (see Table V) indicate that in an H_mXYH_n -type species, in which the X and Y central atoms possess free valence electron pairs, at-

tractive forces exist between a free valence electron pair on one central atom and a hydrogen ligand bonded to the other central atom. In terms of molecular orbital theory, this effect can be considered to be the result of both dipolar attraction and back-donation from lone-pair orbitals of one central atom into antibonding orbitals of the other.⁴⁹ On the other hand, free valence electron pairs on X are repelled by free pairs on Y, and the same holds for vicinal hydrogen ligands. These effects explain the eclipsed configuration of H_2NOH ,⁴⁴ the staggered one of C_2H_6 ,⁵⁵ and the gauche ones⁵⁶⁻⁵⁸ of the remaining species. (ii) When going from HOO^- to $\text{H}_3\text{NNH}_3^{2+}$, one observes that the number of repulsions between vicinal ligands (including the free valence electron pairs) decreases from two for HOO^- to zero for H_2OOH^+ and H_2NNH^+ and then increases again to three for $\text{H}_3\text{NNH}_3^{2+}$. (iii) It is known that for peroxides a weakening of the oxygen-ligand bonds results in a strengthening of the O-O bond (FOOF , $\nu_{\text{O-O}}$ 1257 cm^{-1} ; HOOH , $\nu_{\text{O-O}}$ 864 cm^{-1})^{59,12} and vice versa. Furthermore, it is known⁸ that the $^{\delta-}\text{X}-\text{H}^{\delta+}$ polarity of an X-H bond increases by the addition of a second H^+ to X. This increase in bond polarity upon progressive protonation weakens the X-H bonds and therefore should strengthen the X-X bond. In addition, protonation is expected to shift more s character to the orbital involved in the X-X bond, thereby strengthening this bond. In our opinion, these two effects are the major reasons for the observed increase of the X-X stretching frequency within this series.

The fact that the stepwise increases within the series of Table V are small to the right of H_2XXH and large to the left of it suggests that the attractions between a free valence electron pair and a vicinal hydrogen ligand are at a maximum for H_2XXH and counteract the general polarity effect caused by the progressive protonation. This explanation seems plausible because both dipole interaction and back-donation should decrease the $^{\delta-}\text{X}-\text{H}^{\delta+}$ polarity of the X-H bond by transferring electron density from the free valence electron pair orbital to the vicinal hydrogen ligand. Although this picture is oversimplified and neglects other effects, such as possible changes in hybridization, it can nevertheless qualitatively account for the observed trends within this series. Molecular orbital calculations would be desirable but were beyond the scope of this study. In view of the great difficulties encountered with FOOF ,⁶⁰ such calculations might not be trivial.

The above analysis indicates that the replacement of a free valence electron pair on one of the two central atoms by a hydrogen ligand could either decrease or increase the vicinal ligand (or electron pair) repulsion. The direction of the effect

depends on whether the two central atoms possess less than three or three and more hydrogen ligands. With less than three hydrogen ligands, a free pair-free pair repulsion is replaced by a free pair-XH bond attraction, whereas with three or more hydrogen ligands an attraction is replaced by a vicinal hydrogen-hydrogen ligand repulsion. The importance of the attractive forces in this type of molecule is in agreement with the results from molecular orbital calculations.^{49,61}

The above results suggest that the previously proposed^{8,54} simple free valence electron pair repulsion concept applies only to H_mXYH_n species with $\sum(m+n) < 3$. In these limited cases, replacement of a free valence electron pair by a ligand will result in decreased ligand-ligand repulsion. However, this decreased repulsion counteracts the polarity effect and therefore does not strengthen but actually weakens the bond between the two central atoms. Consequently, the simple free valence electron pair repulsion concept cannot account, even in these limited cases, for the observed increase in the stretching frequency of the two central atoms.

The above results show that for a comparison, such as that given in Table V, a large enough number of molecules and ions must be available to have confidence in the observed trends. Furthermore, the assignments must be well established, the fundamental vibrations used must be highly characteristic, and interionic or intermolecular effects, such as hydrogen bridging in ionic solids or condensed phases, must be less pronounced than the trends to be observed. Finally, force constants should be compared only if their differences are significantly larger than their uncertainties.

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Registry No. $H_2O_2^+SbF_6^-$, 70850-27-0; $H_2O_2^+SbF_6^-$, 70850-28-1; $H_2O_2^+AsF_6^-$, 70850-29-2; H_2NNH , 25415-88-7; H_2NOH , 7803-49-8; AsF_5 , 7784-36-3; SbF_5 , 7783-70-2; BiF_3 , 7787-62-4; H_2O_2 , 7722-84-1; HF , 7664-39-3; $BiF_3 \cdot BiF_5$, 70850-25-8.

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APPENDIX D

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Formation and Decomposition Mechanism of NF_4^+ Salts

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The thermal decompositions of NF_4BF_4 and NF_4AsF_6 were studied in a sapphire reactor at different temperatures by total-pressure measurements. It was found that the rates, previously reported by Solomon and co-workers for NF_4AsF_6 , significantly differ from those of the present investigation, although both studies result in a $3/2$ reaction order. From the temperature dependence of the observed decomposition rates, the following values were obtained for the global activation energies: $E_{\text{NF}_4\text{BF}_4} = 36.6 \pm 0.8 \text{ kcal mol}^{-1}$ and $E_{\text{NF}_4\text{AsF}_6} = 44.7 \pm 4.2 \text{ kcal mol}^{-1}$. The suppression of the decomposition rates by NF_3 , F_2 , and BF_3 or AsF_3 was measured. A critical evaluation of all experimental data available on the NF_4^+ salt formation and decomposition suggests the following reversible reaction mechanism: $\text{F}_2 \rightleftharpoons 2\text{F}$; $\text{F} + \text{NF}_3 \rightleftharpoons \text{NF}_4$; $\text{NF}_4 + \text{AsF}_5 \rightleftharpoons \text{NF}_4^+\text{AsF}_6^-$; $\text{NF}_3^+\text{AsF}_6^- + \text{F} \rightleftharpoons \text{NF}_4^+\text{AsF}_6^-$. A Born-Haber cycle calculated for NF_4BF_4 shows that the global decomposition activation energy and the heat of the formation reaction are identical within experimental errors and that the second step of the above mechanism is approximately thermochemically neutral. The rate of the thermal formation of NF_4SbF_6 at 250 °C was also studied.

Introduction

The formation and decomposition reactions of NF_4^+ salts are of significant theoretical and practical interest. From a

theoretical point of view, the question arises as to whether NF_4 or NF_3 is produced as an unstable intermediate. This would be highly unusual because second-row elements generally do not form hypervalent molecules. From a practical point of view, a better knowledge of the formation and the decom-

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position mechanism is necessary in order to improve on existing synthetic methods.

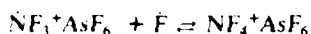
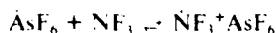
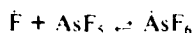
Several mechanisms have previously been postulated for the formation of NF_4^+ salts. In 1966, Christie and co-workers suggested in their original reports^{1,2} on the synthesis of NF_4AsF_6 by low-temperature glow discharge that either NF_3^+ or F^+ (or F_2^+) is generated in the discharge. These radical cations could then react with either F_2 or NF_3 to yield NF_4^+ . In 1972, Solomon and co-workers reported³ the results from a kinetic study of the thermal decomposition of NF_4AsF_6 in Monel. Based on total pressure measurements, their conclusion was that the decomposition involved the equilibrium dissociation step



followed by irreversible decomposition of the unstable NF_3



The latter step was taken to be a $3/2$ -order reaction. From the temperature dependence of the kinetic constants, a value of 41 kcal mol⁻¹ was obtained for the sum of the overall heat of sublimation and the activation energy for the decomposition of NF_3 . In 1973, Christie and co-workers proposed⁴ an alternate mechanism for the formation of NF_4^+ salts. This mechanism accounted for the fact that NF_4^+ salts can be synthesized by UV photolysis. It involved the steps



Part of this mechanism was later experimentally confirmed by ESR studies^{5,7} which showed that the NF_3^+ radical cation is indeed formed as an intermediate in both the low-temperature UV photosynthesis and the γ -irradiation-induced decomposition of NF_4^+ salts.

Since the observation of NF_3^+ as an intermediate^{5,7} is incompatible with the mechanism proposed³ by Solomon and since at elevated temperatures metal reactors rapidly absorb F_2 Lewis acid mixtures, a reinvestigation of the thermal decomposition of NF_4AsF_6 in an inert sapphire reactor was undertaken. In particular, a more detailed investigation of the suppression effects of NF_3 , F_2 , and AsF_5 was expected to yield valuable information. Furthermore, no quantitative data had previously been available on the decomposition rates of NF_4BF_4 and the formation rates of NF_4SbF_6 .

Experimental Section

Thermal Decomposition Studies. The samples of NF_4BF_4 ⁸ and NF_4AsF_6 ^{8,9} were prepared as previously described and showed no detectable impurities. All decomposition experiments were carried out in a sapphire reactor (Tyco Co.). The reactor was connected by a Swagelok compression fitting, containing a Teflon front ferrule, to a stainless steel valve and a pressure transducer (Validyne, Model DP7, 0–1000 mm $\pm$ 0.5%), the output of which was recorded on a strip chart. The reactor had a volume of 38.7 mL and was heated by immersion into a constant-temperature ($\pm$ 0.05 °C) circulating oil bath. The reactor was passivated at 250 °C with F_2 - BF_3 or F_2 - AsF_5 mixtures until the pressure remained constant over a period of several days, and weighed amounts of NF_4^+ salts were added in the dry nitrogen atmosphere of a glovebox. After immersion of the reactor into the hot oil bath, the reactor was evacuated, and the pressure change was monitored as a function of time. Control experiments were carried out at the beginning and end of each series of measurements to ascertain that the rates had not significantly changed during each series. The composition of the gaseous decomposition products was shown by chemical analysis, infrared spectroscopy, and gas chromatography to be 1:1:1 mixtures of NF_3 , F_2 , and the corresponding Lewis acid. For the curve fitting of the kinetic data the

method of linear least squares was used with the listed uncertainties being 2 σ of the calculated slope.

Formation of NF_4SbF_6 . Because of the high corrosivity of high-pressure NF_3 - F_2 - SbF_5 mixtures at elevated temperatures, the NF_3 - F_2 - SbF_5 reaction system could not be monitored directly with a pressure transducer or gage. Consequently, nine identical passivated 95-ml. Monel cylinders were each loaded with 50 mmol of SbF_5 , and a twofold excess of NF_3 and F_2 was added. The cylinders were simultaneously placed into an oven preheated to 250 °C and were removed separately from the oven after certain time intervals. After the cylinders were cooled, all material volatile at 25 °C was pumped off, and the amount of NF_4^+ salt formed was determined by the observed weight increase and spectroscopic analyses.

Results and Discussion

Thermal Decomposition of NF_4BF_4 and NF_4AsF_6 . The thermal decomposition of NF_4BF_4 and NF_4AsF_6 in a constant-volume reactor was studied by total-pressure measurements over a temperature range of about 35 °C for each compound. Since screening experiments had shown that even well-passivated nickel or Monel reactors rapidly reacted with mixtures of hot F_2 and BF_3 or AsF_5 , a sapphire reactor was used. This reactor was found to be completely inert toward these gas mixtures over extended time periods. Furthermore, it was found that the decomposition rates increased with increasing sample size. However, the rates did not increase linearly with the sample size because the increased pressure enhances the suppression of the rates (see below). In order to minimize the effect of changes in the sample size during a given series of experiments, we used the largest feasible samples and the smallest available reactor volume. In this manner, only a small percentage of the sample was decomposed in a given series of experiments. The first and the last experiment of each series were carried out under identical conditions and showed that the change in rate due to the small, but inevitable, sample-size change was indeed negligible.

The results of our measurements on NF_4BF_4 and NF_4AsF_6 are summarized in Tables I and II. In agreement with the previous report³ on the thermal decomposition of NF_4AsF_6 , smooth decomposition curves were obtained. The decomposition rates steadily decreased with increasing pressure in the reactor and the initial rates were restored upon evacuation of the reactor, indicating that the decomposition products suppress the decomposition rates. This was confirmed by studying the influence of different gases on the decomposition rates of NF_4BF_4 and of NF_4AsF_6 . The addition of He did not noticeably influence the rates, whereas F_2 and NF_3 resulted in a weak suppression. However, the addition of BF_3 to NF_4BF_4 or of AsF_5 to NF_4AsF_6 resulted in strong rate suppressions (see Tables I and II).

For all decomposition experiments, plots of $P^{3/2}$ vs. time resulted in straight lines (see Figures 1 and 2) indicating a $3/2$ reaction order. The resulting global kinetic constants are given in Table III. Arrhenius plots of these constants resulted in straight lines (see Figure 3) and in the global decomposition activation energies $E_{\text{NF}_4\text{BF}_4} = 36.6 \pm 0.8$ kcal mol⁻¹ and $E_{\text{NF}_4\text{AsF}_6} = 44.7 \pm 4.2$ kcal mol⁻¹, the latter value being in good agreement with that of 41 kcal mol⁻¹ previously reported.³

The fact that the small mole fraction ranges of sample decomposition studied in these experiments were truly representative for the overall decomposition rates was established by following the decomposition of small samples at somewhat higher temperatures over almost the entire mole fraction (α) range. A typical decomposition curve obtained for NF_4BF_4 at 253 °C (see Figure 4) does not exhibit any sigmoid character, and the $P^{3/2}$ vs. time plot is linear for about the first 25% of α .

Although the results previously reported³ for the decomposition of NF_4AsF_6 in Monel resulted in a linear $P^{3/2}$ vs. time plot, the reported rates were higher than ours by a factor of

Table I. Thermal Decomposition of NF_4BF_4 ^a in a Sapphire Reactor^b

time, h	pressure change, mmHg										
	190.8 °C										
	182.2 °C	188.9 °C	190.8 °C	He (500) ^c	F ₂ (500) ^c	NF ₃ (500) ^c	BF ₃ (500) ^c	197.4 °C	204 °C	213.3 °C	215 °C
0	0	0	0	0	0	0	0	0	0	0	0
1	28	40	45	44	38	38	5	64	91	160	180
2	42	66	74	73	64	64	11	103	142	261	285
3	55	86	97	98	84	87	16	134	191	341	367
4	66.5	102	116	117	102	105	21	161	228	409	440
5	77	117	135	136	122	122	26	186	266	468	509
6	86.5	132	152	153	139	138	31	208	300	522	572
7	96	146	168	169	155	152	35	230	336	579	633
8	104	159	183		169	166	39	250		628	689
9	112	171	197		182	180	43	269		675	741
10	120.5	182	210		195	192	47	288		721	791
12	135	204	236		218	217	56	324		806	891
14	149	225	260		238	239	65	355		895	980
16	162	247	280		258	263	73	390			
18		267	300		277		82				
20					295		91				

^a Sample size 2.65 g. ^b Reactor volume 38.7 mL. ^c The values given in parentheses indicate the pressure (in mmHg) of the added gas at the beginning of each experiment.

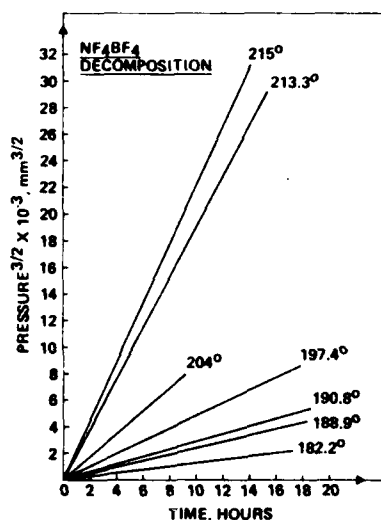


Figure 1. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 2.65 g of NF_4BF_4 at different temperatures (°C).

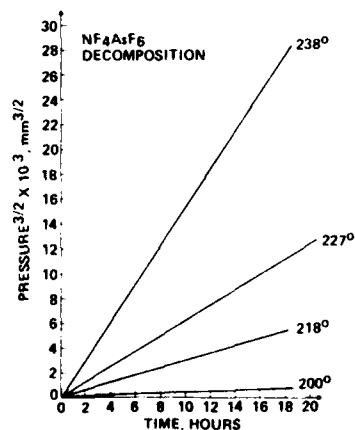


Figure 2. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 1.86 g of NF_4AsF_6 at different temperatures (°C).

about 7. Unfortunately the sample size and the exact reactor volume used in ref 3 were not given. However, the estimated reactor volume (100-cm³ Monel cylinder + Wallace-Tierman

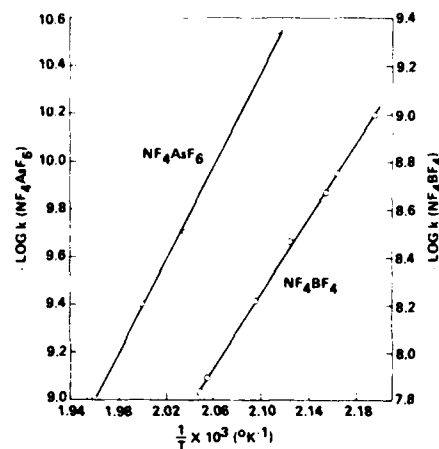


Figure 3. Arrhenius plots for NF_4BF_4 and NF_4AsF_6 .

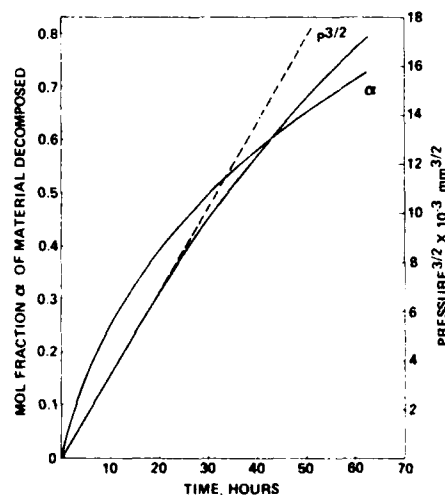


Figure 4. Decomposition curves for 75 mg of NF_4BF_4 at 253 °C. The solid lines are the observed data and the broken line represents the ideal straight line for the $P^{3/2}$ vs. t plot.

FA 145-780 gage) and the reported method of the NF_4AsF_6 synthesis suggest that the previously used sample weight to reactor volume ratios were almost certainly significantly

Table II. Thermal Decomposition of NF_4AsF_6 in a Sapphire Reactor^b

time, h	pressure change, mmHg					238 °C				
	200 °C	218 °C	227 °C	238 °C		He (736) ^c	F ₂ (197) ^c	NF ₃ (567) ^c	AsF ₃ (247) ^c	AsF ₅ (724) ^c
0	0	0	0	0		0	0	0	0	0
1	2.6	9.9	16	27		28	25	21	5	4
2	4.0	16.0	25	44		45	42	34	8.5	7
3	5.2	20.8	33	58		59	55	44	12	9
4	6.2	25.3	40	71		73	68	54	16.5	11
5	7.2	29.4	46.5	83		85	79	63	20	12
6	8.3	32.2	52.5	93.5		95	90	72	24	13
7	9.2	36.6	57	103.5		105	101	81	28	14
8	10.0	40.0	62	113		115	110	90	32	15.5
9	10.8	43.0	67.5	123		124	120	98	35	17
10	11.6	46.0	72.5	132		133	129	106	38	18
12	13.2	51.4	82	149		151	145	122	45	21
14	14.7	56.6	91	165		166	161	140	52	23
16	16.1	61.4	99.5	181		181	176	160	59	25
18	17.4	66.2	107	197.5		196	190	176	65	
20			115.5	214		213	205	192	72	
25			134					226		
30								252		

^a Sample size 1.86 g. ^b Reactor volume 38.7 mL. ^c The values given in parentheses indicate the pressure (mmHg) of the added gas at the beginning of each experiment.

Table III. Global Kinetic Constants^a for the Thermal Decomposition of NF_4BF_4 and NF_4AsF_6

NF_4BF_4		NF_4AsF_6	
temp, °C	$10^3 k$	temp, °C	$10^{10} k$
182.2	0.96 ± 0.01	200	0.284 ± 0.002
188.9	1.74 ± 0.02	218	1.99 ± 0.03
190.8	2.11 ± 0.04	227	4.00 ± 0.02
197.4	3.39 ± 0.05	238	9.69 ± 0.10
204	6.08 ± 0.08	238 (He	9.62 ± 0.08
213.3	12.79 ± 0.22	(736))	
215	14.68 ± 0.18	238 (F ₂	9.22 ± 0.05
190.8 (He	2.29 ± 0.03	(197))	
(500))		238 (NF ₃	8.60 ± 0.16
190.8 (F ₂	1.86 ± 0.04	(567))	
(500))		238 (AsF ₃	1.94 ± 0.12
190.8 (NF ₃	1.92 ± 0.02	(247))	
(500))		238 (AsF ₅	0.48 ± 0.08
190.8 (BF ₃	0.314 ± 0.02	(724))	
(500))			

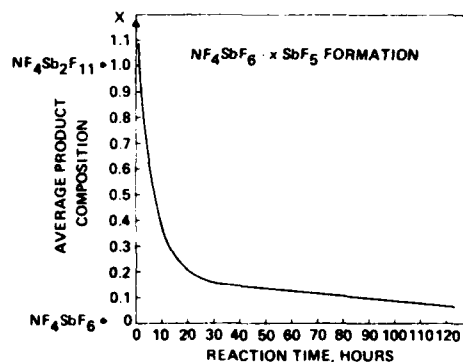
^a Units $\text{mol}^{3/2} \text{L}^{-3/2} \text{s}^{-1}$; error limits 2σ.

smaller than those of our experiments. This should have resulted in rates lower than ours. The only possible explanations for the previously reported³ higher rates are absorption of the suppressing AsF_5 by Monel and/or inaccurate temperature control (heating of the cylinder in a tube furnace).

A large discrepancy of $\sim 10^6$ exists between the previously reported³ results and our kinetic constants (see Table III). Most of this discrepancy ($\sim 10^5$) appears to be computational.

Furthermore, the previously reported³ data for the suppression by AsF_5 are inconsistent. Whereas the experimental data in Tables 6 and 7 of ref 3 show strong rate suppression by AsF_5 , the kinetic constants given in Table 8 of ref 3 imply only mild suppression by AsF_5 . The previously reported³ strong rate suppression by NF_3 could not be confirmed by the present study. Our data (see Table III) show that NF_3 is only a weak suppressor, comparable to F_2 , and that AsF_5 or BF_3 is the only strong suppressor. This is an important observation, because the alleged³ strong suppression by NF_3 had caused us to propose in a previous publication⁴ a mechanism for the formation of NF_4AsF_6 involving the incorrect (see below) steps $\text{F} + \text{AsF}_5 \rightarrow \text{AsF}_6$ and $\text{AsF}_6 + \text{NF}_3 \rightarrow \text{NF}_3^+\text{AsF}_6^-$.

Thermal Synthesis of NF_4SbF_6 . Whereas the thermal synthesis of NF_4AsF_6 proceeds at too slow a rate for practical kinetic measurements, the rate of formation of NF_4SbF_6 is sufficiently fast. However, SbF_6 tends to form poly-

**Figure 5.** Formation rate of $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$ from NF_3 , F_2 , and SbF_5 at 250 °C.**Table IV.** Conversion of $\text{NF}_3 + \text{F}_2 + \text{SbF}_5$ to NF_4SbF_6 at 250 °C^a

reacn time, h	prod compn, $\text{NF}_4^+\text{SbF}_6^- \cdot x\text{SbF}_5$	convsn of SbF_5 to NF_4SbF_6 , mol %
1	1.08	48.1
2	0.89	52.9
3	0.78	56.2
6	0.59	62.9
12	0.34	74.6
24	0.17	85.5
50	0.13	88.5
85	0.106	90.4
120	0.064	94.0

^a Mole ratios of starting materials $\text{NF}_3:\text{F}_2:\text{SbF}_5 = 2:2:1$. Starting pressure 110 atm; residual pressure calculated for 100% conversion to NF_4SbF_6 44 atm. The Monel cylinders (95-mL volume) were placed horizontally in the oven, preheated to 250 °C. One hour was required until the cylinders reached 250 °C. This point was taken as zero reaction time.

antimonates such as $\text{Sb}_2\text{F}_{11}^-$ or $\text{Sb}_3\text{F}_{16}^{3-}$ with SbF_5 , which makes a kinetic evaluation of any experimental data very difficult. In view of the importance of the thermal synthesis of NF_4SbF_6 (this compound serves as a starting material for the metathetical syntheses of most other NF_4^+ salts¹¹⁻¹⁵) and because of the complete absence of data on its formation rate, nine reactions were carried at 250 °C and at a pressure of

about 110 atm to determine its formation rate. The results are summarized in Table IV and Figure 5 and show that at this temperature the initial formation rate of NF_4^+ salts is surprisingly rapid. The subsequent slow-down of the reaction is probably caused by a lowering of the SbF_5 partial pressure in the system due to the formation of polyantimonate anions. Their thermal dissociation equilibria to SbF_6^- and SbF_5 will then control the SbF_5 pressure in the system and become the rate-limiting steps.

Reaction Mechanism. As pointed out in the Introduction, the formation and decomposition mechanism of NF_4^+ salts is of great interest because it appears to involve an unusual hypervalent species such as NF_4 , NF_5 , AsF_6 , or BF_4 . The following experimental data are known, and the correct mechanism must be compatible with all of these conditions.

(1) Certain NF_4^+ salts, such as NF_4SbF_6 and NF_4AsF_6 , can, depending upon the system pressure, be either formed or decomposed at the same temperature.^{5,9,11} This implies pressure-dependent equilibria and reversibility of the formation and decomposition reactions.

(2) ESR measurements have shown^{5,7} that the NF_3^+ radical cation is a crucial intermediate in both the low-temperature UV photolytic synthesis and γ -irradiation-induced decomposition of NF_4^+ salts. Furthermore, the fluorination of NF_3^+ to NF_4^+ appears to require F atoms.

(3) In the thermal decomposition of either NF_4BF_4 or NF_4AsF_6 , BF_3 or AsF_5 acts as a strong rate suppressor, whereas both NF_3 and F_2 suppress the decomposition rates only mildly (see above results).

(4) Filtered UV radiation^{4,8} or heating⁹ to 120 °C supply sufficient activation energy for the formation of NF_4^+ salts. This is a strong indication that the first step in the synthesis must be the dissociation of F_2 into two fluorine atoms ($D^0(\text{F}_2) = 36.8 \text{ kcal mol}^{-1}$).¹⁶

(5) The tendency to form NF_4^+ salts by thermal activation strongly decreases with decreasing Lewis acid strength, i.e., $\text{SbF}_5 > \text{AsF}_5 > \text{PF}_5 > \text{BF}_3$.^{4,8,9} Since the corresponding NF_4^+ salts all possess sufficient thermal stability, a mechanism³ involving the initial formation of NF_5 , followed by its reaction with the corresponding Lewis acid, cannot explain the lack of thermal formation of salts such as NF_4PF_6 or NF_4BF_4 . It can be explained, however, by the formation of intermediates of lower thermal stability such as NF_3^+ salts. For SbF_6^- or AsF_6^- , these NF_3^+ salts were shown to still possess the lifetime required for their efficient conversion to NF_4^+ salts, whereas $\text{NF}_3^+\text{BF}_4^-$ was found to be of considerably lower thermal stability.

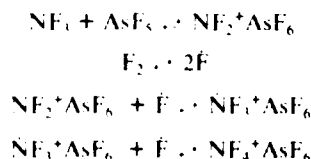
(6) ESR flow-tube experiments¹⁷ gave no indication of interaction between F atoms and AsF_5 , as expected for the reaction step $\text{AsF}_5 + \text{F} \rightarrow \text{AsF}_6$.

(7) Infrared matrix isolation studies of the thermal decomposition products from either NF_4AsF_6 ³ or $(\text{NF}_4)_2\text{NiF}_6$ ¹⁸ gave no evidence for the formation of NF_5 .

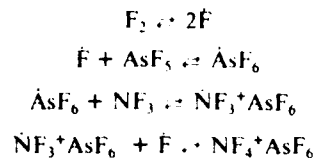
(8) Lewis acids such as BF_3 , PF_5 , AsF_5 , or SbF_5 do not form stable adducts with NF_3 , even at low temperatures.^{18,19}

Since NF_3 , F_2 , and F have ionization potentials of 13.00,²⁰ 15.69,²¹ and 17.44 eV,²² respectively, any mechanism involving the initial formation of either NF_3^+ , F_2^+ , or F^+ can be ruled out, based on condition 4. This leaves us with Schemes I-IV as possibilities.

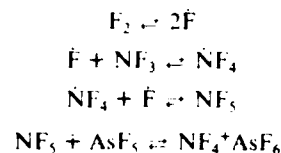
Scheme I



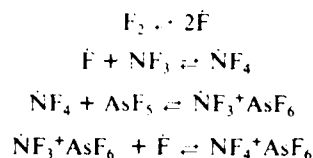
Scheme II



Scheme III



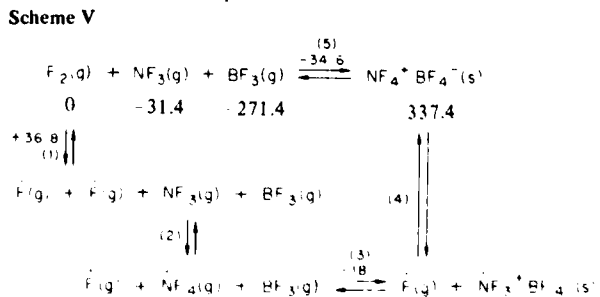
Scheme IV



Scheme I can be ruled out because it does not comply with conditions 8 and 3. In Scheme I, NF_3 would be expected to suppress as strongly as AsF_5 . Scheme II can be eliminated because of the fact that it violates condition 3 (i.e., NF_3 should be a stronger suppressor than AsF_5) and because of condition 6. Scheme III is unacceptable because it does not comply with conditions 2 and 5. Scheme IV is the only mechanism which agrees with all experimental data and therefore is our preferred mechanism. This mechanism differs from all the mechanisms previously proposed. It appears to be generally applicable to NF_4^+ salts, except for certain decomposition reactions in which NF_4^+ oxidatively fluorinates the anion.¹⁸

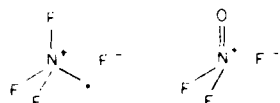
In view of the rather complex mechanism of Scheme IV and the observed fractional reaction order for the decomposition process, a mathematical analysis of the kinetic data was too complex and beyond the scope of the present study.

Born-Haber Cycle for NF_4BF_4 . It was of interest to examine the thermodynamic soundness of Scheme IV. NF_4BF_4 was chosen for this purpose because it is the only NF_4^+ salt for which the heat of formation has experimentally been determined.²³ The Born-Haber cycle is shown in Scheme V, where all heats of formation or reaction are given in kcal mol⁻¹. From the known heats of reaction of NF_3 ,²⁴ BF_3 ,²⁴ and NF_4BF_4 ,²³ the heat of reaction 5 is known to be -34.6 kcal mol⁻¹. Furthermore, the heat of dissociation of F_2 , reaction 1, is known¹⁶ to be 36.8 kcal mol⁻¹. A reasonably close estimate for step 3, the heat of formation of solid $\text{NF}_3^+\text{BF}_4^-$ from NF_3 and BF_3 , can be made from the known heat of dissociation of $\text{NF}_2\text{O}^+\text{BF}_4^-$. Since NF_3O and NF_4 are expected to be quite similar (see below), it is reasonable to assume that step 3 has a heat of reaction similar to that of $\text{NF}_3\text{O} + \text{BF}_3 \rightarrow \text{NF}_2\text{O}^+\text{BF}_4^-$, i.e., -18 kcal mol⁻¹. Consequently, the sum of steps 2 and 4 should be about -53 kcal mol⁻¹. Whereas the heat of reaction of step 2 is difficult to estimate, the heat of

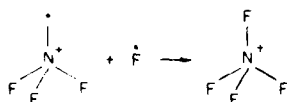


reaction of (4) is easier to estimate because it represents the dissociation energy of the fourth N-F bond in NF_4^+ . In NF_3 , the heat of dissociation of the third N-F bond is 58 kcal mol⁻¹,^{26,27} and it seems reasonable to assume that the dissociation energy of the fourth N-F bond in NF_4^+ is similar to or slightly less than this value. Consequently, step 2 should be approximately thermochemically neutral.

The proposition that steps 2 and 4 should so markedly differ in their heats of reaction, although both involve the formation of one additional N-F bond, is not unreasonable. In step 2 a hypervalent NF_4 radical is formed which would possess nine valence electrons on the central nitrogen atom. By analogy with the known NF_3O molecule,²⁸ this energetically unfavorable structure can be circumvented by assuming strong contributions from resonance structures such as



These resonance structures result in a strong polarization, i.e., weakening of all N-F bonds, when compared to those in NF_3 . This is demonstrated by the bond lengths of 1.371 and 1.43 Å observed for NF_3 ²⁹ and NF_3O ,²⁸ respectively. Thus the energy gained by the formation of a fourth N-F bond in the NF_4 radical is largely compensated by a significant weakening of the remaining N-F bonds. In contrast, the reaction of the NF_3^+ radical cation with a fluorine atom, i.e.



does not significantly change the nature of the existing N-F bonds and, therefore, is expected to result in a heat of reaction close to the energy of this bond.

An alternate, attractively simple, and preferable explanation for the above bond weakening effect in NF_4 can be offered if one assumes that, due to the large energy difference between the 2p and 3s nitrogen orbitals, the ninth nitrogen valence electron occupies an antibonding orbital. Experimental evidence for such a model has recently been reported³⁰ by Nishikida and Williams for the NF_3O radical anion which is isoelectronic with NF_4 . On the basis of the observed ESR data, NF_3O possesses a spin density of 0.27 in the nitrogen 2s orbital suggesting that the unpaired electron indeed occupies an antibonding orbital.

A third possible, although less likely, explanation would be the assumption of a trigonal-bipyramidal structure for NF_4 , in which two axial fluorines and nitrogen form a semiionic three-center, four-electron bond while the three equatorial positions are occupied by two fluorine ligands and the unpaired electron. Although all three models are basically a formalism describing the same net result, i.e., an increase of the bond length and ionicity of the NF bonds, model III should result in significantly different bond angles and therefore be experimentally distinguishable from models I and II.

It should be pointed out that the global activation energy (36.6 ± 0.8 kcal mol⁻¹) of the decomposition of NF_4BF_4 to $\text{NF}_3 + \text{F}_2 + \text{BF}_3$ and the heat of formation of NF_4BF_4 from $\text{NF}_3 + \text{F}_2 + \text{BF}_3$ (-34.6 kcal mol⁻¹) are the same within

experimental error. It is difficult to say whether this is coincidental or if it implies that the corresponding forward reactions, i.e., steps 2-4 of the Born-Haber cycle, occur without activation energy. Examples of the latter case are known for the endothermic dissociation of solids such as carbonates.³¹ If for NF_4^+ salts the global decomposition activation energies should indeed be identical with the heats of formation from NF_3 , F_2 , and the corresponding Lewis acid, a value of about 372 kcal mol⁻¹ can be predicted for $\Delta H_f^\circ(\text{NF}_4\text{AsF}_6)$ on the basis of $E_{\text{NF}_4\text{AsF}_6} = 45$ kcal mol⁻¹ and $\Delta H_f^\circ(\text{AsF}_5) = 29.55$ kcal mol⁻¹.

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Registry No. NF_4BF_4 , 15640-93-4; NF_4AsF_6 , 16871-75-3; NF_4SbF_6 , 16871-76-4; NF_3 , 7783-54-2; F_2 , 7782-41-4; SbF_5 , 7783-70-2.

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Sulfur tetrafluoride. Assignment of vibrational spectra and force field

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Abstract—The i.r. spectra of SF_4 isolated in Ar and Ne matrices were studied. The observed ^{32}S - ^{34}S isotopic shifts were used to resolve the existing ambiguities concerning the assignments of the deformation modes and to obtain an improved valence force field.

INTRODUCTION

Although numerous papers have been published on the vibrational spectra and assignments of SF_4 [1–12], this molecule is still poorly understood and the assignment of most of the deformation modes is still open to question.

In this paper, we report new matrix isolation data and ^{32}S - ^{34}S isotopic shifts which allow unambiguous assignments for the deformation modes and the computation of an improved valence force field.

EXPERIMENTAL

The Ar or Ne matrix isolated samples of SF_4 were prepared by the reaction of S_2Cl_2 with AgF_2 using a previously described flow system [13] and the cryostat [14] altered to use as a He-flowcryostat. The isotopically enriched samples were prepared from ^{32}S (>98% purity) and Cl_2 . The i.r. spectra were recorded on a Perkin-Elmer Model 325 spectrophotometer with an accuracy of $\pm 0.5 \text{ cm}^{-1}$. Most of the ^{32}S - ^{34}S isotopic shifts were determined with an accuracy of $\pm 0.05 \text{ cm}^{-1}$. The methods used for the normal coordinate analyses have previously been described [11].

RESULTS AND DISCUSSION

Infrared spectra

Infrared spectra were recorded of SF_4 in both Ar and Ne matrices at 4 K for SF_4 of natural sulfur isotope abundance, 1:1 mixtures of $^{32}\text{SF}_4$ and $^{34}\text{SF}_4$ and pure $^{32}\text{SF}_4$ using sample to matrix ratios of 1:1000. The observed frequencies and ^{32}S - ^{34}S isotopic shifts are summarized in Table 1.

In agreement with previous experience [6, 13, 15, 16], neon matrices produced the best spectra and exhibited frequencies closest to those of the gas phase values. Because accurate anharmonicity corrections were not possible, all observed isotopic shifts were corrected by a factor of 1.01, a

value close to those previously used for similar molecules [13, 16, 17]. The observed isotopic shifts are in fair agreement with the values previously reported [11] for some of these bands in an N_2 matrix.

For some of the bands, matrix splittings were observed. The use of ^{34}S enriched samples facilitated distinction between isotopic and matrix splittings. For the 353 cm^{-1} fundamental, the splitting observed in a N_2 matrix had previously been interpreted [11] in terms of a coincidence of the two fundamentals ν_1 and ν_9 . Although varying degrees of splitting were observed during the present study for the 353 cm^{-1} fundamental in Ar and Ne matrices (see Fig. 1), these splittings are identical for both $^{32}\text{SF}_4$ and $^{34}\text{SF}_4$. Since it appears unlikely that ν_1 and ν_9 should exhibit identical sulfur isotopic shifts, these splittings are attributed to matrix splittings of a single fundamental. This conclusion is supported by the normal coordinate analysis, given below, which shows that the large isotopic shift observed for the 532 cm^{-1} deformation mode can be explained only by assigning this frequency to ν_1 . Similar matrix splittings were observed and identified for several other bands and are denoted in Table 1.

Normal coordinate analysis and assignments

A listing of the nine fundamentals of SF_4 and their assignment in point group C_{2v} is given in Table 2, together with an approximate description of these modes. Based on the previous studies [1–12], the assignments for ν_1 , ν_2 and ν_3 in the A_1 block, ν_4 in the B_1 block, and ν_5 in the B_2 block are well established. The remaining four modes are all deformation modes. Assuming no coincidences, three fundamentals at 532, 475 and 353 cm^{-1} are available for assignment to these four modes. Based on relative intensity considerations and the fact that all three fundamentals are i.r. active, the missing fundamental should be the torsional mode ν_6 (A_2)

Table 1. Observed frequencies and ^{32}S - ^{34}S isotopic shifts (cm^{-1}) of SF_4 in Ar and Ne matrices

Ar Frequency	$\Delta\nu$	Ne Frequency	$\Delta\nu$	$\Delta\omega^*$	Gas-phase frequencies	Assignment
883.5	11.2 ± 0.1	887.2	11.22 ± 0.05	11.33	892	$\nu_1(A_1)$
858	10.4 ± 0.1	859.7	10.42 ± 0.05	10.52	867	$\nu_8(B_2)$
705†	12.7 ± 0.1	721†	13.00 ± 0.05	13.13	730	$\nu_6(B_1)$
550.5	0	557†	0	0	558	$\nu_2(A_1)$
529†	3.9 ± 0.2	530.1	4.05 ± 0.05	4.09	532	$\nu_3(A_1)$
354†	2.35 ± 0.1	352†	2.4 ± 0.1	2.42	353	$\nu_9(B_2)$

*Corrected for anharmonicity.

†These bands showed matrix splittings.

which is i.r. inactive. In similar molecules, this mode is generally of very low Raman intensity. Therefore, it would not be surprising that this mode has up to date not experimentally been observed for SF_4 .

The assignment of the 532, 475 and 353 cm^{-1} fundamentals was established in the following manner. The 353 cm^{-1} band has previously been assigned [5, 6, 8, 10, 11] to $\nu_9(B_2)$, and this assignment has recently been supported by microwave spectroscopy [1]. Since the ^{32}S - ^{34}S isotopic shifts of ν_8 and of the 353 cm^{-1} fundamental are now both known, a force field computation can be used to test the correctness of this assignment. If the assignment is correct, both observed isotopic shifts must result in an identical force field. As can be seen from Fig. 2, the isotopic shifts observed for the 867 and the 353 cm^{-1} fundamental result in the same force field, thus establishing the 353 cm^{-1} fundamental as $\nu_9(B_2)$.

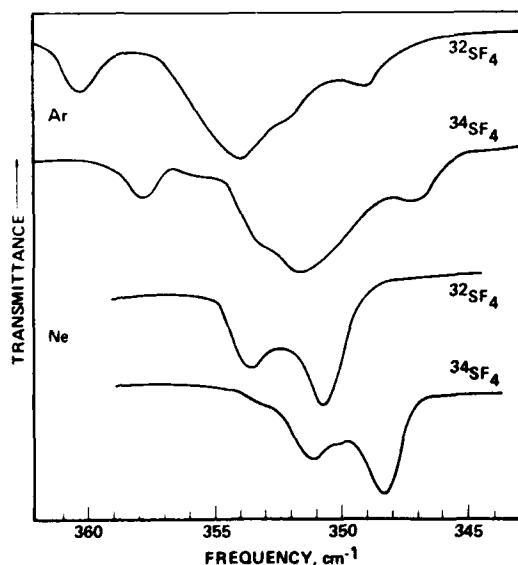


Fig. 1. Infrared spectra of $^{32}\text{SF}_4$ and $^{34}\text{SF}_4$ in argon and neon matrices. The observed splittings are attributed to matrix effects.

A distinction between the two possible assignments (532 and 475 cm^{-1}) for $\nu_3(B_1)$ can be made in a similar manner, since the sulfur isotopic shifts of $\nu_8(B_1)$ and of the 532 cm^{-1} deformation mode (4.05) cm^{-1} are known. From a computation of the B_1 force field (see Fig. 3) it becomes obvious that the sulfur isotopic shift of ν_3 has to be less than 1 cm^{-1} in order to agree with the force field obtained from the isotopic frequencies of ν_8 . Since the isotopic shift of 4.05 cm^{-1} observed for the 532 cm^{-1} band, is much too large for ν_3 , the 532 cm^{-1} fundamental must be $\nu_3(A_1)$ and the 475 cm^{-1} one must be $\nu_3(B_1)$. Additional support for this assignment was obtained from the computation of the A_1 block force field (See Table 3). No difficulty was encountered to duplicate the isotopic shifts observed for ν_1 , ν_2 and ν_4 .

The missing frequency of $\nu_5(A_2)$ was calculated to be 437 cm^{-1} assuming $F_{\text{eq}} = F_{\text{ax}}$. This assumption seemed most plausible because of the three possible f_{int} interaction constants, the one which involves two angles sharing a common equatorial fluorine ligand, i.e. f_{eq} , should have the largest value and because in F_{eq} and F_{ax} f_{int} has the same sign.

The assignments, thus obtained for SF_4 , are summarized in Table 1 and can now be considered as being well established. They are in good agreement with the previously published [3] i.r. gas-phase band contours and compare favorably with those [18] recently published for the closely related SF_4O molecule. Based on the results of this study on SF_4 ,

Table 2. Assignment of normal modes of SF_4

Species	Approximate description of mode	Frequency (cm^{-1})
$A_1 \nu_1$	ν sym XF_2 eq	892
ν_2	ν sym XF_2 ax	558
ν_3	δ sciss XF_2 eq and ax, sym comb	532
ν_4	δ sciss XF_2 ax and eq, asym comb	228
$A_2 \nu_5$	XF_2 twist	[437]*
$B_1 \nu_6$	ν asym XF_2 ax	730
ν_7	XF_2 eq wagging	475
$B_2 \nu_8$	ν asym XF_2 eq	867
ν_9	δ sciss XF_2 ax out of plane	353

*Value calculated from $F_{\text{eq}} = F_{\text{ax}}$.

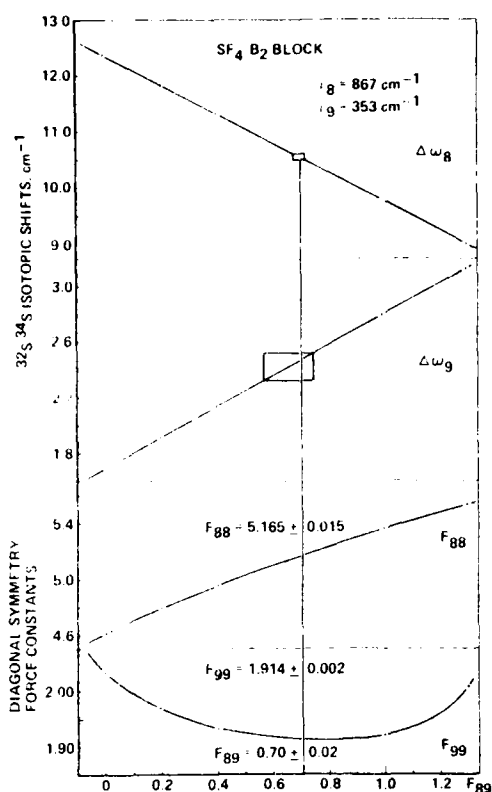


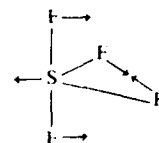
Fig. 2. Solution range of force constants and computed sulfur isotopic shifts for the B_2 block of SF_4 . The rectangles indicate the uncertainties of the observed anharmonicity corrected isotopic shifts and the vertical line the resulting general valence force field. The units are cm^{-1} for the isotopic shifts and $mdyn \text{ \AA}^{-1}$, $mdyn \text{ \AA} \text{ rad}^{-2}$ and $mdyn \text{ rad}^{-1}$ for F_{88} , F_{99} and F_{89} , respectively.

it becomes necessary, however, to exchange the assignments of ν_1 (A_1) and ν_2 (B_1) for SF_4O .

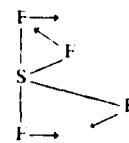
The force field of SF_4 is summarized in Table 3. The B_2 and B_1 block values represent a general valence force field. The A_1 block is still undetermined (ten symmetry force constants and seven frequency values), but is expected to be a good approximation to a general valence force field in view of the good agreement between the observed and calculated isotopic shifts. The off-diagonal symmetry force constants listed in Table 3 were required in order to be able to duplicate the observed sulfur isotopic shifts. The value of F_{34} is necessary to make $\Delta\nu_2$ close to zero. The relatively large isotopic shift of ν_1 can only be achieved by the use of an F_{11} value which concentrates the isotopic shifts of ν_1 and ν_2 almost exclusively in ν_1 and by the use of F_{11} and F_{14} which transfer some of the isotopic shift from ν_1 to ν_2 . Since ν_1 is an almost equal mixture of F_{11} and F_{14} (see PED of Table 3), the isotopic shift balance between ν_1 and ν_2 can be equally well achieved by either F_{11} or F_{14} , as long as their sum equals to about

$0.6 \text{ mdyn rad}^{-1}$. Therefore the chosen ratio between F_{11} and F_{14} is somewhat arbitrary, and their values were made about equal for cosmetic reasons.

The potential energy distribution (PED) is given in Table 3 and shows that all fundamentals are highly characteristic, with the exception of ν_1 and ν_2 . The latter are almost equal mixtures of F_{11} and F_{14} . As previously discussed in detail [10, 11] and shown by their eigenvectors (see Table 3), ν_1 is a symmetric and ν_2 is an antisymmetric combination of the symmetry coordinates S_1 and S_2 , i.e.



ν_1 , symmetric combination of axial and equatorial bending



ν_2 , antisymmetric combination of axial and equatorial bending

In view of these facts, a discussion is rather meaningless whether ν_1 or ν_2 is mainly axial or equatorial bending. Furthermore, it shows that ν_1 is

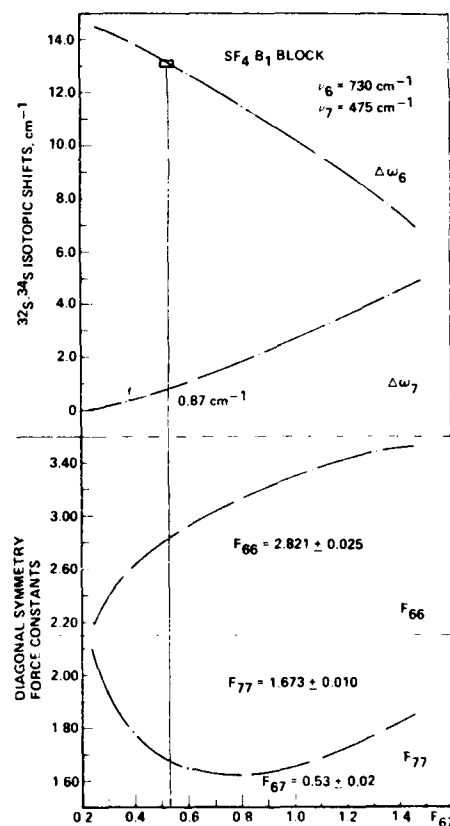


Fig. 3. Solution range of force constants and computed sulfur isotopic shifts for the B_1 block of SF_4 . For further explanations, see caption of Fig. 2.

Table 3. Force field*, computed and observed harmonic sulfur isotopic shifts†, potential energy distribution‡ and eigenvectors of SF₄

		$\Delta\omega$ comp		$\Delta\omega$ observed	PED	Eigenvectors			
						S ₁	S ₂	S ₃	S ₄
A ₁	F ₁₁ = f _r + f _{aa}	5.884	11.37	11.35 ± 0.05	95F ₁₁	0.275	0.014	0.124	0.194
	F ₂₂ = f _{rr} + f _{RR}	3.476	0.07	0	99F ₂₂	-0.010	0.229	0.014	-0.028
	F ₃₃ = 0.99 f _{rr} + 0.01 f _r - 0.15 f _{RR}	1.414	4.14	4.09 ± 0.05	30F ₃₃ + 29F ₄₄ + 26F ₅₅	0.045	0.018	0.187	0.238
	F ₄₄ = 0.004 f _{rr} + 0.71 f _r	0.863	0.08		91F ₁₁ + 89F ₄₄ - 80F ₅₅	0	0.005	0.141	-0.178
	+ 0.29 (f _{aa} + f _{aa} + f _{aa})								
	+ f _{aa}) + 0.13 f _{RR}								
	+ 1.80 f _{rr} + 0.11 f _{rr}								
	F ₁₃	0.320							
	F ₁₄	0.300							
	F ₂₃	0.100							
A ₂	F ₃₄ = f _{aa} - f _{aa} - f _{aa} + f _{aa}	1.673	0			S ₆	S ₇		
	F ₄₅ = f _{rr} - f _{RR}	2.821	13.14	13.13 ± 0.05	101F ₆₆ + 22F ₇₇ - 23F ₈₈	0.335	-0.203		
	F ₅₆ = f _{aa} + f _{aa} - f _{aa} - f _{aa}	1.673	0.87		84F ₃₃ + 10F ₄₄	0.050	0.259		
	F ₆₇ = √2(f _{rr} - f _{RR})	0.530				S ₈	S ₉		
	F ₈₈ = f _r - f _r	5.165	10.53	10.52 ± 0.05	105F ₈₈ - 9F ₉₉	0.297	-0.096		
	F ₉₉ = f _{aa} - f _{aa} + f _{aa} - f _{aa}	1.914	2.48	2.42 ± 0.1	101F ₉₉	-0.003	0.196		
	F ₉₀ = √2(f _{rr} - f _{RR})	0.700							
	f _r	5.525							
	f _{rr}	3.149							
	f _{RR}	0.360							
B ₁	F ₁₁	0.320							
	F ₁₄	0.300							
	F ₂₃	0.100							
	F ₃₄	0.4913							
	F ₄₅ = f _{aa} - f _{aa} - f _{aa} + f _{aa}	1.673	0			S ₆	S ₇		
	F ₄₆ = f _{rr} - f _{RR}	2.821	13.14	13.13 ± 0.05	101F ₆₆ + 22F ₇₇ - 23F ₈₈	0.335	-0.203		
	F ₅₆ = f _{aa} + f _{aa} - f _{aa} - f _{aa}	1.673	0.87		84F ₃₃ + 10F ₄₄	0.050	0.259		
	F ₆₇ = √2(f _{rr} - f _{RR})	0.530				S ₈	S ₉		
	F ₈₈ = f _r - f _r	5.165	10.53	10.52 ± 0.05	105F ₈₈ - 9F ₉₉	0.297	-0.096		
	F ₉₉ = f _{aa} - f _{aa} + f _{aa} - f _{aa}	1.914	2.48	2.42 ± 0.1	101F ₉₉	-0.003	0.196		
B ₂	F ₉₀ = √2(f _{rr} - f _{RR})	0.700							
	f _r	5.525							
	f _{rr}	3.149							
	f _{RR}	0.360							
	f _{RR}	0.328							

*Stretching constants in mdyn Å⁻¹, deformation constants in mdyn Å rad⁻², and stretch-bend interaction constants in mdyn rad⁻¹. For the force field computation, the frequency values of Table 2 were used and fitted to within 0.1 cm⁻¹.

†In cm⁻¹.

‡Per cent contributions. Contributions of less than 10% to the PED are not listed.

the fundamental mainly involved in an intramolecular exchange process as suggested by BERRY [19].

Additional experimental data which could be used as a constraint for the SF₄ assignment and force field, are centrifugal distortion constants [12] and mean amplitudes of vibration [20]. Since the observed centrifugal distortion constants "are not well determined" and have been shown [12] to be insensitive towards changes in the assignment of the deformation modes, they are not a useful constraint. Mean amplitudes of vibration have previously been reported [10] for SF₄ using five different assignments and force fields. These data showed that only $\langle q^2 \rangle^{1/2}$ F₁...F₄ and $\langle q^2 \rangle^{1/2}$ F₁...F₅ are sufficiently sensitive to variation of the assignment of the deformation modes in question. As can be seen from Table 4, the revised force field given in Table 3 results in mean amplitudes of vibration which are in excellent agreement with the observed

values, thus lending additional support to our assignment. It should be pointed out that both the centrifugal distortion constants and the mean amplitudes of vibration, although useful for the detection of gross errors in the assignments, are not sensitive enough to be useful constraints for the force field of SF₄.

Acknowledgements—One of us (KOC) is indebted to DR E. C. CURTIS for the use of his computer programs and helpful discussions and to the Office of Naval Research for financial support.

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Table 4. Computed* (298 K) and observed [20] mean amplitudes (in Å) of vibration of SF₄

S-F _{eq}	0.041	0.041 ± 0.005
S-F _{ax}	0.048	0.047 ± 0.005
F _{eq} -F _{eq}	0.073	0.068 ± 0.010
F _{eq} -F _{ax}	0.069	0.067 ± 0.005
F _{ax} -F _{ax}	0.061	0.059 ± 0.010

*Using the force field of Table 3.

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APPENDIX F

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83

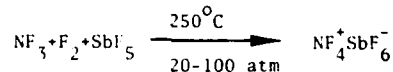
SHORT COMMUNICATION

Simplified Synthesis of $\text{NF}_4^+\text{SbF}_6^-$

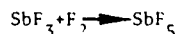
WILLIAM W. WILSON AND KARL O. CHRISTE*

Rocketdyne Division of Rockwell International, Canoga Park, Calif. 91304, (USA)

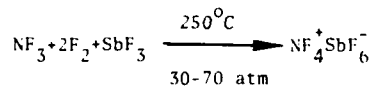
In NF_4^+ chemistry, the $\text{NF}_4^+\text{SbF}_6^-$ salt plays a key role. It is most amenable to large scale production and serves as a starting material for the metathetical syntheses of numerous other NF_4^+ salts [1 - 4]. The most convenient previously reported [5] method involved the reaction of SbF_5 with an excess of NF_3 and F_2 at elevated temperature and pressure according to:



In view of its appreciable cost and its detrimental physical and chemical properties, it was desirable to replace SbF_5 by a starting material which is cheaper, more readily available and easier to handle. Since it is well known [6] that, under conditions similar to those of the above $\text{NF}_4^+\text{SbF}_6^-$ synthesis, SbF_3 can be fluorinated by F_2 to SbF_5 ,



a direct synthesis of $\text{NF}_4^+\text{SbF}_6^-$ from SbF_3 , F_2 and NF_3 was logical. The possible combination of the two steps was experimentally verified, as shown by the following equation:



Although no efforts were made to maximize all the reaction parameters, the high yield and purity of the thus obtained $\text{NF}_4^+\text{SbF}_6^-$ demonstrates the feasibility of this simplified synthesis.

EXPERIMENTAL

A prepassivated (with ClF_3) 95 ml monel cylinder was loaded in the dry nitrogen atmosphere of a glove box with SbF_3 (31 mmol). The cylinder was connected to a metal vacuum system, evacuated, and charged at -196°C with NF_3 (65 mmol) and F_2 (98 mmol). The cylinder was heated for five days to 250°C . The excess of unreacted NF_3 and F_2 was pumped off at ambient temperature, leaving behind a white crystalline residue (10 g, weight expected for 31 mmol of $\text{NF}_4\text{SbF}_6 = 10.1 \text{ g}$). Based on its infrared and Raman spectra and its chemical analysis, this solid consisted of high purity $\text{NF}_4^+\text{SbF}_6^-$. It did not contain any detectable amounts of polyantimonate [7] salts.

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

Synthesis and Properties of $\text{NF}_4^+\text{ClO}_4^-$ and $\text{NF}_4^+\text{HF}_2 \cdot n\text{HF}$ and Some Reaction Chemistry of NF_4^+ Salts

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The possibility of synthesizing $\text{NF}_4^+\text{XO}_4^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) salts by metathesis between NF_4SbF_6 and CsXO_4 in anhydrous HF solution at -78°C was studied. Of these NF_4XO_4 salts, NF_4ClO_4 was isolated and characterized by vibrational and ^{19}F NMR spectroscopy. It is an unstable white solid decomposing at 25°C to give NF_3 and FOClO_3 in high yield. The NF_4BrO_4 salt is of marginal stability in HF solution and decomposes to NF_3 , O_2 , and FBrO_2 . Attempts to isolate NF_4IO_4 as a solid resulted in explosions. The NF_4IO_4 salt could not be prepared due to the facile fluorination of IO_4^- to IF_4O_2 by either HF or BrF_3 . Attempts to prepare $\text{NF}_4^+\text{XF}_6^-$ ($\text{X} = \text{Cl}, \text{Br}$) salts by metathesis between NF_4SbF_6 and CsXF_6 in BrF_3 solution at 25°C were unsuccessful; with BrF_3 , fluoride abstraction occurred, resulting in the formation of NF_3 , F_2 , and BrF_2O , whereas CsClF_6 underwent a displacement reaction with BrF_3 to give CsBrF_6 and ClF_3O . The metathetical synthesis of NF_4NO_3 could not be studied in HF due to the reaction of NO_3^- with HF to give NO_2^+ , H_2O , and HF_2^- . The metathesis between NF_4SbF_6 and CsF in HF at -78°C did not produce NF_4^+F^- but produced an unstable white solid of the composition $\text{NF}_4^+\text{HF}_2 \cdot n\text{HF}$. The composition, thermal stability, spectroscopic properties, and decomposition products of this solid were studied. The NF_4^+HF_2 salt is stable in HF solution at 25°C , and the synthetic usefulness of these solutions for the synthesis of other NF_4^+ salts is briefly discussed. Attempts to prepare NCl_4^+ and NCl_2O^+ salts by F-Cl exchange between BCl_3 and NF_4^+ and NF_2O^+ were unsuccessful.

Introduction

The first report on the successful syntheses of NF_4^+ salts were published^{1,2} in 1966. Since then, numerous NF_4^+ salts have been prepared and characterized which contain as counterions BF_4^- ,³⁻¹⁰ XF_6^- ($\text{X} = \text{Ge}, \text{Ti}, \text{Sn}$), XF_6^- ¹⁰⁻¹² ($\text{X} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$),^{1,2,7,8,10,13,14-18} or XF_6^{2-} ($\text{X} = \text{Ge}, \text{Sn}, \text{Ti}, \text{Ni}$).^{10-12,19} All these anions are derived from strong perfluorinated Lewis acids. It was therefore interesting to investigate the possible synthesis of salts derived from either the simplest anion F^- or oxygen containing anions. Although in 1968 Tolberg and co-workers found evidence for the existence of unstable NF_4^+ salts probably containing the HF_2^- or the ClO_4^- anion,⁴ these salts were not well characterized, and no data were published. In this paper, we describe the synthesis and characterization of $\text{NF}_4^+\text{HF}_2 \cdot n\text{HF}$ and $\text{NF}_4^+\text{ClO}_4^-$ and the attempted syntheses of $\text{NF}_4^+\text{BrO}_4^-$, $\text{NF}_4^+\text{BrF}_2\text{O}$, NF_4^+ ,

ClF_4O , and $\text{NF}_4^+\text{NO}_3^-$. Since the existence of a stable $\text{NOCl}_2^+\text{SbCl}_6^-$ salt has recently been reported,²⁰ it appeared interesting to study the possibility of exchanging chlorine for fluorine in either NF_4^+ or NF_2O^+ salts by using BCl_3 .

Experimental Section

Materials. Literature methods were used for the syntheses of NF_4SbF_6 ,⁷ NF_2OSbF_6 ,²¹ CsClF_6 ,²² and CsBrF_6 .²³ The BrF_3 (Matheson) was treated with 35 atm of F_2 at 200°C for 24 h and then purified by fractional condensation through traps kept at -64 and -95°C , with the material retained in the latter being used. Hydrogen fluoride (Matheson) was dried by treatment with 20 atm of F_2 at room temperature, followed by storage over BiF_3 to remove the last traces of H_2O .¹⁸ The CsF (American Potash) was fused in a platinum crucible and ground in the drybox. The CsClO_4 (ROC/RIC) was used as received. The CsNO_3 was prepared from aqueous Cs_2CO_3 and HNO_3 by using a pH electrode for end point detection. It was purified by recrystallization from H_2O and dried in an oven at 100°C for 24 h. The BCl_3 (Matheson) was treated with Hg and purified by fractional condensation prior to use.

Apparatus. Volatile materials used in this work were handled either in a Monel Teflon FEP, a stainless steel Teflon FEP, or a Teflon PFA vacuum line. The latter was constructed exclusively from injection-molded PFA fittings and valves (Fluoroware, Inc.). The anhydrous HF was preferentially handled in the PFA or Monel line, whereas the halogen fluorides were handled mainly in a steel line. All lines 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 either HF or BrF_3 solution by using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter (see Figure 1 of ref 12). For NMR or low-temperature vibrational spectra, the second FEP U-trap, which served as a receiver, was replaced by either a 4-mm Teflon FEP or thin-walled Kel-F tube.

Infrared spectra were recorded in the range $4000\text{--}200\text{ cm}^{-1}$ on a Perkin-Elmer Model 283 spectrophotometer. Room-temperature spectra of solids were obtained by using dry powders pressed between AgCl disks. Low-temperature spectra were obtained by placing the chilled powder between cold AgCl disks and striking the disks with a hammer. The resulting AgCl sandwich was held in a liquid N_2 cooled

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sample holder of a low-temperature infrared cell²⁴ with external CsI windows. Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter²⁵ for the elimination of plasma lines. Sealed quartz, Teflon FEP, or Kel-tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded by using a previously described²⁶ device. Polarization measurements were carried out according to method VIII listed by Claassen et al.²⁵ Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external CFCl_3 .

Preparation and Properties of $\text{NF}_4^+\text{ClO}_4^-$. The compatibility of the ClO_4^- anion with HF was established by dissolving CsClO_4 in HF and recording the Raman spectra of the solution and of the solid residue recovered after removal of the solvent. Both spectra showed exclusively the bands characteristic for ClO_4^- . In a typical preparation of $\text{NF}_4^+\text{ClO}_4^-$, NF_4SbF_6 (10.03 mmol) and CsClO_4 (10.02 mmol) were placed into the $3/4$ -in. o.d. Teflon FEP bottom U-trap of the metathesis apparatus. Anhydrous HF (8.56 g) was added at -196°C . The mixture was kept at -78°C for 15 h and then for 2 h at -45°C with agitation. The entire metathesis apparatus was cooled to -78°C and inverted to separate the CsSbF_6 precipitate from the $\text{NF}_4^+\text{ClO}_4^-$ solution. Dry N_2 (2 atm) was used to pressurize the solution during this filtration step. The HF solvent was pumped off at -78 and 45°C for 7 days. The resulting white solid residue was allowed to warm to ambient temperature, and the gaseous decomposition products were separated in a dynamic vacuum by fractional condensation through a series of traps kept at -112 , -186 , and -210°C . The -210°C trap contained 8.0 mmol of NF_3 and the -186°C trap had 8.0 mmol of FOClO_3 which were identified by infrared, Raman, and ^{19}F NMR spectroscopy.²⁷ The filter cake (3.60 g, weight calculated for 10 mmol of CsSbF_6 , 3.69 g) was shown by infrared and Raman spectroscopy to be CsSbF_6 and did not contain any detectable impurities. A small amount (80 mg) of a white stable solid residue was left behind after the thermal decomposition of the $\text{NF}_4^+\text{ClO}_4^-$ which, on the basis of its vibrational spectra, consisted of a mixture of NF_4SbF_6 and CsSbF_6 . The 20% of $\text{NF}_4^+\text{ClO}_4^-$ unaccounted for by the above material balance corresponds to the amount of product in the mother liquor typically retained by the CsSbF_6 filter cake in similar metathetical reactions. It is decomposed and pumped off during the HF removal step in which the filter cake is allowed to warm to ambient temperature. On the basis of the above material balance, the $\text{NF}_4^+\text{ClO}_4^-$ prepared in this manner had a purity of 95 wt %.

For the spectroscopic identification of $\text{NF}_4^+\text{ClO}_4^-$ and the determination of its thermal stability, reactions were carried out on a 1–2-mmol scale by using 4-mm o.d. Teflon FEP NMR or thin-walled Kel-F tubes as receivers. The ^{19}F NMR spectrum of an $\text{NF}_4^+\text{ClO}_4^-$ solution in anhydrous HF at 40°C showed the signals characteristic of NF_4^+ (triplet of equal intensity at $\phi = 214.8$ with $J_{\text{NF}} = 229.3$ Hz and a line width of less than 3 Hz),¹⁰ FOClO_3 (singlet at $\phi = 219.4$),²⁷ and NF_3 (broad triplet of equal intensity at $\phi = 142$ with $J_{\text{NF}} = 150$ Hz).^{28,29} When the solution was kept at 20°C and continuously monitored by NMR, the signal due to NF_4^+ was found to steadily decrease, and those due to FOClO_3 and NF_3 were found to correspondingly increase in relative intensity. A solution containing 40 mol % of NF_4^+ and 60 mol % FOClO_3 was found to change within 16 h at 20°C to 17 mol % of NF_4^+ and 83 mol % of FOClO_3 . The decomposition of $\text{NF}_4^+\text{ClO}_4^-$ in HF solution at ambient temperature was also followed by Raman spectroscopy which showed the bands due to FOClO_3 ²⁷ to grow with time at the expense of those due to NF_4^+ and ClO_4^- . Due to its low boiling point and low solubility in HF, NF_3 could not be detected in the HF solution by Raman spectroscopy.

The thermal stability of solid $\text{NF}_4^+\text{ClO}_4^-$ was studied by pumping on a sample at a given temperature for 1 h and measuring the amount of NF_3 and FOClO_3 evolved. Whereas at 13°C $\text{NF}_4^+\text{ClO}_4^-$ essentially is still stable, slow decomposition was observed at 0°C which became rather rapid at 25°C , giving the sample the appearance of a fluidized sand bath. **Caution!** Since the thermal decomposition of $\text{NF}_4^+\text{ClO}_4^-$ yields the very shock-sensitive³⁰ FOClO_3 in high yield, one should take appropriate safety precautions when working with this compound.

Reaction of NF_4SbF_6 with CsBrO_4 . The compatibility of CsBrO_4 with HF was established in the same manner as described above for CsClO_4 . The solubility of CsBrO_4 in HF at 25°C was in excess of 1 g/g of HF. For the metathetical reaction, NF_4SbF_6 and CsBrO_4 (1.0 mmol each) in HF (2 mL) were stirred at 20°C for 1.5 h, then half of the solvent was pumped off, and the mixture was cooled to -78°C and filtered at this temperature into a Teflon FEP NMR tube. The NMR tube was sealed off, and the filter cake was pumped to dryness and shown by vibrational spectroscopy to consist of CsSbF_6 . The Raman spectrum of the solution, which showed signs of gas evolution (O_2), exhibited the bands characteristic for NF_4^+ , BrO_4^- ,³¹ and FBrO_2 ³² with the intensity of the FBrO_2 bands growing with time at the expense of those of NF_4^+ and BrO_4^- . The ^{19}F NMR spectrum showed resonances characteristic of NF_4^+ (sharp triplet of equal intensity at $\phi = 217$ with $J_{\text{NF}} = 227$ Hz) and NF_3 (broad triplet of equal intensity at $\phi = 143$ with $J_{\text{NF}} = 150$ Hz) and a broad line at $\phi = 186$ attributed to HF ($\phi = 196$) undergoing rapid exchange with FBrO_2 ($\phi = 205$).³³ **Caution!** Explosions occurred when attempts were made to isolate solid NF_4BrO_4 from an HF solution which had never been warmed above -78°C .

Reaction of CsNO_3 with HF. Cesium nitrate was dissolved in anhydrous HF. The Raman spectrum of the solution did not show the bands characteristic of NO_3^- but did show only one band at 1411 cm^{-1} which is characteristic³⁴ for NO_3^+ . The solid residue obtained by pumping the solution to dryness was shown by Raman spectroscopy to consist again of CsNO_3 .

Reaction of NF_4SbF_6 with CsBrF_4O in BrF_3 . In a drybox a mixture of NF_4SbF_6 (0.536 mmol) and CsBrF_4O (0.449 mmol) was placed into a $3/4$ -in. o.d. Teflon FEP ampule, and BrF_3 (4 mL, liquid) was added at -196°C by using the vacuum line. The contents of the ampule were warmed to 20°C and stirred with a magnetic stirring bar for 2.5 h. The ampule was cooled to -196°C , and the noncondensable material (0.42 mmol of F_2) was distilled off. The material volatile at -95°C was distilled off and consisted of 0.48 mmol of NF_3 . The material volatile at 20°C was separated by fractional condensation through a series of traps kept at -64 , -78 , and -196°C . The -64°C trap contained BrF_3O (0.43 mmol), in addition to some BrF_3 . The two colder traps contained the bulk of the BrF_3 . The solid nonvolatile reaction product (205 mg, weight calculated for 0.449 mmol CsSbF_6 and 0.087 mmol NF_4SbF_6 , 194 mg) was shown by vibrational spectroscopy to consist mainly of CsSbF_6 containing some NF_4SbF_6 .

Reaction of CsClF_4O with BrF_3 . In a sapphire reactor, CsClF_4O (1.234 mmol) and BrF_3 (15 mmol) were combined at -196°C . The mixture was kept at 20°C for 12 h. The volatile products were distilled off and consisted of BrF_3 and ClF_3O (1.2 mmol). The solid residue (405 mg, weight calculated for 1.234 mmol of CsBrF_6 , 403 mg) was shown by vibrational spectroscopy to consist of CsBrF_6 .³⁵

Preparation and Properties of $\text{NF}_4^+\text{HF}_2^-$ in HF. In a typical experiment, NF_4SbF_6 and CsF (10.0 mmol each) were placed into the metathesis apparatus and HF (10 mL) was added at -196°C . The mixture was stirred at 20°C for 2 h, then cooled to -78°C , and filtered. Most of the HF solvent was removed by pumping at -78°C for 36 h, 64°C for 12 h, 57°C for 6 h, and 45°C for 6 h. At 45°C the residue was still liquid but, when cooled to -78°C , changed its appearance to that of a wet solid. The pumped-off material consisted of HF. The sample was allowed to warm to ambient temperature, and the evolved volatile material was pumped off through traps kept at 126 and 210°C . The amounts and mole ratios of HF (126°C trap) and NF_3 (210°C trap) were periodically

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measured while the sample was cooled back to -45°C . Several hours of warming to ambient temperature and to 40°C was required to achieve complete decomposition of the salt. A total of 8.32 mmol of NF_3 and 19.63 mmol of HF was collected with the $\text{HF}:\text{NF}_3$ mole ratio ranging from 10.1 at the start to 1.54 toward the end of the decomposition. A small amount (80 mg) of a stable white solid residue was left behind after completion of the decomposition which consisted mainly of NF_4SbF_6 and some CsSbF_6 . The filter cake (3.5 g, weight calculated for 10.0 mmol of CsSbF_6 , 3.687 g) consisted of CsSbF_6 . The 15% of the NF_4^+ value unaccounted for by the above material balance is in line with the amount of material in the mother liquor generally retained by the CsSbF_6 filter cake in similar reactions (see NF_4ClO_4 preparation). On the basis of the above material balance, the purity of $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$ obtained in this manner is about 97 mol % with the CsSbF_6 and NF_4SbF_6 impurities being caused by the slight solubility of CsSbF_6 in HF and a small excess of one reagent. During the above-described ambient-temperature decomposition of $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$, the originally liquid sample first turned milky and pasty and then after being recooled to -45°C had the appearance of a white dry solid which melted very slowly when warmed again to 20°C . On melting, it started to bubble and foam.

For the determination of the spectroscopic properties, metathetical reactions were carried out as described above but on a 1-mmol scale. The ^{19}F NMR spectrum of the compound in HF solution showed the signal (triplet of equal intensity at $\delta = 216.2$ with $J_{\text{NF}} = 230\text{ Hz}$ and a line width of less than 3 Hz) characteristic^{13,14} of NF_4^+ and a broad line at $\delta 195$ due to rapidly exchanging HF and HF_2 . The solution appeared to be stable at ambient temperature, and no formation of the NF_3 decomposition product was detectable by NMR.

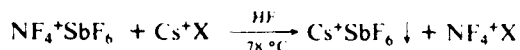
Raman spectra were recorded for the HF solutions at different concentration stages. In all cases, only the characteristic NF_4^+ bands at 1170, 859, 617, and 448 cm^{-1} were observed. For the most dilute solution also a very broad solvent band centered at about 3300 cm^{-1} was observed. After removal of most of the solvent at -57°C , the solvent band had disappeared. When this sample was frozen at -110°C , numerous intense bands in the $1400\text{--}1700\text{--}$ and the $650\text{--}850\text{--cm}^{-1}$ region appeared. However, on further removal of HF , the spectrum of the solid at -110°C showed again only bands due to NF_4^+ .

Reactions of NF_4SbF_6 and NF_4OSbF_6 with BCl_3 . A sample of NF_4SbF_6 (1.85 mmol) was treated in a Teflon FEP ampule with a 10-fold excess of BCl_3 for 3 h at 20°C . The volatile products were separated by fractional condensation and shown to consist of NF_3 and mixed BF_2Cl_2 α -type compounds. A small amount of solid residue (60 mg) was identified by vibrational spectroscopy as $\text{NO}^+\text{SbCl}_6^-$.

A sample of NF_4OSbF_6 was similarly treated with BCl_3 . The volatile products consisted again of mixed BF_2Cl_2 α -type compounds, but $\text{NO}^+\text{SbF}_6^-$ was formed in almost quantitative yield as a nonvolatile residue.

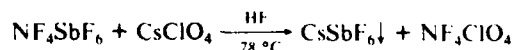
Results and Discussion

The general usefulness of the metathetical reaction



for the syntheses of otherwise inaccessible NF_4^+X^- salts has previously been demonstrated^{7,11,12,18,19} for a number of perfluorinated anions. In this study this approach was extended to oxygen-containing anions, such as the perchlorates and tetrafluorohalates.

Synthesis and Properties of NF_4ClO_4 . The ClO_4^- anion was found to be stable in HF solution. Therefore, NF_4ClO_4 was prepared according to



The reaction must be carried out at low temperature since, even in HF solution, NF_4ClO_4 undergoes decomposition at room temperature. The NF_4ClO_4 salt can be isolated as a white solid, stable up to about -13°C . At 0 and 25°C , respectively, slow and rapid decompositions of the solid were observed according to



In HF solution the rate of decomposition is slower but follows

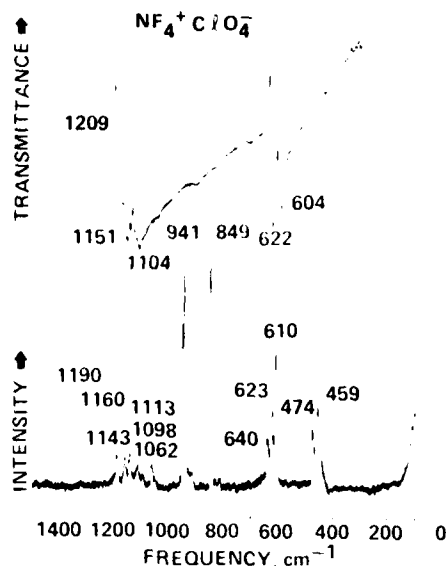


Figure 1. Low-temperature vibrational spectra of solid $\text{NF}_4^+\text{ClO}_4^-$. The infrared spectrum was recorded as a dry powder between AgCl disks at -196°C . The broken line indicates absorption due to the AgCl window material. The Raman spectrum was recorded at -110°C with a spectral slit width of 6 cm^{-1} .

Table I. Vibrational Spectra of Solid NF_4ClO_4

obsd freq, cm^{-1} , and rel intens ^a		assign (point group)	
IR	Raman	$\text{NF}_4^+ (T_d)$	$\text{ClO}_4^- (T_d)$
1209 w		$2\nu_4 (A_1 + E + F_2)$	
1151 s	1190 (1.3)	$\nu_3 (F_2)$	$\nu_3 (F_2)$
	1160 (1)		
	1143 (1.2)		
1104 vs	1113 (0.8)	$\nu_1 (F_2)$	$\nu_1 (F_2)$
	1098 (0.3)		
	1062 (1)		
	950 (6)	$\nu_1 (A_1)$	$\nu_1 (A_1)$
	941 (10)		
	849 (10)		
	640 (2)	$\nu_4 (F_2)$	$\nu_4 (F_2)$
622 s	623 (3)		
604 s	610 (6)		
	474 (2.5)	$\nu_2 (E)$	$\nu_2 (E)$
	459 (3.5)		

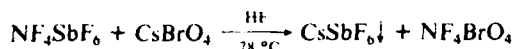
^a Uncorrected Raman intensities.

the same path. The essentially quantitative formation of FOClO_3 is noteworthy and represents a new and convenient synthesis of FOClO_3 . On the basis of the observed material balance, the yield of NF_4ClO_4 is high, and the only significant loss of material is due to the amount of mother liquor retained by the CsSbF_6 filter cake. The purity of the NF_4ClO_4 product is also high, and the impurities present are CsSbF_6 , in an amount corresponding to its solubility in HF at -78°C , and any slight excess of starting material used in the reaction.

