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R-77-112

ANNUAL REPORT
INORGANIC HALOGEN OXIDIZER RESEARCH
(1 January 1976 through 31 December 1976)

4 February 1977

Contract N00014-70-C-0294
G.O. 09263

Office of Naval Research
Power Branch
Code 429

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121

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
R-77-112

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
ANNUAL REPORT, INORGANIC HALOGEN OXIDIZER RESEARCH

5. TYPE OF REPORT & PERIOD COVERED
Annual Report, 1 January 1976 through 31 December 1976

6. PERFORMING ORG. REPORT NUMBER
R-77-112

7. AUTHOR(s)
K. O. Christe, C. J. Schack, and R. D. Wilson

8. CONTRACT OR GRANT NUMBER(s)
N00014-70-C-0294

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Rocketdyne Division, Rockwell International
6633 Canoga Avenue
Canoga Park, California 91304

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research Power Branch

12. REPORT DATE
4 February 1977

13. NUMBER OF PAGES

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)
UNCLASSIFIED

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Synthesis, Novel Oxidizers, Solid Propellant Fluorine Gas Generators, Perfluoroammonium Salts, Fluoronickelates, Fluorostannates, Fluorotitanates, Fluoroborates, Fluorobismutates, Fluoroantimonates, Oxytetrafluorobromate, Chlorine Trifluoride Oxide, Thionyl Tetrafluoride, Sulfur Pentafluoride Bromide, Tungsten Hexafluoride, Molybdenum Hexafluoride, Oxonium Salts, Tungsten Hexaperchlorate.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The novel NF_4^+ salts $(NF_4)_2NiF_6$, $(NF_4)_2TiF_6$, $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, $NF_4Ti_6F_{25}$, and NF_4SnF_5 were synthesized and characterized. The $(NF_4)_2NiF_6$ and $(NF_4)_2TiF_6$ salts are of significant interest as ingredients in solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers. The nickel salt represents the first successful combination of both an energetic perfluoro cation and anion in the form of a stable salt. The theoretical usable fluorine content of this salt is 68 percent higher than that obtainable with KF clinkered NF_4BF_4, the best previously known

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20. ABSTRACT (continued)

system. On thermal decomposition, one cm^3 of solid $(NF_4)_2NiF_6$ is capable of producing 1.5 times as much useful fluorine, i.e. in the form of NF_3 and F_2, as liquid F_2 at -187 C. The metathetical NF_4BF_4 process was refined and high purity (> 99%) metathetical NF_4BF_4 was obtained for the first time, thus eliminating the major drawback of the metathetical route. The process for the synthesis of the NF_4SbF_6 starting material was also improved by elimination of the cumbersome vacuum pyrolysis step. The usefulness of solid propellant NF_3-F_2 gas generators for the rapid destruction of magnetic tape was demonstrated. Information was obtained on the intermediates formed in the uv photolytic synthesis of NF_4BF_4. It was shown by esr spectroscopy that the BF_4 radical is formed as the key intermediate during the low-temperature, uv-photolysis of the NF_3-F_2-BF_3 system. The ESCA spectrum of NF_4BF_4 has been measured.

In the field of halogen fluorides the reactions of $KClO_3$ with ClF_5 and of $MBrO_4$ with BrF_5 were studied. No novel compounds were obtained. Unsuccessful attempts were made to prepare the novel ClF_4O radical by γ-irradiation of ClF_3O in SF_6 matrix at -196 C.

Normal coordinate analyses of SF_5Br and SF_4O were carried out. Attempts to prepare $O_2^+ClO_4^-$ by metathesis were unsuccessful. Evidence for the formation of the novel perchlorate $W(ClO_4)_6$ was obtained, however this compound appears to be unstable. Attempts to synthesize the novel WF_6^+ and MoF_6^+ cations were unsuccessful. The usefulness of the recently discovered stable oxonium salts as polymerization catalysts was demonstrated.

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FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 473, with Dr. R. S. Miller as Scientific Officer. This report covers the period 1 January 1976 through 31 December 1976. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, and Mr. R. D. Wilson. The program was administered by Dr. L. Grant, Manager, Exploratory and Analytical Chemistry, and Dr. K. O. Christe, Program Engineer.

INTRODUCTION

This report covers a 12-month period and describes Rocketdyne's research efforts in the area of halogen chemistry. As in the past years, our research was kept diverse and covered areas ranging from the exploration of new synthetic methods and the syntheses of novel compounds to structural studies. However because of the importance of NF_4^+ salts as ingredients for solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers, our main efforts were concentrated in this area. The existence of stable NF_4^+ salts was originally discovered by one of us in 1965 (Ref. 1) under ONR sponsorship, and much of the development in this field has since been achieved at Rocketdyne under this ONR program.

Particular progress in the field of solid propellant NF_3-F_2 gas generators was made by us during the current program year. Thus, the novel NF_4^+ salts $(NF_4)_2SnF_6$, $(NF_4)_2TiF_6$, and $(NF_4)_2NiF_6$ were discovered, and the concept of self-clinkering formulations was developed. The nickel salt is of particular importance since it constitutes the first known combination of an energetic perfluoro cation with an energetic perfluoro anion in the form of a stable salt. In this manner, we have succeeded to boost within one year the theoretically achieveable fluorine yield from 38.5 weight % (for clinkered NF_4BF_4) to 64.6% for $(NF_4)_2NiF_6$.

The results obtained under this program have been successfully applied to a number of past and ongoing Navy, Army, and Air Force programs, thus demonstrating the usefulness of goal-oriented basic research.

As in the past (Ref. 2), we have summarized completed pieces of work in manuscript form suitable for publication. Thus, time spent for report and manuscript writing is minimized, and widespread dissemination of our data is achieved.

During the past 12 months, the following papers were published, submitted for publication, or presented at meetings. In addition, several patents were either issued or filed. All of these arose from work sponsored under this program.

PUBLICATIONS AND PATENTS DURING PAST CONTRACT YEAR

Papers Published

1. "On the PtF_6-$XeOF_4$ Reaction System," K. O. Christe and R. D. Wilson, J. Fluor. Chem., 7, 356 (1976).
2. "Chlorine Oxyfluorides," by K. O. Christe and C. J. Schack, Advanc. Inorg. Chem. Radiochem., 18, 319 (1976).
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4. "Titanium Tetraperchlorate and Chromyl Perchlorate," C. J. Schack, D. Pilipovich and K. O. Christe, J. Inorg. Nucl. Chem., Supplem., 207 (1976).
5. "Low-Temperature Ultraviolet Photolysis and its Application to the Synthesis of Novel and Known NF_4^+ Salts," K. O. Christe, C. J. Schack and R. D. Wilson, Inorg. Chem., 15, 1275 (1976).
6. "Vibrational Spectra of the Trigonal Bipyramidal Tetrafluorides SF_4 and ClF_4^+," K. O. Christe, E. C. Curtis and C. J. Schack, Spectrochim.Acta, 32A, 1141 (1976).
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11. "Improved Syntheses of NF_4BF_4 and NF_4SbF_6," K. O. Christe, C. J. Schack and R. D. Wilson, J. Fluor. Chem., 8, 541 (1976).

Papers in Press

12. "On the Synthesis and Characterization of NF_4BiF_6 and Some Properties of NF_4SbF_6," K. O. Christe, R. D. Wilson and C. J. Schack, Inorg. Chem.

13. "Synthesis and Characterization of $(NF_4)_2SnF_6$ and NF_4SnF_5," K. O. Christe, C. J. Schack and R. D. Wilson, Inorg. Chem.

14. "Synthesis and Characterization of $(NF_4)_2TiF_6$ and of Higher NF_4^+ and Cs^+ Polyperfluorotitanate (IV) Salts," K. O. Christe and C. J. Schack, Inorg. Chem.

15. "Synthesis and Characterization of $(NF_4)_2NiF_6$," K. O. Christe, Inorg. Chem.

16. "Vibrational Spectrum and Normal Coordinate Analysis of SF_5Br," K. O. Christe, E. C. Curtis, C. J. Schack and A. Roland, Spectrochim.Acta.

17. "Vibrational Spectra of Thionyl Tetrafluoride, SF_4O," K. O. Christe, C. J. Schack and E. C. Curtis, Spectrochim. Acta.

Papers Presented at Meetings

18. "NF_4^+ Chemistry," K. O. Christe, C. J. Schack and R. D. Wilson, 8th International Symposium on Fluorine Chemistry, Kyoto, Japan (August 1976).

19. "Recent Progress in the Chemistry of NF_4^+ Salts," C. J. Schack, K. O. Christe, R. D. Wilson and R. I. Wagner, 172nd ACS National Meeting, San Francisco (August 1976).

20. Invited seminars on "Energetic Halogen Chemistry" were given at Harvard-MIT, University of Arizona, Tucson, and the Science Center of Rockwell International.

Issued Patents

21. "Stable Unsubstituted Sulfonium Salts," K. O. Christe, U.S.P. 3,987,152 (October 19, 1976).

Filed Patents

22. "Germanium Containing NF_4^+ Salts and Process for Preparing Same," K. O. Christe and C. J. Schack.

23. "Photolysis Method for Producing NF_4PF_6," K. O. Christe and C. J. Schack.

24. "Displacement Reaction for Producing NF_4PF_6," K. O. Christe and C. J. Schack.

25. "High Energy Solid Propellant Oxidizer and Method of Producing Same," K. O. Christe.

26. "Self-Clinkering NF_4^+ Compositions for NF_3-F_2 Gas Generators and Method of Producing Same," K. O. Christe, C. J. Schack and R. D. Wilson.

DISCUSSION

NF_4^+ CHEMISTRY

NF_4^+ salts, first discovered by one of us in 1965 under an ONR contract at Stauffer Chemical (Ref. 1), are the most promising oxidizers for solid propellant NF_3-F_2 gas generators. The concept of such a gas generator was conceived (Ref. 3) and to a large extent (Ref. 4 through 8) developed at Rocketdyne. It offers significant logistics and safety advantages over cryogenic or storable liquid oxidizers for use in chemical HF-DF lasers, for example. In a chemical HF-DF laser, F atoms are generated by burning F_2 in a precombustor with a fuel, such as hydrogen:

$$F_2 + H \longrightarrow HF + F^{\bullet}$$

The F atoms are subsequently reacted with a cavity fuel, such as D_2, to produce vibrationally excited DF as the active lasing species:

$$F^{\bullet} + D_2 \longrightarrow DF^* + D$$

In the original solid F atom generator concept (Ref. 3), the F atoms were directly generated by burning the solid propellant grain, thus eliminating the need of a precombustor. This concept is demonstrated for NF_4BF_4 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 NF_3 and F_2 to F atoms and N_2:

$$NF_4BF_4 + (CF_2)_n \longrightarrow CF_4 + BF_3 + NF_3 + Q$$

$$2NF_3 + Q \longrightarrow N_2 + 6F^{\bullet}$$

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 NF_3-F_2 molecule generator, using a gas catch tank. Further modification of this concept became necessary, when system analysis data revealed that gaseous byproducts of high molecular weight and low C_p/C_v significantly degrade the performance of a laser. Consequently, an NF_3-F_2 gas generator was desired which would produce no gases other than NF_3 and F_2. The latter objective can be achieved by a so-called clinker system in which the BF_3 byproduct is converted by an alkali metal fluoride to a nonvolatile BF_4^- salt.

$$NF_4BF_4 + KF \xrightarrow{+Q} KBF_4 + NF_3 + F_2$$

Whereas the feasibility of such a clinker system approach has been well demonstrated, the addition of KF lowers the NF_3-F_2 yield per pound of solid propellant and the possibility always exists of having incomplete clinkering.

Realizing these limitations, we have searched during the past year for novel NF_4^+ salts containing anions that will yield a nonvolatile fluoride, such as SnF_4 (boiling point = 705 C), after thermal decomposition. No such salts had previously been known, owing to the fact that nonvolatile fluorides are highly polymeric and, therefore, do not behave like strong Lewis acids. This makes the direct synthesis of such salts from NF_3, F_2, and the Lewis acid extremely difficult. We found, however, that $(NF_4)_2SnF_6$ can be prepared by the following metathetical reaction in HF solution:

$$Cs_2SnF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF sol}} 2CsSbF_6\downarrow + (NF_4)_2SnF_6$$

This salt was thoroughly characterized and the results were summarized in manuscript form (see Appendix B).

Further improvements were made by synthesizing novel NF_4^+ salts derived from TiF_4 (see Appendix C). Although the usable fluorine content of $(NF_4)_2TiF_6$ (see Table 1) is considerably higher than that of $(NF_4)_2SnF_6$, TiF_4 (sublimation pressure of 760 mm at 284 C) is more volatile than SnF_4 (b.p. = 705 C) and may require alkali metal fluoride based clinkering.

Table 1: Comparison of the Fluorine Yields of Presently Known NF_3-F_2 Gas Generator Systems

Rank	System	Usable F (Weight %) Before	After Burning
1.	$(NF_4)_2NiF_6$	64.6	58.6
2.	$(NF_4)_2TiF_6$*	55.6	49.6
3.	$(NF_4)_2SnF_6$	46.0	40.0
4.	$(NF_4)_2TiF_6 \cdot 2.4KF$	39.5	33.5
5.	$NF_4BF_4 \cdot 1.2KF$	38.5	32.5
6.	$(NF_4)_2GeF_6 \cdot 2.4KF$	37.6	31.6
7.	NF_4SnF_5	31.3	25.3
8.	$NF_4PF_6 \cdot 1.2KF$	31.2	25.2
9.	$NF_4GeF_5 \cdot 1.2KF$	29.0	23.0
10.	$NF_4AsF_6 \cdot 1.2KF$	27.3	21.3
11.	$NF_4SbF_6 \cdot 1.2KF$	24.0	18.0
12.	$NF_4BiF_6 \cdot 1.2KF$	19.7	13.7

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* $(NF_4)_2TiF_6$ might require clinkering with KF which would drop its fluorine yield below that of $(NF_4)_2SnF_6$.

The usable fluorine content was further increased by synthesizing a NF_4^+ salt of an oxidizing anion. This salt is $(NF_4)_2NiF_6$ (see Appendix D). It has the advantages of containing a doubly charged anion which is "self-clinkering", and an oxidizing anion, thus boosting its usable fluorine content to 64.6 weight % (see Table 1). However, its thermal stability is marginal (see Appendix D), which may limit its potential applications.

Since all of the top ranked NF_4^+ salts are prepared by metathetical processes, this process was studied in more detail and was significantly improved (see Appendix G). A major breakthrough in the process development was achieved by demonstrating that essentially pure NF_4BF_4 can be produced by metathesis. Furthermore, the synthesis of the NF_4SbF_6 starting material was improved (see Appendices A and G) and a novel alternate starting material, i.e. NF_4BiF_6, was synthesized and characterized (see Appendix A).

Extensive efforts were undertaken to prepare other novel NF_4^+ salts. Desired compounds included $(NF_4)_3AlF_6$, $(NF_4)_3CoF_6$, $(NF_4)_3FeF_6$, $(NF_4)_3MnF_6$, NF_4AlF_4 and $(NF_4)_2ZrF_6$. Metatheses in either HF or BrF_5 solution were chosen as synthetic approaches. Unfortunately, efforts along these lines were frustrating owing to the low solubilities of the starting materials in these solvents and solvolysis of the triply charged anions according to:

$$MF_6^{---} + 2X \longrightarrow MF_4^- + 2XF^-$$

$$(X{=}HF \text{ or } BrF_5)$$

Efforts to prepare these compounds are being continued and will be summarized in a future report.

In collaboration with Dr. I. Goldberg of Rockwell International's Science Center (who also has an ONR Contract), a joint esr study was carried out to identify some of the intermediates in the uv-photolytic NF_4^+ salt process. For the NF_3-F_2-BF_3 system, the formation of the novel $BF_4^{\cdot}$ radical was established. This radical is a key intermediate in the mechanism previously proposed by us

(Ref. 9). A summary of this work will be given in manuscript form in next year's report.

In collaboration with Dr. C. Christenson of Dow Chemical, the ESCA spectra of NF_4^+ and related salts are being studied. Preliminary results for NF_4BF_4 are summarized in Table 2. A comparison with data previously reported by Rosolovskii (Ref. 10) shows that the latter values are indeed much too high.

With the exception of NF_4BF_4, no thermodynamic data are presently available for NF_4^+ salts. These data are badly needed for performance calculations. A collaborative effort with Prof. R. Peacock of the University of Leicester, England, has been established to acquire such data.

Following the suggestion of Dr. R. Miller, the contract Scientific Officer, the usefulness of solid propellant NF_3-F_2 gas generators for the rapid destruction of films or magnetic tapes was demonstrated (see Appendix H).

In summary, the following major breakthroughs in NF_4^+ chemistry were achieved during the past year:

1. Reduction to practice of the "self-clinkering" concept of NF_4^+ salts
2. The use of doubly charged anions
3. The use of energetic anions, such as NiF_6^{--}
4. The synthesis and characterization of the novel $(NF_4)_2NiF_6$, $(NF_4)_2SnF_6$, $(NF_4)_2TiF_6$ and NF_4BiF_6 salts
5. The synthesis of high purity NF_4BF_4 by metathesis
6. The identification of the novel BF_4 radical as a key intermediate in the photolytic formation of NF_4BF_4

These results clearly demonstrate the importance and usefulness of the work done under this contract.

Table 2: ESCA Data for NF_4BF_4

	NF_4BF_4	CHRISTENSON, CHRISTE (1976)	ROSOLOVSKII ET AL (1972)
BINDING ENERGY (eV)	N1s	413.5	(417.3)
	F1s(NF_4^+)	691.3	(694.4)
	F1s(BF_4^-)	688.9	
	B1s	192.9	(195.4)

	$NH_3(s)$	NH_4^+	NO_2^-	NO_3^-	NF_4^+
BINDING ENERGY	398.8	402	404	407.2	413.5

HALOGEN FLUORIDES

Recently, Bougon reported (Ref. 11) the synthesis of the novel BrF_4O^- anion from BrO_3^- and BrF_5. We have studied the analogous reaction of ClO_3^- with ClF_5 as a possible route to ClF_4O^-. If possible, this reaction would provide a new convenient synthesis for ClF_3O. However instead of the desired ClF_4O^-, the following quantitative reaction occurred:

$$KClO_3 + ClF_5 \longrightarrow KClF_4 + FClO_3$$

Attempts were also undertaken to prepare the yet unknown $BrF_4O_2^-$ anion from BrO_4^- and BrF_5. However instead of $BrF_4O_2^-$, only the known BrF_4O^- anion was formed in high yield. Good vibrational spectra were obtained for BrF_4O^- and a normal coordinate analysis of this anion is under progress. The results will be given in next year's report in manuscript form. Attempts to record the Raman spectrum of $CsBrF_4O$ in HF solution resulted in a displacement reaction accompanied by BrF_3O formation.

In collaboration with Dr. Goldberg of Rockwell's Science Center, attempts were undertaken to prepare the novel $ClF_4O^\cdot$ radical by γ-irradiation of ClF_3O in an SF_6 matrix at -196 C. However, no esr signals attributable to $ClF_4O^\cdot$ could be detected. Control experiments with BrF_5 in SF_6 matrix resulted in the well characterized (Ref. 12, 13) $BrF_6^\cdot$ radical.

SULFUR COMPOUNDS

Normal coordinate analyses of SF_5Br (see Appendix E) and SF_4O (see Appendix F) were carried out. The former is an important starting material for energetic fluorocarbons, and the latter is of interest as a model compound for trigonal bipyramidal halogen compounds. Our results for SF_5Br are in good agreement with those of an independent study recently published by Smardzewski and coworkers (Ref. 14).

PERCHLORATES

Attempts were made to synthesize the novel $O_2^+ClO_4^-$ salt by metathesis in anhydrous HF according to:

$$O_2^+SbF_6^- + Cs^+ClO_4^- \xrightarrow[-78C]{HF} CsSbF_6\downarrow + O_2^+ClO_4^-$$

Although the expected $CsSbF_6$ precipitate was formed, spontaneous decomposition of O_2ClO_4 with strong gas evolution occurred. This indicates that O_2ClO_4 is unstable under these conditions. This compound would have been extremely interesting due to its very high oxygen content (73 weight %).

Anhydrous metal perchlorates are of interest as ingredients in explosives and as burning rate modifiers for solid propellants. The reaction of WF_6 with chlorine perchlorate was carried out to examine whether all six chlorines on tungsten could be replaced by perchlorate groups. A long term reaction at -45 C showed that six equivalents of Cl_2 were formed as expected for the reaction:

$$WCl_6 + 6ClOClO_3 \longrightarrow 6Cl_2 + W(ClO_4)_6$$

However, some Cl_2O_7 was also present indicating that the following decomposition had occurred:

$$W(ClO_4)_6 \longrightarrow OW(ClO_4)_4 + Cl_2O_7$$

TRANSITION METAL FLUORIDES

The interaction of O_2^+ salts with WF_6 and MoF_6 was studied to check whether novel cations can be prepared according to:

$$O_2^+SbF_6^- + MF_6 \xrightarrow{25C} MF_6^+SbF_6^- + O_2$$

However, no interaction was observed in either case.

MICROWAVE STUDY OF O_2F

The O_2F radical is of great interest for chemical lasers. Since work in our laboratory had indicated that this radical posseses appreciable stability at room temperature, a structural study of the O_2F radical in the gas phase appeared feasible. Consequently, contact has been established with Prof. Godfrey of the Monash University in Melbourne, Australia, who will study the $O_2F^{\cdot}$ radical by microwave spectroscopy. A sample of O_2AsF_6 was prepared by us and will be subjected at Monash to slow vacuum pyrolysis for the O_2F generation.

OXONIUM SALTS

The stable OH_3^+ salts, discovered recently under this contract, are of interest as polymerization catalysts. A sample of $OH_3^+SbF_6^-$ was prepared and tested at Ciba-Geigy for the polymerization of epoxy resins. The compound was found to be too powerful for commercial applications, resulting in spontaneous polymerization with high heat release. For practical purposes, salts of weaker Lewis acids would have to be prepared and tested.

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

On the Synthesis and Characterization of NF_4BiF_6 and Some Properties of NF_4SbF_6

Karl O. Christe*, Richard D. Wilson, and Carl J. Schack

Received 9 March 1976

Introduction

Perfluoroammonium salts are known[1] of the following anions: PF_6^-, AsF_6^-, SbF_6^-, $SbF_6 \cdot nSbF_5^-$, BF_4^-, GeF_5^-, and GeF_6^{--}. Very recently, the synthesis and chemistry of NF_4^+ salts have received considerable attention owing to their potential for solid propellant NF_3-F_2 gas generators for chemical DF lasers. The concept of such a gas generator was conceived[2] and to a large extent developed at Rocketdyne. Originally, the fluorine gas generators were aimed at the direct generation of F atoms by burning a highly overoxidized grain, consisting mainly of an NF_4^+ salt, with a small amount of fuel, such as Teflon powder, according to:

$$NF_4MF_6 + (CF_2)_n \longrightarrow CF_4 + NF_3 + MF_5 + Q$$

$$NF_4MF_6 \xrightarrow{+Q} NF_3 + F_2 + MF_5$$

$$2NF_3 + F_2 \xrightarrow{+Q} N_2 + 8F\cdot$$

The heat of reaction (Q) generated in such a system is sufficient to pyrolyze the remaining NF_4MF_6 and to dissociate most of the NF_3 and F_2 to F atoms. For an NF_3-F_2 gas generator, the underlying principle is quite similar, except for keeping the burning temperature lower since dissociation of NF_3 and F_2 to F atoms is not required.

In view of the above developments, we were interested in the synthesis of new NF_4^+ salts and in the characterization of new and known NF_4^+ salts. In this paper, we report on the synthesis of the new salt NF_4BiF_6 and on some properties of the known NF_4SbF_6. Since these two salts can be readily prepared in high yields, they are important starting materials for the syntheses of other NF_4^+ salts used in NF_3-F_2 gas generator compositions.

Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those[1] recently described. The NF_4BF_4 starting material was prepared by low-temperature uv-photolysis[1] and did not contain any detectable impurities. The α-BiF_5 was purchased from Ozark Mahoning Co. and did not contain any impurities detectable by Raman spectroscopy. The $NF_4Sb_2F_{11}$ was prepared as described.[3]

Synthesis of NF_4BiF_6 by Displacement Reaction without Solvent. Pure NF_4BF_4 (10.1 mmol) and α-BiF_5 (10.1 mmol) were powdered, mixed, and placed in a prepassivated (with ClF_3) 95 ml Monel cylinder. The cylinder was heated to 180° for 1.5 h. Products, volatile at 20°, were removed by pumping and separated by fractional condensation. They consisted of 7.8 mmol of BF_3 in addition to a small amount of material noncondensible at -196°. The amount of BF_3 evolution was confirmed by the weight loss of the solid containing cylinder. The conversion of NF_4BF_4 to NF_4BiF_6 was further confirmed by Raman spectroscopy of the solid. The solid was removed from the cylinder, finely powdered, returned to the cylinder, and heated to 175° for an additional 18 hours. This resulted in the evolution of an additional 2.3 mmol of BF_3, in excellent agreement with the observed weight loss. The complete conversion of NF_4BF_4 to NF_4BiF_6 was confirmed by infrared and Raman spectroscopy and elemental analysis. Anal. Calcd for NF_4BiF_6: NF_3, 17.15; BiF_3, 64.49. Found: NF_3, 16.9; BiF_3, 60.0. An explanation for the low BiF_3 value is given below.

Synthesis of NF_4BiF_6 by Displacement Reaction in HF. Dry HF (5 ml liquid) was added at -78° to a Teflon FEP ampoule containing NF_4BF_4 and BiF_5 (9.9 mmol of each). The mixture was agitated at 20° for several hours and gas evolution was observed. The volatile products were pumped off at 20° and the HF treatment was repeated. After removal of the volatile products from the second HF treatment, 4.075 g of a white, stable solid (weight calculated for 9.9 mmol of NF_4BiF_6 = 4.089 g) was left behind which was shown by infrared and Raman spectroscopy to be identical to the analyzed product obtained from the above described thermal displacement reaction.

Direct Synthesis of $NF_4BiF_6 \cdot nBiF_5$. In a typical experiment, a mixture of NF_3 (238 mmol), F_2 (238 mmol), and BiF_5 (10.06 mmol) in a prepassivated 95 ml Monel cylinder was heated for 30 hours to 175° under an autogenous pressure of 167 atm. Unreacted NF_3 and F_2 (~463 mmol total) were pumped off at 20° leaving behind 3.75 g of a white, stable solid (weight calcd for 6.29 mmol of $NF_4BiF_6 \cdot 0.6BiF_5$ = 3.745 g). Anal. Calcd for $NF_4BiF_6 \cdot 0.6BiF_5$: NF_3, 11.92; BiF_3, 71.60. Found: NF_3, 11.9; BiF_3, 69.00.

Pyrolysis of $NF_4BiF_6 \cdot nBiF_5$. A sample (3.29 mmol) of $NF_4BiF_6 \cdot 1.46BiF_5$, prepared as described above except for using a significantly shorter reaction time, was subjected to vacuum pyrolysis at 280° for 1.5 hours. The white crystalline residue (1.13 g) was identified by vibrational spectroscopy and its x-ray diffraction powder pattern to be mainly NF_4BiF_6 (weight calcd for 3.29 mmol of NF_4BiF_6 = 1.36 g) corresponding to a yield of 83%.