The ionic composition of NF_4ClO_4 , in both HF solution and the solid state, was established by vibrational and ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of $\text{NF}_4^+\text{ClO}_4^-$ in HF solution showed the signal characteristic^{13,14} for tetrahedral NF_4^+ . The Raman spectra (cm^{-1}) of this solution confirmed the presence of tetrahedral NF_4^+ (1170 (w, br), 855 (vs, p), 612 (m), 448 (mw))¹⁰ and ClO_4^- (940 (s, p), 620 (w), 460 (w)).¹⁴ The infrared and Raman spectra of solid $\text{NF}_4^+\text{ClO}_4^-$ are given in Figure 1. The observed frequencies and their assignments in point group T_d are summarized in Table I. As expected for a solid, splittings of bands into their degenerate

components and crystal splittings are observed. In addition $\nu_1(\text{A}_1)$ and $\nu_2(\text{E})$ which ideally are infrared inactive were observed in the infrared spectrum as extremely weak bands. The pronounced Christiansen effect³⁶ observed for the infrared spectrum is due to the experimental difficulties in obtaining good pressing of AgCl windows at low temperature. The pressing was achieved by striking the sample sandwiched between the AgCl plates with a hammer. The sample did not detonate under these conditions, indicating that NF_4ClO_4 is considerably less sensitive than its decomposition product FOClO_3 .³⁰

Reaction of NF_4SbF_6 with CsBrO_4 . The BrO_4^- anion was found to be stable in HF solution, thus allowing the metathetical reaction

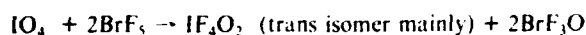
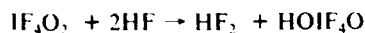
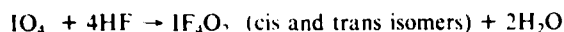


to be carried out. The presence of tetrahedral NF_4^+ ^{10,13,14} and BrO_4^- ³¹ in the resulting HF solution was demonstrated by ¹⁹F NMR and Raman spectroscopy. By analogy with NF_4ClO_4 , slow decomposition of the NF_4BrO_4 solution occurred at room temperature. However, instead of the yet unknown FOBrO_3 , only its expected³⁷ decomposition products, FBrO_2 and O_2 , were obtained in addition to NF_3 .



Attempts to isolate solid NF_4BrO_4 from an HF solution, which had never been warmed above -78°C , were unsuccessful due to a sharp detonation of the sample with flashing. Whether this was caused by NF_4BrO_4 itself or by possibly the presence of some FOBrO_3 could not be established.

The metathetical synthesis of NF_4IO_4 was not possible due to the fact that IO_4^- interacts with either HF ^{27,38} or BrF_5 ²⁷ according to

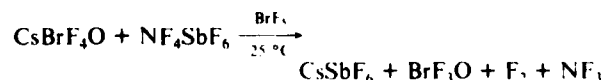


The metathesis between CsIF_4O_2 and NF_4SbF_6 in HF, followed by the thermal decomposition of the metathesis product, produces the novel compounds *cis*- and *trans*- OIF_4OF and will be reported in a separate paper.

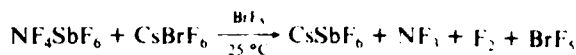
Reaction of NF_4SbF_6 with CsBrF_4O . Although CsBrF_4O reacts with HF ³⁹ according to



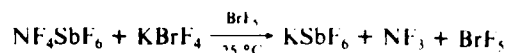
BrF_5 does not interact with CsBrF_4O ²³ and therefore is a suitable solvent for studying the reaction of NF_4SbF_6 with CsBrF_4O . The following reaction was observed:



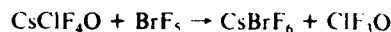
The formation of these products indicates that the salt $\text{NF}_4^+\text{BrF}_4\text{O}^-$ is not stable under these conditions and that, contrary to the $\text{NF}_4^+\text{ClO}_4^-$ and $\text{NF}_4^+\text{IF}_4\text{O}_2^-$ reactions, fluoride abstraction from BrF_4O^- is preferred over the fluorination of BrF_4O^- to either BrF_3OF or BrF_3O . A similar fluoride abstraction has previously been observed⁴ for BrF_6 .



but not for BrF_4 which was fluorinated⁴ to BrF_5 .



The corresponding metathesis between CsClF_4O and NF_4SbF_6 was not studied because it was found that CsClF_4O reacts with BrF_5 according to



The formed CsBrF_6 would be capable of undergoing with NF_4SbF_6 the above-given fluoride abstraction reaction.

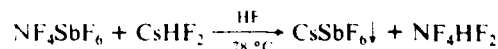
Reaction of CsNO_3 with HF. The compatibility of CsNO_3 with HF was studied in order to explore the feasibility of synthesizing NF_4NO_3 . Although CsNO_3 is quite soluble in HF and can be recovered as such from HF solutions, Raman spectra of these solutions showed the absence of NO_3^- and the presence of NO_2^+ as the only nitrogen-oxygen-containing species. These results imply an equilibrium, such as



which has previously been postulated⁴⁰ for these solutions. In view of the absence of NO_3^- in the HF solution, no metathetical reactions between CsNO_3 and NF_4SbF_6 were attempted.

Preparation and Properties of $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$. The NF_4^+F^- salt, which has an active fluorine content in excess of 90 wt %, would be of extreme interest. However, previous attempts to prepare a stable salt from NF_3 and F_2 at -196°C by either bremsstrahlung³ or UV photolysis¹⁰ were unsuccessful, indicating that the salt is unstable with regard to its decomposition to NF_3 and F_2 . Since most of the metathetical reactions for the production of NF_4^+ salts are carried out in anhydrous HF, which is an acid, it was of interest to define the nature and stability of a possible $\text{NF}_4^+\text{HF}_2^-$ salt. A previous unpublished study⁴ of the $\text{LiF-NF}_4\text{SbF}_6$ system in HF at ambient temperature had provided evidence that after removal of the precipitated LiSbF_6 a stable solution containing the NF_4^+ cation was obtained. All attempts to isolate a salt at temperatures of -44°C and above from this solution resulted in decomposition to NF_3 , F_2 , and HF. Removal of the solvent at -78°C resulted in a wet solid which was not characterized.

Since our previous studies¹⁸ had shown that a low-temperature metathesis using a cesium salt is superior to a lithium salt based process, the following system was studied:



On the basis of the observed material balance, the soluble product consisted of about 97 mol % NF_4HF_2 with the remainder being CsSbF_6 and excess of either starting material. In agreement with the previous observation,⁴ NF_4HF_2 is stable in HF solution at ambient temperature and shows in the ¹⁹F NMR spectrum the characteristic^{13,14} NF_4^+ signal. The presence of the NF_4^+ cation and the virtual absence of anions other than those due to solvated F^- was also demonstrated by Raman spectroscopy of solutions at different concentrations. As shown by trace A of Figure 2, these solutions exhibited only the four bands characteristic¹⁰ of tetrahedral NF_4^+ . The difficulty in observing bands due to solvated HF_2^- is not surprising in view of HF being a weak scatterer and the ex-

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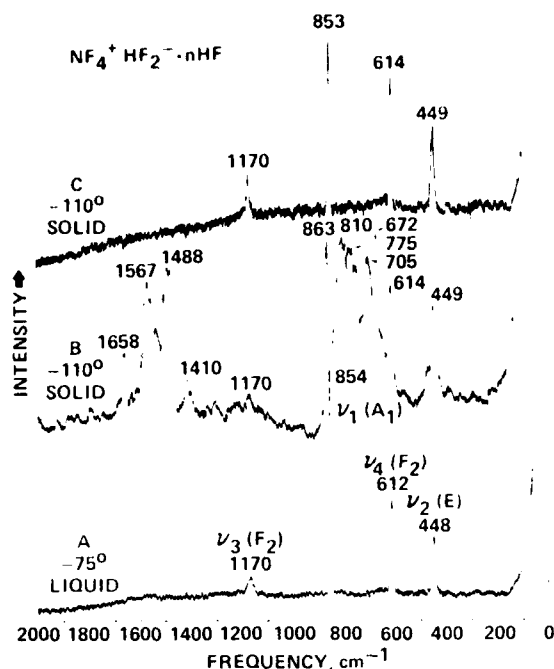
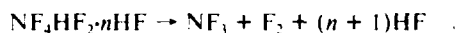


Figure 2. Raman spectra of liquid and solid $\text{NF}_4^+\text{HF}_2^-\cdot n\text{HF}$ in a Kel-F capillary: trace A, spectrum of a concentrated HF solution at -75°C (the given assignments are for tetrahedral NF_4^+); trace B, spectrum for the trace A sample cooled to -110°C (in addition to the NF_4^+ bands, the spectrum shows bands attributed to $\text{HF}_2^-\cdot n\text{HF}$); trace C, spectrum of the solid at -110°C containing only a small excess of HF. The sample of trace B was used after pumping off most of the HF and decomposing most of the sample at about -20°C . All spectra were recorded with a spectral slit width of 8 cm^{-1} .

pected broadness of the lines of HF_2^- undergoing rapid exchange with the solvent HF.

Most of the solvent can be removed by pumping at -45°C . The resulting residue is a clear liquid at -45°C but solidifies at -78°C to give the appearance of a wet solid. The composition of this residue was determined by studying its exhaustive dissociation at 25°C according to



It was found that the mole ratio of $\text{NF}_3:\text{HF}$ was about 10:1 at the beginning and 1.54 toward the end of this decomposition. These results demonstrate that complete removal of solvated HF from NF_4HF_2 is extremely difficult and is accompanied by decomposition of most of the NF_4^+ salt itself. The presence

of a solvated $\text{HF}_2^-\cdot n\text{HF}$ anion was also demonstrated by Raman spectroscopy (see trace B of Figure 2) which shows the presence of broad complex bands in the vicinity of the symmetric (600 cm^{-1}) and the antisymmetric (1455 cm^{-1}) stretching modes³⁴ of HF_2^- . Upon removal of most of the solvated HF, these bands lost intensity, resulting in a spectrum consisting exclusively of the NF_4^+ bands (see trace C of Figure 2).

It is also noteworthy that with decreasing HF content the melting point of $\text{NF}_4^+\text{HF}_2^-\cdot n\text{HF}$ increases and approaches room temperature for n approaching zero. The decomposition of $\text{NF}_4\text{HF}_2\cdot n\text{HF}$ becomes rather slow for decreasing n , particularly in the presence of other stable fluorides. It appears that such fluorides can assume the function of stabilizing the HF_2^- anion. A typical example for such a fluoride is AlF_3 or AlF_4^- .³⁷ A careful analysis of such systems is therefore necessary to avoid the interpretation of such $(\text{NF}_4\text{HF}_2)_n\text{MF}_x$ in terms of $(\text{NF}_4)_n\text{MF}_{1+n}$ salts.

The possibility of preparing stable HF solutions of NF_4HF_2 renders them a very useful intermediate. By addition of a stronger or less volatile Lewis acid, the HF_2^- anion can be displaced and NF_4HF_2 can be converted into other NF_4^+ salts. This was first demonstrated⁴ by reacting NF_4HF_2 solutions with BF_3 to form NF_4BF_4 and has recently been extended⁴¹ to the formation of other salts, which due to the low solubility of their cesium salts are not amenable to direct metathetical reactions.

Halogen Exchange in NF_4^+ and NF_2O^+ . In view of the existence of a stable $\text{NCl}_2\text{O}^+\text{SbCl}_6^-$ salt,²⁰ it was of interest to study the possibility of halogen exchange in either NF_4^+ or NF_2O^+ with BCl_3 . For both salts, the observation of mixed BF_3Cl_3 products indicated that halogen exchange took place. For NF_4^+ the main product was gaseous NF_3 , suggesting that the likely NF_3Cl^+ intermediate might be unstable toward decomposition under the given conditions. For $\text{NF}_2\text{O}^+\text{SbF}_6^-$, the main product was $\text{NO}^+\text{SbF}_6^-$ which could arise again from breaking of the rather weak N-Cl bonds in an NCl_2O^+ intermediate.

Acknowledgment. The authors are indebted to Drs. C. J. Schack and L. R. Grant for helpful discussions and to the Office of Naval Research, Power Branch, and the Army Research Office for financial support.

Registry No. NF_4ClO_4 , 13706-14-4; NF_4BrO_4 , 25483-10-7; NF_4HF_2 , 71485-49-9; NF_4SbF_6 , 16871-76-4; NF_2OSbF_6 , 25562-23-6; CsClF_4O , 39018-38-7; CsBrF_4O , 65391-03-9; CsClO_4 , 13454-84-7; CsBrO_4 , 33259-95-9; CsF , 13400-13-0; BCl_3 , 10294-34-5; BrF_3 , 7789-30-2.

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APPENDIX H

Das Kraftfeld von SF₄

The Force Field of SF₄

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Herrn Prof. Dr.-Ing. Fritz Seel zum 65. Geburtstag gewidmet

Z. Naturforsch. **35b**, 1137–1142 (1980); eingegangen am 9. Mai 1980

Force Constants

As it proved impossible, to compute a unique and meaningful General Valence Force Field for SF₄ from the known experimental data, this was realized by an *ab initio* calculation using a basis set of 3-3-21 + 1d G functions for the S-, and 4-21G functions for the F-atom. The values of the stretching force constants are $f(S-F_{eq})$: 5.36 mdyn/Å, $f(S-F_{ax})$: 3.25 mdyn/Å. Problems of assignment of the deformational modes could be settled conclusively.

Obwohl SF₄ im Grunde eine recht einfache Verbindung darstellt, birgt seine schwingungsspektroskopische Behandlung eine Fülle von Problemen. Dies liegt zum einen an der niedrigen Symmetrie (C_{2v}), die eine eindeutige Zuordnung insbesondere der Deformationsschwingungen erschwert, zum anderen an der starken Assoziation in flüssiger Phase, die für eine Untersuchung des ungestörten Moleküls lediglich Spektren in Gasphase oder in einer Inertgas-Matrix zuläßt. Hinzu kommt, daß die Gewinnung zusätzlicher spektroskopischer Informationen durch das Vorliegen eines asymmetrischen Kreisel und die beschränkten Möglichkeiten einer Isotopen-Substitution sehr begrenzt ist. In einer langen Reihe von Arbeiten [1–13] wurde versucht, wenigstens die Zuordnung der Normalschwingungen zu treffen, was allerdings erst jüngst [13] mit Hilfe der Daten für ³⁴SF₄ einigermaßen zuverlässig gelungen ist. Hiermit war es auch möglich, das allgemeine Valenzkraftfeld (GVFF) für die beiden asymmetrischen Rassen B₁ und B₂ festzulegen, während die 4 Normalschwingungen (und damit 10 Kraftkonstanten) enthaltende Rasse A₁ mangels ausreichender Daten nur näherungsweise behandelt werden konnte. Es soll nun der Versuch unternommen werden, unter

Einbeziehung der bisher unberücksichtigt gebliebenen, aber gemessenen [12] Zentrifugaldehnungskonstanten zu einer genaueren Eingrenzung des Kraftfeldes auch für die Rasse A₁ zu kommen, oder – falls dies nicht zum Ziel führt – durch *ab initio*-Berechnung der Kraftkonstanten eine Lösung zu finden. Durch letzteres kann gleichzeitig die Zuordnung bestätigt werden.

Das Kraftfeld aus experimentellen Daten

Die Normalschwingungen des SF₄ teilen sich nach $4 A_1 + 1 A_2 + 2 B_1 + 2 B_2$ auf die Schwingungsrassen auf. Die Symmetrie-Koordinaten wurden wie in [11] gewählt, die F- und G-Matrizen nach der Wilsonschen Methode abgeleitet. Als experimentelle Größen standen die Schwingungsfrequenzen nach [13] (Werte der IR-Gasspektren; ³²S–³⁴S-Isotopenverschiebungen aus Spektren in Ne-Matrix), 5 Zentrifugaldehnungskonstanten [12] und die mittleren Schwingungsamplituden [14] zur Verfügung, letztere wurden allerdings nicht in die Iteration einbezogen, sondern nachträglich berechnet.

Die Kraftfelder der Rassen B₁ und B₂ lassen sich aus den Isotopendaten ermitteln und wurden aus [13] übernommen, ebenso F₅₅(A₂) mit dem geschätzten Frequenzwert von $\nu_5 = 437 \text{ cm}^{-1}$, nachdem die gleichzeitig angestellten *ab initio*-Rechnungen (siehe unten) dies als sinnvoll bestätigten. Für die 10

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Tab. 1. Kraftfeld für SF₄ aus experimentellen Daten (Valenzkraftkonstanten mdyn/Å = 10² Nm⁻¹, Deformationskonstanten mdyn Å = aJ, Valenz/Deformations-Wechselwirkungskonstanten mdyn = 10 nN).

	[13]	diese Arbeit	Meßdaten [12, 13] Δν in cm ⁻¹ , τ in MHz
A ₁ : F ₁₁ = f _r + f _{rr}	5,884	5,644 ± 0,233	
F ₂₂ = f _R + f _{RR}	3,467	3,479 ± 0,145	
F ₃₃ = 0,99 f _ρ + 0,01 f _γ - 0,15 f _{ργ}	1,414	1,707 ± 0,093	
F ₄₄ = 0,71 f _γ + 0,29 (f _α + f _{αα} + f'αα + f''αα) + 0,004 f _ρ + 0,13 f _{αρ} + 0,18 f _{αγ} + 0,11 f _{ργ}	0,863	0,598 ± 0,023	
F ₁₂	-	-0,495 ± 0,799	
F ₁₃	0,320	0,311 ± 0,144	
F ₁₄	0,300	-0,012 ± 0,213	
F ₂₃	0,100	0,057 ± 0,125	
F ₂₄	-	0,092 ± 0,291	
F ₃₄	0,4913	-0,018 ± 0,092	
A ₂ : F ₅₅ = f _α - f _{αα} - f'αα - f''αα	1,673		
B ₁ : F ₆₆ = f _R - f _{RR}	2,821		
F ₇₇ = f _α + f _{αα} - f'αα - f''αα	1,673		
F ₆₇	0,530	wie [13]	
B ₂ : F ₈₈ = f _r - f _{rr}	5,165		
F ₉₉ = f _α - f _{αα} + f'αα - f''αα	1,914		
F ₈₉	0,700		
Δν ₁	11,37	11,8	11,33 ± 0,05
Δν ₂	0,07	0,8	0
Δν ₃	4,14	2,8	4,09 ± 0,05
Δν ₄	0,08	0,2	
Δν ₆	13,14		13,13 ± 0,05
Δν ₇	0,87		
Δν ₈	10,53		10,52 ± 0,05
Δν ₉	2,48		2,42 ± 0,1
τ _{xxxx}	-10,7	-14,3	-15,2 ± 1,1
τ _{yyyy}	-6,0	-5,9	-7,8 ± 1,1
τ _{zzzz}	-2,1	-3,2	-4,9 ± 1,0
T ₁	-14,0	-16,2	-14,7 ± 2,0
T ₂	-2,4	-2,4	-5,2 ± 1,6

Kraftkonstanten der Rasse A₁ bleiben dann neben den 4 Frequenzen, den Isotopenaufspaltungen für ν₁ und ν₃ (für ν₂ wurde keine beobachtet, ν₄ nicht gemessen) 5 τ-Werte als Bestimmungsgrößen (wobei in T₁ und T₂ die Anteile der Rassen A₂, B₁ und B₂ abgezogen werden). Das Ergebnis der Iteration findet sich in Tab. I. Die großen Standardabweichungen zeigen, daß diese Daten zu einer vernünftigen Festlegung des Kraftfeldes nicht ausreichen, alle Nichtdiagonalglieder der F-Matrix außer allenfalls F₁₃ sind letztlich unbestimmt. Es ergibt sich ferner, daß alle τ-Werte außer τ_{xxxx} und T₁ wesentlich zu klein erhalten werden, und dies trifft nicht nur für das in Tab. I wiedergegebene Kraftfeld zu, sondern auch für weitere, die wir unter Variation der Zuordnung der Deformationsschwingungen gemäß früherer Vorschläge [6, 7, 11] getestet haben. Weiterhin weist das berechnete Kraftfeld für A₁ gegenüber dem nur aus den Isotopenverschiebungen abgeschätzten [13] erhebliche Diskrepanzen auf, die

sich auch in einer unzureichenden Wiedergabe von Δν₃ äußern.

ab-initio-Berechnung der Kraftkonstanten für SF₄

Da sich also mit den derzeit bekannten experimentellen Daten das Kraftfeld des SF₄ in der Rasse A₁ nicht eindeutig bestimmen läßt, sahen wir nur die Möglichkeit, durch eine *ab initio*-Berechnung weiterzukommen. Zuerst wurden nur s- und p-Funktionen verwendet, für Schwefel ein 3-3-21G-Basisatz nach Hehre und Lathan [15], und Skancke *et al.* [16], für Fluor ein 4-21G-Basisatz nach Pulay *et al.* [17]. Die Berechnungen wurden nach der Kräfteformel von Pulay [18] mit Hilfe des TEXAS-Programms [19] durchgeführt. Analog zu Oberhammer und Boggs [20] stellten wir mit diesen Basisätzen starke Abweichungen der berechneten von der experimentellen Geometrie fest. Entsprechend unterscheiden sich auch die für diese beiden Gleichgewichtslagen erhaltenen Kraftkonstanten-

Tab. II. Durch *ab initio*-Rechnung erhaltene Kraftfelder für SF₄ (Dimensionen wie Tab. I), exp. Daten [13, 21].

Basissatz S: F:		3-3-21 G 4-21 G exp. Geom.	3-3-21 G 4-21 G theor. Geom.	3-3-21 + 1d G 4-21 G exp. Geom.
Ort:				
A ₁ : F ₁₁		9,212	6,059	7,580
F ₂₂		6,049	4,523	4,886
F ₃₃		1,104	0,739	1,309
F ₁₄		1,125	1,033	1,233
F ₁₂		0,698	0,584	0,756
F ₁₃		0,041	0,104	0,073
F ₁₄		0,433	0,438	0,422
F ₂₃		0,065	0,155	0,034
F ₂₄		0,176	0,033	0,051
F ₃₄		0,488	0,498	0,513
A ₂ : F ₅₅		1,950	1,966	2,099
B ₁ : F ₆₆		5,028	3,888	4,073
F ₇₇		2,237	2,268	2,413
F ₆₇		0,658	0,679	0,784
B ₂ : F ₈₈		9,133	6,136	7,320
F ₉₉		3,273	2,147	3,008
F ₈₉		0,541	0,625	0,624
ν_1 (.1 ν_1)	892 (11,33)	1124,90 (13,08)	850,72 (10,36)	1033,31 (13,03)
ν_2 (.1 ν_2)	558 (0)	727,11 (0,0)	708,71 (1,94)	648,29 (0,03)
ν_3 (.1 ν_3)	532 (4,09)	547,26 (5,12)	477,71 (2,91)	569,31 (4,72)
ν_4 (.1 ν_4)	228 ()	223,72 (0,01)	153,88 (0,0)	248,50 (0,01)
ν_5 (.1 ν_5)	[437] ()	472,23 (0,0)	461,34 (0,0)	489,94 (0,0)
ν_6 (.1 ν_6)	730 (13,13)	982,52 (17,18)	850,70 (14,67)	874,61 (15,68)
ν_7 (.1 ν_7)	475 (—)	550,80 (1,30)	515,14 (1,19)	571,11 (1,08)
ν_8 (.1 ν_8)	867 (10,52)	1184,66 (15,59)	976,78 (12,84)	1054,18 (13,79)
ν_9 (.1 ν_9)	353 (2,42)	458,68 (2,76)	372,86 (2,14)	440,62 (2,68)
mit obigen Basissätzen berechnet:				
r (Å)	1,545		1,628	1,559
R (Å)	1,646		1,694	1,631
β (°)	101,6°		110,0°	102,2°
γ (°)	173,1°		161,4°	169,7°

sätze (Tab. II) erheblich voneinander. Oberhammer und Boggs [20] zeigten, daß sich die Diskrepanzen bezüglich der Geometrie durch Einbeziehung von d-Funktionen beseitigen lassen. Deshalb wurden auch von uns Rechnungen mit einer um 1d-Funktion (Exponent: 0,6) erweiterten Basis vorgenommen. Die damit ermittelte Geometrie stimmt nun sowohl mit [20] wie mit der aus Mikrowellenspektren erhaltenen [21] befriedigend überein. Den zugehörigen Kraftkonstantensatz und die damit berechneten Schwingungsfrequenzen und Isotopenaufspaltungen zeigt ebenfalls Tab. II.

Zieht man in Betracht, daß bei derartigen Rechnungen die Diagonalglieder der Kraftkonstanten-Matrix und damit die Schwingungsfrequenzen immer zu hoch erhalten werden, insbesondere die Valenzkraftkonstanten und -schwingungen von X-F-Bindungen [22–25], so kann man mit dem Ergebnis

die Richtigkeit der Zuordnung, die ja lange Zeit in der Literatur kontrovers war [1–13], prüfen. Die aus der *ab initio*-Rechnung erhaltenen Frequenzwerte stützen eindeutig die Zuordnung aller Valenzschwingungen und der Deformationen ν_4 und ν_8 nach [6, 10, 13], die Besonderheit einer sehr hohen Deformationsschwingung in A₁ (ν_3 , nur knapp unterhalb der Valenzfrequenz ν_2) wird bestätigt. Die Alternative mit $\nu_3 = 350 \text{ cm}^{-1}$ [11] kann man damit endgültig ausschließen. Lediglich die Zuschreibung der Schwingungen bei 475 und 532 cm^{-1} zu ν_3 (A₁) und ν_7 (B₁) ([6, 10] einerseits, [13] andererseits) läßt sich nicht entscheiden, die Berechnung ergibt hier identische Frequenzwerte. Jedoch wird die Zuordnung $\nu_3 = 532 \text{ cm}^{-1}$, $\nu_7 = 475 \text{ cm}^{-1}$ (wie in [13]) durch die Isotopenverschiebungen (die *ab initio* alle etwas zu hoch erhalten werden) gestützt. Wir haben diese Zuordnung darüber hinaus durch

Tab. III. Das Kraftfeld der Rasse A₁ für SF₄ auf der Basis des *ab initio*-Resultats (Dimensionen wie Tab. I).

	nachiteriertes <i>ab initio</i> -Feld	Modifizierungen: a	b	c	d
F ₁₁	5,533 ± 0,099	5,535	5,522	5,505	5,626
F ₂₂	3,724 ± 0,056	3,683	3,698	3,684	3,662
F ₃₃	1,448 ± 0,229	1,458	1,456	1,465	1,447
F ₄₄	0,891 ± 0,138	0,876	0,879	0,880	0,873
F ₁₂	0,756	0,68	0,70	0,68	0,65
F ₁₃	0,073	0,12	0,11	0,10	0,13
F ₁₁	0,422	0,36	0,37	0,36	0,40
F ₂₃	- 0,034	- 0,034	- 0,05	- 0,034	- 0,034
F ₂₄	- 0,051	- 0,051	- 0,07	- 0,051	- 0,051
F ₃₄	0,513	0,513	0,513	0,518	0,505
v ₁ (lv ₁)	890,60 (11,64)	891,07 (11,82)	891,15 (11,82)	890,96 (11,93)	891,03 (11,56)
v ₂ (lv ₂)	557,95 (0,21)	557,88 (0,11)	557,82 (0,04)	557,90 (0,15)	557,81 (0,02)
v ₃ (lv ₃)	535,41 (3,81)	533,53 (3,80)	533,45 (3,86)	534,11 (3,69)	533,76 (4,03)
v ₄ (lv ₄)	227,56 (0,11)	227,77 (0,10)	227,78 (0,10)	227,71 (0,10)	227,75 (0,10)
T _{xxxx}	- 11,5	- 11,5	- 11,5	- 11,6	- 11,2
T _{yyyy}	- 5,5	- 5,6	- 5,6	- 5,6	- 5,6
T _{zzzz}	- 2,1	- 2,1	- 2,1	- 2,1	- 2,1
T _{xxxy}	- 0,28	- 0,04	- 0,001	- 0,02	- 0,02
T _{xxzz}	- 1,9	- 1,9	- 1,9	- 1,9	- 1,9
T _{yyzz}	- 0,8	- 0,8	- 0,8	- 0,8	- 0,8
T ₁	- 12,6	- 12,9	- 12,9	- 12,9	- 12,9
T ₂	- 2,1	- 2,1	- 2,1	- 2,1	- 2,1

eine Messung der Polarisationsgrade der Linien bei 558 und 532 cm⁻¹ (die Linien bei 475 und 350 cm⁻¹ waren so schwach, daß ihr Polarisationsgrad nicht festgestellt werden konnte) im Raman-Gasspektrum bestätigt: beide Linien sind im Gegensatz zu früheren Angaben [5] polarisiert. Für die inaktive v₅ (A₂) läßt sich aus der *ab initio*-Rechnung ein Bereich von 400–450 cm⁻¹ abschätzen, so daß die Annahme v₅ = 437 cm⁻¹ [13] durchaus plausibel ist.

Angeichts der Erkenntnis, daß die Diagonalglieder der Kraftkonstanten-Matrix *ab initio* auf jeden Fall zu hoch erhalten werden, läßt sich mit einem einfachen Satz von Schwingungsfrequenzen unter Festhaltung aller Nichtdiagonalglieder eine Nachiteration durchführen, die die Diagonal-Kraftkonstanten den experimentellen Werten anpaßt. Dieses Kraftfeld ist für A₁ in Tab. III wiedergegeben.

Einen Hinweis auf die Qualität der erhaltenen Wechselwirkungskonstanten liefern neben früheren Erfahrungen [22–25] auch die Ergebnisse für B₁ und B₂ (vgl. Tab. II mit Tab. I). Sie zeigen, daß die experimentell bestimmten Kopplungskonstanten F₆₇ bzw. F₈₉ von der *ab initio*-Rechnung in Vorzeichen und Größenordnung richtig wiedergegeben werden, aber im Absolutwert Abweichungen zeigen. Unerwartet ist angesichts des gleichen Wechselwir-

kungstyps (Valenz-Deformations-Kopplung) deren unterschiedliche Richtung (F₆₇(exp) > F₆₇(ab in.); F₈₉(exp) < F₈₉(ab in.)). Dies muß nicht unbedingt eine Unzuverlässigkeit der *ab initio*-Rechnung signalisieren: Kontroll-Untersuchungen haben gezeigt, daß etwa bei einer Annahme von F₆₇ = 0,52 mdyn und F₈₉ = 0,65 mdyn (Abweichung vom *ab initio*-Wert in gleicher Richtung und in gleichem Verhältnis) Kraftfelder erhalten werden, die für alle gemessenen lv keine größeren Diskrepanzen als 5% (die T-Werte zeigen überhaupt keine Änderung) aufweisen, was bei einer realistischen Einschätzung der Meßgenauigkeit durchaus tragbar ist (übrigens weichen auch die Diagonal-Kraftkonstanten für diese Lösungen um nicht mehr als 5% von denen in Tab. I ab). Trotzdem übernehmen wir für B₁ und B₂ die in [13] aus den Isotopenverschiebungen ermittelten Kraftkonstanten und nehmen an, daß die für F₆₇ und F₈₉ beobachteten Unterschiede auch für die Kopplungsglieder in A₁ den Rahmen der zu erwartenden Genauigkeit aus der *ab initio*-Rechnung abstecken.

Vergleicht man die Ergebnisse für diese Rasse, so ist festzustellen, daß die durch Iteration unter Einbeziehung auch der Zentrifugaldehnungskonstanten erhaltene Lösung (Tab. I) überhaupt nicht den *ab initio*-Werten entspricht. Bei der nur aus den

Isotopenverschiebungen abgeschätzten Lösung [13] sind zumindest die Konstanten F_{14} und F_{34} ähnlich, die auch im *ab initio*-Feld die größten Werte besitzen (die dritte derartige Konstante F_{12} beschreibt nur einen Potentialeffekt, der durch die Isotopenverschiebung nicht erfaßt werden kann, da das zugehörige $G_{12} = 0$ ist). Trotz der Abweichungen der übrigen Nichtdiagonalglieder zeigen die Diagonalkraftkonstanten eine erstaunlich gute Übereinstimmung, ein Hinweis, daß diese Kopplungskonstanten wohl nur von geringem Einfluß auf sie sind.

Betrachtet man die Wiedergabe der experimentellen Daten durch das nachiterierte *ab initio*-Feld für A_1 (in Kombination mit den experimentell ermittelten Kraftkonstanten für B_1 und B_2), so werden die Isotopenverschiebungen gut reproduziert, die τ -Werte zeigen hingegen noch größere Diskrepanzen als bei der Iteration nach r , Δr und τ gemeinsam. Da aber die τ 's wegen anharmonischer Effekte weniger zuverlässig sind und zudem noch im Gegensatz zu den Isotopenverschiebungen eine wesentlich geringere Meßgenauigkeit aufweisen, erscheint dies aber tragbar, ja man muß sogar vermuten, daß das völlig andere Kraftfeld bei der Iteration nach allen experimentellen Daten gerade durch das Bemühen um eine Angleichung der τ -Werte, die aber trotzdem nur bei τ_{xxxx} und T_1 innerhalb der angegebenen [12] Fehlergrenze erreicht wird, verursacht ist. Beim *ab initio*-Feld werden für alle τ 's zu niedrige Werte erhalten, T_1 könnte aber durch eine Erniedrigung von ν_5 (A_2) angeglichen werden (für $\nu_5 = 400 \text{ cm}^{-1}$: $T_1 = -14.8 \text{ MHz}$). Jedoch zeigt sich bei ihm für das ebenfalls im Summenausdruck T_1 verborgenen τ_{xyxy} sogar ein positiver Wert, was nicht möglich ist. Es ist also zumindest erforderlich, die Nichtdiagonalglieder des *ab initio*-Feldes so zu variieren,

daß τ_{xyxy} negativ wird. Bei der Untersuchung, welchen Einfluß die Nichtdiagonalglieder einzeln auf die Meßdaten haben, zeigte sich, daß dieser bei F_{23} und F_{24} außerordentlich gering ist, für F_{34} hingegen extrem stark: schon eine Änderung unter $0.01 \text{ m dyn. \AA}$ verschiebt τ_{xyxy} erheblich, jedoch werden gleichzeitig ν_5 , $\Delta \nu_3$ und $\Delta \nu_1$ so sehr in negativem Sinne beeinflusst, daß dieser Effekt kaum genutzt werden kann. Eine Verkleinerung von F_{12} , F_{14} und eine Vergrößerung von F_{13} wirken bezüglich τ_{xyxy} in der gewünschten Richtung, wenn auch nicht stark. Sie wurden daher alle drei gemeinsam geändert, um sich nicht mit einer Größe allzuweit vom *ab initio*-Wert zu entfernen. Tab. III zeigt 4 solche Kraftfelder (Modifizierungen a–d), bei denen die Nichtdiagonalglieder gemäß dieser Erfahrungen festgelegt wurden. Sie reproduzieren alle Daten etwa gleich gut. Auf die Diagonalkraftkonstanten haben diese Änderungen kaum Einfluß, und man kann wohl davon ausgehen, daß die korrekte Lösung für die Rasse A_1 des SF₄ tatsächlich in diesem eng umschriebenen Bereich liegen wird. Daraus ergeben sich für SF₄ folgende Valenzkraftkonstanten $f_r(S-F_{eq}) = 5.36 \text{ m dyn. \AA}$ ($f_{rr} 0.19 \text{ m dyn. \AA}$); $f_R(S-F_{ax}) = 3.25 \text{ m dyn. \AA}$ ($f_{RR} 0.43 \text{ m dyn. \AA}$). Die mittleren Schwingungsamplituden bei 298 K für all diese Lösungen betragen (in $\text{\AA}$, in Klammern experimentelle Werte [14]): SF_{ax} : 0.048 (0.047 $\pm$ 0.005); SF_{eq} : 0.041 (0.041 $\pm$ 0.005); $F_{eq}F_{eq}$: 0.074 (0.068 $\pm$ 0.01); $F_{ax}F_{eq}$: 0.069 (0.067 $\pm$ 0.005); $F_{ax}F_{ax}$: 0.060 (0.059 $\pm$ 0.01) und entsprechen so den Werten, die auch mit dem Kraftfeld in [13] erhalten wurden. Auch Eigenvektoren und Potentialenergieverteilung stimmen weitgehend mit den Ergebnissen von [13] überein, insbesondere was die völlige Mischung der Symmetriekoordinaten S_3 und S_4 in den Schwingungen ν_3 und ν_4 anbetrifft.

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Vibrational spectra of $^{15}\text{NF}_4\text{AsF}_6$ and general valence force field of NF_4^+

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Abstract—Samples of $^{15}\text{NF}_4\text{AsF}_6$ and $^{15}\text{NF}_4\text{AsI}_6$ were prepared by low-temperature u.v. photolysis and their vibrational spectra were recorded. The observed spectra are in agreement with space group $P4_3n$ for NF_4AsF_6 and site symmetries of S_4 and C_4 for NF_4^+ and AsF_6^- , respectively. The observed ^{14}N – ^{15}N isotopic shifts were used to compute a general valence force field for NF_4^+ .

INTRODUCTION

Since the first report [1, 2] on the existence of NF_4^+ salts numerous papers [3–25] dealing with NF_4^+ chemistry have been published. The vibrational spectrum of NF_4^+ is well known [5, 7–9, 13–15, 17–19], and its force field has been computed [5, 7]. However, the earlier work permitted only computation of an approximate force field, since the F_2 block has two fundamentals and three symmetry force constants. In view of the general interest in the NF_4^+ cation, the computation of a general valence force field was highly desirable. In addition, it was hoped that the vibrational spectra might allow the determination of the space group of NF_4AsF_6 .

EXPERIMENTAL

The samples of $^{15}\text{NF}_4\text{AsF}_6$ and $^{15}\text{NF}_4\text{AsI}_6$ were prepared by low-temperature u.v.-photolysis of mixtures of F_2 , AsF_5 and $^{14}\text{NF}_3$ or $^{15}\text{NF}_3$, respectively, in a quartz reactor, using a previously described method [15]. The $^{15}\text{NF}_3$ starting material was prepared by glow-discharge of $^{15}\text{N}_2$ (99% ^{15}N , Stohler Isotope Chemicals) and F_2 (Rocketdyne), as previously described [26]. Volatile materials were handled in a stainless steel Teflon-FEP vacuum system and solids in the dry nitrogen atmosphere of a glove box.

The i.r. spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as dry powders pressed between AgCl disks in a Wilks mini press. The spectrometer was calibrated by comparison with standard gas calibration points [27, 28]. The Raman spectra were recorded on Spex Ramalog and Cary Model 83 spectrophotometers using the 4880 Å exciting line and quartz tubes as sample containers. The reported frequencies and isotopic shifts are believed to be accurate to ± 1 and $\pm 0.1 \text{ cm}^{-1}$, respectively.

RESULTS AND DISCUSSION

The sample of $^{15}\text{NF}_4\text{AsF}_6$ was of high isotopic purity and its vibrational spectra did not exhibit any detectable bands due to the ^{14}N isotope. To determine the ^{14}N – ^{15}N isotopic shifts, the corresponding ^{14}N salt was prepared and studied by vibrational spectroscopy under identical conditions. Since the ^{15}N salt spectra were identical to those previously published for the ^{14}N salt [15], except for the isotopic shifts observed for ν_1 and ν_4 of NF_4^+ , the

actual spectra are not shown. The observed frequencies, ^{14}N – ^{15}N isotopic shifts and assignments are summarized in Table 1.

Although the assignments given in Table 1 were made for simplicity for tetrahedral NF_4^+ and octahedral AsF_6^- , the observed splittings of the degenerate modes and deviations from the T_2 and O_h selection rules indicate that the actual site symmetries of the NF_4^+ and AsF_6^- ions must be lower than T_2 and O_h , respectively. Unfortunately, the exact crystal structure of NF_4AsF_6 is unknown, however, based on its reported X-ray powder diffraction data [4], NF_4AsF_6 appears to be isotypic with PCl_4PCl_6 , which belongs to space group $P4_3n$ (C_{4h}^2 , No. 85) [29, 30]. In this space group, the NF_4^+ cation would occupy sites of symmetry S_4 . As can be seen from comparison of Tables 1 and 2, the observed NF_4^+ bands agree well with the predictions for S_4 site symmetry, but not with those for D_2 or D_{2d} . Similarly, the deviations from the O_h selection rules, observed for AsF_6^- , are compatible with a site symmetry of C_4 (see Table 3), but not with D_{3d} , D_{3h} , D_2 or S_6 . Based on these results, alternate probable space groups, such as $P4_3/m$, $P4_3/n$, $P4_3/2_1$, $P4_3/mmc$, $P4_3/mnc$, $P4_3/mnm$ or $P4_3/m$, can be ruled out.

Since the A_1 and E block of tetrahedral NF_4^+ contain only one fundamental vibration each, the values of the corresponding symmetry force constants are uniquely determined. For the F_2 block which contains one stretching and one deformation mode, additional data, such as ^{14}N – ^{15}N isotopic shifts, are needed to allow the calculation of unique values for the three symmetry force constants.

In solid NF_4AsF_6 , the F_2 modes of NF_4^+ are split under S_4 site symmetry into one B and one doubly degenerate E mode. Since the isotopic shifts of both modes are very similar (see Table 2), weighting of the shifts can be neglected and a simple average was used. It should be pointed out however that in certain NF_4^+ salts, such as NF_4BF_4 [31], the ^{14}N – ^{15}N isotopic shifts of the $\nu_2(F_2)$ components can differ by as much as 8 cm^{-1} , thus requiring reliable mode assignments.

As expected from their G matrix elements, the ^{14}N – ^{15}N isotopic shifts of $\nu_1(A_1)$ and $\nu_2(E)$ were

Table 1. Vibrational spectra of $^{14}\text{NF}_4\text{AsF}_6$ and $^{15}\text{NF}_4\text{AsF}_6$.

$^{14}\text{NF}_4\text{AsF}_6$		$^{15}\text{NF}_4\text{AsF}_6$		Assignments (point group)*		$\Delta \nu^{14}\text{N}-^{15}\text{N}$
i.r.	Raman	i.r.	Raman	$\text{NF}_4^+(T_d)$	$\text{AsF}_6^-(O_h)$	
2360 vvw } 2310 vw } 2012 sh } 1997 w } 1780 sh } 1763 vw } 1760 sh }		2310 vvw } 2253 vw } 1984 sh } 1969 w }		$2\nu_1(A_1 + E + F_2)$		
				$\nu_1 + \nu_3(F_2)$		
		1732 vw		$\nu_1 + \nu_4(A_1 + E + F_2)$		29.2 ± 1.8
		1455 sh }		$\nu_1 + \nu_4(F_2)$		2
1453 w }		1451 w }				
1398 vw }		1398 vw }			$\nu_1 + \nu_3(F_{1u})$	
1290 vw }		1290 vw }			$\nu_2 + \nu_3(F_{1u} + F_{2u})$	
1221.9 mw }		1218.2 mw }		$2\nu_2(A_1 + E + F_2)$		1.85
1165 vs, br }	{ 1165.0 (1) 1152.9 (0.6)	1135 vs, br }	{ 1136.0 (1) 1123.4 (0.6)	$\nu_3(F_2)$		{ 29.0 29.5 } 29.25 ± 0.25
1056 sh }		1054 sh }		$\nu_2 + \nu_4(F_1 + F_2)$		
1052 vw }		1050 vw }				
	882 (0+) 848.2 (7.3)		882 (0+) 848.2 (7.3)	$2\nu_2(A_1 + A_2 + E)$ $\nu_1(A_1)$		
826 vw }		826 vw }			$\nu_2 + \nu_6(F_{1u} + F_{2u})$	
710.0 vs, br }	704.5 (1.5)	710 vs, br }	704.5 (1.5)		$\nu_3(F_{1u})$	
685 sh }	685.4 (10)	685 sh }	685.4 (10)		$\nu_1(A_{1g})$	
613.3 s }	613.3 (2.6)	611.5 s }	611.4 (2.6)			1.8, 1.9 } 1.8 ± 0.1
609.0 s }	609.0 (5.2)	607.3 s }	607.2 (5.2)	$\nu_4(F_2)$	$\nu_2(E_g)$	1.7, 1.8 }
579 w }	578.3 (1.2) 445.0 (1.9) 441.6 (2.0)	579 w }	578.3 (1.2) 444.9 (1.9) 441.5 (2.0)	$\nu_2(E)$		0 ± 0.1
395 s }		395 s }			$\nu_4(F_{1u})$ $\nu_5(F_{2g})$	
	369.6 (3.6)		369.6 (3.6)			

* The site symmetry of NF_4^+ and AsF_6^- in NF_4AsF_6 is S_4 and C_4 , respectively (see text). However, since reliable assignments for the nearly degenerate vibrations cannot be made for S_4 and C_4 , the observed spectra were assigned in point group T_d and O_h , respectively.

Table 2. Correlation table for the internal vibrations of NF_4^+ in NF_4AsF_6 for space group $P4/n$ and $Z = 2$.

Point group T_d	Site group S_4	Factor group C_{4h}	Assignment
A_1 — Raman*	A — Raman	A_g — Raman	$\nu_{\text{sym}}\text{NF}_4^+$
		B_u — —	
E — Raman	A — Raman	A_g — Raman	$\delta_{\text{sym}}\text{NF}_4^+$
		B_u — —	
	B i.r. Raman	B_g — Raman	
		A_u i.r. —	
F_2 i.r. Raman	B i.r. Raman	B_g — Raman	$\nu_{\text{as}}\text{NF}_4^+$
		A_u i.r. —	
	E i.r. Raman	E_g — Raman	
		E_u i.r. —	
F_2 i.r. Raman	B i.r. Raman	B_g — Raman	$\delta_{\text{as}}\text{NF}_4^+$
		A_u i.r. —	
	E i.r. Raman	E_g — Raman	
		E_u i.r. —	

* Spectral activity.

Table 3. Correlation table for the internal vibrations of AsF_6^- in NF_4AsF_6 for space group $P4/n$ and $Z = 2$

Point group O_h	Site group C_4	Factor group C_{4h}	Assignment
A_{1g} — Raman	A i.r. Raman	A_g — Raman	$\nu_{\text{sym}}\text{AsF}_6$
		A_u i.r. —	
E_g — Raman	A i.r. Raman	A_g — Raman	$\nu_{\text{sym}}\text{AsF}_6$
		A_u i.r. —	
	B — Raman	B_g — Raman	
		B_u — —	
F_{1u} i.r. —	B — Raman	B_g — Raman	$\nu_{\text{as}}\text{AsF}_6$
		B_u — —	
	E i.r. Raman	E_g — Raman	
		E_u i.r. —	
F_{1u} i.r. —	B — Raman	B_g — Raman	$\delta_{\text{as}}\text{AsF}_6$
		B_u — —	
	E i.r. Raman	E_g — Raman	
		E_u i.r. —	
F_{2g} — Raman	B — Raman	B_g — Raman	$\delta_{\text{sym}}\text{AsF}_6$
		B_u — —	
	E i.r. Raman	E_g — Raman	
		E_u i.r. —	
F_{2u} — —	B — Raman	B_g — Raman	$\delta'\text{AsF}_6$
		B_u — —	
	E i.r. Raman	E_g — Raman	
		E_u i.r. —	

found to be zero within experimental error. Those of $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ were measured to be 29.25 ± 0.25 and $1.8 \pm 0.1 \text{ cm}^{-1}$, respectively. These values were supported by preliminary measurements on $^{14}\text{NF}_4\text{BF}_4$ and $^{15}\text{NF}_4\text{BF}_4$ [31] which shows very similar averaged isotopic shifts for ν_3 and ν_4 .

For the computation of the general valence force field of NF_4^+ the frequencies and isotopic shifts listed in Table 4 were used. For the F_2 block, the possible ranges of the two diagonal symmetry force constants F_{33} and F_{44} and the ^{14}N – ^{15}N isotopic

shifts of ν_3 and ν_4 were computed as a function of the interaction constant F_{34} by trial and error and by the use of the expressions previously reported [32] for the calculation of extremal force constant solutions. The results of these calculations are shown in Fig. 1. The observed ^{14}N – ^{15}N isotopic shifts were used to graphically select the correct F_2 block force field. The isotopic shift of ν_4 was preferred because, due to its smallness, anharmonicity corrections should be unimportant [33].

Since the slopes of the $\Delta\nu_3$ and $\Delta\nu_4$ vs F_{34} plots

Table 4. Frequency values, ^{14}N – ^{15}N isotopic shifts (cm^{-1}), general valence force field* and potential energy distribution for NF_4^+

	$\nu^{14}\text{NF}_4^+$	$\nu^{15}\text{NF}_4^+$	$\Delta\nu$	Symmetry force constants	PED
A_1 ν_1	848.2	848.2	0	$F_{11} = f_r + 3f_{rr} = 8.053$	
E ν_2	443.3	443.3	0	$F_{22} = f_r - 2f_{rr} + f_{\text{asr}} = 0.733$	
F_2 ν_3	1158.95	1129.7	29.25 ± 0.25	$F_{33} = f_r - f_{rr} = 5.52 \pm 0.08$	$96F_{33} + 43F_{44} - 39F_{34}$ $15F_{33} + 67F_{44} + 18F_{34}$
	611.15	609.35	1.8 ± 0.1	$F_{44} = f_r - f_{\text{asr}} = 1.00 \pm 0.02$	
				$F_{34} = \sqrt{2(f_{rr} - f_r)} = 0.73 \pm 0.03$	
				$f_r = 6.153 \pm 0.1$	
				$f_{rr} = 0.633 \pm 0.03$	

* Stretching, bending and stretch-bend interaction force constants have units of mdyn/cm , $\text{mdyn}/\text{\AA}$ and $\text{mdyn}/\text{\AA}$ radian² and $\text{mdyn}/\text{\AA}$ radian, respectively.

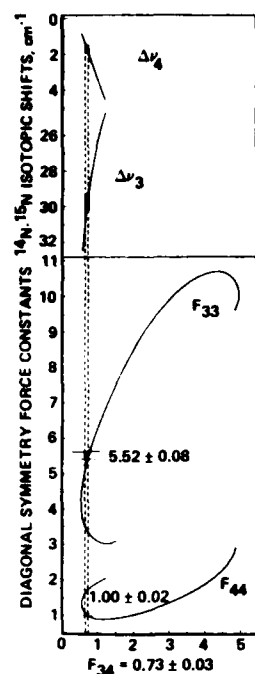


Fig. 1. F_i block force field (mdyn/Å) of NF_3 . The diagonal symmetry force constants and ^{14}N - ^{15}N isotopic shifts are plotted as a function of the interaction constant F_{34} . The rectangles delineate the observed ^{14}N - ^{15}N isotopic shifts and their uncertainties. The broken vertical and solid horizontal lines indicate the resulting force constant ranges.

have opposite signs, the $\Delta\nu_4$ range might be used as a rough estimate for the anharmonicity correction required for $\Delta\nu_3$. Figure 1 indicates an anharmonicity correction of about 1 cm^{-1} for $\Delta\nu_3$, which is in line with previous estimates for similar molecules, such as NF_3 [34].

The general valence force field and the potential energy distribution (PED) of NF_3 are summarized in Table 4. The PED indicates significant mixing of S_1 and S_4 , as expected [32, 36] for a strongly mass coupled system [32, 36]. The close agreement between the general valence force field of this study and the previously reported [5, 7] approximate force field is in line with Pfeiffer's analysis [37] which showed that for similar molecules the method of 'step-wise coupling' gives the best agreement with the general valence force field values. A comparison of the NF stretching force constant of NF_3 (6.15 mdyn/Å) with those of the NF bond distances of FNO ($f_s = 2.15\text{ mdyn/Å}$, $r_{\text{NF}} = 1.512\text{ Å}$) and NF_4 ($f_s = 4.31\text{ mdyn/Å}$, $r_{\text{NF}} = 1.365\text{ Å}$) [35] suggests for NF_3 an unusually strong and short ($r = 1.24\text{ Å}$) NF bond.

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Canoga Park, California 91304

Synthesis and Properties of $\text{NF}_4^+\text{SO}_3\text{F}^-$

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

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The novel salt $\text{NF}_4^+\text{SO}_3\text{F}^-$ was prepared by metathesis between NF_4SbF_6 and CsSO_3F in anhydrous HF solution at -78°C . In HF solution, it is stable at room temperature. Removal of the solvent produces a white solid which is stable at 0°C but slowly decomposes at $+10^\circ\text{C}$ to produce FOSO_2F and NF_3 in high yield. The ionic nature of the compound, both in the solid state and in HF solution, was established by Raman and ^{19}F NMR spectroscopy. Cesium sulfate was found to react with anhydrous HF, producing CsSO_3F as the major product. Similarly, CsPO_2F_2 , the Raman spectrum of which is reported, was found to react with HF to give CsPF_6 in quantitative yield.

Introduction

Among oxidizers, the NF_4^+ cation is unique. In spite of being one of the most powerful oxidizers known, it possesses high kinetic stability,¹ thereby permitting its combination with

a surprisingly large number of anions to form stable or metastable salts. Anions capable of NF_4^+ salt formation include

(1) Christe, K. O.; Wilson, R. D.; Goldberg, I. B. *Inorg. Chem.* 1979, 18, 2572.

BF_4^- ,^{2,9} XF_6^- ($\text{X} = \text{Ge, Ti, Sn}$),^{9,11} XF_6^- ($\text{X} = \text{P, As, Sb, Bi}$),^{6,7,9,12-19} XF_6^{2-} ($\text{X} = \text{Ge, Sn, Ti, Ni, Mn}$),^{9,11,20,21} ClO_4^- ,²² HF_2^- ,²² and several perfluoro polyanions.^{6,10,11,19} Recent studies have shown that NF_4^+ salts of oxygen-containing anions are of particular interest because hypofluorites such as $\text{OIF}_4\text{O}^{23}$ or FOClO_3 ²² can be formed during their thermal decomposition.

In this paper we report results on the possible synthesis of salts derived from sulfur or phosphorus oxyfluorides. We are aware of only one unpublished study¹ in this area, in which the evolution of some FOSO_2F from either an NF_4SbF_6 - $\text{H}_2\text{OSO}_2\text{F}$ solution at -78°C or a supposedly dry mixture of NF_4SbF_6 and LiSO_3F at room temperature was interpreted¹ as evidence that $\text{NF}_4\text{SO}_3\text{F}$, if it exists, is unstable even at -78°C . In view of the relative stability of NF_4ClO_4 ²² and the similarity between ClO_4^- and isoelectronic SO_3F^- and PO_3F_2^- , the isolation of $\text{NF}_4\text{SO}_3\text{F}$ and $\text{NF}_4\text{PO}_3\text{F}_2$ seemed possible.

Experimental Section

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.²² Literature methods were used for the synthesis of NF_4SbF_6 ,⁶ $\text{ClO}_3\text{SO}_2\text{F}$,²⁴ and HOPOF_2 .²⁵ The CsPO_3F_2 was prepared by the addition of Cs_2CO_3 to a 10% excess of HOPOF_2 frozen at -196°C . The mixture was allowed to react at room temperature with agitation, and the volatile products and excess HOPOF_2 were pumped off at 40°C for 12 h. On the basis of observed material balance and vibrational spectra, the solid residue consisted of CsPO_3F_2 of high purity. The Cs_2SO_4 was obtained from aqueous Cs_2CO_3 and H_2SO_4 by using a pH electrode for end point (pH 3.86) detection. The solution was taken to dryness and dried in an oven at 100°C for 24 h. The CsSO_3F was prepared by allowing CsCl (10.3 mmol) and ClOSO_2F (15.5 mmol) to react in a 10-mL stainless-steel cylinder at ambient temperature for several days. All volatile material was removed from the cylinder, and the solid product was pumped on overnight. The weight of the solid (2.43 g vs. 2.40 g theoretical) together with its infrared and Raman spectra confirmed the completeness of the reaction and the identity of the product.

Preparation and Properties of $\text{NF}_4^+\text{SO}_3\text{F}^-$. The compatibility of

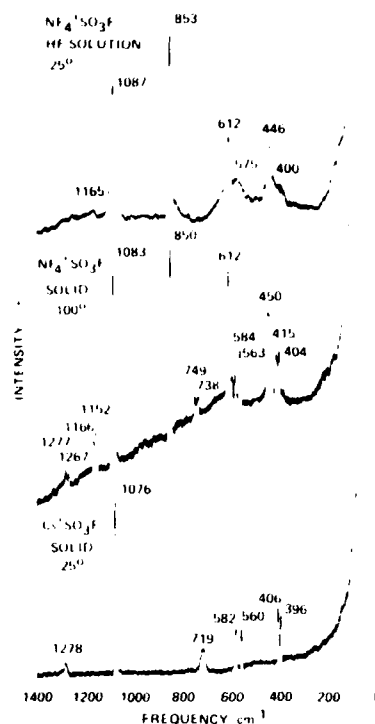


Figure 1. Raman spectra of $\text{NF}_4^+\text{SO}_3\text{F}^-$: upper trace, HF solution at 25°C ; middle trace, neat solid at -100°C . (Weak bands due to the sample tubes and small amounts of CsSbF_6 were subtracted from the spectra.); bottom trace, solid CsSO_3F at 25°C . The spectra were recorded with spectral slit widths of 8, 6, and 4 cm^{-1} , respectively.

Table I. Raman Spectra of $\text{NF}_4\text{SO}_3\text{F}$ and CsSO_3F

obsd freq, cm^{-1} (rel intens ^a)		assign	
$\text{NF}_4\text{SO}_3\text{F}^-$		NF_4^+ (T_d)	SO_3F^- (C_{3v})
HF soln	solid		
	1277 (0.7)		$\nu_4(\text{E})$
	1267 (0.4)		
1165 (0.4)	1166 (1.3)	$\nu_3(\text{F}_2)$	$\nu_1(\text{A}_1)$
	1152 (1.8)		
1087 (6.7) p	1083 (10)		
853 (10) p	850 (9.5)	$\nu_1(\text{A}_1)$	$\nu_2(\text{A}_1)$
	749 (1.1)		
	738 (0.8)		
612 (3)	612 (6)	$\nu_4(\text{F}_2)$	
575 (1.2)	584 (1.7)		$\nu_2(\text{E})$
	563 (2.5)		$\nu_3(\text{A}_1)$
446 (2.8)	450 (4)	$\nu_2(\text{E})$	
	415 (2.5)		$\nu_6(\text{E})$
400 (1)	406 (3.8)		
	404 (2.3)		
	396 (3.5)		

^a Uncorrected Raman intensities.

the SO_3F^- anion with HF was established by dissolving CsSO_3F in dry HF and recording the Raman spectra of the starting material, of the HF solution, and of the solid residue recovered after removal of the solvent. All spectra showed the bands characteristic²⁶ for SO_3F^- . The ^{19}F NMR spectrum of the HF solution was also recorded and consisted of a singlet at $\delta -33.8$ (downfield from external CFCl_3) for SO_3F^- and a relatively narrow HF solvent peak at $\delta 191$.

In a typical preparation of $\text{NF}_4\text{SO}_3\text{F}$, NF_4SbF_6 (3.145 mmol), and CsSO_3F (3.146 mmol) were combined in a previously described²² Teflon metathesis apparatus. Dry HF^{22} (3 mL of liquid) was added, and the resulting mixture was stirred at ambient temperature for 3 h with a magnetic stirring bar, followed by cooling to -78°C and

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Table II. Vibrational Spectra of Solid CsPO_3F_2 and Their Assignments Compared to Those of SO_3F_2

obsd freq, cm^{-1} (rel intens)				assignt (C_{2v})	approx descriptn of mode
$\text{CsPO}_3\text{F}_2^a$		SO_3F_2^b			
Raman	IR	Raman	IR		
1143 (10)	1142 vs	1270 vs	1270 vs	$A_1 \nu_1$	sym PO_2 str
813 (3.7)	825 vs	848 vs	848 vs	ν_2	sym PF_2 str
512 (6)	520 sh	552 m	553 s	ν_3	δ scissoring PO_2
370 sh	370 mw				
353 (5.7)	351 mw	384 m	384 vw	ν_4	δ scissoring PF_2
		[384 + 15] ^c			
1318 (0+)	1325 vs	1504 w	1503 vs	$A_1 \nu_5$	τ
501 (2)	494 s	539 m	540 s	$B_1 \nu_6$	asym PO_2 str
851 (0.7)	850 sh	888 w	886 vs	ν_7	δ rock PF_2
830 (1.2)	825 vs			$B_2 \nu_8$	asym PF_2 str ^d
501 (2)	508 s	544 m	544 s	ν_9	δ rock PO_2

^a Data from this study; uncorrected Raman intensities; since ν_1 and ν_4 have very similar frequencies and intensities, their assignments are tentative. ^b Data from ref 36–38. ^c From microwave data. ^d In Fermi resonance with $\nu_4 + \nu_9 (B_2) = 854 \text{ cm}^{-1}$.

filtration at this temperature. The HF solvent was pumped off from the filtrate at -30°C for 3 h, leaving behind a white solid residue. The thermal stability of this residue was established by incremental warm-up of the solid in a dynamic vacuum and by trapping, measuring (PVT), and identifying (infrared spectroscopy) the volatile decomposition products. Up to 0°C , only HF and small amounts of NF_3 were collected, indicating the possible presence of small amounts of unstable $\text{NF}_4\text{HF}_2\cdot\text{HF}^{22}$ in the product. At temperatures of 9°C or higher, significant decomposition of the solid was observed, producing equimolar amounts of NF_3 and FOSO_2F . When we allow for about 20% of the product solution to be retained, as generally seems to be the case with similar metathetical reactions,²² by the filter cake and to be lost during solvent pump-off, the yield of NF_3 and FOSO_2F was essentially quantitative. The filter cake (1.0 g, weight calculated for 3.15 mmol of $\text{CsSbF}_6 = 1.16 \text{ g}$) was shown by vibrational spectroscopy to be CsSbF_6^{28} and did not show any detectable impurities.

Caution! FOSO_2F has been reported^{29,30} to have explosive properties. The compound should therefore be handled with appropriate safety precautions.

For the spectroscopic identification of $\text{NF}_4\text{SO}_3\text{F}$, reactions were carried out on a 1-mmol scale in a previously described²² manner. The ^{19}F NMR spectrum of a solution of $\text{NF}_4^+\text{SO}_3\text{F}^-$ in HF at -30°C showed the signals characteristic for NF_4^+ (triplet of equal intensity at $\phi = -215$ with $J_{\text{NF}} = 226 \text{ Hz}$ and a line width of less than 3 Hz),⁹ SO_3F^- (singlet at $\phi = -33.5$), and HF (broad singlet at $\phi = 193$). No evidence for the presence of $\text{FOSO}_2\text{F}^{27}$ was observed. The Raman spectra of the HF solution at 25°C and of solid $\text{NF}_4\text{SO}_3\text{F}$ at -100°C were also recorded and are shown in Figure 1. The spectra showed the presence of only small amounts of CsSbF_6^{28} , indicating a purity of $\text{NF}_4\text{SO}_3\text{F}$ in excess of 90 wt %, in agreement with the observed material balance. Raman and ^{19}F NMR spectra of HF solutions of $\text{NF}_4\text{SO}_3\text{F}$, which were kept at 25°C for several days, showed no evidence of FOSO_2F formation.

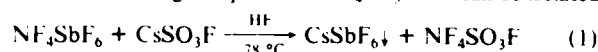
Reaction of Cs_2SO_4 with HF. The Cs_2SO_4 salt was found to be highly soluble in HF. Raman spectra of these solutions and of the solid residue obtained after the solvent removal showed the complete absence of the SO_4^{2-} anion²⁸ and the presence of the SO_3F^- anion.²⁶ The presence of the SO_3F^- anion in the HF solution was confirmed by ^{19}F NMR spectroscopy which showed a strong singlet at $\phi = -33.8$, characteristic for SO_3F^- .

Reaction of CsPO_3F_2 with HF. A sample of CsPO_3F_2 (2.1 mmol) was treated with anhydrous HF (3 mL of liquid) for 12 h at 25°C . The white solid residue, left behind after removal of the solvent, was identified by its infrared and Raman spectrum as CsPF_6^{28} (2.1 mmol) and did not contain detectable amounts of PO_3F_2 .^{31,33}

Results and Discussion

The novel salt $\text{NF}_4^+\text{SO}_3\text{F}^-$ was prepared from NF_4SbF_6 and

CsSO_3F by low-temperature metathesis in anhydrous HF solution according to eq 1. The $\text{NF}_4\text{SO}_3\text{F}$ salt can be isolated



as a white solid which is stable at 0°C but slowly decomposes at $+10^\circ$ to produce NF_3 and FOSO_2F in high yield according to eq 2. Its HF solution appears to be stable at ambient



temperature. The thermal stability of $\text{NF}_4\text{SO}_3\text{F}$ is very similar to that²² of NF_4ClO_4 . This is not surprising since SO_3F^- and ClO_4^- are isoelectronic and chemically very similar. This chemical similarity is also demonstrated by their decomposition modes, which in both cases produce the corresponding hypofluorites in high yield.

The decomposition of $\text{NF}_4^+\text{SO}_3\text{F}^-$ represents a new, high-yield, convenient synthesis of FOSO_2F . The previously reported methods for the preparation of FOSO_2F involved either the fluorination of $\text{SO}_3^{34,35}$ or $\text{S}_2\text{O}_8\text{F}_2$.³⁶ $\text{NF}_4\text{SO}_3\text{F}$ is the third known example of an NF_4^+ salt of an oxyanion producing on thermal decomposition the corresponding hypofluorite. The other two known examples are $\text{NF}_4\text{ClO}_4^{22}$ and $\text{NF}_4\text{IF}_6\text{O}_2$.²³ This indicates that the thermal decomposition of unstable NF_4^+ salts of oxyanions may be a general method for the synthesis of hypofluorites.

The ionic nature of $\text{NF}_4\text{SO}_3\text{F}$, both in the solid state and in HF solution, was verified by Raman and ^{19}F NMR spectroscopy. The Raman spectra are shown in Figure 1 and demonstrate the presence of the bands characteristic for NF_4^+ ^{9,22} and SO_3F^- .²⁶ The observed frequencies and their assignments are summarized in Table I. The SO_3F^- bands in $\text{NF}_4\text{SO}_3\text{F}$ are very similar to those observed for CsSO_3F (see Figure 1). The minor frequency shift observed for the SF stretching mode is not surprising in view of a previous infrared study of the alkali metal salts which showed that the frequency of this fundamental strongly depends on the nature of the cation and varied from 812 cm^{-1} in LiSO_3F to 715 cm^{-1} in CsSO_3F .²⁶ The observed splitting of some of the modes of both the NF_4^+ cation and the SO_3F^- anion into their degenerate components is easily explained by solid-state effects and has also been observed for $\text{NF}_4^+\text{ClO}_4^{22}$.

The ^{19}F NMR spectrum of $\text{NF}_4^+\text{SO}_3\text{F}^-$ in HF solution showed a triplet of equal intensity at $\phi = -215$ with $J_{\text{NF}} = 226 \text{ Hz}$ and a line width of less than 3 Hz, characteristic⁹ for NF_4^+ , a singlet at $\phi = -33.5$, characteristic for SO_3F^- , and the char-

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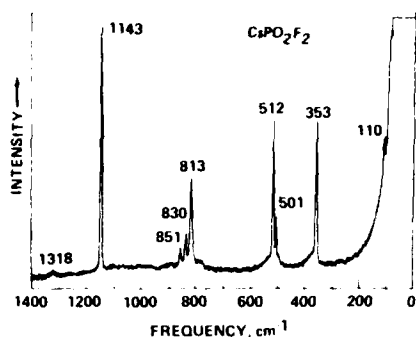
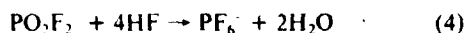
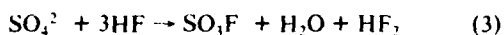


Figure 2. Raman spectrum of solid CsPO_2F_2 recorded at 25 °C with a spectral slit width of 5 cm^{-1} .

acteristic HF signal at ϕ 193. The assignment of the ϕ -33 signal to SO_3F was verified by recording the spectrum of CsSO_3F in HF under the same conditions.

In view of the above-mentioned usefulness of NF_4^+ salts of oxyanions for the preparation of novel hypofluorites, it appeared interesting to attempt the syntheses of $(\text{NF}_4)_2\text{SO}_4$ and $\text{NF}_4\text{PO}_2\text{F}_2$. The thermal decomposition of these two hypothetical salts would offer an opportunity to prepare the yet unknown hypofluorites $\text{SO}_2(\text{OF})_2$ and $\text{POF}_2(\text{OF})$. However, both the SO_4^{2-} and PO_2F_2^- anions were found to interact with anhydrous HF according to eq 3 and 4. Attempts to prepare



$\text{POF}_2(\text{OF})$ by fluorination of HOPOF_2 with atomic fluorine, generated by the controlled decomposition of $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$,²² were also unsuccessful. The main products were NF_4PF_6 ⁹ and an unidentified nonvolatile phosphorus oxyfluoride.

Although vibrational spectra have been reported³¹⁻³³ for the PO_2F_2^- anion, the previous assignment of several fundamentals is open to question. Figure 2 and Table II summarize the vibrational spectra of CsPO_2F_2 , obtained in our study. The given assignment was made by analogy with that of isoelectronic SO_2F_2 which is well established.³⁷⁻³⁹ Whereas, the splitting of $\nu_8(\text{B}_2)$ can easily be explained by Fermi resonance with $(\nu_4 + \nu_9)(\text{B}_2)$, the reason for the observed splitting of ν_4 is less obvious. The possibility of one of the components assigned to ν_4 actually being due to the $\nu_5(\text{A}_2)$ torsional mode cannot be ruled out but is unlikely due to the facts that this mode should be infrared inactive under C_2 selection rules and usually is of such low intensity in the Raman spectra that it is very difficult to observe.

In summary, the present study shows that within the isoelectronic series ClO_4^- , SO_3F^- , PO_2F_2^- , SO_4^{2-} , the first two anions are capable of forming NF_4^+ salts of moderate stability which can decompose to NF_3 and the corresponding hypofluorites. The syntheses of $\text{NF}_4\text{PO}_2\text{F}_2$ and $(\text{NF}_4)_2\text{SO}_4$ by metathesis in HF were prevented by the reaction of PO_2F_2^- and SO_4^{2-} with the solvent to yield PF_6^- and SO_3F^- , respectively.

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Registry No. $\text{NF}_4^+\text{SO}_3\text{F}^-$, 74096-76-7; CsSO_3F , 13530-70-6; CsPO_2F_2 , 17117-59-8; NF_4SbF_6 , 16871-76-4; NF_3 , 7783-54-2; FOSO_2F , 13536-85-1; Cs_2SO_4 , 10294-54-9; CsPF_6 , 16893-41-7.

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

Synthesis and Characterization of $(\text{NF}_4)_2\text{MnF}_6$

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The synthesis of novel NF_4^+ salts containing doubly or triply charged 3d transition-metal fluoride anions was studied. The new compound $(\text{NF}_4)_2\text{MnF}_6$ was prepared and characterized. The combination of good thermal stability and high active fluorine content makes $(\text{NF}_4)_2\text{MnF}_6$ an outstanding solid oxidizer.

Introduction

Due to the high-energy kinetic stability of the NF_4^+ cation,¹ NF_4^+ salts are important high-energy oxidizers. In order to maximize the oxidizing power of such salts, it is desirable to combine as many NF_4^+ cations as possible with a given anion. Furthermore, the anion should be as light as possible and also be an oxidizer. Of the presently known NF_4^+ salts,² $(\text{NF}_4)_2\text{NiF}_6$ ³ has the highest active fluorine content or oxidizing capacity. However, its marginal thermal stability limits its usefulness. Consequently, compounds having comparable fluorine content but possessing better thermal stability are highly desirable. This paper describes the results of a systematic study on the synthesis of NF_4^+ salts derived from 3d transition-metal fluorides and the successful synthesis of the novel $(\text{NF}_4)_2\text{MnF}_6$ salt.

Experimental Section

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.^{1,2} A literature method⁴ was used for the synthesis of NF_4SbF_6 . For the synthesis of Cs_2MnF_6 , a previously reported method⁵ was slightly modified. Anhydrous MnCl_2 and dry CsF , in a 1:2 mole ratio, were fluorinated in a Monel cylinder at 400 °C for 36 h by using a MnCl_2/F_2 mole ratio of 1:10. On the basis of the observed material balance, elemental analysis, X-ray diffraction powder pattern, and vibrational spectra, the resulting yellow solid consisted of high-purity Cs_2MnF_6 .

The Cs_2CuF_6 salt was prepared by high-pressure fluorination of a mixture of CsF and CuCl_2 in a 2:1 mole ratio. The conditions (400 °C, 18 h, 130 atm) were similar to those⁶ previously reported. However, during unsuccessful attempts to prepare Cs_2CuF_6 in a similar manner, it was noticed that very mild fluorination conditions (flow reactor, 200 °C) sufficed to prepare Cs_2CuF_6 . This brick red compound was always formed as the major product, instead of the pale green Cs_3CuF_6 . At the lower fluorination temperatures, the fluorination product also contained CsHF_4 . The infrared spectrum of Cs_2CuF_6 showed major bands at 670, 570, 480, and 430 cm^{-1} . The compatibility of Cs_2CuF_6 with different solvents was studied. In BrF_3 , Cs_2CuF_6 is stable but highly insoluble, whereas in anhydrous HF , it is soluble but undergoes a reaction even at -78 °C, resulting in the formation of a brown solid. When the Cs_2CuF_6 HF solutions were warmed to room temperature, fluorine evolution was observed, in agreement with a previous report.⁷

Preparation of $(\text{NF}_4)_2\text{MnF}_6$. In the N_2 atmosphere of a drybox a mixture of NF_4SbF_6 (37.29 mmol) and Cs_2MnF_6 (18.53 mmol) was placed into the bottom of a prepassivated (with ClF_3) Teflon FEP double U-tube metathesis apparatus. Dry HF^8 (20 ml of liquid) was

added at -78 °C on the vacuum line, and the mixture was warmed to 25 °C for 30 min with stirring. The mixture was cooled to -78 °C and pressure filtered at this temperature. The HF solvent was pumped off at 30 °C for 12 h. The white filter cake (14 g, weight calculated for 37.1 mmol of CsSbF_6 = 13.7 g) was shown by Raman spectroscopy to consist mainly of CsSbF_6 . The yellow filtrate residue (6.1 g, weight calculated for 18.5 mmol of $(\text{NF}_4)_2\text{MnF}_6$ = 6.46 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; CsSbF_6 , 4.46. For the elemental analysis, a sample of $(\text{NF}_4)_2\text{MnF}_6$ was hydrolyzed in H_2O ; the NF_3 and O_2 evolution was measured by *PVT* and gas chromatography, and Cs, Sb, and Mn in the hydrolysate were determined by atomic absorption spectroscopy. Anal. Calcd for $[(\text{NF}_4)_2\text{MnF}_6]_{0.72}[(\text{NF}_4\text{SbF}_6)_{0.27}][(\text{CsSbF}_6)_{0.46}]$: NF_3 , 38.07; Mn, 14.37; Sb, 3.07; Cs, 1.61. Found: NF_3 , 37.8; Mn, 14.5; Sb, 3.10; Cs, 1.62.

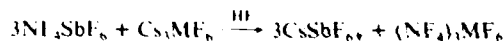
Caution! The reaction of $(\text{NF}_4)_2\text{MnF}_6$ with H_2O is extremely violent, and proper safety precautions must be used.

The $\text{CoF}_3/\text{NF}_4\text{HF}_2$ System. A suspension of CoF_3 (231 mg = 2 mmol) in a freshly prepared concentrated NF_4HF_2 HF solution⁹ (15 mmol of NF_4HF_2) was stirred at 45 °C for 4 h. The tan CoF_3 did not appear to react, and no evidence for the formation of pale blue CoF_6^{3-} was observed. The HF solvent was pumped off while the mixture was allowed to warm slowly toward ambient temperature. At this temperature, the $\text{NF}_4\text{HF}_2/\text{HF}$ underwent decomposition and was also pumped off. To ensure complete decomposition of NF_4HF_2 , we warmed the mixture to 45 °C for 4 h under a dynamic vacuum. The tan solid residue (230 mg) was shown by vibrational spectroscopy to be unreacted CoF_3 .

Results and Discussion

In view of the marginal thermal stability of $(\text{NF}_4)_2\text{NiF}_6$ it was interesting to investigate the possibility of synthesizing other NF_4^+ salts containing multiply charged anions derived from higher oxidation state transition-metal fluorides. It was hoped to obtain a salt which would be comparable to $(\text{NF}_4)_2\text{NiF}_6$ in its active fluorine content but possess better thermal stability. The following anions were considered most promising: CuF_6^{3-} , NiF_6^{3-} , CoF_6^{3-} , MnF_6^{3-} , CuF_6^{2-} , CoF_6^{2-} , and MnF_6^{2-} .

Attempted Syntheses of $(\text{NF}_4)_2\text{MF}_6$ Salts. In a previous study,⁷ it was shown that the above listed triply charged anions undergo solvolysis in HF . Furthermore, it was found that CuF_6^{3-} decomposed with F_2 evolution and NiF_6^{3-} disproportionated with NiF_6^{2-} formation but that for CoF_6^{3-} the solvolysis to $\text{CoF}_4 + 2\text{HF}_2$ could be suppressed by the addition of a 10–20-fold excess of fluoride ion to the solution. In view of these results, a simple metathetical reaction of an MF_6^{3-} salt in HF solution according to

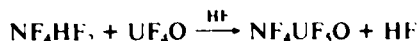


is preempted by the unavoidable solvolysis of MF_6^{3-} . However, the synthesis of a CoF_6^{3-} salt might be possible in the presence of a large excess of fluoride ion, provided the excess of fluoride can be readily removed from the product. Such a method was

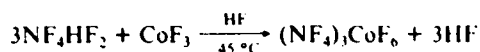
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recently discovered⁹ and successfully applied to the synthesis of NF₄UF₅O according to



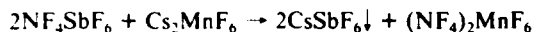
NF₄HF₂ is thermally unstable² and decomposes at 30 °C to NF₃, F₂, and HF, which are all gases. Therefore, the HF solvent can be pumped off first at low temperature, followed by decomposition and removal of the excess NF₄HF₂. Application of this method to the synthesis of (NF₄)₂CoF₆ according to



was unsuccessful, and no evidence for the formation of a cobalt-containing NF₄⁺ salt was obtained. Only unreacted CoF₃ was recovered.

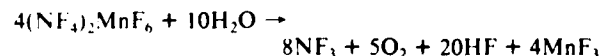
Syntheses of (NF₄)₂MF₆ Salts. Since the MF₆²⁻ anions contain one negative charge less than the MF₆³⁻ ones, they are less basic and, therefore, are less likely to undergo solvolysis in the strongly acidic solvent HF. The compatibility of TiF₆²⁻ and NiF₆²⁻ with HF has previously been demonstrated^{3,7,10} and led to the successful syntheses of (NF₄)₂TiF₆¹⁰ and (NF₄)₂NiF₆.³ During this study the compatibility of Cs₂CuF₆ with HF was studied. It was found that Cs₂CuF₆ reacts, even at low temperature, with HF to form a dark brown solid. At room temperature, decomposition with fluorine evolution occurs. The compatibility of Cs₂CoF₆ with HF was not examined since Court had previously shown⁷ that this salt is unstable in HF solution.

In agreement with a previous report,⁷ MnF₆²⁻ was found to be stable in HF solution. Consequently, the metathetical reaction



was carried out which resulted in the isolation of the novel (NF₄)₂MnF₆ salt. Since the impurities NF₄SbF₆ and CsSbF₆ are well characterized, no attempts were undertaken to purify the compound by well-established⁴ recrystallization techniques.

Properties of (NF₄)₂MnF₆. The (NF₄)₂MnF₆ salt is a yellow, crystalline solid which is highly soluble in anhydrous HF. At 24 °C, its solubility exceeds 1.30 g/g of HF. It is stable at room temperature, and, in the absence of fuels, it is not shock sensitive. With water a violent reaction occurs, similar to that previously reported³ for (NF₄)₂NiF₆. By analogy with the other known NF₄⁺ salts, the hydrolysis was found to result in quantitative NF₃ evolution and, therefore, is a useful analytical method. The hydrolysis also produced oxygen in a NF₃:O₂ mole ratio of 8:5 in excellent agreement with the equation



Thermal Decomposition. At 65 °C, (NF₄)₂MnF₆ appears to be stable, but at about 100 °C it starts to slowly decompose. Its decomposition rate in a sapphire reactor was monitored by total pressure measurements over the temperature range 100–130 °C. Except for a slightly faster rate during the first 20 min, 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 h, whereas, at 130 °C, 0.66% of the sample decomposed in the same time. The gaseous decomposition products consisted of NF₃ and F₂ in a mole ratio of about 1:1.2. For identification of the solid residue, a sample of (NF₄)₂MnF₆

Table I. X-ray Powder Data for (NF₄)₂MF₆ Salts (M = Mn, Ge, Ti, Sn)^a

	tetragonal unit cell dimensions			vol./f, Å ³	calcd density, g/cm ³
	a, Å	c, Å	V, Å ³		
(NF ₄) ₂ TiF ₆	6.99	9.28	453	16.2	2.51
(NF ₄) ₂ MnF ₆	6.90	9.23	440	15.7	2.64
(NF ₄) ₂ NiF ₆ ^b	6.83	9.27	432	15.4	2.71
(NF ₄) ₂ GeF ₆	6.92	9.25	443	15.8	2.75
(NF ₄) ₂ SnF ₆	7.05	9.41	468	16.7	2.93

Table II. Crystallographic Data of (NF₄)₂MF₆ Salts (M = Ti, Mn, Ni, Ge, Sn)^a

	tetragonal unit cell dimensions			vol./f, Å ³	calcd density, g/cm ³
	a, Å	c, Å	V, Å ³		
(NF ₄) ₂ TiF ₆	6.99	9.28	453	16.2	2.51
(NF ₄) ₂ MnF ₆	6.90	9.23	440	15.7	2.64
(NF ₄) ₂ NiF ₆ ^b	6.83	9.27	432	15.4	2.71
(NF ₄) ₂ GeF ₆	6.92	9.25	443	15.8	2.75
(NF ₄) ₂ SnF ₆	7.05	9.41	468	16.7	2.93

^a Space group *I4/m* (No. 87); *Z* = 2. ^b Data from ref 13.

was completely decomposed under a dynamic vacuum at 240 °C. On the basis of its weight, X-ray powder diffraction pattern,¹¹ and mauve color, this residue was identified as MnF₃. Consequently, (NF₄)₂MnF₆ decomposes according to



A comparison with the decomposition data previously published³ for (NF₄)₂NiF₆ shows that the normal stability of (NF₄)₂MnF₆ is significantly higher than that of (NF₄)₂NiF₆, which in 6 h at 100 °C exhibited 9% decomposition.

Crystallographic Data. The X-ray powder diffraction pattern of (NF₄)₂MnF₆ are listed in Table I. The pattern is very similar to those of other (NF₄)₂MF₆ salts (M = Ge, Ti, Sn, Ni),^{3,5,10,12,13} indicating that these salts are isotypic. Recent studies on both powdered and single-crystal (NF₄)₂NiF₆ have shown that this compound crystallizes in a tetragonal form derived from the K₂PtCl₆ structure and belongs to space group *I4/m*. Consequently, the indexing, previously proposed for the (NF₄)₂MF₆ salts (M = Ge, Ti, Sn, Ni),^{3,5,10,12} was revised according to ref 13. The revised patterns and the crystallographic data are given in Tables I and II, respectively. Some of the additional lines, previously observed,^{3,4,10,12} were found to be due to small amounts of polyanion salts such as (NF₄)₂Ge₂F₁₀ or (NF₄)₂Sn₂F₁₀. As expected, the size of the unit cell decreases from (NF₄)₂TiF₆ to (NF₄)₂NiF₆ owing to the transition-metal contraction and then increases again when going from Ni to the main-group elements.

NMR Spectrum. The ionic nature of (NF₄)₂MnF₆ in HF solution was established by its ¹⁹F NMR spectrum which was recorded over the temperature range +20 to -75 °C. It showed at all temperatures a broad resonance at δ -218 (downfield from external CFCl₃), characteristic of NF₄⁺. The lack of observable NF spin-spin coupling, generally seen for

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Table III. Vibrational Spectra of Solid $(\text{NF}_4)_2\text{MnF}_6$ and Cs_2MnF_6

obsd freq. cm^{-1} , and rel intens ^a				assign ^b (point group)	
$(\text{NF}_4)_2\text{MnF}_6$		Cs_2MnF_6		NF_4^+ (T_d)	MnF_6^{2-} (O_h)
IR	Raman	IR	Raman		
2310 vw				$2\nu_1 (A_1 + E + T_2)$	
2000 w				$\nu_2 + \nu_3 (E_g)$	
1759 vw				$\nu_3 + \nu_4 (A_1 + E + T_2)$	
1466 w				$\nu_1 + \nu_4 (E_g)$	
1221 mw				$2\nu_4 (A_1 + E + T_2)$	
		1240 sh			$\left. \begin{array}{l} \nu_1 + \nu_2 (E_{gu}) \\ \nu_2 + \nu_3 (E_{gu} + E_{gu}) \end{array} \right\}$
		1202 vw		$\nu_1 (E_g)$	
1160 vs		1155 vw			$\left. \begin{array}{l} \nu_2 + \nu_3 (E_{gu} + E_{gu}) \\ \nu_1 + \nu_4 (E_{gu}) \end{array} \right\}$
1110 sh		1116 w		$\nu_2 + \nu_4 (E_g + E_g)$	
1061 vw				$\nu_1 (A_1)$	$\nu_1 + \nu_4 (E_{gu})$
915 vw		919 vw			$\left. \begin{array}{l} \nu_2 + \nu_3 (E_{gu} + E_{gu}) \\ \nu_1 (E_{gu}) \\ \nu_1 (A_{1g}) \end{array} \right\}$
856 vvw	855 m	745 sh		$\nu_1 (E_g)$	
760 sh		732 w			
735 sh		620 vs		$\nu_1 (E_g)$	$\nu_1 (E_{gu})$
620 vs	593 vs		590 vs		$\nu_1 (A_{1g})$
		569 vw			$\nu_1 (E_{gu})$
500 vw	505 m		502 m	$\nu_2 (E_g)$	$\nu_1 (E_{gu})$
450 vw	450 w				$\nu_1 (E_{gu})$
338 s	304 s	381 vw			$\nu_1 (E_{gu})$
		338 s			$\nu_1 (E_{gu})$
			304 s		$\nu_1 (E_{gu})$

^a Uncorrected Raman intensities. ^b By analogy with $(\text{NF}_4)_2\text{NiF}_6^{13}$ the actual site symmetries of NF_4^+ and MnF_6^{2-} are probably S_4 and C_{4h} , respectively, thus explaining the observed slight deviations from the selection rules for T_d and O_h .

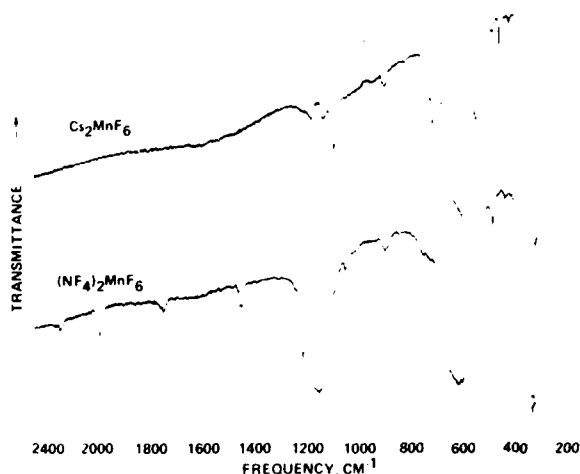


Figure 1. Infrared spectra of solid Cs_2MnF_6 and $(\text{NF}_4)_2\text{MnF}_6$ recorded at 25 °C as dry powders pressed between AgCl disks. The broken lines indicate absorption due to the window material.

tetrahedral NF_4^+ ,^{14,15} is attributed to the influence of the paramagnetic MnF_6^{2-} anion which can provide rapid relaxation.

Vibrational Spectra. 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 for NF_4^+ ¹² and MnF_6^{2-} .¹⁶

Figure 1 shows the infrared spectrum of $(\text{NF}_4)_2\text{MnF}_6$, compared to that of Cs_2MnF_6 . Great difficulties were encountered in obtaining good-quality Raman spectra with the blue 4880-Å exciting line of our spectrometer due to strong luminescence¹⁶ (ruby red light emission). However, the principal Raman lines of NF_4^+ ¹² and MnF_6^{2-} ¹⁶ were observable even under these conditions. The observed vibrational frequencies and their assignments are summarized in Table III. Since the assignments of NF_4^+ ¹² and MnF_6^{2-} ¹⁶ are well established, no further discussion is required.

Summary

The present study shows that, in HF solution, solvolysis preempts the metathetical synthesis of NF_4^+ salts containing triply charged MF_6^{3-} anions derived from 3d transition-metal fluorides. On the other hand, three NF_4^+ salts derived from doubly charged MF_6^{2-} anions are accessible by this method. These salts are $(\text{NF}_4)_2\text{TiF}_6$,¹⁰ $(\text{NF}_4)_2\text{MnF}_6$, and $(\text{NF}_4)_2\text{NiF}_6$.³ All of them are stable at room temperature, with $(\text{NF}_4)_2\text{NiF}_6$ possessing the lowest thermal stability. The existence of stable NF_4^+ salts of TiF_6^{2-} , MnF_6^{2-} , and NiF_6^{2-} can be explained by the favorable d^0 , d^3 (high-spin) and d^6 (low-spin) electron configurations, respectively, of these anions. The combination of good thermal stability with high active fluorine content (1.58 g/cm³) renders $(\text{NF}_4)_2\text{MnF}_6$ a very attractive candidate for solid oxidizer applications.

Acknowledgment. The authors are indebted to Drs. C. J. Schack, L. R. Grant, and M. Lustig for helpful discussion, to Mr. R. Rushworth for the elemental analyses, and to the Army Research Office for financial support.

Registry No. $(\text{NF}_4)_2\text{MnF}_6$, 74449-37-9; NF_4SbF_6 , 16871-76-4; Cs_2MnF_6 , 16962-46-2; CsSbF_6 , 16949-12-5.

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Evidence for the Existence of Directional Repulsion Effects by Lone Valence Electron Pairs and π Bonds in Trigonal-Bipyramidal Molecules

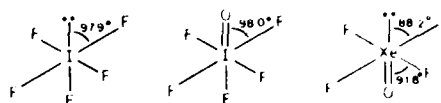
Sir:

The Gillespie-Nyholm valence-shell electron-pair-repulsion (VSEPR) theory^{1,2} is very useful for explaining the basic structural features of many classes of inorganic compounds. The theory assumes that the geometry around a given central atom is determined by the number of electron pairs in its valence shell which are arranged as "points-on-a-sphere" in a manner to minimize the mutual repulsion energy. The finer details of the structure are predicted by assuming lone or nonbonding electron pairs to be more repulsive than single bonds, with double bonds being almost as repulsive as the lone pairs. Since the valence electron pairs are treated as points, their repulsive effect is assumed to be directionally independent. This approximation holds well for highly symmetric molecules such as octahedrons or tetrahedrons and for valence electron pairs which are cylindrically symmetric with respect to their axes. However, if a molecule possesses a structure of lower symmetry such as a trigonal bipyramid and if the valence electron pair is not cylindrically symmetric such as the π bonds of double bonds, directional repulsion effects can be expected which should depend on the nature of the orbital and its electron density distribution.

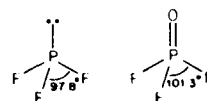
Contrary to the ligands in a tetrahedron or octahedron, those in a trigonal-bipyramidal molecule, when arranged as being equidistant from each other, are no longer on the surface of a sphere and become nonequivalent. The two axial ligands have a greater (ideally by a factor of $2^{1/2}$) central atom-ligand bond length than the three equatorial ligands. Consequently, an equatorial ligand possesses two nonequivalent pairs of neighbors, one axial one of greater bond length and ideally at 90° angles and one equatorial one of shorter bond length and ideally at 120° angles.

In this correspondence, two cases are presented which are strong evidence for the existence of directional repulsion effects in trigonal-bipyramidal molecules. These two cases are (i) a comparison of the structures of SF_4 ^{3,4} and $\text{X}=\text{SF}_4$ (where X is O or CH_3)^{5,10} and (ii) the structure of ClF_3O .¹¹ In the first case, the relative repulsion of the axial and of the equatorial fluorine ligands by either the π bonds of a double bond or a free valence electron pair is compared, whereas in the second case, the combined effect of a lone pair and of a doubly bonded oxygen is described.

For a meaningful comparison, we must first establish the relative repulsive strength of a lone valence electron pair and of a doubly bonded oxygen in the absence of directional effects. Inspection of the known structures of IF_5 ,¹² and $\text{IF}_5\text{O}^{13} and of XeOF_4 ¹⁴$

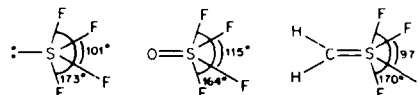


shows that in these pseudooctahedral molecules the repulsive strengths of a lone valence electron pair and of a doubly bonded oxygen are very similar and that, as demonstrated for XeOF_4 , the oxygen can be even slightly more repulsive than a free valence electron pair. In the pseudotetrahedral molecules PF_3 and PF_3O ,² the free valence electron pair appears to be somewhat more repulsive than oxygen:



The above examples show that, for practical purposes, the nondirectional repulsive strengths of a free valence electron pair and of a doubly bonded oxygen are comparable. For a more precise comparison, effects such as changes in the oxidation state of the central atom or in the hybridization of the orbitals should be eliminated. This is best achieved by selecting a compound such as XeOF_4 containing both a free valence electron pair and doubly bonded oxygen at the same time. In this manner, their relative repulsive strengths can be compared under identical conditions.

Returning to the less symmetric case of trigonal-bipyramidal molecules, let us consider the structures of SF_4 , $\text{O}=\text{SF}_4$, and $\text{H}_2\text{C}=\text{SF}_4$:



As recently pointed out by Oberhammer and Boggs,⁶ the FSF bond angles are surprisingly different in these molecules but could be well duplicated by ab initio MO calculations. These calculations showed that the observed differences in the structures of $\text{O}=\text{SF}_4$ and $\text{H}_2\text{C}=\text{SF}_4$ can be satisfactorily explained by the different population of the $\text{X}=\text{S}$ π -bond orbitals in the equatorial and the axial plane (OSF_4 , $\pi_{\text{eq}} = 0.17$ au, $\pi_{\text{ax}} = 0.12$ au; $\text{H}_2\text{C}=\text{SF}_4$, $\pi_{\text{eq}} = 0.23$ au, $\pi_{\text{ax}} = 0.02$ au).

The comparatively small $\text{F}_\text{ax}\text{SF}_\text{eq}$ bond angle of SF_4 can be rationalized in the following manner. A lone electron pair can be delocalized rather easily, as shown, for example, by the structure of BrF_6^- ¹⁵ as opposed to that of IF_6^- .¹⁶ Although

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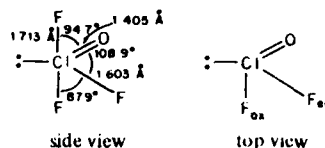
in both ions the central atom possesses a lone valence electron pair, the size of bromine permits only a maximum coordination number of 6 (toward fluorine) and the lone pair in BrF_6^- is sterically inactive and centrosymmetric. In IF_6^- , the larger central atom can readily accept seven or eight ligands, as demonstrated by the existence of IF_7 and IF_8^- ,^{17,18} and, therefore, the lone valence electron pair becomes sterically active and acts as a ligand. On the assumption of a similar ease of delocalization of the free valence electron pair in trigonal-bipyramidal arrangements, a free valence electron pair can then be expected to possess little directional repulsive selectivity and to compress preferentially the most compressible bond angle. In an idealized SF_4 structure, the 120° equatorial FSF angle obviously should be compressed more easily than the 90° angles formed between the axial ligands and the fluorine containing equatorial plane.

On the other hand, the π orbitals of an $\text{S}=\text{X}$ double bond are more localized and concentrated between the sulfur and the X atom in the equatorial and the axial planes of the molecule. Depending on the relative population of these orbitals, preferential repulsion of either the axial or the equatorial fluorines is possible. Thus, the "shape" of the $\text{S}=\text{X}$ π bond is responsible for the preferred direction of the repulsion effect and must be considered when the structure of an unknown molecule is predicted.

In view of these directional repulsion effects, the change in a single bond angle is not a good measure for the overall repulsive strength of a ligand or a free valence electron pair. Since the repulsion of all the other ligands must be considered, the average quadruple angle¹⁰ should be used for such a comparison. In SF_4 , OSF_4 , and H_2CSF_4 , these average quadruple angles are 111.5° , 110.3° , and 113.3° , respectively, indicating that the overall repulsive strengths of a free valence electron pair and of a $\text{S}=\text{X}$ π bond are, within experimental

error, quite similar but that they strongly differ in their directions.

Since the molecular structure of SF_4O has not yet been established beyond doubt (four models have been proposed on the basis of an electron diffraction study)⁵ and since one might argue that secondary effects such as the difference in the oxidation state of the sulfur central atom might be of importance, the structural study of a trigonal-bipyramidal molecule containing both a lone valence electron pair and a doubly bonded oxygen atom was important. Such a molecule is ClF_3O , the structure of which was recently established.¹¹



The fact that the axial fluorine atoms are repelled more strongly by the oxygen ligand than by the lone pair confirms the existence of directional repulsion effects in trigonal-bipyramidal molecules and supports the conclusions reached from the comparison of the SF_4 , OSF_4 , H_2CSF_4 series.

In summary, in trigonal-bipyramidal molecules, cylindrically nonsymmetric valence electron pairs can result in directional repulsion effects. These effects can be rather pronounced and cannot be accounted for by simple VSEPR theory.^{1,2}

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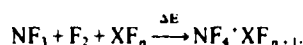
SYNTHESIS AND PROPERTIES OF $\text{NF}_4^+\text{UF}_6\text{O}^-$ WILLIAM W. WILSON, RICHARD D. WILSON and KARL O. CHRISTE*
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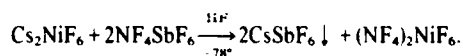
Abstract—A new method for the synthesis of NF_4^+ salts is reported. It permits the synthesis of otherwise inaccessible salts derived from nonvolatile Lewis acids which do not possess HF-soluble cesium salts. The method was successfully applied to the synthesis of the novel salt $\text{NF}_4^+\text{UF}_6\text{O}^-$. This compound is a yellow solid, stable at room temperature. It was characterized by analysis and vibrational spectroscopy.

INTRODUCTION

Most NF_4^+ salts, derived from volatile strong Lewis acids, can be prepared directly from NF_3 , F_2 and the Lewis acid in the presence of a suitable activation energy source [1, 2]:



If the Lewis acid is polymeric and nonvolatile, its NF_4^+ salt can usually be prepared by an indirect metathetical process [3, 4], provided a compatible solvent is available in which the starting materials are soluble and one of the products is insoluble. This metathetical approach has been demonstrated for several NF_4^+ salts [3–7]. A typical example is the synthesis of $(\text{NF}_4)_2\text{NiF}_6$ in anhydrous HF solution [7] using the cesium salts. The latter salts are preferred because they exhibit the most favorable solubility products for a metathesis in HF [4]:



However, in cases where the corresponding cesium salt starting material or both products are insoluble in the solvent and the Lewis acid is nonvolatile, neither one of the above approaches can be used. In this paper a method which circumvents these problems is described and is applied to the synthesis of the novel salt $\text{NF}_4^+\text{UF}_6\text{O}^-$.

EXPERIMENTAL

Materials and apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described [8]. Literature methods were used for the syntheses of UF_6O [9], KUF_6O [10] and NF_4SbF_6 [3]. The CsF (American Potash) was fused in a platinum crucible and ground in the dry box. The HF (Matheson) was dried by treatment with F_2 , followed by storage over BiF_3 to remove last traces of water [4].

Preparation and properties of $\text{NF}_4^+\text{UF}_6\text{O}^-$. In a typical experiment, a solution of NF_4HF_2 (12.5 mmol) in anhydrous HF (12.5 g) was prepared from NF_4SbF_6 and CsF at -78°C , as previously described [8] and added to UOF_4 (6.18 mmol). The resulting mixture was kept at -78°C for 40 hr, then warmed to -31°C for 6 hr with stirring, followed by removal of all volatile products *in vacuo* by slowly raising the temperature from -31 to 20°C . A yellow solid residue (2.70 g, weight calcd for 6.18 mmol of $\text{NF}_4\text{UF}_6\text{O}^- = 2.71$ g) was obtained. This compound was stable at ambient temperature and of low solubility in HF. It was

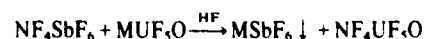
identified by elemental analysis and vibrational spectroscopy as $\text{NF}_4^+\text{UF}_6\text{O}^-$. For the elemental analysis, a weighed amount of sample was hydrolyzed in H_2O and the NF_3 evolution was measured [11]. The hydrolysate was analyzed for Cs and Sb by atomic absorption spectroscopy, and for U gravimetrically as U_3O_8 . Based on this analysis, the composition (wt %) of the yellow solid was: $\text{NF}_4\text{UF}_6\text{O}$, 96.8; NF_4SbF_6 , 1.7; CsSbF_6 , 1.4.

The thermal decomposition of $\text{NF}_4^+\text{UF}_6\text{O}^-$ was studied in a sapphire reactor, equipped with a pressure transducer. The onset and rate of decomposition was determined by total pressure measurements [12] in a closed system over the temperature range 40 – 60°C . For the determination of the decomposition products, a sample of $\text{NF}_4\text{UF}_6\text{O}$ (2 mmol) was rapidly heated to 150°C in a dynamic vacuum, and the volatile products were collected in traps, cooled to -126 and -210°C , and were identified by their IR spectra. The -126°C trap contained 1.1 mmol of UF_6 , and the contents of the -210°C trap consisted of 1.5 mmol of NF_3 and a small amount of OF_2 . The IR spectrum of the pale yellow solid residue (350 mg) showed strong bands characteristic for UF_6O [9], UO_2F_2 [13], NF_4^+ [2–8], and two broad bands at 520 and 410 cm^{-1} , probably due to UF_6 vibrations. In addition, the spectrum indicated the presence of a small amount of UF_6O^- [10, 14, 15].

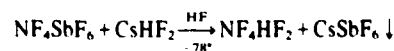
RESULTS AND DISCUSSION

Synthesis

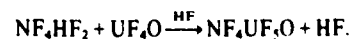
The metathetical synthesis of $\text{NF}_4\text{UF}_6\text{O}$ according to



was not possible because both the MUF_6O (M = Alkali metal) and $\text{NF}_4\text{UF}_6\text{O}$ salts possess very low solubilities in anhydrous HF. Attempts to obtain reasonably pure $\text{NF}_4\text{UF}_6\text{O}$ by a metathetical reaction using stoichiometric amounts of UF_6O , CsF and NF_4SbF_6 in HF as starting materials, were also unsuccessful due to the unfavorable solubilities. However preparation of an HF solution of NF_4HF_2 [8] according to



followed by removal of the insoluble CsSbF_6 by filtration at -78°C and addition of this solution to UF_6O , resulted in $\text{NF}_4\text{UF}_6\text{O}$ of about 97% purity.



A twofold excess of NF_4HF_2 was used to ensure complete conversion of UF_6O to UF_6O^- . After solvent

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Table 1. Vibrational spectra of $\text{NF}_4\text{UF}_5\text{O}$ and KUF_5O and their assignment

Obsd freq, cm^{-1} and rel. intens ^a				Assignment point (group)	
KUF_5O		$\text{NF}_4\text{UF}_5\text{O}$		NF_4^+ (T_d)	UF_5O^- (C_{4v}) ^b
IR	Ra ^b	IR	Ra ^c		
		2310vw		$2\nu_3(A_1 + E + F_2)$	
		2000w		$\nu_1 + \nu_3(F_2)$	
		1765vw		$\nu_3 + \nu_4(A_1 + E + F_2)$	
1630vw		1660vw			$2\nu_1(A_1)$
		1459w		$\nu_1 + \nu_4(F_2)$	
1230vw		1250sh			$\nu_1 + 430$
		1218mw		$2\nu_4(A_1 + E + F_2)$	
		1155vs	1165vw	$\nu_3(F_2)$	
1150vw		1050vw		$\nu_2 + \nu_4(F_1 + F_2)$	$2\nu_2(A_1)$
940m		945mw			(UO_2^{2+})
			850 sh	$\nu_1(A_1)$	
812vs	$\left\{ \begin{array}{l} 815(10) \\ 800 \text{ sh} \end{array} \right.$	834vs	837vs		$\nu_1(A_1)$
			610 sh	$\nu_4(F_2)$	
583vs	$\left\{ \begin{array}{l} 595 \text{ sh} \\ 580(4.4) \end{array} \right.$	600vs	601s		$\nu_2(A_1), \nu_5(A_1)$
480vs, br	$\left\{ \begin{array}{l} 470\text{sh} \\ 460(1.5) \end{array} \right.$	490vs, br	492m		$\nu_8(L)$
			450w	$\nu_2(E)$	
425w	425(0.8)	431w	435w		
370m	365(2)	360m			

(a) uncorrected Raman intensities

(b) data from ref 15

(c) recorded with 4880 Å exciting line at -100 and 25°C

removal, the excess of unreacted NF_4HF_2 was decomposed [8] at 40°C to NF_3 , F_2 and HF which were pumped off.

Properties

$\text{NF}_4\text{UF}_5\text{O}$ is a yellow, crystalline solid, stable up to about 50°C. Its composition was established by elemental analysis. The ionic nature of the salt was demonstrated by vibrational spectroscopy which showed the presence of the NF_4^+ cation [2-8] and UF_5O^- anion [10, 14, 15]. For comparison, a sample of KUF_5O was prepared from KF and UF_4O in HF , as previously reported [10], and its spectra were also recorded. The IR spectra of $\text{NF}_4\text{UF}_5\text{O}$ and KUF_5O are shown in Fig. 1, and the observed IR and Raman frequencies are summarized in Table 1. The recording of the Raman spectra with the available exciting line (4880 Å) was very difficult due to fluorescence, strong color and poor scattering.

The assignments of the bands due to NF_4^+ are well established [2-8] and require no further discussion. For the UF_5O^- anion, the previously proposed [15] assignments were adopted. The IR spectrum of $\text{NF}_4\text{UF}_5\text{O}$ shows an IR band at 360 cm^{-1} . The appearance of an IR and Raman active band in this region has previously been interpreted as evidence for anion-anion fluorine bridging resulting in a coordination number of eight about each uranium [15].

The thermal decomposition of $\text{NF}_4\text{UF}_5\text{O}$ was studied

in more detail since the decomposition of NF_4^+ salts containing oxyanions has been shown [8, 16, 17] to be a useful synthetic route to hypofluorites. The $\text{NF}_4\text{UF}_5\text{O}$ salt is stable up to about 50°C, but started to decompose in a sapphire reactor at 60°C at an approximately linear rate, resulting in a pressure build-up of about 4.6 mm Hg per hour for a 2 mmol sample in a 38.7 cm^3 volume. The nature of the decomposition products was established by rapid pyrolysis at 150°C in a dynamic vacuum. The main decomposition products, condensable at -210°C, were NF_3 , UF_6 , and a small amount of OF_2 . The pale yellow solid residue contained UF_4O and UO_2F_2 as the major products. The formation of UF_4O , UF_6 and UO_2F_2 as main decomposition products can be readily explained by assuming



as the primary decomposition step, followed by the well established [9, 18] decomposition of UF_4O



The fact that the recovered amount of UF_6 exceeded that expected from this reaction sequence, can readily be explained by partial fluorination of UF_4O or UF_5O^- by the formed fluorine.

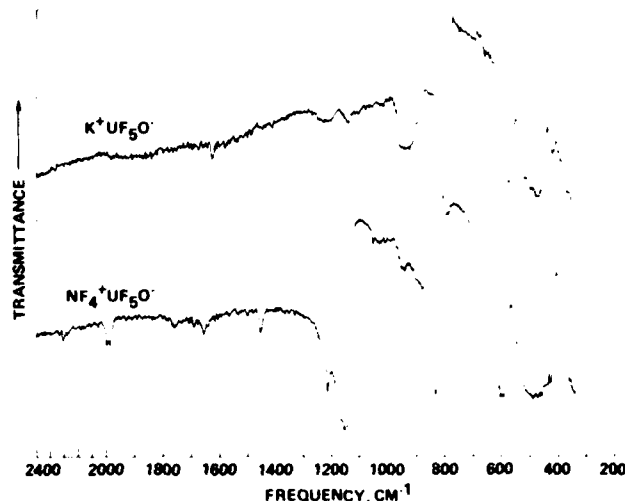


Fig. 1. IR spectra of KUF_6O and $\text{NF}_4^+\text{UF}_6\text{O}^-$ recorded as dry powders pressed between AgCl disks. The broken lines represent absorption due to the AgCl window material.

CONCLUSION

The results of this study show that NF_4^+ salts which are derived from nonvolatile polymeric Lewis acids and are insoluble in HF , are accessible by treating the corresponding Lewis acid with an excess of NF_4HF_2 in HF solution. This approach has also been successfully applied to the synthesis of $\text{NF}_4\text{WF}_6\text{O}$ [19] and might be of general use.

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Determination of Nitrogen Trifluoride in Perfluoroammonium Cation Containing Complex Fluoro Anion Salts

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The NF_4^+ content of complex fluoro anion salts is determined by quantitative measurement of the NF_3 evolved during hydrolysis of 500–1000 mg size samples using gasometric and chromatographic methods. Analytical data are given for NF_4BF_4 , NF_4SbF_6 , NF_4BiF_6 , and NF_4SnF_6 with NF_3 contents ranging from 17 to 40%. These data show a scatter of about ± 2 rel % for the NF_3 analyses. The use of several quantitative, semiquantitative, and qualitative methods for the determination of the anions or for the detection of impurities in the NF_4^+ salts is discussed.

Perfluoroammonium salts are unique. In spite of their unusual oxidizing power, they are capable of forming numerous stable salts. Potential applications of NF_4^+ salts include their use in solid propellant NF_3 - F_2 gas generators for chemical HF-DF lasers (1, 2) and as a fluorinating agent for aromatic compounds (3). Since generally the elemental analyses of powerful oxidizers are difficult to perform, we would like to report the methods developed in our laboratory for analyzing NF_4^+ salts.

EXPERIMENTAL SECTION

Caution. The hydrolysis of NF_4^+ salts is highly exothermic and can be explosive. It must be moderated, as described in the following paragraphs, and appropriate safety precautions must be taken.

Apparatus. The hydrolysis reaction of NF_4^+ salts was carried out in a volume-calibrated stainless steel vacuum line equipped with Teflon FEP U-traps and bellows seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0–760 mm $\pm$ 0.01%). The vacuum line was directly interfaced with the gas chromatograph, F and M Model 700, which was equipped with a $\frac{1}{8}$ in. $\times$ 20 ft column packed with PPQ, 80–100 mesh, and was operated at ambient temperature, with 25 mL/min He and a thermal conductivity detector. Peak area integration was accomplished with a Hewlett-Packard Model 3371 R integrator. Nonvolatile materials were handled outside the vacuum system in the dry nitrogen atmosphere of a glovebox. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line of a Lexel Model 75 Ar ion laser and a Claassen filter (4) for the elimination of plasma lines with sealed glass melting point capillaries as sample containers. Infrared spectra were obtained by using Perkin-Elmer Model 283 or 457 spectrophotometers using a Wilks minipellet press for pressing the dry powders between AgCl disks.

Hydrolysis of the NF_4^+ Salt. The sample to be analyzed (500–1000 mg) was transferred in the glovebox to a previously evacuated, leak-checked, and weighed volume-calibrated Teflon FEP ampule equipped with a stainless steel valve. After removal from the glovebox, the ampule was reevacuated and reweighed. It was attached to the vacuum line, and after the ampule was cooled to -196°C , 2.0 mL of degassed and deionized H_2O was slowly admitted into the sample tube from an inverted bath. The H_2O addition was carried out in such a manner that the water was frozen at -196°C on the upper walls of the tube some distance above the sample. Upon closing of the ampule, the frozen water was knocked down onto the sample. The resulting slush mixture was agitated and carefully warmed toward room temperature. As soon as interaction was noticeable, the mixture was chilled in liquid

Table I. The Determination of NF_3 in Various NF_4^+ Salts by the Gas Chromatographic Method

compound	% NF_3	
	calcd	exptl ^a
NF_4BF_4 ^a	40.16	40.28
NF_4SbF_6 ^b	21.80	21.69
NF_4BiF_6 ^c	21.80	21.71
NF_4BiF_6 ^b	17.19	16.94
NF_4SnF_6 ^d	23.38	23.60

^a From UV photolysis reaction. ^b From direct thermal synthesis. ^c From pyrolysis of $\text{Sb}_2\text{F}_{11}^-$ salt. ^d From displacement reaction. ^e Averaged values from multiple determinations.

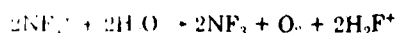
N_2 again to moderate the hydrolysis. Repeating this warming and cooling cycle two or three times accomplished most of the hydrolysis reaction, and at this point the reaction was allowed to go to completion near room temperature.

Determination of the NF_3 - O_2 Content by Gas Chromatography. The tip of the ampule with the resulting hydrolysate was cooled to -78°C . Care was taken that all the hydrolysate was in the tip and that it was frozen to avoid distortion of the ensuing pressure measurement by water vapor pressure. With the solution frozen, the ampule was opened to the calibrated volume of the vacuum line, the gas pressure and temperature were recorded, and the amount of gas was calculated from these PVT measurements. A portion of this gas was analyzed by GC which had previously been calibrated for NF_3 , O_2 , N_2 , and mixtures thereof. Retention times (in minutes) for the gases were as follows: N_2 (2.4), O_2 (2.55), and NF_3 (4.95). The amount of NF_4^+ , originally present in the sample, was calculated from the total amount of gas evolved and the percentage of NF_3 , as found by GC. Analyses carried out on pure samples showed that 1 mol of NF_4^+ generated 1 mol of NF_3 .

Separation of NF_3 and O_2 by Fractional Condensation. The following procedure was also used in place of the gas chromatographic determination of NF_3 and O_2 . After the NF_4^+ salt had been hydrolyzed as described above, the ampule containing the hydrolysis products was cooled to -210°C by a N_2 slush bath prepared by pumping on a Dewar containing liquid N_2 . The contents of the ampule were allowed to slowly warm from -210°C toward 0°C , while the volatile materials were pumped in a dynamic vacuum ($\sim 10^{-4}$ torr) through a series of U-traps kept at -78°C for trapping water vapor and at -210°C for trapping NF_3 . When the hydrolysate in the ampule had melted, the valves between the ampule, the first U-trap, and the second U-trap were closed, and pumping on the second (-210°C) U-trap was continued for another 15 min to remove any trapped oxygen. The -210°C U-trap was then closed off and the contents were allowed to warm to ambient temperature and were measured by PVT.

RESULTS AND DISCUSSION

The analyses of numerous spectroscopically pure NF_4^+ salts of different counterions by the gas chromatographic method have shown (see Table I) that the hydrolysis of NF_4^+ results in quantitative NF_3 evolution according to



The solubility of NF_3 in H_2O is very small (5, 6) and can

therefore be neglected. The hydrolysis reactions must be carefully controlled to avoid violent reactions (7, 8) which (i) are dangerous and (ii) can result in the hydrolysis of some NF_3 to nitrogen oxides. The oxygen evolution was found, even under well-controlled conditions, to be often less than quantitative due to the formation of some H_2O_2 and HOF (2). In addition, certain oxidizing anions, such as NiF_6^{2-} (7), BiF_6^- (2), or MnF_6^{2-} (8) also produced oxygen on hydrolysis. Consequently, determination of the evolved O_2 should not be used for a quantitative determination of the NF_4^+ content.

Two methods were developed for the determination of the amount of NF_3 evolved during hydrolysis. In the first method, the total amount of gas volatile at -78°C is measured by PVT, followed by a gas chromatographic analysis of the gas. In the second method, the evolved NF_3 and O_2 are separated by fractional condensation by use of a -210°C trap; the -210°C trap retains only the NF_3 . The choice of either method depends on the availability of the appropriate equipment.

An error analysis of the method using gas chromatographic separation shows that by far the largest uncertainty stems from the uncertainty in the area integration of the GC peak. This is confirmed by analytical data on high-purity NF_4BF_4 , prepared by low-temperature UV photolysis in a steel-sapphire reactor (9). These data shows a scatter of about ± 2 rel % for the NF_3 analyses.

An error analysis of the second method shows that its accuracy is limited by the effectiveness of the NF_3 - O_2 separation. The NF_3 values obtained for high-purity NF_4BF_4 standards were found to be highly reproducible but were always slightly high due to small amounts (0–0.8 mol %) of residual oxygen, as determined by gas chromatographic analyses of the NF_3 trapped at -210°C .

Despite the minor limitations of either of these two methods, both are well suited for the quantitative determination of NF_3 in NF_4^+ salts.

Often, however, the NF_4^+ -containing salts are obtained by a metathetical reaction (10), rather than in a direct fashion. This results in a product consisting of a mixture of several salts. This fact does not alter the method nor the reliability of the NF_3 determination of such a mixture; however, it does require additional analyses for the remaining constituents using methods such as atomic absorption, X-ray fluorescence spectroscopy, and gravimetry. Typical elements determined in the hydrolysate after the NF_3 analysis include Cs, Ag, B, Sb, Sn, Ti, Ni, Mn, Bi, W, and U. Analyses for the determination of the total fluoride content were not carried out because they do not provide much useful information and require Parr bomb fusion techniques using Na_2O_2 (11, 12) to assure complete hydrolysis of the complex fluoro anions.

If the mixture of the salts to be analyzed can contain polyanions, such as $\text{Sb}_2\text{F}_{11}^-$ (2), $\text{Bi}_2\text{F}_{11}^-$ (2), or $\text{Ti}_2\text{F}_{10}^{2-}$ (13), the mole ratio of total cation central atoms to total anion central atoms provides information about the percentage of polyanions present. The presence of polyanions or of impurities, such as H_3O^+ (14), HF_2^- , or solvated HF, can be further confirmed by qualitative spectroscopic techniques, such as infrared and Raman spectroscopy. The question of which cations are

combined with which anions can be answered by recording the X-ray powder diffraction patterns of the mixture.

Semiquantitative methods for the determination of NF_4^+ and MF_4^+ include Raman and ^{19}F NMR spectroscopy. In the Raman spectra the symmetric stretching mode of tetrahedral NF_4^+ , for example, occurs at about 850 cm^{-1} (15) and always results in an intense and narrow line outside the frequency range of most anion modes. The relative peak height of this line can therefore be taken as a measure of the NF_4^+ concentration, provided that calibration spectra of analyzed samples recorded under identical instrumental conditions are available and that the relative peak heights of the other complex ions are also known. The advantages of this method are its speed and the small amount of sample required. It is routinely used in our laboratory and gives results within a few percent of those obtained by conventional wet analysis techniques. It should be pointed out, however, that this method is not suitable for the detection of weak Raman scatterers, such as HF.

In the ^{19}F NMR spectra of solutions of NF_4^+ salts in solvents, such as anhydrous HF or BrF_3 , a very narrow well-resolved triplet of equal intensity is observed for NF_4^+ at about 220 ppm downfield from external CFCl_3 with a line width of about 5 Hz and $J_{\text{NF}} = 229\text{ Hz}$ (16, 17). It is well suited for accurate peak area integration. However, in many cases rapid fluorine exchange between the complex fluoro anions and the HF solvent preempts the simultaneous determination of the anion concentration, thereby limiting the general applicability of this method.

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The general valence force field of perchloryl fluoride

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Abstract—The i.r. spectra of FCIO_3 in Ne, N_2 and Ar matrices were recorded and the ^{35}Cl – ^{37}Cl isotopic shifts were measured. The Coriolis constants of the E -species vibrations were redetermined and together with the isotopic data used for the computation of a general valence force field. The A_1 block, for which only isotopic frequencies are available, was fixed with the help of *ab initio* force constant calculations. It is shown that ν_2 and ν_3 are best described as an antisymmetric and a symmetric combination, respectively, of the ClF stretching and the ClO_3 bending motions. Comparison with 13 previously published force fields demonstrates the inadequacy of underdetermined force fields for strongly coupled systems, such as FCIO_3 . The ClO and ClF stretching force constants were found to be 9.76 and 3.49 mdyn $\text{\AA}^{-1}$, respectively, in good agreement with those expected for a mainly covalent Cl–F single and Cl=O double bonds.

INTRODUCTION

During a normal coordinate analysis of the fluorine perchlorate, FOClO_3 , molecule [1] we became interested in the force field of the closely related perchloryl fluoride, FCIO_3 , molecule. Although FCIO_3 is a well known and important molecule, and at least 13 force fields [2–14] have previously been published for it, comparison of the literature data revealed large discrepancies. Furthermore, for most of these computations estimated structural parameters had been used. Since the structure of FCIO_3 has been well established by electron diffraction data [6] and since for similar molecules a combination of isotopic frequencies and Coriolis constants have been shown to result in well defined general valence force fields [15–17], it was interesting to apply this approach to FCIO_3 . Further interest was added to the problem by the fact that in several studies [2, 3, 8, 9, 11] FCIO_3 has been used as a model compound to test the quality of approximate force fields. An evaluation of the merits of the different approximating methods, however, requires the knowledge of a reliable general valence force field. Finally, based on the results of a normal coordinate analysis, Gans pointed out [9] that two possible assignments (715 and 549 cm^{-1}) exist in the A_1 block for the Cl–F stretching mode and that, as a result, ν_2 and ν_3 might be mixtures of Cl–F stretching and angle deformations. The purpose of this study was to clarify some of these aspects and to obtain a better understanding of the force field of this interesting molecule.

EXPERIMENTAL

Perchloryl fluoride (Pennsalt) was handled in a passivated stainless steel–Teflon FEP vacuum system and purified prior to use by fractional condensation. Infrared spectra of the gas were recorded using a 5 cm path-length Teflon cell with CsI windows. The infrared spectra of

matrix-isolated FCIO_3 were obtained at 6 K with an Air Products Model DE 202 S helium refrigerator equipped with CsI windows. Research grade Ne, N_2 and Ar (Matheson) were used as matrix materials in a mole ratio of 1000:1. The infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points [18, 19]. The reported frequencies and isotopic shifts are believed to be accurate to ± 2 and $\pm 0.1 \text{ cm}^{-1}$, respectively.

RESULTS AND DISCUSSION

Since the infrared and Raman spectra and the assignments of FCIO_3 are well established [10, 20–25], only the infrared matrix isolation spectra were recorded for the determination of the ^{35}Cl – ^{37}Cl isotopic shifts. These spectra were obtained at 6 K using three different matrix materials, Ne, N_2 and Ar, at a MR of 1000. The observed spectra, frequencies and assignments are shown in Fig. 1 and Table 1. As expected for a five atomic molecule of symmetry C_{3v} , FCIO_3 exhibits a total of six fundamental vibrations classified as $3A_1 + 3E$. By analogy with the similar halogen fluorides, BrF_3 [26], BrF_3O [27] and FBrO_2 [28], neon matrices exhibited the least matrix site effect splittings and showed frequencies closest to those of the gas phase values. The additional splittings observed for the N_2 and the Ar matrices are attributed to matrix site effects.

A general valence force field was computed for FCIO_3 using a previously described machine method [29]. The frequency values were taken from previous gas phase measurements [10, 21, 22, 24, 25] and are summarized in Table 1. The ^{35}Cl – ^{37}Cl isotopic shifts were taken from the present matrix work except for ν_3 and ν_5 which were more accurately determined [22] by a previous high resolution gas phase infrared study (see Table 1). Anharmonic frequencies were used for the force field computations because sufficient experimental

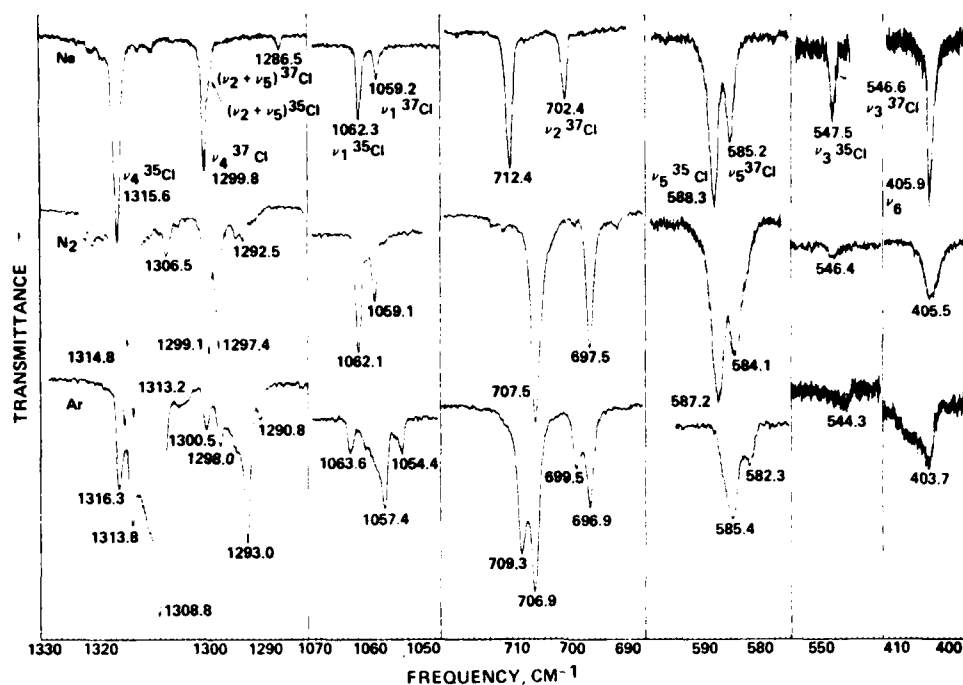


Fig. 1. Infrared matrix isolation spectra of FClO_3 recorded at 6 K in Ne, N_2 and Ar at a MR of 1000.

Table 1. Frequencies* and ^{35}Cl - ^{37}Cl isotopic shifts† of $\text{F}^{35}\text{ClO}_3$

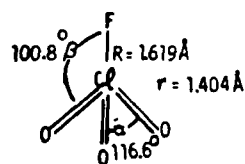
Species	Mode	$\text{F}^{35}\text{ClO}_3$ frequency (cm^{-1})	^{35}Cl - ^{37}Cl isotopic shift (cm^{-1})
A_1	ν_1	1063	3.05
	ν_2	717	10.0
	ν_3	550	0.89
E	ν_4	1315	15.8
	ν_5	591	3.09
	ν_6	405	[0.17]‡

*Frequencies were taken from the gas phase values of Refs. [10, 21, 22, 24, 25].

†Taken from this study, except for $\Delta\nu_3$ and $\Delta\nu_5$ (from Ref. [22]).

‡Calculated value. Splitting was too small to be experimentally observable.

data for anharmonicity corrections were not available. Since the relative signs of the symmetry coordinates are critical for the computation of the Coriolis constants, the symmetry coordinates have been summarized in Table 2. The following internal coordinates and the geometry, determined by an electron diffraction study[6], were used:



As it was clear from the beginning, that the measured isotopic splittings would not suffice to determine the A_1 block force constants unequivocally, *ab initio* force constant calculations were performed too, using the force method[30], a 4-21G basis set[31] for F and O and a 3-3-21 basis set[32] for the chlorine atom, which was augmented by one *d* function with exponent 0.6[33], when it was realized, that the pure basis did not reproduce the geometrical data properly. With the augmented basis set for Cl, the calculated geometry (r_{ClF} 1.628 Å, r_{ClO} 1.402 Å, $\angle\text{ClOF}$ 100.8°) is in good agreement with the experimental values. Table 3 shows the results of the *ab initio* force constant calculations (set I). The usual[34-38] deviation of the diagonal force constants was remedied by a subsequent iteration using the measured frequencies (set II in Table 3).

E-block force field. The ^{37}Cl isotope can provide only two new independent frequencies, due to the product rule. Consequently, the fact that the isotopic splitting for ν_6 could not be measured, is unimportant. Similarly, the Coriolis constants can provide two additional independent data points since they are related by the sum rule, $\zeta_4 + \zeta_5 + \zeta_6 = 2B/A$. Again, the fact that one Coriolis constant could not be measured, does not decrease the number of available independent data points. Thus, there were a total of seven pieces of independent data available to determine six force constants. The least squares computer code, used for our force field computations, did not converge when

Table 2. Symmetry coordinates and symmetry force constants for FCIO_3

A_1	$S_1 = (r_1 + r_2 + r_3)/\sqrt{3}$ $S_2 = R$ $S_3 = 0.4912(\beta_1 + \beta_2 + \beta_3) - 0.3034(\alpha_1 + \alpha_2 + \alpha_3)$ $S^* = 0.3034(\beta_1 + \beta_2 + \beta_3) + 0.4912(\alpha_1 + \alpha_2 + \alpha_3)$
E	$S_{4a} = (r_2 + r_3 - 2r_1)/\sqrt{6}$ $S_{4b} = (r_1 - r_2)/\sqrt{2}$ $S_{5a} = (\alpha_2 + \alpha_3 - 2\alpha_1)/\sqrt{6}$ $S_{5b} = (\alpha_1 - \alpha_2)/\sqrt{2}$ $S_{6a} = (2\beta_1 - \beta_2 - \beta_3)/\sqrt{6}$ $S_{6b} = (\beta_2 - \beta_3)/\sqrt{2}$
	$F_{11} = f_r + 2f_\pi$ $F_{22} = f_R$ $F_{11} = 0.72f_\beta + 0.28f_\alpha + 1.45f_{\beta\beta} + 0.55f_{\alpha\alpha} - 1.79f_{\alpha\beta} - 0.89f_{\alpha\beta'}$ $F_{12} = \sqrt{3}f_{R\beta}$ $F_{13} = 0.85f_{\beta\beta} + 1.70f_{\beta\beta'} - 1.05f_{\beta\alpha} - 0.53f_{\beta\alpha'}$ $F_{23} = 1.47f_{R\beta} - 0.91f_{R\alpha}$ $F_{44} = f_r - f_\pi$ $F_{45} = f_\alpha - f_{\alpha\alpha}$ $F_{66} = f_\beta - f_{\beta\beta}$ $F_{45} = f_{\beta\alpha} - f_{\beta\alpha'}$ $F_{46} = f_{\beta\beta} - f_{\beta\beta'}$ $F_{56} = f_{\alpha\beta} - f_{\alpha\beta'}$

*Redundant coordinate.

the observed frequencies and the previously reported Coriolis ζ constant values[5, 10] were used as input data. Consequently, this code was used to compute five symmetry force constants and the Coriolis constants as a function of the sixth constant, F_{45} , requiring an exact fit of the five observed frequencies. The resulting range of solutions is shown in Fig. 2.

Since neither of the two previously published[5, 10] sets of Coriolis constants (see Table 4) resulted in a unique force field solution (see Fig. 2), the Coriolis constants were reexamined. This examination revealed severe short-comings for both sets. The set calculated from Raman gas phase band contours[10], although quoted with the smaller uncertainties, is effectively useless because the Raman band contours are a function of both the Coriolis constants ζ and the ratio δ of the relative intensities between the set of transitions in J with $\Delta K = \pm 1$ and the same transition in J with $\Delta K = \pm 2$. Since the δ values are unknown, reliable ζ values cannot be obtained in this manner.

The other set of Coriolis constants was calculated[5] from i.r. gas-phase band contours. For the determination of ζ_5 , the accurately known Q branch spacing of ν_5 (0.1581 cm^{-1})[22] was used according to $\zeta_5 = 1 - (B/A) - (0.1581/2A)$, where A and B are the reduced moments of inertia. At the time of the original computation[5] of ζ_5 , an experimental value was available[22, 30] only for B , but A had to be estimated. Reevaluation of ζ_5 with A and B values of 0.1846 and 0.1764 cm^{-1} , respectively, deduced from the electron diffraction structural data[6], resulted in a revised value for ζ_5 of -0.384 ± 0.008 , assuming 1% uncertainties for both the value of A and the value of the Q branch spacing. The values of A and B computed from

the published electron diffraction data[6] are considered to be more precise than $\pm 1\%$ in view of the 0.64% deviation between our value of B ($0.1764 \text{ cm}^{-1} = 5292 \text{ Mcs}$) and that of $5258.682 \pm 0.005 \text{ Mcs}$ obtained[30] by microwave spectroscopy.

The previously reported[5] value of ζ_6 had been computed from an estimated geometry and the PR branch separation of ν_6 which was obtained by doubling the QR branch separation observed in the low resolution work of LIDE and MANN[21]. A re-examination of the complete ν_6 infrared band contour at 30°C resulted in a $P-R$ branch separation of $20.5 \pm 1.0 \text{ cm}^{-1}$, which in turn resulted in $\zeta_6 = 0.32 \pm 0.05$ using previously reported[31-34] graphic interpolation methods.

Determination of ζ_4 from the infrared band contour of ν_4 was not possible due to interference from the strong Q branches of the ^{35}Cl and ^{37}Cl isotopic species and from the $(\nu_2 + \nu_5)$ combination band. Therefore, ζ_4 was determined from the known ζ_5 and ζ_6 values and the sum rule $\zeta_4 + \zeta_5 + \zeta_6 = 2B/A$ and was found to be 0.54 ± 0.05 .

This revised set of Coriolis constants differs significantly from those reported previously[3, 5, 10] (see Table 4). As can be seen from Fig. 2, it results in a single set of force constants, thus lending credibility to the force field chosen. The numerical values of the resulting force constants are summarized in Tables 3 and 5 and Fig. 2 with uncertainties derived from the uncertainty limit of ζ_5 .

There is an excellent agreement of this experimentally derived force field with the *ab initio* results (see Table 3).

The E -block force field appears entirely plausible. All the off-diagonal symmetry constants have relatively small values, and the potential energy

Table 3. Force constants calculated for FCIO_3^*

	I	II	III
	<i>Ab initio</i> calc.	<i>Ab initio</i> calc. diagonal terms adapted to frequencies	Final set†
$A_1: F_{11}$	8.563	9.951	9.90 ± 0.05
F_{12}	4.857	3.267	3.49 ± 0.07
F_{13}	2.754	2.673	2.58 ± 0.05
F_{12}	0.154	0.154	0.13 ± 0.03
F_{13}	0.0	0.0	0.07 ± 0.07
F_{14}	0.481	0.481	0.58 ± 0.01
$E: F_{22}$	8.590	9.675	9.69 ± 0.01
F_{23}	1.403	1.520	1.53 ± 0.01
F_{24}	1.640	1.506	1.49 ± 0.02
F_{25}	-0.267	-0.267	-0.29 ± 0.01
F_{26}	-0.345	-0.345	-0.33 ± 0.11
F_{26}	0.271	0.271	0.26 ± 0.07
$\nu_1(\Delta \nu_1)$	1001.61(5.25)	1062.46(2.78)	1062.93(2.96)
$\nu_2(\Delta \nu_2)$	830.08(8.13)	725.95(10.72)	717.15(9.95)
$\nu_3(\Delta \nu_3)$	578.35(1.72)	540.39(0.32)	549.97(0.76)
$\nu_4(\Delta \nu_4)$	1239.29(15.09)	1314.96(15.85)	1315.05(15.80)
$\nu_5(\Delta \nu_5)$	578.08(3.09)	590.96(3.09)	590.97(3.09)
$\nu_6(\Delta \nu_6)$	414.63(0.06)	404.77(0.16)	404.87(0.17)
ζ_4	0.54	0.53	0.54
ζ_5	-0.30	-0.38	-0.38
ζ_6	0.24	0.32	0.32

*Stretching constants in $\text{mdyn } \text{\AA}^{-1} = 10^3 \text{ Nm}^{-1}$; deformation constants in $\text{mdyn } \text{\AA}^{-1} \text{ rad}^{-1} = aJ$; stretch-bend interaction constants in $\text{mdyn rad}^{-1} = 10 \text{ nN}$.

†A₁ block: optimal adaption to experimental data with minimum deviation from *ab initio* values for off-diagonal force constants. E block: calculated from experimental data.

‡Percent contributions; contributions of less than 5% to the PED are not listed.

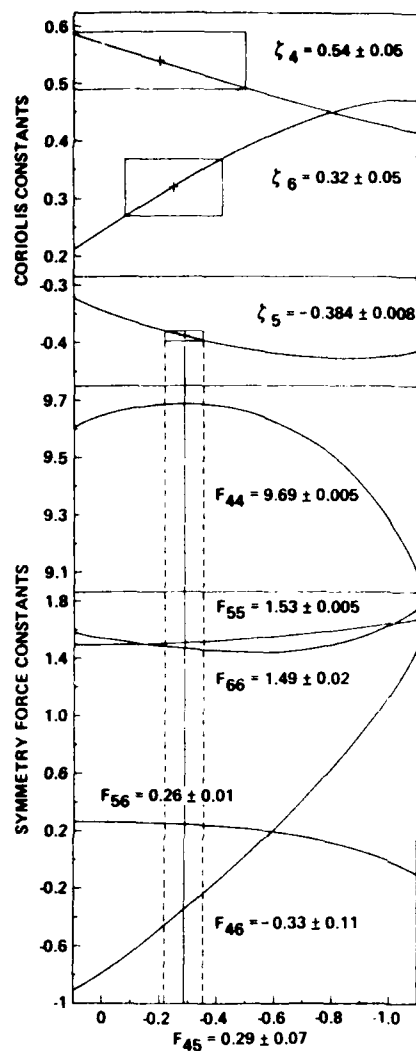


Fig. 2. E-block symmetry force constants and Coriolis constants of FClO_3 plotted as a function of F_{45} . The units of the force constants are given in Table I. The observed Coriolis constants are marked by + and their uncertainties are given by rectangles. The solid and the two broken lines represent the general valence force field and its uncertainties, respectively, derived from the corresponding ζ_5 value.

distribution (see Table 3) shows the fundamentals to be highly characteristic (70–98%). They are well described as an antisymmetric ClO_3 stretch, an antisymmetric ClO_3 deformation and a ClO_3 rocking mode. Fig. 2 also demonstrates that the general valence force field is approximately an extremal solution with F_{44} being a maximum and F_{55} and F_{66} being close to their minima.

A_1 -block force field. For the A_1 block, the product rule reduces the six vibrational frequencies to five independent pieces of data. Therefore, a unique force field cannot be determined. Thus, we had to rely mainly on the *ab initio* calculations (see Table 3), which, however, do not reproduce the vibrational frequencies ν_2 and ν_3 even after iteration of the diagonal terms. This is due to the small value of F_{23} . We have computed the five remaining symmetry force constants as a function of F_{23} , requiring an exact ($\pm 0.05 \text{ cm}^{-1}$) fit of the observed frequencies and chlorine isotopic shifts. The results from this computation are displayed in Fig. 3.

Its inspection allows the following conclusions: (i) F_{23} must be positive and must have a value of at least $0.57 \text{ mdyn rad}^{-1}$. The *ab initio* value ($0.481 \text{ mdyn rad}^{-1}$) is definitely below the range of real solutions. (ii) At $F_{23} = \text{min}$, ν_2 and ν_3 are complete mixtures of the symmetry coordinates S_2 (ClF stretching) and S_3 (ClO_3 deformation) with ν_2 being an antisymmetric and ν_3 a symmetric combination of them. (iii) Except for a very small range close to F_{12} and F_{13} being zero and to $F_{23} = \text{min}$, F_{12} and F_{13} must have the same sign with $F_{12} > F_{13}$. For increasing positive values of F_{12} and F_{13} , the contribution of S_3 to ν_2 and of S_2 to ν_3 increase and for increasing negative values these assignments become reversed [9]. (iv) The diagonal terms of the force constant matrix have their extremal values ($F_{11} = \text{max}$, $F_{22} = \text{min}$, $F_{33} = \text{min}$) close to the minimum of F_{23} . In this range, large changes in the values of F_{12} and F_{13} will be of minor influence on the diagonal force constants. Though for the A_1 block the *ab initio* force constants do not fulfill these requirements exactly (F_{23} is outside the range of real solutions and the difference between F_{12} ($0.154 \text{ mdyn } \text{\AA}^{-1}$) and F_{13} ($0.0 \text{ mdyn rad}^{-1}$) is too large, they may be used to

Table 4. Coriolis constants of FClO_3

	Ref. [5]*	Ref. [10]*	Ref. [3]†	This work*
ζ_4	0.45 ± 0.10	0.38 ± 0.04	0.52	0.54 ± 0.05
ζ_5	-0.25 ± 0.02	-0.29 ± 0.04	0.60	-0.384 ± 0.008
ζ_6	0.23 ± 0.10	0.36 ± 0.04	0.49	0.32 ± 0.05
$\zeta_4 + \zeta_6 + \zeta_6$	0.43	0.45	0.41	$0.477 \pm 0.005\dagger$

* Experimentally determined values.

† Values computed from the approximate force field of Ref. [3].

‡ Calculated from $I_4/2I_H$ assuming a 1% uncertainty in the ratio of the moments of inertia obtained from the structure determination of Ref. [6].

Table 5. Comparison of the different force field of FCIO₃

	This work*	Ref. [2]†	Ref. [3]†	Ref. [3]†	Ref. [4]†	Ref. [5]†	Ref. [6]†	Ref. [7]†	Ref. [8]†	Ref. [9]†	Ref. [10]†	Ref. [11]†	Ref. [12]†	Ref. [13]†
$A_1 F_{11}$	9.90	8.64	8.64									9.49		
F_{12}	3.49	3.91	3.92									3.69		
F_{13}	2.58	1.82	0.85									2.98		
F_{12}	0.13	-0.03	-0.04									-0.19		
F_{13}	0.07	0.13	0.09									-0.07		
F_{23}	0.56 _s	-0.44	-0.30									0.725		
EF_{44}	9.69	9.80	9.82									9.59		
F_{33}	1.53	1.03	1.04									1.50		
F_{44}	1.49	0.62	0.53									1.08		
F_{45}	-0.29	-0.09	-0.09									0.06		
F_{46}	-0.33	0.04	0.04									0		
F_{47}	0.26	0	0									0		
f_r	9.76	9.41	9.43									9.56	9.36-9.55	9.42
f_θ	3.49	3.91	3.92									3.69	3.72-4.10	3.47
f_ϕ	0.07	-0.39	-0.39									-0.03		0.24
$f_{\theta\theta}$	0.08	-0.02	-0.02									-0.11		1.75
$f_{\theta\phi}$														1.84
$f_{\phi\phi}$														0.39
$f_{\theta\theta}$														0.53

*Stretching constants in $\text{mdyn } \text{\AA}^{-1}$, deformation constants in $\text{mdyn } \text{\AA} \text{ rad}^{-2}$ and stretch-bend interaction constants in mdyn rad^{-1} .†All force constants in $\text{mdyn } \text{\AA}^{-1}$. For comments on conversion into units above see text.

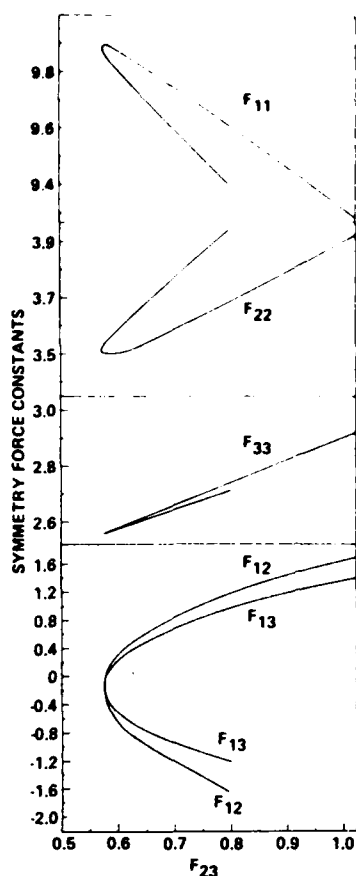


Fig. 3. A_1 block symmetry force constants of FCIO_3 plotted as a function of F_{23} .

fix the force field within narrow limits, provided their sign and order of magnitude is correct, which was proven for many examples (e.g. [34–38]). Thus, the *ab initio* value of F_{12} may be regarded as an upper limit, the value of F_{13} as a lower one, while F_{23} is close to the minimum value. F_{13} exhibits the largest uncertainty. Its lower limit is given by the *ab initio* value (0) and its upper limit by the value for F_{12} . The force field derived in this way with an optimal adaption to the experimental data is given in Table 3 as set III.

The strong mixing of the symmetry coordinates S_2 and S_3 in ν_2 and ν_3 can be easily rationalized. If the three oxygen atoms are treated as one centre of mass X , then the symmetric ClO_3 deformation mode corresponds to a stretching of the hypothetical Cl-X bond. Since such a hypothetical F-Cl-X molecule is linear, the F-Cl and Cl-X stretching motions should be strongly coupled and, therefore, result in an antisymmetric and a symmetric F-Cl-X stretch.

Comparison with Previous Force Fields. Table 5 gives a comparison of our force field with those previously reported. In most cases, an exact com-

parison of the bend-bend and stretch-bend force constants is difficult because for most of the previous force fields all force constants were given in units of $\text{mdyn}\text{\AA}^{-1}$ and the authors were not specific which bond lengths (r , R or possible combinations) were used for their normalization procedures. For a comparison with our force field, approximate values of the previously reported all $\text{mdyn}\text{\AA}^{-1}$ force fields can be obtained by multiplying F_{11} and F_{33} by rR , F_{13} by R or $\sqrt{rR}$, F_{21} and F_{31} by r or $\sqrt{rR}$, F_{22} by r^2 or rR , F_{32} by $\sqrt{rR}$, and F_{23} by rR or $r^{3/2}R^{1/2}$. Furthermore, most of the previously published force fields were computed with estimated geometries of inaccurate Coriolis constants. Consequently, an objective evaluation of the merits of the individual approximating methods is difficult and was not undertaken.

General Comments. We would like to point out the wide range of force constant values previously published for FCIO_3 , which fully supports the previous critical statements[9] by GANS concerning the questionable value of force constant calculations from insufficient or inaccurate data. In such cases, the computation of wide solution ranges is important to determine the range of possible plausible solutions.

The values of 9.76 and 3.49 $\text{mdyn}\text{\AA}^{-1}$ obtained for the Cl=O and the Cl-F stretching force constant, respectively, of FCIO_3 , are in excellent agreement with our expectations[45] for highly covalent Cl=O double and Cl-F single bonds. Higher Cl=O force constants have only been observed for the cations ClF_2O_2^+ (12.1 $\text{mdyn}\text{\AA}^{-1}$) [46] and ClF_2O_2^+ (11.2 $\text{mdyn}\text{\AA}^{-1}$) [47] and are caused by their formal positive charge[45]. Similarly, ClF_2O_2^+ is the only chlorine oxyfluoride species which exhibits a higher (4.46 $\text{mdyn}\text{\AA}^{-1}$) ClF stretching force constant. This can be attributed to the high oxidation state of chlorine (+VII) and the energetically favorable pseudo-tetrahedral structure of FCIO_3 .

The results of the present study are of particular interest because they demonstrate that arguments concerning the assignment of certain modes, capable of undergoing coupling, can be rather meaningless. This has recently been demonstrated[44] for the axial and the equatorial SF_2 scissoring modes in SF_4 and is now further substantiated for FCIO_3 . Rather than resulting in highly characteristic fundamentals, their symmetry coordinates are strongly mixed and the fundamentals correspond to an antisymmetric and a symmetric combination of the corresponding symmetry coordinates.

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Syntheses and Properties of FOIF₄O, ClOIF₄O, HOIF₄O, and Tetrafluoroperiodates

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Mixtures of *cis*- and *trans*-CsIF₄O₂ were prepared by the interaction of CsIO₄ with either anhydrous HF, BrF₃, ClF₃, ClF₅, or F₂. The vibrational spectra of these mixtures were recorded, and partial assignments are given for *cis*- and *trans*-IF₄O₂⁻. The assignments for *trans*-IF₄O₂⁻ were supported by a normal-coordinate analysis. The CsIF₄O₂ salt dissolves in CH₃CN with the formation of IF₄O₂⁻ anions but undergoes solvolysis in anhydrous HF with formation of HOIF₄O. An improved synthesis of HOIF₄O from CsIF₄O₂ and BiF₃ in anhydrous HF is reported, and its Raman and ¹⁹F NMR spectra were recorded. The interaction of CsIF₄O₂ with NF₄SbF₆ in anhydrous HF results in solutions containing NF₄⁺, HF₂⁻, and HOIF₄O. When standing or when pumped to dryness, these mixtures decompose to yield NF₃ and the new compound FOIF₄O in high yield. The latter compound, the first known example of an iodine hypofluorite, was thoroughly characterized and shown by vibrational and NMR spectroscopy to be a mixture of the *cis* and *trans* isomers. For comparison, the vibrational spectra of IF₃O have also been recorded. The reaction of CsIF₄O₂ with ClOSO₂F was shown to yield the novel compound ClOIF₄O. The fluorination reactions of CsIO₄, CsIF₄O₂, IF₃O, and HOIF₄O with elementary fluorine were also studied.

Introduction

The number of elements known to form stable hypofluorites is very limited.¹ Thus stable hypofluorites are known only for carbon-, nitrogen-, sulfur-, selenium-, fluorine-, and chlorine-containing compounds. In addition, the unstable hypofluorous acid, HOF, has been prepared.² Since recent work in our laboratory had shown that the thermal decomposition of certain NF₄⁺ salts of oxyanions such as NF₄ClO₄³ and NF₄SO₃F⁴ produces the corresponding hypofluorites in high yield, it was interesting to apply this method to the synthesis of novel hypofluorites. Preliminary results⁵ showed that FOIF₄O, the first known example of an iodine hypofluorite, can be prepared in this manner. In this paper, detailed information is given on the synthesis, properties, and reaction chemistry of this interesting compound and of related iodine oxyfluoride derivatives such as ClOIF₄O, HOIF₄O, and the IF₄O₂⁻ anion.

The literature on the synthesis and properties of salts containing the IF₄O₂⁻ anion is scant. The first report on the existence of IF₄O₂⁻ salts was published in 1971 by Engelbrecht

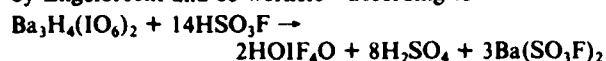
and co-workers⁶ but was limited to a one-sentence statement that HOIF₄O interacts with either alkali-metal fluorides or trifluoroacetates to yield the corresponding salts. In a subsequent paper,⁷ this statement was repeated, but again no data were given. In 1975, Aubke and co-workers reported⁸ that CsF combines with an excess of IF₃O₂ to give Cs⁺IF₄O₂⁻. A melting point, elemental analysis, and incomplete vibrational spectra were given, which were incorrectly interpreted in terms of a *cis* isomer. In 1976, Selig and Elgad reported⁹ that partial hydrolysis of IF₇ produces IF₃O, HOIF₄O, and, with increased water addition, the IF₄O₂⁻ anion, which was identified by ¹⁹F NMR and vibrational spectroscopy as the *cis* isomer. Although Selig and Elgad reported only solution data, their vibrational spectra strongly disagreed with those reported by Aubke for solid Cs⁺IF₄O₂⁻. In 1977, Gillespie and Krasznai reported¹⁰ that solutions of KIO₄ in IF₃ contain a mixture of IO₂F, IOF₃, and *cis*- and *trans*-IF₄O₂⁻. On cooling solutions of KIO₄ dissolved in boiling IF₃, they isolated a KIF₄O₂·2IF₃ adduct, which could be converted into KIF₄O₂. Both compounds were shown by ¹⁹F NMR and Raman spectroscopy to

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contain in the solid state and in CH_3CN solution *trans*- IF_4O_2^- . In IF_5 solution, however, IF_4O_2^- was shown to exist in a *cis-trans* equilibrium, with the *cis* isomer being favored.

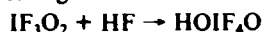
Tetrafluoroorthoperiodic acid, HOIF_4O , was first prepared by Engelbrecht and co-workers¹¹ according to



Since HOIF_4O could not be separated from HSO_3F by distillation, it was converted into the more volatile IF_3O_2



which was distilled off and then reconverted to HOIF_4O by HF addition according to



The acid was characterized^{6,11} by its physical constants and mass and NMR spectra, which showed the compound to be a mixture of the *cis* and *trans* isomers, with the *cis* isomer being more abundant. Selig and Elgad found⁹ that solutions of NaIO_4 in anhydrous HF contain HOIF_4O , as well as other unidentified fluorine species, and reported the ^{19}F NMR spectra of both isomers in HF solution. Gillespie and Krasznai¹⁰ also listed chemical shifts for *cis*- and *trans*- HOIF_4O , without specifying the solvent, and gave a coupling constant of 21 Hz for the *cis* isomer, which disagrees with the values of about 220 Hz reported by others.^{6,9,11}

Experimental Section

Caution. Two explosions were encountered in reactions involving FOIF_4O . Most hypofluorites are shock-sensitive materials¹ and appropriate precautions should therefore be taken when one is working with larger amounts of FOIF_4O .

Materials. Literature methods were used for the syntheses of NF_3 ,¹² SbF_5 ,¹² IF_3 ,^{13,14} and ClOSO_2F .¹⁵ CsIO_4 was prepared by slowly combining, with stirring, stoichiometric amounts of concentrated aqueous solutions of CsCl and NaIO_4 . The mixture was cooled to 0 °C, and the CsIO_4 precipitate was filtered off, washed three times with ice water, and dried for 16 h in an oven at 110 °C. Its vibrational spectra showed no detectable impurities. Bismuth pentafluoride (Ozark Mahoning Co.) was used as received. BrF_3 (Matheson) was treated with 35 atm of F_2 at 200 °C for 24 h and then purified by fractional condensation through traps kept at -64 and -95 °C, with the material retained in the latter being used. Hydrogen fluoride (Matheson) was dried by treatment with 20 atm of F_2 at room temperature, followed by storage over BiF_3 to remove the last traces of H_2O .¹⁶ ClF_3 (Matheson) and ClF_5 (Rocketdyne) were purified by fractional condensation prior to their use.

Apparatus. Volatile materials used in this work were handled in either a Monel-Teflon FEP, a stainless steel-Teflon FEP, or a Teflon PFA vacuum line. The last was constructed exclusively from injection-molded PFA fittings and valves (Fluoroware, Inc.). The anhydrous HF was preferentially handled in the PFA or Monel line, whereas the halogen fluorides were handled mainly in a steel line. All lines 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 glove box. Metathetical reactions were carried out in HF solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter (see Figure 1 of ref 17). For NMR or low-temperature vibrational spectra, the second FEP U-trap, which served as a receiver, was replaced by either a 4-mm Teflon FEP or a thin-walled Kel-F tube.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Room-temperature

spectra of solids were obtained by using dry powders pressed between AgCl disks. Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. The spectra of matrix-isolated FOIF_4O and IF_3O_2 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 1000:1. The spectrometer was calibrated by comparison with standard gas calibration points,^{18,19} and the reported frequencies are believed to be accurate to $\pm 2 \text{ cm}^{-1}$.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter²⁰ for the elimination of plasma lines. Sealed quartz, Teflon FEP, or Kel-F Tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. Polarization measurements were carried out according to method VIII listed by Claassen et al.²⁰ Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer equipped with a variable-temperature probe. Chemical shifts were determined relative to external CFCl_3 , with positive shifts being downfield from CFCl_3 .^{21a}

The mass spectra were recorded with an EAI Quad 300 quadrupole spectrometer at an ionization potential of 70 eV.

Preparation of CsIF_4O_2 . In a typical experiment, CsIO_4 (31.44 mmol) was placed in a 3/4-in. o.d. Teflon FEP ampule equipped with a stainless-steel valve. Anhydrous HF (20 mL of liquid) was condensed into the ampule, and the mixture was stirred with a magnetic stirring bar for 4 days at ambient temperature. Volatile products were pumped off overnight at ambient temperature and for an additional 2 h at 50 °C. The solid residue (11.402 g, weight calculated for 31.44 mmol of CsIF_4O_2 11.564 g) was shown by Raman spectroscopy to still contain some unreacted CsIO_4 . It was treated again, as described above, with fresh anhydrous HF (15 mL of liquid). After the residue was pumped to dryness, the Raman spectrum of the solid residue (11.532 g) showed *cis*- and *trans*- CsIF_4O_2 as the principal products and only a trace of unreacted CsIO_4 .

A total of eight preparations were carried out in a similar manner, with use of shorter reaction times, slightly higher reaction temperatures (~ 50 °C), and rapid HF removal at elevated temperature. The conversion of CsIO_4 to CsIF_4O_2 after the first HF treatment was generally in the range of 75–90%, and the Raman spectra showed the presence of some unreacted CsIO_4 . This unreacted CsIO_4 was readily converted to CsIF_4O_2 by repeated treatment with anhydrous HF; however in most cases, repeated HF treatments resulted in a slight weight decrease and the appearance of bands due to HF_2^- (infrared 1435 s, br, 1228 ms cm^{-1} ; Raman complex band at 790–740 cm^{-1} with maximum at 759 cm^{-1}). This is caused by the solvolysis of CsIF_4O_2 in anhydrous HF and the volatility of the resulting HOIF_4O (see below). The ratio between the *cis* and *trans* isomers of CsIF_4O_2 varied somewhat for the different preparations, with the *trans* isomer being slightly favored at the lower and the *cis* isomer being somewhat favored at the higher reaction temperatures.

The CsIO_4 - BrF_3 System. Cesium periodate (2.453 mmol) was placed in a passivated sapphire reactor equipped with a stainless-steel valve and a magnetic stirring bar. Bromine pentafluoride (14.99 mmol) was added at -196 °C, and the mixture was allowed to react during warm-up to room temperature. A fast reaction with gas evolution occurred, which was moderated by intermittent cooling with liquid N_2 . After completion of the warm-up cycles, the mixture was stirred at 20 °C for 24 h, resulting in a clear, pale yellow solution. The Raman spectrum of this solution showed the presence of BrF_3 , BrF_3O , and IF_4O_2 (mainly *trans* with a small amount of *cis* isomer). The solution was kept at 22 °C for 4 days and then cooled to -196 °C. The materials volatile at -196 °C consisted of 1.92 mmol of oxygen. The materials volatile at 22 °C were separated by fractional condensation and identified by Raman spectroscopy. They consisted of unreacted

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BrF_3 (9.9 mmol) and a mixture of BrF_3 and BrF_3O (found 682 mg, calcd for 3.84 mmol of BrF_3 + 1.06 mmol of BrF_3O 688 mg). The solid residue (found 804 mg, weight calcd for 2.453 mmol of CsIF_4O_2 787 mg) was shown by Raman spectroscopy to consist mainly of *trans*- CsIF_4O_2 , CsBrF_4 , and smaller amounts of *cis*- CsIF_4O_2 , and possibly some solvated BrF_3O . Vacuum pyrolysis at 90 °C resulted in a solid residue consisting again of *trans*- CsIF_4O_2 , CsBrF_4 , and a small amount of *cis*- CsIF_4O_2 and also in the evolution of some IF_3 (~8 weight %).