Synthesis of NF_4SbF_6. The thermal reaction[4] of NF_3-F_2-SbF_5 at 115°, followed by vacuum pyrolysis at 200°, produces[3] a product of the approximate composition $NF_4Sb_2F_{11}$. This product can be converted to NF_4SbF_6 by vacuum pyrolysis at higher temperature, however, this SbF_5 removal is accompanied by a competing reaction, i.e. the thermal decomposition of some of the desired NF_4SbF_6. Pyrolysis at 250-260° for 1 to 1.5 hours in a dynamic vacuum resulted in complete conversion to NF_4SbF_6. Measurement of the NF_3 evolved during this pyrolysis showed that less than 3% of the NF_4SbF_6 had undergone decomposition. When the pyrolysis was carried out at 275-300°, even for relatively short periods of time, significantly higher losses of NF_4SbF_6 due to thermal decomposition occurred.

In a typical experiment, $NF_4Sb_2F_{11}$ (31.0 mmol) in a 95 ml Monel cylinder was pyrolyzed in a dynamic vacuum at 255° for 80 min. The evolved SbF_5 was condensed in a Teflon-FEP U-trap kept at -196°. The white solid residue consisted of 30.4 mmol of NF_4SbF_6 (98 mole % yield based on NF_4^+). Anal. Calcd for NF_4SbF_6: NF_3, 21.80; Sb, 37.38. Found: NF_3, 21.72; Sb, 37.41; Ni, 0.08; Cu, 0.03.

Elemental Analyses. For the elemental analyses, a weighed amount (several mmol) of the NF_4^+ salt was placed in the bottom of a Teflon-FEP U-trap, which was closed off by valves. The trap was cooled to -196° and several ml of distilled water was frozen out in the upper section of the U-trap. The frozen water was shaken down into the cold bottom section of the U-tube and the ice and the NF_4^+ salt were mixed while being cold. This mixing procedure was found important to avoid violent reactions between solid NF_4^+ salts and isolated droplets of liquid water, which sometimes were encountered when thawing the ice in the upper part of the tube and allowing the liquid water to run down onto the NF_4^+ salt. The mixture of ice and NF_4^+ salt was warmed to 20° for 30 min. Upon melting of the ice, gas evolution occurred. The contents of the trap were cooled and the evolved O_2 and NF_3 were distilled off at -196° and -126°, respectively, and were measured volumetrically. For NF_4SbF_6, the aqueous hydrolysate was analyzed for Sb by x-ray fluorescence spectroscopy. For the BiF_5 salts, a white, water-insoluble precipitate formed on hydrolysis. This precipitate was filtered off at 0°, washed with a small amount of cold distilled water, dried at 103°, and weighed. It was identified by its x-ray powder diffraction pattern[4] and by electron microprobe x-ray analysis as BiF_3. Anal. Calcd for BiF_3: Bi, 78.57; F, 21.43; O, 0. Found: Bi, 78.6 ; F, 21.3 ; O, 0. Although 93 to 97% of the BiF_3 could be isolated in this manner, the solubility of BiF_3, particularly in the presence of HF, is not low enough[5] to permit a quantitative precipitation of BiF_3.

Results and Discussion

Syntheses. The new NF_4^+ salt NF_4BiF_6 was prepared either from NF_4BF_4 and BiF_5 by the following displacement reaction

$$NF_4BF_4 + BiF_5 \longrightarrow NF_4BiF_6 + BF_3$$

or directly by the elevated temperature-pressure method[6] followed by vacuum pyrolysis

$$NF_3 + F_2 + (n+1)\ BiF_5 \xrightarrow{175°} NF_4BiF_6 \cdot nBiF_5$$

$$NF_4BiF_6 \cdot nBiF_5 \xrightarrow{280°} NF_4BiF_6 + nBiF_5$$

The displacement reaction can be carried out either at 25° in HF solution or in the absence of a solvent at elevated temperature.

The synthesis of NF_4BiF_6 is more difficult than that of NF_4SbF_6 owing to the fact that at ambient temperature α-BiF_5 is a nonvolatile, polymeric, trans-fluorine bridged solid. Consequently, temperatures above the melting point (151.4°) of BiF_5 are required for both the displacement reaction and the elevated temperature-pressure method. Since removal of excess BiF_5 is inconvenient, the displacement reactions are best carried out with stoichiometric amounts of starting materials. As for SbF_5,[6] the direct synthesis of the NF_4^+ perfluorobismuthate salt at elevated temperature and pressure tends to produce polyanions (mainly $Bi_2F_{11}^-$).[7] The feasibility of converting these salts to NF_4BiF_6 by vacuum pyrolysis was demonstrated, but no effort was made to maximize the reaction conditions.

The pyrolysis of $NF_4Sb_2F_{11}$ to NF_4SbF_6 and SbF_5 was briefly investigated, when we discovered that the reaction conditions (200°) previously recommended[8] for the pyrolysis were not suitable for obtaining pure NF_4SbF_6. In our experience, a significantly higher pyrolysis temperature of about 250° was required for the production of essentially pure NF_4SbF_6. At this temperature, little or no decomposition of the NF_4SbF_6 itself took place. Based on the results obtained in our laboratory, the thermal reaction between approximately equimolar amounts of NF_3, F_2, and SbF_5 at temperatures ranging from 115 to 200° and autogenous pressures of about 200 atm produces a product of the composition $NF_4SbF_6 \cdot nSbF_5$ with n ranging from 2.1 to 3.2 depending on the exact reaction conditions. Vacuum pyrolysis of these products at 200° reduces n to a level ranging from 0.8 to 1.1. Pyrolysis at 260° reduces the value of n to zero.

Properties. The composition of the NF_4^+ salts was established by both the observed material balances and elemental analyses. The NF_4BiF_6 salt is a white crystalline solid melting in a sealed glass capillary at about 341°. The x-ray powder diffraction pattern of the sample prepared by pyrolysis of $NF_4BiF_5 \cdot nBiF_5$ is given as supplementary material. It could readily be indexed for a tetragonal unit cell, analogous to those of NF_4PF_6,[1] NF_4AsF_6,[9] and NF_4SbF_6 (see Table I). Several weak lines were of variable intensity could not be indexed for a tetragonal unit cell, and corresponding lines had not been observed for the other isotypic NF_4MF_6 salts. Consequently, these extra lines are attributed to impurities, such as polyanion salts, and have not been included in the listing.

The NF_4SbF_6 salts melts at about 318°. Its x-ray powder diffraction pattern is given as supplementary material. All the observed lines could be indexed for a tetragonal unit cell, analogous to those observed for the other NF_4MF_6 salts (see Table I). As expected, the unit cell dimensions and calculated densities increase in the order: $PF_6^- < AsF_6^- < SbF_6^- < BiF_6^-$.

The hydrolyses of NF_4SbF_6 and NF_4BiF_6 showed a distinct difference as far as the amount of oxygen evolution is concerned. The NF_4SbF_6 behaved like the previously studied[1] NF_4^+ salts and generated O_2 according to:

$$NF_4^+ + H_2O \longrightarrow NF_3 + H_2F^+ + \tfrac{1}{2}O_2$$

This reaction, however, is not quantitative owing to a competing reaction[1] involving the formation of some H_2O_2. Thus, for NF_4SbF_6, only 0.45 mol of O_2 was observed per mol of NF_3. For NF_4BiF_6, however, 0.86 mol of O_2 was obtained per mol of NF_3. Furthermore, no evidence for the formation of brown Bi_2O_5 (generated when BiF_5 is hydrolyzed) was observed, but white BiF_3 was precipitated. This oxidation of H_2O by BiF_6^- according to

$$BiF_6^- + H_2O \longrightarrow BiF_3\downarrow + HF_2^- + HF + \tfrac{1}{2}O_2$$

can account for the additional O_2 evolution, which by analogy[1] with NF_4^+ might not be quantitative owing to the formation of some H_2O_2.

The oxygen evolution during the hydrolysis of the closely related O_2^+ salts has recently been studied.[10] In agreement with our findings for NF_4^+ salts, the observed O_2 evolution was generally lower than the calculated values. However, for O_2BiF_6, no evidence for the reduction of pentavalent bismuth was reported. Furthermore, the given explanation, i.e. that the low observed O_2 values are due to samples which had undergone partial decomposition according to

$$2O_2MF_6 \longrightarrow O_2M_2F_{11} + O_2 + \tfrac{1}{2}F_2 ,$$

cannot account for the low O_2 value found for salts, such as O_2AsF_6, which contain a volatile Lewis acid and do not form a stable $M_2F_{11}^-$ anion. Therefore, some of the conclusions, such as "all dioxygenyl salts prepared so far are intrinsically unstable at room temperature", which are based on the low observed oxygen values, are open to question. Obviously, competing side reactions, such as those observed for the NF_4^+ salts, might play an important role and give rise to low oxygen values.

Vibrational Spectra. The vibrational spectra of NF_4BiF_6, $NF_4BiF_6 \cdot 0.6BiF_5$, and NF_4SbF_6 are shown in Figure 1. The observed frequencies and their assignments are summarized in Table II. The spectra are in excellent agreement with those previously reported for the NF_4^+ cation[1] and the BiF_6^- [7,11,12] and SbF_6^- [7,12-15] anions, thus confirming the ionic nature of these adducts. By analogy with the previously studied[1] NF_4^+ salts, the degeneracy of some of the modes is lifted and crystal field splittings are observed. For example, the antisymmetric NF_4^+ stretching mode $\nu_3(F_2)$ is split into three components, and the $\nu_3(F_{1u})$ and the $\nu_2(E_g)$ mode of SbF_6^- show a splitting into three and two components, respectively. The presence of polyanions, such as $Bi_2F_{11}^-$,[7] in the $NF_4BiF_6 \cdot nBiF_5$ adducts is apparent from the appearance of a medium intense infrared band at 452 cm^{-1}, which is attributed to the stretching mode of the Bi-F-Bi bridge. Furthermore, additional bands were observed in the region of the BiF stretching and deformation modes. The maximum of the most intense BiF stretching infrared band was found to vary somewhat from sample to sample and varied from 575 to 605 cm^{-1}. In addition, some of the pyrolysis products showed weak infrared bands at 475 and 400 cm^{-1}. A comparison of the spectra of NF_4BiF_6 and $NF_4BiF_6 \cdot nBiF_5$ with those of NF_4SbF_6 and $NF_4Sb_2F_{11}$[1] shows a similar pattern for both when going from MF_6^- to $M_2F_{11}^-$.

Summary. The new NF_4^+ salt NF_4BiF_6 was prepared by the reaction between equimolar amounts of NF_4BF_4 and BiF_5 either at 180° without solvent or at 20° in HF solution. A salt of the composition $NF_4BiF_6 \cdot nBiF_5$ (n=0.6 to 1.5) was prepared directly from NF_3, F_2, and BiF_5 at elevated temperature and pressure. It was converted to NF_4BiF_6 by vacuum pyrolysis at 280°. The salts were characterized by elemental analyses and vibrational spectroscopy, and their hydrolyses were studied. The pyrolysis of $NF_4SbF_6 \cdot nSbF_5$ to NF_4SbF_6 was briefly investigated, and the vibrational spectrum and x-ray powder pattern of NF_4SbF_6 are reported.

Acknowledgement. We are indebted to Dr. L. R. Grant for helpful discussions and to the Office of Naval Research for financial support.

Supplementary Material Available. Listings of the observed x-ray powder diffraction patterns of NF_4BiF_6 and NF_4SbF_6 (2 pages). Ordering information is given on any current masthead page.

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Table 1. Crystalographic Data of NF_4SbF_6 and NF_4BiF_6 Compared to Those of NF_4PF_6 and NF_4AsF_6

	Tetragonal Unit Cell Dimensions					
	a(Å)	c(Å)	V(Å^3)	Z	Volume (Å^3) per F	Calcd Density (g/cm^3)
NF_4PF_6 [a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6 [b]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6	8.006	5.821	373.10	2	18.66	3.68

(a) Ref. 1

(b) Ref. 7

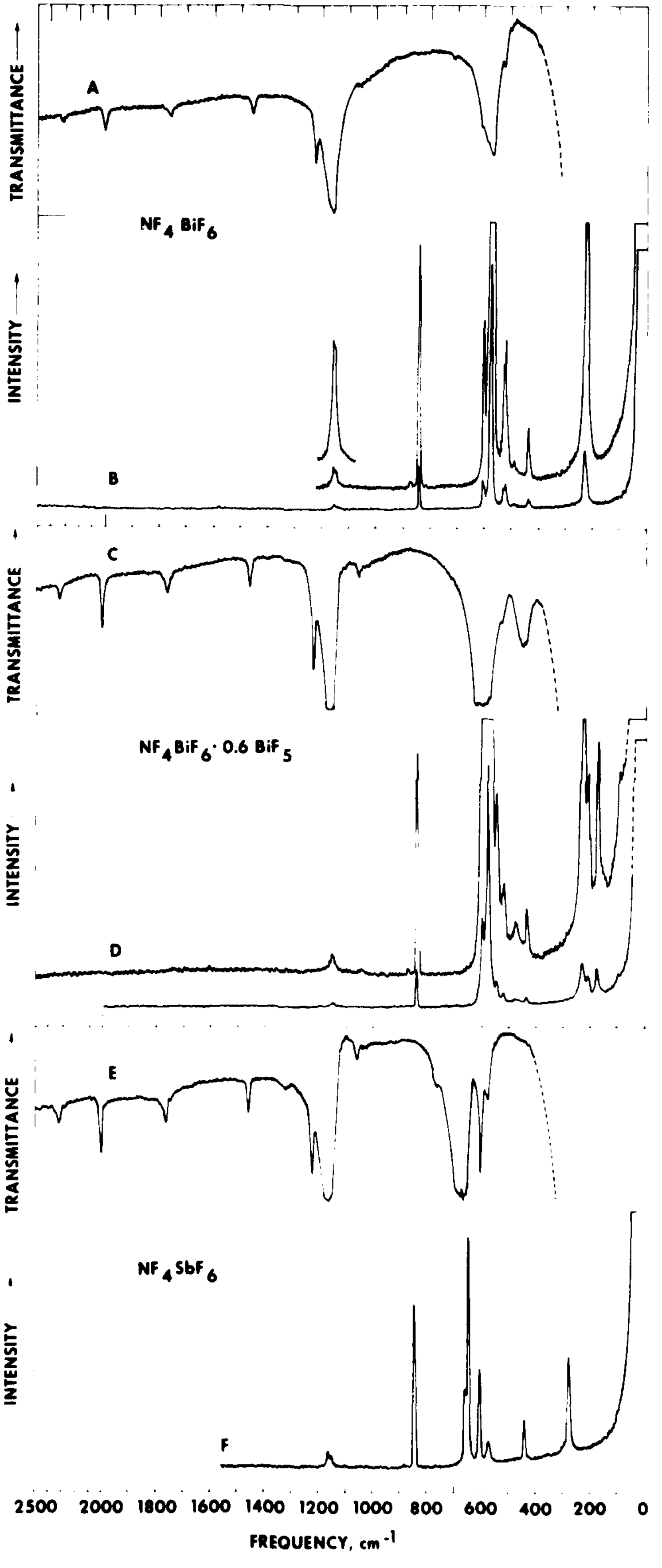
Table 2. Vibrational Spectra of Solid NF_4BiF_6, $NF_4BiF_6 \cdot 0.6BiF_5$, and NF_4SbF_6

Observed frequencies (cm^{-1}) and relative intensities [a]						Assignments (point group)		
NF_4BiF_6		$NF_4BiF_6 \cdot 0.6BiF_5$		NF_4SbF_6		NF_4^+ (T_d)	MF_6^- (O_h)	$M_2F_{11}^-$
IR	RA	IR	RA	IR	RA			
2320vw		2320vw		2320vw		$2\nu_3(A_1+E+F_2)$		
2010w		2010w		2010w		$\nu_1+\nu_3(F_2)$		
1768vw		1768vw		1768vw		$\nu_3+\nu_4(A_1+E+F_2)$		
1462vw		1462vw		1460vw		$\nu_1+\nu_4(F_2)$		
1228mw		1228mw		1227mw		$2\nu_4(A_1+E+F_2)$		
1175sh				1177sh				
1160vs	1159(0.15)	1160vs	1156(0.13)	1162vs	1160(0.6)	$\nu_3(F_2)$		
1145sh	1150sh	1145sh		1145sh	1150(0.2)			
				1323vw			$\nu_1+\nu_3(F_{1u})$	
1056vw		1056vw		1056vw		$\nu_2+\nu_4(F_1+F_2)$		
	878(0+)		875(0+)		878(0.2)	$2\nu_2(A_1+A_2+E)$		
	844(1.8)		844(1.5)		843(7.0)	$\nu_1(A_1)$		
				763vw			$\nu_2+\nu_6(F_{1u}+F_{2u})$	
730vw							$\nu_2+\nu_4(F_{1u}+F_{2u})$	
		600vs	602(2)					BiF stretch
		618m						
610m	608(1)			609m	604(3.9)	$\nu_4(F_2)$		
			602(2)					
	580(10)		580(10)		648(10)		$\nu_1(A_{1g})$	
				675vs				
576vs		575sh		665vs			$\nu_3(F_{1u})$	
				655sh	655(1)			
			548(0.5)					BiF stretch
529w	529sh	531sh		576w				
	521(0.8)		521(0.25)		569(0.9)		$\nu_2(E_g)$	
			475(0.13)					
		452m						BiFBi stretch
	438(0.35)		436(0.25)		437(1.5)	$\nu_2(E)$		
	228(2.1)		230(1.4)		275(3.8)		$\nu_5(F_{2g})$	
			211(0.4)					
			175(0.9)					deformation
			150sh					
	115(0+)br		95(0.1)			lattice vibration		

(a) Uncorrected Raman intensities

Diagram Caption

Figure 1. Vibrational Spectra of NF_4BiF_6, $NF_4BiF_6 \cdot 0.6BiF_5$, and NF_4SbF_6. Traces A, C, and E: Infrared spectra of the solids in silver chloride disks; the absorptions below 300 cm^{-1} (broken lines) are due to the AgCl windows. Traces B, D, and F: Raman spectra of the solids recorded at different sensitivities; the spectral slit width used at the lower sensitivity levels was 2 cm^{-1}.


TRANSMITTANCE
A
NF4 BiF6
INTENSITY
B
TRANSMITTANCE
C
NF4BiF6· 0.6 BiF5
INTENSITY
D
TRANSMITTANCE
E
NF4SbF6
INTENSITY
F
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
0
FREQUENCY, cm-1

Supplementary Material:

"On the Synthesis and Characterization of NF_4BiF_6 and Same Properties of NF_4SbF_6", by K. O. Christe, R. D. Wilson, and C. J. Schack.

Table 3. X-Ray Powder Data for NF_4BiF_6 [a]

d obsd	d calcd	Int	h	k	l
5.62	5.66	s	1	1	0
4.67	4.71	mw	1	0	1
4.09	4.06	w	1	1	1
4.00	4.00	vs	2	0	0
3.30	3.30	mw	2	0	1
3.05	3.05	mw	2	1	1
2.832	2.831	mw	2	2	0
2.735	2.735	mw	1	0	2
2.589	2.588	w	1	1	2
2.547	2.546	mw	2	2	1
2.321	2.320	mw	3	1	1
2.257	2.258	w	2	1	2
2.076	2.075	vw	3	2	1
2.025	2.029	w	2	2	2
1.889	1.889	mw,br	4 3 1	0 3 0	1 0 3
1.848	1.842	w	4	1	1
1.832	1.835	vw	1	1	3
1.800	1.795	mw	3	3	1
1.772	1.765	w	3	2	2
1.706	1.706	w	2	1	3

(a) tetragonal, a=8.006Å, c=5.821Å, Cu K_α radiation Ni filter.

Table 4. X-Ray Powder Data for NF_4SbF_6 [a]

d obsd	d calcd	Int	h	k	l
5.55	5.59	s	1	1	0
4.65	4.68	s	1	0	1
4.03	4.03	vs, br	1	1	1
			2	0	0
3.27	3.27	mw	2	0	1
3.014	3.018	s	2	1	1
2.793	2.793	mw	2	2	0
2.722	2.724	m	1	0	2
2.515	2.517	m	2	2	1
2.296	2.295	m	3	1	1
2.243	2.243	m	2	1	2
2.053	2.050	vw	3	2	1
1.979	1.975	w	4	0	0
1.953	1.950	m	3	0	2
1.879	1.879	m	1	0	3
1.827	1.828	m	1	1	3
1.775	1.773	mw	3	3	1
1.757	1.757	m	4	2	0
			3	2	2
1.699	1.697	ms	2	1	3
1.600	1.599	w	4	1	2
1.558	1.559	w	3	0	3
1.532	1.530	w	3	1	3
1.505	1.509	w	4	2	2
1.453	1.451	w	0	0	4
1.429	1.427	vw	1	0	4
1.405	1.404	vw	1	1	4
1.396	1.397	w	4	4	0
1.366	1.366	w	5	1	2

(a) tetragonal, a=7.903Å, c=5.806Å, Cu K_α radiation Ni filter

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

Synthesis and Characterization of $(NF_4)_2SnF_6$ and NF_4SnF_5

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Received 8 April 1976

Abstract

The novel NF_4^+ salt $(NF_4)_2SnF_6$ was prepared by metathesis between Cs_2SnF_6 and NF_4SbF_6 in HF solution. It is a white solid, stable to above 200°. Based on its x-ray powder data, it crystallizes in the tetragonal system and is isotypic with $(NF_4)_2GeF_6$. Its composition was established by elemental analysis, and the presence of tetrahedral NF_4^+ and octahedral SnF_6^{--} ions in the solid state and in BrF_5 solution was demonstrated by vibrational and ^{19}F nmr spectroscopy, respectively. The salt NF_4SnF_5 was obtained in quantitative yield from the displacement reaction between equimolar amounts of NF_4BF_4 and SnF_4 in HF solution. When a large excess of NF_4BF_4 was used, the main product was again NF_4SnF_5 and only a small amount of $(NF_4)_2SnF_6$ was formed. The NF_4SnF_5 salt was characterized by elemental analysis, vibrational and ^{19}F nmr spectroscopy, and x-ray powder data. The vibrational spectra of the solid and the ^{19}F nmr spectra of BrF_5 solutions show that SnF_5^- possesses a polymeric structure of cis-fluorine bridged SnF_6 octahedra, analogous to that observed for GeF_5^- in NF_4GeF_5. The potential of $(NF_4)_2SnF_6$ for a "self-clinkering" NF_3-F_2 gas generator is briefly discussed.

Introduction

Perfluoroammonium salts are of significant interest owing to their potential for solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers.[1] Salts are known of the following anions: PF_6^-, AsF_6^-, SbF_6^-, $SbF_6^-\cdot nSbF_5$, BiF_6^-,

$BiF_6^-\cdot nBiF_5$, BF_4^-, GeF_5^-, and GeF_6^{--}.[1,2] All these salts are derived from Lewis acids which are volatile and either completely or at least partially monomeric at temperatures below the thermal decomposition temperature of their NF_4^+ salts. Since these volatile Lewis acids are undesirable for NF_3-F_2 gas generators, they must be removed by complexing (clinker formation) with a strong Lewis base, such as KF. Since the addition of a clinker forming component degrades the performance of an NF_3-F_2 gas generator, the synthesis of NF_4^+ salts, derived from nonvolatile Lewis acids, became very desirable. However, this objective presented a synthetic challenge, since nonvolatile Lewis acids are highly polymeric and already possess favorable high coordination numbers. Consequently, these polymeric compounds are quite unreactive and do not behave like strong Lewis acids, thus rendering a direct synthesis[3] from NF_3, F_2, and the Lewis acid impossible. In this paper we report the synthesis of NF_4^+ salts derived from SnF_4, a doubly trans-fluorine bridged polymer[4,5] subliming at 704°, using metathetical[6,7] and displacement[1,2] reactions.

Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those recently described.[1,2] The NF_4BF_4[1] and NF_4SbF_6[2] starting materials were prepared as previously reported. The SnF_4 (Ozark Mahoning) and $SnCl_4$ (Baker) were used as received. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,[8] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. The CsF was fused in a platinum crucible and powdered in the dry box.

Synthesis of Cs_2SnF_6. Dry CsF (10.45 mmol) and $SnCl_4$ (5.22 mmol) were combined in a passivated Teflon FEP ampoule. Anhydrous HF (10 ml liquid) was added, and the mixture was agitated at 20° for several hours until HCl evolution had ceased and a clear solution was obtained. The volatile materials were pumped off at 50°. The white solid residue (2.604 g, weight calcd for 5.22 mmol of Cs_2SnF_6 = 2.600 g) was shown by infrared and Raman spectroscopy[9,10] and its x-ray diffraction powder pattern[11] to be of excellent purity.

If SnF_4 is readily available, the following synthesis of Cs_2SnF_6 was found to be somewhat more convenient. A mixture of CsF and SnF_4 (2:1 mol ratio) was fused in a covered platinum crucible until a clear melt was obtained. Alternately, CsF and SnF_4 (2:1 mol ratio) was agitated in anhydrous HF until a clear solution was obtained (SnF_4 is only very sparingly soluble in HF). In both cases the resulting products were shown by spectroscopic techniques to be undistinguishable from that obtained by the above method.

Synthesis of $(NF_4)_2SnF_6$. The small-scale metathetical reactions were carried out in the apparatus depicted in Figure 1. It consisted of three Teflon FEP U-traps interconnected by Monel unions (Swagelok) and closed off at both ends by a Monel valve. The union between trap II and trap III contained a Teflon filter (porous Teflon sheet, 1/16" thickness from Russel Assoc. Inc.) 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°. 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 $(NF_4)_2SnF_6$.

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 $(NF_4)_2SnF_6$ = 2.01 g). Elemental analysis for solid from trap III. Found: NF_3, 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3. Calcd for a mixture (mol %) of 82.8 $(NF_4)_2SnF_6$, 12.9 NF_4SbF_6, and 4.3 $CsSbF_6$: NF_3, 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43.

Synthesis of NF_4SnF_5. 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°, and the resulting suspension was stirred at 25° for 2 hours. The volatile material was pumped off at 35° 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 nonvolatile 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.

When a mixture of NF_4BF_4 and SnF_4 in a mol ratio of 2:1 was treated 8 times, as described above, with liquid HF for a total of 35 days, the resulting nonvolatile residue consisted mainly of NF_4SnF_5, unreacted NF_4BF_4, and a small amount of $(NF_4)_2SnF_6$.