The CsIO_4 - ClF_3 System. A well-passivated (with ClF_3) sapphire tube equipped with a stainless-steel valve and containing a Teflon-coated stirring bar was loaded with CsIO_4 (1.14 mmol), followed by ClF_3 (10.6 mmol). The liquid ClF_3 and solid periodate were stirred magnetically overnight at 0–20 °C. This resulted in a clear, very pale yellow solution. Upon removal of the volatile material and several hours of pumping at ambient temperature, a white powder (0.493 g) remained in the tube, which was identified by vibrational spectroscopy as a mixture of CsF_3IF_2 and CsClF_4 (weight calculated for the conversion of 1.14 mmol of CsIO_4 to 0.38 mmol of CsF_3IF_2 and 0.76 mmol of CsClF_4 was 0.497 g). The volatile materials consisted of ClF , FClO_2 , and unreacted ClF_3 .

The CsIO_4 - ClF_3 System. When CsIO_4 was allowed to interact with a large excess of ClF_3 in a stainless-steel reactor at room temperature, the composition of the solid reaction product depended on the reaction time. After short reaction times (about several hours) the solid consisted, on the basis of its weight change and Raman spectra, mainly of unreacted CsIO_4 and smaller amounts of *trans*- CsIF_4O_2 . After longer reaction times (in excess of 1 month), the solid consisted mainly of CsIF_8 and *trans*- CsIF_4O_2 and some CsIF_4O .

The CsIO_4 - F_2 System. The fluorination of CsIO_4 with elemental fluorine in a static system at temperatures up to 60 °C resulted in a solid product, which, on the basis of its vibrational spectra, was a mixture of mainly CsIF_8 , CsIF_6 , and CsIO_4 with smaller amounts of CsIF_4O and *cis*- and *trans*- CsIF_4O_2 also being present.

Synthesis of HOIF_4O . In a typical experiment, CsIF_4O_2 (2.0 mmol) and BiF_3 (2.0 mmol) were placed in a passivated Teflon FEP U-trap containing a magnetic stirring bar. One arm of the trap was closed off by the stainless-steel valve, while the other one was connected through a porous Teflon filter to a second Teflon U-trap, which was capped off by another valve. Anhydrous HF (5 mL of liquid) was condensed into the U-trap, and the CsIF_4O_2 - BiF_3 -HF mixture was stirred at 25 °C for 1 h. The double U-trap assembly was cooled to -78 °C and inverted, and the HOIF_4O -containing HF solution was separated from the CsBiF_6 precipitate by pressure filtration. The HF solvent was pumped off at -45 and -13 °C. The residue was allowed to warm to ambient temperature, and the material volatile at 25 °C was collected at -78 °C in a 4-mm o.d. external Teflon U-trap. This trap was shown to contain HOIF_4O (~2 mmol), which was identified by its Raman and ^{19}F NMR spectra. The filter cake (0.9 g) was identified by its Raman spectrum as CsBiF_6 .

Synthesis of FOIF_4O . In a typical experiment, CsIF_4O_2 (5.0 mmol) and NF_3/SbF_5 (5.0 mmol) were placed in the Teflon FEP metathesis apparatus (see above), and anhydrous HF (5 mL of liquid) was condensed in at -78 °C. The mixture was stirred for 1 h at room temperature. The apparatus was cooled to -78 °C and 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 temperature. 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 -78 °C trap contained a small amount of unidentified material, which was discarded, the -95 °C fraction consisted of pure FOIF_4O (2.36 mmol), the -112 °C trap had 1.69 mmol of FOIF_4O containing a small amount of IF_3O as an impurity, and the -210 °C trap contained NF_3 (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*- CsIF_4O_2 . The filter cake (1.8 g) was identified by Raman spectroscopy as CsSbF_6 . The -95 °C fraction was used for the characterization of FOIF_4O and was shown by vibrational and ^{19}F NMR analysis to be free of IF_3O .

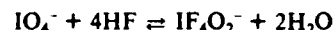
For the elemental analysis, 278.7 mg of the material was condensed at -196 °C into an ampule containing 12 mL of frozen 1 N NaOH. The mixture was warmed to ambient temperature for 12 h and then

analyzed for total iodine by energy-dispersive X-ray fluorescence spectrometry, for IO_4^- by iodometric titration, for base consumption by back-titration with 0.1 N HCl using a pH electrode and for fluoride by titration using $\text{La}(\text{NO}_3)_3$ and an Orion specific-ion electrode. Anal. Calcd for FOIF_4O : I, 49.98; F, 37.42; OH⁻ consumed, 6.0 equiv/mol; iodometric titration, 8.0 equiv/mol, with the assumption of the hydrolysis reaction $\text{FOIF}_4\text{O} + 6\text{OH}^- \rightarrow \text{IO}_4^- + 5\text{F}^- + 0.5\text{O}_2(\text{g}) + 3\text{H}_2\text{O}$. Found: I, 50.0; F, 36.0; OH⁻ consumed, 6.1 equiv/mol; iodometric titration, 7.8 equiv/mol.

Synthesis of CFOIF_4O . A 30-mL stainless-steel cylinder was loaded with 2.32 mmol of CsIF_4O_2 and 2.12 mmol of ClSO_3F was added at -196 °C. After the cylinder was kept for 5 days at -78 °C, the volatile products were removed from the cylinder. The solid residue was identified by vibrational spectroscopy as CsSO_3F . The volatiles were fractionated through traps cooled to -45, -78, and -196 °C. The lowest temperature fraction (0.77 mmol) was mainly Cl_2 together with some FClO_2 , while the -45 °C trap contained a white solid, which melted above 0 °C and which was identified by its infrared spectra as IF_3 . The -78 °C trap contained a yellow-orange solid, which on slight warming melted to an orange liquid. Its gas-phase infrared spectrum was recorded at 25 °C and showed the following bands (cm^{-1} ; relative intensity, assignment): 912 m, I=O stretch; 763 mw, O—Cl stretch; 678 vs, 635 s, 532 mw, I—F and I—O stretching. The compound was found to be thermally unstable and very difficult to handle. It readily decomposed to IF_3 , and its synthesis required careful temperature control. When the synthesis was carried out for example at -45 °C, only decomposition products were obtained. Attempts to isolate fluorocarbon derivatives of CFOIF_4O by adding it across the C=C double bond of C_2F_4 resulted at -78 °C in no reaction and at room temperature in the oxygenation, fluorination, and decomposition products COF_2 , CF_3COF , ClCF_2COF , $\text{C}_2\text{F}_5\text{Cl}$, and IF_3 .

Results and Discussion

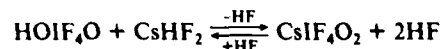
Synthesis of CsIO_2F_4 . In our work the known⁹ equilibrium



was utilized for a convenient synthesis of CsIF_4O_2 . So that this equilibrium can be shifted to the right, a large excess of HF must be used and the HF treatment must be repeated at least once. The resulting CsIF_4O_2 consists of a mixture of the *cis* and *trans* isomers, as shown by ^{19}F NMR and vibrational spectroscopy (see below). The ratio of *cis* to *trans* isomer varies somewhat with the reaction conditions used, but the formation of the *cis* isomer appears to be slightly favored. The ^{19}F NMR and Raman spectra were recorded for solutions of CsIF_4O_2 in anhydrous HF and CH_3CN . Whereas the CH_3CN solution spectra show the presence of the IF_4O_2^- anion, the spectra of the HF solutions are characteristic (see below) for those of HOIF_4O . This finding is in excellent agreement with the previous report by Selig and Elgud⁹ that solutions of NaIO_4 in anhydrous HF contain HOIF_4O and the report by Engelbrecht and co-workers^{6,7} that HOIF_4O interacts with alkali-metal fluorides to form IF_4O_2^- salts. Consequently, the above equilibrium reaction involves at least two reactions, the first being



and, upon HF and H_2O removal, the second being



The intermediate formation and the slight volatility of HOIF_4O also explain why in some of our CsIF_4O_2 preparations, when the HF was rapidly pumped off at elevated temperature, a weight loss accompanied by some CsHF_2 formation was observed.

The above synthesis of CsIF_4O_2 from CsIO_4 and HF appears more convenient than the previously reported methods involving either the difficult to obtain IF_3O_2 as a starting material or the isolation and recrystallization of $\text{MIF}_4\text{O}_2 \cdot 2\text{HF}$ from IF_3 , followed by its pyrolysis. However, the latter method produces almost exclusively the *trans* isomer and might be the

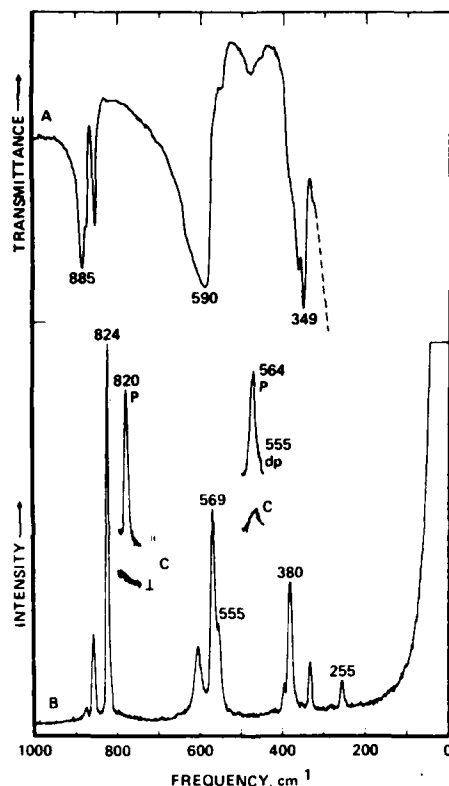
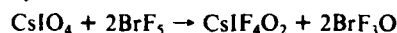


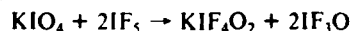
Figure 1. Vibrational spectra of a CsIF_4O_2 sample containing mainly *trans*- IF_4O_2^- (bands marked by their frequency values) and smaller amounts of *cis*- IF_4O_2^- . Trace A is an infrared spectrum of the solid as a dry powder pressed between AgCl disks; the broken line indicates absorption due to the window material. Trace B is a Raman spectrum of the solid. Inserts C are Raman bands of the CH_3CN solution, recorded with parallel and perpendicular polarization.

preferred method if pure *trans*- IF_4O_2^- is desired. The fact that the *cis*-*trans* isomer ratio strongly depends on the nature of the reactants suggests that this ratio is kinetically and not thermodynamically controlled. This conclusion is in excellent agreement with those reached by Toetsch and Sladky for the closely related $\text{TeF}_6(\text{OH})_2$ system.^{21b}

An alternate method for the formation of CsIF_4O_2 involves the reaction of CsIO_4 with BrF_3 . The main reaction can be described by

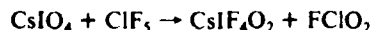


This reaction is analogous to that¹⁰ previously reported for $\text{KIO}_4 + \text{IF}_3$, i.e.



and produces almost entirely the *trans* isomer. Compared to the IF_3 reaction, the BrF_3 reaction offers the advantage that the BrF_3O and BrF_3 byproducts are volatile and can easily be pumped off. However, the resulting product was contaminated by nonvolatile CsBrF_4 , which could not be readily separated from the CsIF_4O_2 .

The reactions of CsIO_4 with chlorine fluorides were also briefly studied. With ClF_3 , *trans*- CsIF_4O_2 was formed in low conversion according to



Attempts to achieve higher conversions by the use of longer reaction times failed due to the formation of CsIF_6 as the main product and of CsIF_4O as a minor product.

When ClF_3 was replaced by the more reactive ClF_5 , complete conversion of the CsIO_4 was obtained; however, all the

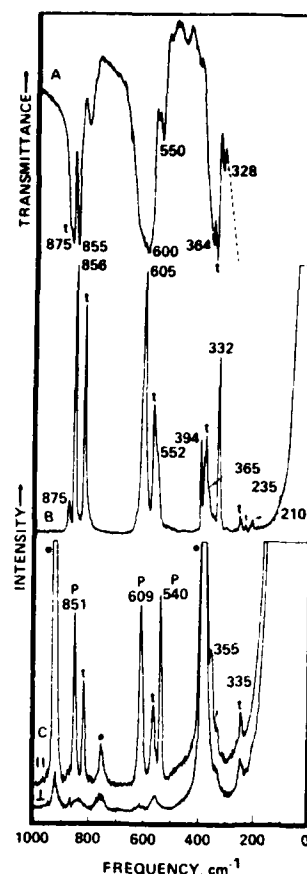


Figure 2. Vibrational spectra of a CsIF_4O_2 sample containing mainly *cis*- IF_4O_2^- (bands marked by frequency values) and smaller amounts of *trans*- IF_4O_2^- (marked by t). Trace A is an infrared spectrum of the solid as a dry powder pressed between AgCl disks. The weak bands at 815 and 470 cm^{-1} probably do not belong to IF_4O_2^- . Trace B is a Raman spectrum of the solid. Traces C are Raman spectra of a CH_3CN solution. Solvent bands are marked by an asterisk.

oxygens in IO_4^- were exchanged for fluorine, and the solid product consisted of a mixture of $\text{CsIF}_6 \cdot 2\text{IF}_3$ ²² and CsClF_4 .²³ Based on the observed material balance, the following reaction occurred:



The formation of ClF and of half of the FCIO_2 can be readily explained by the well-known²⁴ disproportionation of the expected unstable FCIO intermediate:



The fluorination of CsIO_4 by elemental fluorine at temperatures up to 60 °C in a static system was also studied. The main products were CsIF_6 and CsIF_6 , with CsIF_4O and *cis*- and *trans*- CsIF_4O_2 as minor products.

In view of the fact that the fluorination reactions of CsIO_4 with ClF_5 , BrF_5 , ClF_3 , or F_2 do not result in pure compounds, they are less attractive synthetic methods for the preparation of CsIF_4O_2 .

Vibrational Spectra of CsIF_4O_2 . The vibrational spectra of solid CsIF_4O_2 were recorded for samples that differed in their *cis* and *trans* isomer content. The observed spectra are given

(22) Christe, K. O. *Inorg. Chem.* 1972, 11, 1215.

(23) Christe, K. O.; Sawodny, W. Z. *Anorg. Allg. Chem.* 1970, 374, 306.

(24) Cooper, T. D.; Dost, F. N.; Wang, C. H. *J. Inorg. Nucl. Chem.* 1972, 34, 3564.

Table I. Vibrational Spectra of $\text{trans-IF}_4\text{O}_2^-$ and Their Assignments in Point Group D_{4h} Compared to Those of Closely Related Molecules

obsd freq, cm^{-1} , and rel intens									
<i>trans-CsIF₄O₂</i>									
solid		CH ₃ CN soln		IF ₃ O ⁺ gas		IF ₄ ⁺ solid		IF ₃ O ⁺ gas	
IR	Raman ^a	IR	Raman ^a	IR	Raman	IR	Raman	IR	Raman
...	569 (5.5)	...	540 (5.8)	...	522 (10)	...	640 s	...	616 vs, p
...	824 (10)	...	887 (10)	...	...	...	927 vs	...	...
885 s	...	...	283 (0.3)	...	...	...	363 m	...	...
349 s	...	...	...	271 ms	...	...	...	318 m	...
...	555 (2)	...	478 (2.3)	...	455 (7.2)	...	647 s, dp	...	...
...	255 (0.7)	...	224 (0.5)	...	195 (0+)	...	330 w	...	...
...	...	...	...	...	...	...	...	...	...
...	380 (3.5)	...	368 (1)	...	...	...	375 m, dp	...	...
...	...	...	...	...	...	...	712 w, dp	...	...
590 vs, br	...	...	...	...	...	...	205 vw	...	...
...	...	...	140 (0+)	...	...	...	208 vw, dp	...	...

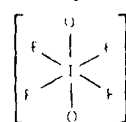
^a Uncorrected Raman intensities (peak heights). ^b Obscured by solvent band. ^c Data from ref 26. ^d Data from ref 25. ^e Data from ref 14 and 29. ^f Data from ref 27 and 28.

Table II. Vibrational Spectra of $\text{cis-IF}_4\text{O}_2^-$

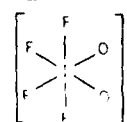
obsd freq, cm^{-1} , and rel intens ^a				
solid		CH ₃ CN soln	assign for	approx
IR	Raman	Raman	point group C_{2v}	description of mode
875 vs	875	870 sh	ν_{12} (B_2)	ν_{12} (B_2)
855 vs	856 (10)	851 (9) p	ν_1 (A_1)	ν_1 (A_1)
600 vs, br	...	...	ν_2 (B_1)	ν_{12} (B_2)
600 vs, br	605 (9.8)	609 (10) p	ν_2 (A_1)	ν_{12} (B_2)
550 mw	552 sh	540 (10) p	ν_3 (A_1)	ν_{12} (B_2)
395 sh	394 (3.4)	...	ν_4 (A_1)	ν_{12} (B_2)
364 s	365 sh	355 sh	...	ν_{12} (B_2)
328 mw	332 (6.5)	335 sh	...	ν_{12} (B_2)
...	235 (0.2)	...	...	ν_{12} (B_2)
...	210 (0.5)	...	...	ν_{12} (B_2)

^a Uncorrected Raman intensities (peak height).

in Figures 1 and 2, and the observed frequencies and their assignments in point group D_{4h} and C_{2v} .



D_{4h} , trans



C_{2v} , cis

are summarized in Tables I and II, respectively. The bands belonging to the trans isomer could be readily distinguished from those of the cis isomer due to the fact that only the trans isomer has a center of symmetry, which causes the infrared and Raman bands to be mutually exclusive. Furthermore, the ^{19}F NMR spectrum (see below) clearly distinguished the trans from the cis isomer and established which isomer was more abundant in a given sample.

Assignments and Normal-Coordinate Analysis for $\text{trans-IF}_4\text{O}_2^-$. The $\text{trans-IF}_4\text{O}_2^-$ anion of symmetry D_{4h} should possess 11 fundamental modes classified as $2A_{1g} + 2A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 3E_u$. Of these, the A_{1g} , B_{1g} , B_{2g} , and E_g modes should be Raman active only and the A_{2u} and E_u modes should be infrared active only, whereas the B_{2u} mode should be inactive in both spectra. Of the 10 active modes, all five Raman-active modes and three out of the five infrared-active modes have been observed and can be readily assigned on the basis of their activity, polarization data, and comparison with the closely related species IF_4^- ,²⁵ IF_4O^- ,²⁶ IF_5 ,^{27,28} and $\text{IF}_5\text{O}^{14,29} (see Table I). The correctness of these assignments was confirmed by a normal-coordinate analysis using the symmetry coordinates and G matrix elements previously published³⁰ by Beattie and co-workers. The bond distances were estimated to be $r_{\text{IF}} = 1.92 \text{ \AA}$ and $d_{\text{IO}} = 1.72 \text{ \AA}$, on the basis of the known structures and stretching frequencies of the related IF_5 ,^{14,29,31} and IF_5 ,^{27,28,32} molecules and the IF_4O^- anion.^{26,33} The force constants of the B_{1g} , B_{2g} , and E_g species are uniquely determined. In the A_{1g} block, the G_{12} element is zero, and therefore F_{12} can be ignored. For the A_{2u} block, the extremal solution³⁴ $F_{44} = \text{minimum}$ was used, which has previously been shown²⁵ for the closely related IF_4^- anion$

(25) Christe, K. O.; Naumann, D. *Inorg. Chem.* **1973**, *12*, 59.

(26) Christe, K. O.; Wilson, R. D.; Curtis, E. C.; Sawodny, W.; Kuhlmann, W. *Inorg. Chem.* **1978**, *17*, 533.

(27) Begun, G. M.; Fletcher, W. H.; Smith, D. F. *J. Chem. Phys.* **1965**, *42*, 2236.

(28) Selig, H.; Holzman, A. *Isr. J. Chem.* **1969**, *7*, 417.

(29) Smith, D. F.; Begun, G. M. *J. Chem. Phys.* **1965**, *43*, 2001.

(30) Beattie, J. R.; Webster, M.; Chantry, G. W. *J. Chem. Soc.* **1964**, 6172.

(31) Pierce, S. B.; Cornwell, C. D. *J. Chem. Phys.* **1967**, *47*, 1731.

(32) Richey, A. S.; Bradley, R. H.; Brier, P. N. *J. Chem. Soc. D* **1971**, 186.

(33) Ryan, R. R.; Asprey, I. B. *Acta Crystallogr., Sect. B* **1972**, *B28*, 979.

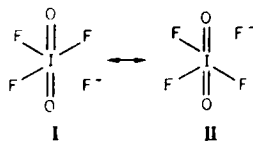
(34) Sawodny, W. *J. Mol. Spectrosc.* **1969**, *30*, 56.

Table III. Symmetry Force Constants^a of *trans*-IF₄O₂⁻

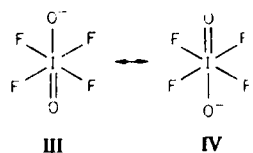
A _{1g}	ν ₁ 569	F ₁₁ = f _r + 2f _{rr} + f _{rr'}	3.623
	ν ₂ 824	F ₂₂ = f _α + f _{αα}	6.400
A _{2u}	ν ₃ 885	F ₃₃ = f _d - f _{dd}	5.903
	ν ₄ 349	F ₄₄ = f _β + 2f _{ββ} + f _{ββ'} - f _{ββ''} - 2f _{ββ°} - f _{ββ†}	1.700
		F ₃₄ = 2f _{dβ} - 2f _{dβ'}	-0.036
B _{1g}	ν ₅ 555	F ₅₅ = f _r - 2f _{rr} + f _{rr'}	3.447
B _{2g}	ν ₆ 255	F ₆₆ = f _γ - 2f _{γγ} + f _{γγ'}	0.671
B _{2u}	ν ₇	F ₇₇ = f _β - 2f _{ββ} + f _{ββ'} - f _{ββ''} + 2f _{ββ°} - f _{ββ†}	
E _g	ν ₈ 380	F ₈₈ = f _β - f _{ββ'} - f _{ββ''} + f _{ββ†}	1.201
E _u	ν ₉ 590	F ₉₉ = f _r - f _{rr'}	2.998

^a stretching constants in mdyn/Å, deformation constants in mdyn/Å/rad², and stretch-bend interaction constants in mdyn/rad.

to be an excellent approximation to a general valence force field for these weakly coupled systems. For the E_u block, only the frequency value of the stretching mode is experimentally known. A comparison with the force field of the related IF₄⁻ anion²⁵ showed that, due to the heavy iodine central atom, the approximation $F_{99} = \lambda_9/G_{99}$ yields an almost exact value for the stretching force constant in the E_u block and was therefore used for IF₄O₂⁻. The resulting force field is listed in Table III and strongly supports our assignments. Table IV gives a comparison of the internal stretching force constants of *trans*-IF₄O₂⁻ with those of the closely related species IF₄⁻,²⁵ IF₄O⁻,²⁶ IF₅,³⁵ IF₅O⁻,²⁹ and IF₆⁺.³⁶ As previously discussed³⁷ for chlorine oxyfluorides, the IF stretching force constants increase in the sequence anions < neutral molecules < cations and within a given group with increasing oxidation state of the iodine central atom. The IO stretching force constants are in the range expected for I=O double bonds and demonstrate that, even in the anions, the formal negative charge is located mainly on the more electronegative fluorine ligands rather than on the oxygen ligand. Consequently, contributions from resonance structures such as I and II are more important



than those from III and IV to explain the bonding in IF₄O₂⁻.



Resonance structures such as I and II also account for the decrease of the IF stretching force constants with increasing formal negative charges and also with decreasing oxidation state of the central atom. Both effects increase the I^{δ+}-F^{δ-} polarity of the IF bonds, thereby causing the bonds to become more ionic, longer, and therefore weaker. This weakening of the IF bonds can be very significant as is demonstrated by the low value of f_r in IF₄⁻, which is only 41% of that in IF₆⁺. The fact that the IO stretching force constant drops from IF₄O⁻ (6.56 mdyn/Å) toward IF₄O₂⁻ (6.15 mdyn/Å), in spite of an increase in the oxidation state of the iodine atom, is interesting and parallels the trends previously noted³⁷ for chlorine oxyfluorides, i.e., the electron-releasing effect of oxygen ligands

in highly electronegative compounds.

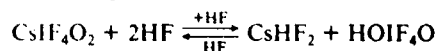
Assignments for *cis*-IF₄O₂⁻. Our assignments for *cis*-IF₄O₂⁻ have been limited to the stretching modes because only 10 of the 15 fundamentals expected for point group C_{2v} have been observed and because no reliable assignments have been published for similar XF₄O₂ species. The assignment of the two IO₂ stretching modes is straightforward on the basis of their high frequencies, relative intensities, and the previously published ¹⁸O spectra.⁹ The symmetric IF₂ axial and the symmetric IF₂ equatorial stretches must belong to the two intense polarized Raman bands at 540 and 609 cm⁻¹, respectively, with the axial mode resulting in a weak and the equatorial mode resulting in a strong infrared counterpart. The antisymmetric axial and the antisymmetric equatorial IF₂ stretches should both be very intense in the infrared spectrum and therefore are assumed to coincide at about 600 cm⁻¹, resulting in a very strong, broad band.

Comparison with Previous IF₄O₂⁻ Assignments. Disregarding some solvent-induced shifts, we find the above assignments for *cis*-IF₄O₂⁻ agree well with those previously reported⁹ by Selig and Elgud for an aqueous solution. The only minor discrepancy is the assignment of the antisymmetric axial IF₂ stretch. For *trans*-IF₄O₂⁻, the assignments proposed by Gillespie and Krasznai for six of the modes have been revised for three of them. The vibrational spectra reported by Carter et al.⁸ show that their sample contained mainly *trans*-IF₄O₂⁻ but was incorrectly interpreted in terms of the *cis* isomer.

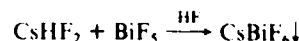
¹⁹F NMR Spectra of IF₄O₂⁻ and HOIF₄O. The presence and the relative amounts of *cis*- and of *trans*-IF₄O₂⁻ in the above samples were verified by ¹⁹F NMR spectroscopy. The spectra were recorded in CH₃CN solution at -70 °C and showed a narrow singlet at δ 65.1 for the *trans* isomer and a broader A₂B₂ pattern at δ 66.0 and 112.8 with $J_{FF} = 204$ Hz for the *cis* isomer. The observed shifts and coupling constant are in fair agreement with the value previously reported for solutions in CH₃CN (*trans* δ 62.0),¹⁰ IF₅ [*cis* δ 68.5, 102.1 ($J_{FF} = 202$ Hz); *trans* δ 70.6], and aqueous HF [*cis* δ 64, 105 ($J_{FF} = 196$ Hz)].⁹

Solutions of CsIF₄O₂ in anhydrous HF at -75 °C resulted in a sharp singlet at δ 62.0 and a broadened A₂B₂ pattern at δ 61.8 and 85.9 with $J_{FF} = 220$ Hz. At room temperature, the A₂B₂ pattern was broadened to the extent that it could barely be detected. Although these spectra are similar to those of IF₄O₂⁻, it was conclusively shown (see below) by Raman spectroscopy that they are due to *cis*- and *trans*-HOIF₄O and not to IF₄O₂⁻. This finding is in excellent agreement with the conclusion⁹ reached by Selig and Elgud that their signals 1 and 2 observed for solutions of NaIO₄ in HF are due to *cis*- and *trans*-HOIF₄O. The observed chemical shifts and coupling constant are in fair agreement with previous reports,^{6,7,9,10} considering the different solvents and conditions used for recording the spectra. The coupling constant of 21 Hz previously reported by Gillespie and Krasznai¹⁰ appears to be a typographical error.

Synthesis and Properties of HOIF₄O. The above described experiments involving CsIF₄O₂ in HF solutions indicate the existence of the equilibrium



which, in the presence of a large excess of HF, is shifted all the way to the right side. In view of the lack of a convenient synthesis of HOIF₄O,^{6,7} this reaction was utilized to prepare HOIF₄O. Since during HF removal the above equilibrium is shifted back to the left, the CsHF₂ was converted into an insoluble BiF₃ salt according to



which can be filtered off at -78 °C. The resulting mixture

(35) Christie, K. O.; Curtis, E. C.; Wilson, R. D. *J. Inorg. Nucl. Chem. Suppl.* 1976, 437.

(36) Christie, K. O.; Sawodny, W. *Inorg. Chem.* 1967, 6, 1783.

(37) Christie, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* 1976, 18, 331.

Table IV. Stretching Force Constants (mdyn/A) of *trans*-IF₄O₂⁻ Compared to Those of Similar Molecules and Ions

	anions			molecules		cation IF ₄ ⁺ (+VII) ^e
	IF ₄ ⁻ (+III) ^a	IF ₄ O ⁻ (+V) ^b	IF ₄ O ₂ ⁻ (+VII)	IF ₄ (+V) ^c	IF ₄ O (+VII) ^d	
<i>f_r</i> (IF)	2.22	2.46	3.27	3.77	4.42	5.42
<i>f_{rr}</i>	0.18	0.16	0.04	0.04	0.00	-0.07
<i>f_{rr'}</i>	0.47	0.45	0.27	0.38	0.18	0.19
<i>f_d</i> (IO)		6.56	6.15		6.99	
<i>f_{da}</i>			0.25			

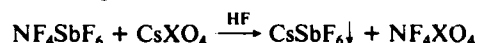
^a Data from ref 25; iodine oxidation state in parentheses for all species. ^b Data from ref 26. ^c Data from ref 35. ^d Data from ref 29. ^e Data from ref 36.

of HOIF₄O and HF can be easily separated by fractional condensation or distillation.

The ¹⁹F NMR spectrum of HOIF₄O in HF solution was recorded at -78 °C and was identical with that of the product obtained by dissolving CsIF₄O₂ in HF (see above). The ratio of *cis* to *trans* isomer in the HOIF₄O sample appeared to be similar to that in the CsIF₄O₂ starting material. It should be pointed out that at room temperature the signal due to the *cis* isomer can be so broad that it is difficult to detect, thereby giving the false impression of dealing with samples containing exclusively the *trans* isomer.

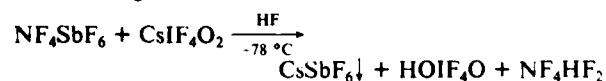
The Raman spectra of liquid HOIF₄O showed some variation. Freshly prepared samples and HF solutions exhibited spectra similar to that of trace A of Figure 3. After the solutions were allowed to stand, the 872 cm⁻¹ band decreased in intensity and bands at 828 and 799 cm⁻¹ started to grow. In addition the bands in the 600–700 cm⁻¹ region became broader and shifted to slightly lower frequencies, as shown by trace B of Figure 3. On the basis of its ¹⁹F NMR spectrum, a sample of HOIF₄O in HF solution, which showed a Raman spectrum very similar to that of trace A of Figure 3, consisted mainly of the *cis* isomer. Whether the change from Raman spectrum A to spectrum B involves a change in the isomer ratio or is caused by association effects was not clearly established.

Synthesis of FOIF₄O. Previous studies have shown that unstable NF₄⁺ salts containing oxyanions such as ClO₄⁻³ or SO₃F⁻⁴ can be prepared by metathesis in anhydrous HF solution according to

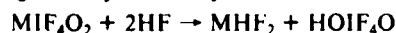


Thermal decomposition of these NF₄⁺ salts provided a new high-yield synthetic route to hypofluorites.^{3,4} Since no examples of iodine hypofluorites had previously been known, it was interesting to examine the applicability of this method to periodates.

Since the IO₄⁻ anion is fluorinated to IF₄O₂⁻ in anhydrous HF, as shown by the above studies and the previous report by Selig and Elgadi,⁹ the metathetical reaction of IC₄⁻ itself could not be studied. However, when IO₄⁻ was replaced by IF₄O₂⁻, the following metathetical reaction occurred:



The CsSbF₆ precipitate could be easily filtered off at -78 °C, and Raman and ¹⁹F NMR spectroscopy of the filtrate showed the presence of NF₄⁺³⁸ and HOIF₄O (see above) with no evidence for the IF₄O₂⁻ anion. This is in agreement with the above results for CsIF₄O₂, which demonstrated that MIF₄O₂ salts undergo solvolysis in anhydrous HF according to



Raman and ¹⁹F NMR spectra showed that these NF₄HF₂/HOIF₄O-containing HF solutions are unstable at room tem-

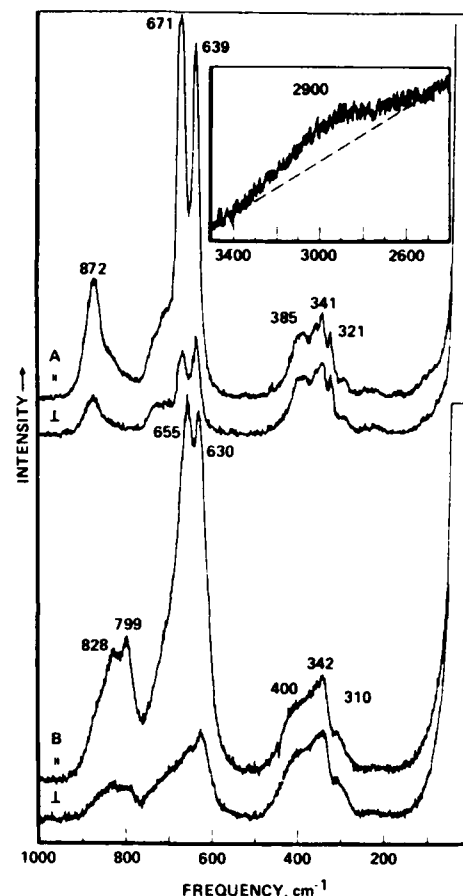


Figure 3. Raman spectra of liquid HOIF₄O, recorded in Teflon FEP tubes at room temperature.

perature and slowly decompose to NF₃^{39,40} and a new compound identified (see below) as a mixture of *cis*- and *trans*-FOIF₄O. At the same time, the relative intensities of the NF₄⁺ and HOIF₄O signals decreased accordingly. When the HF solvent was pumped off at -30 °C from a freshly prepared NF₄HF₂-HOIF₄O solution, a white solid residue was obtained. The low-temperature Raman spectrum of this solid showed the presence of the NF₄⁺ cation, but the remaining bands were too broad to permit a positive distinction among IF₄O₂⁻, HOIF₄O, and possibly some HF₂⁻·*n*HF.³ The new compound FOIF₄O was obtained in high yield by decomposing at room temperature this thermally unstable solid, with the byproduct being NF₃. Since the same products were obtained from HF solutions that, on the basis of their ¹⁹F NMR and Raman spectra, contained only HOIF₄O but not IF₄O₂⁻, it appears

(38) Christe, K. O.; Guertin, J. P.; Pavlath, A. E.; Sawodny, W. *Inorg. Chem.* **1967**, *6*, 533.

(39) Rose, W. B.; Nebgen, J. W.; Metz, F. I. *Rev. Sci. Instrum.* **1966**, *37*, 238.

(40) Shamir, J.; Hyman, I. *J. Spectrochim. Acta, Part A* **1967**, *23A*, 1899.

that FOIF₄O is formed by fluorination of HOIF₄O by either NF₄⁺ or nascent fluorine formed during the thermal decomposition of the marginally stable NF₄⁺HF₂⁻·*n*HF.³ Consequently, it was interesting to investigate whether FOIF₄O could also be obtained by the fluorination of HOIF₄O with elemental fluorine. However, fluorination reactions carried out at 25 °C with the use of either neat or HF solutions of HOIF₄O, 2 atm of F₂ pressure, and a shaker for agitation did not result in any fluorination of HOIF₄O, and only unchanged starting materials were recovered.

Since the fluorination reactions of alkali-metal salts such as CsSF₃O, CsCF₃O, CsClO₄, or KNO₃ with elemental fluorine yield the corresponding hypofluorites,¹ it was interesting to study the analogous fluorination reaction of CsIF₄O₂. In static systems up to 60 °C slow reactions between CsIF₄O₂ and F₂ were observed, producing IF₃O in low yield as the only volatile product. Since IF₃O is the primary decomposition product of FOIF₄O (see below), the intermediate formation of some FOIF₄O in this reaction cannot be ruled out. Similarly, the fluorination of CsIO₄ with F₂ under comparable conditions produced small amounts of IF₃O as the only volatile product. The Raman spectra of the solid residues from both reaction systems showed the presence of CsIF₈,⁴¹ CsIF₆,²² *cis*- and *trans*-CsIF₄O₂, and CsIF₄O.²⁶ The low reactivity of the I=O double bond in IF₃O was further demonstrated by separate experiments, showing that F₂ is not added across the I=O double bond, even in the presence of CsF as a catalyst, at temperature between -196 and +25 °C with the use of an excess of F₂.

Properties of FOIF₄O. As shown by NMR and vibrational spectroscopy (see below), FOIF₄O exists in the form of two isomers, one in which the two oxygens are *cis* and one in which they are *trans* to each other. Attempts were unsuccessful to separate the two isomers by gas chromatography at 25 °C using a 30-ft, 3/16-in. o.d. stainless-steel column containing 50% Halocarbon oil No. 4-11V on Kel-F 300 (70-80 mesh).⁴² Consequently, the physical properties could only be determined for a mixture of both isomers. On the basis of their ¹⁹F NMR peak areas, the ratio of *cis* to *trans* isomers in the sample used for the physical property measurements was 1.92:1. FOIF₄O is colorless as a gas, pale yellow as a liquid, and white in the solid state. The given sample melted at -33.1 °C. Vapor pressures were fitted by the method of least squares to the equation

$$\log [P(\text{mm})] = 7.62925 - 1432.0/[T(\text{K})]$$

the index of correlation being 0.99991. The extrapolated boiling point is 28.37 °C. Measured vapor pressures at the noted temperatures are as follows [*T* (°C), *P* (mm)]: -45.3, 22; -33.1, 47; -23.0, 80; -13.7, 129; 0, 244. The latent heat of vaporization of FOIF₄O is 6.55 kcal/mol and the derived Trouton constant is 21.73, indicating little association in the liquid phase. This is in agreement with the relatively low boiling point and the small changes between the vibrational spectra of the gas and the liquid (see below). The molecular weight was determined from the vapor density and found to be 254.5 (calcd for FOIF₄O 253.9). The good agreement indicates little or no association in the gas phase at the pressure used (*P* ~ 1 atm).

FOIF₄O is marginally stable at room temperature and can be handled in well-passivated metal and Teflon equipment without rapid decomposition. The fact that IF₃O was frequently observed as an impurity in the vibrational and NMR spectra suggests the primary decomposition mode

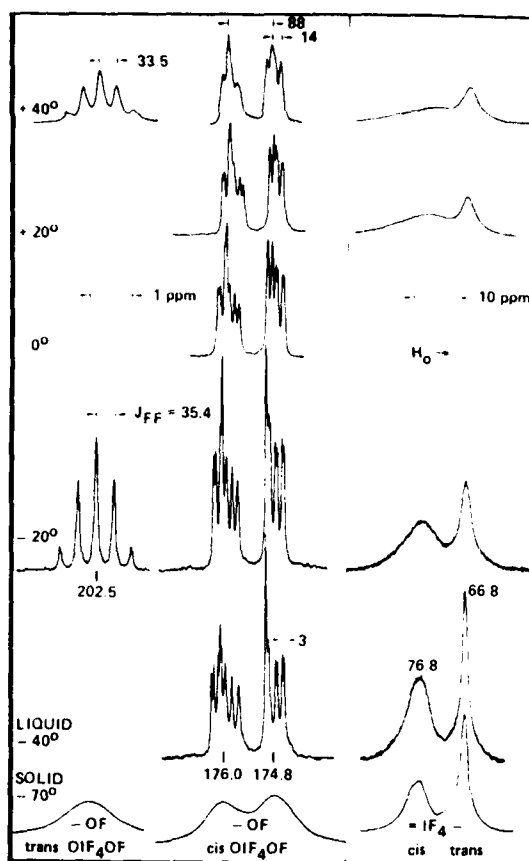


Figure 4. ¹⁹F NMR spectra of *cis*- and *trans*-FOIF₄O recorded at different temperatures. The signals due to the O-F fluorines are given at a 10 times wider scale than those due to fluorines on iodine. Positive shifts are downfield from the external CFCl₃ standard.

When a sample of FOIF₄O has heated in a stainless-steel cylinder to 120 °C for 388 h, decomposition to IF₃ and O₂ was observed. This is not surprising in view of a previous report¹³ that IF₃O readily decomposed to IF₃ and O₂. As expected for a hexacoordinated iodine species, FOIF₄O is neither a good fluoride ion acceptor nor a good donor. Thus, it does not form stable adducts at room temperature with either the strong Lewis acid SbF₅ or the strong Lewis base CsF. Attempts to add FOIF₄O across the C=C double bond in C₂F₄ were unsuccessful. Fluorination and oxygenation of C₂F₄ occurred with COF₂, CF₃COF, and C₂F₆ being the principal reaction products.

¹⁹F NMR Spectra of FOIF₄O. The ¹⁹F NMR spectra of FOIF₄O were recorded for the neat material and HF solutions and were essentially identical. The spectra of the neat liquid and solid are shown in Figure 4, together with the observed chemical shifts and coupling constants. Peak-area measurements showed that the 202 and 67 ppm signals belong to an AX₄ and the 176, 175, and 77 ppm signals to an A₂BCX system. The AX₄ system is readily assigned to the *trans* isomer



The chemical shift of 66.8 ppm of the four equatorial fluorines is almost identical with that in IF₃O (68.5 ppm for neat IF₃O at -20 °C), and that of 202.5 ppm of the fluorine on oxygen

(41) Adams, C. J. *Inorg. Nucl. Chem. Lett.* 1974, 10, 831.

(42) Dayan, V. H.; Neale, C. B. *Adv. Chem. Ser.* 1966, No. 54, 223.

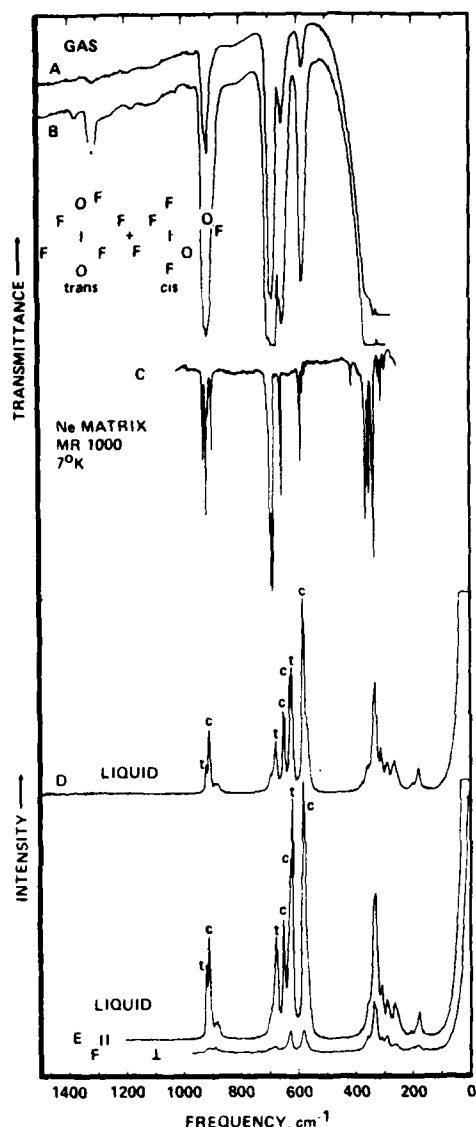


Figure 5. Vibrational spectra of a mixture of *cis*- and *trans*-FOIF₄O in a ratio of about 1.9:1. Traces A and B are infrared spectra of the gas, recorded at pressures of 10 and 95 mm, respectively, in a 5-cm path length cell equipped with AgCl windows. Most of the absorption below 400 cm⁻¹ is due to the window material. Trace C is an infrared spectrum of FOIF₄O isolated in a neon matrix [mole ratio (MR) 1000:1] and recorded at 6 K. Traces D-F are Raman spectra of liquid FOIF₄O recorded in 4-mm o.d. quartz tubes at -20 °C for two samples containing somewhat different ratios of *cis* (c) to *trans* (t) isomers, with the incident polarization parallel and perpendicular.

is similar to those of other hypofluorites such as O₃ClOF (219 ppm),⁴³ SF₃OF (189 ppm),⁴⁴ or *trans*-SeF₄(OF)₂ (179 ppm).⁴⁵ The fluorine-fluorine coupling constant, $J_{FF} = 34$ Hz, is in good agreement with the value of 27 Hz previously reported for the coupling constant of the four equatorial fluorines to the two hypofluorite fluorines in *trans*-SeF₄(OF)₂.⁴⁵ The broadened fluorine on iodine resonance and the lack of observable fine structure of FOIF₄O is attributed to unresolved IF coupling ($I_1 = 5/2$) due to decreased quadrupole relaxation caused by the approximately spherically symmetric electric

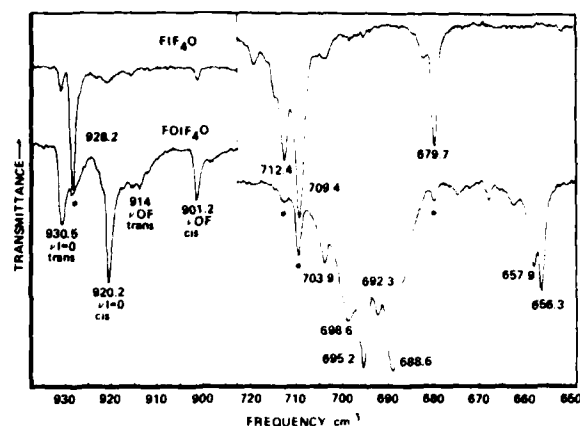


Figure 6. Infrared spectra of IF₃O and FOIF₄O in a Ne matrix (MR 1000:1) at 6 K recorded at 20-fold scale expansion. The bands due to IF₃O in the FOIF₄O spectrum are marked by an asterisk.

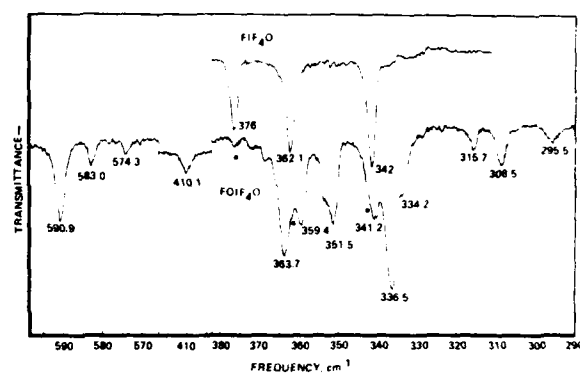
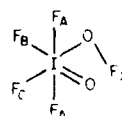


Figure 7. Infrared spectra of IF₃O and FOIF₄O in a Ne matrix (MR 1000:1).

field about the iodine.⁶ The A₂BCX system is assigned to the *cis* isomer



and also shows an unresolved IF signal (at about 77 ppm) and a resolved hypofluorite signal (at about 202 ppm), which exhibits a pronounced temperature dependence. At 40 °C, the OF signal approximates a first-order doublet ($J = 88$ Hz) of triplets ($J = 14$ Hz). Since coupling should be stronger to the *cis* fluorines than to the *trans* fluorine,⁴⁴ this spectrum could then be interpreted as being due to the *cis* isomer with free rotation around the I—O single bond and $J_{BX} = 88$ Hz, $J_{AX} = 14$ Hz, and J_{CX} being too small to be resolved. When the solution is cooled, the line width becomes smaller and the CX coupling becomes observable. As can be seen from Figure 4, the spectrum exhibits pronounced second-order effects, and a computer-aided analysis will be required to obtain precise coupling constants. The fact that the unresolved fluorine on iodine signal has a significantly larger line width for the *cis* than for the *trans* isomer is not surprising because the *cis* isomer possesses three similar but nevertheless nonequivalent types of fluorine on iodine.

Vibrational Spectra of FOIF₄O and IF₃O. The infrared spectra of the gas and of the neon matrix isolated solid and the Raman spectra of liquid and solid FOIF₄O were recorded (see Figures 5–7), and the observed frequencies are summa-

(43) Christe, K. O., unpublished results.

(44) Harris, R. K.; Packer, K. J. *J. Chem. Soc.* 1962, 3077.

(45) Smith, J. E.; Cady, G. H. *Inorg. Chem.* 1970, 9, 1293.

Table V. Vibrational Spectra of FOIF₃O^a

obsd freq, cm ⁻¹ , and rel intens ^b		Raman		tentative assigns to to cis and trans isomers
IR		liquid, -20 °C	solid, -80 °C	
gas	Ne matrix			
1375 vw				2 × 688
1315 w				2 × 655
916 s	930.5 m 920.2 ms 914 mw	926 (2.9) p	924 (1.7)	$\nu(\text{I}=\text{O})_{\text{trans}}$
900 sh	901.2 m	890 (0.6) p	891 (0.4)	$\nu(\text{I}=\text{O})_{\text{cis}}$
701 sh	703.9 m 698.6 s			$\nu(\text{OF})_{\text{trans}}$ $\nu(\text{OF})_{\text{cis}}$
693 vs	695.2 vs 692.3 m	695 sh	690 sh	$\nu_{\text{as}}(\text{IF}_4)_{\text{trans}}$ $\nu_{\text{as}}(\text{IF}_4)_{\text{ax,cis}}$
688 vs	688.6 vs 686 sh 657.9 m	680 (3.9) p	679 (3.3)	$\nu(\text{I}-\text{O})_{\text{trans}}$
653 s	656.3 ms	654 (4.5) p	652 (2.9)	$\nu(\text{I}-\text{O})_{\text{cis}}$
		631 (6) p	630 (5)	$\nu_{\text{as}}(\text{IF}_4)_{\text{ax,cis}}$
		624 (9.2) p	622 (6.8)	$\nu_{\text{as}}(\text{IF}_4)_{\text{trans}}$
584 ms	590.9 ms 583.0 mw 574.3 w 410.1 mw 363.7 ms 359.4 m 353.5 sh 351.5 ms 341.2 m	585 (10) p	586 (10)	$\nu_{\text{as}}(\text{IF}_4)_{\text{eq,cis and}}$ $\nu_{\text{as}}(\text{IF}_4)_{\text{eq,cis}}$
		575 sh	577 (4)	
			570 sh	
		360 sh	358 (1)	
		340 sh		
335 s	336.5 vs 334.2 sh 315.7 mw 308.5 m 295.5 mw	334 (5.4) p	333 (4)	
		311 (0.4) p	311 (0.4)	
		291 (0.7)	291 (1)	
		264 (1) p	263 (0.8)	
		205 (0.1)	203 (0+)	
		182 (0.9) p	183 (0.6)	

^a Mixture of cis and trans isomers. ^b Uncorrected Raman intensities based on trace E of Figure 5.

rized in Table V. The studied samples were mixtures of *cis*- and *trans*-FOIF₃O with a *cis*:*trans* ratio of about 1.9 based on the NMR spectra and, in the matrix study, also contained a small amount of IF₃O, formed during manipulation of the sample. Since the vibrational spectra of *cis*- and *trans*-FOIF₃O and of IF₃O (see Figure 8) are all very similar, the gas-phase infrared spectra are only of limited value for distinguishing the three compounds. However, the Raman spectra of the liquid and solid and particularly the infrared spectra of the matrix-isolated samples definitely confirm the presence of the two FOIF₃O isomers established by the ¹⁹F NMR study. Some distinction of the *cis* from the *trans* isomer bands was possible from a comparison of spectra of samples having different *cis* to *trans* ratios (see for example traces D and E of Figure 5).

Tentative assignments for the stretching modes of *cis*- and *trans*-FOIF₃O are given in Table V and were made by comparison with those established for IF₃O^{14,29} and IF₄O₂⁻ (see above), relying mainly on the observed relative infrared and Raman intensities.

The vibrational spectra observed for IF₃O are in excellent agreement with those previously reported,^{14,29} except for the fact that our spectra do not show a strong infrared band at 640 cm⁻¹. As previously suggested,²⁹ this band is due to IF₃, the principal decomposition product of IF₃O.

Mass Spectra. The recording of the mass spectrum of FOIF₃O presented difficulties due to reaction of the compound with the inlet system, resulting in the formation of some IF₃O. Furthermore, I₂ has almost the same mass (253.8) as the parent FOIF₃O (253.9) thus making a distinction of the two

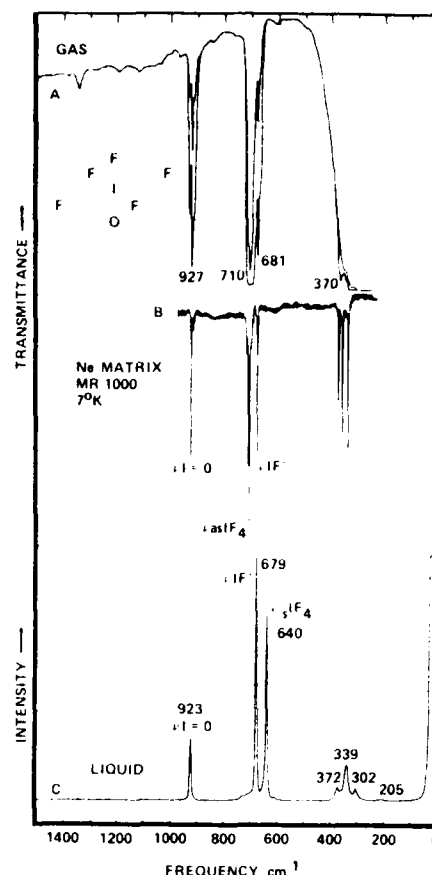


Figure 8. Vibrational spectra of IF₃O. Trace A is infrared spectra of the gas, trace B is an infrared spectrum in a Ne matrix, and trace C is a Raman spectrum of the liquid. All were recorded under conditions identical with those of Figure 5.

Table VI. Mass Spectrum^a of a Mixture of *cis*- and *trans*-FOIF₃O

m/e	rel intens	ion	m/e	rel intens	ion
219	72	IF ₃ O ⁺	165	18	IF ₂ ⁺
203	100	IF ₃ O ⁺	162	38	IOI ⁺
200	32	IF ₃ O ⁺	146	15	IF ⁺
184	18	IF ₃ O ⁺	143	7	IO ⁺
181	73	IF ₃ O ⁺	127	38	I ⁺
178	1	IO ₂ F ⁺			

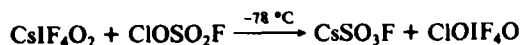
^a Recorded with an ionization potential of 70 eV, with the use of a 1:1 mixture of FOIF₃O and ClF₃. Peaks due to ClF₃ and IF₃O have been subtracted from the pattern.

molecules difficult. These problems were overcome by recording the spectra of pure IF₃O under the same conditions and subtracting the IF₃O pattern from that of the FOIF₃O-containing sample. The interference from I₂ was eliminated by recording spectra of 1:1 mixtures of ClF₃ and FOIF₃O. The ClF₃ oxidized I₂ rapidly to iodine fluorides but did not appear to interact with FOIF₃O. The mass cracking pattern obtained in this manner for FOIF₃O is listed in Table VI and agrees with the expectations⁴⁶ for a hypofluorite. The I-OF single bond is readily broken to yield an intense IF₄O⁺ fragment, which can undergo additional oxygen and/or fluorine loss.

Synthesis of ClOIF₃O. Since FOIF₃O was found to be stable, the synthesis of the analogous hypochlorite, ClOIF₃O, appeared feasible. Using CsIF₄O₂ and ClOSO₂F, a generally

(46) Huston, J. L.; Studier, M. H. *J. Fluorine Chem.* 1979, 13, 235.

useful reagent for the syntheses of hypochlorites,⁴⁷ the synthesis of ClOIF₄O was accomplished according to



The resulting ClOIF₄O appears to be highly reactive, difficult to handle, and thermally unstable. Consequently, the compound could not be well characterized. The main evidence for its existence is the infrared spectrum of the gas, which is similar to that of FOIF₄O except that the O—F stretch is replaced by a band at 763 cm⁻¹, characteristic of an O—Cl stretch,⁴⁷ and the I=O, IF, and I—O stretching modes are shifted to slightly lower frequencies. The compound decomposes to IF₃, and attempts to add it across the C=C double bond of C₂F₄ did not result in stable adducts.

Conclusion. Although the isolation of NF₄⁺ salts of either IO₄⁻ or IF₄O₂⁻ was not possible, solutions containing NF₄⁺ and HOIF₄O were found to decompose to produce FOIF₄O in high yield. This is in marked contrast to the similar syntheses of FOClO₃ and FOSO₂F where the corresponding NF₄⁺ClO₄⁻³

and NF₄⁺SO₃F⁻⁴ salts were shown to be the actual intermediates. FOIF₄O is the first known example of an iodine hypofluorite and exists as cis and trans isomers. It is a stable compound and was thoroughly characterized. The analogous hypochlorite, ClOIF₄O, was also prepared for the first time but, as expected, is considerably less stable than FOIF₄O. The reaction of CsIO₄ with HF was found to be a convenient synthesis of CsIF₄O₂, which, by reaction with BiF₃ in HF, can readily be converted into HOIF₄O, thus providing easy access to tetrafluoroperiodates. The bonding in *trans*-IF₄O₂⁻ was studied by vibrational spectroscopy, and the results of a normal-coordinate analysis are in excellent agreement with the trends previously established³⁷ for chlorine oxyfluorides.

Acknowledgment. The authors are grateful for financial support by the Office of Naval Research, Power Branch, and the U.S. Army Research Office.

Registry No. *trans*-CsIF₄O₂, 77224-44-3; *cis*-CsIF₄O₂, 55188-51-7; *trans*-HOIF₄O, 25685-16-9; *cis*-HOIF₄O, 25685-15-8; *trans*-FOIF₄O, 72151-31-6; *cis*-FOIF₄O, 72123-55-8; ClOIF₄O, 77224-34-1; CsIO₄, 13478-04-1; HF, 7664-39-3; BrF₃, 7789-30-2; ClF₃, 7790-91-2; ClF₂, 13637-63-3; F₂, 7782-41-4; BiF₃, 7787-62-4; NF₄SbF₆, 16871-76-4; ClSO₃F, 13997-90-5; IF₃O, 16056-61-4.

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

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

Properties of Azidotrifluoromethane

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The infrared spectrum of gaseous and the Raman spectrum of liquid CF_3N_3 were recorded. A total of 14 fundamental vibrations out of 15, expected for a model of symmetry C_1 with hindered rotation, were observed and assigned. The UV, ^{19}F NMR, and mass spectra were also recorded and confirm the presence of a covalent azido group. The melting point and vapor pressure curve of CF_3N_3 are reported.

Introduction

Although the existence of CF_3N_3 has been known for almost 2 decades,¹ very little is known about this interesting molecule. In 1961 Makarov and co-workers mentioned¹ that CF_3N_3 is formed during the chlorination of CF_3NNNH_2 , and in 1968 they described its synthesis in more detail.² However, the compound was only characterized by elemental analysis, its boiling point, and a statement concerning its explosive properties at elevated temperature.² No further information on CF_3N_3 could be found in the literature. This is not surprising in view of the explosive character generally exhibited by covalent azides.^{3,4} In view of this paucity of data, a characterization of CF_3N_3 was carried out, the results of which are summarized in this paper.

Experimental Section

Caution! Although no explosions were encountered in this study, covalent azides are in general explosive,^{3,4} and Makarov and co-workers reported that CF_3N_3 explodes at 330 °C.² Consequently, appropriate safety precautions should be taken when working with larger amounts of CF_3N_3 .

Materials and Apparatus. Volatile materials were manipulated in a 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. Gas chromatographic data were obtained with use of a Varian GC under isothermal conditions with a stainless-steel column (1/8 in. $\times$ 10 ft) packed with Poropak PS. Trifluoronitrosomethane (PCR Research Chemicals, Inc.) and hydrazine (Olin-Mathieson) were used as received.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer using a Teflon cell of 5-cm path length equipped with CsI windows. The spectrometer was calibrated by comparison with standard gas calibration points,^{5,6} and the reported frequencies are believed to be accurate to $\pm 2 \text{ cm}^{-1}$.

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 filter⁷ for the elimination of plasma lines. Quartz tubes (4-mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A previously described⁸ device was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al.⁷

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 .⁹

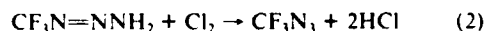
The mass spectra were recorded with an LAI Quad 300 quadrupole spectrometer at an ionization potential of 40 eV.

The UV spectra were recorded on Cary Model 14 spectrophotometer using a stainless-steel cell of 10-cm path length equipped with sapphire windows.

Synthesis of CF_3N_3 . A 200-ml. glass ampule containing a stirring bar was loaded with 78.1 mmol of N_2H_4 and 40 ml. of CH_3OH , stirred and cooled to -78°C . After removal of air, CF_3NO (83 mmol) was bled into the cooled ampule during 2.5 h resulting in a blue-green solution. Trifluoronitrosomethane in the vapor phase was removed, and Cl_2 was added (78 mmol during 2 h) to the stirred -78°C solution giving a light yellow liquid phase. The solution was allowed to warm slowly, and the gas generated was passed through a coarse glass frit, NaOH scrubber. In 4 h approximately 76 mmol of crude CF_3N_3 passed the scrubber. Final purification was effected by fractional condensation through traps cooled at -78 , -126 , -142 , and -196°C . The -196°C fraction was mainly CF_3NO while the -78°C trap contained traces of material which was discarded without examination. The remaining traps contained the colorless CF_3N_3 (70 mmol, 89% yield on the basis of N_2H_4 taken) whose GC indicated purity was 98–99%. Storage in stainless-steel cylinders for several weeks at ambient temperature at several atmospheres pressure did not result in any significant decomposition.

Results and Discussion

Synthesis and Properties of CF_3N_3 . For the synthesis of CF_3N_3 the procedure of Makarov and coworkers² was followed. It involves reactions 1 and 2.



Azidotrifluoromethane is white as a solid and colorless as a liquid and a gas. It melts at -152°C . It is stable at room temperature and can be handled without noticeable decomposition. Vapor pressures were measured over the range -95 to -45°C , and the data were fitted by the method of least squares to eq 3 with an index of correlation of 0.9998. The

$$\log P (\text{mm}) = 7.8748 - 1221.7/T (\text{K}) \quad (3)$$

extrapolated boiling point is -28.5°C , in good agreement with that of -28.5°C at 743 mm, previously reported.² Measured vapor pressures at the noted temperatures are as follows (T , $^\circ\text{C}$; P , mm): -95.2 , 10; -78.6 , 40; -64.6 , 108; -45.5 , 324. The latent heat of vaporization of CF_3N_3 is 5.591 kcal/mol, and the derived Trouton constant is 22.9, indicating little association in the liquid phase.

Vibrational Spectra. Figure 1 shows the infrared spectrum of gaseous and the Raman spectrum of liquid CF_3N_3 . The observed frequencies are listed in Table I. By analogy with the known structures of CH_3N_3 ,^{10,11} CF_3OF ,^{12,13} and ClN_3 ,¹⁴

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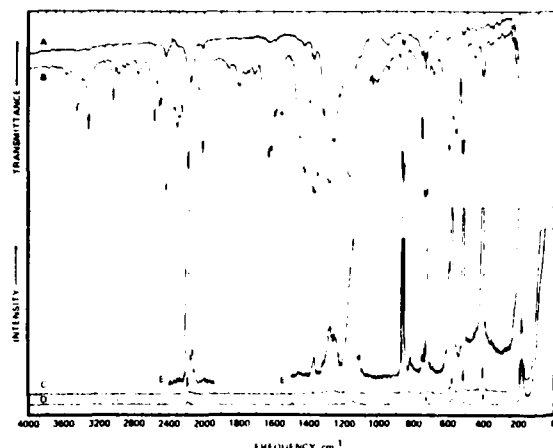
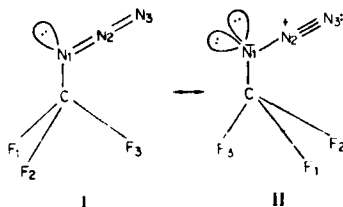


Figure 1. Vibrational spectra of CF_3N_3 . Traces A and B: infrared spectra of the gas recorded in a 5-cm path length cell equipped with CsI windows at pressures of 8 and 255 mm, respectively. The bands marked by a diamond and an asterisk are believed to be due to an impurity and CF_3NO , respectively. Traces C-E: Raman spectra of the liquid, recorded at -100°C at two different sensitivities and with the incident polarization parallel and perpendicular.

the CF_3N_3 molecule is expected to possess a structure of symmetry C_s with a planar CN_3 backbone, an approximately linear N_3 group, a staggered CF_3 group, and $r_{\text{N}_1\text{N}_2}$ ($\sim 1.25 \text{ \AA}$) being significantly longer than $r_{\text{N}_2\text{N}_3}$ ($\sim 1.13 \text{ \AA}$) due to II being



the most important resonance structure. Structure I would be analogous to that of $\text{CF}_3\text{N}=\text{O}^{15}$ in which the CF_3 and NO group are eclipsed. Whether the CF_3 is eclipsed or staggered depends on the coordination number of N_1 , including its sterically active valence electron pairs as ligands. If N_1 is three-coordinated, as in CF_3NO or structure I, the highly repulsive free valence electron pair of N_1 will avoid the fluorine ligands of the CF_3 group and therefore cause the free valence electron pair of N_1 to be staggered and the $\text{N}=\text{X}$ ligand to be eclipsed relative to the CF_3 group. However, if N_1 is four-coordinated, as in II, the two free valence electron pairs on N_1 and the $\text{N}-\text{X}$ group should all be staggered with respect to the CF_3 group.

Assuming hindered rotation of the CF_3 group, CF_3N_3 should exhibit 15 fundamental modes of vibration, all active in both the infrared and the Raman spectra. Of these, 10 belong to species a' and can be either polarized or depolarized, while 5 belong to species a'' and should be depolarized in the Raman spectrum. An approximate description of these 15 fundamental vibrations is given in Table II. Eight of them involve motions of the CF_3 group, four are due to the N_3 group, and three involve the $\text{C}-\text{N}$ linkage.

Assignments for the four N_3 modes were made by comparison with the known spectra of the covalent azides, FN_3^{16} ,

Table I. Vibrational Spectra of CF_3N_3 .

obsd freq, cm^{-1} , and intens ^a		
IR (gas)	Raman (liquid)	assign in point group C_s
3465 w		$\nu_1 + \nu_2$ - 3466 (a')
3436 sh		$\nu_1 + \nu_2$ - 3436 (a')
3327 w		$\nu_1 + \nu_2$ - 3332 (a')
3039 w		$\nu_1 + \nu_2$ - 3041 (a')
2755 vw		$\nu_1 + \nu_2$ - 2762 (a')
2567 w		$2\nu_2$ - 2568 (a')
2510 w		$2\nu_2$ - 2508 (a')
2440 mw		$\nu_2 + \nu_4$ - 2434 (a')
2410 sh		$\nu_2 + \nu_4$ - 2404 (a')
2354 vw		$\nu_1 + \nu_{11}$ - 2361 (a')
2302 vw		$2\nu_4$ - 2300 (a')
2270 vw		
2183 s	2182 (1.1) p	ν_1 (a')
2140 m	2137 (0.1)	$\nu_2 + \nu_6$ - 2143 (a')
2018 mw		$\nu_2 + \nu_6$ - 2014 (a')
1856 vw		$\nu_2 + \nu_7$ - 1864 (a')
1798 w		$\nu_2 + \nu_6$ - 1797 (a')
1713 vw		$2\nu_2$ - 1718 (a')
1629 mw		{impurity?
1613 mw		
1590 w		$\nu_1 + \nu_6$ - 1589 (a') or CF_3NO ?
1455 w		$2\nu_6$ - 1460 (a')
1427 mw		$\nu_1 + \nu_{10}$ - 1432 (a')
1370 mw	1370 (0.1)	$\nu_1 + \nu_6$ - 1372 (a')
1316 m		$\nu_6 + \nu_7$ - 1310 (a')
1284 vs, PQR	1280 (0.2) p	ν_3 (a')
1255 ms	1253 (0.2) p	ν_3 (a')
1223 mw		C_2F_3 impurity?
1169 vs	1165 sh, dp?	ν_{11} (a'')
1152 sh	1149 (0.5) p	ν_4 (a')
1110 sh	1110 (0+)	C_2F_3 impurity or $2\nu_{11}$ = 1112 (a')?
1034 vw		$\nu_1 + \nu_{10}$ - 1038 (a')
1009 vw		
859 mw, PQR	859 (10) p	ν_1 (a')
	814 (0+)	?
751 w, PQR	751 (0+)	$\nu_2 + \nu_{10}$ - 759 (a')
731 m, PQR	730 (3.8) p	ν_6 (a')
687 vw	685 (0+)	$\nu_6 + \nu_{10}$ = 692 (a')
594 mw	594 (0.2) dp	ν_{12} (a'')
582 sh	580 (1.1) p	ν_7 (a')
557 w	555 sh	ν_{13} (a'')
513 mw, PQR	514 (1.7) p	ν_3 (a')
450 vw		ν_{14} (a'')
402 w, PQR	403 (1.6) p	ν_4 (a')
	179 (4.3) p	ν_{10} (a')

^a Uncorrected Raman intensities representing relative peak height.

ClN_3 ,^{16,17} BrN_3 ,¹⁶ IN_3 ,¹⁸ CH_3N_3 ,¹⁹⁻²² CD_3N_3 ,^{21,22} HN_3 ,²³⁻²⁷ DN_3 ,²³⁻²⁷ and OPF_2N_3 ²⁸ (see Table II). Of the four N_3 modes, two are due to stretching motions, one antisymmetric and one symmetric. Since the two NN bonds significantly differ in their bond strength, the higher frequency mode might equally well be described as mainly a stretching of the N_2N_3 bond and the lower one as mainly a stretching of the N_1N_2 bond; however, due to the linear N_3 structure, both modes should be strongly coupled.²² On the basis of its high frequency and relative intensity, the N_2N_3 stretch is readily assignable to the

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Table II. Assignment of the 15 Fundamental Vibrations of Cl_3N Compared to Those of Closely Related Molecules

assign	approx description of mode for CF_3N_3	obsd freq, cm^{-1}									
		CF_3N_3	Cl_3NO^a	Cl_3COOH^b	N_2	CN^c	BrN_3^e	IN^d	CH_3N_3^f	CD_3N_3^f	HN^f
ν_1	$\nu_{\text{as}}(\text{N}_3)$ or $\nu(\text{N}_2\text{N}_3)$	1282	1291	1254	2034	2066	2062	2058	2106	2118	2140
ν_2	$\nu_{\text{g}}(\text{Cl}_3)$	1284	1284	1211							
ν_3	$\nu_{\text{as}}(\text{CF}_3)$	1254	1230	1211							
ν_4	$\nu_2(\text{N}_3)$ or $\nu(\text{N}_1\text{N}_2)$	1150	809		1086	1144	1160	1176	1272	1285	1151
ν_5	$\nu(\text{C}-\text{N})$	859	730	781					910	830	
ν_6	$\delta_3(\text{CF}_3)$	730	730		503	520	530	578	666	640	534
ν_7	$\delta(\text{N}_3)$ in plane	580									
ν_8	$\delta_{\text{as}}(\text{CF}_3)$	513	533	508							
ν_9	$\delta_{\text{rock}}(\text{CF}_3)$	402	428						245	231	
ν_{10}	$\delta(\text{CNN})$	179	296								
ν_{11}	$\nu_{\text{as}}(\text{CF}_3)$	1168	1175	1189					560	560	607
ν_{12}	$\delta(\text{N}_3)$ out of plane	594									
ν_{13}	$\delta_{\text{as}}(\text{CF}_3)$	556	551	591							
ν_{14}	$\delta_{\text{rock}}(\text{CF}_3)$	450	428								
ν_{15}	τ		[50] ^h						126	90	

^a Data from ref 29 and 30 with some revised assignments. ^b Data from ref 32. ^c Data from ref 16. ^d Data from ref 18. ^e Data from ref 12-22. ^f Data from ref 27. ^g Data from ref 28. ^h Estimated value from ref 29.

band at about 2180 cm^{-1} . The N_1N_2 stretch should occur in the frequency range between 1090 and 1270 cm^{-1} and most likely be of higher Raman intensity than the CF_3 stretching modes. It is therefore assigned to the Raman band at about 1150 cm^{-1} . This assignment agrees well with those reported for ClN_3 ,¹⁶ BrN_3 ,¹⁶ and IN_3 ,¹⁸ for which this mode occurs at 1144 , 1160 , and 1176 cm^{-1} , respectively.

The in plane (a') and out of plane (a'') N_3 deformation modes should occur in the 500 – 660 cm^{-1} range (see Table II). Two polarized Raman bands were observed in this range at 580 and 514 cm^{-1} , respectively, and must be due to the in plane N_3 deformation and the antisymmetric a' CF_3 deformation mode. Based on the similarity of the frequencies of the CF_3 modes in CF_3N_3 and CF_3NO ,^{29,30} (see Table II), we prefer to assign the 580 cm^{-1} fundamental to the N_3 a' deformation and the 514 cm^{-1} one to the CF_3 a' deformation mode. A similar choice exists for the two corresponding a'' modes for which two bands at 594 and 556 cm^{-1} are available for assignment. By comparison with the related compounds listed in Table II and based on intensity arguments, we prefer to assign 594 cm^{-1} to $\delta(\text{N}_3)$ (a'') and 556 cm^{-1} to $\delta_{\text{as}}(\text{CF}_3)$ (a''). Spectra of ^{15}N -substituted CF_3N_3 would be required to confirm these assignments.

The assignment of the three fundamental vibrations involving mainly the C–N linkage presents no difficulties because they occur at frequencies outside of the ranges expected for the CF_3 and N_3 modes. Thus, the C–N stretching mode obviously²² must be assigned to the strongest Raman band at 859 cm^{-1} , and the second strongest Raman band at 179 cm^{-1} must be due to the CNN angle deformation. The latter mode was observed²² at 245 and 231 cm^{-1} for CH_3N_3 and CD_3N_3 , respectively, and the further mass increase of the methyl group in CF_3N_3 can account for the observed additional frequency decrease. The C–N torsional modes in CH_3N_3 and CD_3N_3 have frequencies of 126 and 90 cm^{-1} , respectively.¹⁹ On the basis of the larger mass of the CF_3 group, this mode should show again a frequency decrease for CF_3N_3 and should occur well below 90 cm^{-1} . Due to its low frequency, this mode could not experimentally be observed in the present study.

Assignments for a CF_3 group with hindered rotation (C_2 symmetry) are generally difficult; however, several recent thorough studies of the vibrational spectra of CF_3X type compounds such as CF_3COX ,^{31,32} CF_3NO ,^{29,30} and CF_3OF ,^{33–37} have provided valuable information and permit assignments for most of the CF_3 modes.

As previously pointed out by Redington,³² the CF_3 modes of molecules of symmetry C_3 can be related to those of molecules of symmetry C_{3v} , for which the assignments are well established. Such a correlation is shown in Table III for CF_3N_3 , CF_3NO ,^{29,30} CF_3COOH ,³² CF_3CN ,³⁸ CF_3CCH ,³⁸ and CF_3H .³⁹ Under C_3 symmetry the doubly degenerate e modes of C_{3v} split into one a' and one a'' component. Although the degree of splitting can significantly vary from compound to compound, the average of the a' and the a'' frequency is similar

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Table III. Spectral Correlation between the Fundamental Vibrations of the CF_3 Group in Molecules of Symmetry C_{3v} and Those of Symmetry C_{30}

C_{3v}					C_s				
class	description of mode	obsd freq, cm^{-1}			obsd freq, cm^{-1}			class	description of mode
		CF_3CN^a	CF_3CCH^a	CF_3H^b	CF_3COOH^c	CF_3N_3^d	CF_3NO		
a_1	$\nu_s(\text{CF}_3)$	1227 ^a	1253 ^a	1117	1254	1284	1291	a'	$\nu_s(\text{CF}_3)$
	$\delta_s(\text{CF}_3)$ (umbrella)	522 ^a	536 ^a	700	781	730p	730	a'	$\delta_s(\text{CF}_3)$
e	$\nu_{as}(\text{CF}_3)$	1214	1179	1152	1211	1254	1230	a'	$\nu_{as}(\text{CF}_3)$
					1200	1211	1203	f	
					1189	1168dp	1175	a''	$\nu_{as}(\text{CF}_3)$
					591	556	551	a''	$\delta_{as}(\text{CF}_3)$
	$\delta_{as}(\text{CF}_3)$ (scissor)	618	612	507	549	535	542	f	
					508	513p	533	a'	$\delta_{as}(\text{CF}_3)$
	$\delta_{rock}(\text{CF}_3)$	463	453		434	450	428	a'	$\delta_{rock}(\text{CF}_3)$
					402p		a'	$\delta_{rock}(\text{CF}_3)$	

^a Data from ref 38. ^b Data from ref 39. ^c Data from ref 32. ^d p and dp indicate polarization in the Raman spectra. In C_{3v} symmetry, a' modes cannot be polarized. ^e Strongly coupled modes (see text). ^f Average frequency of a' and a'' .

to that of the corresponding degenerate e mode. However, the following secondary effects which can influence the frequencies must be kept in mind: (i) the covalency, and thereby the bond strength and frequency values, of the C-F bonds in CF_3X increases with increasing electronegativity of X, and (ii) coupling between certain modes can result in large frequency shifts. The tendency for strong coupling is particularly pronounced in the a' block, when the symmetric CF_3 stretching, the C-X stretching, and the symmetric CF_3 deformation strongly mix with each other.

In CF_3N_3 , the corresponding three fundamentals occur at 1284, 859, and 730 cm^{-1} and are readily identified by their PQR band contours (parallel bands of an approximate accidental spherical top molecule) and highly polarized Raman bands. On the basis of our experience with related molecules and the observed infrared and Raman intensities, the 1284-cm^{-1} fundamental might be described as an antisymmetric combination of the symmetry coordinates of $\nu_s(\text{CF}_3)$ and those of $\nu(\text{C-N})$, the 859-cm^{-1} fundamental as a symmetric combination of the same symmetry coordinates with some contribution from $\delta_s(\text{CF}_3)$, and the 730-cm^{-1} fundamental as mainly a symmetric combination of the symmetry coordinates of the $\nu(\text{C-N})$ and $\delta_s(\text{CF}_3)$. Due to this pronounced mixing, arguments concerning the identity of these modes are not very meaningful. It should be kept in mind, however, that, particularly in the a' block of CF_3X type molecules, the above described coupling can cause the frequencies of $\nu_s(\text{CF}_3)$ and $\delta_s(\text{CF}_3)$ to move apart, resulting in an unexpected high frequency for $\nu_s(\text{CF}_3)$ and a low one for $\delta_s(\text{CF}_3)$. This in turn may result for different CF_3X type compounds in a different sequence of the a' and a'' fundamentals and is one of the principal reasons for the existing confusion concerning the proper assignment of CF_3 group fundamental vibrations. The coupling between $\nu_s(\text{CF}_3)$ and $\delta_s(\text{CF}_3)$ in a' of a CF_3X type molecule is enhanced when the C-X stretch has a frequency intermediate between those of $\nu_s(\text{CF}_3)$ and $\delta_s(\text{CF}_3)$, and in these cases great care should be exercised when the CF_3 fundamentals are assigned.