Results and Discussion

Syntheses. As pointed out in the introduction, SnF_4 is polymeric with Sn being hexacoordinated. Consequently, solid SnF_4 does not act as a strong Lewis acid. This was experimentally confirmed by demonstrating that mixtures of NF_3, F_2, and SnF_4, when heated to temperatures of up to 300° 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 it has previously been shown[12] that SnF_6^{--} salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. Based on the reported solubilities of $CsSbF_6$ (5.6 g/100 g HF)[6], NF_4SbF_6 (280 g/100 g HF)[6], Cs_2SnF_6 (~250 g/100 g HF)[12], and the predicted high solubility of $(NF_4)_2SnF_6$ (the analogous $(NF_4)_2GeF_6$ is very soluble in HF)[2], the following methathetical reaction

$$2\ NF_4SbF_6 + Cs_2SnF_6 \xrightarrow{\text{HF solution}} 2\ CsSbF_6\downarrow + (NF_4)_2SnF_6$$

should be capable of producing $(NF_4)_2SnF_6$ in a purity of about 93 mol percent. The soundness of these predictions was experimentally verified. A product was obtained which based on its elemental analysis had the composition (mol %): $(NF_4)_2SnF_6$, 82.8; NF_4SbF_6, 12.9; $CsSbF_6$, 4.3. Whereas the amount of $CsSbF_6$ found in the product approximates that predicted, the presence of about 13 percent NF_4SbF_6 indicates the loss of some Cs_2SnF_6. This was probably caused by the hold up of some of the Cs_2SnF_6 solution in trap I (see Figure 1) during its transfer to trap II. It should be possible to eliminate most of the NF_4SbF_6 from the product by either minimizing the relative loss of Cs_2SnF_6 during transfer by scaling up the reaction or by recrystallization of the product. However, both approaches were beyond the scope of the present study.

Whereas SnF_4 is quite insoluble in anhydrous HF (contrary to a previous literature report[13]), it dissolves reasonably fast in HF solutions containing an excess of an alkali metal fluoride with formation of the corresponding alkali metal SnF_6^{--} salt. SnF_4 has also been reported to act as a relatively strong acid in HF solution.[13] Furthermore, GeF_4 is capable of displacing BF_4^- in NF_4BF_4,[2] and the strength of a Lewis acid generally increases within a group of the periodic system with increasing atomic weight of the central atom. Consequently, SnF_4 in HF might be expected to also be capable of displacing BF_4^- in NF_4BF_4.

When equimolar mixtures of NF_4BF_4 and SnF_4 were stirred in anhydrous HF, the following quantitative reaction occurred:

$$NF_4BF_4 + SnF_4 \xrightarrow{HF} NF_4SnF_5 + BF_3$$

However, BF_3 interacts with HF and the above reaction appears to be an equilibrium reaction. Consequently, it was found advantageous to pump off the volatile products and to repeat the HF treatment at least once to obtain complete conversion to NF_4SnF_5. No evidence for SnF_6^{--} formation was observed under these conditions. The quantitative formation of SnF_5^- was surprising, since for the alkali metal fluoride - SnF_4 systems exclusive SnF_6^{--} formation was observed during our study. We could not find any previous literature reports on SnF_5^-, except for a recent low-temperature ^{19}F nmr study by Dean[14] which demonstrated the presence of polyanions in SO_2 solutions of mixtures of SnF_6^{--} and SnF_4.

The possibility of preparing $(NF_4)_2SnF_6$ from a 2:1 mixture of NF_4BF_4 and SnF_4 was examined. However, even after 8 HF treatments for a total of 35 days only a small amount of SnF_6^{--} had formed. The main products were NF_4SnF_5 and unreacted NF_4BF_4. These results indicate that the Lewis acid strength of SnF_5^- in HF is insufficient to displace most of the BF_4^- from its NF_4^+ salt and that, in agreement with Dean's observations for SO_2 solutions,[14] the equilibrium is shifted far to the right.

$$SnF_6^{--} + SnF_4 \rightleftharpoons 2\ SnF_5^-$$

Properties. Both salts, $(NF_4)_2SnF_6$ and NF_4SnF_5, are white, stable, crystallinic, moisture sensitive solids. As previously pointed out,[2] the onset of thermal decomposition is difficult to define for NF_4^+ salts owing to the absence of a sharp decomposition point. For the SnF_4 salts, one of the decomposition products is nonvolatile solid SnF_4 and, therefore, no melting point could be observed. Visual observation for $(NF_4)_2SnF_6$ in sealed glass capillaries indicated the first signs of decomposition at about 240°. The occurrence of decomposition in this temperature range was confirmed by a DSC study which showed the onset of an irreversible endotherm at about 225° which was accompanied by F_2 evolution. Furthermore, sealed glass capillaries, when heated above 300°, exploded due to pressure build up from the gaseous decomposition products. For NF_4SnF_5 in a sealed glass capillary, slight shrinkage of the solid was observed at about 120°. The DSC curve did not show any evidence for a sharp change in slope up to a temperature of about 270°, where a large exotherm started. It should be kept in mind, however, that for powerful oxidizers, such as NF_4^+ salts, exotherms can be caused by reaction of the oxidizer with the aluminum sample container.

The hydrolyses of $(NF_4)_2SnF_6$ and NF_4SnF_5 proceeds, as previously established for other NF_4^+ salts,[2,15] with quantitative NF_3 evolution. This reaction was also used for the elemental analyses. In anhydrous HF, the $(NF_4)_2SnF_6$ salt is highly soluble, whereas NF_4SnF_5 is of moderate solubility. Both salts are also soluble in BrF_5, however the solubilities are considerably lower than those in HF.

X-Ray Powder Data. The powder pattern of $(NF_4)_2SnF_6$ is given as supplementary material. The observed pattern, after correction for several weak lines due to the presence of the metathesis by-products NF_4SbF_6[1] and $CsSbF_6$[16], is very similar to that[2] of $(NF_4)_2GeF_6$, indicating that the two compounds are isotypic. The pattern was indexed for a tetragonal unit cell, and the reulting crystallographic parameters of $(NF_4)_2SnF_6$ are compared in Table I with those of other NF_4^+ salts. As can be seen, the agreement is excellent. Since $(NF_4)_2GeF_6$ has been prepared in high purity and is well characterized,[2] the x-ray powder data establish beyond doubt that the major crystalline product from the $NF_4SbF_6 + Cs_2SnF_6$ metathesis is indeed $(NF_4)_2SnF_6$.

The powder pattern of NF_4SnF_5 was also recorded and is given as supplementary material. It did not contain any lines which could be attributed to either NF_4BF_4,[2] SnF_4, or $(NF_4)_2SnF_6$. Reliable indexing of the pattern was not possible owing to the large number of observed lines, but it somewhat resembles that previously observed[2] for NF_4GeF_5.

NMR Spectra. The ^{19}F nmr spectra were recorded for both $(NF_4)_2SnF_6$ and NF_4SnF_5 in BrF_5 solution. In spite of its higher melting point (-60.5°) and lower solubilities, this solvent was preferred over HF, because it was found difficult[2] to suppress rapid fluoride exchange between HF and the anions. In BrF_5 solution, no such problems were encountered. Well resolved spectra were observed for both the NF_4^+ cation and the corresponding anions, in addition to the sharp quintet (ϕ = -272) and doublet (ϕ = -136) with J_{FF} = 74.7 Hz characteristic for BrF_5.[2,17] For both the $(NF_4)_2SnF_6$ and the NF_4SnF_5 solution a triplet of equal intensity with ϕ = -220, J_{NF} = 229.6 Hz, and a line width at half height of about 5 Hz was observed which is characteristic for tetrahedral NF_4^+.[2,15,18] The $(NF_4)_2SnF_6$ solution showed in addition to these resonances a narrow singlet at ϕ = 149 with the appropriate $^{117/119}Sn$ satellites (average J_{SnF} = 1549 Hz). These values are in good agreement with those previously reported[14,19] for octahedral SnF_6^{--} in different solvents. This assignment was further confirmed by recording the spectrum of Cs_2SnF_6 in BrF_5 solution.

Table I. Crystallographic Data of $(NF_4)_2SnF_6$ Compared to Those of Other NF_4^+ Salts

	Tetragonal Unit Cell Dimensions			Z	Volume (Å^3) per F	Calcd Density (g/cm^3)
	a(Å)	c(Å)	V(Å^3)			
NF_4PF_6 [a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6 [a]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6 [a]	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6 [a]	8.006	5.821	373.10	2	18.66	3.68
NF_4BF_4 [b]	9.944	5.229	517.04	4	16.16	2.27
$(NF_4)_2GeF_6$ [b]	10.627	11.114	1255.14	16/3	16.81	2.59
$(NF_4)_2SnF_6$	10.828	11.406	1337.35	16/3	17.91	2.73

(a) Ref. 1

(b) Ref. 2

Two resonances were observed for SnF_5^- of NF_4SnF_5 at ϕ = 145.4 and 162.4, respectively, with an area ratio of 1:4. At -20° the resonances consisted of broad lines, but at lower temperatures the ϕ = 162.4 signal showed splittings. These splittings exhibited a pronounced temperature dependence (see Figure 2). The observed spectrum can be interpreted by comparison with the data previously reported[14] by Dean for $(SnF_5)_n^{n-}$ in SO_2 solution. For this ion, Dean observed a singlet at 140.4 ppm and two approximately 1:2:1 triplets at 154.2 and 158.1 ppm, respectively, with area ratios of 1:2:2. The lower field triplet was broader than the higher field triplet and the coupling constant was 58 Hz. These data unambigously showed[14] that $(SnF_5)_n^{n-}$ must have a polymeric structure consisting of cis fluorine bridged SnF_6 octahedrons. Our data for $(SnF_5)_n^{n-}$ in NF_4SnF_5 are quite similar with the only exception that the difference in chemical shift between the two triplets has decreased and decreases further with decreasing temperature. Thus the resonance at 164.2 ppm (area 4) can be interpreted as an A_2B_2 system strongly distorted by second order effects.[20] The singlet at 145.4 ppm (area 1) must then be due to the bridging fluorines. The 4:1 area ratio results from the fact that only the two bridging fluorines are shared by two octahedrons. As found by Dean, the coupling between the axial and the terminal equatorial fluorines is much larger (about 40-60 Hz) than that between the terminal and the bridging fluorines. Furthermore, the lower field half of the 162.4 ppm resonance shows a greater line width than the upper half, indicating weak, but differing, coupling between the bridging and the two types of terminal fluorines.

Our observations for NF_4SnF_5 are in excellent agreement with the data of Dean[14] and demonstrate the polymeric cis fluorine bridged nature of SnF_5^-. However, we are less confident than Dean that in $(SnF_5)_n^{n-}$, n equals 2. Higher values of n can certainly not be excluded and n might vary within and from sample to sample, as indicated by varying solubilities observed for different samples during this study. Attempts were unsuccessful to observe the spectrum of a 1:1 mol ratio mixture of Cs_2SnF_6 and SnF_4 in BrF_5 solution owing to its low solubility. Only a signal due to SnF_6^{--} was observed.

Vibrational Spectra. The infrared and Raman spectra of $(NF_4)_2SnF_6$ and NF_4SnF_5 were recorded and are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are listed in Tables II and III. Comparison with the known spectra[1,2] of other NF_4^+ salts clearly demonstrates the presence of tetrahedral NF_4^+ cations, and the bands due to NF_4^+ can be easily assigned. The observation of small splittings for the degenerate modes of NF_4^+ and the observation of the ideally infrared inactive $\nu_1(A_1)$ mode as a very weak band in the infrared spectra indicate that the site symmetry of NF_4^+ in these solids is lower than T_d. This is not surprising in view of the above given x-ray powder data, and has previously been also observed[1,2] for other NF_4^+ salts.

The assignments for the anion bands in $(NF_4)_2SnF_6$ are also straightforward. The vibrational spectra of octahedral SnF_6^{--} are well known[19,21-24] and establish the presence of SnF_6^{--} in $(NF_4)_2SnF_6$ (see Table II).

The anion spectrum in NF_4SnF_5 shows a pattern very similar to that of the anion in NF_4GeF_5. Furthermore, the general appearance of these anion spectra closely resembles the spectrum previously reported[25] for solid TaF_5. The structure of the latter has been established by x-ray diffraction data[26] as a cis fluorine bridged tetramer. Consequently, the observed vibrational spectra indicate a value of 4 for n in these $(MF_5)_n^{n-}$ polyanions. A thorough vibrational analysis has been carried out[25] for tetrameric NbF_5 and TaF_5 by Beattie and coworkers. Using their data, we have made tentative assignments for the stretching modes of SnF_5^- and GeF_5^- based on tetrameric anions, which are given in Table V. The assumption of a low degree of polymerization, such as a cyclic tetramer, for the anions in these NF_4MF_5 salts is not unreasonable in view of their appreciable solubility in solvents, such as HF or BrF_5. However, a crystal structure determination is desirable to confirm the above conclusions.

Summary. The successful syntheses of NF_4SnF_5 and $(NF_4)_2SnF_6$ demonstrate the possibility of preparing NF_4^+ salts derived from nonvolatile and unreactive polymeric Lewis acids. Such salts are important for solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers, because they do not require the

Table II. Vibrational Spectra of Solid $(NF_4)_2SnF_6$ Compared to Those of Cs_2SnF_6

obsd freq (cm^{-1}) and rel intens [a]				assignments (point group)	
$(NF_4)_2SnF_6$		Cs_2SnF_6		NF_4^+ (T_d)	SnF_6^{--} (O_h)
IR	RA	IR	RA		
2310 vw				$2\nu_3$ (A_1+E+F_2)	
2005 vw				$\nu_1+\nu_3$ (F_2)	
1764 vw				$\nu_3+\nu_4$ (A_1+E+F_2)	
1463 vw				$\nu_1+\nu_4$ (F_2)	
1224 mw				$2\nu_4$ (A_1+E+F_2)	
1160 vs	1158 (1.5)			ν_3 (F_2)	
1132 sh,vw					$\nu_1+\nu_3$ (F_{1u})
1059 vw				$\nu_2+\nu_4$ (F_1+F_2)	
1026 vw					$\nu_2+\nu_3$ (F_{1u}+F_{2u})
	881 (0.1)			$2\nu_2$ (A_1+A_2+E)	
854 vvw	853 (10)			ν_1 (A_1)	
613 mw	613 (5.0)			ν_4 (F_2)	
605 mw	607 (1.5)				
	579 (8.3)		573 (10)		ν_1 (A_{1g})
550 vs		555 vs			ν_3 (F_{1u})
	470 (0+) br		460 (1.2)		ν_2 (E_g)
	449 (3.1)			ν_2 (E)	
	442 (2.9)				
	251 (3.3)		249 (4.5)		ν_5 (F_{2g})
	84 (0.3)			lattice vibration	

(a) uncorrected Raman intensities

Table III. Vibrational Spectra of Solid NF_4SnF_5 Compared to Those of NF_4GeF_5

obsd freq (cm^{-1}) and rel intens [a]				assignments[c] (point group)	
NF_4SnF_5		NF_4GeF_5 [b]		NF_4^+ (T_d)	$(MF_5)_4^{4-}$
IR	RA	IR	RA		
		2380 vw		$2\nu_3$ (A_1+E+F_2)	
2320 w		2320 w			
2000 w		2010 w		$\nu_1+\nu_3$ (F_2)	
1760 w		1766 w		$\nu_3+\nu_4$ (A_1+E+F_2)	
1464 vw		1465 w		$\nu_1+\nu_4$ (F_2)	
1456 w		1456 vw			
1222 mw		1221 mw		$2\nu_4$ (A_1+E+F_2)	
	1168 (0.4)		1168 (0.8)		
1165 vs	1159 (0.8)	1160 vs	1159 (0.8)	ν_3 (F_2)	
	1150 sh		1149 (0.9)		
1134 w,sh					
1061 w		1055 w		$\nu_2+\nu_4$ (F_1+F_2)	
1048 w					
	881 (0.2)		881 (0+)	$2\nu_2$ (A_1+A_2+E)	
850 vw	851 (10)		848 (10)	ν_1 (A_1)	
635 vs		701 vs			ν_{as} MF_2 ax (ν_{22}) and ν_{as} MF_2 eq (ν_{25})
		690 sh	689 (1.0)		ν_{as} MF_2 ax (ν_{17}) and ν_{sym} MF_2 eq (ν_7)
	622 (9.2)	673 mw	672 (4.9)		ν_{sym} MF_2 eq (ν_1)
		613 m	615 (0.8)		
605 mw	606 (3.3)	604 m	604 (3.2)	ν_4 (F_2)	
		593 m	594 (2.6)		
575 vs		630 vs			ν_{as} MF_2 eq (ν_{26})
	574 (0.5)				ν_{as} MF_2 eq (ν_{13})
559 w,sh	558 (2.0)		578 (1.6)		ν_{sym} MF_2 ax (ν_2)
490 m	490 (0+)		490 (0+)		ν_{sym} MFM bridge (ν_9)
458 m		474 mw			ν_{as} MFM bridge (ν_{28})
	448 (2.5)		440 (2.6)	ν_2 (E)	
	440 (2.3)		431 (2.2)		
		386 m			
		373 w	373 (0+) br		
			343 (0+) br		
		335 m			
	272 (0.6)		321 (0.8)		deformation modes
	247 (1.4)		281 (1.0)		
	222 (1.1)		249 (0.6)		
	197 (0.6)		212 (0.4)		
	154 (0+)				
	135 (0.2)		132 (0.4)		

(a) uncorrected Raman intensities
(b) data from ref 2
(c) assignments for $(MF_5)_4^{4-}$ were made by analogy with the data of ref 25

addition of a clinker forming reagent. The synthesis of NF_4SnF_5 was achieved by depolymerizing SnF_4 in anhydrous HF and displacing BF_4^- from NF_4BF_4 as BF_3 gas. For the synthesis of $(NF_4)_2SnF_6$ a metathetical process was required. Both NF_4^+ salts were characterized by material balance, elemental analysis, infrared, Raman, and ^{19}F nmr spectroscopy, x-ray powder diffraction data, and DSC. Whereas $(NF_4)_2SnF_6$ contains monomeric SnF_6^{--} anions, NF_4SnF_5 contains polymeric, cis fluorine bridged, hexacoordinated anions. The vibrational spectra indicate that in solid NF_4SnF_5 the anion is probably present as a cyclic tetramer.

Acknowledgment. We are grateful to Dr. L. R. Grant for helpful discussions and to the Office of Naval Research, Power Branch, for financial support.

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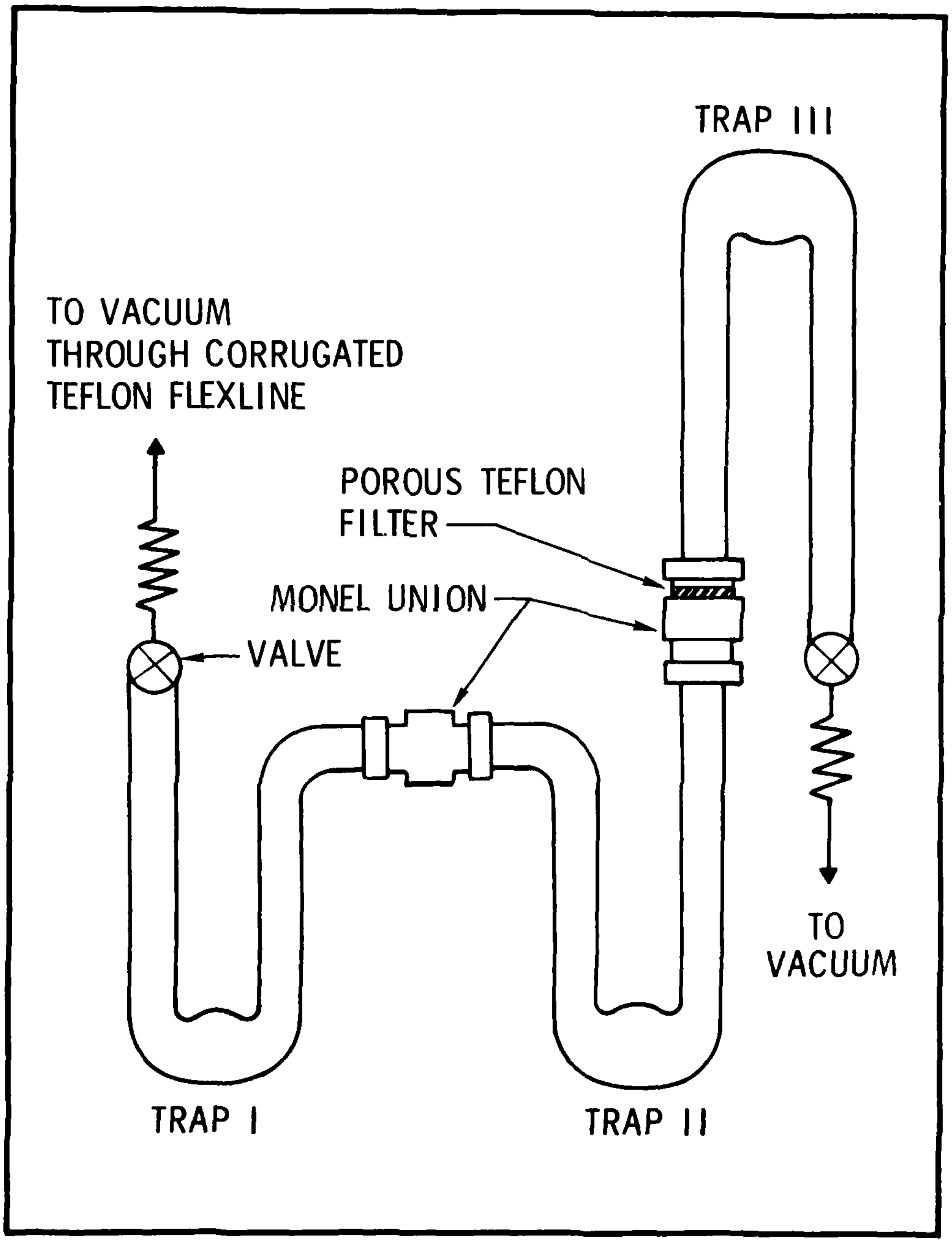
Diagram Captions

Figure 1. Apparatus for small-scale metathetical reactions consisting of three interconnected Teflon-FEP U-traps.

Figure 2. Temperature dependence of the ^{19}F nmr spectrum of the $(SnF_5)_n^{n-}$ part of NF_4SnF_5 in BrF_5 solution, recorded at 56.4 MHz using $CFCl_3$ as external standard.

Figure 3. Vibrational spectra of solid $(NF_4)_2SnF_6$. Trace A: Infrared spectrum of the dry powder in a silver chloride disk; the absorption below 400 cm^{-1} (broken line) is due to the AgCl windows. Trace B: Raman spectrum recorded at a spectral slit width of 3 cm^{-1}. Weak bands due to SbF_6^- were deleted from the spectra.

Figure 4. Vibrational spectra of solid NF_4SnF_5, recorded under the same conditions as those of Figure 3.


TRAP III
TO VACUUM
THROUGH CORRUGATED
TEFLON FLEXLINE
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MONEL UNION
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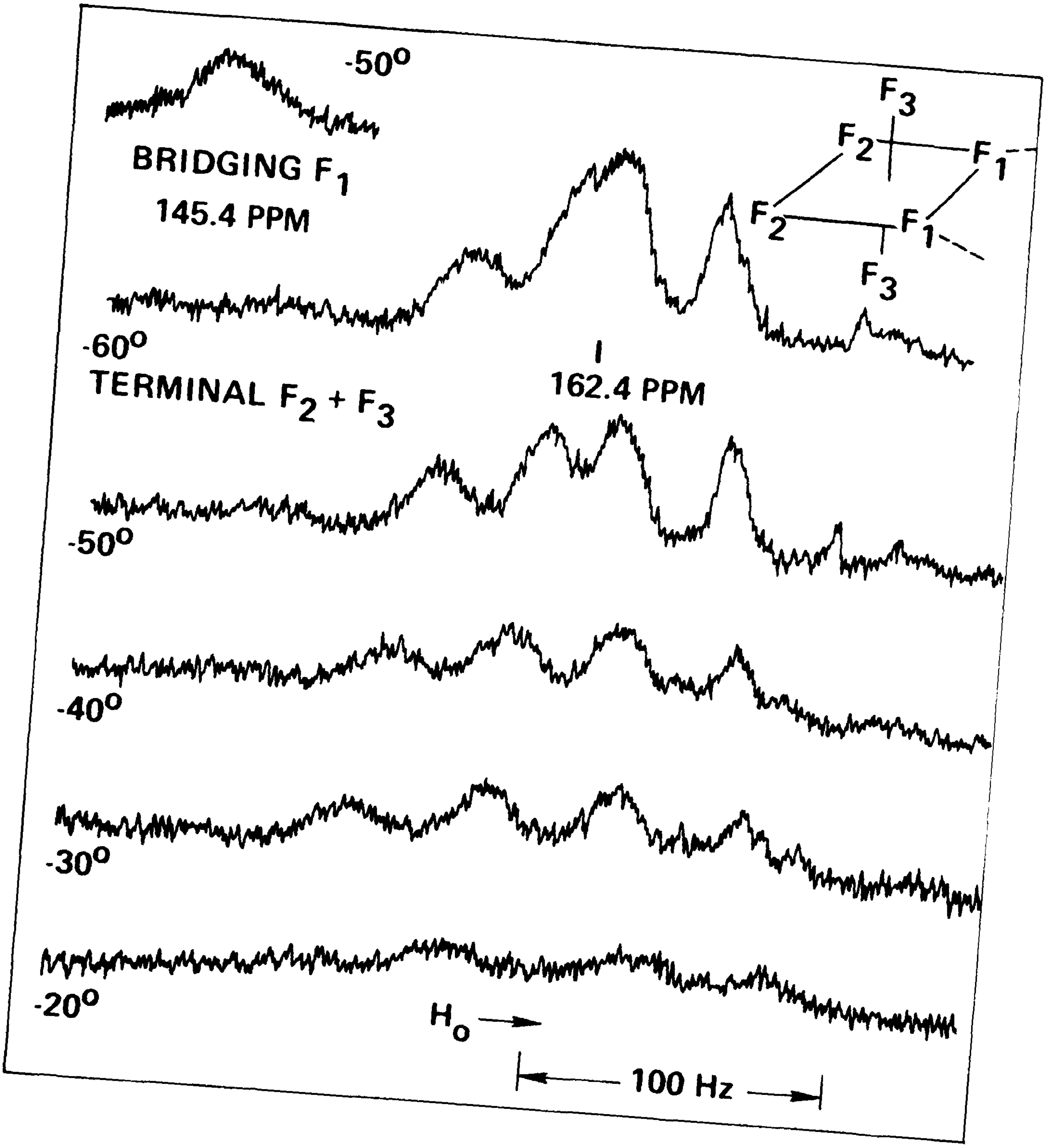
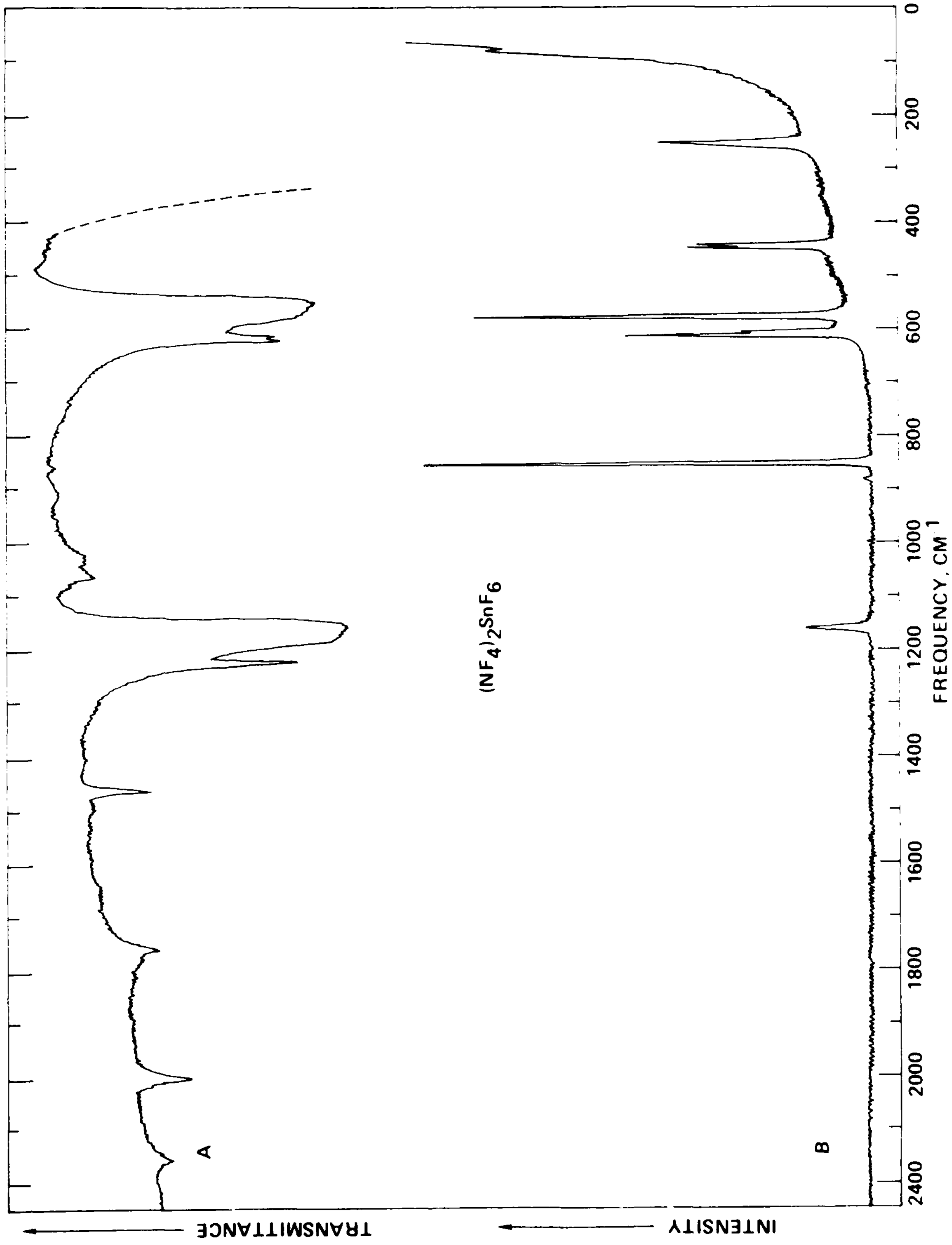
TRAP II


-50°
BRIDGING F1
145.4 PPM
F3
F2
F1
F2
F1
F3
-60°
TERMINAL F2 + F3
162.4 PPM
-50°
-40°
-30°
-20°
Ho →
100 Hz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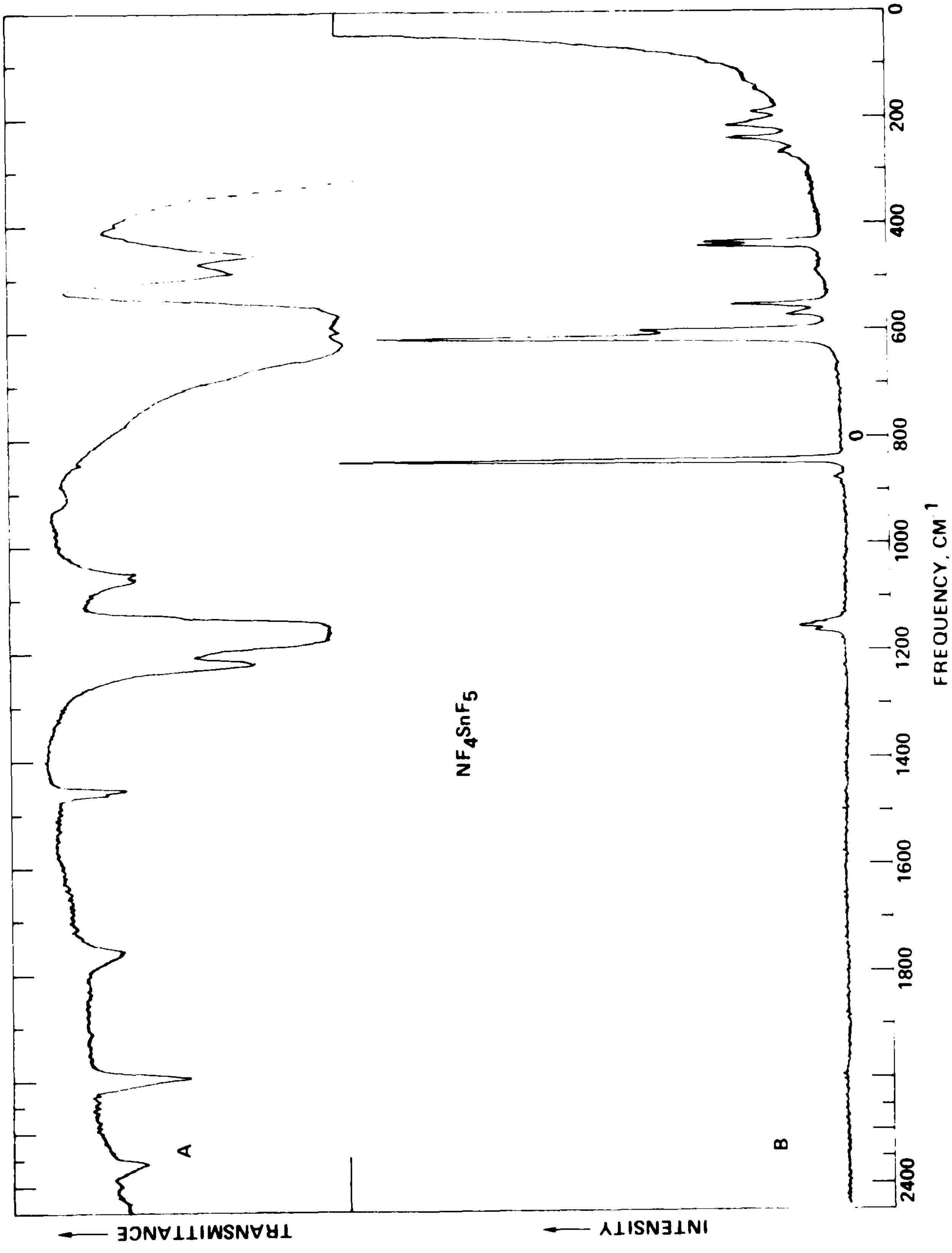

NF4SnF5
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Contribution from Rocketdyne, A Division of
Rockwell International, Canoga Park, California 91304

Synthesis and Characterization of $(NF_4)_2TiF_6$ and of Higher NF_4^+ and Cs^+ Polyperfluorotitanate (IV) Salts

Karl O. Christe* and Carl J. Schack

Received . . . .

Abstract

Metathesis between Cs_2TiF_6 and NF_4SbF_6 in HF solution was used to prepare the novel perfluoroammonium salt $(NF_4)_2TiF_6$. The compound is a white crystalline solid, stable to about 200°. It was characterized by elemental analysis and infrared, Raman and ^{19}F nmr spectroscopy. X-ray powder data show that the compound (tetragonal, a = 10.715Å, c = 11.114Å) is isotypic with $(NF_4)_2GeF_6$ and $(NF_4)_2SnF_6$. Thermal or HF solution displacement reactions between NF_4BF_4 and TiF_4 produced the polyperfluorotitanate (IV) salts $NF_4Ti_2F_9$ and $NF_4Ti_3F_{13}$. Heating of NF_3, F_2, and TiF_4 to 190° at an autogenous pressure of 160 atm produced a salt of the approximate composition $NF_4Ti_6F_{25}$. For comparison, TiF_4 and the salts Cs_2TiF_6, $Cs_2Ti_2F_{10}$ and $CsTi_2F_9$ were synthesized and characterized by vibrational spectroscopy.

Introduction

Although the nonexistence of an NF_5 parent molecule and the high ionization potentials of NF_3 and fluorine made the original synthesis of NF_4^+ salts difficult,[1] their surprisingly high thermal stability permits the syntheses of salts of relatively weak Lewis acids. Thus, the preparation of stable

NF_4^+ salts [2,3] containing GeF_5^-, GeF_6^{--}, SnF_5^-, and SnF_6^{--} anions has been recently reported. Since NF_4^+ salts are of significant interest for solid propellant NF_3-F_2 gas generators [4] for chemical HF-DF lasers, the synthesis of novel higher performing NF_4^+ salts is desirable. In this paper, we report on the syntheses and properties of NF_4^+ salts derived from TiF_4.

Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those previously described. [2-4] The CsF was fused in a platinum crucible and powdered in the dry box. The NF_3 and F_2 were prepared at Rocketdyne, the HF (Matheson) was dried as previously described, [5] and the BrF_5 (Matheson) was purified by fractional condensation prior to use. Pure NF_4BF_4 was prepared from NF_3, F_2, and BF_3 by uv-photolysis [2] at -196° and the NF_4SbF_6 was synthesized as previously described. [4] A 10 year old sample of commercial TiF_4 (Allied) had undergone partial hydrolysis, but was converted back to pure TiF_4 by fluorinating it in a Monel cylinder for 2 days at 250° with F_2 at 70 atm pressure. Both, treated and untreated, samples of TiF_4 were used in the displacement reactions with NF_4BF_4. In some cases the course of the reactions was influenced by the choice of the TiF_4.

Synthesis of Cs_2TiF_6. Dry CsF (40.3 mmol) and TiF_4 (20.15 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (3 ml liquid) was added at -78°. The mixture was warmed to 24° and stirred for 1 hour until all solid material had dissolved. The volatile materials were pumped off at 70° for 2 hours. The white solid residue (8.621 g, weight calcd for 20.15 mmol of Cs_2TiF_6 = 8.619 g) was shown by infrared and Raman spectroscopy to be Cs_2TiF_6 of excellent purity. The products obtained from both, untreated and prefluorinated TiF_4, were undistinguishable. The solubility of Cs_2TiF_6 in anhydrous HF at 24° was found to be about 4 g per g of HF.

Synthesis of $Cs_2Ti_2F_{10}$. This salt was synthesized from equimolar amounts of Cs_2TiF_6 and prefluorinated TiF_4 by either heating in a Monel cylinder to 180° for 7 days or by stirring the mixture in liquid anhydrous HF for 4 days at

25° and pumping off the volatile material at 50° for 3 hours. The observed weights closely corresponded to those expected for $Cs_2Ti_2F_{10}$. Vibrational spectroscopy showed only small amounts of TiF_6^{--} and $Ti_2F_9^-$ for the product of the thermal reaction and of TiF_4, $Ti_2F_9^-$, TiF_6^{--}, and a higher polyanion (Ra band at 778 cm^{-1}) for the HF displacement reaction.

Synthesis of $CsTi_2F_9$. This salt was prepared as described above for $Cs_2Ti_2F_{10}$, except for using Cs_2TiF_6 and TiF_4 in a 1:3 mole ratio. Vibrational spectroscopy showed that the product from the HF reaction contained mainly $Ti_2F_9^-$ with traces of TiF_4 and $Ti_2F_{10}^{--}$ being present. The product from the thermal reaction was a mixture of approximately $4TiF_4$, $4CsTi_2F_9$, and $2Cs_2Ti_2F_{10}$.

The synthesis of higher polyperfluorotitanate (IV) anions was attempted by heating a 1:5 mol ratio mixture of Cs_2TiF_6 and TiF_4 to 180° for 7 days. Vibrational spectroscopy, however, showed the presence of only $Ti_2F_{10}^{--}$, $Ti_2F_9^-$, and unreacted TiF_4.

Synthesis of $(NF_4)_2TiF_6$. The metathetical synthesis of $(NF_4)_2TiF_6$ from saturated HF solutions of NF_4SbF_6 (10.00 mmol) and Cs_2TiF_6 (5.00 mmol) was carried out in the apparatus previously described [3] for the synthesis of $(NF_4)_2SnF_6$. 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° and filtered. The volatile materials were pumped off at 50° 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 $(NF_4)_2TiF_6$. The filtrate residue (1.55 g, weight calcd for 5 mmol of $(NF_4)_2TiF_6$ = 1.71 g) had the composition (mol %): 88.5 $(NF_4)_2TiF_6$ and 11.5 $CsSbF_6$. Found: NF_3, 8.77; Ti, 12.21; Sb, 4.11; Cs, 4.4. Calcd for a mixture of 88.5 $(NF_4)_2TiF_6$ and 11.5 $CsSbF_6$: NF_3, 8.72; 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 $(NF_4)_2TiF_6$ and 10 $CsSbF_6$, in good agreement with the above elemental analysis.

Displacement Reactions between NF_4BF_4 and TiF_4. These 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° 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 1.

Direct Synthesis of NF_4^+ Polyperfluorotitanates (IV). Prefluorinated 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° 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 $Ti_6F_{25}^-$, see below) having its strongest Raman line at 784 cm^{-1}. During the next two heating cycles (190-195° for 14 days and 180° 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° 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 $NF_4Ti_6F_{25}$ (calcd weight increase, 205 mg; obsd weight increase 198 mg).

Results and Discussion

Syntheses of NF_4^+ Salts. Perfluoroammonium salts of TiF_4 were prepared by the following methods.

(1) Metathesis:

$$Cs_2TiF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF solution}} 2CsSbF_6\downarrow + (NF_4)_2TiF_6$$

The yield of $(NF_4)_2TiF_6$ in this reaction is practically quantitative, except for material losses caused by the retention of a certain amount of mother liquor by the filter cake. The purity of the material obtained in this manner was approximately 88.5 mol percent, the remainder being $CsSbF_6$.

(2) Direct synthesis from NF_3, F_2, and TiF_4:

$$NF_3 + F_2 + 6TiF_4 \xrightarrow[160\text{ atm}]{190°} NF_4Ti_6F_{25}$$

Heating of TiF_4 with a large excess of NF_3 and F_2 to 180-195° for 50 days under an autogenous pressure of about 160 atm produced a solid of the approximate composition $NF_4Ti_6F_{25}$. Significant increases or decreases of the reaction temperature resulted in lower conversions of NF_3 to NF_4^+.

(3) Displacement reactions:

$$NF_4BF_4 + nTiF_4 \longrightarrow NF_4TiF_5\cdot(n-1)TiF_4 + BF_3$$

These reactions were carried out either in anhydrous HF solution at room temperature or by heating the solid starting materials in a Monel cylinder to 160-190°. The composition of the products was influenced by both the reaction conditions and the choice of the TiF_4 starting material (see Table 1). For the HF solution displacement reactions, the use of prefluorinated TiF_4 (see below) resulted in the following approximate stoichiometry, independent of the mol ratio of the starting materials:

$$NF_4BF_4 + 3TiF_4 \xrightarrow{\text{HF, }24°} NF_4Ti_3F_{13} + BF_3$$

When untreated TiF_4 was used, the reaction stoichiometry changed from 1:3 to 1:2, again independent of the mol ratio of the starting materials:

$$NF_4BF_4 + 2TiF_4 \xrightarrow{HF,\ 24^\circ} NF_4Ti_2F_9 + BF_3$$

In the thermal displacement reactions, the use of prefluorinated TiF_4 at 170° resulted in a clean 1:2 reaction between NF_4BF_4 and TiF_4 according to:

$$NF_4BF_4 + 2TiF_4 \xrightarrow{170^\circ} NF_4Ti_2F_9 + BF_3$$

When an excess of NF_4BF_4 was used, the reaction was complete in 20 hours, producing a mixture of $NF_4Ti_2F_9$ and unreacted NF_4BF_4. Using a 1:2 mol ratio of NF_4BF_4 and TiF_4, however, longer heating periods were required to avoid the formation of some $NF_4Ti_3F_{13}$ as a by-product.

With untreated TiF_4, some of the NF_4^+ salt was used up for the fluorination of the partially hydrolyzed TiF_4, however, the main product formed at 190° was again $NF_4Ti_2F_9$. When the reaction temperature was lowered to 160°, the main product was $NF_4Ti_3F_{13}$.

The above results are not surprising in view of our present understanding of NF_4^+ chemistry. It appears that the nature of the Lewis acid determines the possible synthetic routes towards their NF_4^+ salts. If a sufficiently strong Lewis acid is monomeric at the reaction temperature, a direct synthesis from NF_3, F_2, and the Lewis acid is possible. The initial step in this direct synthesis is the generation of F atoms [1] from F_2 by either discharge,[6,7] radiation,[1,[illegible],8] or heating.[4,9] These F atoms then react with the monomeric Lewis acid to form a Lewis acid·F radical,[10] a species which might be capable [1,11] of supplying the energy (ionization potential of NF_3 minus the energy released by the formation of the ion pair) required for the oxidation of NF_3 to NF_3^+. The latter cation can then be readily fluorinated by either F· or F_2 to NF_4^+. A typical example for this scheme is the low temperature uv photolysis of the NF_3-F_2-BF_3 system:[1,[illegible],1[illegible]]

$$F_2 \xrightarrow{hv} 2F^\cdot$$
$$F^\cdot + BF_3 \longrightarrow BF_4^\cdot$$
$$BF_4^\cdot + NF_3 \longrightarrow NF_3^+BF_4^-$$
$$NF_3^+BF_4^- + F^\cdot \longrightarrow NF_4^+BF_4^-$$

On the other hand, if the Lewis acid is polymeric at temperatures above the thermal decomposition point of its NF_4^+ salt, indirect synthetic methods must be used. A typical example is SnF_4 (sublimation point 704°), where metathesis

$$Cs_2SnF_6 + 2NF_4SbF_6 \xrightarrow{\text{HF solution}} 2CsSbF_6{\downarrow} + (NF_4)_2SnF_6$$

and the displacement reaction

$$2NF_4BF_4 + 2SnF_4 \xrightarrow{\text{HF solution}} (NF_4)_2Sn_2F_{10} + 2BF_3$$

have successfully been applied [3] to the syntheses of its NF_4^+ salts.

The physical properties of TiF_4 (polymeric solid at room temperature with a vapor pressure of 1 atm at 284°) are intermediate between those of BF_3 (b.p. -101°) or GeF_4 (1 atm vapor pressure at -36°) and SnF_4 (b.p. 705°). Consequently, the successful, although slow, direct thermal synthesis of an NF_4^+ salt of TiF_4 and the pronounced tendency of TiF_4 to form polyanions are not unexpected. However, the actual composition of the polyanions was surprising. Whereas both GeF_4 and SnF_4 in their displacement reactions [2,3] with NF_4BF_4 *form exclusively the* $Ge_2F_{10}^{--}$ *and* $Sn_2F_{10}^{--}$ anions, respectively, no evidence was obtained for the formation of $Ti_2F_{10}^{--}$ in the corresponding reactions of TiF_4. Instead, only the polymeric anions $Ti_2F_9^-$ and $Ti_3F_{13}^-$ were observed. Since TiF_6^{--} is known [12] to associate with TiF_5^- or TiF_4 to form $Ti_2F_{11}^{3-}$ and $Ti_2F_{10}^{--}$, respectively, the failure to observe the two latter anions in the NF_4BF_4-TiF_4 displacement reactions suggests that TiF_6^{--} is not formed as an intermediate in appreciable quantities. Furthermore, the absence of observable amounts of $Ti_2F_{10}^{--}$ indicates either that TiF_5^- preferentially associates with TiF_4 rather than with itself, or that the smallest TiF_4 units present which will accept a fluoride ion, are dimers. Unfortunately, the structures of both solid TiF_4 and of the species present in its HF solutions are unknown. Consequently, it is at present inappropriate to rationalize the different behavior of TiF_4 and of the two main group tetrafluorides.

The fact that the displacement reaction in HF solution resulted for untreated TiF_4 in a lower polyanion ($Ti_2F_9^-$) than for prefluorinated TiF_4, is consistent with previous reports [13] on the solubility of TiF_4 in HF. Thus TiF_4 is only sparingly soluble in anhydrous HF, but its solubility is significantly increased by the addition of a Lewis base, such as an alkali metal fluoride or water. Apparently, the base, i.e. F^- ions, helps to depolymerize the TiF_4. Since the untreated TiF_4 was partially hydrolyzed, it probably generated upon addition to the HF solution some H_2O, which in the presence of HF and TiF_4 would be protonated to yield OH_3^+ and a polytitanate anion. No chemical interaction between OH_3^+ and NF_4^+ is expected, since it has previously been demonstrated that $OH_3^+SbF_6^-$ and $NF_4^+SbF_6^-$ can coexist in HF solution.[14]

A previous study [13] on the relative strength of fluoroacids in HF solution had placed BF_3, SnF_4, and TiF_4 in categories 2, 3, and 5, respectively, where the acid strength decreased with increasing category number. The results from our studies, i.e. the fact that both SnF_4 and TiF_4 are capable of quantitatively displacing BF_4^- from NF_4BF_4 in HF solution, indicate that this acid classification is not generally valid.

Syntheses of Cs Salts. For the characterization of the polyperfluorotitanate (IV) anions in their NF_4^+ salts, a better knowledge of these anions was required. Very little information on polyperfluorotitanates (IV) has previously been published. Except for a recent DSC study on $NOTiF_5$, which was shown to decompose at 225° to $NOTi_2F_9$ and FNO, [15] the only detailed study on polyperfluorotitanates was carried out by Dean.[12] Studying the TiF_4 - $(Pr_2NH_2)_2TiF_6$ system in SO_2 solution by ^{19}F nmr spectroscopy, he established the presence of the $Ti_2F_{11}^{3-}$, $Ti_2F_{10}^{--}$, and $Ti_2F_9^-$ anions, in addition to other unidentified polymeric anions.

Our study in anhydrous HF as a solvent showed that pure Cs_2TiF_6 is formed from stoichiometric amounts of CsF and either untreated or prefluorinated TiF_4:

$$2CsF + TiF_4 \xrightarrow{HF} Cs_2TiF_6$$

The compound $Cs_2Ti_2F_{10}$ can be produced from an equimolar mixture of Cs_2TiF_6 and TiF_4 by either HF treatment at room temperature or heating of the solids to 180°:

$$Cs_2TiF_6 + TiF_4 \xrightarrow[HF,\ 25°]{180°\ or} Cs_2Ti_2F_{10}$$

Vibrational spectroscopy showed only traces of TiF_4, TiF_6^{--}, and $Ti_2F_9^-$, indicating that under these conditions $Ti_2F_{10}^{--}$ is clearly the favored species.

When the mol ratio of Cs_2TiF_6 to TiF_4 was changed to 1:3, the reaction in HF solution produced almost exclusively $Ti_2F_9^-$ according to:

$$Cs_2TiF_6 + 3TiF_4 \xrightarrow{HF,\ 25°} 2CsTi_2F_9$$

Only traces of TiF_4 and $Ti_2F_{10}^{--}$ were present. The thermal reaction, however, produced a mixture of approximately $4TiF_4$, $4CsTi_2F_9$, and $2Cs_2Ti_2F_{10}$.

A further increase of the TiF_4 ratio in the thermal reactions did not produce any evidence for the formation of polyanions higher than $Ti_2F_9^-$, but resulted in unreacted TiF_4. The HF solution study was not extended beyond the 1:3 Cs_2TiF_6:TiF_4 mol ratio.

Properties. The most interesting one of the novel salts prepared during this study is $(NF_4)_2TiF_6$, since it has the highest usable fluorine content of any presently known NF_4^+ salt. All the NF_4^+ perfluorotitanates (IV) are white crystalline solids. Based on observations of their thermal decompositions in sealed glass capillaries and on the results of the direct thermal synthesis and of the thermal displacement reactions, these NF_4^+ salts are stable to at least 200°. By analogy with the other known NF_4^+ salts, it is difficult to obtain meaningful decomposition temperatures from either m.p. determinations or DSC data.[2,3] All salts are hygroscopic and hydrolyze in water with quantitative NF_3 and less than quantitative O_2 evolution, in agreement with previous findings.[2] The hydrolysate shows the yellow color characteristic for titanyl salts. The $(NF_4)_2TiF_6$ salt is highly soluble in HF and moderately soluble in BrF_5. For the polyanion salts, the solubility decreases with increasing anion size.

The Cs^+ salts are also stable, white, crystallinic solids. The Cs_2TiF_6 salt is very soluble in HF (about 4 g/g of HF), but the solubility sharply decreases for the polyanion salts. The hydrolysis of the cesium perfluoropolytitanates (IV) was followed by Raman spectroscopy. The spectra obtained for the solid phase in equilibrium with the aqueous phase showed that the bands due to TiF_4 and the higher polyanion impurities disappeared first, accompanied by a simultaneous growth of the TiF_6^{--} bands. The aqueous phase showed TiF_6^{--} as the main constituent.

X-Ray Powder Data. The powder pattern of $(NF_4)_2TiF_6$ is listed in Table 2. After correction for weak lines due to $CsSbF_6$ and NF_4SbF_6, all observed lines could be indexed for a tetragonal unit cell. The resulting crystallographic parameters are compared in Table 3 to those of similar NF_4^+ salts. The similarity of the patterns of $(NF_4)_2TiF_6$, $(NF_4)_2SnF_6$,[3] and $(NF_4)_2GeF_6$ [2] indicates that the three compounds are isotypic.

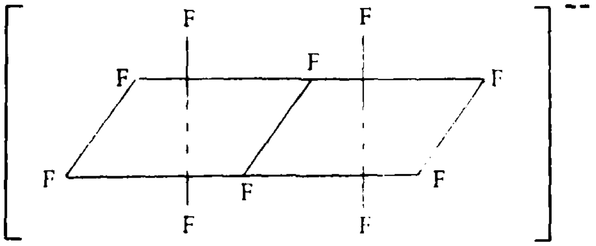
NMR Spectra. Since in HF solution rapid exchange between the solvent and the anion prevents observation of well resolved anion spectra, the ^{19}F nmr spectrum of $(NF_4)_2TiF_6$ was recorded in BrF_5 solution. In addition to the solvent lines, [2] the spectrum showed the characteristic [9,16] triplet ($\phi = -220.8$, $J_{NF} = 229$ Hz) for NF_4^+ and the characteristic [12,17] TiF_6^{--} signal at $\phi = -81.7$. The solubility of the NF_4^+ polytitanate salts in BrF_5 was too low to permit the observation of useful spectra. Since the ^{19}F nmr spectra of $Ti_2F_{11}^{3-}$, $Ti_2F_{10}^{--}$, and $Ti_2F_9^-$ in SO_2 solution have previously been studied and assigned in detail by Dean,[12] no further work in this direction was undertaken.

Vibrational Spectra. The infrared and Raman spectrum of solid $(NF_4)_2TiF_6$ is shown in Figure 1. The observed frequencies are listed in Table 4. Comparison with the previously reported [2-4,8,16,18] spectra of other NF_4^+ salts demonstrates beyond doubt the presence of the NF_4^+ cation. The remaining bands are due to the anion and are in excellent agreement with those previously reported for TiF_6^{--} in Cs_2TiF_6 [17,19] and $(HgI)_2TiF_6$.[20] The observation of small splittings for some of the degenerate modes of NF_4^+ indicate that the site symmetry of NF_4^+ in the solid is lower than T_d. The same effect has previously been observed [3] for isotypic $(NF_4)_2SnF_6$.