For CF_3N_3 , the following CF_3 modes can be assigned with reasonable confidence. The three CF_3 stretching modes are expected to occur in the $1150\text{--}1300\text{-cm}^{-1}$ region and therefore are assigned to the fundamental vibrations at about 1168, 1254, and 1284 cm^{-1} . Since the two higher frequency bands are definitely polarized in the Raman spectrum, the 1168-cm^{-1} band must represent the antisymmetric CF_3 stretch of species a'' , in good agreement with previous conclusions.^{31,32,40} On the basis of its PQR infrared band contour,

its higher Raman intensity and a comparison with similar molecules,^{31,32,40} the highest frequency fundamental vibration is assigned to $\nu_s(\text{CF}_3)$ (a'). On the basis of analogous arguments, the 730-cm^{-1} fundamental vibration must be assigned to the symmetric CF_3 deformation of species a' . Adopting the above assignments for the two N_3 deformation modes, the antisymmetric CF_3 deformation modes are ascribed to the 556- and 513-cm^{-1} bands with the Raman polarization data unambiguously distinguishing the a' from the a'' mode. The CF_3N_3 assignments also suggest that in Redington's³² and Berney's³¹ previous studies the assignments of the $\delta_{as}(\text{CF}_3)$ (a'), and $\delta_{as}(\text{CF}_3)$ (a'') might need to be interchanged. Although intensity arguments were cited against such an exchange, it is supported by Raman polarization data.^{31,32}

The two modes which in most studies could be assigned only with difficulties are the a' and a'' CF_3 rocking modes. As can be seen from Table III, the corresponding degenerate e mode of symmetry C_{30} occurs at about 460 cm^{-1} . Therefore, the polarized Raman band, generally observed for CF_3X compounds of symmetry C_{3v} in the range $400\text{--}430\text{ cm}^{-1}$ should represent the a' CF_3 rocking mode. Since the a'' CF_3 rocking mode must be depolarized in the Raman spectrum, the 179-cm^{-1} fundamental vibration of CF_3N_3 cannot be assigned to this mode. The only vibration left for a possible assignment to the a'' CF_3 rocking mode is the weak infrared band at 450 cm^{-1} , unless a coincidence of the symmetric and of the antisymmetric CF_3 rocking mode is assumed at 403 cm^{-1} , which would leave no plausible assignment for the 450-cm^{-1} band.

A normal coordinate analysis was not carried out because of the grossly underdetermined nature of the problem and the strong coupling experienced by us and others^{30,36} for CF_3X type species. Since the force constants and the resulting potential energy distributions can be varied over a wide range with exact reproduction of the observed frequencies, PED-based conclusions concerning the identities of certain fundamental vibrations should be treated with the necessary scepticism.

Numerous overtones and combination bands were observed in the infrared spectrum at higher sample pressures. Almost all of them could be readily assigned (see Table I) and confirm the proposed assignments. The only detectable impurities were possibly traces of C_2F_6 and CF_3NO .

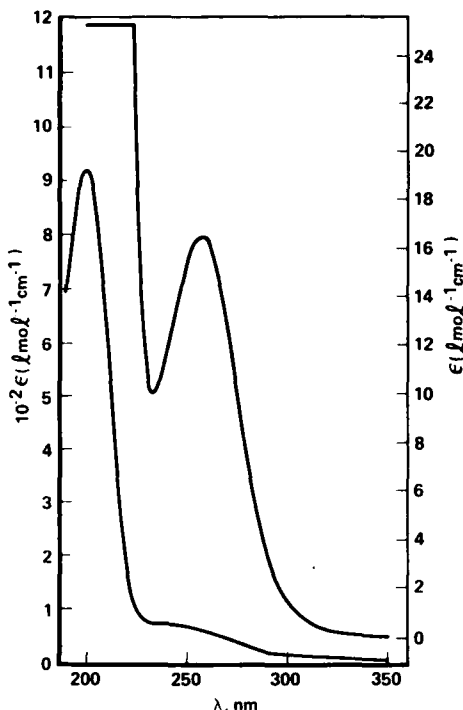
¹⁹F NMR Spectrum. The ¹⁹F NMR spectrum of CF_3N_3 was recorded at 27°C in CFCl_3 solution. It consisted of a sharp singlet at 57.6 ppm , upfield from internal CFCl_3 , characteristic for a CF_3 group with all three fluorines being equivalent on a NMR time scale. This is not surprising in view of the relatively low barrier to internal rotation expected^{19,29,37} for a molecule such as CF_3N_3 .

Mass Spectrum. The mass spectrum of CF_3N_3 is listed in Table IV. It shows a strong parent ion at $m/e\ 111$ and a

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Table IV. Mass Spectrum of CF_3N_3

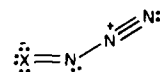
<i>m/e</i>	rel intens	assignt	<i>m/e</i>	rel intens	assignt
28	90	N_2	64	52	CF_2N
31	68	CF	69	100	CF_3
42	27	N_2	92	31	CF_2N_2
45	37	CFN	111	79	CF_3N_2
50	39	CF_2			

Figure 2. UV absorption spectrum of gaseous CF_3N_3 .

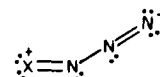
strong N_3^+ fragment, typical for covalent azides. As expected, the base peak is due to CF_3^+ , but surprisingly, the CF_3N^+ peak at m/e 83 was extremely weak (less than 1%), in contrast to organic azides which generally show RN^+ as base peak. However, the high intensity of the N_2^+ and CF_2N^+ peaks indicate that in CF_3N_3 N_2 elimination is also important, but that CF_3N readily loses a fluorine to form the relatively stable CF_2N radical.⁴¹

UV Spectrum. The UV absorption spectrum of gaseous CF_3N_3 is shown in Figure 2. The spectrum shows two strong

absorptions at 200 and 258 nm, which by analogy to previous assignments for similar covalent azides⁴² might be assigned to the $\text{sp}_x \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the azido group, respectively. The previous suggestions,⁴² that the energy difference between these two electronic transitions in a given XN_3 molecule is both a measure for the polarity of the $\text{X}-\text{N}$ bond and an indication for a negatively polarized chlorine in ClN_3 , appear questionable. If these suggestions were correct, the replacement of the three hydrogens in CH_3N_3 by three fluorines should result in a closer match of the electronegativities of the methyl and the azido group and hence an increased covalency and a larger energy difference between the two electronic transitions. However, this is clearly not the case. The previously postulated $\text{Cl}-\text{N}_3^+$ polarization is also incompatible with the well-established⁴ reaction chemistry of ClN_3 which clearly demonstrates the electropositive character of chlorine in this compound. The principle argument previously presented⁴ for the $\text{Cl}-\text{N}_3^+$ polarization in ClN_3 was the relatively high frequency of the $\text{N}-\text{Hal}$ stretching modes in ClN_3 and BrN_3 . It was suggested that these high frequencies are due to partial $\text{N}=\text{X}$ double bonding and that this partial double-bond character can only be explained by the following resonance structure invoking a formal negative charge on the halogen atom



Obviously, the possibility of the more likely resonance structure



which results also in an $\text{X}=\text{N}$ double bond but with a positively polarized halogen was overlooked.

Summary. Azidotrifluoromethane is a relatively stable compound, and some of its physical properties were determined. The spectroscopic data show that CF_3N_3 contains a covalent azido group, similar to those of other covalent azides of known structure, such as CH_3N_3 or ClN_3 . Whether the azido group is linear, as in CH_3N_3 or HN_3 , or slightly bent, as in ClN_3 , is difficult to say on the basis of the available data.

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Perfluoroammonium and Cesium Fluorotungstates

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The syntheses of NF_4^+ salts containing fluorotungstate anions were studied. The new NF_4WOF_3 salt was prepared by the reaction of WOF_4 with a concentrated solution of NF_4HF_2 in anhydrous HF. It is a white solid, stable up to 60 °C. At higher temperatures it decomposes to $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$, NF_3 , OF_2 , and WF_6 . The ionic nature of NF_4WOF_3 in the solid state was established by vibrational spectroscopy, but in dilute HF solutions the WOF_3^- anion solvolyzes according to $2\text{WOF}_3^- + \text{HF} \rightleftharpoons \text{W}_2\text{O}_2\text{F}_9 + \text{HF}_2^-$. In HF solution WF_6 is readily oxidized by NF_4^+ to yield WF_6 and NF_3 . The syntheses and some reaction chemistry and properties of CsWOF_3 , $\text{CsW}_2\text{O}_2\text{F}_9$, $\text{Cs}_2\text{W}_2\text{O}_2\text{F}_4$, and CsWF_6 are discussed.

Introduction

The synthesis of a stable NF_4^+ salt containing a fluorotungstate anion is of significant interest for solid-propellant WF_6 gas generators. In this paper the synthesis and characterization of the first known example of a stable NF_4^+ fluorotungstate salt are reported, and some reaction chemistry of various cesium fluorotungstates in anhydrous HF is discussed.

Experimental Section

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 were carried out in HF solution with use of an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter.¹ Thermal decomposition measurements were carried out in a previously described² 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 a Claassen filter³ 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.

The ^{19}F NMR spectra were 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 the standard.⁴

Elemental analyses were carried out as previously described.⁵

Materials. Literature methods were used for the syntheses of NF_4SbF_6 ,⁶ NF_4HF_2 solutions in HF,⁷ and WOF_4 .⁸ Hydrogen fluoride (Matheson) was dried by storage over BiF_3 to remove the H_2O .⁹ Tungsten hexafluoride (Alfa) and CsI (Alfa, 99.9%) were used as received. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox. Sulfur dioxide (Matheson) was dried over P_2O_5 and purified by fractional condensation prior to use.

Preparation of CsWOF_3 . Cesium fluoride (9.93 mmol) was loaded inside the drybox into a prepassivated Teflon FEP ampule. Anhydrous

HF (15 mL, liquid) was added to the ampule on the vacuum line, and 9.9 mmol of distilled H_2O was added with a syringe. The mixture was allowed to homogenize, and WF_6 (9.96 mmol) was added in vacuo at -196 °C. After the ampule was kept at ambient temperature for several hours, all material volatile at 55 °C was pumped off. On the basis of its weight and vibrational spectra, the solid residue was mainly CsWOF_3 ^{10,11} containing only small amounts of $\text{CsW}_2\text{O}_2\text{F}_9$ ¹² and CsHF_2 .

Preparation of $\text{CsW}_2\text{O}_2\text{F}_9$ by Solvolysis of CsWOF_3 in HF. A sample of CsWOF_3 (2.35 mmol) in a Teflon ampule was stirred in anhydrous HF (10 mL, liquid) for 12 h at 24 °C. The undissolved material was separated from the solution by filtration at 24 °C, and all volatile material was pumped off at 55 °C. On the basis of the observed mass balance and vibrational spectra, the filter cake consisted of $\text{CsW}_2\text{O}_2\text{F}_9$ ¹² (~1.1 mmol) and the filtrate residue consisted of CsHF_2 (~1.2 mmol) containing as an impurity $\text{Cs}_2\text{W}_2\text{O}_2\text{F}_4$,¹³ which was formed by hydrolysis of some CsWOF_3 .

Preparation of $\text{Cs}_2\text{W}_2\text{O}_2\text{F}_4$. Cesium fluoride (37 mmol) and 20 mL of 48% aqueous HF were combined in a Teflon FEP ampule to which WF_6 (18.47 mmol) was added at -196 °C on the vacuum line. When the mixture warmed to room temperature, initially a white precipitate formed, which subsequently dissolved, resulting in a clear solution. The solution was poured into a 250-mL Teflon beaker, and the aqueous HF solvent was evaporated on a hot plate at 60 °C. The resulting white residue (10.24 g, weight calculated for 18.47 mmol of $\text{Cs}_2\text{W}_2\text{O}_2\text{F}_4$ = 10.40 g) was shown by vibrational spectroscopy to be essentially pure *cis*- $\text{Cs}_2\text{W}_2\text{O}_2\text{F}_4$.¹³ Treatment of $\text{Cs}_2\text{W}_2\text{O}_2\text{F}_4$ with anhydrous HF resulted in the partial conversion of $\text{Cs}_2\text{W}_2\text{O}_2\text{F}_4$ to CsWOF_3 , $\text{CsW}_2\text{O}_2\text{F}_9$, and CsHF_2 .

Preparation of CsWF_6 . Cesium iodide (21.2 mmol) was loaded in the drybox into a prepassivated Teflon U-tube, equipped with a Teflon filter, and anhydrous HF (26 mL, liquid) was added at -196 °C on the vacuum line. On warming toward ambient temperature, the HF reacted with the CsI to form HI, which accumulated in the bottom of the U-tube as a separate liquid phase. Tungsten hexafluoride (32.46 mmol) was added to the U-tube at -196 °C, and the mixture was allowed to warm to ambient temperature. A copious precipitate of black iodine crystals formed. The mixture was kept at 25 °C for 12 h, and the clear solution was filtered into a second prepassivated Teflon U-tube attached through Teflon tubing and valves to the first U-tube. The HF solvent and small amounts of I_2 were pumped off from the contents of the second U-tube at 55 °C for 2 h, resulting in a slightly off-white solid (4.856 g, weight calculated for 21.2 mmol of CsWF_6 = 9.144 g), which was identified by vibrational spectroscopy^{14,15} as CsWF_6 . A second extraction of the precipitate with 16 mL of liquid HF resulted in an additional 3.011 g of CsWF_6 , indicating that CsWF_6 is only moderately soluble in HF.

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Reaction of CsI with SO₂. Dry CsI (6.30 mmol) was loaded in the drybox into a Teflon ampule, and SO₂ (51.4 mmol), which had been stored over P₂O₅, was added at -196 °C on the vacuum line. On warming, all the CsI reacted with SO₂ to form a red solution. Removal of the excess of unreacted SO₂ at -10 °C resulted in a red-orange solid of the approximate composition CsI·4SO₂, which at 25.5 °C exhibited a dissociation pressure of 450 torr. Exhaustive dissociation of the adduct at 25.5 °C produced pure SO₂ and CsI (6.3 mmol).

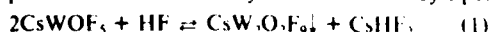
Preparation of NF₄WOF₅. A mixture of CsF (21.99 mmol) and NF₄SbF₆ (22.14 mmol) was loaded in the drybox into one half and WOF₄ (14.59 mmol) into the other half of a prepassivated Teflon double-U metathesis apparatus. Dry HF (16 mL, liquid) was added on the vacuum line to the half containing the NF₄SbF₆-CsF mixture and was warmed to 25 °C for 30 min with stirring. After this mixture was cooled to -78 °C, the metathesis apparatus was inverted and the NF₄HF₂ solution was filtered into the other half of the apparatus containing the WOF₄. The NF₄HF₂·WOF₄ mixture in HF was stirred for 30 min at 25 °C, and then the volatile material was pumped off for 12 h at 25 °C and 0.8 h at 50 °C. The volatile material, trapped at -196 °C, was shown by infrared spectroscopy to consist of HF and NF₃ and did not contain any tungsten species. The filter cake (8.06 g; weight calculated for 21.99 mmol of CsSbF₆ = 8.11 g) and the filtrate residue (4.99 g; weight calculated for 14.59 mmol of NF₄WOF₅ = 5.61 g) were shown by vibrational spectroscopy to consist of CsSbF₆ and mainly NF₄WOF₅, respectively. On the basis of its elemental analysis, the filtrate residue had the composition (wt %): NF₄WOF₅, 96.1; CsSbF₆, 2.0; NF₄SbF₆, 1.9. Anal. Calcd: NF₄, 18.14; Cs, 0.72; W, 45.91; Sb, 1.37. Found: NF₄, 18.05; Cs, 0.7; W, 46.0; Sb, 1.32.

Preparation of NF₄W₂O₂F₉. A sample of NF₄WOF₅ was placed into a sapphire tube equipped with a stainless steel valve. The contents of the tube were heated in a dynamic vacuum to 155 °C for 6.5 h and to 180 °C for 4 h. On the basis of the observed weight change and the vibrational spectra, the conversion of NF₄WOF₅ to NF₄W₂O₂F₉ was essentially complete.

In an alternate method, NF₄WOF₅ was dissolved in anhydrous HF and formed a precipitate. This precipitate was separated from the solution by filtration and, on the basis of its vibrational spectra, consisted of NF₄W₂O₂F₉.

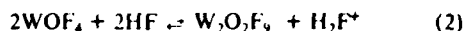
Results and Discussion

Syntheses and Reaction Chemistry of CsWOF₅, CsW₂O₂F₉, Cs₂WO₂F₄, CsWF₆, WOF₄, and H₃O⁺WOF₅. The synthesis of CsWOF₅ was first reported¹⁹ in 1958 by Hargreaves and Peacock and involved the reaction of moist CsF with WF₆ in IF₃ solution. In subsequent reports,^{10,20} either the original or slightly modified methods were used replacing the IF₃ solvent by CH₃CN and using WOF₄ as a starting material. Since in Hargreaves and Peacock's method an excess of water can result in WO₃F₄² formation, a better control of the amount of water used in the reaction was desirable. Furthermore, the intended reactions with NF₄⁺ salts required the use of anhydrous HF as a solvent. Consequently, our CsWOF₅ preparation was carried out in such a manner that dry CsF, WF₆, and a stoichiometric amount of water were used in anhydrous HF solution. On the basis of its vibrational spectra, the resulting solid product consisted of CsWOF₅^{10,11} containing small amounts of CsW₂O₂F₉¹² and CsHF₂. During an attempt to determine the solubility of CsWOF₅ in anhydrous HF, it was found that the salt did not completely dissolve in anhydrous HF. The insoluble material was filtered off and identified by vibrational spectroscopy as CsW₂O₂F₉.¹² The residue isolated from the filtrate after solvent removal consisted mainly of CsHF₂ contaminated by a small amount of *cis*-Cs₂WO₂F₄.¹³ The latter was most likely produced by hydrolysis of some CsWOF₅ by a trace of water present in the large amount of HF used as a solvent. These results demonstrate the existence of the equilibrium reaction in anhydrous HF shown by eq 1.



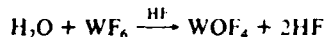
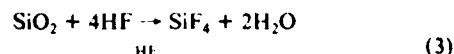
A large excess of HF and the low solubility of CsW₂O₂F₉ can

shift this equilibrium all the way to the right. Separation of the CsW₂O₂F₉ precipitate from the CsHF₂ solution, followed by washing with anhydrous HF, affords essentially pure CsW₂O₂F₉ and thus offers a convenient synthetic method for the preparation of this compound. Equilibrium 1 is in excellent agreement with that observed by Bougon and co-workers¹² for the HF-WOF₄ system (eq 2). If the CsHF₂ and CsW₂O₂F₉

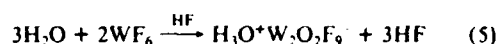
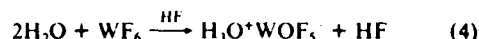


are not separated prior to HF removal, equilibrium 1 is shifted back to the left on HF removal and in our experiments resulted in a mixture containing about 95 mol % CsWOF₅ and 5 mol % CsW₂O₂F₉.

The above described synthesis of CsWOF₅ by controlled hydrolysis of WF₆ in a CsF-containing HF solution is similar to the previously reported⁸ hydrolysis of WF₆ in HF according to eq 3. However, on the basis of the results of this study,

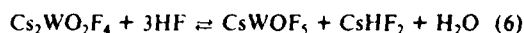


care must be taken to use an excess of WF₆ in this reaction. In the presence of an excess of water, H₃O⁺WOF₅⁻ and H₃O⁺W₂O₂F₉⁻ are formed according to eq 4 and 5. Since



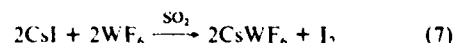
these oxonium salts are also volatile, they are difficult to separate from WOF₄ by sublimation. It should be noted that in the previous report²¹ on the synthesis of H₃O⁺WOF₅⁻ the observed anion spectra were incorrectly ascribed to a distorted WOF₅⁻ anion. The reported spectra²¹ are identical with those published¹² for W₂O₂F₉⁻, which were also confirmed by the results of this study (see below).

For the synthesis of Cs₂WO₂F₄, the use of an HF-soluble tungsten species²² and of an aqueous HF solution are important. In agreement with a previous report,²² WO₃ or H₂WO₄²³ was found difficult to dissolve completely in aqueous HF, but WF₆ and CsF in a 1:2 mole ratio were found to be a convenient alternate to Cs₂WO₄²² as a starting material for the preparation of pure *cis*-Cs₂WO₂F₄. If anhydrous HF is used in place of aqueous HF as a solvent, equilibria 6 and 1



were found to become important. Equilibrium 1 results in a precipitation of CsW₂O₂F₉, which can be isolated by filtration, while the residue obtained from the filtrate consists of Cs₂WO₂F₄ and CsHF₂. The vibrational spectra observed for Cs₂WO₂F₄ agree well with those^{13,23,24} previously reported and confirm that WO₃F₄² is present as the *cis* isomer.

For the synthesis of CsWF₆, the original method²⁵ based on the reaction given by eq 7 did not lead to a pure product,



in agreement with previous reports.^{16,26} Even when the reaction was carried out in a well-passivated sapphire reactor with carefully dried reagents, the product always contained

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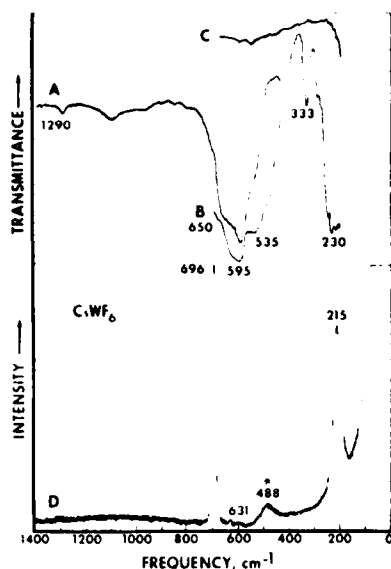


Figure 1. Vibrational spectra of solid CsWF_6 : trace A, infrared spectrum of the dry powder pressed between AgCl disks; trace B, Nujol mull between CsI windows; trace C, Nujol alone between CsI windows; trace D, Raman spectrum of the solid. The Raman band at 488 cm^{-1} , marked by an asterisk, is probably due to the Pyrex capillary.

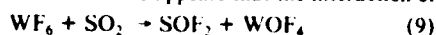
significant amounts of CsWOF_5 , and sometimes $\text{CsW}_2\text{O}_7\text{F}_9$, as byproducts. The replacement of SO_2 as a solvent by HF eliminated this problem and offered the additional advantage of easy separation of the HF-insoluble I_2 from HF-soluble CsWF_6 . This preparation of the CsWF_6 is similar to that²⁶ previously published for NaWF_6 with HF as a solvent, NaF, and cadmium in place of iodide as a reducing agent. Other solvents that have successfully been used for the syntheses of WF_6^- salts include CH_3CN ,^{16,17} CH_3NO_2 ,¹⁷ and SF_4 .²⁷

Since only incomplete spectroscopic data had previously been reported for CsWF_6 , its vibrational and ^{19}F NMR spectra were recorded. The vibrational spectra and observed frequencies are given in Figure 1. The observed spectra, particularly the infrared spectra, are too complicated for an ideal octahedral anion. It must be kept in mind, however, that CsWF_6 samples usually are poor Raman scatterers and also hydrolyze very easily to CsWOF_5 . The ^{19}F NMR spectrum of CsWF_6 in HF solution at 80°C consisted of a singlet at δ 159 with J_{WF_6} of about 53 Hz.

The compatibility of SO_2 with CsI and WF_6 was briefly studied in an effort to explain the above described side reaction resulting in CsWOF_5 formation. In agreement with a previous report,²⁸ CsI was found to form with SO_2 an orange-red 1:4 adduct according to eq 8. This adduct was unstable at room



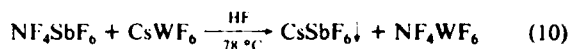
temperature, possessing a dissociation pressure of about 450 torr at 25.5°C . Its decomposition resulted in SO_2 and CsI as the only products. For the WF_6 - SO_2 system, little interaction was noted. Even after an equimolar mixture of WF_6 and SO_2 was kept at 25°C for 5 days, less than 0.2% of the starting material had reacted to form WOF_4 and SOF_2 according to eq 9. It therefore appears that the interaction of



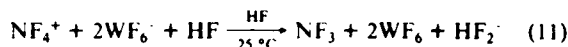
WF_6 with SO_2 is either catalyzed by CsI or one of its reaction products or that the desired CsWF_6 product is more reactive than WF_6 toward SO_2 . Such behavior is in accord with a previous report²⁹ on the enhanced reactivity of SO_2 toward WF_6 in the presence of bases capable of forming adducts with WF_6 .

Syntheses of NF_4^+ Fluorotungstate Salts. The possibility was explored to synthesize stable NF_4^+ salts derived from one of the following complex fluorotungstate anions: WF_6^- , $\text{WO}_2\text{F}_4^{2-}$, WOF_5^- , and $\text{W}_2\text{O}_7\text{F}_9^-$.

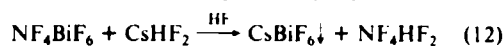
For the synthesis of NF_4WF_6 the metathetical reaction eq 10 proved unsatisfactory because of product separation



problems due to the limited solubility of the WF_6^- salts in HF especially at low temperature and because of the competing redox reaction (eq 11) during removal. Although the solubility

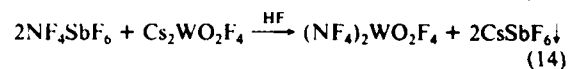


problem was successfully circumvented by separately generating HF solutions of NF_4HF_2 and WF_5 (eq 12 and 13) and



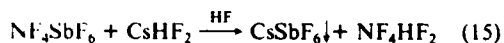
combining them, the redox reaction (12) remained a major obstacle, particularly when an excess of NF_4HF_2 was employed in the reaction.

The synthesis of $(\text{NF}_4)_2\text{WO}_2\text{F}_4$ was attempted with use of the metathetical reaction given by eq 14. Although $\text{WO}_2\text{F}_4^{2-}$



appeared to be compatible with NF_4^+ , the desired $(\text{NF}_4)_2\text{W}_2\text{O}_7\text{F}_9$ could not be isolated due to $\text{WO}_2\text{F}_4^{2-}$ interacting with anhydrous HF according to reactions 6 and 1. Consequently, the filter cake contained a significant amount of $\text{W}_2\text{O}_7\text{F}_9^-$ salts, whereas the filtrate residue contained a significant amount of WOF_5^- salts. The volatile reaction products contained some NF_3 and OF_2 . Nitrogen trifluoride is the product expected for either thermal decomposition of NF_4HF_2 or redox reactions involving NF_4^+ . Oxygen difluoride could have been formed by fluorination of H_2O generated from $\text{WO}_2\text{F}_4^{2-}$ and HF according to reaction 6.

Since the products from the $\text{NF}_4\text{SbF}_6 + \text{Cs}_2\text{WO}_2\text{F}_4$ metathetical reactions had indicated that NF_4WOF_5 and $\text{NF}_4\text{W}_2\text{O}_7\text{F}_9$ might be stable but are difficult to separate from the CsSbF_6 precipitate, this separation problem was overcome by first preparing an NF_4HF_2 solution according to eq 15, then



separating the CsSbF_6 precipitate from the highly soluble NF_4HF_2 by filtration, and reacting a twofold excess of this NF_4HF_2 solution with WOF_4 according to eq 16. The excess



of unreacted NF_4HF_2 was decomposed at room temperature to NF_3 , F_2 , and HF, leaving behind the thermally more stable NF_4WOF_5 salt.

The $\text{NF}_4\text{W}_2\text{O}_7\text{F}_9$ salt was obtained by controlled vacuum pyrolysis of NF_4WOF_5 at 180°C in a sapphire reactor. The vibrational spectra of the solid residue showed only the bands characteristic for NF_4^+ ^{1,7,9} and $\text{W}_2\text{O}_7\text{F}_9^-$.¹² The volatile

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Table I. Vibrational Spectra of Solid $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$, $\text{CsW}_2\text{O}_2\text{F}_9$, and NF_4WOF_5

obsd freq, cm^{-1} , and rel intens ^a						assignment (point group) ^b		
$\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$		$\text{CsW}_2\text{O}_2\text{F}_9$		NF_4WOF_5		NF_4^+ (T_d)	$\text{W}_2\text{O}_2\text{F}_9^-$	WOF_5 (C_{4v})
IR	Raman	IR	Raman	IR	Raman			
2320 vw				2315 vw		$2\nu_1$ ($A_1 + E + F_2$)		
2060 vw		2060 vw					(2×1035)	
2015 w				1996 w		$\nu_1 + \nu_2$ (F_2)		
1768 vw				1760 wv		$\nu_1 + \nu_4$ ($A_1 + E + F_2$)		
1461 w				1453 w		$\nu_1 + \nu_4$ (F_2)		
1343 w		1338 w					(709 + 640)	
1240 sh		1240 w					(640 + 610)	
1224 mw				1221 mw		$2\nu_4$ ($A_1 + E + F_2$)		
1165 vs	1165 (0.2)			1160 vs	1165 (0.7)	ν_3 (F_2)		
1035 vs	1034 (10)	1048 vs		991 vs	996 (10)		ν W-O out of phase	ν_1 (A_1)
		1035 vs	1036 (10)				ν W-O in phase	
900 vw	850 (1.5)				852 (8.4)	ν_1 (A_1)		
		822 vw						
		790 vw						
709 s	698 (5.4)			688 vs	690 (5.4)		ν_3 WF_6 in phase	ν_2 (A_1)
640 vs, br		704 s	700 (6.3)	620 vs, br			ν_{as} WF_6	ν_3 (E)
610 s	610 (0.9)	628 vs, br			613 (4.9)	ν_4 (F_2)	ν_3 WF_6 out of phase	ν_3 (B_1)
			610 (0.6)	515 vs				ν_3 (A_1)
462 s								
440 s	440 (0.4)	440 vs			446 (1.6)	ν_1 (E)	ν_{as} WF_6	
400 vw		400 vw						
	335 sh		340 (0.6)					
	316 (6.2)		320 (5.3)		329 (6.8)			ν_3 (E)
	305 sh		309 sh					
	283 (0.5)		284 (0.2)		285 (0.5)		def vibrations	ν_4 (A_1)
	211 (0.6)		217 (0.5)					
	194 (0.2)		200 (0.2)					
	120 sh		122 (0.3)		140 sh			

^a Uncorrected Raman intensities. ^b The actual site symmetry of NF_4^+ and WOF_5 might be lower than T_d and C_{4v} , respectively. ^c Assignments from ref 10 and 12.

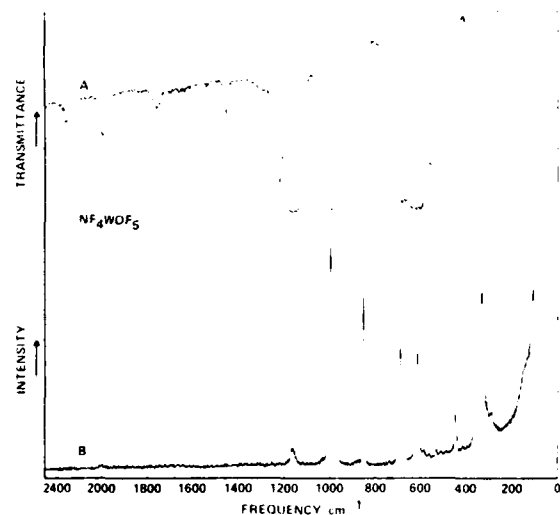
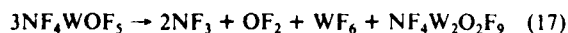


Figure 2. Infrared and Raman spectra of solid NF_4WOF_5 . The broken line indicates absorption due to the AgCl window material.

products consisted of NF_3 , OF_2 , and WF_6 in a mole ratio of about 2:1:1, indicating the reaction shown in eq 17.



Properties of NF_4WOF_5 and $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$. Both salts are white crystalline solids stable at room temperature. The thermal stability of the salts was studied in a static vacuum with a sapphire reactor equipped with a pressure transducer. The NF_4WOF_5 salt was found to be stable at 55 °C but at 85 °C started to undergo slow decomposition according to reaction 17 at an approximate rate of 0.03% h^{-1} . At 155 °C the pyrolysis proceeded at a much faster rate, and after 6.5

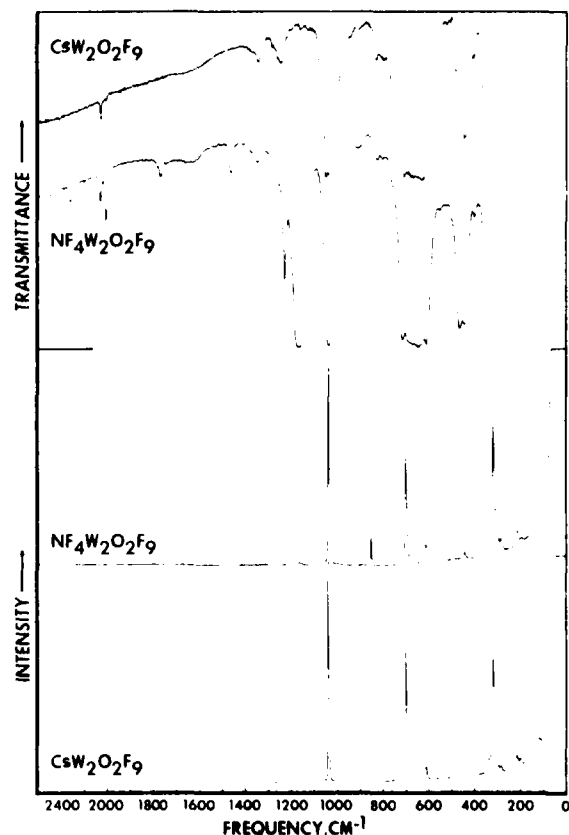


Figure 3. Infrared and Raman spectra of solid $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$ compared to those of solid $\text{CsW}_2\text{O}_2\text{F}_9$.

h about 90% of the starting material was converted to $\text{NF}_4\text{-W}_2\text{O}_2\text{F}_9$ and to the other products shown in reaction 17. Complete conversion to $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$ was achieved by heating to 180 °C for an additional 4 h.

The ionic structure of NF_4WOF_5 and $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$ in both the solid state and HF solution was demonstrated by vibrational and ^{19}F NMR spectroscopy. The infrared and Raman spectra of solid NF_4WOF_5 and $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$ are shown in Figures 2 and 3, respectively. For comparison, the vibrational spectra of $\text{CsW}_2\text{O}_2\text{F}_9$ are also shown in Figure 3. The observed frequencies, together with their assignments to the NF_4^+ ,^{1,7,9} WOF_5^- ,^{10,11} and $\text{W}_2\text{O}_2\text{F}_9^-$ ¹² ions, are summarized in Table I and clearly establish the nature of these salts in the solid state. In HF solution, however, a significant change was observed. First of all, both NF_4WOF_5 and $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$ were only partially soluble in anhydrous HF. In both cases the insoluble phases were shown by Raman spectroscopy to consist of $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$, and the HF solution showed only NF_4^+ and $\text{W}_2\text{O}_2\text{F}_9^-$ ions. In the HF solution obtained from dissolving NF_4WOF_5 , the ratio of $\text{NF}_4^+:\text{W}_2\text{O}_2\text{F}_9^-$ was, as expected from eq 18, considerably higher than that found for the $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$



solution. The presence of these ions and the lack of WOF_5^- in these solutions were confirmed by ^{19}F NMR spectroscopy. These spectra showed a triplet of equal intensity at δ 215.5 with $J_{\text{NF}} = 239.5$ Hz, characteristic for NF_4^+ ,^{1,7} and a singlet at δ 54 with two ^{183}W satellites with $J_{\text{WF}} = 84$ Hz, characteristic for $\text{W}_2\text{O}_2\text{F}_9^-$ in HF solution.¹² The latter signal has

been attributed to the eight equivalent fluorines of $\text{W}_2\text{O}_2\text{F}_9^-$ with the bridging ninth fluorine undergoing rapid exchange with the HF solvent.¹² This exchange was still rapid at -60 °C, and no evidence for F-F coupling was observed. These Raman and NMR data suggest that NF_4WOF_5 undergoes the solvolysis in anhydrous HF given by eq 18. This solvolysis is analogous to that observed for CsWOF_5 in reaction 1 and explains why NF_4WOF_5 could not be prepared by a direct metathesis. Due to their limited solubility in anhydrous HF, some of the $\text{W}_2\text{O}_2\text{F}_9^-$ salt is precipitated out. This was confirmed by ^{19}F NMR peak area measurements on the HF solution of the original NF_4WOF_5 sample; it was shown that the ratio of the fluorines on nitrogen to the equivalent fluorines on tungsten was 1.5:1, indicating that on the basis of (18) about half of the $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$ had precipitated out under the given conditions.

Conclusion. The perfluoroammonium cation is capable of forming stable salts derived from the WOF_5^- and the $\text{W}_2\text{O}_2\text{F}_9^-$ anion but rapidly oxidizes the WF_6^- anion to WF_6 . The new NF_4WOF_5 and $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$ salts were characterized, and the syntheses and reaction chemistry of tungsten fluoride and oxyfluoride anions were studied in more detail.

Acknowledgment. We thank Drs. C. J. Schack and L. R. Grant and Mr. R. D. Wilson for helpful support and the Office of Naval Research and the Army Research Office for financial support of this work.

Registry No. NF_4WOF_5 , 79028-46-9; $\text{NF}_4\text{W}_2\text{O}_2\text{F}_9$, 79056-35-2; CsWOF_5 , 58341-09-6; $\text{CsW}_2\text{O}_2\text{F}_9$, 79056-36-3; *cis*- $\text{Cs}_2\text{WO}_2\text{F}_4$, 79005-35-9; CsWF_6 , 19175-38-3; WF_6 , 7783-82-6; WOF_4 , 52049-91-9.

APPENDIX S

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253

SYNTHESIS AND PROPERTIES OF $(\text{NF}_4)_2\text{SiF}_6$ AND INTERACTION OF SiF_4 WITH ANHYDROUS HF AND CsHF_2

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SUMMARY

The scope of the metathetical process for the production of NF_4^+ salts from HF solutions was extended to the synthesis of salts derived from Lewis acids which are weaker than the HF solvent. The new salt $(\text{NF}_4)_2\text{SiF}_6$ was prepared by this process and was characterized. The solubility of SiF_4 in anhydrous HF and the reversibility of the $\text{Cs}_2\text{SiF}_6 + 2\text{HF} \rightleftharpoons 2\text{CsHF}_2 + \text{SiF}_4$ reaction were demonstrated.

INTRODUCTION

Highly energetic NF_4^+ salts containing multiply charged light anions are of significant interest for solid propellant $\text{NF}_3\text{-F}_2$ gas generators [1] and high detonation pressure explosives [2]. Whereas NF_4^+ salts containing triply charged anions are unknown, the following NF_4^+ salts containing doubly charged anions have been prepared: $(\text{NF}_4)_2\text{GeF}_6$ [3], $(\text{NF}_4)_2\text{SnF}_6$ [4], $(\text{NF}_4)_2\text{TiF}_6$ [5], $(\text{NF}_4)_2\text{NiF}_6$ [6], and $(\text{NF}_4)_2\text{MnF}_6$ [7].

Since the fourth main group elements Sn and Ge are known to form stable $(\text{NF}_4)_2\text{MF}_6$ salts [3,4], the synthesis of the more energetic $(\text{NF}_4)_2\text{SiF}_6$ salt seemed also possible. However, previous attempts were unsuccessful to prepare an NF_4^+ salt derived from SiF_4 by either direct methods, such as low-temperature uv-photolysis [3], or by indirect methods, such as a standard metathesis between NF_4SbF_6 and Cs_2SiF_6 in anhydrous HF solution. The metathetical approach failed because anhydrous HF displaces SiF_4 from hexafluorosilicates [8] according to



Since recent studies [9] in our laboratory had shown that under suitable reaction conditions even very weak Lewis acids, such as WF_6 , UF_6 or XeF_6 , can form stable NF_4^+ salts, an extension of this method to SiF_4 was investigated.

In connection with this study previous reports [8] were reexamined that SiF_4 is insoluble in and does not react with liquid anhydrous HF, a seemingly surprising behavior in view of the well established existence of H_2SiF_6 in aqueous HF solution.

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. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove-box. Metathetical reactions were carried out in HF solution using 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 described [10] sapphire reactor.

Infrared spectra were recorded in the range $4000\text{--}200\text{ cm}^{-1}$ 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 $4880\text{-}\text{\AA}$ exciting line of an Ar-ion laser and Claassen filter [11] 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 [12].

Materials

Literature methods were used for the syntheses of NF_4SbF_6 [13] and NF_4HF_2 solutions in HF [14]. Hydrogen fluoride (Matheson) was dried by storage over BiF_5 to remove the H_2O [15]. Silicon tetrafluoride (Matheson) was used as received. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox.

Interaction of SiF_4 with Anhydrous HF

Anhydrous HF (80 mmol) was condensed into a sapphire tube equipped with a metal valve and a pressure transducer (Validyne). The tube was cooled to -78°C and briefly pressurized with 997 torr of SiF_4 . The valve was quickly closed and during a 5 minute time period the pressure inside the tube dropped to 320 torr. The tube was pressurized again briefly with SiF_4 to 902 torr, and after closing the valve the pressure inside the tube gradually decreased during the next ten minutes to 509 torr. When the sapphire tube was warmed from -78° to 25°C , the pressure inside the tube increased to 1472 torr. For no interaction or solubility of SiF_4 in HF, the amount of added SiF_4 (3.50 mmol) should have resulted in a total pressure of 2675 torr. A Raman spectrum of the liquid phase in the sapphire tube at 25° showed only bands due to HF and SiF_4 . An infrared spectrum of a mixture of HF and SiF_4 in the gas phase also showed only the bands characteristic for HF and SiF_4 .

Preparation of Cs_2SiF_6 from CsF and SiF_4 in HF

Dry CsF (33.4 mmol) was loaded into a 50 ml Teflon tube containing a Teflon coated magnetic stirring bar. Anhydrous HF (316 mmol) was added to the tube on the vacuum line at -196°C . The tube was warmed to -78°C and the CsF was dissolved in the HF. The tube was cooled again to -196°C and SiF_4 (37.0 mmol) was added. The mixture was allowed to warm up to ambient temperature with stirring. The material volatile at 25°C was pumped off, separated by fractional condensation through -126° and -196°C traps, and consisted of SiF_4 (34.9 mmol) and HF. The residue consisted of a mushy solid and the tube had gained 1.696 g in weight. This residue was pressurized for 2.5 hours with 720 torr of SiF_4 at 25°C which resulted in an exothermic reaction and the formation of a white crystalline solid. The material volatile at 25°C was pumped off and consisted of HF and unreacted SiF_4 . The white solid residue (6.7 g, weight calcd for 16.7 mmol of Cs_2SiF_6 6.8 g) was shown by infrared and Raman spectroscopy to be Cs_2SiF_6 [16], and did not exhibit any bands due to SiF_5^- [17], HF_2^- or any HF adducts [14]. A third treatment of the solid with SiF_4 did not result in any further weight uptake, HF evolution or change in the spectra of the solid.

Preparation of $(\text{NF}_4)_2\text{SiF}_6$

A mixture of CsF (29.1 mmol) and NF_4SbF_6 (29.17 mmol) was loaded in the drybox into one half of a prepassivated Teflon double U metathesis apparatus. Dry HF (20 ml liquid) was added on the vacuum line and the mixture was stirred

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. Most of the HF solvent was pumped off during warm-up towards 0°C until the first signs of decomposition of NF_4HF_2 were noted. The resulting residue was cooled to -196° and SiF_4 (32.7 mmol) was added. The mixture was allowed to warm to ambient temperature while providing a 912 ml ullage in the vacuum line. During warm-up of the apparatus the SiF_4 evaporated first and upon melting of the $\text{NF}_4\text{HF}_2 \cdot \text{nHF}$ phase a significant reduction in the SiF_4 pressure was noted, resulting in a final pressure of 400 torr. A clear colorless solution was obtained with no sign of solid formation. The material volatile at 0°C was pumped off, separated by fractional condensation through -210° and -126°C traps, and consisted of SiF_4 (22.6 mmol) and HF (75 mmol). The residue, a white fluffy solid, was treated at 25°C with 400 torr of SiF_4 (15.6 mmol) for 24 hours. The volatile material was pumped off at 24°C for 3 hours and consisted of SiF_4 (13.2 mmol) and HF (14 mmol). The white solid residue was treated one more time at 25°C with SiF_4 (17.4 mmol) for 14 hours. The materials volatile at 25°C were pumped off and consisted of SiF_4 (16.7 mmol) and HF (0.7 mmol). Since the vibrational spectra of the solid residue still showed the presence of HF type material, the solid was transferred to a sapphire tube and heated in a dynamic vacuum at 50°C for a total of 28 hours until no further HF evolution was noted. A total of 9 mmol of HF, but only traces of NF_3 and SiF_4 were collected during this pyrolysis. The white solid residue (3.759 g, 80% yield) was shown by vibrational spectroscopy to consist mainly of $(\text{NF}_4)_2\text{SiF}_6$ with small amounts of SbF_6^- as the only detectable impurity. Based on its elemental analysis, the product had the following composition (weight %): $(\text{NF}_4)_2\text{SiF}_6$, 95.5; CsSbF_6 , 2.2; NF_4SbF_6 , 2.3. Anal. Calcd: NF_3 , 42.6; Cs, 0.79; Si, 8.3; Sb, 1.6. Found: NF_3 , 42.6; Cs, 0.78; Si, 8.3; Sb, 1.6.

The filter cake from the metathetical preparation of the NF_4HF_2 solution consisted of 11.1 g of CsSbF_6 (weight calcd for 29.1 mmol of CsSbF_6 10.7 g), containing small amounts of $(\text{NF}_4)_2\text{SiF}_6$, formed by hang-up of some mother liquor on the filter cake and its subsequent conversion to $(\text{NF}_4)_2\text{SiF}_6$ during pressurization of the apparatus with SiF_4 .

Thermal Decomposition of $(\text{NF}_4)_2\text{SiF}_6$

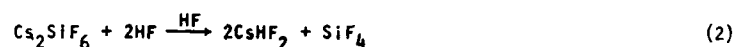
The thermal decomposition of $(\text{NF}_4)_2\text{SiF}_6$ in a constant-volume sapphire reactor was studied by total pressure measurements using a Validyne pressure transducer and a strip chart recorder. In order to minimize the effect of

changes in the sample size during a given experiment, the largest feasible sample (1.55 g) and the smallest available reactor volume (27.8 mL) were used. In this manner, less than 0.4 percent of the sample was decomposed in any given experiment. Analysis of the gaseous decomposition products showed NF_3 , F_2 and SiF_4 in a 2.0:2.0:1.0 mol ratio.

RESULTS AND DISCUSSION

Interaction of SiF_4 with HF and CsHF_2

In agreement with previous reports [8], a large excess of anhydrous HF was found to quantitatively displace SiF_4 from Cs_2SiF_6



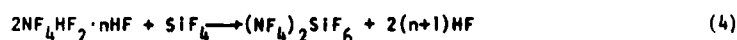
However, experiments using CsHF_2 and a large excess of SiF_4 showed that reaction (2) is actually an equilibrium which can be shifted all the way to the left by a large excess of SiF_4 and removal of the evolved HF. During these experiments it was also noted that, contrary to previous literature reports [8], SiF_4 exhibited a pronounced solubility in anhydrous HF. This observation was confirmed in a study of the binary HF- SiF_4 system at -78° and 25°C . Infrared spectra of a mixture of gaseous HF and SiF_4 and Raman spectra of liquid HF pressurized with two atmospheres of SiF_4 at 25°C showed only the presence of bands due to HF and SiF_4 , but no evidence for H_2SiF_6 . It therefore appears that under the given conditions SiF_4 dissolves in liquid HF, but does not form H_2SiF_6 to an easily observable extent.

Synthesis of $(\text{NF}_4)_2\text{SiF}_6$

Based on the above observations for the CsHF_2 - SiF_4 system, the synthesis of $(\text{NF}_4)_2\text{SiF}_6$ was successfully carried out by first preparing a solution of NF_4HF_2 in HF according to



followed by removal of as much HF as possible from the system without decomposing NF_4HF_2 , and finally repeatedly pressurizing the resulting residue with SiF_4 and pumping off any displaced HF



The yield of $(\text{NF}_4)_2\text{SiF}_6$ (based on the limiting reagent CsF) was 80 mol percent, with the lost materials being principally due to hang up of mother liquor on the CsSbF_6 filter cake during reaction (3). The purity of the product was 95.5 mol percent which is typical for similar metathetical reactions [9, 18]. Purification by recrystallization from either HF or BrF_5 solution was not possible owing to displacement of SiF_4 by HF and low solubility in BrF_5 .

Contrary to $(\text{NF}_4)_2\text{GeF}_6$, for which treatment with an excess of GeF_4 resulted in NF_4GeF_5 formation [3]



$(\text{NF}_4)_2\text{SiF}_6$ when treated with an excess of SiF_4 , did not exhibit any tendency to form a stable NF_4SiF_5 salt. This reluctance of SiF_4 to form a stable NF_4SiF_5 salt might also account for the failure to obtain NF_4SiF_5 by low-temperature uv-photolysis of $\text{NF}_3\text{-F}_2\text{-SiF}_4$ mixtures [3].

Properties of $(\text{NF}_4)_2\text{SiF}_6$

$(\text{NF}_4)_2\text{SiF}_6$ is a white crystalline solid stable at ambient temperature. It slowly decomposes at 90°C according to



Its rate of decomposition was studied by total-pressure measurements at 88.3°C and 99.3°C . For all experiments, plots of log pressure versus log time resulted in a straight line with a slope corresponding to a 1.12 fractional reaction order. Assuming x to be the amount of $(\text{NF}_4)_2\text{SiF}_6$ at any time, the rate of decomposition equals

$$-\frac{dx}{dt} = kx^{1.12} \quad (7)$$

Substituting x in this equation by $x_0 - \frac{PV}{5RT}$ where V is the reactor volume and x_0 the amount of $(\text{NF}_4)_2\text{SiF}_6$ at the beginning of the experiment, (7) becomes

$$\frac{V}{5RT} \frac{dP}{dt} = k \left(x_0 - \frac{PV}{5RT} \right)^{1.12} \quad (8)$$

and

$$k = \frac{V}{5RT \left(x_0 - \frac{PV}{5RT} \right)^{1.12}} \frac{dP}{dt} \quad (9)$$

From (9) and the observed dP/dt decomposition rates at a given decomposition pressure P the following global kinetic constants were calculated, $k(88.3^\circ\text{C}) =$

$1.03 \times 10^{-7} \text{ mol}^{-0.12} \text{ sec}^{-1}$ and $k(99.3^\circ\text{C}) = 3.08 \times 10^{-7} \text{ mol}^{-0.12} \text{ sec}^{-1}$. From the Arrhenius relation, a global decomposition activation energy $E = 26.6 \text{ kcal mol}^{-1}$ was obtained which compares favorably with the corresponding value of $36.6 \text{ kcal mol}^{-1}$ previously obtained [10] for the considerably more stable NF_4BF_4 salt.

The ionic structure of $(\text{NF}_4)_2\text{SiF}_6$ was established by the infrared and Raman spectra of the solid. The observed spectra are shown in Figure 1, and the assignment of the bands to NF_4^+ and SiF_6^{2-} is summarized in Table I. The splittings observed for some of the degenerate modes and violation of some of the selection rules indicate that the actual site symmetries of NF_4^+ and SiF_6^{2-} in the crystal are actually lower than T_d and O_h , respectively, which were used for simplicity in Table I.

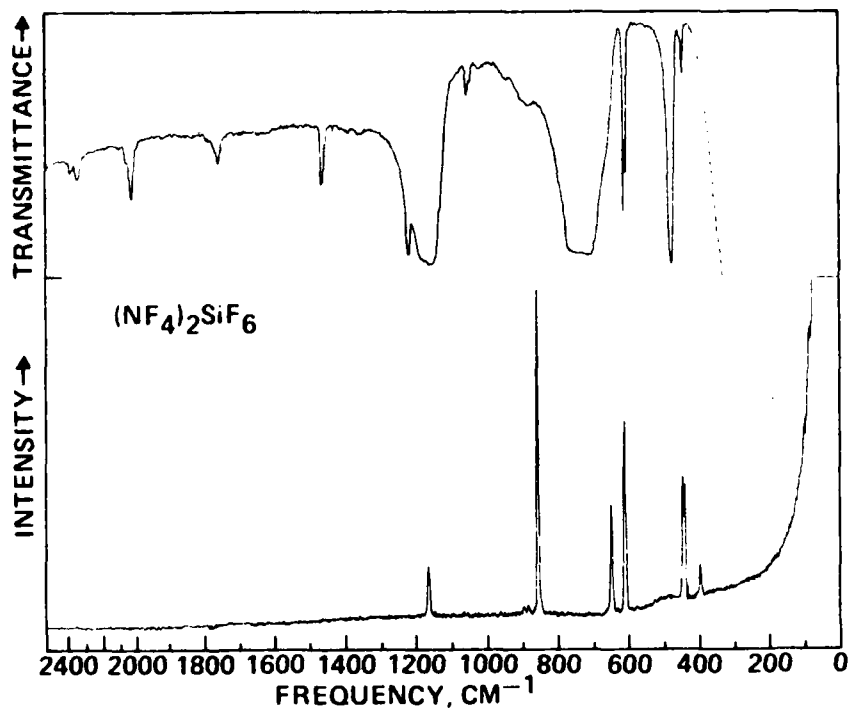


Fig. 1. Infrared and Raman Spectra of Solid $(\text{NF}_4)_2\text{SiF}_6$. The broken line indicates absorption due to the AgCl window material.

TABLE I

Vibrational Spectra of Solid $(\text{NF}_4)_2\text{SiF}_6$

obsd freq. cm^{-1} , and rel intens ^a		assignment (point group) b	
IR	RA	$\text{NF}_4^+(\text{T}_d)$	$\text{SiF}_6^{2-}(\text{O}_h)$
2350 sh		$2\nu_3(\text{A}_1+\text{E}+\text{F}_2)$	
2310 vw		$\nu_1+\nu_3(\text{F}_2)$	
2010 w		$\nu_3+\nu_4(\text{A}_1+\text{E}+\text{F}_2)$	
1760 vw		$\nu_1+\nu_4(\text{F}_2)$	
1468 w		$2\nu_4(\text{A}_1+\text{E}+\text{F}_2)$	
1223 mw		$\nu_3(\text{F}_2)$	
1165 vs	1164 (1.5)	$\nu_2+\nu_4(\text{F}_1+\text{F}_2)$	
1060 vw		$2\nu_2(\text{A}_1+\text{A}_2+\text{E})$	
1050 sh		$\nu_1(\text{A}_1)$	
890	895(0+) 885(0+)		$\nu_3(\text{F}_{1u})$ $\nu_1(\text{A}_{1g})$
	859(10)		
735 vs, br	649(3.2)		$\nu_4(\text{F}_2)$
614 m	611(5.8)		
609 mw			$\nu_4(\text{F}_{1u})$
478 s	447(3.8)		$\nu_2(\text{E}_g)$
448 w	441		$\nu_5(\text{F}_{2g})$
	398(1.0)		

(a) Uncorrected Raman intensities.

(b) The splitting observed for $\nu_4(\text{F}_2)$ indicates that the actual site symmetry of NF_4^+ is lower than T_d .

CONCLUSION

The scope of the metathetical NF_4^+ salt process in HF solution has been extended to the synthesis of salts, derived from Lewis acids which are weaker than the HF solvent. This modified process has been demonstrated for the synthesis of $(\text{NF}_4)_2\text{SIF}_6$, a new salt not accessible by previously known direct [3] or indirect [15,19] methods.

ACKNOWLEDGEMENT

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APPENDIX T

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263

THERMOCHEMISTRY OF NF_4^+ SALTS

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SUMMARY

The decomposition, solid phase change, and the formation enthalpies were determined for NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4SbF_6 , NF_4GeF_5 and $(\text{NF}_4)_2\text{GeF}_6$ by differential scanning calorimetry. It is shown that $(\text{NF}_4)_2\text{GeF}_6$ is an intermediate in the decomposition of NF_4GeF_5 . The enthalpies of reaction in water of NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 and NF_4SbF_6 were measured and used to obtain an alternate set of formation enthalpies for these compounds. Recommended values for $H_f^\circ(\text{NF}_4\text{XF})(s)$ are: $\text{NF}_4\text{BF}_4 = -1410 \pm 5$, $\text{NF}_4\text{SbF}_6 = -1669 \pm 12$, $\text{NF}_4\text{AsF}_6 = -1538 \pm 11$, $\text{NF}_4\text{PF}_6 = -1841 \pm 7$, $\text{NF}_4\text{GeF}_5 = -1473 \pm 1$, and $(\text{NF}_4)_2\text{GeF}_6 = -1606 \pm 5 \text{ kJ mol}^{-1}$. The formation enthalpies of the NF_4^+ salts were used to estimate the F^+ ion affinity of NF_3 and the enthalpy of formation of gaseous NF_4^+ . The reaction enthalpy of the process $\text{NF}_3(g) + \text{F}_2(g) \rightarrow \text{NF}_4^+\text{F}^-(s)$ was estimated.

INTRODUCTION

Although NF_4^+ salts have now been known for a number of years [1,2], thermodynamic data on these compounds are few. Thus, until very recently, the only available experimental data were in an unpublished report on the enthalpy of formation of NF_4BF_4 from its calorimetrically determined enthalpy of decomposition [3], and overall activation energies obtained from kinetic measurements on the thermal decomposition of NF_4BF_4 and NF_4AsF_6 [4]. Since NF_4^+ salts have considerable potential as principal ingredients in solid-propellant gas generators [5-7] and as high detonation pressure explosives [8],

reliable thermochemical data are clearly needed for the computation of parameters such as theoretical performance and flame temperatures. In addition, from the enthalpies of formation of NF_4^+ salts it is possible to obtain the enthalpy of formation of gaseous NF_4^+ ion and hence the F^+ ion affinity of NF_3 ; knowledge of these quantities allows, for example, conclusions to be reached about the possible existence of NF_5 in the ionic form NF_4^+F^- . The existence of NF_5 has previously been claimed [9], however experiments carried out at Rocketdyne using UV-photolysis of $\text{NF}_3 - \text{F}_2$ mixtures at 77K [10] have failed to confirm this.

The major problem in the thermochemistry of NF_4^+ salts is the scarcity of suitable quantitative reactions leading to well defined products. In the present work two very different approaches have been used, viz. differential scanning calorimetry at 150-350°C [11], and solution calorimetry at 25°C [12, 13]. Under ideal conditions, the results from both methods should agree closely; the actual discrepancies are some measure of the experimental difficulties in preventing side reactions and, in some cases, of the lack of reliable auxiliary data. Very recent work by two of us [11] on NF_4SbF_6 is also referred to in the present communication.

EXPERIMENTAL AND RESULTS

Materials. The compounds NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4SbF_6 , NF_4GeF_5 and $(\text{NF}_4)_2\text{GeF}_6$ were prepared by literature methods [10,14,15], and, except for the last named compound, did not show impurities detectable by analytical or spectroscopic techniques [16]. The amount of impurities in $(\text{NF}_4)_2\text{GeF}_6$, mainly NF_4BF_4 , and NF_4GeF_5 , was only a few percent and was too low to significantly disturb the measurement of the thermal effects.

Differential Scanning Calorimetric Measurements. Thermograms (i.e. thermal effect vs time) of samples loaded in an evacuable prefluorinated Monel cell were obtained using an Arion M.C.B. microcalorimeter. The heat effect calibration was achieved by Joule effect generation of a known heat, the heat changes involved during the phenomena were evaluated by comparison of experimental and calibration peaks, the areas of which were measured with a planimeter. The principle of the microcalorimeter based upon differential calorimetric analysis has been described previously [17], and the method has already been shown to be successful in the thermal decomposition of other NF_4^+ salts [11]. For all runs the completion of decomposition was confirmed

by weighing. The resulting data for NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4GeF_5 and $(\text{NF}_4)_2\text{GeF}_6$ are given in Table 1 and are based on the average of five runs for each compound. The necessary ancillary data are listed in Table 2 together with those required for the thermochemical measurements. The previously observed [9,10] phase transitions were confirmed for NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 and NF_4SbF_6 . For the latter two compounds, x-ray powder patterns of the high temperature phases were also recorded. For NF_4AsF_6 , a cubic phase with $a=9.13 \pm 0.03 \text{ \AA}$ was observed at 166°C . For NF_4SbF_6 a cubic phase with $a=5.66 \pm 0.08 \text{ \AA}$, which was observed at ambient temperature in one of the sample preparations, might be due to the "frozen" high temperature form. For NF_4GeF_5 , a three step decomposition was observed. The first two steps were shown by vibrational spectroscopy to mainly involve the chemical transformation of NF_4GeF_5 to $(\text{NF}_4)_2\text{GeF}_6$.



whereas the third step is mainly due to the thermal decomposition of $(\text{NF}_4)_2\text{GeF}_6$



The latter step was also confirmed by comparison with the decomposition curve of an authentic sample of $(\text{NF}_4)_2\text{GeF}_6$. From these data, the enthalpy change for reaction (1) was found to be 148 kJ mol^{-1} .

The enthalpies of formation of the NF_4^+ salts (see Table 1) were calculated assuming the decomposition mode



well established [4,9,10] for closed containers. The validity of this assumption for the dynamic vacuum conditions of this study was confirmed by collection and identification of the decomposition products and by the excellent agreement between the results of this study for NF_4BF_4 and those previously carried out in a closed container [3]. The enthalpies of formation of the solid NF_4^+ salts are given by

$$\begin{aligned} \Delta H_f^\circ(\text{NF}_4\text{XF})_{(s)} &= \Delta H_f^\circ(\text{NF}_3)_{(g)} + \Delta H_f^\circ(\text{X})_{(g)} - \Delta H_{\text{decomp}}^\circ(\text{NF}_4\text{XF})_{(s)} + \\ &+ [\text{H}^\circ - \text{H}^\circ](\text{NF}_3)_{(g)} + [\text{H}^\circ - \text{H}^\circ](\text{F}_2)_{(g)} + [\text{H}^\circ - \text{H}^\circ](\text{X})_{(g)} - [\text{H}^\circ - \text{H}^\circ](\text{NF}_4\text{XF})_{(s)} \end{aligned}$$

TABLE I

Results^a of the DSC Study of NF_4 Salts

	Phase Change			Decomposition			Total ΔH_{dec} (RT form)	ΔH_{f298} (NF_4 salt) ^b
	T_{onset}	T_{max}	ΔH	T_{onset}	T_{max}	ΔH		
NF_4BF_4	224 $\pm$ 2	237 $\pm$ 3	7.58 $\pm$ 0.5	162 $\pm$ 7	257 $\pm$ 11	134.3 $\pm$ 4.2	141.9 $\pm$ 5.8	-1409 $\pm$ 6
NF_4PF_6	131 $\pm$ 2	142 $\pm$ 0.5	5.90 $\pm$ 0.37	173 $\pm$ 3	260 $\pm$ 3	126.5 $\pm$ 6.8	132.4 $\pm$ 7.0	-1841 $\pm$ 7
NF_4AsF_6	145 $\pm$ 1	155 $\pm$ 2	4.62 $\pm$ 0.38	245 $\pm$ 7	323 $\pm$ 5	164.7 $\pm$ 10.6	169.3 $\pm$ 10.9	-1538 $\pm$ 11
$\text{NF}_4\text{SbF}_6^c$				305 $\pm$ 4	382 $\pm$ 7	245.6 $\pm$ 12	245.6 $\pm$ 12	-1674 $\pm$ 12
$\text{NF}_4\text{GeF}_5^d$				101 $\pm$ 6 ^d	202 $\pm$ 5 ^d	149.6 $\pm$ 1.2 ^d	149.6 $\pm$ 1.2	-1473 $\pm$ 1
$(\text{NF}_4)_2\text{GeF}_6^e$				167 $\pm$ 0.7	208 $\pm$ 1.6	151.3 $\pm$ 5.3	151.3 $\pm$ 5.3	-1606 $\pm$ 5

^a Units: T , $^{\circ}\text{C}$; H , kJ mol^{-1} ; S , $\text{JK}^{-1}\text{mol}^{-1}$. ^b The given standard deviations (1 σ) are based on the uncertainties of H decomp. and do not include uncertainties in the heats of formation of the decomposition products.

^c For NF_4SbF_6 , the phase transition was observed as a shoulder on the decomposition peak and therefore could not accurately be measured. T_{onset} is estimated to be 325 $^{\circ}\text{C}$. ^d The decomposition of NF_4GeF_5 involves three steps (see text); T_{onset} (temp. of beginning decomp.) refers to step 1 and T_{max} (temp. of maximum heat effect) to step 3; step 1 and 2 = 45.0 kJ mol^{-1} , step 3 = 104.6 kJ mol^{-1} . ^e Due to the rapid decomposition rate of $(\text{NF}_4)_2\text{GeF}_6$, a slower heating rate ($1^{\circ}\text{C min}^{-1}$) and smaller sample sizes had to be used to avoid solids to be blown out of the reactor.

TABLE 2

Ancillary Thermochemical Data (kJ mol^{-1})

ΔH_f°	$\text{NF}_3(\text{g}) = -131.4$ [18]	ΔH_f°	$\text{F}^-(\text{g}) = -249$ [23]
ΔH_f°	$\text{BF}_3(\text{g}) = -1136.0$ [18]	E.A.	$\text{F} = -328$ [23]
ΔH_f°	$\text{PF}_5(\text{g}) = -1577.6$ [18]	ΔH° diss	$\text{F}_2(\text{g}) = +159$ [23,24]
ΔH_f°	$\text{AsF}_5(\text{g}) = -1236.8$ [19]	ΔH_f°	$\text{F}^+(\text{g}) = +1760$ [23,24]
ΔH_f°	$\text{SbF}_5(\text{l}) = -1328$ [20]	ΔH_f°	$\text{K}^+(\text{g}) = +514.9$ [22]
ΔH_f°	$\text{GeF}_4(\text{g}) = -1191.9$ [19]	ΔH_f°	$\text{K}^+(\text{aq}) = -251$ [22]
$\Delta H_{\text{vap}}^{418\text{K}}$	$\text{SbF}_5(\text{l}) = 43.4^a$ [21]	ΔH_{sol}	$\text{K}^+(\text{g}) = -766$ [22]
ΔH_f°	$\text{SbF}_5(\text{g, monomer}) = -1297.1^b$		
ΔH_f°	$\text{H}_2\text{O}(\text{l}) = -286$ [22]		
ΔH_f°	$\text{HF}(\text{aq}) = -332$ [22]		
ΔH_f°	$\text{F}^-(\text{aq}) = -335$ [22]		

^a Refers to an approximately trimeric vapor (see text).^b See text

Since the temperature dependence of the enthalpy of the solid NF_4XF salts is unknown, and since the $[\text{H}^T - \text{H}^\circ]$ terms of the solid starting material and of the gaseous decomposition products might cancel each other to a large extent, all $[\text{H}^T - \text{H}^\circ]$ terms were ignored in our calculations of $\Delta H_f^\circ(\text{NF}_4\text{XF})_{(\text{s})}$. In the case of NF_4SbF_6 , ΔH_f° was recalculated in the same manner using the previously given [11] experimental data and $\Delta H_f^\circ(\text{SbF}_5)_{(\text{g, monomer})} = -1297.1$ kJ mol^{-1} (see below) to conform with the other values listed in Table 1.

TABLE 3

Enthalpies of Solution Reactions (kJ mol^{-1}) of NF_4XF Salts

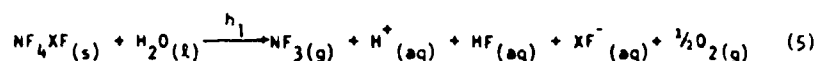
	NF_4BF_4 ^d	NF_4PF_6	NF_4AsF_6	NF_4SbF_6
H_2O	(-244±18)	(-269±10)	-330±10	(-269±10)
$\text{H}_2\text{O/Pt}$	-298±30	-309±20	-329±16	-304±20
0.1M KI ^a	(-472±15)	(-471±17)	(-505±17)	(-504±18)
0.1M KI ^b	-300±15	-299±17	-333±17	(-332±18)
1M KOH	(-345±20)	(-390±20)	(-429±20)	(-748±40)
1M KOH/Pt				(-872±30)
1M HClO ₄		(-220±9)		
1M/3M HCl	-327±27	-293±9		-310±10
1M HBr	(-390±20)			
Average value ^c	308±26	300±16	330±13	307±15

^a Experimental values based on equation (5)^b Recalculated values corresponding to equation (6)^c Average of the unbracketed values^d Bracketed values refer to non-stoichiometric reactions

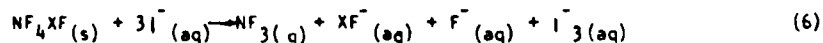
Solution Calorimetry Measurements. These were made in a LKB calorimeter with ancillary apparatus as described previously [12]; the performance of the calorimeter was monitored from time to time via determination of the enthalpy of solution of potassium chloride in water [25]. Samples of between 10 and 40 mg were used, with 30 or 100 cm^3 of water or other aqueous hydrolyzing medium.

In agreement with previous reports [10,16], it was found that the hydrolysis of NF_4^+ salts resulted in rapid and quantitative NF_3 evolution, but that quantitative O_2 evolution was more difficult to achieve. Hence,

different reaction conditions were studied. Of the various reactions listed in Table 3, those in water, 1M- or 3M-HCl and in 0.1M-KI are the most significant since in these cases quantitative or almost quantitative results were most likely achieved. Ideally, all the compounds studied should react with water according to the general equation,



but O_2 evolution is not quantitative (except, apparently, for NF_4AsF_6), unless sufficient Pt black is present to decompose intermediates such as H_2O_2 [10]. If H_2O_2 were to be formed quantitatively as a hydrolysis product, then the measured enthalpy should be about 95 kJ mol^{-1} less exothermic than if the final product is oxygen; a situation that was approximated for NF_4PF_6 in 1M- HClO_4 . Freshly prepared solutions of NF_4PF_6 in water showed considerable oxidizing power and decolorized permanganate, which indicates the presence of H_2O_2 . Another significant side reaction is the formation of ozone. A recent study at Rocketdyne has shown that several mol percent of ozone are always formed in the hydrolyses of NF_4^+ salts in water, even under very carefully controlled reactions. If O_3 were to be formed quantitatively, then the measured enthalpy should be about 48 kJ per mol of NF_4^+ less exothermic than if the final product is oxygen. The results with alkali show that non-quantitative reactions were taking place which involved the hydrolysis of the anion as well as that of the cation; as expected, this phenomenon is most apparent for SbF_6^- . Although the alkali metal salts (except Li^+) of PF_6^- and AsF_6^- are kinetically nearly inert towards dilute alkali at 298K, it should be noted that with the highly exothermic NF_4^+ salt hydrolyses there is always the possibility of anion involvement even under carefully controlled reaction conditions. The large uncertainties in many of the hydrolysis values are probably the results of such factors and perhaps of others, such as incomplete decomposition of H_2O_2 or O_3 formation which would act in the opposite sense. Assuming the following reaction with KI



and recalculating the measured values according to equation (5) excellent agreement with the H_2O -Pt black values is obtained (Table 3), except for NF_4SbF_6 , where the redox reaction between Sb(V) and excess of I^- is important.

In choosing final values for the hydrolyses of NF_4XF salts according to equation (5) (Table 4), we have taken the average of the unbracketed values of Table 3 which, in our opinion, are least affected by side reactions.

From the data of Table 3, together with measured enthalpies of solution of KBF_4 , KPF_6 , and KSbF_6 and their known enthalpies of formation, the enthalpies of formation of the corresponding NF_4^+ salts may be determined (Table 4), using equations (5), (7), and (8)

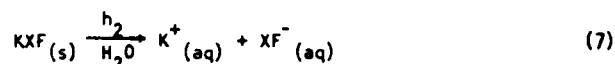
TABLE 4

Thermochemical Data (kJ mol^{-1}) for NF_4XF Salts at 298.2K

Anion	BF_4^-	PF_6^-	AsF_6^-	SbF_6^-
$\Delta H_{\text{sol}}(\text{NF}_4^+ \text{ salt})$	-308 ± 26^a	-300 ± 16^a	-330 ± 13^a	-307 ± 15^a
$\Delta H_{\text{sol}}(\text{K}^+ \text{ salt})$	$+35.0^a$	$+38.1^a$	$+42.8^a$	$+38.5^a$
$\Delta H_f^\circ(\text{K}^+ \text{ salt})$	$-1884[26-28]$	$-2312[29]$	-	$-2083[29]$
$\Delta H_f(\text{NF}_4^+ \text{ salt})$	-1467	-1900		-1663

^a

This work



$$\begin{aligned} \Delta H_f^\circ(\text{NF}_4\text{XF})(\text{s}) &= h_2 - h_1 + \Delta H_f^\circ(\text{NF}_3)(\text{g}) + \Delta H_f^\circ(\text{H}^+)(\text{aq}) + \Delta H_f^\circ(\text{HF})(\text{aq}) \\ &- \Delta H_f^\circ(\text{K}^+)(\text{aq}) - \Delta H_f^\circ(\text{H}_2\text{O})(\text{l}) + \Delta H_f^\circ(\text{KXF})(\text{s}) \end{aligned} \quad (8)$$

Substituting the appropriate ancillary data from Table 2, equation (8) becomes

$$\Delta H_f^\circ(\text{NF}_4\text{XF})(\text{s}) = h_2 - h_1 + \Delta H_f^\circ(\text{KXF})(\text{s}) + 74 \text{ kJ mol}^{-1} \quad (9)$$

The solubility of NF_3 in water is small[30,31] so $\Delta H_{\text{sol}}(\text{NF}_3)(\text{g})$ has been neglected. Assuming that the uncertainties in the values of h_1 are most significant, the uncertainties in the $\Delta H_f(\text{NF}_4\text{XF})(\text{s})$ values of Table 4 are probably $\pm 30 \text{ kJ mol}^{-1}$ or less, depending on the nature of the anion.

DISCUSSION

The data for enthalpies of formation of NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4SbF_6 , NF_4GeF_5 and $(\text{NF}_4)_2\text{GeF}_6$ are brought together in Table 5, which

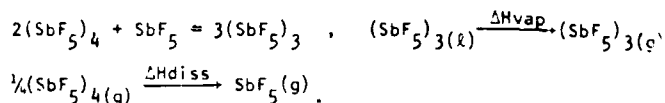
TABLE 5

Enthalpies of Formation and Dissociation of Some NF_4^+ Salts (kJ mol^{-1})

Anion	BF_4^-	PF_6^-	AsF_6^-	SbF_6^-	GeF_5^-	GeF_6^{2-}
$\Delta H_f^\circ(\text{NF}_4\text{XF})(\text{s})$						
DSC	-1409±6	-1841±7	-1538±11	-1674±12	-1473±1	-1606±5
Sol. Cal.	-1467	-1900		-1663		
TDC ^a	-1412±5					
$\Delta H(\text{NF}_4\text{XF}(\text{s}) \rightarrow \text{NF}_3(\text{g}) + \text{F}_2(\text{g}) + \text{X}(\text{g}))$						
DSC	142	132	169	246	150	151
Sol. Cal	200	191		232		
TDC ^a	145					

^a Unpublished results from [3] determined by thermal decomposition calorimetry.

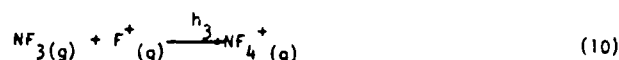
indicates clearly the agreement for NF_4SbF_6 and the divergences for NF_4BF_4 and NF_4PF_6 using the two very different approaches. The results for NF_4SbF_6 are based upon $\Delta H_f(\text{SbF}_5)(\ell) = -1328 \text{ kJ mol}^{-1}$ rather than the previously used [11] value of $-1336 \text{ kJ mol}^{-1}$, and it has been necessary to assume the equilibrium $\frac{1}{4}(\text{SbF}_5)_4(\text{g}) \rightleftharpoons \text{SbF}_5(\text{g})$ with a relative molecular mass corresponding to trimers at the b.p. [32] and to monomers at the decomposition temperature of NF_4SbF_6 . The enthalpy of dissociation of $\frac{1}{4}(\text{SbF}_5)_4$ has recently been estimated to be 18.5 kJ mol^{-1} from vapor density measurements, assuming a mixture of two tetrameric and one monomeric SbF_5 corresponding to an average trimeric molecular weight [32]. Although gaseous SbF_5 has recently been shown by electron diffraction to consist at ambient temperature principally of the trimer [33], the above value, combined with the enthalpy of vaporization of liquid SbF_5 to the gaseous trimer [21], can be used to estimate $\Delta H(\text{SbF}_5(\ell) \rightarrow \text{SbF}_5(\text{g}) (\text{monomer})) = 8/9 \Delta H_{\text{diss}} + 1/3 \Delta H_{\text{vap}} = 30.9 \text{ kJ mol}^{-1}$, based on the following equations:



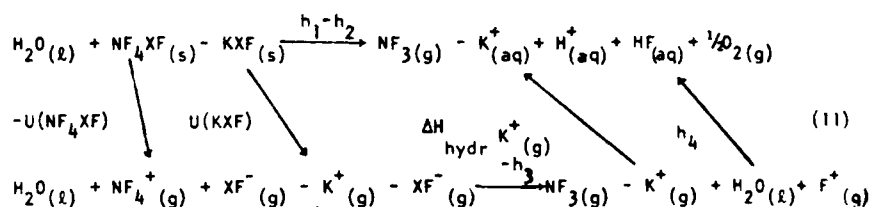
A comparison of the data of Table 5 shows that for NF_4BF_4 the DSC and the previously found [3] thermal decomposition calorimetry value are in excellent agreement. Both values were obtained with relatively small uncertainties by direct methods and support a value of $-1410 \pm 5 \text{ kJ mol}^{-1}$ for $\Delta H_f^\circ(\text{NF}_4\text{BF}_4)(\text{s})$. For NF_4SbF_6 , the DSC and the solution calorimetry value are in good agreement and support a value of $-1669 \pm 12 \text{ kJ mol}^{-1}$ for $\Delta H_f^\circ(\text{NF}_4\text{SbF}_6)(\text{s})$. For NF_4AsF_6 , NF_4GeF_5 and $(\text{NF}_4)_2\text{GeF}_6$ only a DSC value is available, and for NF_4PF_6 the DSC and the solution calorimetry value differ by 59 kJ mol^{-1} . For the latter compound, we prefer the DSC value because it was obtained by a direct method with a relatively small uncertainty, and because two of the other DSC values have been confirmed by independent methods. It should be kept in mind, however, that all these values still need correction for the $[\text{H}^+ - \text{H}^0]$ terms, when these become available.

The relatively large discrepancies between the DSC and the solution calorimetry values for NF_4BF_4 and NF_4PF_6 are not surprising in view of the experimental difficulties encountered with finding and selecting suitable hydrolysis conditions, the relatively large uncertainties and variation in

values as a function of the hydrolysis media, and perhaps most of all, the additional uncertainties in certain of the required ancillary data. Our present preference for the DSC values is also supported by the dissociation enthalpy values of Table 5, since the DSC values exhibit values and trends which are more in line with our expectations based on the strongly differing F^- affinities of the corresponding Lewis acids. To obtain the F^+ ion affinity, h_3 , of NF_3 (equation 10), and the



enthalpy of formation of gaseous NF_4^+ , a knowledge of the lattice enthalpies of the NF_4^+ salt and of the corresponding K^+ salt of the same anion is required. The appropriate thermochemical cycle and equations are given by (10) to (12).



$$h_4 = \Delta H(H_2O(l) + F^+(g) \rightarrow H^+(aq) + HF(aq) + \frac{1}{2}O_2(g)) = -1806 \text{ kJ mol}^{-1} \quad (12)$$

Substitution of the known thermochemical values given in Table 2 yields

$$h_3 = h_2 - h_1 + U_{KXF} - U_{NF_4XF} - 1040 \text{ kJ mol}^{-1} \quad (13)$$

The lattice enthalpy of $KSbF_6$ is known (-585 kJ mol^{-1}) [29], and that of NF_4SbF_6 may be estimated, utilizing incomplete structural data [34]. NF_4SbF_6 has a tetragonal unit cell; the NF_4^+ ions have been placed in the structure with $r_{N-F} = 1.25\text{\AA}$, but the SbF_6^- ions are disordered. Using $q(Sb) = 1.7$, as in $KSbF_6$, we have estimated lattice enthalpies for NF_4SbF_6 from $q(N) = 0$ to $q(N) = 1.0$, using the real structural information, as far as it can be determined. In practice, the variation of lattice enthalpy

with both $q(N)$ and $q(Sb)$ is small, and we estimate a value for $U(NF_4SbF_6)$ ($q(N)=1.0$) of $-435 \pm 10 \text{ kJ mol}^{-1}$. From (13), the F^+ affinity of NF_3 is -845 kJ mol^{-1} and the enthalpy of formation of gaseous NF_4^+ is $+784 \text{ kJ mol}^{-1}$. In view of the various assumptions involved, it is difficult to gauge the error in these quantities, but it is likely to be of the order of $\pm 30 \text{ kJ mol}^{-1}$. Our value of $+784 \pm 30 \text{ kJ mol}^{-1}$ for $\Delta H_f^0(NF_4^+)(g)$ is in fair agreement with a previous estimate [9] of $+854 \pm 40 \text{ kJ mol}^{-1}$, derived from the thermal calorimetric $\Delta H_f^0(NF_4BF_4)(s)$ value [3], $\Delta H_f^0(BF_4^-)(g)$ and an estimated lattice energy of -494 kJ mol^{-1} for NF_4BF_4 .