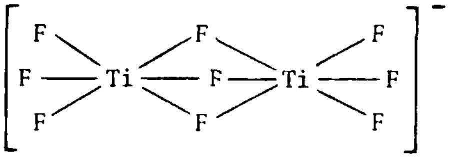
The vibrational spectra of $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$ are shown in Figures 1 and 2, respectively, and the observed frequencies are listed in Table 5. Again, the presence of NF_4^+ is clearly established.

For a better characterization of the anion bands, the vibrational spectra of several cesium salts and of solid TiF_4 were also recorded (see Figures 3 and 4, and Tables 4-6). Since Cs_2TiF_6 can be prepared in high purity and since higher polytitanate impurities preferentially underwent hydrolysis, no problems were encountered with defining the principal bands belonging to each anion. The single most useful band for the identification of a polyperfluorotitanate (IV) anion is the symmetric, in phase, terminal TiF stretching mode. This mode results in a narrow and very intense Raman band, the frequencies of which have been denoted in Figures 1-3. As can be seen, the frequency of this band increases with increasing TiF_4 content and decreasing negative charge of the anion, i.e. $TiF_6^{--} < Ti_2F_{10}^{--} < Ti_2F_9^- < Ti_3F_{13}^- < Ti_6F_{25}^- < (TiF_4)_n$.

The structure of $Ti_2F_{10}^{--}$ has been well established [12] by ^{19}F nmr spectroscopy as the cis-fluorine bridged dimer and a thorough vibrational analysis has previously been carried [21,22] out for the isostructural molecule Nb_2Cl_{10}. Consequently, sufficient information was available to allow some tentative assignments for $Ti_2F_{10}^{--}$. These assignments are summarized in Table 6 and are based on the symmetry coordinates defined for Nb_2Cl_{10} by Beattie and coworkers.[21]



No attempts were made to assign the spectra of the remaining polyperfluorotitanate (IV) anions and TiF_4 itself, although some data are available for $Ti_2F_9^-$. Dean suggested [12] on the basis of ^{19}F nmr data for $Ti_2F_9^-$ the triply fluorine bridged structure and Beattie has analyzed [21] the vibrational spectrum



of the isostructural $Tl_2Cl_9^{3-}$ anion. Our spectra of prefluorinated TiF_4 (see Figures 3 and 4) significantly differ from those of untreated TiF_4 and those [23-25] previously reported in the literature.

Summary. The synthesis of NF_4^+ salts has successfully been extended to a subgroup element. The results of this study show that TiF_4 can act as a much stronger Lewis acid than predicted on the basis of previous literature data.[13] Thus, stable NF_4^+ salts derived from TiF_4 can be prepared either directly or indirectly. Of all the presently known NF_4^+ salts, $(NF_4)_2TiF_6$ contains the highest percentage of usable fluorine and, therefore, is an excellent candidate for a solid propellant NF_3-F_2 gas generator.

Acknowledgement. We are grateful to Dr. L. R. Grant and R. D. Wilson for their help and to the Office of Naval Research, Power Branch, for financial support.

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Diagram Captions

Figure 1. Vibrational spectra of solid $(NF_4)_2TiF_6$ and $NF_4Ti_2F_9$. Traces A and B, infrared and Raman spectra of $(NF_4)_2TiF_6$, respectively. Traces C and D, corresponding spectra of $NF_4Ti_2F_9$, prepared by the thermal (170°) displacement reaction between NF_4BF_4 and TiF_4 (1:2). The absorptions below 400 cm^{-1} in the infrared spectra (broken lines) are due to the AgCl windows. Weak bands, due to impurities, were deleted from the spectra. Raman spectra were recorded with a spectral slit width of 3 cm^{-1}. The insert was recorded at a higher recorder gain.

Figure 2. Vibrational spectra of solid $NF_4Ti_3F_{13}$ and $NF_4Ti_6F_{25}$, recorded under the same conditions as those of Figure 1. The samples of $NF_4Ti_3F_{13}$ and $NF_4Ti_6F_{25}$ were prepared by the displacement reaction between NF_4BF_4 and prefluorinated TiF_4 in HF and by direct synthesis from NF_3, F_2, and TiF_4 at 190°, respectively.

Figure 3. Raman spectra of solid Cs_2TiF_6, $Cs_2Ti_2F_{10}$, $CsTi_2F_9$, and prefluorinated TiF_4.

Figure 4. Infrared spectra of solid Cs_2TiF_6, $Cs_2Ti_2F_{10}$, $CsTi_2F_9$, and prefluorinated TiF_4 as dry powders in AgCl disks.

Table 1. Results from the Displacement Reactions between NF_4BF_4 and TiF_4

Reactants (mol)	Reaction Conditions	Products (mol)
NF_4BF_4(6), untreated TiF_4(6)	HF, 24°, 18h	$NF_4Ti_2F_9$(4), NF_4BF_4(4)
NF_4BF_4(6), untreated TiF_4(12)	HF, 24°, 72h	$NF_4Ti_2F_9$(6)
NF_4BF_4(6), prefluor. TiF_4(6)	HF, 24°, 138h	$NF_4Ti_3F_{13}$(~2), NF_4BF_4(~4), small amount of $NF_4Ti_2F_9$
NF_4BF_4(6), prefluor. TiF_4(12)	HF, 24°, 96h	$NF_4Ti_3F_{13}$(4), NF_4BF_4(2),
NF_4BF_4(6), untreated TiF_4(6)	190°, 18h	$NF_4Ti_2F_9$(~3), NF_3(~3), BF_3(~6), small amounts of NF_4BF_4 and $NF_4Ti_3F_{13}$
NF_4BF_4(6), untreated TiF_4(6)	160°, 60h	$NF_4Ti_3F_{13}$(2), NF_4BF_4(1.4), NF_3(2.6), BF_3(4.6)
NF_4BF_4(6), prefluor. TiF_4(6)	170°, 20h	$NF_4Ti_2F_9$(3), NF_4BF_4(3),BF_3(3)
NF_4BF_4(6), prefluor. TiF_4(12)	170°, 20h	$NF_4Ti_2F_9$(3.6), $NF_4Ti_3F_{13}$(1.6), BF_3(5.4), NF_4BF_4(0.6)
NF_4BF_4(6), prefluor. TiF_4(12)	170°, 192h	$NF_4Ti_2F_9$(6), BF_3(6)

Table 2. X-Ray Powder Data for $(NF_4)_2TiF_6$ [a]

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

(a) tetragonal, a = 10.715Å, c = 11.114Å, Cu K_α radiation Ni filter

Table 3. Crystallographic Data of $(NF_4)_2TiF_6$ Compared to Those of Other NF_4^+ Salts

	Tetragonal Unit Cell Dimensions			Z	Volume ($\mathring{A}^3$) per F	Calcd Density (g/cm^3)
	a($\mathring{A}$)	c($\mathring{A}$)	V($\mathring{A}^3$)			
NF_4PF_6 [a]	7.577	5.653	324.53	2	16.23	2.41
NF_4AsF_6 [b]	7.70	5.73	339.73	2	16.99	2.72
NF_4SbF_6 [c]	7.903	5.806	362.63	2	18.13	2.98
NF_4BiF_6 [c]	8.006	5.821	373.10	2	18.66	3.68
NF_4BF_4 [a]	9.944	5.229	517.04	4	16.16	2.27
$(NF_4)_2GeF_6$ [a]	10.627	11.114	1255.14	16/3	16.81	2.59
$(NF_4)_2SnF_6$ [d]	10.828	11.406	1337.35	16/3	17.91	2.73
$(NF_4)_2TiF_6$	10.715	11.114	1276.01	16/3	17.09	2.37

(a) Ref. 2

(b) Ref. 6

(c) Ref. 4

(d) Ref. 3

Table 4. Vibrational Spectra of Solid $(NF_4)_2TiF_6$ Compared to Those of Cs_2TiF_6

obsd freq (cm^{-1}) and rel intens [a]				assignments (point group)	
$(NF_4)_2TiF_6$		Cs_2TiF_6		$NF_4^+ (T_d)$	$TiF_6^{--} (O_h)$ [b]
IR	RA	IR	RA		
2340sh				$2\nu_3(A_1+E+F_2)$	
2320vw					
2003w				$\nu_1+\nu_3(F_2)$	
1780sh				$\nu_3+\nu_4(A_1+E+F_2)$	
1760vw					
1463w				$\nu_1+\nu_4(F_2)$	
1219mw				$2\nu_4(A_1+E+F_2)$	
1160vs	1158(1.4)			$\nu_3(F_2)$	
1132sh,vw					
1060vw				$\nu_2+\nu_4(F_1+F_2)$	
1021w					
910vw					$\nu_1+\nu_4(F_{1u})$
	883(0.1)			$2\nu_2(A_1+A_2+E)$	
850sh,vw	853(10)			$\nu_1(A_1)$	
804w					
611mw	612(5)			$\nu_4(F_2)$	
	607sh				
	601(8.0)		599(10)		$\nu_1(A_{1g})$
563vs		562vs			$\nu_3(F_{1u})$
452vw	450(3.3)			$\nu_2(E)$	
	442(2.6)				
	289(8.2)		284(9.8)		$\nu_5(F_{2g})$
	107(0+)		84(1.2)		
	86(2)		68(3.2)	Lattice vibrations	
			56(1.7)		

(a) uncorrected Raman intensities

(b) the site symmetry of TiF_6^{--} in Cs_2TiF_6 is D_{3d}, but for simplicity and in view of the unknown site symmetry of TiF_6^{--} in $(NF_4)_2TiF_6$, the assignments for TiF_6^{--} were made for the point group (O_h) of the free ion.

Table 5. Vibrational Spectra of Solid $CsTi_2F_9$, $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$

obsd freq (cm^{-1}) and rel intens[a]								assignments for NF_4^+ in point group T_d
$CsTi_2F_9$		$NF_4Ti_2F_9$		$NF_4Ti_3F_{13}$		$NF_4Ti_6F_{25}$		
IR	RA	IR	RA	IR	RA	IR	RA	
				2360sh }		2350sh }		$2\nu_3(A_1+E+F_2)$
		2320vw		2320vw }		2320vw }		
		2004w		2002w		2002w		$\nu_1+\nu_3(F_2)$
		1765vw		1766vw		1768vw		$\nu_3+\nu_4(A_1+E+F_2)$
		1458w		1458w		1457w		$\nu_1+\nu_4(F_2)$
		1400vw						
		1322vw						
		1223vw }		1220mw		1220mw		$2\nu_4(A_1+E+F_2)$
		1216w }						
		1164vs	1169(0.2) }	1166vs	1175sh	1165vs	1165(0.1)	$\nu_3(F_2)$
			1158(0.5) }		1160(0.2)			
		1054vw		1055vw		1051vw		$\nu_2+\nu_4(F_1+F_2)$
		904vw		905sh				
		853vw	851(3.8)		851(3.2)		851(2.4)	$\nu_1(A_1)$
725vs,br	752(10)	725vs,br	752(10)	760vs,br	770(10)	765vs	784(10)	
	701(0.7)		702(0.7)		731(0.3)		735(1.2)	
650vs	670(0.4)	650vs	670(0.5)	702vs		712vs		
	645(0+)		645(0+)		696(0.8)		698(0.1)	
				675s		661s		
		615s	615(0.5) }	615s	611(1.6)	610s	611(0.9)	$\nu_4(F_2)$
		608s	608(1.6) }					
530vs,br		530vs,br		578vs		585vs	588(0+)	
446vs		446vs		502vs		492vs	500(0+)	
			444(0.5) }		446(0.9)		445(0.7)	$\nu_2(E)$
			439(1.1) }					
390sh	388(0.9)	390sh	389(0.9)		371(1.0)		363(1.0)	
	327(0.3)		326(0.3)		252(0.5)		251sh	
	290(0.8)		290(0.9)		241(2.0)		242(1.5)	
	247(2.4)		247(2.4)		223(0.5)		223sh	
	238(2.4)		237(2.4)		190(1.0)		188(1.7)	
	225sh		225sh		168(0.8)		165sh	
	192(0.5)		192(0.5)				139(0.4)	
	162(0.4)		162(0.4)					

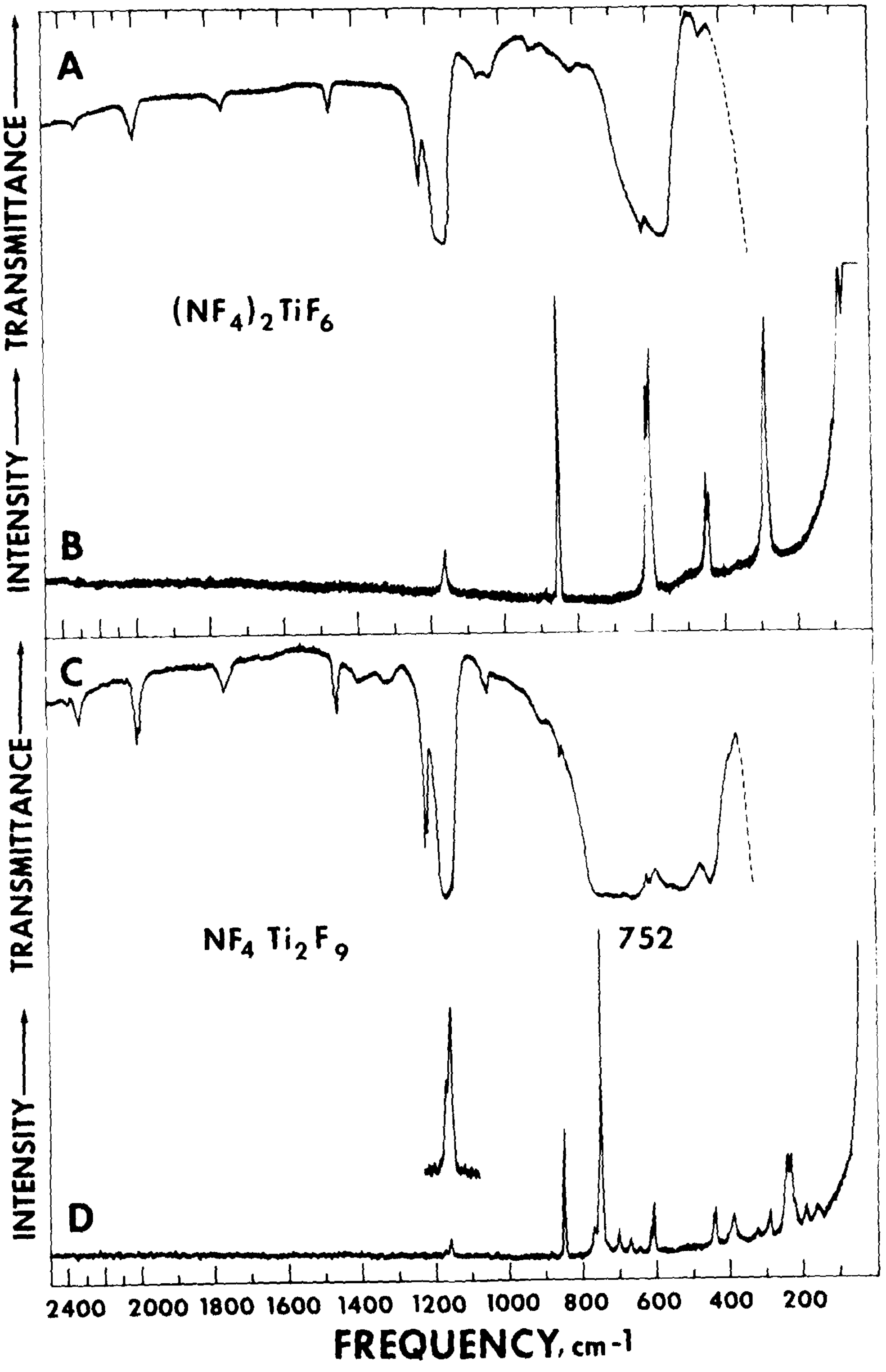
(a) uncorrected Raman intensities

Table 6. Vibrational Spectra of Solid $Cs_2Ti_2F_{10}$ and Prefluorinated TiF_4

$Cs_2Ti_2F_{10}$ obsd freq (cm^{-1}) and rel intens [a] IR	$Cs_2Ti_2F_{10}$ obsd freq (cm^{-1}) and rel intens [a] RA	assignments [b] for point group D_{2h}	TiF_4 obsd freq and rel intens [a] IR	TiF_4 obsd freq and rel intens [a] RA
	703(10)	$\nu_1(A_g)$		829(5.0)
		$\nu_{17}(B_{2g})$		817(0.4)
	620(0.2)	$\nu_9(B_{1g})$	840-730vs,br	807(10)
	577(3)	$\nu_2(A_g)$		761(1.7)
730-600vs,br		$\nu_{13}(B_{1u})$		731(0.4)
		$\nu_{26}(B_{3u})$	580vs,br	
		$\nu_{20}(B_{2u})$	481vs	
		$\nu_{27}(B_{3u})$		471(0.5)
468m		$\nu_{28}(B_{3u})$		370(1.7)
441s		$\nu_{21}(B_{2u})$		291(0.9)
	335(0.5)	$\nu_{18}(B_{2g})$		239(1.8)
		$\nu_{11}(B_{1g})$		221(0+)
	284(1.7)	$\nu_4(A_g)$		201(2.0)
	248(4.8)	$\nu_{24}(B_{3g})$		179(6.1)
	218(2.8)	$\nu_5(A_g)$		140(2.0)
	199(0.8)	$\nu_{12}(B_{1g})$		99(0+)
				87(0+)
				70(0+)

(a) uncorrected Raman intensities

(b) using the symmetry co-ordinates of ref. 21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B
INTENSITY
TRANSMITTANCE
C
TRANSMITTANCE
NF$_4$ Ti$_2$F$_9$
752
D
INTENSITY
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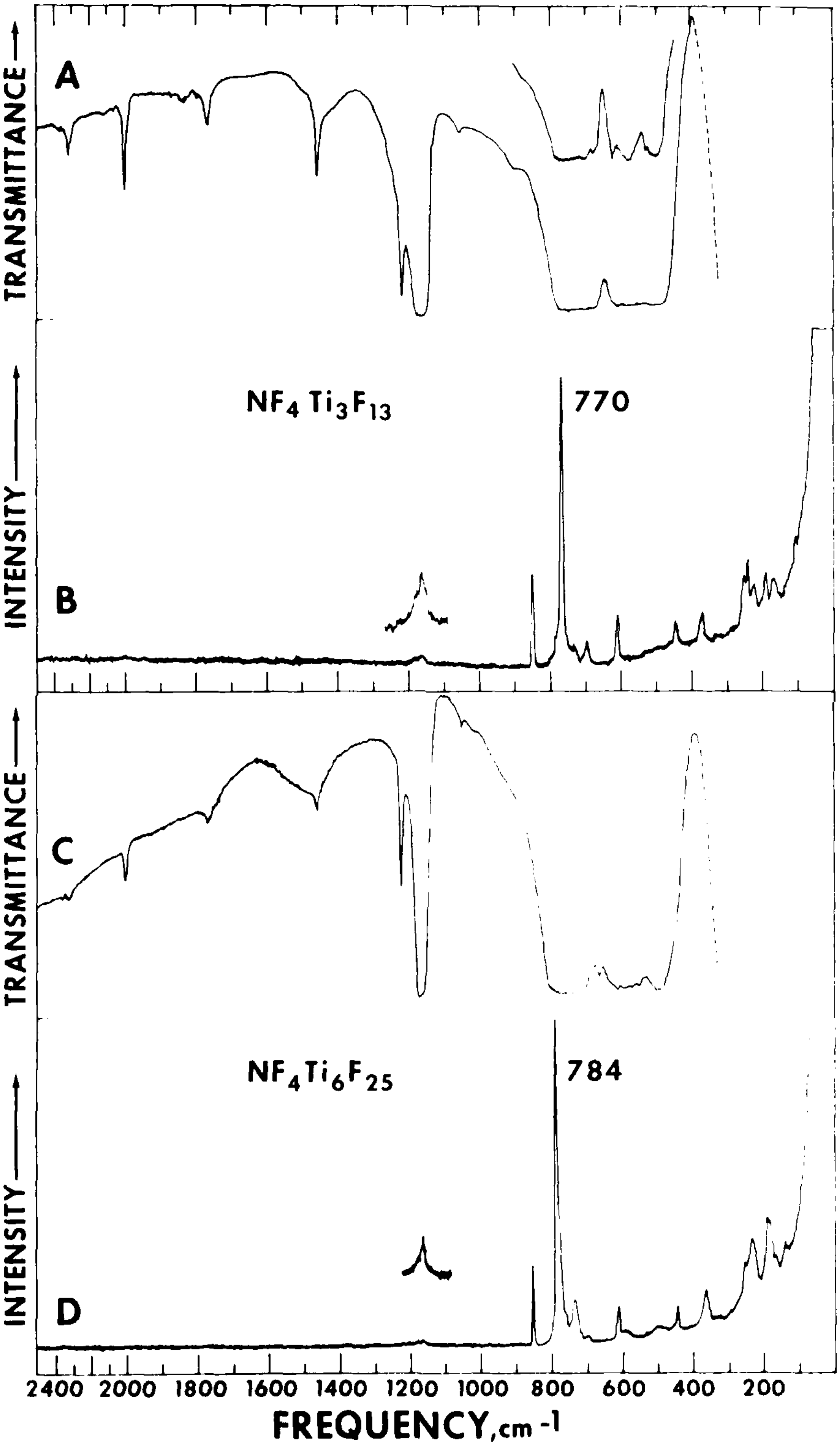
FREQUENCY, cm-1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TRANSMITTANCE
B
INTENSITY
$NF_4Ti_3F_{13}$
770
C
TRANSMITTANCE
D
INTENSITY
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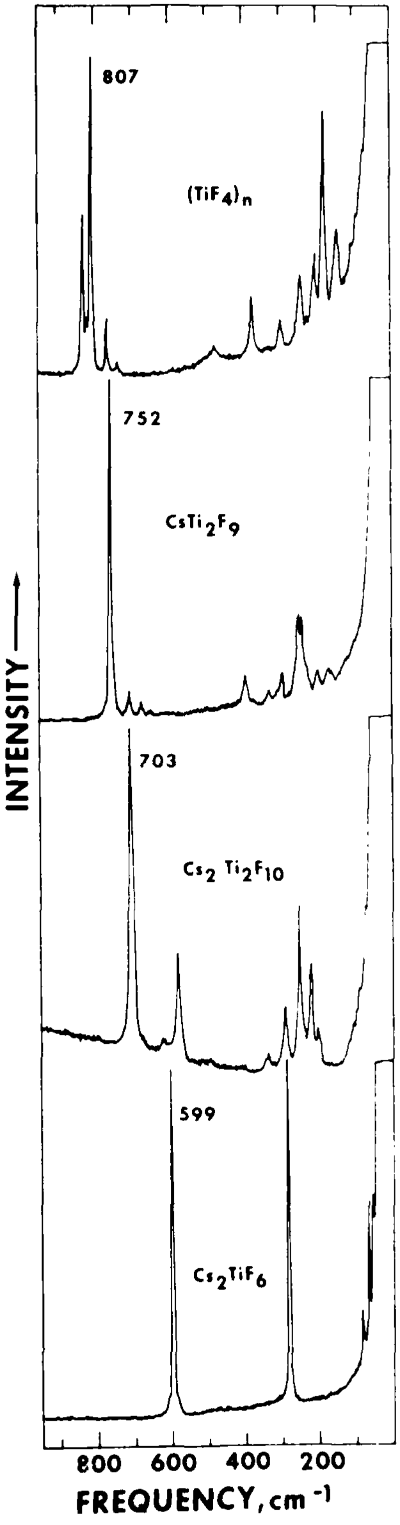
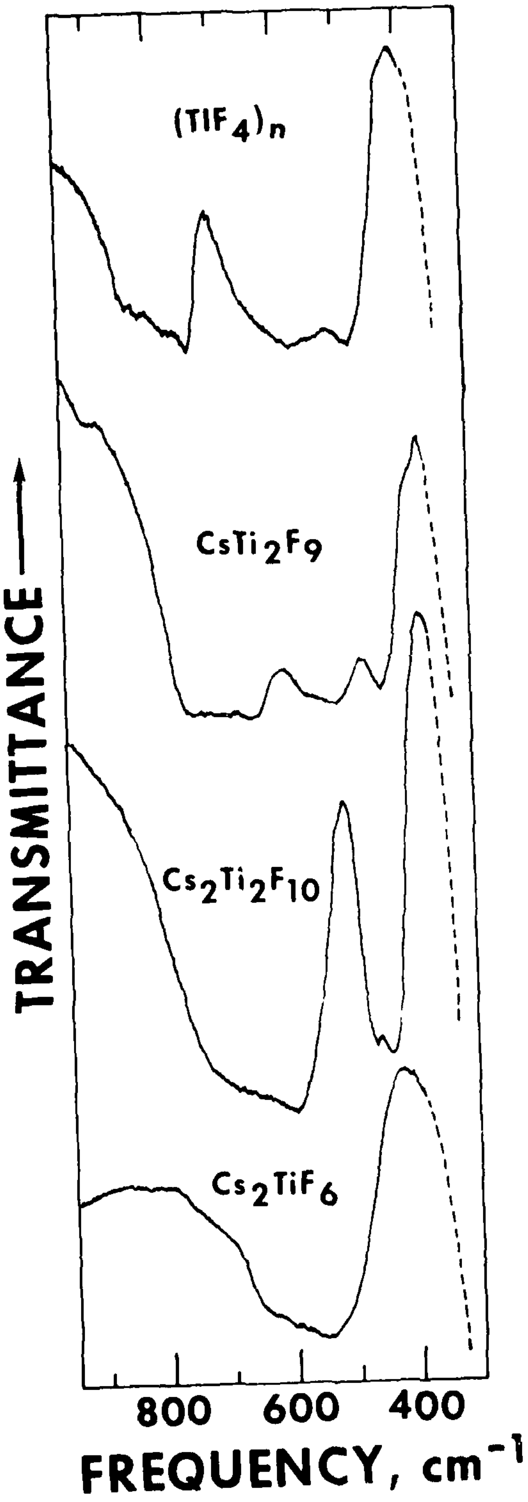
784
2400 2000 1800 1600 1400 1200 1000 800 600 400 200
FREQUENCY, cm -1



807
$(TiF_4)_n$
752
$CsTi_2F_9$
703
$Cs_2Ti_2F_{10}$
599
Cs_2TiF_6
INTENSITY
800
600
400
200
FREQUENCY, cm -1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CsTi$_2$F$_9$
Cs$_2$Ti$_2$F$_{10}$
Cs$_2$TiF$_6$
TRANSMITTANCE
800
600
400
FREQUENCY, cm^{-1}

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

Synthesis and Characterization of $(NF_4)_2NiF_6$

Karl O. Christe

Received . . . .

Abstract

The NF_4^+ cation has successfully been coupled with the energetic NiF_6^{--} anion in the form of the stable $(NF_4)_2NiF_6$ salt. The salt was prepared from Cs_2NiF_6 and NF_4SbF_6 by metathesis in HF. It was characterized by elemental analysis, vibrational spectroscopy, and its x-ray powder diffraction pattern. Its hydrolysis and thermal decomposition were studied.

Introduction

A large number of strongly oxidizing complex fluoro cations and anions are known. However, their potential application as energetic oxidizers had been handicapped by the fact that they formed stable salts only with nonenergetic counter ions. The recent syntheses[1-3] of several stable NF_4^+ salts, derived from relatively weak Lewis acids, indicated that the NF_4^+ cation might possess the necessary stability required for its successful combination with energetic anions.