The value of $\Delta H(NF_3(g) + F^+(g) \rightarrow NF_4^+(g)) = -845 \text{ kJ mol}^{-1}$ is close to the proton affinity of NH_3 ($-860.5 \pm 2.0 \text{ kJ mol}^{-1}$) [35,36]. Although the average bond energy in NF_3 (278 kJ mol^{-1}) is significantly lower than that in NH_3 (391 kJ mol^{-1}) [37], the addition of a positively charged fourth ligand to NH_3 enhances the $\delta^+\delta^-$ polarity of the existing N-H bonds and thereby weakens them. In NF_3 , the polarity of the bonds is reverse, i.e. $\delta^-\delta^+$, and the addition of F^+ results in more covalent and stronger N-F bonds. This opposite effect of X^+ addition to NH_3 and NF_3 is also reflected by their bond distances and stretching force constants [38-40] shown in the Table 6. The dramatic strengthening of the N-F bonds of NF_3 by addition of F^+ is further demonstrated by the large dissociation enthalpy of the first N-F bond in $NF_4^+(g)$, $\Delta H(NF_4^+(g) \rightarrow NF_3^+(g) + F(g)) = 419 \text{ kJ mol}^{-1}$, obtained from the above $\Delta H_f^0(NF_4^+)(g)$ value and the known $\Delta H_f^0(F)(g) = 80 \text{ kJ mol}^{-1}$ [24] and $\Delta H_f^0(NF_3^+)(g) = 1123 \text{ kJ mol}^{-1}$ values. The latter value was calculated from the enthalpy of formation [18] and the first ionization potential [41] of NF_3 .

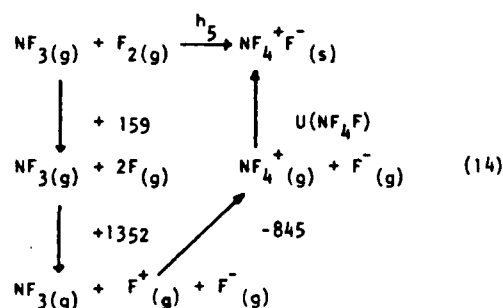
TABLE 6

Comparison of Bond Distances ($\bar{R}$) and Stretching Force Constants (mdyn/ $\bar{R}$) in NX_3 and NX_4^+ .

	r	f_r
NH_3	1.01	6.54[38]
NH_4^+	1.03	6.0[38]
NF_3	1.365	4.31[40]
NF_4^+	1.25-1.30 ^a	6.15[39]

^a Estimated from force constants [39] and incomplete structural data [34].

The Existence of NF_5 . For the hypothetical NF_5 molecule, the ionic NF_4^+F^- form should energetically be more favorable than a covalent NF_5 [42]. The above derived value for the F^+ ion affinity of NF_3 may be utilized to derive a value for the enthalpy of formation of solid NF_4^+F^- from NF_3 and F_2 . In the following cycle



all the quantities are known except for the lattice enthalpy of NF_4^+F^- . Using the configuration of NF_4^+ from the NF_4SbF_6 structure [34], it is possible to estimate $U(\text{NF}_4\text{F})$, assuming a CsCl type of structure as in NH_4Cl , and suitable F-F distances. A cell dimension of $a_0 = 4.51\text{\AA}$ gives $\text{N-F} = 1.25\text{\AA}$ and $\text{F-F} = 2.66\text{\AA}$, which yields a lattice enthalpy for $q(\text{N}) = 1.0$ of -630 kJ mol^{-1} . This value is not sensitive to changes in $q(\text{N})$ and is similar to a previous estimate [9] of -615 kJ mol^{-1} . Substitution in (14) yields $\Delta H(\text{NF}_3(\text{g}) + \text{F}_2(\text{g}) \rightarrow \text{NF}_4\text{F}(\text{s})) = +36(+40)\text{ kJ mol}^{-1}$. The free energy change would, of course, be even less favorable and it is very unlikely that a covalent NF_5 would be more stable. These conclusions are in agreement with previous failures [10] to synthesize NF_4F at temperatures down to 77K from $\text{NF}_3 + \text{F}_2$ by uv-photolysis.

ACKNOWLEDGEMENTS

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Gas-Phase Structure of Chlorine Trifluoride Oxide, ClF₃O

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The molecular structure of ClF₃O has been studied by gas electron diffraction. A distorted trigonal bipyramid with the following geometric parameters (r_a values) was obtained: Cl=O = 1.405 (3) Å, Cl-F_e = 1.603 (4) Å, Cl-F_a = 1.713 (3) Å, $\angle F_eClO$ = 108.9 (0.9)°, $\angle F_eClF_e$ = 87.9 (1.2)°, and $\angle F_aClO$ = 94.7 (2.0)°. Steric repulsion effects in equatorial and axial directions for the double bond and the lone electron pair of chlorine are discussed. The position of the lone pair was derived from ab initio calculations.

Introduction

Chlorine trifluoride oxide was independently discovered in 1965 at Rocketdyne¹ and 1970 at Saclay.² No structural data have been published for this interesting compound, except for its vibrational^{3,4} and ¹⁹F^{1,4} and ¹⁷O⁵ NMR spectra, which were in agreement with a pseudo-trigonal-bipyramidal structure of symmetry C_{2v}. In this structure, two fluorines occupy the axial positions and one fluorine, one oxygen, and one sterically active free valence electron pair occupy the equatorial positions. It was recently proposed⁶ that free valence electron pairs and π bonds can result in directional repulsion effects for trigonal-bipyramidal molecules. Since ClF₃O possesses both a free valence electron pair and a π bond, a knowledge of its exact molecular structure was of great interest. In this paper, the results of a structure determination of ClF₃O by gas-phase electron diffraction are given in support of the previously proposed⁶ directional repulsion effects.

Experimental Section

The sample of ClF₃O used for this study was prepared by low-temperature fluorination of ClONO₂ using a previously described method.¹ The sample was purified by fractional condensation, followed by complexation with KF and controlled vacuum pyrolysis of the resulting KClF₃O adduct.⁷ The product showed no impurities detectable by vibrational and NMR spectroscopy¹⁻⁴ and was handled exclusively in well-passivated (with ClF₃) Teflon-stainless steel equipment.

The electron diffraction intensities were recorded with a Balzer diffractograph KD-G2⁸ at two camera distances (50 and 25 cm) and an accelerating voltage of about 60 kV. The nozzle temperature was 10 °C, and the sample was kept at -35 °C. The camera pressure never exceeded 1×10^{-5} torr during the experiment (throughout this paper $1 \text{ Å} = 100 \text{ pm}$, $1 \text{ torr} = 101.325/760 \text{ kPa}$). The electron wavelength was determined from ZnO diffraction patterns. s ranges ($s = (4\pi/\lambda) \sin(\theta/2)$, λ = electron wavelength, θ = scattering angle) of $1.4\text{--}17 \text{ Å}^{-1}$ and $8\text{--}35 \text{ Å}^{-1}$, for the two camera distances, were covered in the experiment. For each camera distance two plates were selected and the intensity data were evaluated in the usual way.⁹ The averaged molecular intensities were measured in steps of $\Delta s = 0.2 \text{ Å}^{-1}$.

Results and Discussion

Structure Analysis. The observed molecular intensities are given in Figure 1. A preliminary geometric model was derived from the radial distribution function (Figure 2) and then refined by a least-squares analysis based on the molecular intensities. A diagonal-weight matrix was used,⁹ and theoretical intensities were calculated with the scattering amplitudes and phases of Haase.¹⁰ The only geometric constraint was an assumed C_{2v} symmetry. The ratios between the vibrational amplitudes of the bonded distances and of some nonbonded distances were constrained to the spectroscopic values (see Table I). Parallel vibrational amplitudes and

Table I. Results of the Electron Diffraction Experiment and Spectroscopic Calculations

(a) Geometric Parameters (r_a Values) (Å and Deg) ^a			
Cl=O	1.405 (3)	$\angle F_eClF_e$	87.9 (1.2)
Cl-F _e	1.603 (4)	$\angle F_aClO$	94.7 (2.0)
Cl-F _a	1.713 (3)	$\angle F_aClF_a$ ^b	170.5 (4.1)
$\angle F_eClO$	108.9 (0.9)		
(b) Vibrational Amplitudes from Electron Diffraction and Spectroscopic Data and Harmonic Vibrational Corrections (Å)			
	vibrational amplitudes		
	ed	spectr	$r_a - r_{ed}$
Cl=O	0.032 (7) ^c	0.036	0.0010
Cl-F _e	0.041 (7) ^c	0.047	0.0001
Cl-F _a	0.048 (7) ^c	0.053	0.0010
F _e ...O	0.066 (6) ^c	0.065	-0.0008
F _a ...O	0.073 (6) ^c	0.072	0.0000
F _a ...F _e	0.079 (6) ^c	0.078	-0.0007
F _a ...F _a	0.061 (10)	0.067	-0.0010

(c) Agreement Factors for Both Camera Distances (°)
 $R_{50} = 5.2$ $R_{25} = 7.0$

^a See text for estimated uncertainties. ^b Dependent parameter. ^c Ratio constrained to the spectroscopic value.

Table II. Atomic Net Charges, Dipole Moment, and Overlap Populations for ClF₃O

	net charge		overlap pop., au
Cl	1.76 +	Cl-F _e	0.092
F _e	0.31-	Cl-F _a	0.070
F _a	0.46-	Cl-O, π_e	0.103
O	0.53-	π_a	0.091

$\mu^a = 1.74 \text{ D}$

^a See Figure 3 for the direction of dipole moment.

harmonic vibrational corrections $\Delta r = r_a - r_{ed}$ (Table I) were calculated from the force field of ref 3 with the program NORCOR.¹¹ Two correlation coefficients had values larger than

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Table III. Geometric Parameters of Some Chlorine-Fluorine-Oxygen Compounds (Å and Deg)

							
Cl-F	1.628	1.598 (5)	1.571 (14)	1.603 (4)	1.697 (3)	1.619 (4)	
Cl-F _a		1.698 (5)	1.669 (15)	1.713 (3)			
Cl-O				1.405 (3)	1.418 (2)	1.404 (2)	1.475 (3)
∠F _a ClF _a		87.5 (5)	86.0 (15)	87.9 (12)			
∠F _a ClF _e		175.0 (7)		170.5 (41)			
∠OCIF				108.9 (9) ^h	101.7 (1)	100.8 (8)	
∠OCIO				94.7 (20) ⁱ	115.2 (1)	116.6 (5)	117.7 (17)

^a r_e values from ref 19. ^b r_O values from ref 20. ^c r_a values from ref 21. ^d r_a values from this work. ^e r_O values from ref 22. ^f r_a values from ref 23. ^g r_a values from ref 24. ^h $\angle O=Cl-F_e$. ⁱ $\angle O=Cl-F_a$.

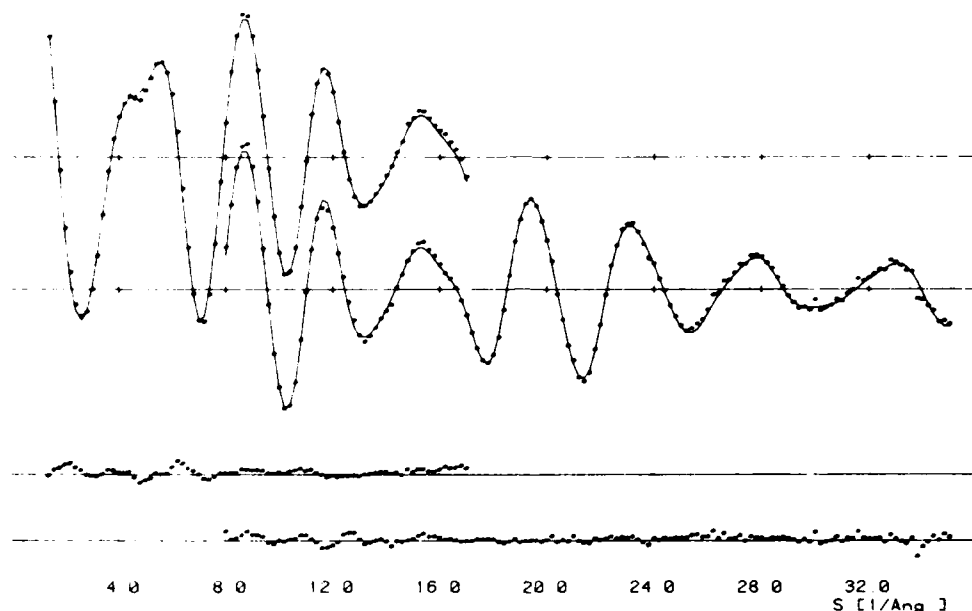


Figure 1. Experimental (points) and calculated (—) molecular intensities and differences.

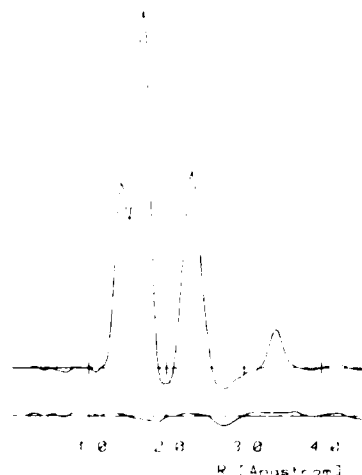


Figure 2. Experimental radial distribution function and difference curve.

0.5: $[\angle F_a Cl F_e / \angle F_a Cl O] = 0.88$ and $[I(\text{bonded}) / (F_a \cdots F_a)] = 0.61$. The results of the least-squares analysis are summarized in Table I. Estimated uncertainties are 3σ values, and a

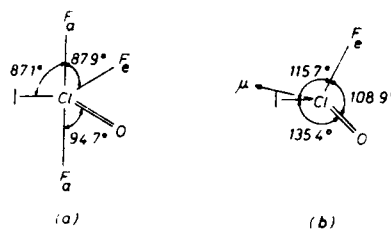


Figure 3. Bond angles in axial (a) and equatorial (b) directions.

possible scale error of 0.1% is included for bonded distances.

Ab Initio Calculations. The molecular wave function at the experimental geometry was calculated with the program TEXAS.¹² For second-row atoms, 4-21 basis sets¹³ were used, and for chlorine, a 3-3-21 basis set,¹⁴ supplemented by d functions,¹² was used. The position of the chlorine lone electron pair (Figure 3) was obtained by transformation to localized orbitals, using Boys' criterion.¹⁵ Atomic net charges and

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overlap populations (Table II) were derived by a Mulliken population analysis.¹⁶

Molecular Structure of ClF₃O. Chlorine trifluoride oxide is a distorted-trigonal-bipyramidal molecule with three different ligands in the equatorial plane: a single bond, a double bond, and a lone valence electron pair. The angles (Figure 3) between the axial bonds and the double bond are larger (by about 7°) than the angles between the axial bonds and the single bond or the lone electron pair; i.e., the axial fluorine atoms are bent away from the double bond into the sector between the single bond and the lone electron pair. This demonstrates that in the axial direction the steric repulsion of the double bond is larger than the repulsion from either the lone pair or the single bond. The angles in the equatorial plane, however, indicate that in the equatorial direction the repulsion by the lone pair is largest, followed by the double bond, with the single bond being smallest. This directional repulsion effect of double bonds, which has been pointed out previously,⁶ correlates well with the different populations of the π -bond orbitals in the axial and the equatorial planes.¹⁷ For ClF₃O, these populations (Table II) are almost equal.

The observed bond distances (Cl=O = 1.405 Å, Cl—F_e = 1.603 Å, Cl—F_a = 1.713 Å) agree well with previous estimates (Cl=O = 1.42 Å, Cl—F_e = 1.62 Å, Cl—F_a = 1.72 Å)³ derived from the observed vibrational spectra and a comparison with related molecules. They confirm the conclusions, previously reached from the results of a normal-coordinate analysis,³ that the chlorine-oxygen bond has double-bond character and that the axial Cl—F bond is significantly weaker than the equatorial one. These results support a previously outlined bonding scheme assuming mainly sp² hybridization for the bonding of the three equatorial ligands (ClF, ClO σ bond, and free valence electron pair) and the use of a chlorine p orbital for the bonding of the two axial fluorines by means of a semiionic

three-center-four-electron bond pair.^{3,7,18}

A comparison of the bond lengths in ClF₃O with those in closely related molecules (see Table III) also correlates well with the conclusions previously derived from force field computations.^{3,7,18} These computations had shown that, if the bonds are separated according to the two possible types (i.e., mainly covalent and mainly semiionic 3c-4e), the bond strength within each type increases with increasing formal oxidation state of the central atom and decreases with increasing oxygen substitution. The first effect is due to an increase in the effective electronegativity of the central atom with increasing oxidation state. This increase causes the electronegativities of the central atom and the ligands to become more similar and therefore the bonds to become more covalent. The second effect is caused by oxygen being less electronegative than fluorine, thereby releasing electron density to the molecule and increasing the ionicity of the Cl—F bonds.^{7,18} Although the previous force field computations clearly reflected these trends, the uncertainties in force constants, obtained from an underdetermined force field, were rather large and certainly are not as precise as the more reliable bond length measurements from this study.

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APPENDIX V

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 .

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. Non-volatile materials were handled in the dry nitrogen atmosphere of a glovebox. Metathetical reactions were carried out in HF solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter [3].

Infrared spectra were recorded in the range $4000\text{--}200\text{ cm}^{-1}$ 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 $4880\text{-}\text{\AA}$ exciting line of an Ar-ion laser and Claassen filter [4] 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 [5].

Materials. Literature methods were used for the syntheses of NF_4SbF_6 [6] and NF_4HF_2 solutions in HF [7]. Hydrogen fluoride (Matheson) was dried by storage over BiF_5 to remove the H_2O [8]. Cesium fluoride (KBI) was dried by fusion in a platinum crucible and ground in the drybox. Beryllium difluoride was prepared by pyrolysis of $(\text{NH}_4)_2\text{BeF}_4$ at 270° to 360°C in a N_2 flow tube using Al boats as sample containers. The $(\text{NH}_4)_2\text{BeF}_4$ was prepared by combining solutions of beryllium metal in 12% aqueous HF and of NH_4HF_2 (15% excess) in 5% aqueous HF. Most of the solvent was evaporated at 120°C and the resulting slurry was filtered at 0°C , washed three times with an ice cold 20% ethanol solution, and dried at 110°C for 24 hours. The purity of BeF_2 and $(\text{NH}_4)_2\text{BeF}_4$ was checked by vibrational spectroscopy, and no impurities could be detected. Aluminum trifluoride was prepared by treating freshly sublimed AlCl_3 twice

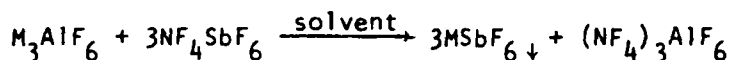
with a large excess of anhydrous HF at ambient temperature, followed by removal of HCl and the excess of HF in vacuo at elevated temperature.

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; CsSbF₆, 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.

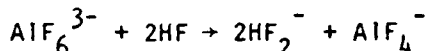
Preparation of NF_4AlF_4 . Freshly prepared AlF_3 (0.469g, 5.58 mmol) was combined with NF_4HF_2 (generated as described above from 33.8 mmol of NF_4SbF_6) in 35 ml of HF. The mixture was stirred at 25°C for 1 hour, then most of the HF solvent was pumped off until incipient decomposition of NF_4HF_2 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 CsSbF₆. 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 $(\text{NF}_4)_2\text{BeF}_4$ 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

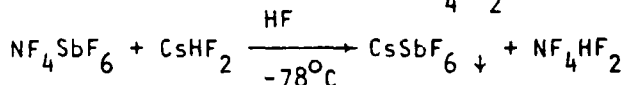


were also investigated where M was either Cs or Na and the solvents were either BrF_5 at 25°C , HF at -78°C or molten NF_4SbF_6 at 275°C under 1000 psi NF_3 and F_2 pressure. In all cases, no evidence for $(\text{NF}_4)_3\text{AlF}_6$ was obtained, probably because the AlF_6^{3-} and BeF_4^{2-} anions are very strong Lewis bases which undergo rapid solvolysis, such as

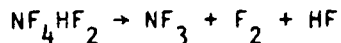


This metathetical approach was further complicated by the fact that the AlF_4^- salts appear to be quite insoluble and therefore cannot be separated from the highly insoluble alkali metal SbF_6^- salts. Since previous studies in our laboratory had demonstrated that these solubility and separation problems can be overcome by digesting a polymeric insoluble Lewis acid, such as UOF_4 [10] or WOF_4 [11], in a large excess of a highly concentrated NF_4HF_2 solution, this approach was also applied to AlF_3 and BeF_2 .

The concentrated solutions of NF_4HF_2 in HF were prepared according to

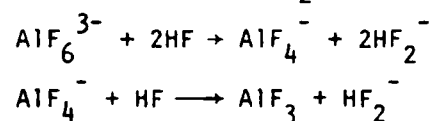


followed by its addition to either AlF_3 or BeF_2 . After digesting these mixtures at 25°C until clear solutions were obtained, the excess of unreacted NF_4HF_2 , which in the absence of a solvent is unstable at 25°C , was decomposed at 55°C



and pumped off. Based on the observed material balances and spectroscopic and elemental analyses, the solid residues consisted of mainly $\text{NF}_4\text{Be}_2\text{F}_5$ and NF_4AlF_4 with some NF_4SbF_6 and CsSbF_6 as the expected impurities. Attempts

to purify NF_4AlF_4 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 HF_2^- ion concentration is required to diminish the acidity of the HF solvent and to suppress the solvolyses of the strong Lewis bases AlF_6^{3-} , AlF_4^- or BeF_4^{2-} . The fact that at the end of the digestion periods of AlF_3 or BeF_2 in HF solutions of NF_4HF_2 clear solutions were obtained, while NF_4AlF_4 and $\text{NF}_4\text{Be}_2\text{F}_5$ appear to possess only limited solubilities in HF, suggests the possibility that, in the presence of a large excess of HF_2^- , either AlF_6^{3-} or BeF_4^{2-} might exist in these solutions. Obviously, an excess of HF_2^- 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 1.

TABLE 1. 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 }		
1220 } mw		$2\nu_4 (A_1 + E + F_2)$
1210 }		
1185 sh }	1189 (1.0) }	
1160 vs }	1158 (1.0) }	$\nu_3 (F_2)$
1145 sh }	1141 (1.0) }	
975 s, br		Be_2F_5^-
	851 (10)	$\nu_1 (A_1)$
765 ms, br }		
690 ms, br }		Be_2F_5^-
623 mw }	621 (1.9) }	
611 m }	610 (3.3) }	$\nu_4 (F_2)$
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 }		

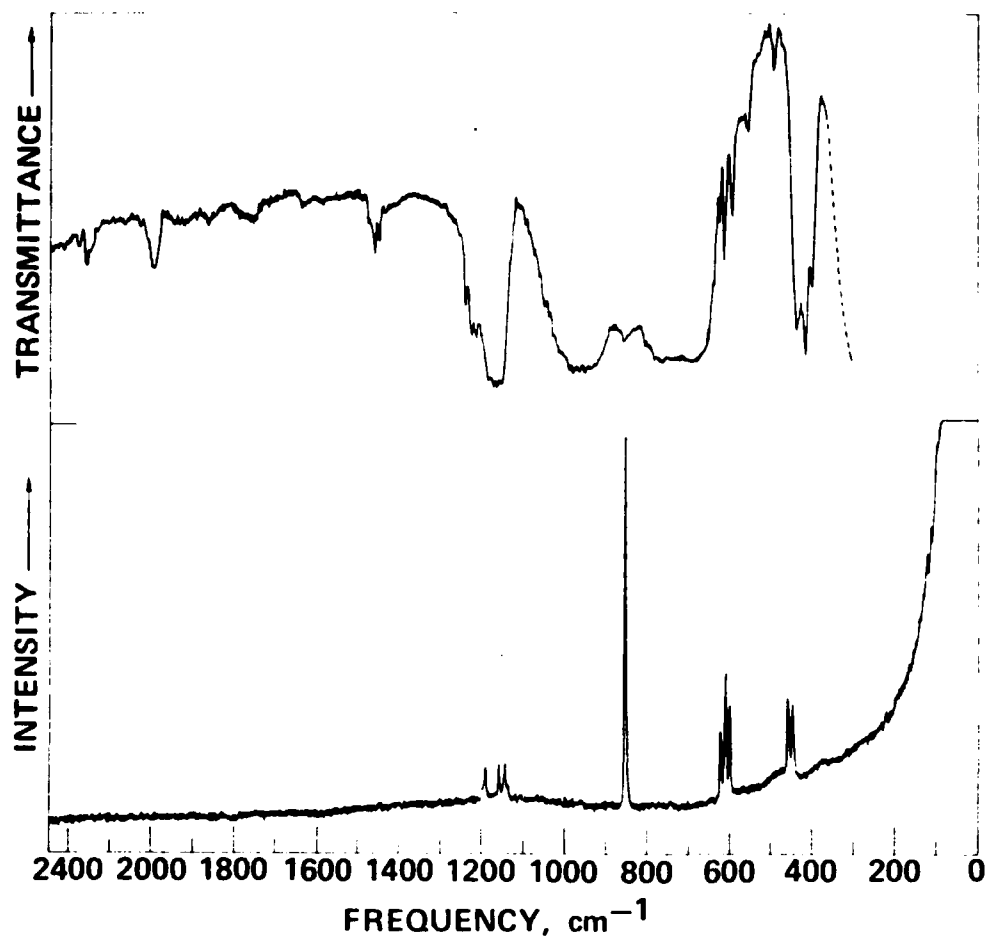


Figure 1. Infrared and Raman Spectrum of Solid $\text{NF}_4\text{Be}_2\text{F}_5$

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

Acknowledgement

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2.2.7 Preparation of Halogen Oxyfluorides

Halogen oxyfluorides are prepared by forming either halogen-fluorine or halogen-oxygen bonds. Since this chapter deals exclusively with the formation of the halogen-halogen bond, preparative methods for halogen oxyfluorides based on the formation of halogen-oxygen bonds are not included.

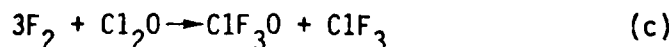
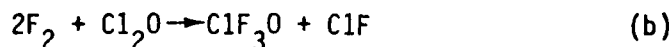
2.2.7.1 By Reaction of Halogen Oxides with Elemental Fluorine

The interaction of F_2 with chlorine oxides, such as ClO_2^{1-5} , $Cl_2O_6^{6-7}$, or $Cl_2O_7^8$ produces $FClO_2$. Quantitative yields of $FClO_2$ are obtained with ClO_2 as a starting material and moderated reaction conditions. Inert solvents, such as $CFCl_3$, or diluents, such as air or N_2 , are recommended to avoid hazards owing to the explosive nature of the chlorine oxides. For the higher chlorine oxides, the need for elevated temperature and the decreased yields of $FClO_2$ suggest that the primary step in these reactions involves the thermal decomposition to ClO_2 which is then fluorinated. Therefore, all of these reactions are likely to involve the step:



In view of the shock sensitivity of chlorine oxides, none of the above methods is recommended for the large-scale production of $FClO_2$, and necessary safety precautions must be used. The recommended method for the preparation of $FClO_2$ is the reaction of $NaClO_3$ with ClF_3 (see section 2.2.7.6).

The low temperature ($-78^\circ C$) fluorination of Cl_2O with elemental fluorine produces ClF_3O as the main product⁹. Depending on the reaction conditions, the by-products can be either ClF or ClF_3 :



When no catalyst is used, or if KF and NaF are present as catalysts, ClF is the main byproduct. When the more basic alkali metal fluorides, RbF and CsF , are used, ClF_3 is the coproduct. The formation of ClF_3 rather than ClF is

associated with the more ready formation of ClF_2^- intermediates with RbF and CsF . Yields of ClF_3O from Cl_2O vary and are affected by the alkali fluoride present. Yields of >40% are obtained and reach >80% using either NaF or CsF . Since NaF does not form an adduct with $\text{ClF}_3\text{O}^{10}$, stabilization of the product by complex formation does not influence the ClF_3O yields.

Owing to unpredictable explosions experienced with liquid Cl_2O , attempts are made to circumvent the Cl_2O isolation step, and the crude Cl_2O , still absorbed on the mercury(II) salts, is directly fluorinated. Again, ClF_3O is formed, but its yield is too low to make this synthetic route attractive.

The fluorination of solid Cl_2O to ClF_3O proceeds at -196°C provided the fluorine is suitably activated by methods such as glow discharge. Unactivated fluorine does not interact with Cl_2O at -196°C . The low yield of ClF_3O (1-2%) makes this modification impractical.

Owing to the shocksensitivity of Cl_2O , its fluorination reaction is not the preferred method for the preparation of ClF_3O . Replacement of Cl_2O by the more stable ClONO_2 results in a safer process (see Section 2.2.7.5).

By analogy with ClO_2 , BrO_2 is readily fluorinated by elemental F_2 to give FBrO_2 in high yield¹¹:



However, direct reaction with F_2 is not practical because even at -78°C the reaction is exceedingly vigorous resulting in spontaneous decomposition of the BrO_2 and explosions. Liquid Cl_2 or perfluoropentane is used as a diluent to moderate the reaction; BrO_2 is not soluble in these solvents and must be suspended. Again, this method is not recommended for larger-scale preparations of FBrO_2 and appropriate safety precautions must be taken.

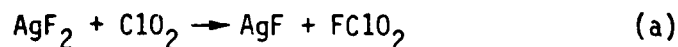
The fluorination of I_2O_5 with elemental fluorine in anhydrous HF may¹² result in $FI O_2$, but this claim is refuted by a subsequent study¹³ which shows that anhydrous HF quantitatively converts I_2O_5 or $FI O_2$ to IF_5 .

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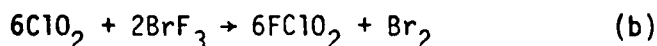
2.2.7.2 By Reaction of Halogen Oxides with Fluorinating Agents other than F_2

In the $FCIO_2$ synthesis from ClO_2 and F_2 , the latter can be replaced by other fluorinating agents. Thus, the passage of ClO_2 , diluted by N_2 , over AgF_2 ¹ or CoF_3 ² at RT produces pure $FCIO_2$ in high yield:

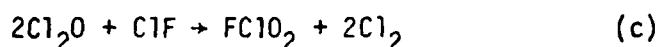


The consumption of AgF_2 can be followed by the color change of AgF_2 (dark brown) to AgF (yellow).

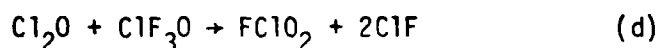
Halogen fluorides can also fluorinate ClO_2 to FClO_2 . Thus, the passage of ClO_2 through liquid BrF_3 at 30°C proceeds¹:



The risk of explosions in the $\text{ClO}_2 - \text{AgF}_2$ reaction is reduced when ClO_2 is replaced by the less dangerous Cl_2O . The yields of FClO_2 is 35%^{3,4}. Similarly, Cl_2O can be fluorinated at -78°C with either ClF ⁵:

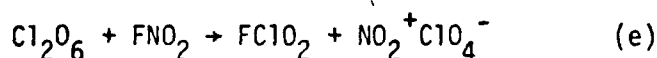


or ClF_3 ⁶:

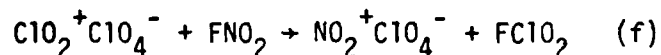


In these two reactions the unstable FClO molecule is formed as an intermediate, but disproportionates to yield FClO_2 and ClF (see section 2.2.7.4).

The fluorination of Cl_2O_6 with a variety of fluorinating agents also yields FClO_2 principally. Fluorinating agents used with Cl_2O_6 include BrF_3 or BrF_5 ⁷, HF ⁸ and FNO_2 ¹. The latter reaction is carried out in CFCl_3 at 0°C :

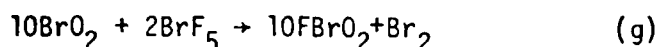


These reactions of Cl_2O_6 are carried out at low temperatures at which decomposition of Cl_2O_6 to $2\text{ClO}_2 + \text{O}_2$ can be excluded. They can be rationalized by polarization of Cl_2O_6 to $\text{ClO}_2^+ \text{ClO}_4^-$ ².

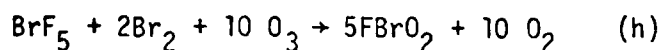


The ionic structure of Cl_2O_6 in the solid state has been established by vibrational spectroscopy⁹.

Fluorination of BrO_2 to FBrO_2 is achieved using BrF_5 as a fluorinating agent^{2,10}:



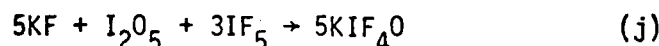
The reaction is carried out at -55°C in liquid BrF_5 , and the FBrO_2 is separated from the Br_2 byproduct and excess of BrF_5 by vacuum fractionation. This reaction can be further simplified by preparing the BrO_2 in situ by passing O_3 through a solution of Br_2 in BrF_5 ^{2,10,11}.



When I_2O_5 is dissolved in boiling IF_5 , white hygroscopic needles of IF_3O separate on cooling¹²:



A modification of this reaction is used to¹³ prepare KIF_4O :



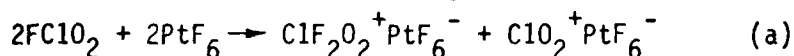
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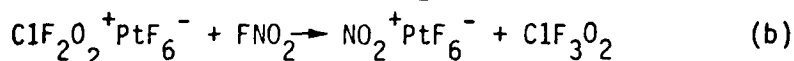
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2.2.7.3. By Reaction of Halogen Oxyfluorides with Fluorinating Agents

The fluorination of a chlorine oxyfluoride to one of higher oxidation state is difficult owing to the scarcity of stable low (+III) and high (+VII) oxidation state oxyfluorides. Only one case ^{1,2} is known, where FClO_2 is fluorinated by the strong oxidizer PtF_6 :

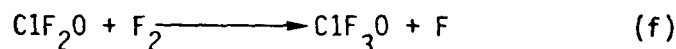
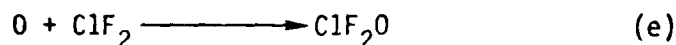
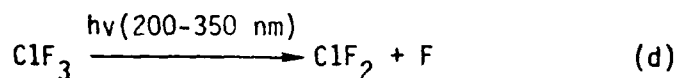
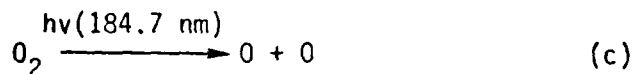


Several side reactions compete, and the yield of ClF_2O_2^+ varies with changes in the reaction conditions. The $\text{ClF}_2\text{O}_2^+\text{PtF}_6^-$ can be converted to ClF_3O_2 by a displacement reaction using FNO_2 :



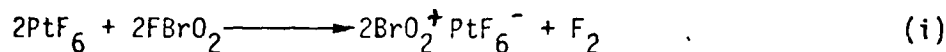
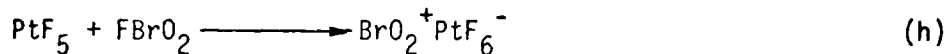
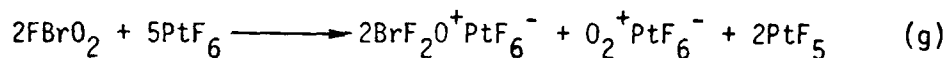
Oxygen and fluorine ligands scramble in the synthesis of ClF_3O from mixtures of chlorine-, fluorine-, and oxygen- containing starting materials using uv-photolysis³⁻⁵. A claim⁵ for the formation of ClF_5O in the uv-photolysis of the $\text{ClF}_5\text{-OF}_2$ system cannot be confirmed⁶.

Kinetic study of the photolyses of the $\text{ClF}_3\text{-O}_2$ and $\text{Cl}_2\text{-F}_2\text{-O}_2$ systems⁷ shows that contrary to the original report³, the rate of ClF_3O formation is the same for both systems, increasing with O_2 concentration, and independent of irradiation time. Furthermore, the rate of ClF_3O formation is proportional to the intensity of the 184.7 nm band of the Hg spectrum indicating that the dissociation of O_2 to two ground-state, ³p, oxygen atoms is the primary photochemical process. The mechanism requires photochemical dissociation of ClF_3 as well:

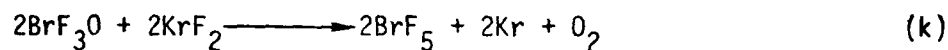
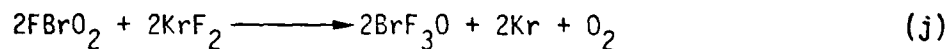


In the photolysis of ClF_3 under similar conditions, a photochemical steady state is quickly achieved, where $(\text{F}_2) = (\text{ClF}) = \alpha(\text{ClF}_3)$, and α - has a value of ~1 at low and of ~3 at high pressures. These results together with the known photochemical decomposition of OF_2 ⁸ explain why ClF_3O can be readily generated by the photolysis of so many different starting materials, including the halogen oxyfluorides FClO_2 , FClO_3 and IF_5O .

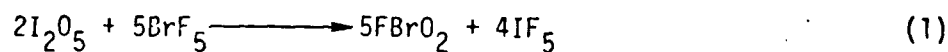
For bromine oxyfluorides, fluorinations use the powerful oxidizers PtF_6 and KrF_2 . With PtF_6 , the following reactions are observed⁹

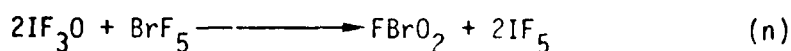
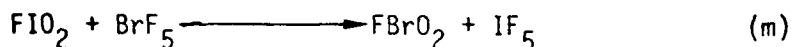


but no evidence for the formation of BrO_2F_2^+ is obtained. Similarly, the reactions of KrF_2 with either FBrO_2 , BrF_3O or FBrO_3 ^{10, 11} do not produce any novel bromine (+VII) compounds, but proceed according to:

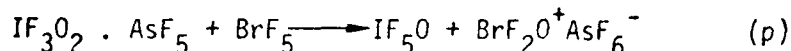
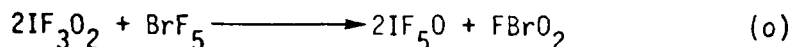


Iodine (+V) oxyfluorides or oxide are fluorinated by BrF_5 to yield FBrO_2 and IF_5 :

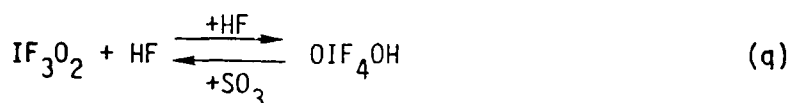




but heptavalent IF_3O_2 or its AsF_5 or SbF_5 adducts are fluorinated to give IF_5O^{11} :



The addition of HF to IF_3O_2 forms OIF_4OH reversibly¹²:



and represents an example for the addition of HF across an $\text{X}=\text{O}$ double bond with formation of a new $\text{X}-\text{F}$ bond.

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2.2.7.4 By Disproportionation of Halogen Oxyfluorides

The thermally unstable FClO readily disproportionates at $\text{RT}^{1,2}$:



This reaction explains the formation of FClO_2 and ClF where FClO would be the expected product (see section 2.2.7.2).

Iodine trifluoride oxide is stable at RT , but at 100°C undergoes a reversible change into IF_5 and FIO_2^3 :



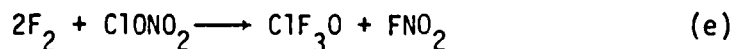
This reaction is also involved in the thermal and photochemical decomposition of IF_3O_2^4



- 1 K. O. Christe, C. J. Schack, Adv. Inorg. Chem. Radiochem., 18, 319 (1976).
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2.2.7.5 By Reaction of Positive Halogen Compounds with Fluorinating Agents

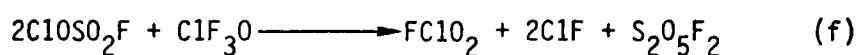
For the synthesis of ClF_3O , fluorination of ClONO_2 by F_2 at -35°C^1 is best:



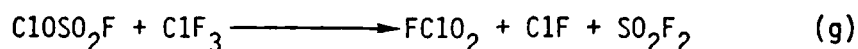
Contrary to the chlorine oxides, ClONO_2 has the advantage of not being shock sensitive. Other advantages include (a) less fluorine is required than in the fluorination reactions of Cl_2O which yield ClF_3 as co-product, (b) the differences in the volatilities of the products FNO_2 and ClF_3O ($\Delta T_{\text{bp}} \sim 100^\circ\text{C}$) permit easy separation by fractional condensation, (c) ClONO_2 can be prepared more conveniently, and (d) yields of ClF_3O are higher.

In the fluorination of ClONO_2 , side reactions compete with the fluorination step. These are caused by thermal decomposition of the starting material owing to inefficient removal of the heat of reaction. Hence, the rate of the competing reactions is markedly affected by the reaction temperature. At reaction temperatures near or above ambient, the decomposition of the hypochlorite appears to be favored, and little or no ClF_3O is formed, resulting in rapid, uncontrolled reactions. Thermal decomposition preceding the fluorination step yields only intermediates incapable of producing ClF_3O . Thus, in order to maximize the desired fluorination reaction, long reaction times at low temperature ($T < 0^\circ\text{C}$) are indicated.

Similarly, ClOSO_2F interacts with ClF_3O^2 :



and



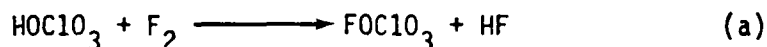
These reactions can be rationalized in terms of a reduction of ClF_3O to the unstable FClO which decomposes to FClO_2 and ClF .

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2.2.7.6 By Reaction of Halogen Oxyacids and their Salts with
Fluorinating Agents

Whereas fluorination of halogen oxyacids results in the formation of the corresponding fluorooxy compounds:



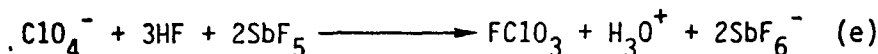
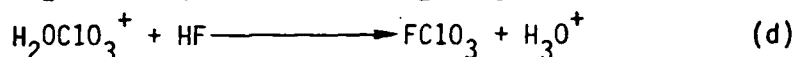
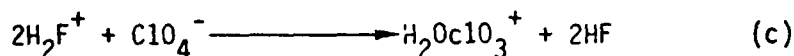
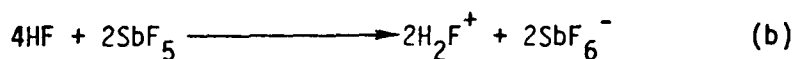
fluorination of the salts of these halogen oxyacids is a more useful method for the synthesis of halogen oxyfluorides. The nature of the halogen oxyfluoride product depends on the starting material and the reaction conditions. Thus the fluorination of perchlorates is a high yield synthesis of perchloryl fluoride. Heating of KC10_4 to $70^\circ - 120^\circ \text{C}$ in an excess of SbF_5 produces FC10_3 in 50% yield.² The yield of FC10_3 can be increased to 90% and the reaction temperature can be lowered to $20^\circ - 50^\circ \text{C}$, when a mixture of $\text{HF} - \text{SbF}_5$ is used.³ Slightly lower yields are obtained when the HF solvent is replaced by AsF_3 , IF_5 , or BrF_5 .

Most of the commercial processes are based on the use of HOSO_2F .⁴ Evolution of FC10_3 starts at 50°C and goes to completion at $85^\circ - 110^\circ \text{C}$. The yields of FC10_3 vary from 50 to 80%^{4,5,6,7} and, if necessary, the HOSO_2F can be regenerated.⁵ The reaction can be carried out in glass apparatus. The addition of certain additives like 5 to 25% SbF_3 to the HOSO_2F increases the yield of FC10_3 to 90%, but hinders the regeneration of HOSO_2F .⁸ The addition of $\text{HF} - \text{BF}_3$ increases the FC10_3 yield to 85%, but requires elevated pressure. Zinc, aluminum, silver, and lead fluorides decrease the yield of FC10_3 .

The highest yield of perchloryl fluoride (97%) is achieved with a mixture of fluorosulfonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction. Commercial reagents are used, but their additional purification is not necessary; unlike all the previous methods, this preparation of perchloryl fluoride can be carried out at RT. At high temperatures ($100^\circ - 135^\circ \text{C}$) the reaction time is 1 - 10 min., which

allows the process to be carried out continuously in a packed column. The purity of product obtained after the usual purification reaches $\geq 98\%$; air and carbon dioxide are present as trace impurities.⁹

The mechanism of the reaction between ClO_4^- and superacids is not established.^{3,10,14} Based on present understanding of superacid chemistry^{15,17} and of complex formation of FClO_3 , a mechanism involving ClO_3^+ as an intermediate is unlikely. Furthermore, the high yields of FClO_3 ($\geq 97\%$) would be surprising in view of the expected instability of ClO_3^+ . Other mechanisms involving protonated perchloric acid¹⁸ are more plausible:

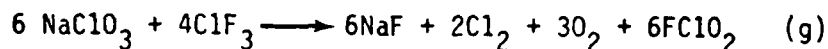


Other syntheses of FClO_3 from metal perchlorates include the electrolysis of a saturated solution of NaClO_4 in anhydrous HF with a current efficiency of 10%,¹⁹ and the fluorination of NO_2ClO_4 by ClF_3 at RT which results in the formation of FClO_3 and smaller amounts of FClO_2 , ClO_2 , and ClNO_2 .²⁰ The corresponding reaction of KClO_4 with BrF_3 yields FClO_2 in 97% yield.²¹

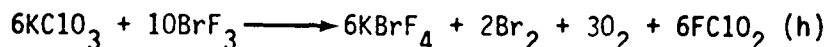


If the MClO_4 starting material is replaced by MClO_3 , the main fluorination product is FClO_2 , e.g., the reaction of NaClO_3 with an equimolar amount of ClF_3 produces FClO_2 in high yield²¹. This method is based on reports^{19,20,21,22} that gaseous ClF_3 reacts with KClO_3 to give FClO_2 in high yield. The substitution of KClO_3 by NaClO_3 is significant since the product NaF does not form an adduct with ClF_3 , whereas KF does. This decreases by 60% the amount of ClF_3 required for the reaction. By analogy with the KClO_3 reaction with

BrF_3 ²³, the idealized stoichiometry is:



The use of a slight excess of ClF_3 is recommended to avoid the possible formation of shock-sensitive chlorine oxides. The KClO_3 reaction with BrF_3 ²³:

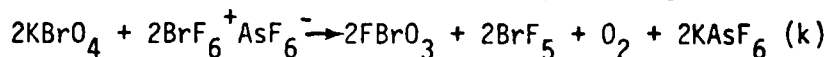
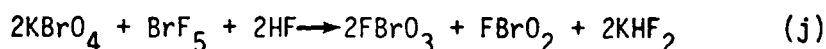
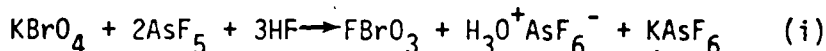


also produces FCIO_2 in high yield, but it is difficult to obtain pure, colorless FCIO_2 by this method.

The action of elemental fluorine on KClO_3 is not synthetically useful for preparing FCIO_2 owing to the large amounts of FCIO_3 always formed.^{19,24,25,26}

Low temperature fluorination of NaClO_2 with F_2 produces FCIO_2 as the main product, however, small amounts of ClF_3O are also obtained in addition to ClF_3 , ClF and Cl_2 .²⁷

Fluorination of alkali metal perbromates with HF and Lewis acids is analogous to that of the perchlorates, and produces FBrO_3 as the main product in high yield. The reactions are carried out in HF solution using SbF_5 ,²⁸ AsF_5 , BrF_5 or $\text{BrF}_6^+ \text{AsF}_6^-$:²⁹



In the absence of HF, CsBrO_4 ³⁰ reacts with BrF_5 and F_2 at RT to produce CsBrF_4O as the solid, and FBrO_3 and FBrO_2 as the volatile products. Potassium perbromate is less reactive than the cesium salt and required prolonged heating at 80°C to achieve a substantial conversion to KBrF_4O . In the absence of F_2 , the conversion of CsBrO_4 to CsBrF_4O is low, even at 80°C , and is not catalyzed by HF.

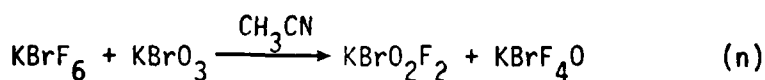
The reaction of KBrO_3 with BrF_5 is complex. According to the original report³¹ KBrO_3 reacts with BrF_5 at -50°C .



Subsequent work³² shows that the reaction of KBrO_3 with equimolar amounts of BrF_5 at RT proceeds:



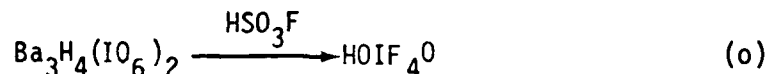
and that the reaction is slow when excess BrF_5 is used; KBrO_3 and BrF_5 at a mole ratio of 1:2.5 do not react at RT,³³ but a rapid reaction occurs when catalytic amounts of HF are added. The solid product of this reaction consists of KBrO_2F_2 and KBrF_4O , and FBrO_2 is the volatile product. The formation of KBrF_4O ³⁴ is shown by using an excess of BrF_5 and F_2 at 80°C which results in quantitative formation of KBrF_4O . This reaction, however, can be difficult to duplicate and can easily result in the formation of KBrF_4 .³⁰ The KBrO_3 reaction with BrF_5 is further modified³³ by reacting KBrF_6 with KBrO_3 in CH_3CN solution:



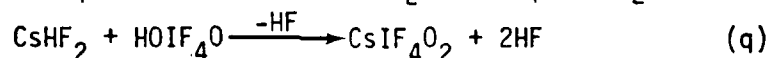
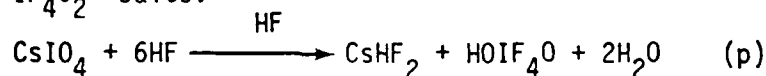
The KBrF_4O produced is soluble in CH_3CN , whereas KBrO_2F_2 is not, and the two products can be separated by extraction with CH_3CN .

The reactions of BrF_5 with BrO_3^- or BrO_4^- are interesting mechanistically since they involve oxygen-fluorine exchange. From the quantitative yields of BrF_4O^- , a free radical mechanism involving the addition of oxygen atoms to bromine fluorides is unlikely. A mechanism involving the addition of BrF_5 or BrF_6^- across a $\text{Br}=\text{O}$ double bond of BrO_4^- or BrO_3^- , followed by FBrO_3 or FBrO_2 elimination with BrF_4O^- formation is plausible.

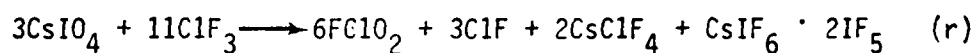
Periodates are fluorinated, e.g. $\text{Ba}_3\text{H}_4(\text{IO}_6)_2$ by HSO_3F to tetrafluoro orthoperiodic acid³⁵:



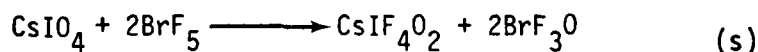
The same product is also formed from HOIO_3 or NaIO_4 in anhydrous HF ³⁶. When CsIO_4 is repeatedly treated with anhydrous HF , and the solvent is pumped off, the less volatile acid HOIF_4O displaces HF from the CsHF_2 with quantitative formation of CsIF_4O_2 (cis:trans $\approx$ 2:1)³⁷. This is a convenient synthesis of IF_4O_2^- salts:



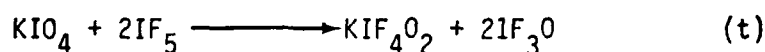
With elemental fluorine at 60°C, CsIO_4 is converted³⁷ to mainly CsIF_8 and CsIF_6 , but the product also contains lesser amounts of CsIF_4O and cis- and trans- CsIF_4O_2 . With an excess of ClF_5 at RT, CsIO_4 is slowly converted to CsIF_8 , trans- CsIF_4O_2 and some CsIF_4O . With the more reactive fluorinating agent, ClF_3 , complete conversion of CsIO_4 is obtained at RT:



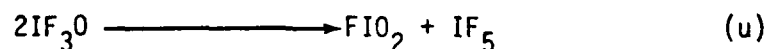
With BrF_5 the main reaction is:



This reaction is analogous to that reported³⁸ for KIO_4 and IF_5 , i.e.:



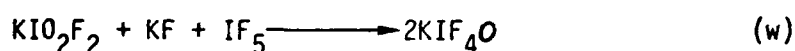
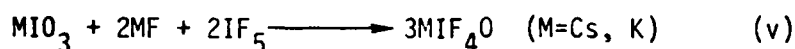
and produces trans- IF_4O_2^- . Under the experimental conditions (120°C, vacuum) used for the removal of the excess IF_5 , the IF_3O disproportionates:



resulting in FIO_2 and KIF_4O_2 as the final products. Compared to the IF_5

reaction, the BrF_5 synthesis offers the advantage that the BrF_3O and BrF_3 byproducts are volatile and can easily be pumped off. However the resulting solid product is contaminated with CsBrF_4 .

Iodates are fluorinated but, whereas the fluorination of HIO_3 in aqueous HF forms the IO_2F_2^- anion³⁹, solutions of NaIO_3 in anhydrous HF contain IF_5 .⁴⁰ With IF_5 as a fluorinating agent, MIO_3 or KIO_2F_2 produces the corresponding IF_4O^- salts⁴¹:



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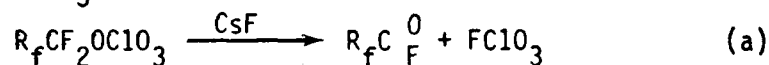
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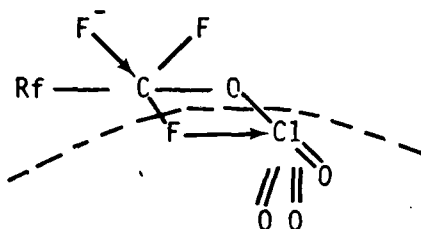
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2.2.7.7 By Elimination Reactions

The only reaction involving the elimination of halogen oxyfluorides is the CsF-catalyzed FClO_3 elimination of fluorocarbon perchlorates¹.



which proceeds at 60°C and involves the attack of the CF_2 carbon atom by the fluoride anion, followed by an internal nucleophilic displacement reaction and FClO_3 elimination:



The reactions of BrF_5 with BrO_3^- or BrO_4^- (see section 2.2.7.6) may also involve similar intermediates which decompose with FBrO_2 or FBrO_3 elimination, but these intermediates are not isolated.

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APPENDIX X

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

PERFLUORO AMMONIUM SALTS OF METAL HEPTAFLUORIDE ANIONS

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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 lasers¹, ingredients in high detonation pressure explosives², and fluorinating agents for aromatic compounds³. 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 FEP vacuum line. The line and other hardware used were well passivated with ClF_3 and, if HF was to be used, with HF. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove-box. Metathetical reactions were carried out in HF solution using an apparatus

consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter⁴. Thermal decomposition measurements were carried out in a previously described⁵ sapphire reactor.

Infrared spectra were recorded in the range $4000\text{--}200\text{ cm}^{-1}$ 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 $4880\text{-}\text{\AA}$ 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 described⁷.

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_5 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 one half of a prepassivated Teflon double U metathesis apparatus. Dry HF (15 ml liquid) 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. 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 vigorous stirring for 30 minutes at 25°C , the

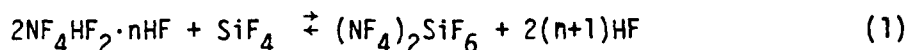
lower WF_6 layer dissolved in the upper HF phase. Most of the volatile products were pumped off at ambient temperature until the onset of NF_4HF_2 decomposition became noticeable (NF_3 evolution). An additional 8.0 mmol of WF_6 was added at -196°C to the residue. When the mixture was warmed to ambient temperature, a white solid product appeared in the form of a slurry. All material volatile at -31°C was pumped off for 1 hour 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 hours. All material volatile at -13°C was pumped off for 2 hours 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 hours and at 22°C for 4 hours. The volatiles, collected at -210°C , consisted of some HF and small amounts of NF_3 and WF_6 . The white solid residue (5.138g, 84% yield) was shown by vibrational and ^{19}F NMR spectroscopy to consist mainly of NF_4WF_7 with small amounts of SbF_6^- as the only detectable impurity. Based on 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 warm up from -78°C towards 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 hours. The material volatile at 25°C was briefly pumped off and separated by fractional condensation 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 hours 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 (5.711g, 88% yield) was shown by vibrational and ^{19}F NMR spectroscopy

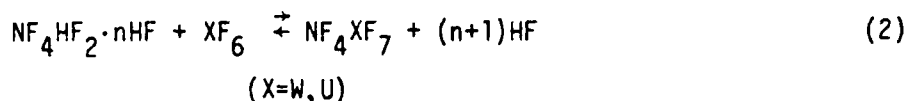
and elemental analysis to have the following composition (weight %): NF_4UF_7 , 97.47; NF_4SbF_6 , 1.50; CsSbF_6 , 1.03. Anal. Calcd: NF_3 , 15.34; U, 50.32; Sb, 0.90; Cs, 0.37. Found: NF_3 , 15.31; U, 50.2; Sb, 0.90; Cs, 0.37.

Results and Discussion

Synthesis of NF_4XF_7 Salts. The synthesis of NF_4XF_7 salts proved rather difficult because metalhexafluorides 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 solution,¹⁰ could be used. For example, anhydrous HF displaces UF_6 from NOUF_7 or CsUF_7 .¹³ However, in the course of a recent study in our laboratory a method for the preparation of $(\text{NF}_4)_2\text{SiF}_6$ was discovered¹⁴ in which the equilibrium (1)



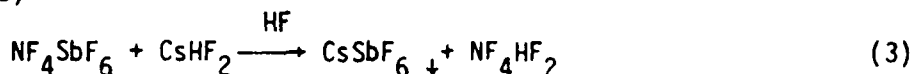
was successfully shifted to the right by repeatedly treating a highly concentrated NF_4HF_2 -HF solution⁹ with an excess of SiF_4 while periodically stripping off the HF. This method has now been extended to the synthesis of NF_4WF_7 and NF_4UF_7 according to (2)



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 percent 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%, based on 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_5 . They are crystalline, hygroscopic solids which are stable in a dynamic vacuum at 125°C . At higher temperatures, both salts decompose according to



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



nor reductive



decomposition, previously observed for the alkali metal salts,¹³ 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 per hour; NF_4WF_7 , 1.4% decomposition per hour), 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_7^- ¹⁶ and UF_7^- anions¹³ and also demonstrate that, under the given reaction conditions, no significant amounts of XF_8^{2-} salts are formed.

^{19}F NMR Spectra. The ionic nature of the NF_4XF_7 salts in BrF_5 solution was established by ^{19}F NMR spectroscopy. For NF_4WF_7 at -60°C two signals, a triplet of equal intensity at $\delta = 222.7$ with $J_{\text{NF}} = 232.7\text{Hz}$ and a

half-line width of 2Hz, and a singlet at $\delta = 142.2$ with a half-line width of 2.8Hz and missing ^{183}W satellites were observed which are characteristic for NF_4^+ ^{4,9} and WF_7^- ^{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_5 solvent and NF_4^+ were observed, but the UF_7^- signal could not be detected. These observations rule out a rapid exchange between UF_7^- and either the BrF_5 solvent or NF_4^+ , but can be explained by the relatively large (400-600Hz) half-line width previously reported¹³ for UF_7^- .

Conclusion. The successful synthesis of NF_4WF_7 and NF_4UF_7 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.

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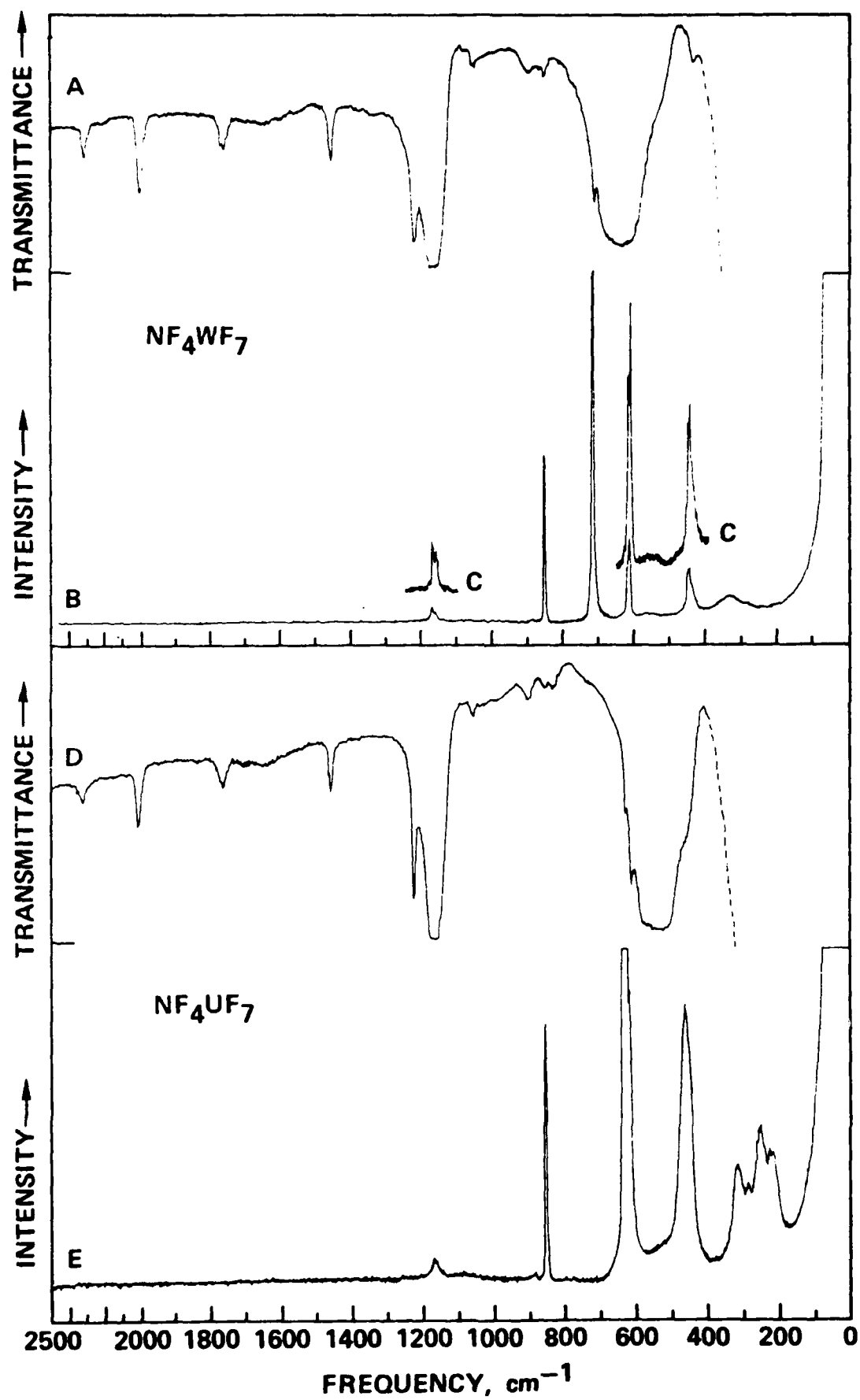
Diagram Caption

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.

Table 1. Vibrational Spectra of Solid NF_4WF_7 and NF_4UF_7

obsd freq, cm^{-1} , and rel intens ^a			Assignment (point group) ^b	
NF_4WF_7		NF_4UF_7	$\text{NF}_4^+(T_d)$	$\text{WF}_7^-(D_{5h})$ ^c
IR	Raman	IR	Raman	
2315 vw		2315 vw		$2\nu_3(A_1 + E + F_2)$
2000 w		2001 w		$\nu_1 + \nu_3(F_2)$
1760 vw		1760 vw		$\nu_3 + \nu_4(A_1 + E + F_2)$
1456 w		1458 w		$\nu_1 + \nu_4(F_2)$
1220 mw		1222 mw		$2\nu_4(A_1 + E + F_2)$
1165 vs	$\left\{ \begin{array}{l} 1165(0.3) \\ 1155 \text{ sh} \end{array} \right\}$	1165 vs	1164(0.1)	$\nu_3(F_2)$
1055 vw		1052 vw		$\nu_2 + \nu_4(F_1 + F_2)$
895 vw		898 vw	885(0+)	$2\nu_2(A_1 + A_2 + E)$
851 vw			851(1.1)	$\nu_1(A_1)$
711 w		626 w	628(10)	$\nu_1(A_1')$
630 vs, br		530 vs, br		$\nu_3(A_2''), \nu_5(E_1')$
610 sh	$\left\{ \begin{array}{l} 614(1.3) \\ 609(2.0) \end{array} \right\}$	610 m	613(9X10.0)	$\nu_4(F_2)$
	$\left\{ \begin{array}{l} 446(0.9) \\ 441(1.1) \end{array} \right\}$		457(1.0)	$\nu_2(E)$
436 w	435 sh	460 sh	457(1.0)	$\nu_8(E_1'')$
	328(0.3) br		311(0.4)	$\nu_6(E_1')$
	285 sh		283(0+)	$\nu_4(A_2'')$
			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_{5h} . c) Assignments based on ref. 16.



APPENDIX Y

Contribution from Rocketdyne, a Division of
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PERFLUORO AMMONIUM AND ALKALI METAL SALTS OF THE HEPTAFLUORO XENON (VI) AND OCTAFLUORO XENON (VI) ANIONS

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Received

Abstract

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

Perfluoro ammonium salts are the major ingredient in solid propellant $\text{NF}_3\text{-F}_2$ gas generator compositions for chemical lasers¹. 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 clinkering 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 by-product. 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 one half of a prepassivated Teflon U metathesis apparatus. Dry HF (9 ml liquid) was added on the vacuum line and the mixture was stirred with a Teflon coated magnetic stirring bar for 45 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. Most of the HF solvent was pumped off during warm up from -78°C towards 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 hours. 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 in a static vacuum and separated by fractional condensation through traps kept at -64°C and -196°C. Immediately, a white copious precipitate formed in the reactor, but disappeared after about 10 minutes 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 in a dynamic vacuum. The volatiles were separated by fractional condensation through traps kept at -210°, -126° and -64°C and consisted of NF₃ (~0.3 mmol), HF (~11 mmol), and XeF₆, respectively. The reactor was taken to the drybox and the solid products were weighed. The yellow filtrate residue (5.149g, weight calcd for 15.54 mmol NF₄XeF₇ = 5.506g, corresponding to a yield of 93.5 percent) consisted of NF₄XeF₇, and the white filter cake (5.78g, weight calcd for 15.54 mmol of CsSbF₆ = 5.72g) consisted of CsSbF₆. The composition of these solids was confirmed by vibrational and ¹⁹F NMR spectroscopy, pyrolysis and analysis of the pyrolysis residue for NF₄⁺, Cs⁺ and SbF₆⁻. Based on these results, the reaction product had the following composition (weight %): NF₄XeF₇ (98.01), NF₄SbF₆ (0.88) and CsSbF₆ (1.11).

Results and Discussion

The XeF₇⁻ and XeF₈²⁻ anions are thermally quite stable⁵ and, therefore, were a logical choice for the synthesis of the corresponding NF₄⁺ salts. Although the syntheses of MXeF₇ (M=Cs, Rb, NO₂)^{5,7} and M₂XeF₈ (M=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 (NO)₂XeF₈.⁹ Therefore, a better characterization of the XeF₇⁻ and the XeF₈²⁻ anion was necessary to allow proper identification of their NF₄⁺ salts.

Synthesis and Characterization of CsXeF₇, Cs₂XeF₈, and XeF₆. In agreement with a previous report⁵ it was found that CsF reacts with XeF₆ at 60°C to form CsXeF₇. However, the following observations deviate from the previous report.⁵ (i) It was not necessary to carefully add the XeF₆ 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 CsXeF₇. Even with a thirteenfold excess of XeF₆ and three weeks reaction time at 60°C, followed by one week at ambient temperature, the XeF₆ uptake by the CsF was less than that 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 hours at ambient temperature was required to obtain a constant weight and for the complete removal of 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 $4880\text{\AA}$ exciting line of our laser. To avoid decomposition of the samples in the laser beam, the Raman spectra of XeF_7^- salts were recorded at low temperature. Although the Raman spectrum of solid XeF_6 has previously been recorded at 40°C ¹¹, its low temperature spectrum was required to allow its comparison with those of XeF_7^- and XeF_8^{2-} . The spectrum observed for XeF_6 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 both at -120°C (trace D of Figure 2) and 25°C (trace E of Figure 2). Since XeF_6 is known to exist in at least four different crystalline modifications,¹² the different spectra are attributed to the presence of more than one XeF_6 phase. The observed frequencies are summarized in Table 1.

As expected from the previously known MF_6 , MF_7^- , MF_8^{2-} series spectra¹⁰, the strongest Raman line in the spectra of XeF_6 and XeF_7^- and XeF_8^{2-} shows a frequency decrease with increasing negative charge (see Figure 1). For Cs_2XeF_8 , two different spectra were observed, depending on its method of preparation. When the sample was prepared by laser photolysis at ambient temperature (XeF_7^- is yellow and strongly absorbs the blue 4880 Å line of the Ar ion laser, whereas XeF_8^{2-} is white and does not decompose in the laser beam), the spectrum shown by trace D of Figure 1 was observed. When the Cs_2XeF_8 sample was prepared by vacuum pyrolysis of CsXeF_7 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 2). These shifts might be caused by solid state effects.

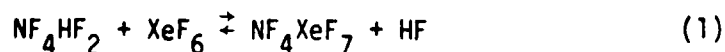
On the Existence of NaXeF_7 . Based on a previous report⁵, only CsF and RbF form 1:1 adducts with XeF_6 , while for NaF only a 2:1 adduct can be isolated. However, the experimental evidence given by the same authors⁵ (combining ratios of NaF: XeF_6 were as low as 1.73) suggested that NaXeF_7 might exist in addition to Na_2XeF_8 . This was now verified by Raman spectroscopy. As can be seen from Table 2 and trace F of Figure 1, the product obtained by reacting Xe with a large excess of F_2 and NaF at 250°C, followed by removal of all material volatile at 55°C in vacuo,⁴ clearly contains XeF_7^- in addition to XeF_8^{2-} . Consequently, NaF can form a 1:1 adduct with XeF_6 which is stable up to at least 55°C. Since KF generally forms more stable adducts than NaF, it appears safe to predict that KXeF_7 should also exist. The difficulty in obtaining 1:1 combining ratios for MF (M=Na or K) with XeF_6 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 XeF_7^- and XeF_8^{2-} . From a crystal structure determination of $(\text{NO})_2\text{XeF}_8$,⁹ the XeF_8^{2-} anion is known to possess a square antiprismatic structure. The observed Raman spectra of Cs_2XeF_8 are in excellent agreement with such a structure of symmetry D_{4d} . Three Raman active stretching

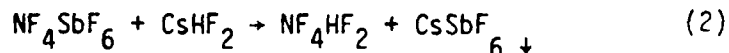
modes should be observed, one each in species A_1 , E_2 and E_3 . Of these, the A_1 mode is assigned to the most intense and single band at about 510 to 530 cm^{-1} , while the two doubly degenerate E modes are assigned to the two doublets at about 430 and 370 cm^{-1} (see Table 2). The observed frequencies agree well with those reported for TaF_8^{3-} (622, 426, and 377 cm^{-1}),¹⁰ which is also known from x-ray data¹³ to be a square antiprism. The fact that XeF_8^{2-} has a square antiprismatic structure suggests that the free valence electron pair on xenon is sterically inactive, analogous to the observations previously made for BrF_6^- .¹⁴

For XeF_7^- no structural data are available and several structural models must be considered. The free valence electron pair on xenon could be sterically either active or inactive. If it is active, one would expect a structure derived from a square antiprism with one of the positions being occupied by the free pair. Such a structure would be of low symmetry and result in 18 mutually nonexclusive infrared and Raman bands. If the free pair is sterically inactive, two models are most likely. One model is a pentagonal bipyramid of symmetry D_{5h} , as observed for MF_7 ($M=\text{I, Re}$), ZrF_7^{3-} and certain CsMF_7 ($M=\text{W, Mo, Re}$) salts.¹⁰ In this case, 5 infrared and 5 Raman active bands are expected which should be mutually exclusive. The other model is a monocapped trigonal prism of symmetry C_{2v} , as in MF_7^{2-} ($M=\text{Nb, Ta}$),¹³ for which 18 Raman and 15 mutually nonexclusive infrared bands are expected. The spectra observed for CsXeF_7 (Table 2, trace B of Figure 1 and trace A of Figure 3) show at least 10 Raman bands, most of which are also observed in the infrared spectrum. Therefore, a model of symmetry D_{5h} appears unlikely. However, a distinction between the two remaining models is not possible based on the available data.

Syntheses and Properties of NF_4XeF_7 and $(\text{NF}_4)_2\text{XeF}_8$. The NF_4XeF_7 salt, the first example of an NF_4^+ salt containing a noble gas fluoride anion, was prepared by repeatedly treating a highly concentrated solution of NF_4HF_2 in anhydrous HF with an excess of XeF_6 in order to shift the equilibrium

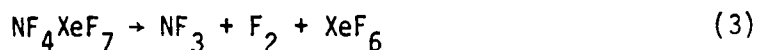


to the right hand side. The displaced HF was removed together with unreacted XeF_6 . The XeF_6 was separated from the HF by fractional condensation and was recycled. In this manner, NF_4XeF_7 was prepared in 94% yield and 98% purity. The yield is based on NF_4SbF_6 used in the NF_4HF_2 preparation step⁶



and is less than quantitative due to hang-up of some mother liquor on the CsSbF_6 filter cake. The 2% impurities consisted of CsSbF_6 and NF_4SbF_6 and are typical^{3,15} for metathetical reactions involving NF_4HF_2 .

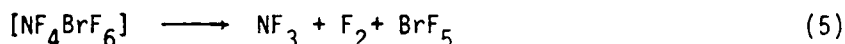
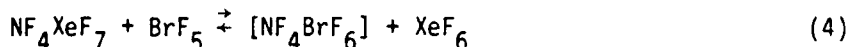
The NF_4XeF_7 salt is a light yellow solid. It is stable at ambient temperature and starts to slowly decompose at about 75°C. In a dynamic vacuum, the decomposition rates at 75°C and 100°C were found to be 1.6% and 28% per hour, respectively. The decomposition mode



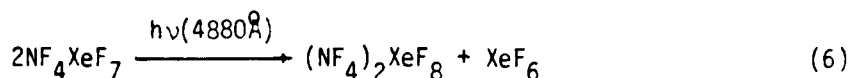
was established by mass balance and the observed decomposition products. Since the NF_4XeF_7 salt violently explodes on contact with water and therefore could not be analyzed by standard hydrolytic methods,¹⁶ an exhaustive vacuum pyrolysis at 120°C, followed by an analysis of the solid residue, was used to assay the compound.

The ionic nature of solid NF_4XeF_7 was established by vibrational spectroscopy (see Table 2 and Figure 3, traces B-F), which showed the bands characteristic for tetrahedral NF_4^+ ¹⁷ and XeF_7^- (see above). When solid NF_4XeF_7 was dissolved in anhydrous HF, ¹⁹F NMR and Raman spectra of the resulting solution showed XeF_6 and NF_4^+ as the principal species suggesting that in a large excess of HF, equilibrium (1) is shifted all the way to the left hand side. In BrF_5 solution at -40°C, the ¹⁹F NMR spectra originally showed the presence of NF_4^+ (triplet of equal intensity at 221 ppm below external CFCl_3 with $J_{\text{NF}} = 232$ Hz),¹⁵ which was slowly replaced by the signal of NF_3 (triplet of equal intensity at 145 ppm below CFCl_3 with $J_{\text{NF}} = 290$ Hz)¹⁸

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 75mW, 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 to I of Figure 3 and Table 2, the spectra clearly show the presence of the NF_4^+ ¹⁷ and XeF_8^{2-} ions (see above). The observed splittings are due to lifting of the degeneracies for the E and F modes in the solid state. ¹⁷

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 not only the first known examples 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_8^{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.

Acknowledgement. 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.

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Diagram Captions

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 of a mixture of NaXeF_7 and Na_2XeF_8 (trace F).

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).

Figure 3. Infrared spectra of CsXeF_7 recorded at 25°C between AgCl windows (trace A), and of NF_4XeF_7 recorded at -196°C between CsI windows (trace B) and 25°C between AgCl windows (trace C); the broken lines indicate absorption due to the AgCl windows. Raman spectra of NF_4XeF_7 and $(\text{NF}_4)_2\text{XeF}_8$ recorded at different temperatures and sensitivities (traces D-I).

Table 1. Raman Spectra of Solid XeF_6 ^a

obsd freq, cm^{-1} , and rel intens ^b			
A		B	
25°C	-120°C	25°C	-120°C
656(10)	{ 658(10) 649(9.7)	652sh	658(5)
636(6)	633(7.1)	646(10)	649(10)
	620(1)		620sh
	613(1)		613sh
	597(2)		589sh
582(4.2)	{ 576(5.0) 564(4.5)	579(4.1)	579(4.3)
404(0.1)	396(0.4)		564sh
365(0.2)	365(1.0)	398(0.3)	396(0.2)
	346(0+)	362(0.4)	365(0+),br
294(0.3)	{ 296(0.4) 284(0.5)	291(0.6)	296(0.4)br
236	232(0.4)	235-180(0+)br	235-180(0.4)br
220 } (0.2)	205sh		
204 }	195(0.3)		
	179sh		
	142(0+)		140(0+)
105(0+)	110(0.2)		107(0+)
	93(0.3)		86(0+)
	64sh		

(a) The observed differences in the A and B type spectra are attributed to the presence of more than one phase in different ratios.

(b) Uncorrected Raman intensities

Table 2. Vibrational Spectra of MXeF_7 and M_2XeF_8 Salts ($\text{M}=\text{NF}_4$, Cs and Na).

Assignment (point group)	obsd freq, cm ⁻¹ , and rel intens ^a										Assignment (point group)
	NaXeF ₇ + Na ₂ XeF ₈		Cs ₂ XeF ₈		(NF ₄) ₂ XeF ₈		NF ₄ XeF ₇		CsXeF ₇		
	Ra	Thermal	Thermal	Photolytic	Ra	Ra	Ra	Ra	Ir	Ra	
	250C	25°C	25°C	25°C	-120°C	25°C	-120°C	25°C	-196°C	-120°C	
XeF ₈ ²⁻ (D _{4d}) ^b		Ir 250C									

- (a) Uncorrected Raman intensities
 (b) Tentative assignments.
 (c) Observed splittings into degenerate components are caused by solid state effects.