In this paper we report the synthesis and properties of $(NF_4)_2NiF_6$ which, to our knowledge, is the first known example of a stable salt containing both a strongly oxidizing complex fluoro cation and anion. The NiF_6^{--} anion is well known[4-19] and is a strong oxidizer owing to the fact that the parent molecule NiF_4 is unstable and decomposes to lower nickel fluorides and elemental fluorine.[17,18]

Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those previously described.[2,3] The NF_4SbF_6 was prepared as previously[20] reported. The HF (Matheson) was dried by F_2 treatment[22] and was stored over K_2NiF_6 (Ozark Mahoning) prior to use. The Cs_2NiF_6 was prepared by heating a finely ground 2:1 molar mixture of dried CsF and $NiCl_2$ (Alfa) with 15 mol of F_2 per mol of $NiCl_2$ in a nickel cylinder to 250°C for 16 hours. The volatile products were pumped off at room temperature. The solid product was finely powdered in the dry box and the fluorination step was repeated as described above. The weight and the vibrational spectra of the resulting crimson red solid were in excellent agreement with those expected[9,15,16] for Cs_2NiF_6.

In the infrared spectrum of Cs_2NiF_6 several relatively intense previously unreported combination bands (cm^{-1}) were observed. These were $\nu_1+\nu_3$ (1205 w, 1187 mw), $\nu_2+\nu_3$ (1164 mw, 1144 m), $\nu_3+\nu_5$ (954 sh, 936 w), $\nu_1+\nu_4$ (884 vw), and $\nu_2+\nu_4$ (842 vw). From these combination bands a splitting of ν_3 into two components with frequencies of 660 and 641 cm^{-1} can be deduced. The observed frequencies (cm^{-1}) and relative intensities of the fundamentals were: infrared, ν_3 (645 vs, br), ν_4 (331 s); Raman, ν_1 [545(10)], ν_2 [503(7.5)], ν_5 [294(4)].

Synthesis of $(NF_4)_2NiF_6$. In the glove box a mixture of Cs_2NiF_6 (13.50 mmol) and NF_4SbF_6 (27.94 mmol) was placed in a 3/4 inch o.d Teflon FEP U-trap which was connected through a 180° coupling to a second U-trap. This coupling contained a porous Teflon filter (Pall Corporation). The free ends of both U-traps were closed off by valves. Both valves were connected through flexible, corrugated Teflon FEP tubing to a vacuum manifold. Dry HF (10 ml liquid) was added at -78°C to the trap containing the reactants. The mixture was warmed to 25°C and stirred with a Teflon coated magnetic stirring bar for 30 minutes. The U-tube and filter coupling were cooled to -78°C and the trap was inverted. The receiving trap was also cooled to -78°C and the solution above the filter was pressurized by 2 atm of dry nitrogen to accelerate the filtration. After completion of the filtration, the HF solvent was removed by pumping for 12 hours at 25°C. The filter cake consisted of 10.15 g of a light brown solid (weight calcd for 27.0 mmol of $CsSbF_6$ 9.95 g) which was identified by analysis and vibrational spectroscopy as mainly $CsSbF_6$ containing a small amount of NF_4^+ and NiF_6^{--} salts. The filtrate residue consisted of 4.36 g of a deep red solid (weight calcd for 13.5 mmol of $(NF_4)_2NiF_6$ 4.76 g) which on the basis of elemental and spectroscopic analyses had the composition (weight %): $(NF_4)_2NiF_6$, 82.35; NF_4SbF_6, 13.98; $CsSbF_6$, 3.56.

Anal. Calcd: Ni, 13.71; Sb, 6.40; Cs, 1.28; NF_3, 36.20. Found: Ni, 13.70; Sb, 6.44; Cs, 1.31; NF_3, 36.19. The method for purifying this material by recrystallization from anhydrous HF at ambient temperature has previously been described[20] for NF_4BF_4.

Hydrolysis of $(NF_4)_2NiF_6$. Caution! The reaction of $(NF_4)_2NiF_6$ with water is very violent and can result in explosions. About 5 ml of distilled water was frozen out at -196° in the upper section of a Teflon FEP U-trap containing about one mmol of $(NF_4)_2NiF_6$. The frozen water was knocked down into the bottom section of the tube containing the sample and the ice and sample were mixed by agitation at low temperature. After good mixing was achieved, the mixture was carefully warmed towards room temperature and as soon as interaction was noticeable, the mixture was chilled again by liquid N_2. This procedure was repeated until the color of the sample had completely changed from red to the green color characteristic for divalent nickel. The products volatile at -78°C consisted of O_2, NF_3, and OF_2. The oxygen was separated from the NF_3 and OF_2 at -210°C, and the NF_3:OF_2 ratio was determined by infrared spectroscopy. The hydrolysate was analyzed for Ni, Cs, and Sb by both x-ray fluorescense and atomic absorption spectroscopy. The mol ratio of O_2 to OF_2 was found to vary somewhat from experiment to experiment, but approached 2:1 with the total amount being close to that expected for the reduction of N(+V) and Ni(+IV) to N(+III) and Ni(+II), respectively. Control experiments on the hydrolysis of Cs_2NiF_6 under identical conditions resulted in the evolution of O_2 only in amounts corresponding to the reduction of Ni(+IV) to Ni(+II).

Pyrolysis of $(NF_4)_2NiF_6$. A sample of $(NF_4)_2NiF_6$ (296 mg) was placed into a prepassivated (with ClF_3, followed by F_2 at 130°C) 1/4" o.d. stainless steel U-tube (volume 10.46 cc) closed off on both ends by Hoke valves (3132M25). One side of the U was connected to a pressure transducer (Validyne, Model AP10) and the other side to the vacuum line. The U-tube was kept at a constant temperature with an oil bath and the pressure build up was measured as a function of time. Periodic evacuation of the system revealed that the decomposition rate was not influenced by the pressure of the gaseous decomposition products. The decomposition rates of $(NF_4)_2NiF_6$ were determined over the temperature range 80-128°C. All measurements were carried out on one sample starting at the lowest temperature. At the highest temperature (128°C), an exhaustive pyrolysis of the remaining undecomposed 82% of the original sample was carried out until gas evolution practically ceased. The evolved gas was shown by infrared and mass spectroscopy to be a mixture of NF_3 and F_2 in a mole ratio of about 2:3. Based on its weight loss and vibrational spectrum, the solid residue from the exhaustive pyrolysis was shown to consist of the thermally more stable NF_4SbF_6 and $CsSbF_6$ impurities and the previously described[9,17] nonstoichiometric brown nickel fluoride $NiF_{2.x}$.

The thermal decomposition was also visually followed by heating a sample of $(NF_4)_2NiF_6$ in a sealed glass capillary. At 130°C the color of the sample changed from dask red to brown ($NiF_{2.x}$) which at higher temperatures changed to grey. Vibrational spectra of these decomposition products and those obtained from the yellow pyrolysis product of Cs_2NiF_6 showed that in all cases the main product was NiF_2(Ra, 520 vs, 425 s, IR, 520 sh, 425 s, br).

Results and Discussion

Synthesis and Properties. Since the NiF_6^{--} anion is stable in anhydrous HF solution[9,12,17], the synthesis of $(NF_4)_2NiF_6$ by metathesis appeared feasible. Both NF_4SbF_6 and Cs_2NiF_6 are highly soluble in HF, whereas $CsSbF_6$ is of relatively low solubility, particularly at lower temperature. Consequently, the following reaction was used to prepare $(NF_4)_2NiF_6$:

$$2NF_4SbF_6 + Cs_2NiF_6 \xrightarrow[-78^\circ \ \text{filtr.}]{HF} 2CsSbF_6\downarrow + (NF_4)_2NiF_6$$

The optimization of a NF_4SbF_6 - cesium salt based metathetical process and the possible product purification have previously been discussed in detail for the corresponding NF_4BF_4 process[20], and hence are not being reiterated.

The resulting $(NF_4)_2NiF_6$ is a deep red hygroscopic solid, stable at room temperature. It crystallizes in the tetragonal system (see Table I) and is isotypic with the other known $(NF_4)_2MF_6$ (M=Ge, Sn, Ti)[1-3] salts (see Table II). As expected, the size of the unit cell decreases from $(NF_4)_2TiF_6$ to $(NF_4)_2NiF_6$ owing to the transition metal contraction and then increases again when going from Ni to the main group elements.

The vibrational spectra of $(NF_4)_2NiF_6$ are shown in Figure 1 and the observed frequencies and their assignments are summarized in Table III. The observed frequencies and itensities are in excellent agreement with those previously reported for other NF_4^+ salts[1-3] and K_2NiF_6[9,15] and Cs_2NiF_6 (see Experimental), thus establishing the ionic nature of $(NF_4)_2NiF_6$.

Thermal Decomposition. The thermal decomposition of $(NF_4)_2NiF_6$ was investigated by DSC and visual observation of samples sealed in glass melting point capillaries. The DSC curves of samples sealed in aluminum pans indicated the onset of very slow endothermic decomposition between 110 and 120°C, which increased with increasing temperature and became rapid between 200 and 210°C. The fact that $(NF_4)_2NiF_6$ undergoes appreciable decomposition well below 200°C was confirmed by visual observation of samples sealed in glass melting point capillaries. Heating to 130°C resulted in the formation of the brown nonstoichiometric $NiF_{2.x}$[9,17] (see Experimental). As previously discussed,[1-3] these data are only qualitative.

Since the thermal stability of a powerful oxidizer, such as $(NF_4)_2NiF_6$, is of great practical importance, its rate of decomposition was quantitatively studied by total pressure measurements over the temperature range 80 to 128°C. The decomposition follows the equation:

$$(NF_4)_2NiF_6 \longrightarrow 2NF_3 + (3-\frac{x}{2})F_2 + NiF_{2.x}$$

The decomposition rate was found to be independent of the gas pressure, as expected for an irreversible reaction involving the decomposition of the thermodynamically unstable NiF_4 to $NiF_{2.x}$. Owing to the limited amount of sample available, all measurements were carried out on the same sample. From 80 to 110°C the decomposition rates were measured only for low α (fraction of material decomposed) values. At 128°C an exhaustive decomposition was carried out (see Figure 2) for the α range 0.18 to 1. Plots of α as a function of time t resulted in straight lines for the α range 0-0.18 from 80 to 110°C and for α 0.18-0.6 at 128°C. From these straight lines, rate constants, k, were calculated for each temperature (see Table IV). An Arrhenius plot of log k versus $\frac{1}{T}$ resulted in a straight line. The fact that this plot included the data points obtained for both low and high α values strongly suggests that the decomposition rates are independent of α at $\alpha < 0.6$. From the Arrhenius plot, the following expressions can be derived for the specific reaction rate constant (sec^{-1}) and activation energy of the $(NF_4)_2NiF_6$ decomposition:

$$k = 4.840 \circ 10^{14} \cdot e^{-\frac{35161}{RT(^\circ K)}} \quad \text{and } \Delta H_a = 35.161 \text{ kcal/mol}$$

A detailed study of the exact decomposition mechanism was beyond the scope of this study. However, the failure to observe significant sigmoid character for the decomposition curves indicates that the decomposition is not autocatalytic. Furthermore, the fact that the decomposition rates were independent of α over a large range of α suggests that the decomposition occurs at active sites and that the number of these sites is fixed.[22]

The thermal decomposition of $(NF_4)_2NiF_6$ strongly differs from that previously reported[23] for NF_4AsF_6. Contrary to our findings for $(NF_4)_2NiF_6$, the decomposition of NF_4AsF_6 was found to be pressure dependent indicating the equilibrium:

$$NF_3 + F_2 + AsF_5 \rightleftharpoons NF_4AsF_6$$

Because of the irreversibility of the $(NF_4)_2NiF_6$ decomposition, the heat of dissociation and thereby the heat of formation of solid $(NF_4)_2NiF_6$ cannot be computed. However, in view of its importance for performance calculations, the heat of formation of solid $(NF_4)_2NiF_6$ was estimated to be about -230 kcal/mol based on the following sequence:

$$\begin{tikzcd}
(NF_4)_2NiF_{6(s)} \arrow[r, "-105"] & \overset{-62.8}{2NF_{3(g)}} + 2F_{2(g)} + & \overset{(-60)}{NiF_{4(g)}} \arrow[d, "-20"] \\
& & NiF_{2(g)} + F_{2(g)} \arrow[d, "-79.4"] \\
& & NiF_{2(s)}\ -159.5
\end{tikzcd}$$

The values for the heat of formation[24] and heat of sublimation[25] of solid NiF_2 and for the heat of formation of gaseous NF_3[26] are literature values. The heats of decomposition of gaseous NiF_4 and solid $(NF_4)_2NiF_6$ are estimates. The latter estimate[27] is based on the known[28] value of -34.6 kcal/mol of the reaction $NF_4BF_{4(s)} \longrightarrow NF_{3(g)} + F_{2(g)} + BF_{3(g)}$. A value for the heat of formation of $(NF_4)_2NiF_6$ being slightly more negative than -222 kcal/mol $(\Delta H^\circ_f\ NiF_{2(s)} + 2\Delta H^\circ_f NF_{3(g)})$ is supported by our DSC measurements which showed the decomposition of $(NF_4)_2NiF_6$ to be mildly endothermic.

Hydrolysis. The hydrolysis of $(NF_4)_2NiF_6$ can be approximately described by the following equation:

$$2(NF_4)_2NiF_6 + 5H_2O \longrightarrow 4NF_3 + 10HF + 2O_2 + OF_2 + 2NiF_2$$

Whereas the NF_3 evolution and formation of +II Ni were quantitative, the ratio of $O_2{:}OF_2$ varied from experiment to experiment. The observation of significant amounts of OF_2 was quite unexpected since neither NF_4^+ nor NiF_6^{--} alone produce OF_2 during hydrolysis. This was verified by studying the hydrolysis of Cs_2NiF_6

which, in agreement with a previous report[9], produced only O_2 according to:

$$2NiF_6^{--} + 2H_2O \longrightarrow 4HF_2^- + 2NiF_2 + O_2$$

The hydrolysis of NF_4^+ salts containing nonoxidizing anions have previously been studied. Although O_2 evolution had not always been quantitative, H_2O_2 and not OF_2 had been the only observed by-product[3]. It thus appears that the combination of NF_4^+ and NiF_6^{--} are required to produce significant amounts of OF_2. A plausible explanation for the formation of OF_2 is the fluorination of HOF, a likely intermediate in the rapid hydrolysis of NF_4^+,[3] by the hydrolytically more stable NiF_6^{--} according to:

$$NF_4^+ + 2HOH \longrightarrow FOH + H_3O^+ + NF_3$$

$$FOH + NiF_6^{--} \longrightarrow FOF + HF + NiF_4^{--}$$

Summary. The successful synthesis of $(NF_4)_2NiF_6$ is significant since, to our knowledge, it is the first combination of a strongly oxidizing complex fluoro cation with a strongly oxidizing complex fluoro anion in the form of a stable salt. Its potential as an oxidizer becomes evident from the following comparison. On thermal decomposition, one cm^3 of solid $(NF_4)_2NiF_6$ is capable of producing 1.5 times as much useful fluorine, i.e. in the form of F_2 and NF_3, as liquid F_2 at -187°C. Furthermore, $(NF_4)_2NiF_6$ is a stable solid at ambient temperature which can be safely stored without requiring cryogenic cooling. The physical and spectroscopic properties of $(NF_4)_2NiF_6$ are in excellent agreement with those predicted for a solid containing NF_4^+ and NiF_6^{--} ions. The only unexpected property was the observation of significant amounts of OF_2 during hydrolysis.

Acknowledgement. The author thanks Mr. R. D. Wilson for his help with some of the experiments, Drs. L. R. Grant, C. J. Schack, A. E. Axworthy, and G. Schneider for helpful discussions, Dr. L. B. Asprey for the recording of the Raman spectrum of $(NF_4)_2NiF_6$, and the Office of Naval Research, Power Branch, for financial support.

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Diagram Captions

Figure 1. - Vibrational spectra of solid $(NF_4)_2NiF_6$. Trace A, infrared spectrum of the dry powder in a silver chloride disk, the absorption below 400 cm^{-1} (broken line) being due to the AgCl windows. Trace B, Raman spectrum, recorded on a Cary Model 83 using the 6471$\mathring{A}$ line of a Kr ion laser and a spectral slitwidth of 2 cm^{-1}.

Figure 2. - Thermal decomposition curve of $(NF_4)_2NiF_6$ measured at 128°C.

Table 1. X-Ray Powder Data for $(NF_4)_2NiF_6^a$

d obsd	d calcd	Int	h k l
5.46	5.49	vs	0 0 2
3.42	3.45	ms	1 0 3
3.31	3.31	s	3 1 0
2.880	2.878	ms	2 1 3
2.742	2.738	mw	0 0 4
2.407	2.405	mw	3 3 1
2.150	2.150	s	4 2 2
1.954	1.954	w	5 0 2 4 3 2
1.846	1.849	m	4 4 0

(a) tetragonal, a = 10.457Å, C = 10.953Å, CuK_α radiation Ni filter

Table 2. Crystallographic Data of $(NF_4)_2NiF_6$ Compared to Those of Other $(NF_4)_2MF_6$ Salts[a]

	Tetragonal Unit Cell Dimensions			Volume (Å^3) per F	Calcd Density (g/cm^3)
	a (A)	C (A)	V (A^3)		
$(NF_4)_2TiF_6$[b]	10.715	11.114	1276.0	17.09	2.57
$(NF_4)_2NiF_6$	10.457	10.953	1197.7	16.04	2.61
$(NF_4)_2GeF_6$[c]	10.627	11.114	1255.1	16.81	2.59
$(NF_4)_2SnF_6$[d]	10.828	11.406	1337.4	17.91	2.75

(a) For all compounds Z = 16/3

(b) Ref. 1

(c) Ref. 3

(d) Ref. 2

Table 3. Vibrational Spectra of Solid $(NF_4)_2NiF_6$

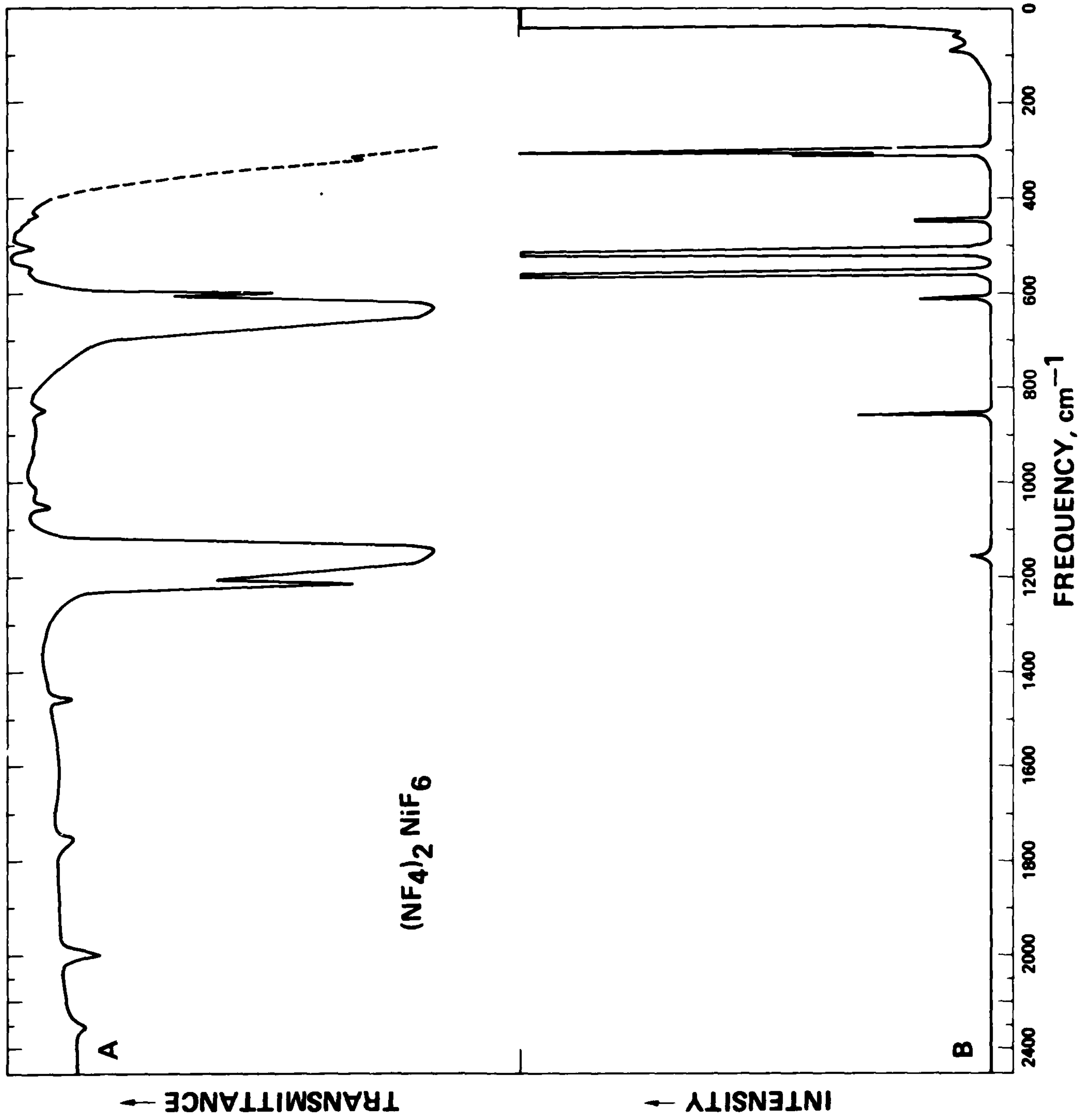
obsd freq (cm^{-1}) and rel intens[a]		assignments (point group)[b]	
IR	RA	NF_4^+ (T_d)	NiF_6^{--} (O_h)
2301 vw		$2\nu_3(A_1+E+F_2)$	
1998 w		$\nu_1+\nu_3(F_2)$	
1756 vw		$\nu_3+\nu_4(A_2+E+F_2)$	
1460 vw		$\nu_1+\nu_4(F_2)$	
1218 m		$2\nu_4(A_1+E+F_2)$	
1156 vs	1157 (0.1)	$\nu_3(F_2)$	
1055 vw		$\nu_2+\nu_4(F_1+F_2)$	
854 vw	854 (1)	$\nu_1(A_1)$	
648 vs			$\nu_3(F_{1u})$
609 m	609 (0.5)	$\nu_4(F_2)$	
604 sh			
556 vw	555 (10)		$\nu_1(A_{1g})$
512 vw	512 (7)		$\nu_2(E_g)$
	457 (0.5)	$\nu_2(E)$	
	454 (0.5)		
443 vw			
332 mw			$\nu_4(F_{1u})$
	307 (1.5)		$\nu_5(F_{2g})$
	298 (4)		
	90 (0.1)	LATTICE VIBRATIONS	
	60 (0+)		

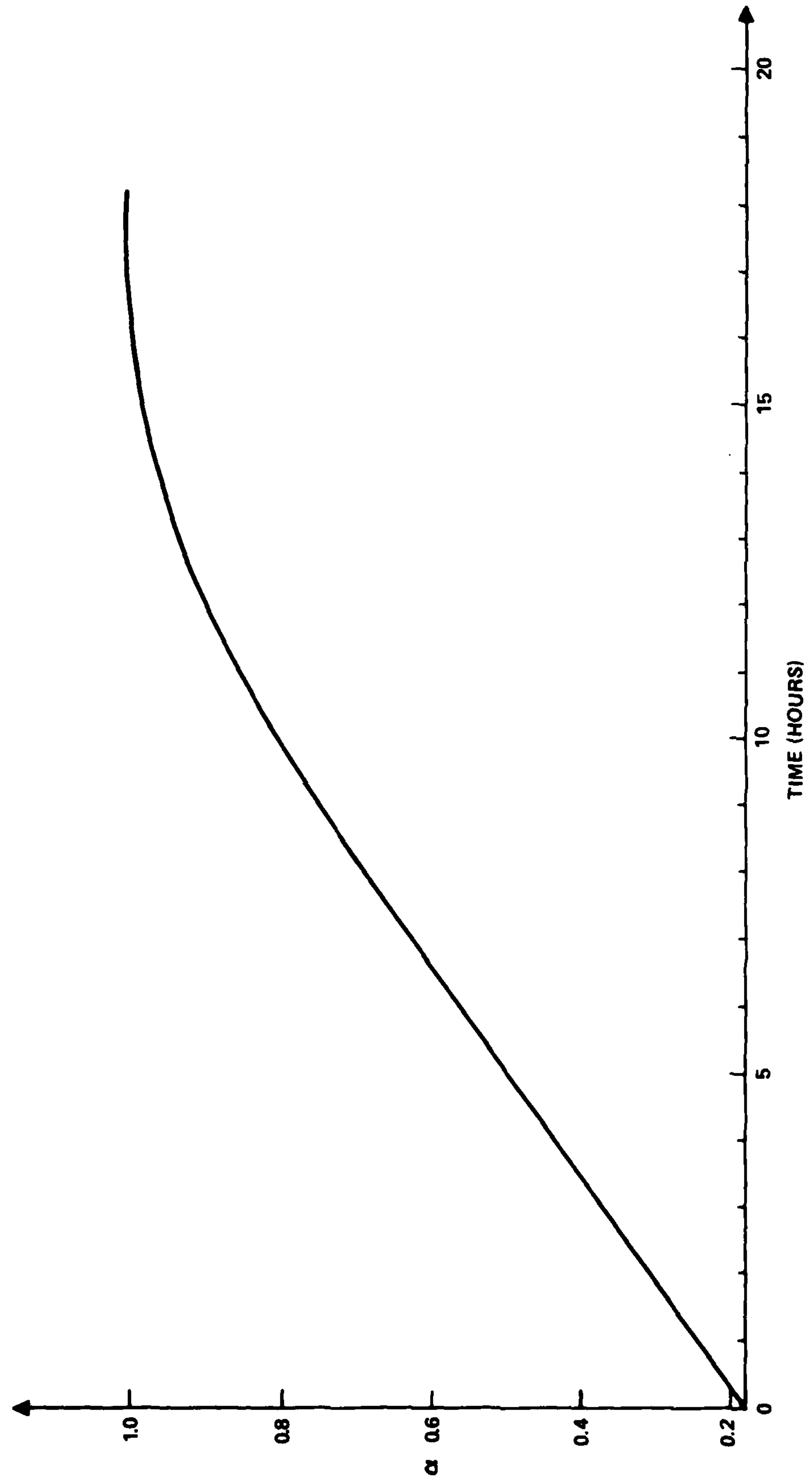
(a) uncorrected Raman intensities

(b) the actual site symmetries of NF_4^+ and NiF_6^{--} in this salt are probably lower than T_d and O_h, respectively, as indicated by the large unit cell (Z = 16/3) and the observed slight deviations from the selection rules and the lifting of the degeneracy for some of the modes; however, since the actual site symmetries are unknown, the assignments are given for the idealized point groups.

Table 4. Rate Constants Observed for the Thermal Decomposition of $(NF_4)_2NiF_6$

T (°C)	k (sec^{-1})
80	$8.279 \cdot 10^{-8}$
90	$2.739 \cdot 10^{-7}$
99	$1.165 \cdot 10^{-6}$
110	$4.197 \cdot 10^{-6}$
128	$3.012 \cdot 10^{-5}$


$(NF_4)_2NiF_6$
A
B
TRANSMITTANCE →
INTENSITY →
FREQUENCY, cm^{-1}
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2400


α
1.0
0.8
0.6
0.4
0.2
0
5
10
15
20
TIME (HOURS)

Spectrochimica Acta, Vol A, pp to Pergamon Press 1976 Printed in Northern Ireland

Vibrational spectrum and normal coordinate analysis of SF_5Br

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(*Received* 11 *March* 1976)

Abstract—The i.r. spectrum of gaseous and the Raman spectrum of liquid SF_5Br are reported. Ten out of 11 fundamentals expected for symmetry C_{4v} were observed and assigned. A normal coordinate analysis was carried out and thermodynamic properties in the range 0–2000 K were computed.

INTRODUCTION

Whereas the vibrational spectra and force fields of SF_5Cl [1–3], SeF_5Cl [4], and TeF_5Cl [5] have been well characterized, similar data on the corresponding bromine compounds are lacking. Since SF_5Br is an important intermediate for the synthesis of SF_5 substituted compounds, a thorough characterization of this molecule was desired. In this paper, we report its vibrational spectrum and the results of a normal coordinate analysis.

EXPERIMENTAL

The SF_5Br was prepared by the interaction of BrF with SF_4 in the presence of CsF in a stainless steel reactor at 90° for 24 hr. The reaction products were separated by repeated fractional condensation through a series of traps maintained at −95 and −112°. The SF_5Br was retained in the −112° trap. It was found difficult to obtain a colorless product, free of traces of Br_2, owing to its tendency to decompose to S_2F_{10} and Br_2 under the influence of light.

The i.r. spectra were recorded at Rocketdyne on both a Perkin–Elmer Model 457 and a Beckman Model 4250 spectrophotometer, calibrated by comparison with standard calibration points [6]. Stainless steel cells of 5 and 10-cm path length fitted with AgCl or high density polyethylene windows (seasoned with ClF_3) were used as sample containers. The Raman spectrum of liquid SF_5Br was recorded at UC Berkeley on a Spex Model 1400 double monochromator, using the 6764 Å exciting line for a Kr ion laser and quartz capillaries as sample containers.

RESULTS AND DISCUSSION

Vibrational spectra of SF_5Br.

The i.r. spectrum of SF_5Br is shown in Fig. 1. Three very weak bands at 945, 820 and 545 cm^{-1} were deleted from the figure, since their relative intensities varied from sample to sample and bands of similar frequencies have previously been reported [7] for S_2F_{10}, the photolytic decomposition product of SF_5Br. The frequencies observed for the i.r. spectrum of the gas and the Raman spectrum of the liquid, together with their assignments for point group C_{4v}, are given in Table 1. The agreement between the frequencies of the gas and the liquid is good indicating very little or no association in the liquid phase.

Since SF_5Br can be considered as a monosubstituted derivative of octahedral SF_6, it should belong to point group C_{4v}. The 11 fundamentals of SF_5Br of symmetry C_{4v} can be classified as $4A_1+2B_1+B_2+4E$. Of these, all 11 modes should be Raman active, whereas only the A_1 and E modes should be i.r. active. Of the Raman lines, only the four A_1 modes should be polarized.

The observed spectrum agrees with these predictions. The assignment of the bands to the individual modes was done by analogy with the known spectra of closely related SF_5Cl [1–3], SeF_5Cl [4], and SF_5O^- [8] (see Table 2) and, therefore, requires only little discussion. For SF_5Cl the revised assignment [4] was used. The frequencies of SF_5Br, which mainly involve motions of the SF_5 part of the molecule, deviate by less than 24 cm^{-1} from those previously reported for SF_5Cl [1–3]. The vibrations involving mainly an S–Br motion show the expected pronounced mass effect. The frequency of

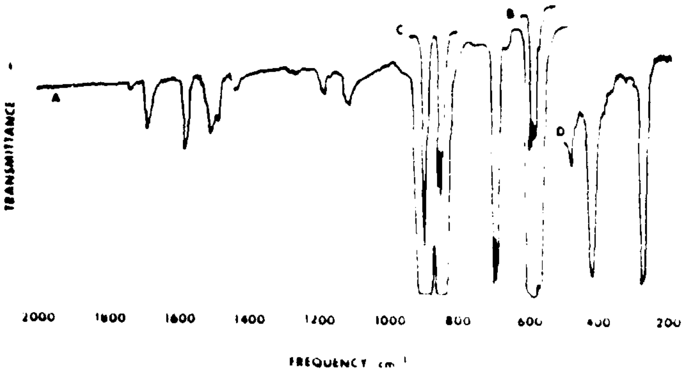

Fig. 1. Infrared spectrum of gaseous SF_5Br. Traces *A*, *B* and *C*: 100, 4.5 and 1 mm, respectively, in a 5 cm pathlength cell with AgCl windows; trace *D*: 700 mm in a 10 cm pathlength cell with polyethylene windows.

275 cm^{-1} assigned to the S–Br stretch in SF_5Br is in good agreement with the value of 305 cm^{-1} found for this mode in $BrSO_2F$ [9].

The above assignments are further supported by the observed i.r. band contours (PQR structure for the A_1 modes), the Raman polarization data, and the fact that all the observed combination bands (see Table 1) can be assigned without violation of the C_{4v} selection rules. The failure to detect ν_6 in the Raman spectrum is no surprise since for this type of molecules this mode is generally of very low intensity and also was not observed for the related molecules SF_5Cl [1–3] and SeF_5Cl [5]. By analogy with SF_5Cl [3], ν_{11} of SF_5Br is of very low intensity in the i.r. spectrum, but is readily observed in the Raman spectrum.

Table 1. Vibrational spectra of SF_5Br and their assignment in point group C_{4v}

Obsd freq, cm^{-1}, and intensity*		
Infrared gas	Raman liquid	Assignment
1745 vw		$\nu_1 + \nu_8 = 1743\ (E)$
1696 w		$2\nu_1 = 1698\ (A_1)$
1588 w		$\nu_2 + \nu_8 = 1586\ (E)$
1540 vw		$\nu_1 + \nu_2 = 1541\ (A_1)$
1514 w		$\nu_5 + \nu_8 = 1514\ (E)$
1489 vw		$\nu_3 + \nu_8 = 1485\ (E)$
1443 vw		$\nu_1 + \nu_3 = 1440\ (A_1)$
1280 vw		$\nu_2 + \nu_3 = 1283\ (A_1)$
1268 vw		$\nu_1 + \nu_{10} = 1267\ (E)$ or $\nu_2 + \nu_9 = 1267\ (E)$
1193 vw		$\nu_5 + \nu_9 = 1195\ (E)$
1175 vvw		$2\nu_3 = 1182\ (A_1)$
1120 vw		$\nu_1 + \nu_4 = 1120\ (A_1)$
894 vs	898 (0.2) dp	$\nu_8\ (E)$
849 vs, P, Q, R	848 (0.02) p	$\nu_1\ (A_1)$
692 m, P, Q, R	691 (7.6) p	$\nu_2\ (A_1)$
	620 (0.3) dp	$\nu_5\ (B_1)$
591 m, P, Q, R	586 (0.2) p	$\nu_3\ (A_1)$
575 m	575 (0.02) dp	$\nu_9\ (E)$
	500 (0.2) dp	$\nu_7\ (B_2)$
477 vw		$\nu_2 - \nu_{11} = 470\ (E)$
418 mw	419 (0.4) dp	$\nu_{10}\ (E)$
271 mw	272 (10) p	$\nu_4\ (A_1)$
	222 (0.6) dp	$\nu_{11}\ (E)$

* Uncorrected Raman intensities

Table 2. Vibrational spectrum of SF_5Br compared to those of SF_5Cl, SF_5O and SeF_5Cl

Obsd freq, cm^{-1}, and intensity									
SF_5Br		SF_5Cl [1-4]		SF_5O [8]		SeF_5Cl [4]		Assignment in point group C_{4v}	Approximate description of vibration
i.r. gas	Ra liquid	i.r. gas	Ra liquid	i.r.	Ra	i.r. gas	Ra liquid		
849 vs	848 (0.02) p	855 vs	833 (0.2) p	735 vs	722 (0.2)	729 ms	721 (1.8) p	A_1 ν_1	ν (XF')
692 m	691 (7.6) p	707 s	704 (3) p	697 m	697 (10)	654 w	656 (10) p	ν_2	ν sym (XF_4)
591 m	586 (0.2) p	602 s	603 (0.2) p	506 s	506 (1)	440 vs	443 (2.2) p	ν_3	δ sym out of plane (XF_4)
271 mw	272 (10) p	402 s	403 (10) p	1154 vs	1153 (1)	384 mw	385 (8.5) p	ν_4	ν (XY)
	620 (0.3) dp		625 (0.7) dp		541 (3.3)		636 (0.6) dp	B_1 ν_5	ν sym out of phase (XF_4)
					472 (0.2)			ν_6	δ asym out of plane (XF_4)
	500 (0.2) dp		505 (0.2) dp		452 (0.9)		380 dp	B_2 ν_7	δ sym in plane (XF_4)
894 vs	898 (0.2) dp	909 vs	927 (0.2) dp	785 vs	780 (0.1)	745 vs	745 (0.3) dp	E ν_8	ν asym (XF_4)
575 m	575 (0.02) dp	579 mw	584 (0.1) dp	530 sh	530 (2)	421 s	424 (0.4) dp	ν_9	δ ($F'XF_4$)
418 mw	419 (0.4) dp	441 m	442 (0.8) dp	325 mw		334 m	336 (1.2) dp	ν_{10}	δ asym in plane (XF_4)
	222 (0.6) dp	287 vw	271 (0.6) dp	606 s	607 (2.2)		213 (1.4) dp	ν_{11}	δ (YXF_4)

Force constants

A normal-coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method [10], assuming the following geometry and coordinate definitions: $R_{SF'} = r_{SF} = 1.60$ Å, $D_{SBr} = 2.27$ Å [11], $\alpha = {<}FSF = 90°$, $\beta = {<}F'SF = 90°$ and $\gamma = {<}BrSF = 90°$, where F' refers to the axial (unique) fluorine ligand. The symmetry coordinates used were identical with those previously reported [12] for IF_5O. The deformation coordinates were weighted by unit (1 Å) distance.

The force constants were calculated by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies using the simplest possible modified valence force field. Unique force constants could not be computed since the general valence force field has 24 symmetry force constants and there are only 11 frequencies. It was found that in both the A_1 and E block off-diagonal force constants are required to fit the observed frequencies. In the A_1 block, the F_{12}, F_{23} and F_{24} terms may be neglected [13] since their corresponding G matrix elements are zero. In the E block, however, all G matrix elements are nonzero. Based on our experience with related molecules, the most plausible interaction constants were selected and their values were kept as small as possible. Additional criteria for selecting the off-diagonal F terms were a plausible potential energy distribution and the condition to make $F_{11} = f_R = f_r$. The resulting force constants are listed in Tables 3 and 4. Uncertainty estimates are difficult to make

Table 3. Symmetry force constants of SF_5Br*

A_1 ν_1	849	$F_{11} = f_R$	=	4.50
ν_2	692	$F_{22} = f_r + 2f_{rr} + f_{rr}'$	=	5.36
ν_3	591	$F_{33} = \frac{1}{2}(f_\beta + 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma + 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} + 4f_{\beta\gamma}' - 2f_{\beta\gamma}'')$	=	2.35
ν_4	271	$F_{44} = f_D$	=	2.23
		$F_{13} = \sqrt{2}(f_{R\beta} - f_{R\gamma})$	=	0.48
		$F_{14} = f_{RD}$	=	0.67
		$F_{34} = \sqrt{2}(f_{D\beta} - f_{D\gamma})$	=	0.30
B_1 ν_5	620	$F_{55} = f_r - 2f_{rr} + f_{rr}'$	=	4.30
ν_6	[470]†	$F_{66} = \frac{1}{2}(f_\beta - 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} - 4f_{\beta\gamma}' - 2f_{\beta\gamma}'')$	=	3.16
B_2 ν_7	500	$F_{77} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	=	1.79
E ν_8	894	$F_{88} = f_r - f_{rr}'$	=	3.74
ν_9	575	$F_{99} = f_\beta - f_{\beta\beta}'$	=	2.62
ν_{10}	418	$F_{1010} = f_\alpha - f_{\alpha\alpha}'$	=	1.90
ν_{11}	222	$F_{1111} = f_\gamma - f_{\gamma\gamma}'$	=	1.26
		$F_{89} = f_{r\beta} - f_{r\beta}''$	=	0.66
		$F_{811} = f_{r\gamma} - f_{r\gamma}''$	=	0.45

* Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interaction constants in mdyn/radian.
† estimated value.

Table 4. Internal force constants of SF_5Br*†

$f_R = 4.50$	$f_{\beta\beta}' = 0.596$
$f_D = 2.23$	$f_\gamma = 1.479$
$f_r = 4.285$	$f_{\gamma\gamma} = -0.128$
$f_{rr} = 0.265$	$f_{\gamma\gamma}' = 0.219$
$f_{rr}' = 0.545$	$f_{R\beta} = 0.34$
$f_{RD} = 0.67$	$f_{D\gamma} = 0.212$
$f_\alpha = 1.955$	$f_{r\beta} = -f_{r\beta}'' = 0.33$
$f_{\alpha\alpha} = -f_{\alpha\alpha}' = 0.055$	$f_{r\gamma} = -f_{r\gamma}'' = 0.225$
$f_\beta = 3.216$	
$f_{\beta\beta} = -0.277$	

* Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch–bend interaction constants in mdyn/radian.

† Only the values of the stretching force constants can be uniquely determined from the symmetry force constants; for the computation of the remaining constants, the following assumptions were made:

$$f_{\beta\gamma} = f_{\beta\gamma}' = f_{\beta\gamma}'' = f_{R\gamma} = f_{D\beta} = 0, \quad f_{r\beta} = -f_{r\beta}'',$$

$$f_{r\gamma} = -f_{r\gamma}'', \quad \text{and} \quad \frac{f_\beta}{f_\gamma} = \frac{f_{\beta\beta}}{f_{\gamma\gamma}} = \frac{f_{\beta\beta}'}{f_{\gamma\gamma}'}$$

owing to the underdetermined nature of the force field. However, numerical experiments and comparisons with related molecules (see Table 5) indicate that the listed *principal force constants* might be expected to be a reasonable approximation of the general valence force field values.

Comparison of the SF_5Br stretching force constants with those of SF_6 [14], SF_5Cl [5, 15], SF_5O [8] and SeF_5Cl [4] (see Table 5) shows the expected trends. The SF stretching force constant values decrease in the order: $SF_6 > SF_5Cl > SF_5Br > SF_5O$. This may be explained [4] by the decreasing electronegativity from F towards Br and the formal negative charge in SF_5O which all tend to release electron density to the remaining fluorine ligands. This results in an increased polarity ($S^{\delta+} - F^{\delta-}$) of these S—F bonds and, consequently, a lowering of the SF stretching force constants. The stretch-stretch interaction constants also show continuous trends, although it is difficult to rationalize why in SF_6 (for which a GVFF is known [14]) the value of f_{rr}' becomes smaller than that of f_{rr}. Generally, the interaction between linear bonds (f_{rr}') is larger than that between bones at right angles (f_{rr}).

The potential energy distribution [16] for SF_5Br is given in Table 6. As can be seen, most fundamentals are reasonably characteristic, thus supporting the above assignments. The mixing of the axial SF stretch (ν_1) with the equatorial SF_4 umbrella

Table 5. Stretching force constants (in mdyn/Å) of SF_5Br compared to those of SF_5O , SF_5Cl, SF_6, SeF_5Cl and SeF_6

		SF_5Cl					
	SF_6 [14]	[15]	[5]	SF_5Br	SF_5O [8]	SeF_6*	SeF_5Cl [4]
f_R		4.83	4.62	4.50	3.75		4.42
f_D	5.26	2.94	2.75	2.23	6.46	5.01	2.75
f_r		4.51	4.59	4.29	3.60		4.31
f_{rr}	0.341	0.30	0.26	0.27	0.54	0.12	0.07
f_{rr}'	0.002	0.47	0.35	0.55	0.75	0.14	0.35
f_{RD}		0.44	0.4	0.67	0.66		

* Abramowitz and I. W. Levin, *Inorg. Chem.*, **6**, 538 (1967)..

Table 6. Potential energy distribution for SF_5Br*

A_1	ν_1	849	$72F_{11} + 54F_{33} + 11F_{44} - 18F_{13} - 12F_{14}$
	ν_2	692	$100F_{22}$
	ν_3	591	$36F_{11} + 46F_{33} + 12F_{13}$
	ν_4	271	$92F_{44}$
B_1	ν_5	620	$100F_{55}$
	ν_6	470	$100F_{66}$
B_2	ν_7	500	$100F_{77}$
E	ν_8	894	$85F_{88} + 14F_{99} + 19F_{10,10} - 14F_{89}$
	ν_9	575	$78F_{99} + 11F_{89}$
	ν_{10}	418	$14F_{88} + 71F_{10,10}$
	ν_{11}	222	$93F_{11,11}$

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

Table 7. Computed thermodynamic properties of SF_5Br*

T, K	$C_p°$	H° − H°o	−(F° − H°o)/T	S°
0	0	0	0	0
100	9.916	0.844	51.584	60.020
200	15.763	2.121	58.033	68.637
298.15	20.527	3.918	62.744	75.883
300	20.598	3.956	62.825	76.010
400	23.619	6.179	66.938	82.386
500	25.459	8.640	70.590	87.870
600	26.619	11.248	73.875	92.622
700	27.382	13.951	76.857	96.787
800	27.909	16.717	79.583	100.480
900	28.284	19.528	82.092	103.790
1000	28.559	22.371	84.414	106.785
1100	28.767	25.237	86.574	109.517
1200	28.928	28.122	88.592	112.027
1300	29.054	31.022	90.485	114.348
1400	29.155	33.932	92.267	116.505
1500	29.238	36.852	93.953	118.519
1600	29.305	39.779	95.546	120.408
1700	29.362	42.713	97.063	122.187
1800	29.409	45.651	98.504	123.866
1900	29.450	48.594	99.881	125.457
2000	29.484	51.541	101.198	126.969

* Units for $C_p°$, S°, and F° are calories, moles, and degrees Kelvin; for H° units are kilocalories and moles.

deformation (ν_3) is no surprise in view of their similar motions and frequencies.

Thermodynamic properties

The thermodynamic properties of SF_5Br were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation [17]. These properties are given for the range 0–2000 K in Table 7.

Acknowledgments—The work at Rocketdyne was financially supported by the Office of Naval Research, Power Branch. The work at Berkeley was supported by the Molecular and materials Research Division of the Lawrence Berkeley Laboratory under Contract W-7405-ENG-48 and during the tenure of a DAAD fellowship (1972–73) with Prof. Neil Bartlett.

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Vibrational spectra of thionyl tetrafluoride, SF_4O

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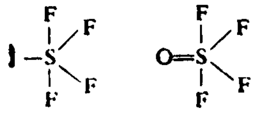
(*Received* 10 *June* 1976)

Abstract—The i.r. spectra of gaseous, solid, and matrix-isolated SF_4O and the Raman spectra of gaseous, liquid and solid SF_4O are reported. It is shown that several bands previously attributed to SF_4O belong to impurities, and 8 of the 12 fundamentals of SF_4O were reassigned. A normal coordinate analysis was carried out and indicates for SF_4O a structural model with significantly longer axial than equatorial S—F bonds, in disagreement with Gundersen and Hedberg's favored Model A. Thermodynamic properties are also reported for SF_4O.

INTRODUCTION

During a study of the vibrational spectra of SF_4 [1], we became also interested in those of SF_4O. The molecular structures of these two molecules [2–6] are closely related and can both be derived from a trigonal bipyramid. The main difference between them is that in SF_4 one of the equatorial positions is occupied by a sterically active free valence electron pair, whereas in SF_4O it is occupied by a doubly bonded oxygen atom.



A closer examination of the available literature data [7–9] on the vibrational spectra of SF_4O revealed many discrepancies and indicated the need for a thorough reinvestigation. Our experimental data, which are reported in this paper, showed that several bands, previously attributed [7–9] to SF_4O, actually belong to impurities, and resulted in the reassignment of 8 of the 12 fundamentals of SF_4O.

EXPERIMENTAL

Pure SF_4O was prepared by vacuum pyrolysis of $CsSF_5O$ [10]. The complexing of crude SF_4O with CsF [10] was found necessary in order to completely remove any SO_2F_2 present. The latter does not form a stable adduct with CsF and can therefore be readily removed from $CsSF_5O$ by pumping.

Volatile compounds were manipulated in a well passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves.

The i.r. spectra were recorded on a Perkin–Elmer Model 457 spectrophotometer in the range of 4000–250 cm^{-1}. The instrument was calibrated by comparison with standard gas calibration points [11]. The gas cells were made of stainless steel with path lengths of either 5 or 10 cm. The windows were made of either AgCl, AgBr, or high density polyethylene seasoned by ClF_3. The apparatus, materials, and technique used for the matrix-isolation study have previously been described [12, 13].

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line. A Claassen filter was used to eliminate plasma lines [14]. Polarization measurements were carried out by method VIII as described by Claassen *et al.* [14]. For the low-temperature spectra an apparatus was used similar to that described by Miller and Harney [15]. A stainless steel cell with Teflon O-rings and sapphire windows [16] was used to obtain the spectrum of the gas. The sample containers for liquid and solid SF_4O were either 3 mm o.d. quartz tubes or Teflon-FEP capillaries used in the transverse excitation-transverse viewing mode.

The ^{19}F NMR spectra were recorded at 56.4 MHz on a Varian Model DA-60 high resolution NMR spectrometer, equipped with a variable temperature probe. Chemical shifts were determined by the side-band technique relative to the external standard $CFCl_3$. Teflon FEP tubes (Wilmad Glass Co.) were used as sample containers. Samples of neat SF_4O, of SF_4O over NaF (for removal of any HF possibly present), and of SF_4O–$FClO_3$ mixtures (1:3 mole ratio) over NaF showed only a single signal for SF_4O over the entire liquid range (mp of $FClO_3$ −147.75°C).

RESULTS AND DISCUSSION

Vibrational spectra. Figure 1 shows the i.r. spectra of gaseous, solid and N_2-matrix-isolated SF_4O. Figure 2 shows the Raman spectra of gaseous, liquid, and solid SF_4O. For the liquid phase, some variation in the spectra was observed. The spectra generally observed over a fairly wide temperature range are shown by traces *D–F* in Fig. 2. During one occasion, however, a spectrum was observed at −80°C which more closely resembled that of gaseous SF_4O. It is shown as trace *G* in Fig. 2. Attempts to reproduce the spectrum with the same or other samples were unsuccessful, and the reason for its deviation could not be established. Figure 3 shows the most intense i.r. bands of gaseous and matrix-isolated SF_4O at higher resolution

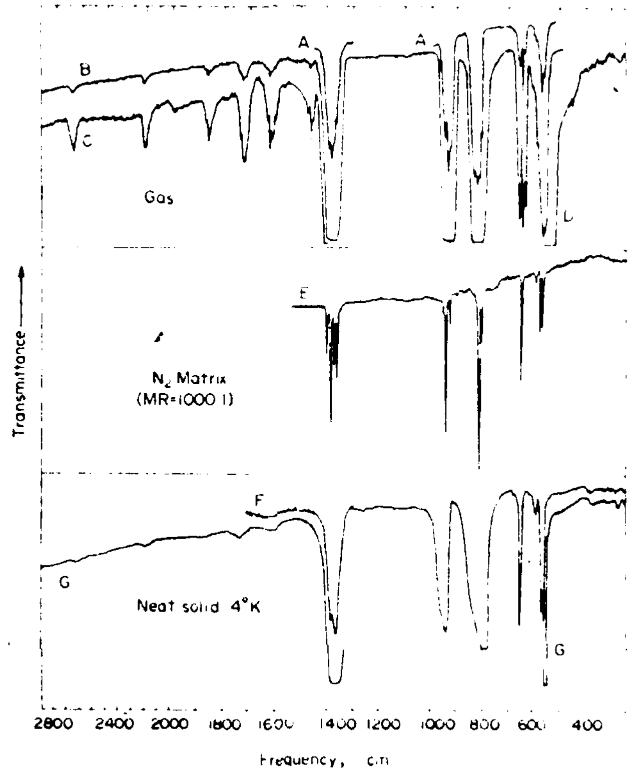


Fig. 1. Infrared spectra of SF_4O. Traces A–D, spectra of the gas at different pressures in a 5-cm path length cell. Trace A, 10 mm (AgBr windows); trace B, 75 mm (AgCl windows); trace C, 500 mm (AgBr windows); trace D, 1500 mm (polyethylene windows). Trace E, spectrum of SF_4O in a N_2 matrix (mole ratio 1 : 1000) at 4 K. Traces F and G, spectra of neat solid SF_4O at two different sample thicknesses at 4 K (CsI windows).

and scale expansion, allowing some conclusions about the band contours and the determination of the ^{32}S—^{34}S isotopic shifts. The observed frequencies are listed in Table 1.

Comparison of the spectra of the gas, the liquid, and the solid shows only minor frequency shifts, indicating little association in the liquid and solid phase. This is in good agreement with its relatively low boiling point (−35.1°C) and Trouton constant (21.9) [7] and with the observations made for the similar molecule ClF_3O_2 [17].

The trigonal-bipyramidal structure of SF_4O has been established by electron diffraction [3–5] and microwave [6] studies. However, four different models of symmetry C_{2v} were found [5] which were all in excellent agreement with the experimental electron diffraction data. No distinction between the four models was possible, but fortunately all of them are very similar as far as the vibrational assignments are concerned. Consequently, knowledge of the exact model is not necessary for making the assignments for SF_4O.

The 12 fundamentals expected for an XY_4Z molecule of symmetry C_{2v} can be classified as $5A_1 + A_2 + 3B_1 + 3B_2$. All of these should be active in both the i.r. and Raman spectra, except for the A_2 mode which should be only Raman active.