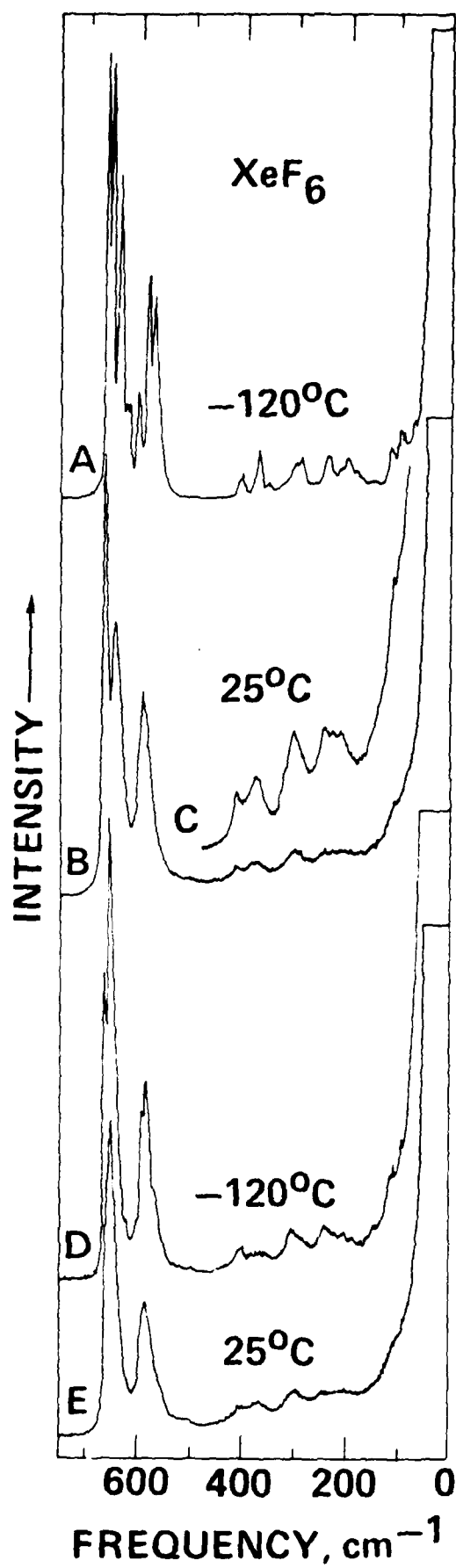


FIGURE 1 Y-14

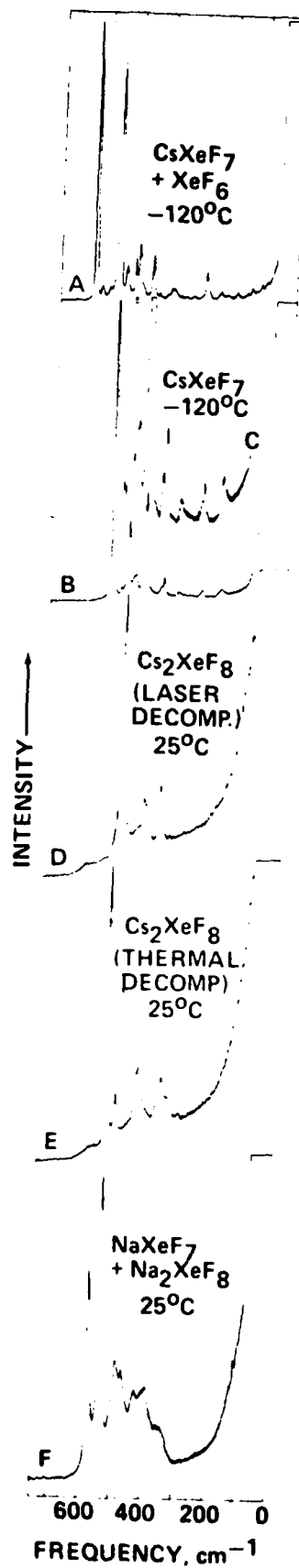


FIGURE 2

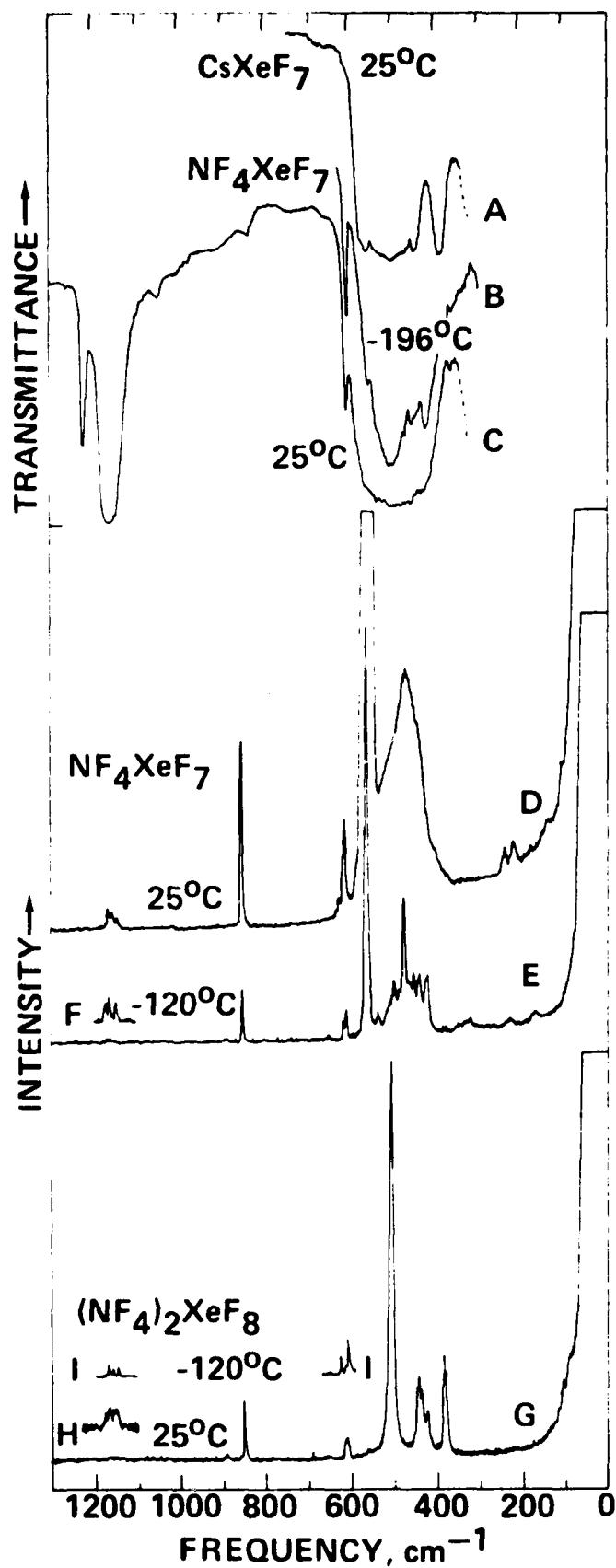


FIGURE 3

APPENDIX Z

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

SYNTHESIS AND CHARACTERIZATION OF TeF_5OF

Carl J. Schack, William W. Wilson, and Karl O. Christe

Received

Abstract

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_5OF . The compound was also prepared in lower yield by the fluorination of TeF_5OH with a concentrated NF_4HF_2 solution. The physical properties, infrared, Raman, ^{19}F NMR and mass spectra of TeF_5OF are reported. The vibrational spectra of TeF_5OCl were redetermined, and complete vibrational assignments are given for TeF_5OF and TeF_5OCl .

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 Cl¹. 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_5OF . This failure to prepare TeF_5OF , but the success to synthesize TeF_5OCl by an analogous method², led to the conclusion³ that TeF_5OF 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_5OF should not only exist, but should also be stable. In this paper we present data which show that TeF_5OF indeed exists and is stable.

Experimental

Materials and Apparatus. Volatile materials were manipulated in a 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. 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 received (light brown color) and after distillation to obtain the clear colorless material. Fluorine fluorosulfate was synthesized as described⁶. The reaction of TeF_5OH with either ClOSO_2F or ClF was used to prepare TeF_5OCl ⁷. Cesium and potassium chloride were oven dried, then cooled and powdered in the dry N_2 atmosphere of a glove box.

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 using either a Teflon cell of 5-cm path length equipped with AgCl windows or a 10-cm stainless steel cell equipped with polyethylene windows which were seasoned with ClF_3 . The spectra of matrix isolated TeF_5OF and TeF_5OCl were obtained at 6K 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 using 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 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_5OH . 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_5OH by the method of Seppelt and Nothe² using HSO_3F as the fluorinating agent. This technique calls for the use of distilled HSO_3F and initially we encountered difficulty in producing TeF_5OH . Subsequently it was discovered that addition of a few ml of H_2O to the reaction mixture and heating the reaction mixture at $160\text{--}170^\circ\text{C}$ for 5-6 hours resulted in continuous evolution of TeF_5OH at a slow to moderate rate. Finally, undistilled HSO_3F was employed which furnished TeF_5OH in 70% purified yield; 93.9 mmol TeF_5OH from 135 mmol $\text{Te}(\text{OH})_6$ and 1.75 ml 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 KOTeF_5^{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 8d at -45°C . The only volatile product condensable at -196°C was TeF_6 (0.38 mmol, 26%). Similarly at -10°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°C for 6 weeks, again TeF_6 (2.35 mmol, 80%) was the only volatile tellurium compound observed.

Synthesis of TeF_5OF from CsTeF_5O and FOSO_2F . A 30 ml stainless steel Hoke cylinder was loaded with CsTeF_5O (3.42 mmol) in the glove box. After evacuation and cooling of the cylinder to -196°C , FOSO_2F (2.79 mmol) was added from the vacuum line. The closed cylinder was slowly warmed to -78°C in a liquid nitrogen- CO_2 slush bath and finally kept at -45°C for 9d. Upon recooling to -196°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°C . The -78°C fraction was TeF_5OH (0.19 mmol) while the -196°C fraction was TeF_6 (0.49 mmol).

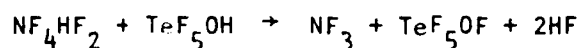
A white solid was retained at -126°C which changed to a colorless glass and melted, over a range of a few degrees, near -80°C to a clear, colorless liquid. This material was identified as TeF_5OF (1.91 mmol, 68% yield) based on its vapor density molecular weight; found, 256.2; calc., 257.6 g/mol. Further identification was based on its spectroscopic properties (see below) and on the preparation of derivatives¹⁶. The observed weight loss of the solid (0.375 g) agreed well with that calculated (0.389 g) for the conversion of 2.79 mmol CsTeF_5O to CsSO_3F . Vapor pressure-temperature data of TeF_5OF were measured: $T^{\circ}\text{C}$, Pmm; -79.3 , 16; -64.2 , 45; -57.6 , 63; -46.9 , 108; -32.5 , 210; -23.0 , 312.

Synthesis of TeF_5OF from TeF_5OH and NF_4HF_2 . A sample of $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$ (10.5 mmol) was prepared and concentrated in a Teflon double U metathesis apparatus, as previously described¹⁷. To this reactor, TeF_5OH (10.5 mmol) was added 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 hours in a dynamic vacuum. The volatile products were separated by fractional condensation through traps kept at -95 , -126 , -142 and -210°C . Based on their infrared and ^{19}F NMR spectra the following products were collected in these traps: -210°C , NF_3 and a trace of TeF_6 ; -142°C TeF_6 and TeF_5OF in a mol ratio of about 3:1; -126°C , HF and some TeF_5OF ; -95°C , TeF_5OH and some HF . The white solid residue (0.57 g) decomposed during an attempt to transfer it at ambient temperature to a dry box for further characterization. The overall yield of TeF_5OF was estimated to be about 10-20% with TeF_6 and unreacted TeF_5OH being the principal products.

Results and Discussion

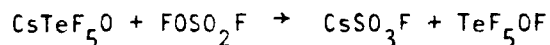
Synthesis of TeF_5OF . By analogy to a previous attempt² to synthesize TeF_5OF from $\text{Hg}(\text{TeF}_5\text{O})$ and F_2 , the fluorination of either CsTeF_5O or KTeF_5O with F_2 at -45 to -10°C was unsuccessful and resulted only in TeF_6 formation. Since the decomposition of NF_4XO salts had recently been shown to provide new high yield syntheses for hypofluorites, such as FOClO_3 ¹⁸, FOSO_2F ¹⁹, and FOIF_4O ⁴, the synthesis of $\text{NF}_4\text{TeF}_5\text{O}$ by metathesis of NF_4SbF_6 and CsTeF_5O in anhydrous HF was attempted. This attempt, however, was preempted by the

fact that CsTeF_5O was found to react with anhydrous HF undergoing a displacement reaction. Since recent work¹⁷ in our laboratory had shown that even in cases of Lewis acids which are weaker than HF their NF_4^+ salts can be prepared by treating $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$ with the weak Lewis acid, this approach was studied for $\text{NF}_4\text{TeF}_5\text{O}$. Although the $\text{NF}_4\text{TeF}_5\text{O}$ salt itself could not be isolated, it was found that TeF_5OH (which is equivalent to an equimolar mixture of the Lewis acid TeF_4O and HF) reacted with $\text{NF}_4\text{HF}_2 \cdot n\text{HF}$ at -23°C to produce TeF_5OF in moderate yield



Since TeF_6 was the major product, we prefer to interpret this reaction in terms of a fluorination of TeF_5OH by nascent fluorine formed in the decomposition of NF_4HF_2 , rather than in terms of a decomposition of an unstable $\text{NF}_4\text{TeF}_5\text{O}$ intermediate. In the latter case, we would expect a near quantitative yield of TeF_5OF .

A more facile high yield synthesis of TeF_5OF was discovered by reacting CsTeF_5O with FOSO_2F at -45°C



This reaction represents a new synthetic route to hypofluorites. Based on the general usefulness of the analogous ClOSO_2F reagent for the syntheses of hypochlorites,²⁰ we predict FOSO_2F will become a similarly useful, versatile and general reagent for the synthesis of hypofluorites.

When the synthesis of TeF_5OF from CsTeF_5O and FOSO_2F was carried out above -45°C , the amount of TeF_6 by-product sharply increased. For example, at -10°C and with a reaction time of 7 days, the TeF_6 to TeF_5OF ratio in the product increased to 1:1. The use of an excess of CsTeF_5O in this reaction was found advantageous for the product purification since it eliminates the need for separating TeF_5OF from FOSO_2F .

Properties of TeF_5OF . 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

$$\log P_{\text{mm}} = 6.9022 - 1101.2/T^\circ\text{K}$$

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 TeF_5OF 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 four months without any sign of decomposition.

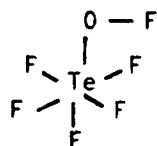
^{19}F NMR Spectrum. The ^{19}F NMR spectrum of TeF_5OF in CFCl_3 solution at 28°C is shown in Figures 1 and 2 and is characteristic for a second order AB_4X spin system. A computer aided analysis of the spectrum resulted in the following parameters: $\delta\text{A} = -52.5$, $\delta\text{B}_4 = -54.0$, $\delta\text{X} = 128.3$, $J_{\text{AB}} = 180 \text{ Hz}$, $J_{\text{AX}} = 4.9 \text{ Hz}$, $J_{\text{BX}} = 19.0 \text{ Hz}$, $R = 1.20$, $J_{125\text{Te}^{19}\text{F}} = 3800 \text{ Hz}$. These values are in excellent agreement with those found for numerous other covalent TeF_5O -type compounds.²¹

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 fragments 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 2. Since the assignments previously reported²² 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 3). The following deviations from the previous literature data²² 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 established²³ assignments of TeF_5Cl and the revised experimental data of TeF_5OCl for comparison, the vibrational spectra of TeF_5OF can be readily assigned (see Table 4) assuming a model with C_{4v} symmetry for the TeF_5O part and C_s symmetry for the TeOF part of the molecule.



Except for the symmetric out of phase, out of plane TeF_4 deformation mode in species B_1 which is usually not observed for pseudo-octahedral 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 4) are straight forward and show for the three molecules almost identical frequencies for the TeF_5 part of the molecules. The modes involving the XY group of this TeF_5XY molecule show the expected mass effects for different X and Y. Since the Te-O stretching mode is expected to strongly couple with the O-Hal stretch and to moderately couple with $\delta_s \text{TeF}_4 (A_1)^{24}$, these modes also exhibit a mass effect.

Comparison of the assignments of Table 4 with those previously given²² for TeF_5OCl shows that with the exception of $\nu_7(\text{B}_2)$ and ν_{13} all the previously given assignments for the deformation modes should be revised. Since a thorough normal coordinate analysis has previously been carried out²³ for TeF_5Cl and in view of the similarity of the TeF_5Cl and TeF_5XY spectra, a normal coordinate analysis of the latter molecules appears unwarranted.

Conclusion. The results of this study show that FOSO_2F is a useful reagent for the synthesis of hypofluorites.²⁵ Furthermore, it is shown that TeF_5OF , as expected from comparison with TeF_5OCl , TeF_5OBr and FOIF_4O , indeed exists and is a stable molecule. The TeF_5OF molecule was characterized and the vibrational assignments were made for TeF_5OF and TeF_5OCl .

Acknowledgement. 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 TeF_5OH 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.

Diagram Captions

Figure 1. Observed and calculated ^{19}F NMR spectra of the AB_4 part of TeF_5OF .

Figure 2. Observed and calculated ^{19}F NMR spectra of the X part of TeF_5OF .

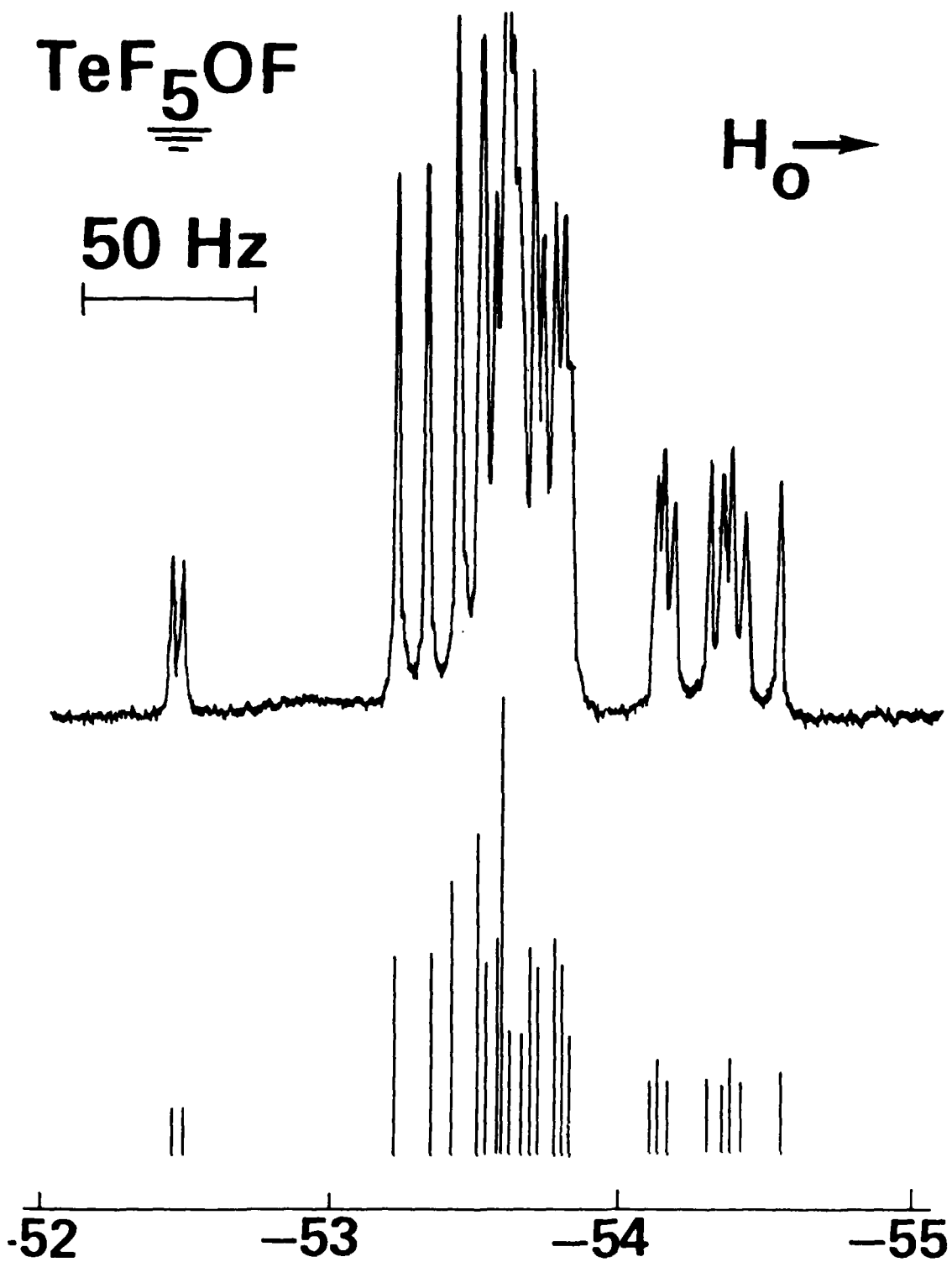
Figure 3. Vibrational spectra of TeF_5OF . Trace A, infrared spectrum of TeF_5OF isolated in a neon matrix (mole ratio 400:1) and recorded at 6K. Traces B and C, infrared spectra of the gas, recorded at pressures of 74 and 3 mm, respectively, in a 5-cm path length cell equipped with AgCl windows. The 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.

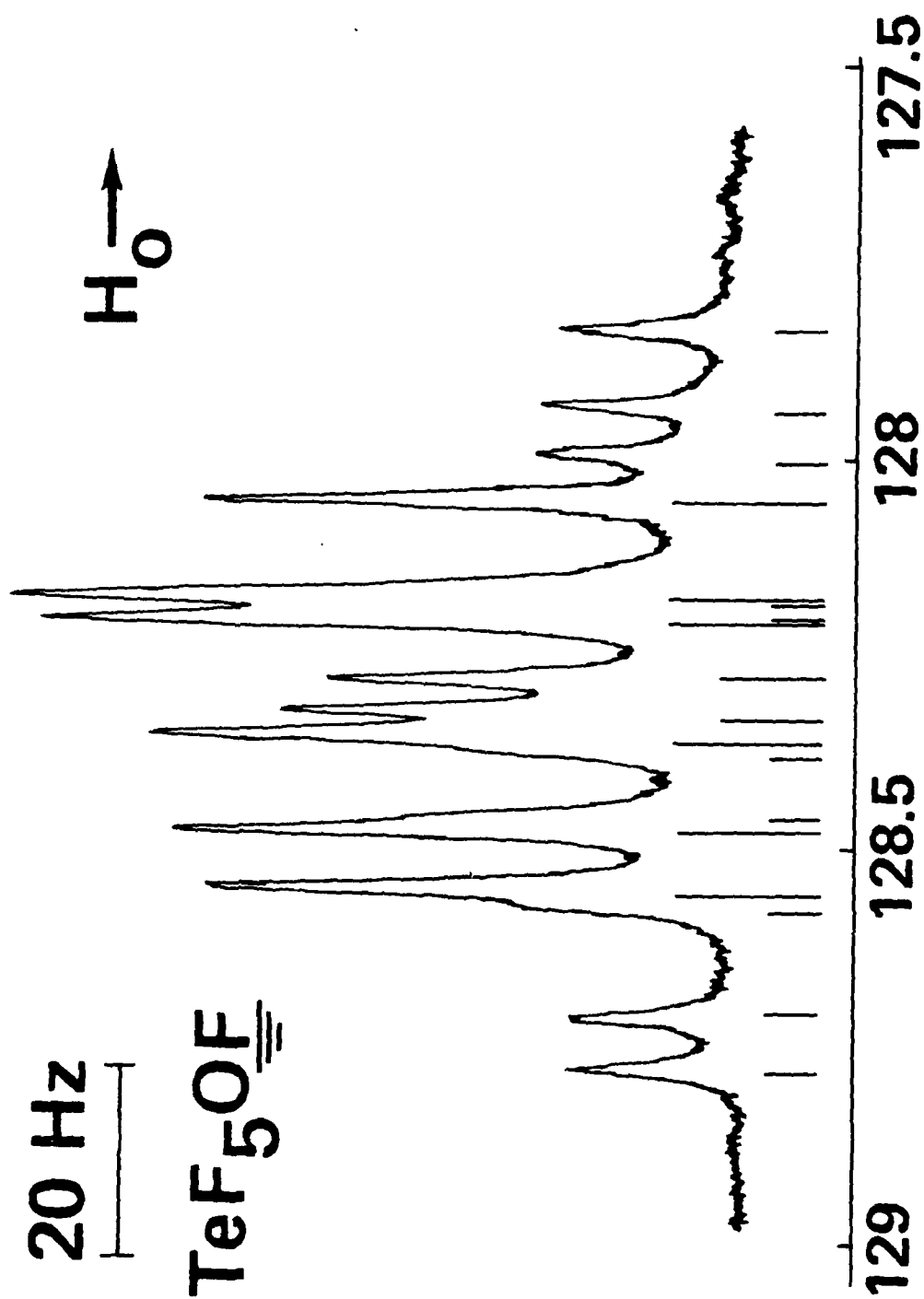
Figure 4. Vibrational spectra of TeF_5OCl . Trace A and C, infrared spectra of TeF_5OCl isolated in a neon matrix (MR = 400:1) at 6 K. Trace B, infrared spectrum of the gas, recorded at a pressure of 27 mm in a 5-cm path length cell equipped with AgCl windows. Traces D and E, Raman spectra of the liquid,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

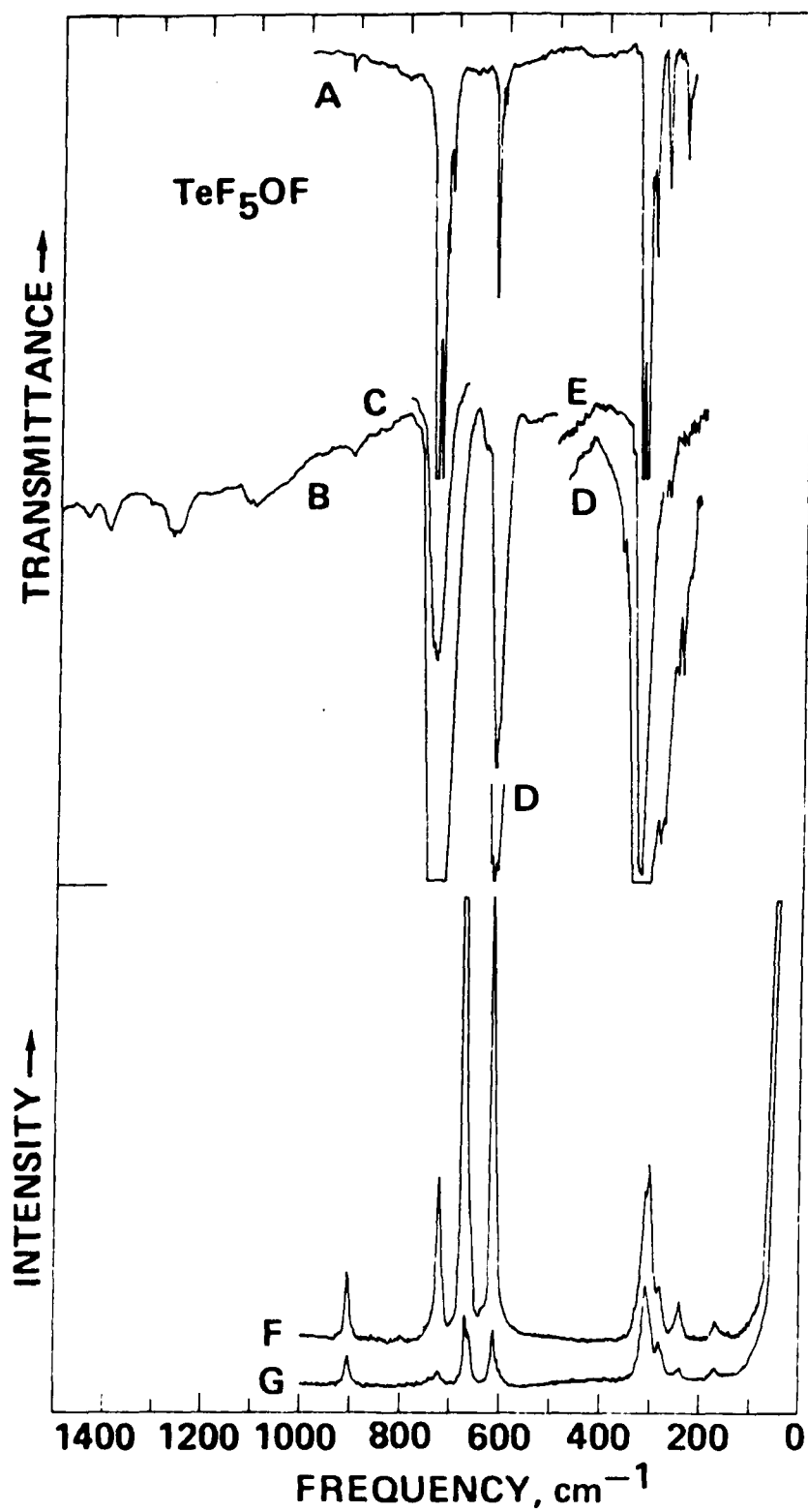
TeF_5OF

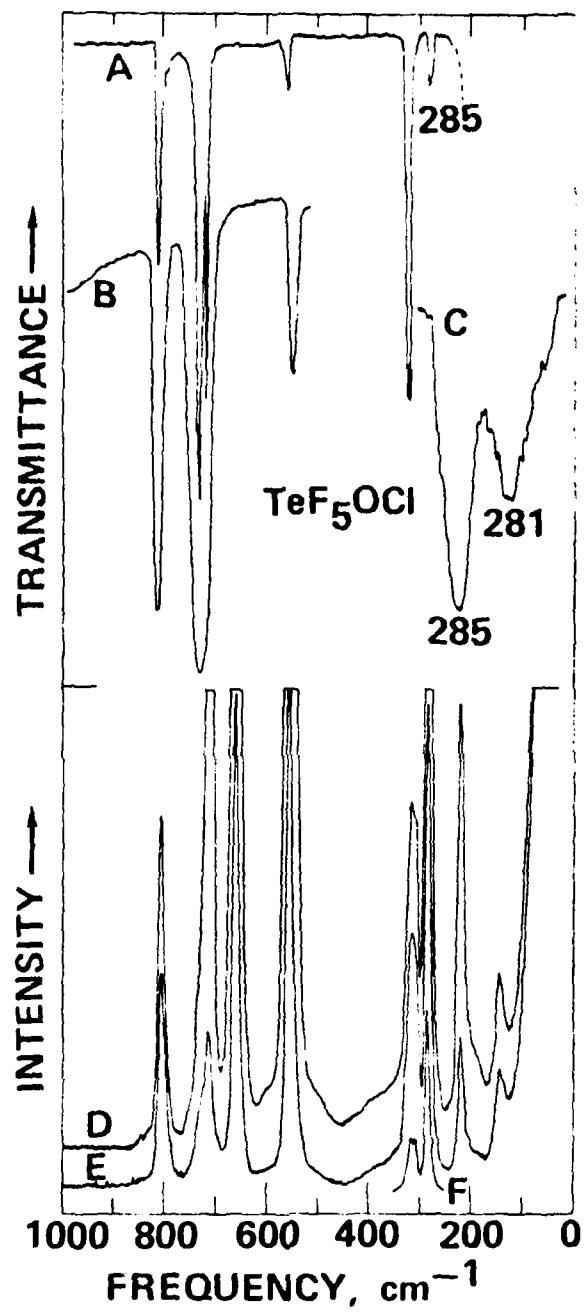
$\text{H}_2\text{O} \rightarrow$

50 Hz









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Table 1. Mass Spectrum of TeF_5OF Compared to Those of $\text{TeF}_5\text{OC1}$ and TeF_5OH

TeF_5OF		$\text{TeF}_5\text{OC1}$		TeF_5OH	
assignt	intens	assignt	intens	assignt	intens
TeF_5OF^+	vW	$\text{TeF}_5\text{OC1}^+$	vW	TeF_5OH^+	W
TeF_4OF^+		$\text{TeF}_4\text{OC1}^+$	vW	TeF_4OH^+	vW
TeF_3OF^+					
TeF_5^+	S	TeF_5^+	S	TeF_5^+	VS
TeF_4^+	W	TeF_4^+	VW	TeF_4^+	W
TeF_3O^+	m	TeF_3O^+	ms	TeF_3O^+	S
TeF_3^+	VS	TeF_3^+	VS	TeF_3^+	VS
TeF_2^+	m	TeF_2^+	m	TeF_2^+	m
TeFO^+	VW	TeFO^+	W	TeFO^+	W
TeF^+	W	TeF^+	W	TeF^+	W
Te^+	W	Te^+	W	Te^+	W

Table 2. Vibrational Spectra of TeF_5OF

obsd freq, cm ⁻¹ , and rel intens ^a				assignment ^b
IR		Raman		
gas	Ne matrix	liquid -55°C	solid -110°C	
1800 vw				2ν ₁₂
1449 vw				2ν ₁
1403 w				ν ₂ + ν ₈
908 vw		905(0.4)p	904(0.8)	ν ₁₂
738 vs	{ 738 ^c vs 727 vs 718 vw } 709 vw }	738 sh dp	735 sh	ν ₈
		721(1.1)p	721(1.3)	ν ₁
	668 vw	659(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	{ 327 vs 318 vs 308 vw }	325 sh, dp	325 sh	ν ₉
			319 sh	ν ₁₀
		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 4.

c) Band shows tellurium isotope fine structure with splittings of about 1.30 cm^{-1} .

Table 3. Vibrational Spectra of TeF_5OCl

obsd freq, cm^{-1} , and rel intens ^a			
IR		Raman liquid -80°C	assignment ^b
gas	Ne matrix		
1365 vw			$\nu_3 + \nu_{12}$
812 s	814 s	809(0.9)p	ν_{12}
	811 s		
732 vs	732 vs ^c	730 sh, dp	ν_8
	718 s	713(1.6)!	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) For mode description see Table 4.

c) Band shows fine structure with splittings of about 1.30 cm^{-1} due to tellurium isotopes.

Table 4. Vibrational Spectra of TeF₅OF and TeF₅OCF and their Assignment Compared to Those of TeF₅Cl^a

assignment		approx descrip- tion of mode	obsd freq, cm ⁻¹ , and rel intens ^a					
			TeF ₅ Cl ^b IR (gas)	TeF ₅ Cl ^b RA (liquid)	TeF ₅ OCl ^b IR(gas,matrix)	TeF ₅ OCl ^b RA (liquid)	TeF ₅ OF ^b IR(gas,matrix) RA(liquid)	
C _{4v}								
A ₁	ν ₁	νTeF	711 sh,m	708(3.1)p	718 s	713(1.6)p	727 vs	721(1.1)p
	ν ₂	ν _s TeF ₄	662 vw	659(10)p		663(10)p		669(10)p
	ν ₃	νTeX	411 ms	413(7.7)p	551 m	554(6.5)p	616 m	613(3.8)p
	ν ₄	δ _s TeF ₄	317 s	312(0.8)p	281 m	281(2.8)p	301 m	301(0.5)p
B ₁	ν ₅	ν _s TeF ₄		651(0.8)dp		655 sh, dp		660(0.3)dp
	ν ₆	δTeF ₄ 						
B ₂	ν ₇	δ _{sciss} TeF ₄		302(0.5)dp		308(0.8)dp	308 vw	309(1.0)dp
E	ν ₈	ν _{as} TeF ₄	726 vvs	726(0.6)dp	732 vs	730 sh, dp	738 vs	738 sh, dp
	ν ₉	δTeF ₄	325 ms	327(0.9)dp	327 vs	328 sh, dp	327 vs	325 sh, dp
	ν ₁₀	δXTeF ₄		167(1.8)dp	322 vs	316(0.8)dp	318 vs	(309-325)
	ν ₁₁	δ _{as} TeF ₄	259 m	259(1.7)dp	285 m		280 mw	279(0.2)dp
C _s								
A'	ν ₁₂	νXY	—		812 s	809(0.9)p	908 vw	905(0.4)p
	ν ₁₃	δTeXY	—			218(1.1)p	240 mw	240(0.2)p
A''	ν ₁₄	τTeXY	—			141(0.3)dp		166(0.1)dp

a) Uncorrected Raman intensities (peak heights). b) Data from ref. 23.

APPENDIX AA

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

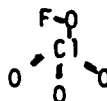
FLUORINE PERCHLORATE, VIBRATIONAL SPECTRA, FORCE FIELD AND THERMODYNAMIC PROPERTIES

Karl O. Christe* and E. C. Curtis

Received . . .

Abstract

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_s were observed

and assigned. A modified valence force field was computed for ClO_3OF 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 FSO_2OF 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 Corporation in which the heat of hydrolysis was measured for ClO_3OF . Macheteau and Gillardeau studied⁵ the thermal decomposition of ClO_3OF and confirmed the four infrared bands previously reported.^{3,4} Small amounts of ClO_3OF have been reported to form as by-products 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 Hamaker 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

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 slowly pass 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 using a Teflon cell of 5 cm pathlength 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 using an Air Products Model ACL3 helium refrigerator equipped with CsI windows. Research grade N_2 or Ne (Matheson) were used as matrices in mole ratios of 1000:1.

The Raman spectra were recorded on a Cary Model 83 spectrometer using the $4880\text{\AA}$ 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 .

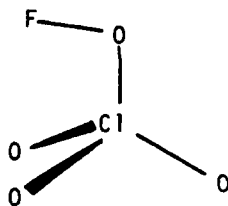
Results and Discussion

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 Rohrbach and Cady², explosions were not incurred on either freezing or melting ClO_3OF . Since Rohrbach 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 sensitive¹⁸.

The ^{19}F NMR chemical shift of ClO_3OF has been reported³ to be 225.9 ppm downfield from CFCl_3 . However, since the shift for FClO_3 , reported in the same paper, is in error by about 35 ppm,¹⁹ we have redetermined the shift for ClO_3OF . In HF solution, a single line, 219.4 ppm downfield from external CFCl_3 , was observed, in fair agreement with the previously reported³ value of 225.9 ppm.

Vibrational Spectra. The infrared spectra of ClO_3OF 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 ClO_3OF , recorded at -100°C , are given in Figure 4. The observed frequencies and their assignments are summarized in Table 1. The four infrared bands previously reported³⁻⁵ for gaseous ClO_3OF agree well with our results.

Assignments. By analogy with closely related molecules, such as CF_3OF ,^{20,21} fluorine perchlorate should possess a staggered structure of symmetry C_s .



The 12 fundamental vibrations expected for ClO_3OF of symmetry C_s can be classified as $8\text{A}'$ and $4\text{A}''$, where all modes are allowed in both the infrared and the Raman spectrum. In 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 2.

By comparison with the known spectra of the related molecules ClO_3OCl ,¹⁰ ClO_3OBr ,¹⁰ ClO_3OH ,²² ClO_3OD ,²² $\text{O}_3\text{ClOClO}_3$,^{9,23,24} CF_3OCIO_3 ,²⁵ FCIO_3 ,²⁶⁻³⁰ FOSO_2F ,³¹⁻³³ and CF_3OF ,³⁴⁻³⁹ the assignments for most fundamental vibrations of ClO_3OF (see Table 2) are straight forward. Additional 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 the Raman polarization data. Consequently, only the less straight forward 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 appears to be in Fermi resonance with the A' combination band ($2\nu_7 + \nu_6$). 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 linewidth, 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, $\nu_7(A')$ and $\nu_{11}(A'')$, almost coincide and are readily assigned on the basis of their Raman polarization ratios. The splitting of $\nu_{11}(A'')$ (see Fig. 3) into two components in the matrix isolated infrared spectra is attributed to Fermi resonance with $3\nu_{12}(A'')$.

The symmetric (umbrella) ClO_3 deformation mode, $\nu_5(A')$, and the two antisymmetric ClO_3 deformation modes, $\nu_{10}(A'')$ and $\nu_6(A')$, 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 $\nu_5(A')$ is established by the observed PQR band contour in the infrared spectrum of the gas, its large $^{35}\text{Cl} - ^{37}\text{Cl}$ isotopic shift and, in particular, by the results from the normal coordinate analysis (see below). By analogy with CF_3OF , $^{35}\text{ClO}_3\text{OF}$ 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 $C=0.0931\text{ cm}^{-1}$. Therefore, the band contours for ClO_3OF are expected⁴⁰ to be analogous to those of CF_3OF for which the PQR band contour of the umbrella deformation mode is well established. By analogy with FCIO_3 ³⁰ and ClO_3OCl ,¹⁰ the Cl-O stretching and the ClO_3 umbrella deformation mode in ClO_3OF are expected to exhibit a total of about 11 cm^{-1} in $^{35}\text{Cl} - ^{37}\text{Cl}$ isotopic shift whose distribution between the two modes is governed by their degree of coupling. In ClO_3OF , 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 ClO_3 umbrella

deformation mode. This condition is met by the 599 cm^{-1} fundamental ($\Delta\nu=3.8\text{ cm}^{-1}$), but not by that at 529 cm^{-1} ($\Delta\nu=1\text{ cm}^{-1}$). Furthermore, the normal coordinate analysis strongly preferred a Cl isotopic shift of about 3.0 cm^{-1} for $\nu_{10}(A'')$ and could accommodate a 3.8 cm^{-1} 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 $\nu_6(A')$ and $\nu_{10}(A'')$ are unambiguous on the basis of the Raman polarization data.

The frequency of 127 cm^{-1} for the Cl-OF torsional mode in ClO_3OF is in excellent agreement with that^{36,39} found for the closely related CF_3OF molecule and confirmed by microwave spectroscopy²⁰. Since the reduced moment of inertia for internal rotation r_{A} of CF_3OF and ClO_3OF should be comparable, the potential barrier to internal rotation in ClO_3OF is expected to be similar to that of CF_3OF (about 4 kcal mol^{-1})^{20,39}. The remaining assignments for ClO_3OF are all unambiguous and require no further comment.

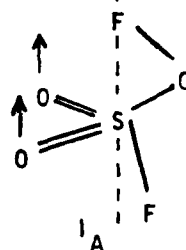
Only minor frequency shifts were observed for ClO_3OF when going from the gas to the liquid and the solid. This indicates little or no association in the condensed phases.

Comparison of the ClO_3OF Assignments with Those of Similar Molecules.

In Table 2, the assignments for ClO_3OF 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 ClO_3 deformation mode of ClO_3OCl ,¹⁰ ClO_3OBr ,¹⁰ and Cl_2O_7 ⁹ should be reversed and the assignments for ClO_3OCF_3 should be revised to conform with those of ClO_3OF .

For FSO_2OF , different mode descriptions were used in Table 2, although its vibrational spectra are closely related to those of the other molecules given in this Table. In ClO_3OF , the three doubly bonded oxygens are almost equivalent. Therefore, their motions are strongly coupled and best described in terms of ClO_3 modes. In contrast, the SF and the SO_2 bonds in FSO_2OF are quite different and consequently, are best described in terms of separate SF and SO_2 motions. It should be kept in mind, however, that the symmetry coordinates of ClO_3OF and FSO_2OF are closely related and are linear combinations of each other.

For FSO_2OF , the assignment of the deformation modes, given in Table 2, is based on the reported Raman polarization data³² and infrared band contours. The SO_2 wagging or SO_2 parallel rocking mode is the only mode which should result in a dipole moment change predominantly along the axis of the smallest moment of inertia (I_A). Consequently, this mode should be assigned to the



575 cm^{-1} infrared band which is the only band exhibiting a pronounced A type contour. By analogy, the 523 cm^{-1} infrared band exhibits a typical perpendicular band contour and is therefore assigned to the out of plane SO_2 rocking mode.

Chlorine Isotopic Shifts. The ^{35}Cl - ^{37}Cl isotopic shifts observed for ClO_3OF are summarized in Table 3. 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 $(2\nu_7 + \nu_6)^{37}\text{Cl}$ and $\nu_1^{37}\text{Cl}$ most likely shifts the latter to higher frequency and decreases its relative intensity, and the apparent $^{35}\text{Cl} - ^{37}\text{Cl}$ separation of ν_1 . Using a weighted average of the 1285.9 and 1289.7 cm^{-1} bands for the frequency of $\nu_1^{37}\text{Cl}$, results in a Cl isotopic shift of about 14.5 cm^{-1} , similar to that (14.6 cm^{-1}) observed for the almost degenerate $\nu_9(\text{A}')$ fundamental.

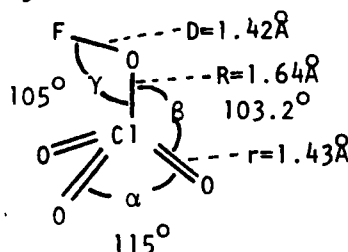
For ν_2 a discrepancy exists between the matrix isolation and the gas-phase data. Whereas two Q branches with a frequency separation of 2.4 cm^{-1} were observed in the gas phase spectrum, the matrix isolation data show that in the Ne and the N_2 matrix the isotopic shifts are 3.3 cm^{-1} . Two combination 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 ClO_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 3 cm^{-1} in the Ne matrix spectrum, but in the N_2 matrix and gas phase spectra this 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 ($\text{X}=\text{F}, \text{Cl}$)^{34,38,41} and FSO_2F 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 first determine 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 as both a starting point for the ClO_3OF computations and as a criterion for judging the plausibility of the resulting force field, a force field was determined which met all our criteria.

For the computation of the ClO_3OF force field, the vibrational frequencies, Cl isotopic shifts and assignments of Tables 2 and 3 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 reference 38, except 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 3. 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 method to reproduce the observed frequencies and isotopic shifts. Due to the symmetry relations between the A' and the A'' block ($F_{11} = F_{99}$, $F_{66} = F_{1010}$, $F_{77} = F_{1111}$, $F_{16} = -F_{910}$, $F_{17} = F_{911}$, and $F_{67} = -F_{1011}$), both blocks were refined simultaneously. Due to its low frequency and weak coupling with other modes, the torsional mode ν_{12} was omitted from the analysis.

Using 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, $\nu_7(A')$ and $\nu_{11}(A'')$, are not completely degenerate and therefore the $F_{77} = F_{1111}$ constraint was removed. Removal of this constraint significantly improved the force field, but again the results suggested that removal of the $F_{66} = F_{1010}$ constraint would significantly benefit the force field. In this manner, a very satisfactory force field (see Table 3) was obtained which 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 4). Removal of the $F_{11} = F_{99}$ constraint 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_9 , however, it must be kept in mind that (i) 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 3, contains in addition to the interaction terms transferred from FCIO_3 only one relatively small ($F_{46} = 0.22$ mdyne rad^{-1}) off-diagonal symmetry force constant. This is not surprising in view of the near degeneracy of the -OClO_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 group can be non-zero because they both belong now to species A' . However, their numerical values should be very small or zero, as can be shown by semi-quantitative 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 percent 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 constants the difference between A' and A'' values amounts to only four percent 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 that 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 three fold 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 , the range of possible solutions was calculated for the A'' block and 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_{911} . 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 FClO_3 E block force field³⁰. The differences in the signs of some of the off-diagonal force constants between FClO_3 and ClO_3OF is 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 3. It shows that the approximate mode descriptions used in Table 2 are appropriate. The largest amount of mixing was observed for ν_4 which, by analogy with ν_2 of FClO_3 ,³⁰ is an antisymmetric combination of S_4 (Cl-O stretch) and S_5 ($\delta s\text{ClO}_3$).

In order to test the possibility of interchanging the assignments of ν_5 , ν_6 and ν_{10} , force fields were computed for all possible assignments and 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 2, assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator, rigid-rotor approximation.⁴⁶ These properties for the range 0-2000°K are given in Table 5.

Conclusions. The observed spectra of ClO_3OF agree well with a covalent perchlorate structure of symmetry C_s . 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 FClO_3 , as constraints. The resulting force field exactly duplicates the experimental data, retains the most important force constant features of FClO_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 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 FClO_3 , but, as expected from the replacement of F by the somewhat less electronegative -OF group, are slightly lowered.

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Diagram Captions

Figure 1. Traces A, B, and C infrared spectra of gaseous ClO_3OF recorded in a 5cm pathlength 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 using CsI windows.

Figure 2. Infrared spectra of N_2 and Ne matrix-isolated and of gaseous ClO_3OF recorded with 20 fold scale expansion under higher resolution conditions.

Figure 3. See Caption of Figure 2.

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

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_{911} . The units are identical to those given in Table 3. The broken line indicates the preferred force field.

Obsd freq, cm ⁻¹ , and Intens						Assignment in point group C _s
Infrared			Raman			
Gas	N ₂ Matrix	Ne Matrix	Solid	Liquid	HF Solution	
2588 vs					1302 + 1295 = 2597 2 x 1295 = 2590	$\nu_1 + \nu_9$ (A ⁺) $2\nu_9$ (A ⁺)
2335 w					1295 + 1149 = 2344	$\nu_9 + \nu_2$ (A ⁻)
2183 vvw					1302 + 885 = 2187 1295 + 885 = 2180	$\nu_1 + \nu_3$ (A ⁻) $\nu_9 + \nu_3$ (A ⁻)
2092 vs					2 x 1049 = 2098	$2\nu_2$ (A ⁺)
1968 vs					1295 + 677 = 1972	$\nu_9 + \nu_4$ (A ⁻)
1891 vvw					1295 + 599 = 1894	$\nu_9 + \nu_5$ (A ⁻)
1749 vs					2 x 885 = 1770	$2\nu_3$ (A ⁺)
1670 vvw, sh					1295 + 379 = 1674	$\nu_9 + \nu_7$ (A ⁻)
1645 vvw					1049 + 599 = 1648	$\nu_2 + \nu_5$ (A ⁻)
1610 vs, sh					1049 + 563 = 1612	$\nu_2 + \nu_{10}$ (A ⁻)
1555 vvw, sh					885 + 677 = 1562	$\nu_3 + \nu_4$ (A ⁺)
1538 vvw					1302 + 230 = 1532	$\nu_1 + \nu_8$ (A ⁻)
1480 vvw					885 + 599 = 1484	$\nu_3 + \nu_5$ (A ⁻)
1394 vvw					563 + 559 + 230 = 1392	$\nu_5 + \nu_{10} + \nu_6$ (A ⁻)
1345 vvw, sh					2 x 677 = 1354	$2\nu_4$ (A ⁺)
			1307 sh			
	1304.6 vs	1303.6 vs	1284 vs	1289(0.3)br	1289(0.3)	ν_1 (A ⁺) ³⁵ Cl
	1303.0 vs	1302 sh				2 x 386 + 529 = 1301 $2\nu_{11} + \nu_6$ (A ⁺)
	1301.8 sh	1297.4 vs				
	1294.8 vs	1296.1 vs	1284 vs	1289(0.3)br	1289(0.3)	ν_9 (A ⁻) ³⁵ Cl
	1293.7 sh	1295.2 vs				
1299 vs	1289.8 m	1289.7 m				ν_1 (A ⁺) ³⁷ Cl
		1286.4 m				
	1286.4 m	1285.9 m			2 x 378 + 529 = 1285	$2\nu_7 + \nu_6$ (A ⁺) ν_9 (A ⁻) ³⁷ Cl
		1281.6 w				
	1280.2 ms	1280.6 ms				
1195 vs	1276 sh					
		1063 w				
	1055 vs	1056.0 w				2 x 599 = 1198 $2\nu_5$ (A ⁺) 2 x 529 = 1058 $2\nu_6$ (A ⁺)
	1051.2 sh 1050.0 ms				678 + 379 = 1057	$\nu_4 + \nu_7$ (A ⁺) ³⁵ Cl
					671 + 379 = 1050	$\nu_4 + \nu_7$ (A ⁺) ³⁷ Cl
1049.2 s	1047.3 ms	1047.5 ms	1042 ms	1044(10)p	1045(10)	ν_2 (A ⁺) ³⁵ Cl
	1046.5 ms					
1046.8 ms	1044.2 ms	1044.2 m				ν_2 (A ⁺) ³⁷ Cl
975 vvw					599 + 379 = 978	$\nu_5 + \nu_7$ (A ⁺)
943 vvw					563 + 379 = 942	$\nu_{10} + \nu_7$ (A ⁻)
886.7 w	883.3 ms	882.3 ms			2 x 379 + 127 = 885	$2\nu_7 + \nu_{12}$ (A ⁻)
884.6 ms	881.6 m	887.2 m	879 m	882(4.3)p	882(1.9)	ν_3 (A ⁺)
751 w			750 w		2 x 379 = 758	$2\nu_7$ (A ⁺)
		683.7 ms			563 + 127 = 690	$\nu_{10} + \nu_{12}$ (A ⁺)
682.1						
679.2						
676.8						
674.6 s	674.6	677.7 s	669 s	670(2.8)p	670(1.5)	ν_4 (A ⁺) ³⁵ Cl ν_4 (A ⁺) ³⁷ Cl
672.3	667.6 ms	670.7 ms				
671.0						
668						
599 ms	597.1 ms	597.6 ms	595 ms	596(0.8) dp		ν_5 (A ⁺) ³⁵ Cl ν_5 (A ⁺) ³⁷ Cl
	593.3 m	593.8 m				
563 ms	561.8 ms	562.9 ms	558 ms	559(0.8)dp		ν_{10} (A ⁺) ³⁵ Cl ν_{10} (A ⁺) ³⁷ Cl
	558.9 m	560.0 m				
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 ms	383 sh	382 sh, dp	382 sh	ν_{11} (A ⁻) and $3\nu_{12}$ (A ⁻)
	377.3 ms	378 ms	377 ms	377(8.9)p	377(4.7)	ν_7 (A ⁺)
				230(1.4)p	232(0.8)	ν_8 (A ⁺)
				127(0.6)dp		ν_{12} (A ⁺)

Table 2. Vibrational Spectra of ClO_3OF Compared to Those of Closely Related Molecules

Related Molecules												
Assignment for ClO_3OF in point group C_s		Approx. description of mode for ClO_3OF	obsd freq, cm^{-1}					Approx. descrip of mode for FSO_2OF				
			FCIO_3	ClO_3OH	ClO_3OF	ClO_3OCl	$\text{O}_3\text{ClOClO}_3$	ClO_3OBr	CF_3OF	FSO_2OF		
A'	ν_1	$\nu_{\text{asym}} \text{ClO}_3$	1314(15.8) ^g	$\begin{Bmatrix} 1326 \\ 1201 \end{Bmatrix}$	1282	1302(14.5) ^g	1287(15) ^g	1279	1294	1248	$\nu_{\text{sym}} \text{SO}_2$	
	ν_2	$\nu_{\text{sym}} \text{ClO}_3$	1062(3.05)	1048	1050	1049(3.3)	1040	1039	1223	852	$\nu \text{ S-F}$	
	ν_3	$\nu \text{ O-F}$	--	3553	2624	885(-0)	749(3.8)	683	882	879	$\nu \text{ O-F}$	
	ν_4	$\nu \text{ Cl-O}$	717(10.0)	726	725	677(7.0)	646(8.5)	648	946	789	$\nu \text{ S-O}$	
	ν_5	$\delta_{\text{umbrella}} \text{ClO}_3$	549(0.89)	582	587	599(3.8)	580(2.5)	572	679	575	$\delta_{\text{diag}} \text{SO}_2$	
	ν_6	$\delta_{\text{asym}} \text{ClO}_3(\alpha)$	589(3.1)	555	555	529(-1)	511(<1.5)	509	584	497	$\delta_{\text{sciss}} \text{SO}_2$	
	ν_7	δ in plane ClO_3 rock (μ)	405(0.2)	421	420	379(<1)	355	387	429	395	$\delta_{\text{diag}} \text{SF}$	
	ν_8	$\delta \text{ Cl-O-F}$ in plane	--	$\begin{Bmatrix} 1326 \\ 1201 \end{Bmatrix}$	930	230	198	154	250	242	$\delta \text{ SOF}$	
A''	ν_9	$\nu_{\text{asym}} \text{ClO}_3$	1314(15.8)	1263	1282	1295(14.6)	1271(15)	1262	1258	1501	$\nu_{\text{asym}} \text{SO}_2$	
	ν_{10}	$\delta_{\text{asym}} \text{ClO}_3(\alpha)$	589(3.1)	582	577	563(2.9)	561(2.5)	566	608	523	$\delta_{\text{rock}} \text{SO}_2$	
	ν_{11}	out of plane ClO_3 rock (μ)	405(0.2)	421	420	385(<1)	382(<1)	387	431	385	$\tau \text{ SO}_2$	
	ν_{12}	$\tau \text{ Cl-OX}$	--	306	177	92			127	137	$\tau \text{ S-OF}$	

(a) ref. 28-30.

(b) ref. 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) ref. 10.

(d) ref. 9, but with revised assignment for ν_5 , ν_6 and ν_7 .

(e) ref. 34-38, it should be noted that for the A' block of CF_3OF the mode description is inaccurate due to strong mixing (ref. 38).

(f) ref. 32 and 33.

(g) ^{35}Cl - ^{37}Cl isotopic shifts.

Table 3. Symmetry Force Constants, ^a Observed and Calculated Frequencies and ³⁵Cl - ³⁷Cl Shifts and Potential Energy Distribution ^b of ClO₂DF

Assignment	freq., cm ⁻¹ obsd clcd	Cl isotopic shift, cm ⁻¹ obsd clcd	Symmetry force constants	Potential energy distribution
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	$F_{55} = 0.65f_E + 0.35f_{\alpha} + 1.30f_{\beta} + 0.70f_{\alpha\alpha} - 1.91f_{\alpha\beta} - 0.95f_{\alpha\delta}$	2.38 54(5) + 20(6) + 8(8) +
ν ₆	579 579	-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	$F_{77} = f_{\beta} - f_{\alpha\beta}$	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(1011)
ν ₁₁	385 385	0.3	$F_{11,11} = f_{\beta} - f_{\beta\beta}$	1.21 94(11) + 18(10) - 12(1011)
ν ₁₂	127		$F_{12,12} = f_T$	—
			$F_{16} = -f_{9,10} = f_{\alpha\alpha} - f_{\alpha\beta}$	-0.27
			$F_{17} = F_{9,11} = f_{\alpha\beta} - f_{\alpha\delta}$	0.35
			$F_{24} = \sqrt{3}f_{RR}$	0.16
			$F_{25} = 0.81f_{rR} - 1.18f_{r\alpha} + 1.61f_{r\beta} - 0.59f_{r\alpha}$	0
			$F_{45} + 1.39f_{R\beta} - 1.02f_{R\alpha}$	0.51
			$F_{46} = f_{R\alpha}$	0.218
			$F_{67} = -f_{10,11} = f_{\alpha\beta} - f_{\alpha\delta}$	-0.2

(a) Stretching constants in mdyn/Å, deformation constants in mdyn Å/rad² and stretch-bend interaction constants in mdyn/rad. Although identical explicit F terms are given for F₁₁, F₆₆, F₇₇ and F₉₉, 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.

Table 4. Comparison of Internal Force Constants^a of ClO_3OF with Those of FClO_3

	ClO_3OF	FClO_3
f_r	9.52	9.76
f_{rr}	-0.01	0.07
f_{rR}	0.09	0.08
$f_\alpha - f_{\alpha\alpha}$	1.62 (A') 1.55 (A'')	1.53
$f_\beta - f_{\beta\beta}$	1.54 (A') 1.21 (A'')	1.49
$f_{r\alpha} - f_{r\alpha'}$	0.27	-0.29 ^b
$f_{r\beta} - f_{r\beta'}$	0.35	-0.33 ^b
$f_{\alpha\beta} - f_{\alpha\beta'}$	0.2	0.26

(a) For dimensions of force constants see footnote (a) of Table 3.

(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.

Table 5. Thermodynamic Properties of C10₃OF

T, K	C_p^0 , cal/(mol deg)	$(H_T^0 - H_0^0)$, kcal/mol	$-(F_T^0 - H_0^0)/T$, cal/(mol deg)	S_T^0 , eu
0	0	0	0	0
100	9.438	0.831	50.106	58.411
200	14.097	2.003	56.334	66.347
298.15	18.111	3.592	60.712	72.761
300	18.176	3.626	60.787	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

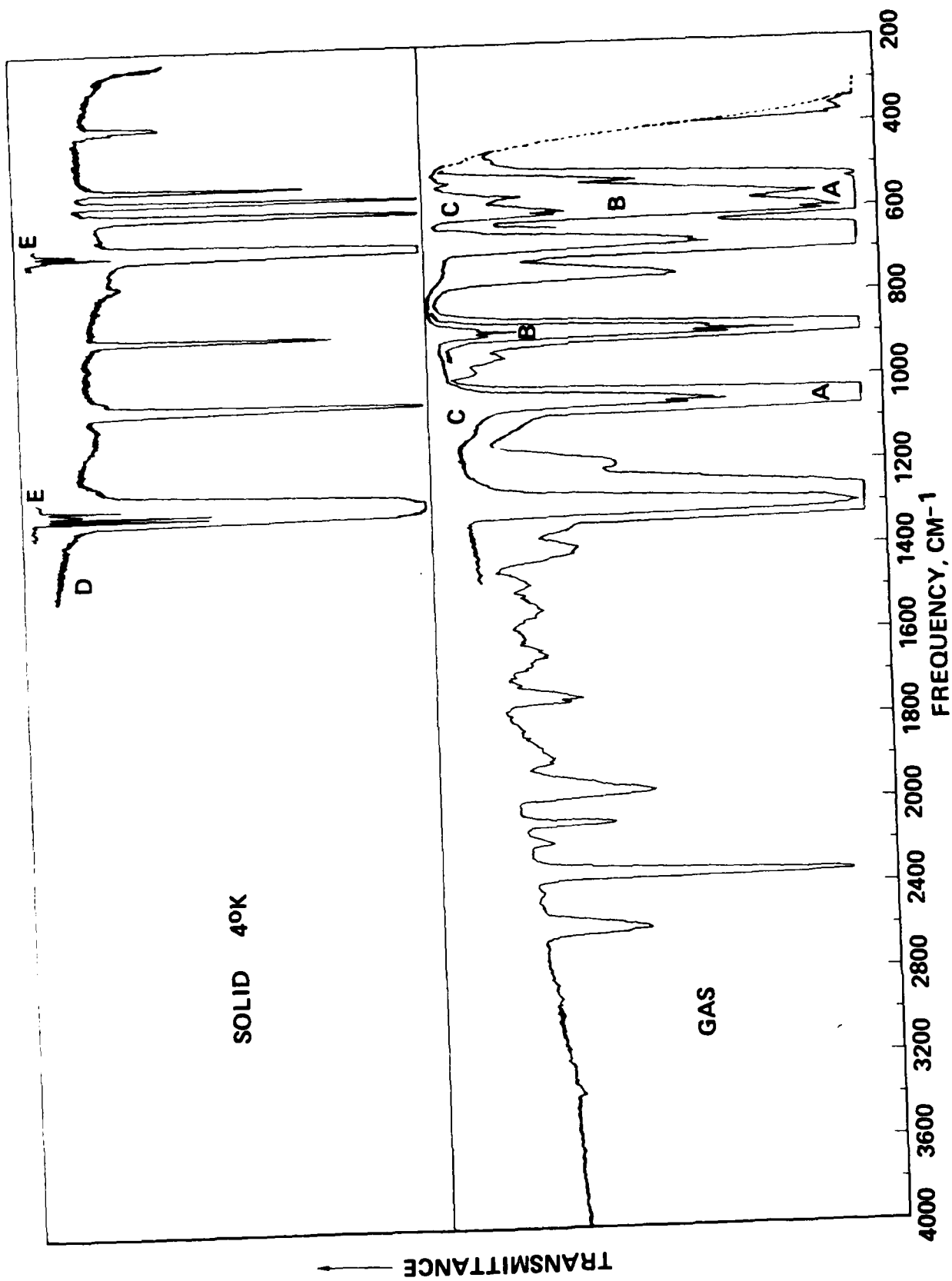


FIGURE 1

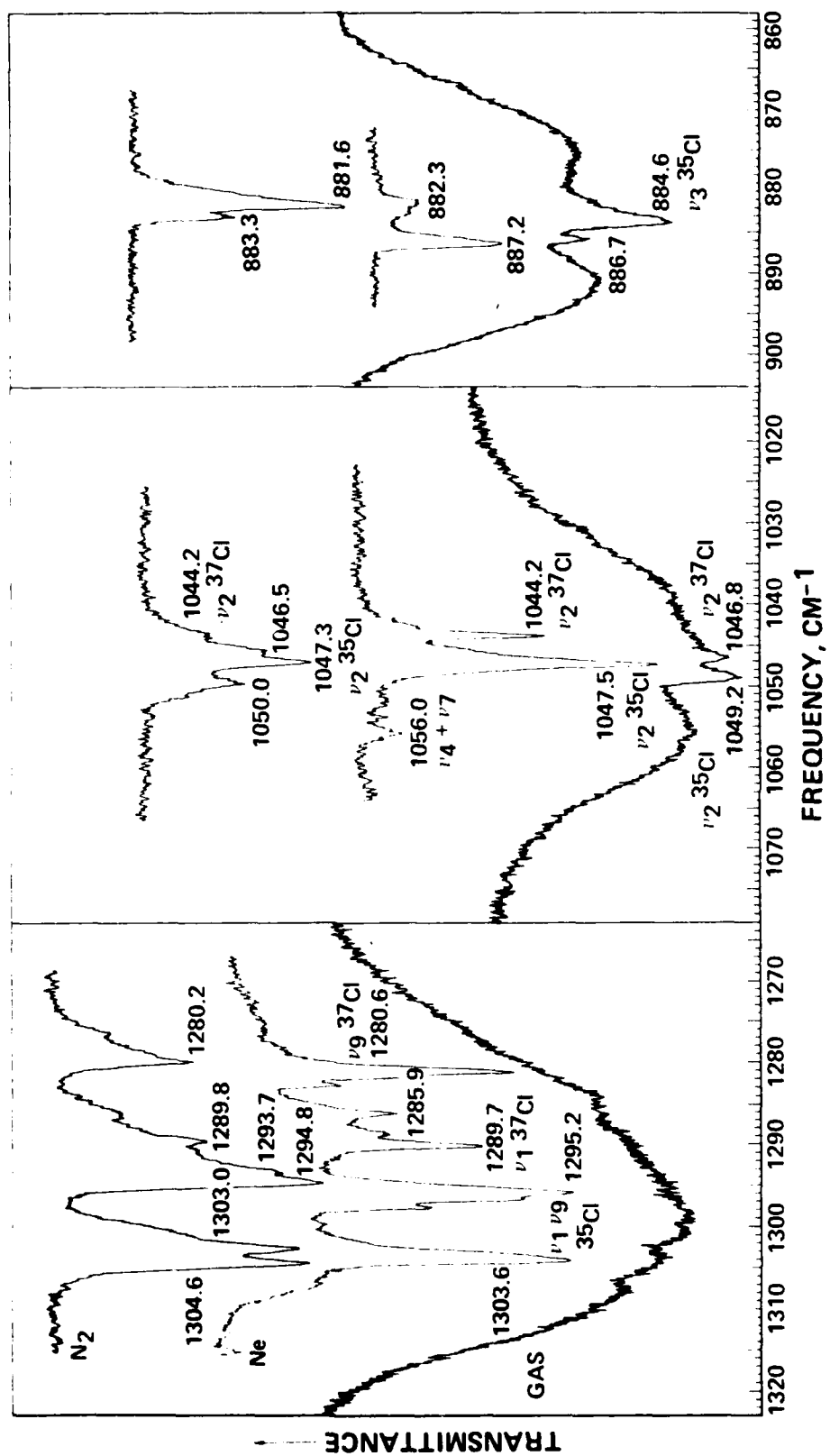


FIGURE 2

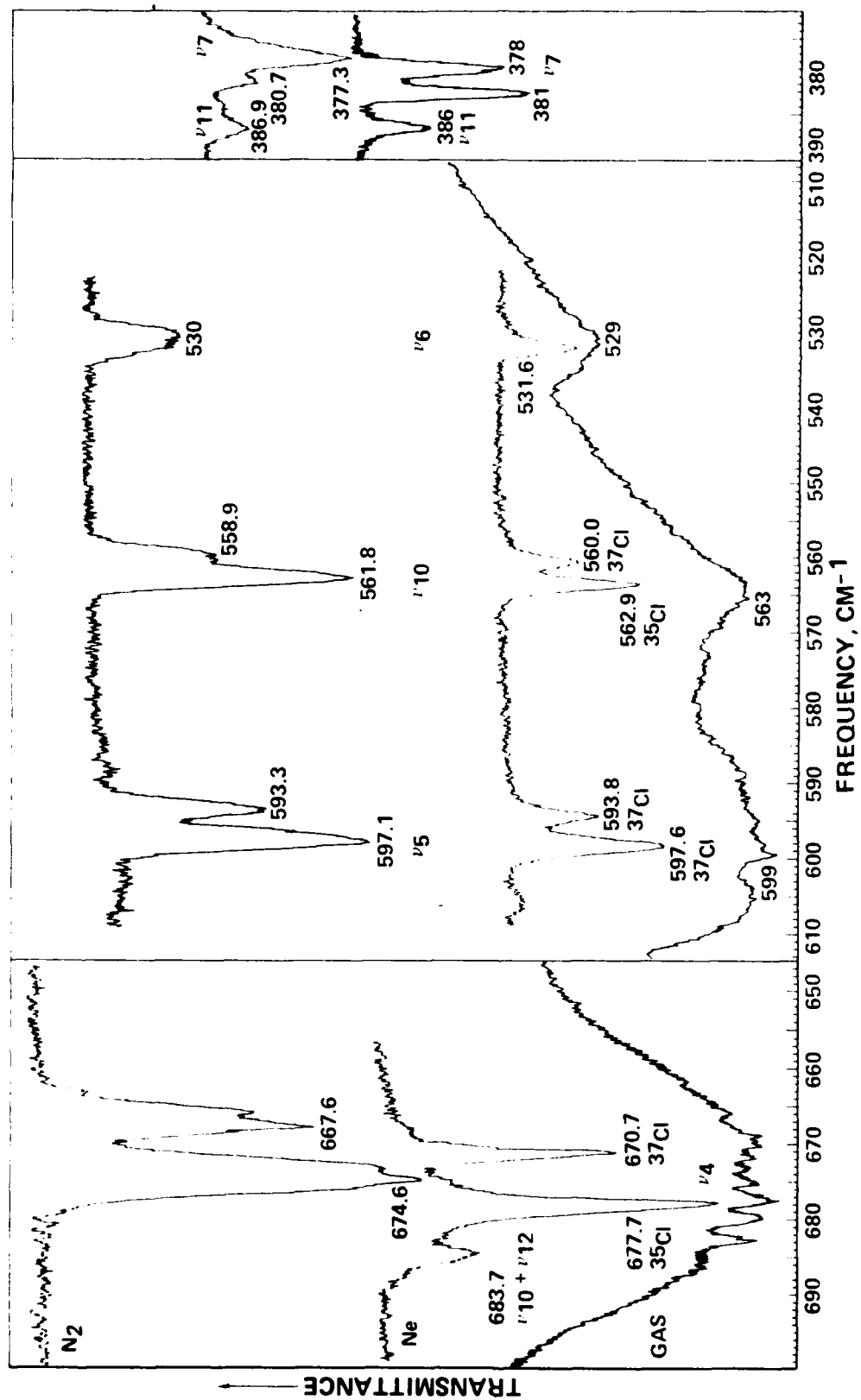
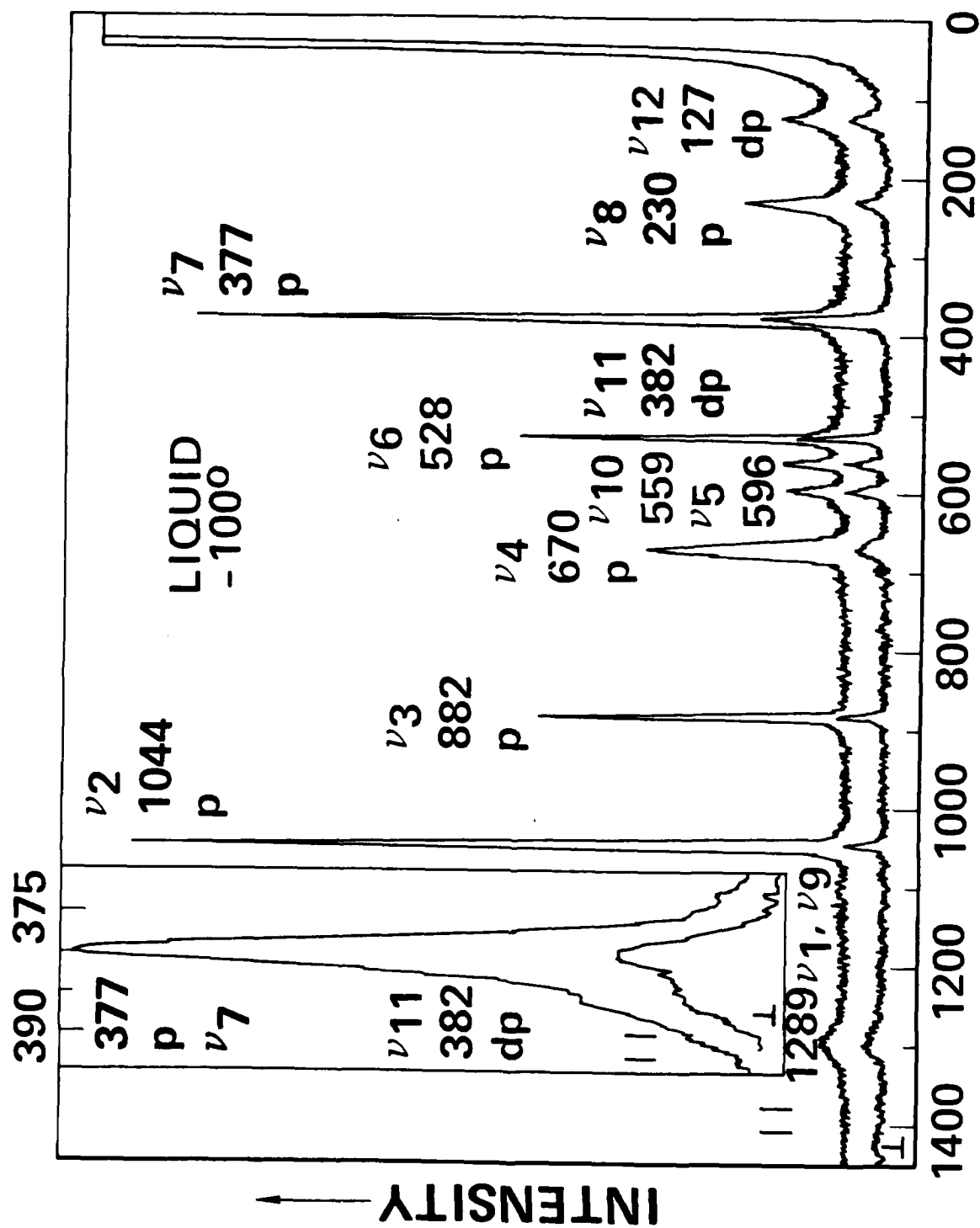


FIGURE 3



FREQUENCY, CM⁻¹

FIGURE 4

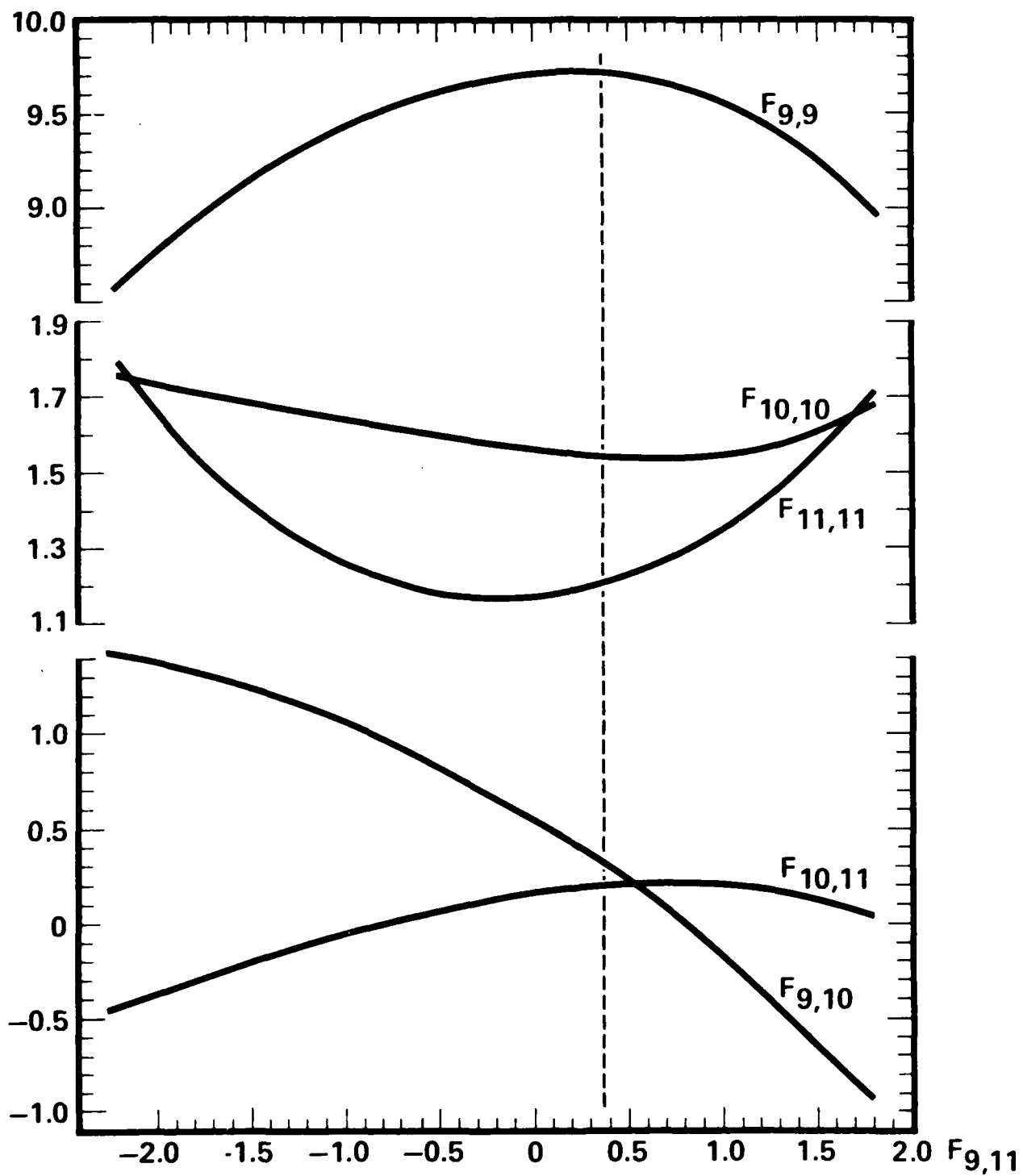


FIGURE 5

AA-26

United States Patent [19]

[11]

4,152,406**Christe et al.**

[45]

May 1, 1979

[54] **SELF-CLINKERING NF_4^+ COMPOSITIONS
FOR NF_3 - F_2 GAS GENERATORS AND
METHOD OF PRODUCING SAME**

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[73] **Assignee:** Rockwell International Corporation, El Segundo, Calif.

[21] **Appl. No.:** 734,153

[22] **Filed:** Oct. 20, 1976

[51] **Int. Cl.²** C01G 21/52; C01G 23/02

[52] **U.S. Cl.** 423/351; 149/119;
149/109.4; 423/472

[58] **Field of Search** 149/119, 19.3, 109.4;
423/351, 472

[56]

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Christe et al., "Inorganic Halogen Oxidizer Research," abstract, Report R-9262 (publ. 1974).
Bailor et al., "Comprehensive Inorganic Chemistry," vol. 3, pp. 1330-1333 and 1370, Pergamon Press Ltd. (1973) Oxford.

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[57]

ABSTRACT

Improved NF_4^+ compositions for solid propellant NF_3 - F_2 gas generators are described which produce NF_3 and F_2 free of gaseous Lewis acids and do not require clinker forming additives for their complexing. The novel self-clinkering compositions $(\text{NF}_4)_2\text{SnF}_6$, NF_4SnF_5 , $(\text{NF}_4)_2\text{TiF}_6$, $\text{NF}_4\text{Ti}_2\text{F}_9$, $\text{NF}_4\text{Ti}_3\text{F}_{13}$, and $\text{NF}_4\text{Ti}_6\text{F}_{25}$ and processes for their production are disclosed.

8 Claims, No Drawings

SELF-CLINKERING NF_4^+ COMPOSITIONS FOR NF_3 - F_2 GAS GENERATORS AND METHOD OF PRODUCING SAME

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions of matter and methods of producing the same and is particularly directed to improved solid propellant NF_3 - F_2 gas generators derived from self-clinkering NF_4^+ salts, together with methods for producing such gas generators.

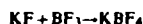
2. Description of the Prior Art

NF_4^+ salts are the key ingredients for solid propellant NF_3 - F_2 gas generators, as shown by D. Pilipovich 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 for 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 byproduct is shared by all the previously known NF_4^+ compositions. These volatile Lewis acids possess a relatively high molecular weight and a low γ value ($\gamma = \frac{C_p}{C_v}$), 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, heretofore, this would be achieved by adding a clinker forming agent, such as KF, to the solid propellant formulation. The function of this additive served to convert the volatile Lewis acid, such as BF_3 , to a non-volatile salt as shown by the following equation:



The principal disadvantages of this approach are that, even if an excess of KF is used, complete clinkering cannot always be guaranteed, and that the addition of the KF severely degrades the yield of NF_3 - F_2 obtainable per pound of formulation. This problem could be solved by using NF_4^+ containing compositions derived from non-volatile Lewis acids. However, the synthesis of such compositions has previously been unknown, since highly stable and non-volatile Lewis acids are polymeric and contain coordination-wise saturated central atoms. Consequently, these compounds possess very little or no acidity, which renders the synthesis of such salts very difficult.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

The above described problem of obtaining a Lewis acid free NF_3 - F_2 gas stream from NF_4^+ compositions without clinker forming additives is overcome by the present invention. We have found that NF_4^+ salts, derived from the polymeric non-volatile Lewis acids SnF_4 (subliming at $704^\circ \text{C}.$) and TiF_4 (1 atm vapor pres-

sure at $284^\circ \text{C}.$) can be prepared. The lack of acidity of SnF_4 at temperatures, at which NF_4^+ salts can be formed and exist, was demonstrated. It was shown that mixtures of NF_3 , F_2 , and SnF_4 , when heated to temperatures of up to $300^\circ \text{C}.$ at autogenous pressures of about 150 atm, did not show any evidence for NF_4^+ formation.

Since a direct synthesis of an NF_4^+ salt derived from SnF_4 was not possible, we have studied metathetical and displacement reactions. Because SnF_6^{2-} salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. The following metathetical reaction

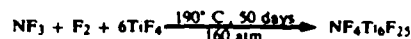


was carried out. It resulted in the precipitation of the rather insoluble salt CsSbF_6 , while the soluble $(\text{NF}_4)_2\text{SnF}_6$ remained in solution. The two products were separated by a simple filtration step. The composition (in mol%) of the crude product was: $(\text{NF}_4)_2\text{SnF}_6$, 83; NF_4SbF_6 , 13; CsSbF_6 , 4. The purity of this product can be easily increased by following the procedures outlined for NF_4BF_4 in our co-pending application Ser. No. 731,198 filed Oct. 12, 1976, and now U.S. Pat. No. 4,107,275.

Another NF_4^+ salt derived from SnF_4 was obtained by the following quantitative displacement reaction in anhydrous HF as a solvent.



For TiF_4 , the direct synthesis of an NF_4^+ salt from NF_3 , F_2 , and TiF_4 is still possible, since TiF_4 possesses already some vapor pressure at temperatures where NF_4^+ salts can be formed. However, the product thus obtained is very rich in TiF_4 , as shown by the following equation:



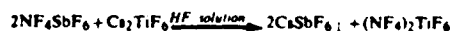
The NF_4^+ content of this salt could not be significantly increased by any changes in the reaction conditions.

Displacement reactions between NF_4BF_4 and TiF_4 , either in HF solution or in the absence of a solvent, produced NF_4^+ salts according to



where, depending on the exact reaction conditions, n equals either 3 or 2.

A further increase in the NF_4^+ content was possible by the following metathetical reaction which yielded $(\text{NF}_4)_2\text{TiF}_6$:



The separation and purification procedure for this product is analogous to that outlined above for $(\text{NF}_4)_2\text{SnF}_6$.

The advantages of the above disclosed concept of using these novel self-clinkering NF_4^+ composition for NF_3 - F_2 gas generators become obvious from a comparison of their theoretical performance data. In Table I, the theoretical yields of usable fluorine, expressed in weight percent, of $(\text{NF}_4)_2\text{SnF}_6$ and $(\text{NF}_4)_2\text{TiF}_6$ are

3 compared to that of KF clinkered NF_4BF_4 , the highest performing presently known system. The novel self-clinkering compositions clearly outperform KF clinkered NF_4BF_4 . Furthermore, the risk of incomplete clinkering which always exists for a clinkered formulation is avoided.

TABLE I

A Comparison of the Theoretical Performance of Self-clinkering $(\text{NF}_4)_2\text{SnF}_6$ and $(\text{NF}_4)_2\text{TiF}_6$ with KF-clinkered NF_4BF_4		
System	Performance (Weight % Usable F)	
NF_4BF_4 12KF	38.5	
$(\text{NF}_4)_2\text{SnF}_6$	40.0	
$(\text{NF}_4)_2\text{TiF}_6$	55.6	

Accordingly, it is an object of the present invention to provide higher performing solid propellant NF_3 - F_2 gas generator compositions.

Another object of the present invention is to provide self-clinkering NF_4^+ compositions capable of generating Lewis acid free NF_3 and F_2 .

Another object of the present invention is to provide processes for the production of self-clinkering NF_4^+ compositions.

These and other objects and features of the present invention will be apparent from the following examples. 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.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLE I

Metathetical reactions were carried out in an apparatus consisting of three Teflon FEP U-traps interconnected by Monel unions and closed off at each end by a Monel valve. The union between trap II and trap III contained a Teflon filter and was held in place by a press fit. The passivated apparatus was taken to the dry box and Cs_2SnF_6 and NF_4SbF_6 (in a 1:2 mole ratio) were placed into traps I and II, respectively. The apparatus was connected to the vacuum line through flexible corrugated Teflon FEP tubing. Anhydrous HF, in an amount sufficient to just dissolve the starting materials, was added to traps I and II. Trap I was flexed to allow the Cs_2SnF_6 solution to run into trap II containing the NF_4SbF_6 solution. Upon contact of the two solutions, copious amounts of a white precipitate (CsSbF_6) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to -80°C . After completion of the filtration step, trap III was warmed to ambient temperature and the HF solvent was pumped off. The solid residue on top of the filter consisted mainly of CsSbF_6 , whereas the solid collected in trap III was mainly the desired $(\text{NF}_4)_2\text{SnF}_6$.

The following example gives a typical product distribution obtainable with the above procedure and apparatus. Starting materials: NF_4SbF_6 (9.72 mmol), Cs_2SnF_6 (4.86 mmol), weight of solid on filter = 4.24 g; weight of solid in trap III = 1.36 g (weight calcd for 4.86 mmol of $(\text{NF}_4)_2\text{SnF}_6$ = 2.01 g). Elemental analysis for solid from trap III. Found: NF_3 , 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3. Calculated analysis for a mixture (mol %) of 82.8

$(\text{NF}_4)_2\text{SnF}_6$, 12.9 NF_4SbF_6 , and 4.3 CsSbF_6 : NF_3 , 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43.

$(\text{NF}_4)_2\text{SnF}_6$ is a white, crystalline, hygroscopic solid, stable at room temperature but decomposing at 240°C . Its characteristic x-ray powder pattern is listed in Table II. Its ionic composition, i. e. the presence of discrete NF_4^+ cations and SnF_6^{2-} anions was established by ^{19}F nmr, infrared and Raman spectroscopy.

The ^{19}F nmr spectrum, recorded for a BrF_3 solution, showed in addition to the solvent lines a triplet of equal intensity with $\phi = -220$, $J_{\text{NF}} = 229.6$ Hz, and a line width at half height of about 5 Hz, which is characteristic of tetrahedral NF_4^+ . In addition, a narrow singlet at $\phi = 149$ was observed with the appropriate 117/119Sn satellites (average $J_{\text{SnF}} = 1549$ Hz), characteristic of octahedral SnF_6^{2-} . The vibrational spectra of $(\text{NF}_4)_2\text{SnF}_6$ and their assignments are summarized in Table III.

EXAMPLE II

A mixture of NF_4BF_4 and SnF_4 (9.82 mmol each) was placed into a passivated Teflon-FEP ampoule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10 ml liquid) was added at -78°C , and the resulting suspension was stirred at 25°C for 2 hours. The volatile material was pumped off at 35°C leaving behind a white stable solid which, on the basis of its weight (3.094 g) and Raman spectrum, consisted of 83 mol percent NF_4SnF_3 and 17 mol percent unreacted starting materials. The HF treatment was repeated (again for 2 hours) and the non-volatile residue (2.980 g, weight calcd for 9.82 mmol of NF_4SnF_3 = 2.982 g) was shown by infrared, Raman, and ^{19}F nmr spectroscopy to be essentially pure NF_4SnF_3 . Anal. Calcd for NF_4SnF_3 : NF_3 , 23.38; Sn, 39.08. Found: NF_3 , 23.6; Sn, 38.7.

TABLE II

X-RAY POWDER DATA FOR $(\text{NF}_4)_2\text{SnF}_6$				
d obsd	d calcd	Int	h k l	
6.27	6.36	w	1	1
5.67	5.70	vs	0	0
4.99	5.04	vw	1	0
3.67	3.69	w	2	1
3.55	3.59	s	1	0
3.42	3.42	s	3	1
2.990	2.990	s	2	1
2.851	2.851	ms	0	0
2.492	2.490	m	3	1
2.347	2.356	w	3	2
2.230	2.228	s	4	2
2.120	2.123	mw	5	1
2.023	2.024	mw	5	0
1.961	1.963	w	4	0
1.917	1.914	m	4	0
1.882	1.881	mw	5	0
1.834	1.832	w	5	1
1.813	1.814	mw	4	2
1.763	1.765	vw	5	2
1.712	1.712	w	6	2
1.686	1.686	m	5	4
1.662	1.662	m	3	1
1.616	1.614	mw	6	0
1.570	1.570	mw	5	0
1.500	1.501	mw	6	4
1.397	1.396	mw	6	4
1.387	1.386	w	6	5
1.359	1.359	mw	7	0
1.331		mw		
1.314		mw		
1.263		w		
1.231		w		
1.212		mw		
1.192		w		
1.177		mw		

Tetragonal, $a = 10.828 \text{ \AA}$, $c = 11.406 \text{ \AA}$, Cu K α radiation Ni filter

TABLE III

VIBRATIONAL SPECTRA OF SOLID $(\text{NF}_4)_2\text{SnF}_6$			
Obsd Freq (cm^{-1}) and Rel Inten		Assignments (Point Group)	
IR	Raman	$\text{NF}_4^+ (\text{T}_d)$	$\text{SnF}_6^{2-} (\text{O}_h)$
1224 mw		$2\nu_4 (\text{A}_1 + \text{E} + \text{F}_2)$	
1160 vs.	1158 (1.5)	$\nu_3 (\text{F}_2)$	$\nu_1 + \nu_3 (\text{F}_{1u})$
1132 sh, vw			
1059 vw		$\nu_2 + \nu_4 (\text{F}_1 + \text{F}_2)$	
1026 vw			$\nu_2 + \nu_3 (\text{F}_{1u} + \text{F}_{2u})$
	881 (0.1)	$2\nu_2 (\text{A}_1 + \text{A}_2 + \text{E})$	
854 vvw	853 (10)	$\nu_1 (\text{A}_1)$	
613 mw	613 (5.0)		
		$\nu_4 (\text{F}_2)$	
605 mw	607 (1.5)		$\nu_1 (\text{A}_{1g})$
			$\nu_3 (\text{F}_{1u})$
550 vs	470 (0+) br		$\nu_2 (\text{E}_g)$
	449 (3.1)		
	442 (2.9)	$\nu_2 (\text{E})$	
	251 (3.3)		$\nu_5 (\text{F}_{2g})$
	84 (0.3)	Lattice Vibration	

NF_4SnF_5 is a white, crystalline, hygroscopic solid, stable at room temperature and decomposing above 200°C . Its characteristic x-ray powder pattern is listed in Table IV.

TABLE IV

X-RAY POWDER DATA FOR NF_4SnF_5			
d obsd	Int	d obsd	Int
7.72	mw	2.571	mw
6.32	vs	2.519	vw
5.69	w	2.276	w
5.29	w	2.146	w
4.51	m	2.064	ms
4.19	m	1.965	mw
3.80	vs	1.929	w
3.46	m	1.820	m
3.32	m	1.780	mw
3.17	mw	1.757	mw
2.868	w	1.732	mw
2.802	w	1.700	mw
2.743	m	1.661	vw
2.683	w	1.639	w
		1.615	w

its ionic structure, i.e., presence of NF_4^+ cations, was established by its ^{19}F nmr spectrum in BrF_3 solution. In addition to the solvent lines, it showed the triplet (see above) at $\phi = -220$, characteristic of NF_4^+ . Two resonances were observed for SnF_5^- at $\phi = 145.4$ and 162.4 , respectively, with an area ratio of 1:4. At -20°C , the resonances consisted of broad lines, but at lower temperatures the $\phi = 162.4$ signal showed splittings. Based on a more detailed analysis of these data, the SnF_5^- anion appears to have a diameric or polymeric structure. The vibrational spectrum of NF_4SnF_5 is listed in Table V and again establishes the presence of discrete NF_4^+ cations.

EXAMPLE III

When a mixture of NF_4BF_4 and SnF_4 in a mol ratio of 2:1 was treated 8 times, as described in Example II, with liquid HF for a total of 35 days, the resulting non-volatile residue consisted mainly of NF_4SnF_5 , unreacted NF_4BF_4 , and only a small amount of $(\text{NF}_4)_2\text{SnF}_6$.

EXAMPLE IV

The metathetical synthesis of $(\text{NF}_4)_2\text{TiF}_6$ from saturated HF solutions of NF_4SbF_6 (10.00 mmol) and Cs_2TiF_6 (5.00 mmol) was carried out in the apparatus described in Example I for the synthesis of $(\text{NF}_4)_2\text{SnF}_6$. After combination of the solutions of the two starting materials at room temperature and formation of a CsSbF_6 precipitate, the mixture was cooled to -78°C and filtered. The volatile materials were pumped off at 50°C for 1 hour. The filter cake (3.85 g) was shown by its x-ray powder diffraction pattern and vibrational spectroscopy to be mainly CsSbF_6 containing, due to the hold up of some mother liquor, a small amount of $(\text{NF}_4)_2\text{TiF}_6$. The filtrate residue (1.55 g, weight calcd for 5 mmol of $(\text{NF}_4)_2\text{TiF}_6 = 1.71$ g) had the composition (mol%): 88.5 $(\text{NF}_4)_2\text{TiF}_6$ and 11.5 CsSbF_6 . Found: NF_3 , 36.2; Ti, 12.21; Sb, 4.11; Cs, 4.4. Calcd for a mixture of 88.5 $(\text{NF}_4)_2\text{TiF}_6$ and 11.5 CsSbF_6 : NF_3 , 36.43; Ti, 12.29; Sb, 4.06; Cs, 4.43. Based on the observed Raman spectrum, the composition of the filtrate residue was estimated to be 9% $(\text{NF}_4)_2\text{TiF}_6$ and 10% CsSbF_6 , in good agreement with the above elemental analysis.

$(\text{NF}_4)_2\text{TiF}_6$ is a white, crystalline, hygroscopic solid, stable at room temperature, but decomposing above 200°C . Its characteristic x-ray powder pattern is listed in Table VI.

TABLE V

VIBRATIONAL SPECTRA OF SOLID NF_4SnF_5			
Obsd Freq (cm^{-1}) and Rel Inten		Assignments (Point Group)	
IR	Raman	$\text{NF}_4^+ (\text{T}_d)$	
1222 mw		$2\nu_4 (\text{A}_1 + \text{E} + \text{F}_2)$	
1165 vs	1168 (0.4)	$\nu_3 (\text{F}_2)$	
	1159 (0.8)		
	1150 sh		
1134 w, sh			
1061 w		$\nu_2 + \nu_4 (\text{F}_1 + \text{F}_2)$	
1048 w			
	811 (0.2)	$2\nu_2 (\text{A}_1 + \text{A}_2 + \text{E})$	
850 vv	851 (10)	$\nu_1 (\text{A}_1)$	
635 vs			
	622 (9.2)		
605 mw	606 (3.3)	$\nu_4 (\text{F}_2)$	
575 vs			
	574 (0.5)		
559 w, sh	558 (2.0)		
490 m	490 (0+)		
458 m			
	448 (2.5)	$\nu_2 (\text{E})$	
	440 (2.3)		
	272 (0.6)		
	247 (1.4)		
	222 (1.1)		
	197 (0.6)		
	154 (0+)		
	135 (0.2)		

TABLE VI

X-RAY POWDER DATA FOR $(\text{NF}_4)_2\text{TiF}_6$			
d obsd	d calcd	Int	h k l
6.23	6.26	vw	1 1 1
5.57	5.56	vs	0 0 2
4.93	4.93	w	1 0 2
3.49	3.50	s	1 0 3
3.39	3.39	s	3 1 0
2.94	2.93	ms	2 1 3
2.782	2.778	m	0 0 4

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TABLE VI-continued

X-RAY POWDER DATE FOR $(\text{NF}_4)_2\text{TiF}_6$			
d obsd	d calcd	Int	h k l
2.465	2.463	w	3 3 1
2.315	2.318	mw	3 2 3
2.201	2.200	s	4 2 2
2.100	2.101	w	5 1 0
1.990	1.990	vw	5 2 0, 5 0 2
1.892	1.894	m	4 4 0
1.789	1.789	mw	6 0 0, 4 4 2
1.663	1.664	mw	2 2 6
1.641	1.644	mw	3 0 6

*tetragonal, $a = 10.715 \text{ \AA}$, $c = 11.114 \text{ \AA}$, Cu K α radiation Ni filter

Its ionic structure, i.e. the presence of discrete NF_4^+ cations and TiF_6^{2-} anions was established by ^{19}F nmr and vibrational spectroscopy. The ^{19}F nmr spectrum showed the triplet at $\phi = -220$, characteristic for NF_4^+ as shown above, and the characteristic TiF_6^{2-} signal at $\phi = -81.7$. The vibrational spectra are listed in Table VII.

TABLE VII

VIBRATIONAL SPECTRA OF SOLID $(\text{NF}_4)_2\text{TiF}_6$			
Obsd Freq (cm^{-1}) and Rel Intens		Assignments (Point Group)	
IR	Raman	$\text{NF}_4^+(\text{T}_d)$	$\text{TiF}_6^{2-}(\text{Oh})$
1219 mw		$2\nu_4(\text{A}_1 + \text{E} + \text{F}_2)$	
1160 vs	1158 (1.4)	$\nu_3(\text{F}_2)$	
1132 sh, vw		$\nu_2 + \nu_4(\text{F}_1 + \text{F}_2)$	
1060 vw		$\nu_1 + \nu_4(\text{F}_{1u})$	
1021 w			
910 vw			
	883 (0.1)	$2\nu_2(\text{A}_1 + \text{A}_2 + \text{E})$	
850 sh, vw	853 (10)	$\nu_1(\text{A}_1)$	
804 w			
611 mw	612 (5)	$\nu_4(\text{F}_2)$	
	607 sh		
	601 (8.0)	$\nu_1(\text{A}_{1g})$	
563 vs		$\nu_3(\text{F}_{1u})$	
452 vw	450 (3.3)		
	442 (2.6)	$\nu_2(\text{E})$	
	289 (8.2)	$\nu_5(\text{F}_{2g})$	
	107 (0+)		
	86 (2)	Lattice Vibrations	

fluorotitanate (IV) anion (probably $\text{Ti}_6\text{F}_{25}^-$) having its strongest Raman line at 784 cm^{-1} . During the next two heating cycles (190° – 195° C . for 14 days and 180° C . for 35 days) the solid gained 149 and 41 mg, respectively, in weight. The vibrational spectra did not show any evidence of unreacted TiF_4 , and the relative intensities of the bands due to NF_4^+ had significantly increased. Furthermore, the 784 cm^{-1} Raman line had become by far the most intense Raman line. Additional heating to 230° C . for 3 days did not result in significant changes in either the weight or the vibrational spectra of the solid. Based on the observed weight increase and on the lack of spectroscopic evidence for the presence of lower polyperfluorotitanate (IV) anions, the solid product appears to have the approximate composition $\text{NF}_4\text{Ti}_6\text{F}_{25}$ (calcd weight increase, 205 mg; obsd weight increase 198 mg).

EXAMPLE VI

Displacement reactions were carried out either in HF solution at room temperature or by heating the starting materials in the absence of a solvent in a Monel cylinder. For the HF solution reactions, the solid starting materials (6 mmol of NF_4BF_4 in each experiment) were placed in a passivated Teflon FEP ampoule and 15 ml of liquid anhydrous HF was added. The mixture was stirred with a Teflon coated magnetic stirring bar at room temperature for a given time period. The volatile products were pumped off at 50° C . for 3 hours and the composition of the solid residue was determined by elemental and spectroscopic analyses and from the observed material balances.

The thermal displacement reactions were carried out in a prepassivated 90 ml Monel cylinder which was heated in an electric oven for a specified time period. The volatile products were separated by fractional condensation in a vacuum line, measured by PVT, and identified by infrared spectroscopy. The solid residues were weighed and characterized by elemental and spectroscopic analyses. The results of these experiments are summarized in Table VIII.

TABLE VIII

Results from the Displacement Reactions between NF_4BF_4 and TiF_4		
Reactants (mol)	Reaction Conditions	Products (mol)
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(6)$	HF, 24° C , 18h	$\text{NF}_4\text{Ti}_2\text{F}_9(4)$, $\text{NF}_4\text{BF}_4(4)$
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(12)$	HF, 24° C , 72h	$\text{NF}_4\text{Ti}_2\text{F}_9(6)$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(6)$	HF, 24° C , 138h	$\text{HF}_4\text{Ti}_3\text{F}_{11}(\sim 2)$, $\text{NF}_4\text{BF}_4(\sim 4)$, small amount of $\text{NF}_4\text{Ti}_2\text{F}_9$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(12)$	HF, 24° C , 96h	$\text{NF}_4\text{Ti}_3\text{F}_{11}(4)$, $\text{NF}_4\text{BF}_4(2)$
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(6)$	190° C , 18h	$\text{NF}_4\text{Ti}_2\text{F}_9(\sim 3)$, $\text{NF}_3(\sim 3)$, $\text{BF}_3(\sim 6)$, small amounts of NF_4BF_4 and $\text{NF}_4\text{Ti}_3\text{F}_{11}$
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(6)$	160° C , 60h	$\text{NF}_4\text{Ti}_3\text{F}_{11}(2)$, $\text{NF}_4\text{BF}_4(1.4)$, $\text{NF}_3(2.6)$, $\text{BF}_3(4.6)$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(6)$	170° C , 20h	$\text{NF}_4\text{Ti}_3\text{F}_9(3)$, $\text{NF}_4\text{BF}_4(1)$, $\text{BF}_3(3)$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(12)$	170° C , 20h	$\text{NF}_4\text{Ti}_3\text{F}_9(3.6)$, $\text{NF}_4\text{Ti}_3\text{F}_{11}(1.6)$, $\text{BF}_3(5.4)$, $\text{NF}_4\text{BF}_4(0.6)$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(12)$	170° C , 192h	$\text{NF}_4\text{Ti}_3\text{F}_9(6)$, $\text{BF}_3(6)$

EXAMPLE V

TiF_4 (11.3 mmol), NF_3 (200 mmol), and F_2 (200 mmol) were heated in a passivated 90 ml Monel cylinder to various temperatures for different time periods. After each heating cycle, the volatile products were temporarily removed and the progress of the reaction was followed by determining the weight gain of the solid and recording its vibrational spectra. Heating to 200° C . for 3 days resulted in a weight gain of 8 mg and the vibrational spectra showed mainly unreacted TiF_4 in addition to a small amount of NF_4^+ and a polyper-

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. A compound for use in an improved NF_3 – F_2 gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is derived from TiF_4 and is self-clinkering

2. A compound for use in an improved $\text{NF}_3\text{--F}_2$ gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is TiF_6^{3-} and is self-clinkering.

3. A compound for use in an improved $\text{NF}_3\text{--F}_2$ gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is $\text{Ti}_2\text{F}_9^{3-}$ and is self-clinkering.

4. A compound for use in an improved $\text{NF}_3\text{--F}_2$ gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is $\text{Ti}_3\text{F}_{13}^{3-}$ and is self-clinkering.

5. A compound for use in an improved $\text{NF}_3\text{--F}_2$ gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is $\text{Ti}_6\text{F}_{25}^{3-}$ and is self-clinkering.

5 6. A process for the production of $\text{NF}_4^+\text{TiF}_5^-$, $n\text{TiF}_4$, comprising the steps of treating NF_4BF_4 with TiF_4 in anhydrous HF solution at room temperature.

7. A process for the production of $\text{NF}_4^+\text{TiF}_5^-$, $n\text{TiF}_4$, comprising the step of treating NF_4BF_4 with TiF_4 at temperatures ranging from 150° to 200° C.

10 8. A process for the production of $\text{NF}_4\text{Ti}_6\text{F}_{25}$, comprising the step of heating a mixture of NF_3 , F_2 and TiF_4 to 170° C. to 200° C. at elevated pressure.

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United States Patent [19]

Christe et al.

[11] 4,163,773

[43] Aug. 7, 1979

[54] SELF-CLINKERING BURNING RATE
MODIFIER FOR SOLID PROPELLANT
NF₃-F₂ GAS GENERATORS FOR CHEMICAL
HF-DF LASERS

[75] Inventors: Karl O. Christe, Calabasas; Carl J.
Schack, Chatsworth, both of Calif.

[73] Assignee: The United States of America as
represented by the Secretary of the
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[21] Appl. No.: 970,775

[22] Filed: Dec. 18, 1978

[51] Int. Cl.² C01B 21/18

[52] U.S. Cl. 423/351; 423/462;

149/119

[58] Field of Search 423/351, 462, 466;
149/19.3, 119

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16, No. 4, pp. 937-940, 1977.

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Assistant Examiner—Thomas W. Ray

Attorney, Agent, or Firm—R. S. Sciascia; W. Thom
Skeer; L.E.K. Pohl

[57]

ABSTRACT

N₂F₃SnF₅ is formed by reacting N₂F₃SbF₆ and
Cs₂SnF₆ in the presence of HF. N₂F₃SnF₅ is useful as a
component of NF₃-F₂ gas generating compositions.

2 Claims, No Drawings

SELF-CLINKERING BURNING RATE MODIFIER FOR SOLID PROPELLANT $\text{NF}_3\text{-F}_2$ GAS GENERATORS FOR CHEMICAL HF-DF LASERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a composition of matter which is useful in $\text{NF}_3\text{-F}_2$ gas generator formulations.

2. Description of the Prior Art

In the recent past, certain new self-clinkering NF_4^+ salts have been synthesized. Among these are $(\text{NF}_4)_2\text{SnF}_6$, NF_4SnF_5 , $(\text{NF}_4)_2\text{TiF}_6$, NF_4TiF_5 , NF_4TiF_3 , NF_4TiF_2 and $(\text{NF}_4)_2\text{NiF}_6$. When such self-clinkering salts are utilized as oxidizers and combined with a fuel such as aluminum, NF_3 gas, F_2 gas and solids are produced when the combination is burned. The gases are useful as lasing materials. The fact that solids or "clinkers" are produced is important in that it overcomes a disadvantage present when, for example NF_4BF_4 is used as the oxidizer. When NF_4BF_4 is used, NF_3 , F_2 and another gas, BF_3 , are produced. The gaseous BF_3 is not useful as a laser material and acts to deactivate the laser. By producing a solid or "clinker" instead of gases other than NF_3 and F_2 , the self-clinkering salts overcome this problem.

Frequently, formulations containing NF_4^+ salts require burning rate modifiers. Typically, N_2F_3^+ salts which are more reactive than NF_4^+ salts can be used. However, insofar as is known from the prior art, no self-clinkering N_2F_3^+ salts are available.

SUMMARY OF THE INVENTION

According to this invention, a self-clinkering N_2F_3^+ salt which is useful as a burning rate modifier has been prepared. The salt has the formula $\text{N}_2\text{F}_3\text{SnF}_5$. Synthesis is accomplished by means of a reaction between $\text{N}_2\text{F}_3\text{SbF}_6$ and Cs_2SnF_6 in HF. Insofar as is known by the inventors, the salt of this invention is the first self-clinkering N_2F_3^+ salt ever produced.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The salt, $\text{N}_2\text{F}_3\text{SbF}_6$, may be prepared according to the procedure set forth in the following example

EXAMPLE I

Synthesis of $\text{N}_2\text{F}_3\text{SbF}_6$. A Teflon ampule, containing a Teflon coated magnetic stirring bar and equipped with a stainless steel valve, was loaded with 14.4 mmol of SbF_5 in a glovebox. The ampule was then attached to a vacuum line and 2 ml of anhydrous HF was condensed into the ampule at -78°C . while stirring and warming to ambient temperature. The system was then pressur-

ized with N_2F_4 (1 atm). A gradual decrease in the pressure was noted due to uptake of N_2F_4 . Periodic cycling to below 0°C . seemed to increase the rate of N_2F_4 uptake. After several hours the unreacted N_2F_4 and HF solvent were pumped off at 40°C . until constant weight was achieved. The observed weight gain corresponded to the reaction of 12.1 mmol of N_2F_4 . When the reaction was repeated on a larger scale with 8 ml HF for 3 days, it was found that 74.0 mmol of SbF_5 reacted with 73.5 mmol of N_2F_4 to give 23.66 g of $\text{N}_2\text{F}_3\text{SbF}_6$ (weight calcd for 74.0 mmol of $\text{N}_2\text{F}_3\text{SbF}_6$ 23.74 g), which was characterized by ^{19}F NMR and vibrational spectroscopy.

To produce the salt of this invention, $\text{N}_2\text{F}_3\text{SnF}_5$, one utilizes $\text{N}_2\text{F}_3\text{SbF}_6$ obtained from Example I and Cs_2SnF_6 and carries out the procedure set forth in the following example.

EXAMPLE II

Solid $\text{N}_2\text{F}_3\text{SbF}_6$ (6.43 mmol) and Cs_2SnF_6 (3.24 mmol) were placed in a well passivated (with ClF_3) Monel vacuum line equipped with Teflon-FEP U traps and diaphragm valves. Approximately 2 ml of anhydrous HF was added. After stirring and shaking vigorously for 30 minutes at room temperature, some of the HF was removed under vacuum and the mixture was cooled to -78°C . The solid and liquid phases were separated by pressure filtration and the volatile products were removed by pumping at 25°C . for 15 hours. The volatile material was separated by fractional consideration and consisted of the HF solvent and N_2F_4 (3.2 mmol). The filtrate residue (0.3 g) was analyzed by means of vibrational and NMR spectroscopy and shown to be $\text{N}_2\text{F}_3\text{SnF}_5$.

When $\text{N}_2\text{F}_3\text{SnF}_5$ is combined with a fuel such as aluminum and burned NF_3 gas, F_2 gas, N_2 gas and a solid are obtained. (Since N_2 is normally used as an inert diluent its formation does not degrade the performance of a laser.) Thus $\text{N}_2\text{F}_3\text{SnF}_5$ is self-clinkering. That is, a non-gaseous product (the solid or "clinker") rather than a gaseous product (such as the BF_3 produced when NF_4BF_4 is burned) results upon burning of $\text{N}_2\text{F}_3\text{SnF}_5$. In addition, the useful gases NF_3 and F_2 (and N_2) are produced. Insofar as is known by the inventors, $\text{N}_2\text{F}_3\text{SnF}_5$ is the only self-clinkering N_2F_3^+ salt that has ever been produced to date.

What is claimed is:

1. $\text{N}_2\text{F}_3\text{SnF}_5$.
2. A method for preparing $\text{N}_2\text{F}_3\text{SnF}_5$ comprising the steps of:
 - forming a solution of $\text{N}_2\text{F}_3\text{SbF}_6$ salt and Cs_2SnF_6 salt in HF;
 - allowing the salts to react.

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United States Patent [19]

[11] 4,163,774

Schack et al.

[45] Aug. 7, 1979

[54] $N_2F_3SbF_6$ AND ITS PREPARATION

[75] Inventors: Carl J. Schack, Chatsworth; Karl O. Christe, Calabasas, both of Calif.

[73] Assignee: The United States of America as represented by the Secretary of the Navy, Washington, D.C.

[21] Appl. No.: 964,025

[22] Filed: Nov. 27, 1978

[51] Int. Cl.¹ C01B 21/18[52] U.S. Cl. 423/351; 423/462;
149/119[58] Field of Search 423/351, 462, 466;
149/19.3, 119

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Primary Examiner—O. R. Vertiz

Assistant Examiner—Thomas W. Roy

Attorney, Agent, or Firm—R. S. Sciascia; W. Thom
Skeer; L. E. K. Pohl

[57]

ABSTRACT

N_2F_4 and SbF_3 react in anhydrous HF to produce $N_2F_3SbF_6$. The salt is useful as a burn rate modifier in NF_3 - F_2 gas generators.

3 Claims, No Drawings

$\text{N}_2\text{F}_3\text{SbF}_6$ AND ITS PREPARATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the salt $\text{N}_2\text{F}_3\text{SbF}_6$ and to its preparation.

2. Description of the Prior Art

The use of solid compositions to produce fluorine and NF_3 for chemical lasers is known. For example, Pilipovich in U.S. Pat. No. 3,963,542, describes such a composition. The need for burn rate modifiers for solid gas generating compositions is also well known.

SUMMARY OF THE INVENTION

According to this invention, a salt that is useful as a burn rate modifier for $\text{NF}_3\text{-F}_2$ gas generators is provided. The salt is a fluorine containing salt having the formula $\text{N}_2\text{F}_3\text{SbF}_6$ and is prepared by reacting N_2F_4 and SbF_5 in anhydrous HF. Insofar as is known by the inventors, $\text{N}_2\text{F}_3\text{SbF}_6$ has not been previously synthesized.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preparation of the salt of this invention is illustrated by the following example.

EXAMPLE

Synthesis of $\text{N}_2\text{F}_3\text{SbF}_6$. A Teflon ampule, containing a Teflon coated magnetic stirring bar and equipped with a stainless steel valve, was loaded with 14.4 mmol of SbF_5 in a glovebox. The ampule was then attached to a

vacuum line and 2 ml of anhydrous HF was condensed into the ampule at -78°C . while stirring and warming to ambient temperature. The system was then pressurized with N_2F_4 (1 atm). A gradual decrease in the pressure was noted due to uptake of N_2F_4 . Periodic cycling to below 0°C . seemed to increase the rate of N_2F_4 uptake. After several hours the unreacted N_2F_4 and HF solvent were pumped off at 40°C . until constant weight was achieved. The observed weight gain corresponded to the reaction of 12.1 mmol of N_2F_4 . When the reaction was repeated on a larger scale with 8 ml HF for 3 days, it was found that 74.0 mmol of SbF_5 reacted with 73.5 mmol of N_2F_4 to give 23.66 g of $\text{N}_2\text{F}_3\text{SbF}_6$ (weight calcd for 74.0 mmol of $\text{N}_2\text{F}_3\text{SbF}_6$ 23.74 g), which was characterized by ^{19}F NMR and vibrational spectroscopy.

Tests in which small amounts of $\text{N}_2\text{F}_3\text{SbF}_6$ were incorporated into aluminized $\text{NF}_3\text{-F}_2$ gas generator compositions showed that the salt was effective as a burn rate modifier.

What is claimed is:

1. The salt having the formula:



2. A method for preparing the salt having the formula $\text{N}_2\text{F}_3\text{SbF}_6$ comprising the steps of:
forming a solution of N_2F_4 and SbF_5 in anhydrous HF; and
reacting the N_2F_4 and SbF_5 at room temperature.
3. A method according to claim 2 wherein the HF solvent is removed by distillation.

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APPENDIX EE

United States Patent [19]
Christe et al.

[11] **4,172,881**
[45] **Oct. 30, 1979**

[54] **DISPLACEMENT REACTION FOR
PRODUCING NF_4PF_6**

[75] **Inventors:** Karl O. Christe, Calabasas; Carl J.
Schack, Chatsworth, both of Calif.

[73] **Assignee:** Rockwell International Corporation,
El Segundo, Calif.

[21] **Appl. No.:** 849,377

[22] **Filed:** Nov. 7, 1977

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 732,275, Oct. 14, 1976,
abandoned.

[51] **Int. Cl.²** C01B 25/10

[52] **U.S. Cl.** 423/301; 423/351;
149/119

[58] **Field of Search** 423/301, 293, 351;
149/119

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dizer Research, 1/26/76, pp. A-1 to A-4, A-10 to
A-13, A-25, Cover Page.

Primary Examiner—O. R. Vertiz
Assistant Examiner—Thomas W. Roy
Attorney, Agent, or Firm—L. Lee Humphries; Robert M.
Sperry

[57] **ABSTRACT**

A method of producing NF_4PF_6 by a displacement
reaction between NF_4BF_4 and PF_5 .

1 Claim, No Drawings

DISPLACEMENT REACTION FOR PRODUCING NF_4PF_6

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 732,275 filed Oct. 14, 1976, and abandoned Dec. 5, 1977, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

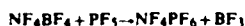
This invention relates to methods of producing compositions and is particularly directed to a method of producing NF_4PF_6 by a displacement reaction between NF_4BF_4 and PF_5 .

2. Description of the Prior Art

NF_4^+ salts are the key ingredients for solid propellant NF_3 - F_2 gas generators, such as that disclosed by D. Pilipovich in U.S. Pat. No. 3,963,542, for chemical HF-DF lasers. Whereas NF_4SbF_6 and NF_4AsF_6 can be prepared with relative ease, according to the methods taught by W. E. Tolberg et al, in U.S. Pat. No. 3,708,570, and K. O. Christe et al, in U.S. Pat. No. 3,503,719, these compounds suffer from the disadvantage of containing a relatively heavy anion, thus decreasing their performance in an NF_3 - F_2 gas generator. This disadvantage can be overcome by replacing the SbF_6^- or AsF_6^- anion by the lighter PF_6^- anion. The existence of this salt has previously been claimed by Tolbert et al in U. S. Pat. No. 3,708,570, but their production process was so inefficient that they could not isolate an amount of material sufficient for its isolation, identification and characterization.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

This problem of synthesizing NF_4PF_6 is overcome by the present invention. The method of the present invention involves a displacement reaction between the readily available NF_4BF_4 and PF_5 according to:



Applicants have found that the displacement reaction can be carried out at any temperature above the melting point of PF_5 (-94°C .) and below the decomposition temperature of NF_4PF_6 (above 245°C .) Moreover, the pressure is not essential and is given by the reaction temperature (that is, the vapor pressure of PF_5).

This method provides NF_4PF_6 of high purity.

Accordingly, it is an object of the present invention to provide an improved process for the production of NF_4PF_6 .

This and other objects and features of the present invention will be apparent from the following examples.

DETAILED DESCRIPTION OF THE INVENTION

In a typical experiment, pure NF_4BF_4 (2.07 mmol) was combined at -196°C . with an excess of PF_5 (40.01 mmol) in a 10-ml 316 stainless steel cylinder. The mixture was kept at 25°C . for 64 h. The volatile materials were removed in vacuo and separated by fractional condensation. They consisted of BF_3 (2.05 mmol) and

unreacted PF_5 (37.93 mmol). The white solid residue had gained 120 mg in weight. Based on the above material balance, the conversion of NF_4BF_4 to NF_4PF_6 was essentially complete. This was further confirmed by vibrational spectroscopy which showed the solid to be NF_4PF_6 containing no detectable amounts of NF_4BF_4 .

The salt NF_4PF_6 is a white, crystalline, hygroscopic solid, stable at room temperature, but rapidly decomposing at 245°C . Its characteristic x-ray diffraction powder pattern is listed in Table I. Its vibrational spectrum is listed in Table II and establishes the ionic nature of the salt, i.e. the presence of discrete NF_4^+ cations and PF_6^- anions. This was further confirmed by ^{19}F nmr spectroscopy in HF solution which showed the triplet ($J_{\text{NF}} = 230\text{ Hz}$ at $\phi = -217$) characteristic for NF_4^+ .

TABLE I

X-RAY POWDER DATA FOR NF_4PF_6			
d obsd	d calcd	Int	h k l
5.40	5.36	ms	1 1 0
4.55	4.53	s	1 0 1
3.91	3.89	vs	1 1 1
3.79	3.79	s	2 0 0
2.91	2.91	ms	2 1 1
2.65	2.65	m	1 0 2
2.40	2.40	vw	3 1 0
2.307	2.305	m	3 0 1
2.204	2.205	vw	3 1 1
2.171	2.171	mw	2 1 2
1.882	1.883	ms	3 0 2 0 3
1.825	1.827	vw	3 1 2 1 0 3
1.784	1.785	w	3 3 0
1.747	1.747	mw	4 1 1
1.685	1.685	w	3 2 2 0 3
1.646	1.646	w	2 1 3
1.622	1.622	w	4 2 1
1.536	1.540	vw	4 1 2
1.485	1.486	vw	5 1 0
1.464	1.463	vw	5 0 1
1.437	1.437	w	5 1 1
1.408	1.407	vw	5 2 0
1.365	1.365	vw	5 2 1 1 1 4
1.333	1.335	w	5 0 2
1.318	1.319	vw	4 4 0
1.302	1.304	vw	2 1 4
1.259	1.259	w	4 2 3
1.214	1.216	w	6 1 1

*Tetragonal. $a = 7.577$, $c = 5.653\text{ \AA}$. Cu K_α radiation Ni filter

TABLE II

VIBRATIONAL SPECTRUM OF NF_4PF_6		
Obsd Frequency (cm^{-1})	Assignments for $\text{NF}_4^+(\text{T}_d)$	
Ir	Raman	
2380 vw	}	$2\nu_3(\text{A}_1 + \text{E} + \text{F}_2) = 2320$
2320 w		
2005 w		$\nu_1 + \nu_3(\text{F}_2) = 2008$
1765 w		$\nu_3 + \nu_4(\text{A}_1 + \text{E} + \text{F}_2) = 1769$
1457 w		$\nu_1 + \nu_4(\text{F}_2) = 1457$
1221 mw		$2\nu_4(\text{A}_1 + \text{E} + \text{F}_2) = 1218$
1166 vs	}	$\nu_1(\text{F}_2)$
1135 vw		$\nu_2 + \nu_4(\text{F}_1 + \text{F}_2) = 1049$
1056 vw		$2\nu_2(\text{A}_1 + \text{A}_2 + \text{E}) = 880$
	880(0.2)	$\nu_1(\text{A}_1)$
	849(8.2)	
611 m	}	$\nu_4(\text{F}_2)$
608 m	}	$\nu_2(\text{E})$
	441(2.9)	

TABLE II-continued

VIBRATIONAL SPECTRUM OF NF_4PF_6

Assignments for PF_6^- (O_h)		
1590 w		$\nu_1 + \nu_3(\text{F}_{1u}) = 1590$
1414 w		$\nu_2 + \nu_3(\text{F}_{1u} + \text{F}_{2u}) = 1413$
1308 vw		$\nu_1 + \nu_4(\text{F}_{1u}) = 1307$
842 vs	838(1.5)	$\nu_3(\text{F}_{1u})$
789 w		
749 w	748(10)	$\nu_1(\text{A}_{1g})$
	571(0.8)	$\nu_2(\text{E}_g)$
559 s		$\nu_4(\text{F}_{1u})$
474 vw		

TABLE II-continued

VIBRATIONAL SPECTRUM OF NF_4PF_6 469(1.2) $\nu_5(\text{F}_{2g})$

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the form of the present invention described above is illustrative only and is not intended to limit the scope of the present invention.

We claim:

1. A process for the production of NF_4PF_6 characterized by combining NF_4BF_4 with an excess of PF_5 at above about -196°C ., reacting the reactants while warming the reaction system to a temperature less than about 25°C . and removing the volatile reaction products by pumping.

• • • • •

APPENDIX FF

United States Patent [19]

[11] **4,172,884**

Christe et al.

[45] **Oct. 30, 1979**

[54] **SELF-CLINKERING NF_4^+ COMPOSITIONS
FOR NF_3 - F_2 GAS GENERATORS AND
METHOD OF PRODUCING SAME**

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[21] **Appl. No.:** 927,713

[22] **Filed:** Jul. 24, 1978

Related U.S. Application Data

[62] Division of Ser. No. 734,153, Oct. 20, 1976, Pat. No.
4,152,406.

[51] **Int. Cl.²** C01G 19/00

[52] **U.S. Cl.** 423/351; 149/19.3;
149/119

[58] **Field of Search** 423/351; 149/19.3, 119

[56] References Cited

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Primary Examiner—Edward A. Miller
Attorney, Agent, or Firm—L. Lee Humphries; Robert M.
Sperry

[57] ABSTRACT

Improved NF_4^+ compositions for solid propellant NF_3 - F_2 gas generators are described which produce NF_3 and F_2 free of gaseous Lewis acids and do not require clinker forming additives for their complexing. The novel self-clinkering compositions $(\text{NF}_4)_2\text{SnF}_6$, NF_4SnF_5 , $(\text{NF}_4)_2\text{TiF}_6$, $\text{NF}_4\text{Ti}_2\text{F}_9$, $\text{NF}_4\text{Ti}_3\text{F}_{13}$, and $\text{NF}_4\text{Ti}_6\text{F}_{25}$ and processes for their production are disclosed.

5 Claims, No Drawings

SELF-CLINKERING NF_4^+ COMPOSITIONS FOR NF_3 - F_2 GAS GENERATORS AND METHOD OF PRODUCING SAME

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of Ser. No. 734,153 filed Oct. 20, 1976, and now U.S. Pat. No. 4,152,406.

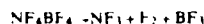
BACKGROUND OF THE INVENTION

1. Field of the Invention

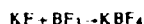
This invention relates to compositions of matter and methods of producing the same and is particularly directed to improved solid propellant NF_3 - F_2 gas generators derived from self-clinkering NF_4^+ salts, together with methods for producing such gas generators.

2. Description of the Prior Art

NF_4^+ salts are the key ingredients for solid propellant NF_3 - F_2 gas generators, as shown by D. Pilipovich 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 for 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 byproduct is shared by all 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, heretofore, this would be achieved by adding a clinker forming agent, such as KF, to the solid propellant formulation. The function of this additive served to convert the volatile Lewis acid, such as BF_3 , to a non-volatile salt as shown by the following equation:

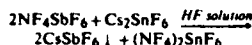


The principal disadvantages of this approach are that, even if an excess of KF is used, complete clinkering cannot always be guaranteed, and that the addition of the KF severely degrades the yield of NF_3 - F_2 obtainable per pound of formulation. This problem could be solved by using NF_4^+ containing compositions derived from non-volatile Lewis acids. However, the synthesis of such compositions has previously been unknown, since highly stable and non-volatile Lewis acids are polymeric and contain coordination-wise saturated central atoms. Consequently, these compounds possess very little or no acidity, which renders the synthesis of such salts very difficult

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

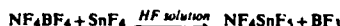
The above described problem of obtaining a Lewis acid free NF_3 - F_2 gas stream from NF_4^+ compositions without clinker forming additives is overcome by the present invention. We have found that NF_4^+ salts, derived from the polymeric non-volatile Lewis acids SnF_4 (subliming at 704°C .) and TiF_4 (1 atm vapor pressure at 284°C .) can be prepared. The lack of acidity of SnF_4 at temperatures, at which NF_4^+ salts can be formed and exist, was demonstrated. It was shown that mixtures of NF_3 , F_2 , and SnF_4 , when heated to temperatures of up to 300°C . at autogenous pressures of about 150 atm, did not show any evidence for NF_4^+ formation.

Since a direct synthesis of an NF_4^+ salt derived from SnF_4 was not possible, we have studied metathetical and displacement reactions. Because SnF_6^{2-} salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. The following methathetical reaction

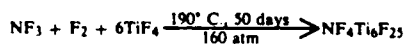


was carried out. It resulted in the precipitation of the rather insoluble salt CsSbF_6 , while the soluble $(\text{NF}_4)_2\text{SnF}_6$ remained in solution. The two products were separated by a simple filtration step. The composition (in mol%) of the crude product was: $(\text{NF}_4)_2\text{SnF}_6$, 83; NF_4SbF_6 , 13; CsSbF_6 , 4. The purity of this product can be easily increased by following the procedures outlined for NF_4BF_4 in our co-pending application Serial No. , filed

Another NF_4^+ salt derived from SnF_4 was obtained by the following quantitative displacement reaction in anhydrous HF as a solvent.



For TiF_4 , the direct synthesis of an NF_4^+ salt from NF_3 , F_2 , and TiF_4 is still possible, since TiF_4 possesses already some vapor pressure at temperatures where NF_4^+ salts can be formed. However, the product thus obtained is very rich in TiF_4 , as shown by the following equation:



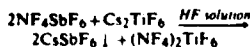
The NF_4^+ content of this salt could not be significantly increased by any changes in the reaction conditions.

Displacement reactions between NF_4BF_4 and TiF_4 , either in HF solution or in the absence of a solvent, produced NF_4^+ salts according to



where, depending on the exact reaction conditions, n equals either 3 or 2.

A further increase in the NF_4^+ content was possible by the following metathetical reaction which yielded $(\text{NF}_4)_2\text{TiF}_6$:



The separation and purification procedure for this product is analogous to that outlined above for $(\text{NF}_4)_2\text{SnF}_6$.

The advantages of the above disclosed concept of using these novel self-clinkering NF_4^+ composition for $\text{NF}_3\text{--F}_2$ gas generators become obvious from a comparison of their theoretical performance data. In Table I, the theoretical yields of usable fluorine, expressed in weight percent, of $(\text{NF}_4)_2\text{SnF}_6$ and $(\text{NF}_4)_2\text{TiF}_6$ are compared to that of KF clinkered NF_4BF_4 , the highest performing presently known system. The novel self-clinkering compositions clearly outperform KF clinkered NF_4BF_4 . Furthermore, the risk of incomplete clinkering which always exists for a clinkered formulation is avoided.

TABLE I

A COMPARISON OF THE THEORETICAL PERFORMANCE OF SELF-CLINKERING $(\text{NF}_4)_2\text{SnF}_6$ AND $(\text{NF}_4)_2\text{TiF}_6$ WITH KF-CLINKERED NF_4BF_4

System	Performance (Weight % Usable F)
$\text{NF}_4\text{BF}_4 \cdot 12\text{KF}$	38.5
$(\text{NF}_4)_2\text{SnF}_6$	46.0
$(\text{NF}_4)_2\text{TiF}_6$	55.6

Accordingly, it is an object of the present invention to provide higher performing solid propellant $\text{NF}_3\text{--F}_2$ gas generator compositions.

Another object of the present invention is to provide self-clinkering NF_4^+ compositions capable of generating Lewis acid free NF_3 and F_2 .

Another object of the present invention is to provide processes for the production of self-clinkering NF_4^+ compositions.

These and other objects and features of the present invention will be apparent from the following examples. 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.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLE I

Metathetical reactions were carried out in an apparatus consisting of three Teflon FEP U-traps interconnected by Monel unions and closed off at each end by a Monel valve. The union between trap II and trap III contained a Teflon filter and was held in place by a press fit. The passivated apparatus was taken to the dry box and Cs_2SnF_6 and NF_4SbF_6 (in a 1:2 mole ratio) were placed into traps I and II, respectively. The apparatus was connected to the vacuum line through flexible corrugated Teflon FEP tubing. Anhydrous HF, in an amount sufficient to just dissolve the starting materials, was added to traps I and II. Trap I was flexed to allow the Cs_2SnF_6 solution to run into trap II containing the NF_4SbF_6 solution. Upon contact of the two solutions, copious amounts of a white precipitate (CsSbF_6) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to -80°C . After completion of the filtration step, trap III was warmed to ambient temperature and the HF solvent was pumped off. The solid residue on top of the filter consisted mainly of CsSbF_6 , whereas the solid collected in trap II was mainly the desired $(\text{NF}_4)_2\text{SnF}_6$.

The following example gives a typical product distribution obtainable with the above procedure and apparatus.

Starting materials: NF_4SbF_6 (9.72 mmol), Cs_2SnF_6 (4.86 mmol); weight of solid on filter = 4.24 g; weight of solid in trap III = 1.36 g (weight calcd for 4.86 mmol of $(\text{NF}_4)_2\text{SnF}_6$ = 2.01 g). Elemental analysis for solid from trap III. Found: NF_3 , 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3. Calculated analysis for a mixture (mol %) of 82.8 $(\text{NF}_4)_2\text{SnF}_6$, 12.9 NF_4SbF_6 , and 4.3 CsSbF_6 . NF_3 , 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43.

$(\text{NF}_4)_2\text{SnF}_6$ is a white, crystalline, hygroscopic solid, stable at room temperature but decomposing at 240°C . Its characteristic x-ray powder pattern is listed in Table II. Its ionic composition, i.e. the presence of discrete NF_4^+ cations and SnF_6^{2-} anions was established by ^{19}F nmr, infrared and Raman spectroscopy.

The ^{19}F nmr spectrum, recorded for a BrF_3 solution, showed in addition to the solvent lines a triplet of equal intensity with $\phi = -220$, $J_{\text{NF}} = 229.6$ Hz, and a line width at half height of about 5 Hz, which is characteristic of tetrahedral NF_4^+ . In addition, a narrow singlet at $\phi = 149$ was observed with the appropriate $^{117/119}\text{Sn}$ satellites (average $J_{\text{SnF}} = 1549$ Hz), characteristic of octahedral SnF_6^{2-} . The vibrational spectra of $(\text{NF}_4)_2\text{SnF}_6$ and their assignments are summarized in Table III.

EXAMPLE II

A mixture of NF_4BF_4 and SnF_4 (9.82 mmol each) was placed into a passivated Teflon-FEP ampoule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10 ml liquid) was added at -78°C , and the resulting suspension was stirred at 25°C for 2 hours. The volatile material was pumped off at 35°C leaving behind a white stable solid which, on the basis of its weight (3.094 g) and Raman spectrum, consisted of 83 mol percent NF_4SnF_5 and 17 mol percent unreacted starting materials. The HF treatment was repeated (again for 2 hours) and the non-volatile residue (2.980 g, weight calcd for 9.82 mmol of NF_4SnF_5 = 2.982 g) was shown by infrared, Raman, and ^{19}F nmr spectroscopy to be essentially pure NF_4SnF_5 . Anal. Calcd for NF_4SnF_5 : NF_3 , 23.38; Sn, 39.08. Found: NF_3 , 23.6; Sn, 38.7.

TABLE II

X-RAY POWDER DATA FOR $(\text{NF}_4)_2\text{SnF}_6$			
d obsd	d calcd	Int	h k l
6.27	6.36	w	1 1 1
5.67	5.70	vs	0 0 2
4.99	5.04	vw	1 0 2
3.67	3.69	w	2 1 2
3.55	3.59	s	1 0 3
3.42	3.42	s	3 1 0
2.990	2.990	s	2 1 3
2.851	2.851	ms	0 0 4
2.492	2.490	m	3 3 1
2.347	2.356	w	3 2 3
2.230	2.228	s	4 2 2
2.120	2.123	mw	5 1 0
2.023	2.024	mw	5 0 2
1.961	1.963	w	4 0 4
1.917	1.914	m	4 4 0
1.882	1.881	mw	5 0 3
1.834	1.832	w	5 3 1
1.813	1.814	mw	4 4 2
1.763	1.765	vw	5 3 2
1.712	1.712	w	6 2 0
1.686	1.686	m	5 4 0, 3 0 6
1.662	1.662	m	3 1 6
1.616	1.614	mw	6 3 0
1.570	1.570	mw	5 0 5
1.500	1.501	mw	6 4 0
1.397	1.396	mw	6 4 3

TABLE II-continued

X-RAY POWDER DATA FOR $(\text{NF}_4)_2\text{SnF}_6$ ^a			
d obsd	d calcd	Int	h k l
1 387	1 386	w	6 5 0
1 359	1 359	mw	7 0 6, 5 4 5
1 331		mw	
1 314		mw	
1 263		w	
1 231		w	
1 212		mw	
1 192		w	
1 177		mw	

^a tetragonal $a = 10.828 \text{ \AA}$, $c = 11.406 \text{ \AA}$, Cu K α radiation Ni filter

TABLE III

Vibrational Spectra of Solid $(\text{NF}_4)_2\text{SnF}_6$			
Obsd Freq (cm^{-1}) and Rel Inten		Assignments (Point Group)	
IR	Raman	$\text{NF}_4^+ (\text{T}_d)$	$\text{SnF}_6^{2-} (\text{O}_h)$
1224 mw		$2\nu_4 (\text{A}_1 + \text{E} + \text{F}_2)$	
1190 vs	1158 (1.5)	$\nu_3 (\text{F}_2)$	$\nu_1 + \nu_3 (\text{F}_{1u})$
1132 sh, vw			
1059 vw		$\nu_2 + \nu_4 (\text{F}_1 + \text{F}_2)$	$\nu_2 + \nu_3 (\text{F}_{1u} + \text{F}_{2u})$
1026 vw			
	811 (0.1)	$2\nu_2 (\text{A}_1 + \text{A}_2 + \text{E})$	
854 vvw	853 (10)	$\nu_1 (\text{A}_1)$	
613 mw	613 (5.0)		
605 mw	607 (1.5)	$\nu_4 (\text{F}_2)$	$\nu_1 (\text{A}_{1g})$
	579 (8.3)		$\nu_3 (\text{F}_{1u})$
550 vs			$\nu_2 (\text{E}_g)$
	470 (0+) br		
	449 (3.1)		
	442 (2.9)	$\nu_2 (\text{E})$	
	251 (3.3)		$\nu_3 (\text{F}_{2g})$
	84 (0.3)	Lattice Vibration	

NF_4SnF_5 is a white, crystalline, hygroscopic solid, stable at room temperature and decomposing above 200°C . Its characteristic x-ray powder pattern is listed in Table IV.

TABLE IV

X-RAY POWDER DATA FOR NF_4SnF_5			
d obsd	Int	d obsd	Int
7.72	mw	2.571	mw
6.32	vs	2.519	vw
5.69	w	2.276	w
5.29	w	2.146	w
4.51	m	2.064	ms
4.19	m	1.965	mw
3.80	vs	1.929	w
3.46	m	1.820	m
3.32	m	1.780	mw
3.17	mw	1.757	mw
2.868	w	1.732	mw
2.802	w	1.700	mw
2.743	m	1.661	vw
2.683	w	1.639	w
		1.615	w

Its ionic structure, i.e., presence of NF_4^+ cations, was established by its ^{19}F nmr spectrum in BrF_3 solution. In addition to the solvent lines, it showed the triplet (see above) at $\phi = -220$, characteristic of NF_4^+ . Two resonances were observed for SnF_5^- at $\phi = 145.4$ and 162.4 , respectively, with an area ratio of 1:4. At -20°C , the resonances consisted of broad lines, but at lower temperatures the $\phi = 162.4$ signal showed splittings. Based on a more detailed analysis of these data, the SnF_5^- anion appears to have a dimeric or polymeric structure. The vibrational spectrum of NF_4SnF_5 is listed in

Table V and again establishes the presence of discrete NF_4^+ cations.

EXAMPLE III

When a mixture of NF_4BF_4 and SnF_4 in a mol ratio of 2:1 was treated 8 times, as described in Example II, with liquid HF for a total of 35 days, the resulting non-volatile residue consisted mainly of NF_4SnF_5 , unreacted NF_4BF_4 , and only a small amount of $(\text{NF}_4)_2\text{SnF}_6$.

EXAMPLE IV

The metathetical synthesis of $(\text{NF}_4)_2\text{TiF}_6$ from saturated HF solutions of NF_4SbF_6 (10.00 mmol) and

Cs_2TiF_6 (5.00 mmol) was carried out in the apparatus described in Example I for the synthesis of $(\text{NF}_4)_2\text{SnF}_6$. After combination of the solutions of the two starting materials at room temperature and formation of a CsSbF_6 precipitate, the mixture was cooled to -78°C . and filtered. The volatile materials were pumped off at 50°C . for 1 hour. The filter cake (3.85 g) was shown by its x-ray powder diffraction pattern and vibrational spectroscopy to be mainly CsSbF_6 containing, due to the hold up of some mother liquor, a small amount of $(\text{NF}_4)_2\text{TiF}_6$. The filtrate residue (1.55 g, weight calcd for 5 mmol of $(\text{NF}_4)_2\text{TiF}_6 = 1.71 \text{ g}$) had the composition (mol%): 88.5 $(\text{NF}_4)_2\text{TiF}_6$ and 11.5 CsSbF_6 . Found: NF_3 , 36.2; Ti, 12.21; Sb, 4.11; Cs, 4.4. Calcd for a mixture of 88.5 $(\text{NF}_4)_2\text{TiF}_6$ and 11.5 CsSbF_6 : NF_3 , 36.43; Ti, 12.29; Sb, 4.06; Cs, 4.43. Based on the observed Raman spectrum, the composition of the filtrate residue was estimated to be 90 $(\text{NF}_4)_2\text{TiF}_6$ and 10 CsSbF_6 , in good agreement with the above elemental analysis.

$(\text{NF}_4)_2\text{TiF}_6$ is a white, crystalline, hygroscopic solid, stable at room temperature, but decomposing above 200°C . Its characteristic x-ray powder pattern is listed in Table VI.

TABLE V

Vibrational Spectra of Solid NF_4SnF_5			
Obsd Freq (cm^{-1}) and Rel Inten		Assignments (Point Group)	
IR	Raman	$\text{NF}_4^+ (\text{T}_d)$	
1222 mw		$2\nu_4 (\text{A}_1 + \text{F} + \text{F}_2)$	
1165 vs	1168 (0.4) 1159 (0.8) 1150 sh	$\nu_3 (\text{F}_2)$	
1134 w, sh			

TABLE V-continued

Vibrational Spectra of Solid NF_4SnF_3		
Obsd Freq (cm^{-1}) and Rel Intens		Assignments (Point Group)
IR	Raman	$\text{NF}_4^+ (\text{T}_d)$
1061 w		$\nu_2 + \nu_4 (\text{F}_1 + \text{F}_2)$
1048 w		
850 vw	881 (0.2)	$2\nu_2 (\text{A}_1 + \text{A}_2 + \text{E})$
635 vs	851 (10)	$\nu_1 (\text{A}_1)$
	622 (9.2)	
605 mw	606 (3.1)	$\nu_4 (\text{F}_2)$
575 vs		
	574 (0.5)	
	558 (2.0)	
559 w, sh		
490 m	490 (0+)	
458 m		
	448 (2.5)	$\nu_2 (\text{E})$
	440 (2.3)	
	272 (0.6)	
	247 (1.4)	
	222 (1.1)	
	197 (0.6)	
	154 (0+)	
	135 (0.2)	

TABLE VI

X-RAY POWDER DATA FOR $(\text{NF}_4)_2\text{TiF}_6$				
d obsd	d calcd	Int	h k l	
6.23	6.26	vw	1 1 1	
5.57	5.56	vs	0 0 2	
4.93	4.93	w	1 0 2	
3.49	3.50	s	1 0 3	
3.39	3.39	s	3 1 0	
2.94	2.93	ms	2 1 3	
2.782	2.778	m	0 0 4	
2.465	2.463	w	3 3 1	
2.315	2.318	mw	3 2 3	
2.201	2.200	s	4 2 2	
2.100	2.101	w	5 1 0	
1.990	1.990	vw	5 2 0, 5 0 2	
1.892	1.894	m	4 4 0	
1.789	1.789	mw	6 0 0, 4 4 2	
1.663	1.664	mw	2 2 6	
1.641	1.644	mw	3 0 6	

*tetragonal. a = 10.715 Å, c = 11.114 Å. Cu K_α radiation Ni filter

Its ionic structure, i.e. the presence of discrete NF_4^+ cations and TiF_6^{2-} anions was established by ^{19}F nmr and vibrational spectroscopy. The ^{19}F nmr spectrum showed the triplet at $\phi = -220$, characteristic for NF_4^+ as shown above, and the characteristic TiF_6^{2-} signal at $\phi = -81.7$. The vibrational spectra are listed in Table VII.

TABLE VII

VIBRATIONAL SPECTRA OF SOLID $(\text{NF}_4)_2\text{TiF}_6$			
Obsd Freq (cm^{-1}) and Rel Intens		Assignments (Point Group)	
IR	Raman	$\text{NF}_4^+ (\text{T}_d)$	$\text{TiF}_6^{2-} (\text{O}_h)$
1219 mw		$2\nu_4 (\text{A}_1 + \text{E} + \text{F}_2)$	
1160 vs	1158 (1.4)		
1132 sh, vw		$\nu_3 (\text{F}_2)$	
1060 vw		$\nu_2 + \nu_4 (\text{F}_1 + \text{F}_2)$	
1021 w			
910 vw			$\nu_1 + \nu_4 (\text{F}_{1g})$
	883 (0.1)	$2\nu_2 (\text{A}_1 + \text{A}_2 + \text{E})$	
850 sh, vw	853 (10)	$\nu_1 (\text{A}_1)$	
804 w			
611 mw	612 (5)	$\nu_4 (\text{F}_2)$	
	607 sh		

TABLE VII-continued

VIBRATIONAL SPECTRA OF SOLID $(\text{NF}_4)_2\text{TiF}_6$			
Obsd Freq (cm^{-1}) and Rel Intens		Assignments (Point Group)	
IR	Raman	$\text{NF}_4^+ (\text{T}_d)$	$\text{TiF}_6^{2-} (\text{O}_h)$
563 vs	601 (8.0)		$\nu_1 (\text{A}_{1g})$
452 vw	450 (3.3)		$\nu_3 (\text{F}_{1g})$
	442 (2.6)	$\nu_2 (\text{E})$	
	289 (8.2)		$\nu_3 (\text{F}_{2g})$
	107 (0+)		
	86 (2)		Lattice Vibrations

EXAMPLE V

TiF_4 (11.3 mmol), NF_3 (200 mmol), and F_2 (200 mmol) were heated in a passivated 90 ml Monel cylinder to various temperatures for different time periods. After each heating cycle, the volatile products were temporarily removed and the progress of the reaction was followed by determining the weight gain of the solid and recording its vibrational spectra. Heating to 200°C . for 3 days resulted in a weight gain of 8 mg and the vibrational spectra showed mainly unreacted TiF_4 in addition to a small amount of NF_4^+ and a polyperfluorotitanate (IV) anion (probably $\text{Ti}_6\text{F}_{25}^-$) having its strongest Raman line at 784 cm^{-1} . During the next two heating cycles (190° – 195°C . for 14 days and 180°C . for 35 days) the solid gained 149 and 41 mg, respectively, in weight. The vibrational spectra did not show any evidence of unreacted TiF_4 , and the relative intensities of the bands due to NF_4^+ had significantly increased. Furthermore, the 784 cm^{-1} Raman line had become by far the most intense Raman line. Additional heating to 230°C . for 3 days did not result in significant changes in either the weight or the vibrational spectra of the solid. Based on the observed weight increase and on the lack of spectroscopic evidence for the presence of lower polyperfluorotitanate (IV) anions, the solid product appears to have the approximate composition $\text{NF}_4\text{Ti}_6\text{F}_{25}$ (calcd weight increase, 205 mg; obsd weight increase 198 mg).

EXAMPLE VI

Displacement reactions were carried out either in HF solution at room temperature or by heating the starting materials in the absence of a solvent in a Monel cylinder. For the HF solution reactions, the solid starting materials (6 mmol of NF_4BF_4 in each experiment) were placed in a passivated Teflon FEP ampoule and 15 ml of liquid anhydrous HF was added. The mixture was stirred with a Teflon coated magnetic stirring bar at room temperature for a given time period. The volatile products were pumped off at 50°C . for 3 hours and the composition of the solid residue was determined by elemental and spectroscopic analyses and from the observed material balances.

The thermal displacement reactions were carried out in a prepassivated 90 ml Monel cylinder which was heated in an electric oven for a specified time period. The volatile products were separated by fractional condensation in a vacuum line, measured by PVT, and identified by infrared spectroscopy. The solid residues were weighed and characterized by elemental and spectroscopic analyses. The results of these experiments are summarized in Table VIII.

TABLE VIII

RESULTS FROM THE DISPLACEMENT REACTIONS BETWEEN NF_4BF_4 AND TiF_4		
Reactants (mol)	Reaction Conditions	Products (mol)
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(6)$	HF, 24° C., 18h	$\text{NF}_4\text{Ti}_2\text{F}_9(4)$, $\text{NF}_4\text{BF}_4(4)$
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(12)$	HF, 24° C., 72h	$\text{NF}_4\text{Ti}_2\text{F}_9(6)$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(6)$	HF, 24° C., 138h	$\text{NF}_4\text{Ti}_3\text{F}_{13}(-2)$, $\text{NF}_4\text{BF}_4(-4)$, small amount of $\text{NF}_4\text{Ti}_2\text{F}_9$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(12)$	HF, 24° C., 96h	$\text{NF}_4\text{Ti}_3\text{F}_{13}(4)$, $\text{NF}_4\text{BF}_4(2)$
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(6)$	190° C., 18h	$\text{NF}_4\text{Ti}_2\text{F}_9(-3)$, $\text{NF}_3(-3)$, $\text{BF}_3(-6)$, small amounts of NF_4BF_4 and $\text{NF}_4\text{Ti}_3\text{F}_{13}$
$\text{NF}_4\text{BF}_4(6)$, untreated $\text{TiF}_4(6)$	160° C., 60h	$\text{NF}_4\text{Ti}_3\text{F}_{13}(2)$, $\text{NF}_4\text{BF}_4(1.4)$, $\text{NF}_3(2.6)$, $\text{BF}_3(4.6)$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(6)$	170° C., 20h	$\text{NF}_4\text{Ti}_2\text{F}_9(3)$, $\text{NF}_4\text{BF}_4(3)$, $\text{BF}_3(3)$
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(12)$	170° C., 20h	
	$\text{NF}_4\text{Ti}_2\text{F}_9(3.6)$, $\text{NF}_4\text{Ti}_3\text{F}_{13}(1.6)$	
$\text{NF}_4\text{BF}_4(6)$, prefluor. $\text{TiF}_4(12)$	170° C., 192h	$\text{BF}_3(5.4)$, $\text{NF}_4\text{BF}_4(0.6)$ $\text{NF}_4\text{Ti}_2\text{F}_9(6)$, $\text{BF}_3(6)$

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. A compound for use in an improved NF_3-F_2 gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is derived from SnF_4 and is self-clinkering.

2. A compound for use in an improved NF_3-F_2 gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is SnF_6^{2-} and is self-clinkering.

3. A compound for use in an improved NF_3-F_2 gas generator, said compound having the general composition $(\text{NF}_4^+)_n\text{A}^{n-}$, wherein A^{n-} is SnF_5^- and is self-clinkering.

4. A process for the production of $(\text{NF}_4^+)_2\text{SnF}_6^{2-}$, comprising the steps of combining a soluble NF_4^+X^- salt with a soluble alkali metal salt of SnF_6^{2-} in a suitable solvent to produce an insoluble alkali metal X salt, and filtering off the precipitated insoluble alkali metal X salt from the solution containing the soluble $(\text{NF}_4^+)_2\text{SnF}_6^{2-}$ salt.

5. A process for the production of NF_4SnF_5 , comprising the steps of treating NF_4BF_4 in an anhydrous HF solution with an equimolar amount of SnF_4 and removing all products volatile at room temperature.

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United States Patent [19]

[11] 4,207,124

Christe

[45] Jun. 10, 1980

[54] HIGH DETONATION PRESSURE
EXPLOSIVES

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[73] Assignee: The United States of America as
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Navy, Washington, D.C.

[21] Appl. No.: 902,642

[22] Filed: May 4, 1978

[51] Int. Cl.² C06B 25/34

[52] U.S. Cl. 149/92; 149/88;

149/119

[58] Field of Search 149/92, 119, 19.1, 19.9,

149/88

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[57] ABSTRACT

Insensitive, high performance explosives obtained by combining certain energetic, high density inorganic compounds with insensitive, underoxidized organic nitro compounds.

7 Claims, No Drawings

HIGH DETONATION PRESSURE EXPLOSIVES

BACKGROUND OF THE INVENTION

1. Field of the Invention.

This invention relates to insensitive, high performance explosives.

2. Description of the Prior Art.

The use of organic nitro compounds as explosives is well known. These compounds are self-oxidizing, i.e., the nitro groups provide the oxygen used in oxidation.

The highest detonation pressures achievable with the currently used organic nitro compounds are about 390 kbar. Further, the best performers (those from which detonation pressures approaching 390 Kbar are achievable) are highly sensitive. Thus, the use of the highest performing organic nitro compounds as explosives is risky and impractical. On the other hand, the lower performing explosives which possess acceptable stability are, without exception, underoxidized and generally exhibit low densities. The densities of the stable explosives are generally less than two grams per cm³. These two factors, i.e., the underoxidized nature of the stable organic nitro compounds and their low densities, severely limit their performance.

SUMMARY OF THE INVENTION

It has now been found that the performance of explosives based on commonly used organic nitro compounds can be increased to about 530 kbar by adding certain dense and stable but highly energetic inorganic oxidizers. Among the suitable oxidizers are: (NF₄)₂TiF₆, NF₄BF₄, Ti(ClO₄)₄, (NF₄)₂NiF₆ and other hereinafter named compounds.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typical examples of performance increases achievable by the use of the inorganic oxidizers of this invention are illustrated in the following table.

TABLE

Examples of Theoretical Performance Improvements		
System	Weight %	Detonation Pressure (kb)
Nitroguanidine (NQ)	100	255
NQ + (NF ₄) ₂ TiF ₆	43-57	349
Triaminotrinitrobenzene (TATB)	100	280
TATB + NF ₄ BF ₄	29-71	375
TATB + (NF ₄) ₂ TiF ₆	30-70	408
HMX	100	382
HMX + NF ₄ BF ₄	51-49	449
HMX + Ti(ClO ₄) ₄	70-30	456
HMX + (NF ₄) ₂ TiF ₆	52-48	471
HMX + (NF ₄) ₂ NiF ₆	56-44	527

The detonation pressures set forth in the foregoing table were calculated by means of the Kamlet correlation (*J. Chem. Phys.*, 48, 23 (1968)), a method commonly used for the performance evaluation of explosives. The percentage of oxidizer used was chosen to obtain complete combustion of the organic nitro compound (to CO₂, N₂ and HF in the case of HMX or NQ and to COF₂, N₂ and HF in the case of TATB). As can be seen from the table, the performance of organic nitro explosives is significantly increased by the addition of dense energetic inorganic oxidizers.

Laboratory tests have shown that the oxidizers and explosives are mutually compatible. For example, HMX

and NF₄BF₄ were found to be stable at 150° C. and drop weight tests of the HMX/NF₄BF₄ mixtures showed only a moderate increase in sensitivity over that of pure HMX.

The examples given in the above table are illustrative only and are not intended to limit the scope of the invention. Other commonly used, underoxidized organic nitro compounds of suitable stability could be substituted for the explosives given as examples in the table. Similarly, other inorganic oxidizers could be substituted for those listed in the table.

The primary requirements for suitable oxidizers are high energy content, high density, high thermal stability and low reactivity with the organic nitro compounds. From this point of view, NF₄⁺ containing salts are ideally suited. The NF₄⁺ cation is isoelectronic with the extremely inert CF₄ molecule and, therefore, in spite of its high energy content, a relatively high activation energy is required to cause it to react with other compounds.

The concept of this invention is not limited to fluorine containing oxidizers. As can be seen from the example of Ti(ClO₄)₄ in the table, this fluorine-free oxidizer is equally useful. By analogy with the NF₄⁺ salts, Ti(ClO₄)₄ possesses all the necessary properties for use as an explosive ingredient.

Although oxygen containing oxidizers will be as effective as fluorine containing oxidizers in most explosives, fluorine containing oxidizers are advantageous in aluminized formulations. The addition of aluminum is known to increase the performance of an explosive, but the Al₂O₃ combustion product formed in a fluorine-free system may not remain for a long enough time in the gas phase. AlF₃, on the other hand, is formed as a combustion product when fluorine containing oxidizers are used. Since AlF₃ (sublimation point 1270° C.) is much more volatile than Al₂O₃ (boiling point 2250° C.), the use of fluorine containing oxidizers offers a distinct advantage for aluminized systems in that efficiencies higher than those obtainable with oxygen containing oxidizers are achieved.

It has been stated above that the oxidizers listed in the table are illustrative only. Examples of other suitable oxidizers are NF₄⁺ salts such as: NF₄SbF₆, NF₄SbF₆, NF₄HF₂, NF₄BiF₆, NF₄PF₆, NF₄GeF₅, NF₄AsF₆, NF₄Ti₂F₉, NF₄Ti₃F₁₃, NF₄Ti₆F₂₅, (NF₄)₂SnF₆ and NF₄SnF₅ and other metal perchlorates.

The salts disclosed herein are not soluble in organic nitro compounds so their use in liquid explosives in conjunction with liquid organic compounds is not possible. However, they may be used in plastic bonded (solid) explosives of the type wherein explosive ingredients are bound in a suitable binder (many of which are known in the art) and in slurries where oxidizer particles are suspended in liquid organic nitro compounds.

What is claimed is:

1. An explosive composition comprising an explosive organic nitro compound, and enough of a dense inorganic oxidizer having an NF₄⁺ ion in conjunction with said organic nitro compound to improve detonation pressure.

2. An explosive composition according to claim 1 wherein said NF₄⁺ containing oxidizer is selected from the group consisting of (NF₄)₂TiF₆, NF₄BF₄, (NF₄)₂NiF₆, NF₄SbF₆, NF₄SbF₆, NF₄HF₂, NF₄BiF₆, NF₄PF₆, NF₄GeF₅, NF₄AsF₆, NF₄Ti₂F₉, NF₄Ti₃F₁₃, NF₄Ti₆F₂₅, (NF₄)₂SnF₆ and NF₄SnF₅.

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3. An explosive composition according to claim 1 which is a slurried explosive wherein particles of said dense inorganic oxidizer are suspended in a liquid organic nitro compound.

4. An explosive composition according to claim 1 wherein said organic nitro compound is selected from the group consisting of triaminotrinitrobenzene, nitroguanidine and cyclotetra-ethylenetetranitramine.

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5. An explosive composition according to claim 4 wherein said organic nitro compound is nitroguanidine and said dense inorganic oxidizer is $(\text{NF}_4)_2\text{TiF}_6$.

6. An explosive composition according to claim 1 wherein said organic nitro compound is triaminotrinitrobenzene and said dense inorganic oxidizer is selected from the group consisting of NF_4BF_4 and $(\text{NF}_4)_2\text{TiF}_6$.

7. An explosive composition according to claim 1 wherein said organic nitro compound is HMX and said dense inorganic oxidizer is selected from the group consisting of NF_4BF_4 , $(\text{NF}_4)_2\text{TiF}_6$ and $(\text{NF}_4)_2\text{NiF}_6$.

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APPENDIX HH

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