Assignment of the stretching modes. The assignment of the stretching modes of SF_4O is relatively easy. There are three stretching modes in species A_1, i.e., the S=O stretch and the symmetric axial SF_2 and the symmetric equatorial SF_2 stretch. Of these, the SO double bond stretch, ν_1, should have the highest frequency, should result in an intense i.r. and a polarized Raman band, and should occur above 1000 cm^{-1}. Obviously, this fundamental must be assigned to the bands in the 1350–1390 cm^{-1} region. The splitting into four components in the matrix-isolation spectrum and the complex band contour in the i.r. spectrum of the gas are

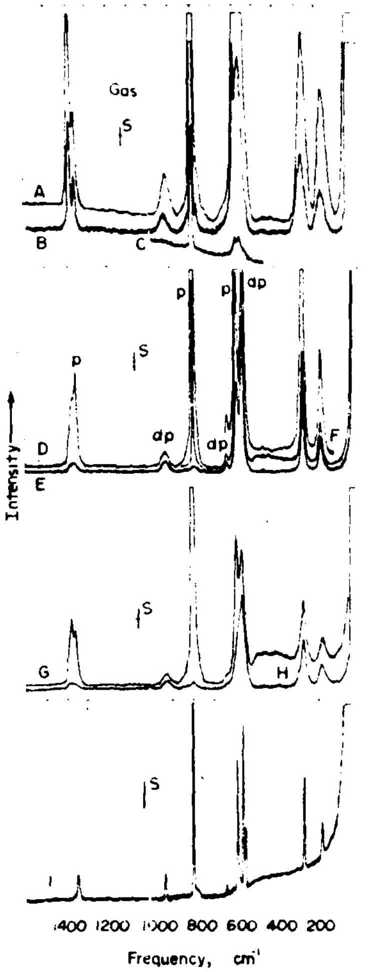


Fig. 2. Raman spectra of SF_4O. Traces A–C, spectra of the gas at 10 atm pressure in a stainless steel cell with sapphire windows recorded at three different sensitivities. Traces *D* and *E*, characteristic spectrum of the liquid in a quartz capillary at −80° with the incident polarization perpendicular and parallel, respectively. The broad band between 300 and 500 cm^{-1} is mainly due to quartz, as shown by trace *F* which was recorded for a sample contained in a Teflon-FEP capillary. Traces *G* and *H*, irreproducible spectrum of the liquid in a quartz capillary at −80° with the incident polarization perpendicular and parallel, respectively. Trace I, spectrum of solid SF_4O in a quartz tube at −130°C.

caused by Fermi resonance between ν_1 and several A_1 combination bands (see Table 1).

The symmetric equatorial SF_2 and axial SF_2 stretching modes ν_2 and ν_3 should give rise to two strong polarized Raman bands in the frequency range 500–1000 cm^{-1}. Since the equatorial SF_2 group is strongly bent, its symmetric stretching mode should result in an intense i.r. band, whereas for the almost linear axial SF_2 group the symmetric stretch should be of low i.r. intensity. Furthermore, by comparison with similar pseudo-trigonal bipyramidal molecules [1, 17], the symmetric equatorial stretch should have a significantly higher frequency than the axial one. Accordingly, the symmetric equatorial SF_2 and the symmetric axial SF_2 stretching modes are readily assigned to the bands at about 796 and 588 cm^{-1}, respectively. For the observation of ν_2 and ν_3 in the i.r. spectra, the matrix isolation data (see Fig. 3) were helpful since ν_2 almost coincides with ν_7 (B_1), and ν_3 occurs in the vicinity of two i.r. bands of higher intensity.

There are two antisymmetric SF_2 stretching modes, the equatorial one, ν_{10} (B_2), and the axial one, ν_7 (B_1). Both should occur in the frequency range 700–1000 cm^{-1} and be very intense in the i.r. spectrum. In the Raman spectra, ν_{10} should be considerably more intense than ν_7 because of the large difference in the equatorial and axial SF_2 bond angles. Consequently, ν_{10} (B_2) and ν_7 (B_1) can be assigned with confidence to the bands at about 926 and 819 cm^{-1}, respectively. The i.r. band contour of ν_7 (see Fig. 3) is complicated by ν_2 (A_1) which has a similar frequency (see above) and by Fermi resonance with $\nu_5 + \nu_8$ (B_1).

Assignment of the deformation modes. The assignment of the remaining bands to the seven deformation modes is more difficult, since only five intense bands (at about 639, 567, 560, 265 and 174 cm^{-1}) were observed with the possibility of a sixth weak fundamental at about 455 cm^{-1}. A similar situation was encountered for SF_4 [1]. It is very difficult to decide if the lack of observation of a fundamental is caused either by its low intensity or by a coincidence of two fundamentals. Tentative assignments for the SF_4O deformation modes can be made based on the following arguments.

The 639 cm^{-1} band has too high a frequency for an SF_2 deformation and, therefore, should be due to the S=O wagging mode, ν_8 (B_1). Additional support for this assignment comes from the i.r. gas phase band contour which is similar to ν_7 (B_1) (see Fig. 3). Furthermore, there is some evidence in the i.r. spectrum of the gas for Fermi resonance between ν_7 (B_1) and the 174+639 cm^{-1} combination band. Since the 174 cm^{-1} band belongs to species A_1 (see below), the 639 cm^{-1} mode must belong to species B_1.

The lowest frequency mode (174 cm^{-1}) should be the one involved in an intramolecular Berry-type

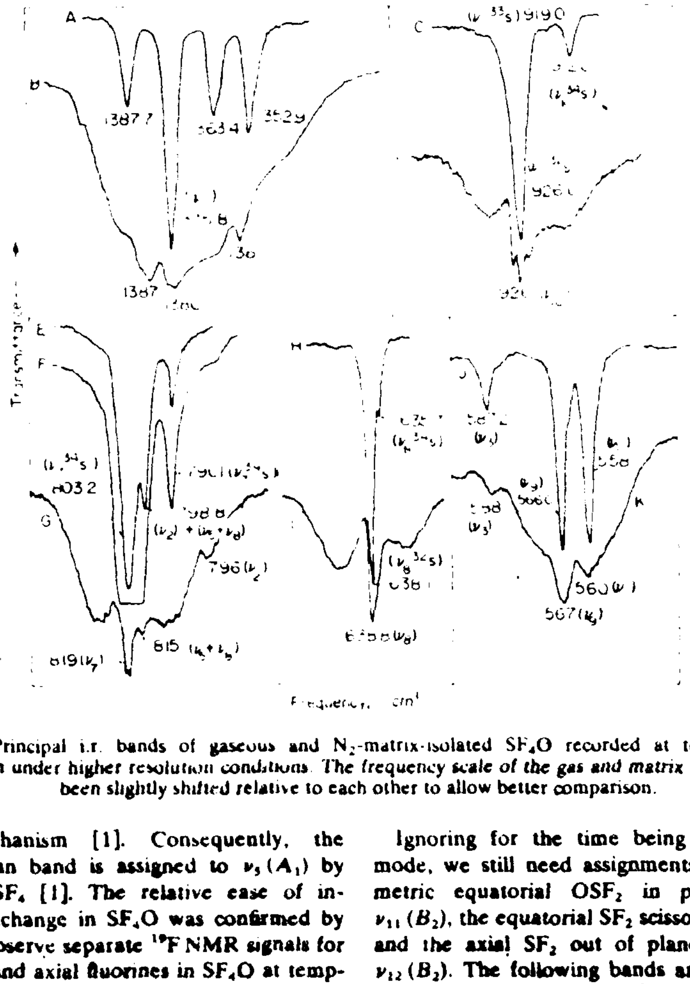


Fig. 3. Principal i.r. bands of gaseous and N_2-matrix-isolated SF_4O recorded at tenfold scale expansion under higher resolution conditions. *The frequency scale of the gas and matrix spectra have been slightly shifted relative to each other to allow better comparison.*

exchange mechanism [1]. Consequently, the $174\ cm^{-1}$ Raman band is assigned to $\nu_5(A_1)$ by analogy with SF_4 [1]. The relative ease of intramolecular exchange in SF_4O was confirmed by our failure to observe separate ^{19}F NMR signals for the equatorial and axial fluorines in SF_4O at temperatures as low as −145°C. Polarization measurements on the liquid provided no direct evidence for the $174\ cm^{-1}$ fundamental being polarized. Similarly, all the other deformation modes also had a depolarization ratio of 0.75. However, a polarized combination band (588 + 174) in Fermi resonance with $\nu_2(A_1)$ was observed. Since the $588\ cm^{-1}$ band has been established (see above) as an A_1 mode, the $174\ cm^{-1}$ band must also belong to species A_1.

By comparison with the closely related PF_5 [18] and SF_4 [1] molecules, the equatorial SF_2 wagging deformation $\nu_9(B_2)$ of SF_4O should be of high Raman and of medium i.r. intensity and have a frequency between 500 and $600\ cm^{-1}$. It is therefore assigned to the higher frequency component of the two bands observed in the 550–$570\ cm^{-1}$ region.

Ignoring for the time being the A_2 torsional mode, we still need assignments for the antisymmetric equatorial OSF_2 in plane deformation $\nu_{11}(B_2)$, the equatorial SF_2 scissoring mode $\nu_4(A_1)$, and the axial SF_2 out of plane scissoring mode $\nu_{12}(B_2)$. The following bands are still unassigned: (i) a band at about $560\ cm^{-1}$ of medium intensity in both the i.r. and Raman spectrum; (ii) a band at about $270\ cm^{-1}$ of medium strong Raman and of low i.r. intensity; (iii) a band at about $450\ cm^{-1}$ of low intensity in both the i.r. and Raman spectrum. By comparison with the known spectrum of planar OCF_2 [19], ν_{11} of SF_4O is expected to have a higher frequency and Raman intensity than ν_4. Furthermore, the frequency of $\nu_{12}(B_2)$ should be lower than those of ν_{11} and ν_4 and by comparison with other similar molecules [1, 17, 18, 20] might be expected to be either degenerate with or close to that of the in plane axial SF_2 scissoring mode ν_5 ($174\ cm^{-1}$). Consequently, the $560\ cm^{-1}$ band of SF_4O should be due to $\nu_{11}(B_2)$.

For the assignment of the $270\ cm^{-1}$ band of SF_4O, two alternatives remain, $\nu_4(A_1)$ and $\nu_{12}(B_2)$.

We prefer its assignment to $\nu_{12}(B_2)$ for the following reasons: (i) its relatively low frequency value is more in line with our expectations for ν_{12} (see above); (ii) its relative i.r. and Raman intensities do not correspond well to those observed for the CF_2 scissoring in planar OCF_2 [19]; (iii) for ClF_3O_2 two intense low-frequency Raman bands were observed [17] at 222 and 285 cm^{-1}, respectively, which resemble those at 185 and 268 cm^{-1} observed for SF_4O. Therefore, these two Raman bands should belong to a structural element common to both ClF_3O_2 and SF_4O. Since ClF_3O_2 contains only one equatorial F atom [17, 21], this common structural element must be the axial FXF group, and the two modes should be due to the axial in plane and out of plane scissoring modes. The assignments previously made [17] for these two modes in ClF_3O_2 should be reversed.

All the observed bands are now assigned, except for a very weak i.r. and Raman band at about 450 cm^{-1}. This band could either be due to the still unassigned $\nu_4(A_1)$ fundamental or the $174 + 265 = 439$ cm^{-1} combination band. Its assignment to the $\nu_5(A_2)$ torsional mode is unlikely based on its activity in the i.r. spectrum of gaseous SF_4O. Since the observed frequency (~ 450 cm^{-1}) does not agree too well with that of 439 cm^{-1}, calculated for $\nu_5 + \nu_{12}$, we tentatively assign the 450 cm^{-1} band to $\nu_4(A_1)$. However, the relatively low i.r. intensity of the 450 cm^{-1} band is disturbing for this assignment, and the possibility cannot be ruled out that $\nu_4(A_1)$ might occur in the 560 cm^{-1} region, but is difficult to detect owing to the presence of three other nearby fundamentals.

Except for the A_2 torsional mode, all fundamentals of SF_4O have thus been assigned. The assignments for all stretching modes and most of the deformations can be considered firm. The A_2 torsional mode which should be only Raman active could not be positively identified. It is expected to occur in the region 400–550 cm^{-1} in which several extremely weak and therefore questionable Raman features were observed.

Combination bands. A further point in support of the above assignments are the combination bands. All observed combination bands could be assigned (see Table 1) without violation of the selection rules for C_{2v} ($B_1 + B_2 = A_2$ and $A_1 + A_2 = A_2$ combinations are i.r. forbidden). Furthermore, for cases involving Fermi resonance, the corresponding fundamentals and combination bands belonged always to the same symmetry species.

Band contours. The i.r. gas phase band contours were also examined. Based on the published microwave data ($A = 0.13663$, $B = 0.11204$, $C = 0.10808$ cm^{-1}) [6], the band contours of SF_4O should approximate those of set 39 in the tables of UEDA and SHIMANOUCHI [22]. Since the B and C values are quite similar, the B and C type bands should be similar under our resolution conditions, and the A type bands should show a narrower Q branch. Since the A axis (smallest moment of inertia) obviously must lie in the direction of the F_{ax}—S—F_{ax} bonds, the B_1 modes should exhibit a narrower Q branch. The observed band contours of ν_7 and ν_8 (see Fig. 3) agree well with this prediction. The largest moment of inertia should be along the S=O axis. Therefore, the A_1 modes should exhibit C type band contours, and the B_2 modes should show a B type contour with a double Q branch. Based on these arguments, we prefer to attribute the complex structure observed for the Q branch of the 926 cm^{-1} $\nu_{10}(B_2)$ band to hot bands. Unfortunately, most of the band contours observed for SF_4O are complicated by effects, such as coincidence of several fundamentals, Fermi resonance, ^{32}S—^{34}S isotopic splittings, and possibly hot bands. The only band having a relatively undisturbed contour is $\nu_8(B_1)$ at 639 cm^{-1}.

Isotopic splittings. The natural abundances of the sulfur isotopes are: $^{32}S = 95.06$, $^{33}S = 0.74$ and $^{34}S = 4.18\%$. For some of the fundamentals splittings due to these isotopes were observed in the matrix isolation i.r. spectra and are listed in Table 1 and Fig. 3.

Comparison with related molecules. A comparison of the assignments for SF_4O to those previously made for the related molecules SF_4 [1], ClF_3 [20], and ClF_3O_2 [17] is given in Table 2. For ClF_3 and ClF_3O_2 only the modes associated with the F_{ax}—Cl—F_{ax} group are listed to avoid confusion. The general agreement is relatively good, if the following points are kept in mind: (i) In the chlorine fluorides, the central atom is more electronegative than oxygen. Consequently, oxygen addition results in an electron release to chlorine and weakens the Cl—F bonds by increasing their polarity. For sulfur fluorides, the effect is reverse because oxygen is more electronegative than the sulfur atom. (ii) In SF_4O, coupling between ν_1 and ν_2 increases their frequency difference and results in a frequency value for ν_2 which is surprisingly low by comparison with that found for SF_4.

As can be seen from Table 2, the problems associated with the assignment of the deformation modes in these pseudo-trigonal bipyramidal molecules are not trivial and more information is required before these assignments should be

Table 1. Vibrational spectra of SF_4O and their assignment in point group C_{2v}

Obsd freq, cm^{-1}, and intensity*							Assignment†	
				Raman				
Gas		Solid	Gas‡	Liquid		Solid		
	Matrix Isolated	Neat		A§	B**			
2740 vw		2720 vw					$2 \times 1380 = 2760$	$2\nu_1(A_1)$
2188 vw		2180 vw					$\{1380 + 819 = 2199$	$\nu_1 + \nu_7(B_1)$
							$1380 + 796 = 2176$	$\nu_1 + \nu_2(A_1)$
1852 vw							$2 \times 926 = 1852$	$2\nu_{10}(A_1)$
1716 vw		1725 vw					$796 + 926 = 1722$	$\nu_2 + \nu_{10}(B_2)$
1619} vw		1600 vw					$796 + 819 = 1615$	$\nu_2 + \nu_7(B_1)$
1600}							$2 \times 796 = 1492$	$2\nu_2(A_1)$
1459 vw							$819 + 639 = 1458$	$\nu_7 + \nu_8(A_1)$
1387}	1387.7 m						$\{819 + 566 = 1385$	$\nu_7 + \nu_9(A_1)$
1380} vs	1375.8 s	1378 ms	1380(0.7) p	1376(0.7) p	1370 sh}			$\nu_1(A_1)$
	1363.4 m				} p	1353(0.6)	$796 + 588 = 1384$	$\nu_2 + \nu_3(A_1)$
1361}		1359 s	1357(0.3) p	1359(0.5) p	1358(0.6)}			
	1352.9 ms						$174 + 639 + 566 = 1379$	$\nu_5 + \nu_8 + \nu_9(A_1)$
	1339.7 w						$174 + 926 + 265 = 1365$	$\nu_5 + \nu_{10} + \nu_{12}(A_1)$
							$2 \times 588 + 174 = 1350$	$2\nu_3 + \nu_5(A_1)$
926 s	926.0 s	929 s	924(0.2)	925(0.2) dp	930(0.1) dp	934(0.5)		$\nu_{10}(^{32}S)(B_2)$
	919.0 w							$\nu_{10}(^{33}S)(B_2)$
	912.0 mw							$\nu_{10}(^{34}S)(B_2)$
819 vs	803.2 vs	820–} vs	815 sh					$\nu_7(^{32}S)(B_1)$
815 m	798.8 m	780}					$174 + 639 = 813$	$\nu_5 + \nu_8(B_1)$
	790.1 m							$\nu_7(^{34}S)(B_1)$
796 m	798.8 mw	798 mw	795(10) p	797(10) p	799(10) p	799(10)		$\nu_2(A_1)$
			766(0.1)	772 sh, p	774 sh, p	777(0.2)	$588 + 174 = 762$	$\nu_3 + \nu_5(A_1)$
638.8 ms	638.1 ms	636 ms	640 sh	639(0.05) dp	639(0.06) dp	638(0.2)		$\nu_8(^{32}S)(B_1)$
	635.7 w							$\nu_8(^{34}S)(B_1)$
588 mw	587.2 mw	588 mw	587(1.7) p	588(1.7) p	588(1.4) p	588(2.4)		$\nu_3(A_1)$
567 ms	566.0 ms	562 ms	566(1.7)	561(1.8) dp	559(1.4) dp	560(3.0)		$\nu_9(B_1)$
560 ms	558.1 ms	554 ms				551(1.0)		$\nu_{11}(B_2)$
447 vvw			455(0+)		460(0+)		$174 + 265 = 439$	$\nu_5 + \nu_{12}(B_2)$ or $\nu_4(A_1)$
270 vw		270 vw	265(0.7)	268(0.9) dp	268(0.7) dp	269(1.5)		$\nu_{12}(B_2)$
			174(0.4)	179(0.4) dp	185(0.3) dp	184(0.6)		$\nu_5(A_1)$

* Uncorrected Raman intensities representing the relative peak height; the relative peak widths and, hence, the relative peak heights change for the different phases.

† The assignments for some of the deformation modes are tentative.

‡ Only qualitative polarization measurements could be obtained for the gas, owing to the optical activity of the sapphire windows of the gas cell.

§ Spectrum of trace *G* of Fig. 2.

** Spectrum of traces *D–F* of Fig. 2.

Table 2. Vibrational spectra of SF_4O compared to those of SF_4, ClF_3 and ClF_3O_2

ClF_3 [20]		ClF_3O_2 [17]		SF_4 [1]		SF_4O		Assignment for SF_4O in point group C_{2v}	Approx. description of mode for SF_4O
i.r.	Ra	i.r.	Ra	i.r.	Ra	i.r.	Ra		
						1380 vs	1380(0.7) p	$A_1\nu_1$	S═O stretch
				892 s	893(9.2) p	796 m	795(10) p	ν_2	sym equat SF_2 stretch
530 m	529 vs,p	487 vw	487(6) p	558 m	558(10) p	588 mw	587(1.7) p	ν_3	sym axial SF_2 stretch
				353	356(0+)	447 vvw	455(0+)	ν_4	equat SF_2 scissor
328	329 w, p		222(1)	226 w	229(1.0)		174(0.4)	ν_5	axial SF_2 scissor in $F_{ax}SO$ plane
					474(0.7)			$A_2\nu_6$	torsion
702 vs		695 vs		728 vs	730(0.5)	819 vs	815 sh	$B_1\nu_7$	antisym axial SF_2 stretch
						639 ms	640 sh	ν_8	S═O wagging
				532 ms	535(3.5)	567 ms	566(1.7)	ν_9	equat SF_2 wagging
				867 s	865 sh	926 s	924(0.2)	$B_2\nu_{10}$	antisym equat SF_2 stretch
				353 ms	356(0+)	560 ms	566	ν_{11}	equat SF_2 rocking
328 s	329 w	287 w	285(1)			270 vw	265(0.7)	ν_{12}	axial SF_2 scissor out of $F_{ax}SO$ plane

considered as being well established. A large number of suitable molecules, such as SF_4, SF_4O, ClF_3, ClF_3O, ClF_3O_2, PF_5, PF_4X and PF_3X_2, are available and are ideally suited for a systematic study. Unfortunately, such a systematic study is beyond the scope of the present investigation.

Force constants. A normal coordinate analysis was carried out for SF_4O to support the above assignments. The potential and kinetic energy metrics were computed by a machine method [23]. The geometry used for the computation was model *D* of GUNDERSEN and HEDBERG [5] since it agrees best with the microwave data [6]. The symmetry coordinates used were analogous to those previously given for ClF_3O_2 [17], except for exchanging the equatorial oxygen atoms for fluorines and vice versa (see Fig. 4). As in that work, the redundant coordinate in the A_1 block was found from the numerical *B* matrix, and the deformation coordinates were made orthogonal to the redundancy by the Gram-Schmidt process. The bending coordinates were weighted by unit (1 Å) distance. The *G* matrix and *Z* transformation were found numerically by the computer and, hence, only the coefficients for the more important force constants are given in Table 3.

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. The observed ^{32}S—^{34}S isotopic shifts were used as additional constraints (see Table 3). For example, for the A_1 block a diagonal valence force field (DVFF) results in an isotopic shift of 17.4 cm^{-1} for ν_1 and an *unreasonably (see below)* low value of 11.05 mdyn/Å for the SO stretching force constant. Based on intensity arguments, ν_1 (^{34}S) is best ascribed to the shoulder on the 1363.4 cm^{-1} band (see trace A of Fig. 3) indicating an isotopic shift of 15 cm^{-1} for ν_1. With this constraint, a force field (MVFF I) is obtained which results in a more plausible value for F_{11} (see below) and a more characteristic potential energy distribution (see Table 3).

For the B_1 block two solutions were found (see Table 3) which were capable of duplicating the *observed isotopic shifts*. Their main difference is the sign of f_{RR}. Since a value of 0.28 mdyn/Å for f_{RR} agrees much better with the values found for related molecules (see Table 4), we prefer set I of Table 3 over set II, although the PED of set II is more characteristic. Strong mixing of the modes in B_1 would not be surprising in view of their similar frequencies and their ease of coupling. An exact duplication of the observed matrix isolation isotopic shifts could be achieved by using for ν_7 the observed matrix isolation frequency value (803 cm^{-1}) in place of the gas phase value (819 cm^{-1}). The resulting force field was almost identical to MVFF I (see Table 3) and, therefore, is not separately listed. Contrary to the findings for the B_1 block, the potential energy distribution for the A_1 and B_2 blocks is highly characteristic.

A comparison of the stretching force constants of SF_4O with those previously reported for similar molecules [24–35] is given in Table 4 and shows the expected trends. The equatorial SF bonds in SF_4O are significantly stronger than the axial ones (even if MVFF II is chosen), thus supporting our choice of an electron diffraction data model [5] in which rSF_{eq} is significantly shorter than rSF_{ax}. By analogy with the other related pseudotrigonal-bipyramidal sulfur or chlorine fluorides or oxyfluorides, the bonding in SF_4O might be described

Table 3. Observed frequencies (cm^{-1}), symmetry force constants,* computed and observed ^{32}S—^{34}S isotopic shifts (cm^{-1}), and potential energy distribution† for SF_4O

		Frequency				MVFF I		DVFF		
				F	ΔνCOMP	ΔνOBSD	PED	F	ΔνCOMP	PED
A_1	ν_1	1380	$F_{11} = f_D$	11.990	14.8	~15	$100F_{11}$	11.05	17.4	$89F_{11}$
	ν_2	796	$F_{22} = f_r + f_{rr}$	5.951	2.4		$100F_{22}$	5.98	1.8	$88F_{22} + 10F_{11}$
	ν_3	588	$F_{33} = f_R + f_{RR}$	3.825	0.1		$98F_{33}$	3.83	0.1	$99F_{33}$
	ν_4	450	$F_{44} = 0.32(2f_\alpha + f_\beta) + 0.15(2f_\alpha + f_\gamma)$	1.440	1.6		$100F_{44}$	1.45	1.0	$94F_{44}$
	ν_5	174	$F_{55} = 0.24(2f_\alpha + f_\beta) + 0.16f_\delta + 0.27(2f_\alpha + f_\gamma)$	0.1486	0.7		$96F_{55}$	0.1475	0.8	$97F_{55}$
			$F_{12} = \sqrt{2}f_{Dr}$	1.1						
			$F_{24} = 0.56(2f_{r\alpha} - f_{r\beta} - f_{r\beta'}) + 0.24(f_{r\gamma} - f_{r\gamma'})$	−0.7						
A_2	ν_6	400	$F_{66} = f_\delta - f_{\delta\delta} - f_{\delta\delta'} + f_{\delta\delta''}$	1.279	0		$100F_{66}$			
		475		1.803					MVFF II	
		550		2.417						
B_1	ν_7	819	$F_{77} = f_R - f_{RR}$	3.26	13.4	13.1	$63F_{77} + 64F_{88} + 10F_{99} - 13F_{78} - 17F_{79}$	4.303	13.0	$124F_{77} + 10F_{88} + 18F_{99}$ $- 23F_{78} - 28F_{79}$
	ν_8	639	$F_{88} = f_\gamma - f_{\gamma\gamma}$	2.77	2.4	2.4	$41F_{77} + 25F_{88} + 48F_{99} - 31F_{79}$	2.359	1.8	$104F_{88}$
	ν_9	566	$F_{99} = f_\delta - f_{\delta\delta} + f_{\delta\delta'} - f_{\delta\delta''}$	2.63	1.0	1–2	$12F_{77} + 15F_{88} + 60F_{99} + 18F_{79}$	2.470	1.9	$94F_{99}$
			$F_{78} = f_{R\gamma} - f_{R\gamma'}$	0.31				1.02		
			$F_{79} = \sqrt{2}(f_{R\delta} - f_{R\delta'})$	1.01				0.95		
			$F_{89} = \sqrt{2}(f_{\gamma\delta} - f_{\gamma\delta'})$	−0.37				−0.15		
B_2	ν_{10}	926	$F_{10,10} = f_r - f_{rr}$	5.415	14.0	14.0	$103F_{10,10} + 11F_{11,11} - 18F_{10,11}$			
	ν_{11}	560	$F_{11,11} = f_\beta - f_{\beta\beta}$	1.459	2.7		$91F_{11,11}$			
	ν_{12}	265	$F_{12,12} = f_\delta - f_{\delta\delta} - f_{\delta\delta} - f_{\delta\delta'}$	1.023	0.6		$94F_{12,12}$			
			$F_{10,11} = f_{r\beta} - f_{r\beta'}$	0.75						
MATRIX FREQUENCIES										
B_1	ν_7	803	F_{77}	3.24	13.1	13.1	$66F_{77} + 64F_{88} + 10F_{99} - 15F_{78} - 18F_{79}$			
	ν_8	638	F_{88}	2.70	2.4	2.4	$41F_{77} + 26F_{88} + 47F_{99} - 31F_{79} + 9F_{89}$			
	ν_9	566	F_{99}	2.62	1.1	1–2	$11F_{77} + 15F_{88} + 62F_{62} + 18F_{79}$			
			F_{78}	0.35						
			F_{79}	1.02						
			F_{89}	−0.36						

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* Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interaction constants in mdyn/radian.

† Percent contributions. Contributions of less than 9% to the PED are not listed

Table 4. Stretching force constants (mdyn Å) of SF_4O compared to those of similar molecules

	SF_6[24]	SF_4O	SF_2O_2[25]	SO_3[26]	SF_4[1]	SF_2O[27]	SO_2[28]	SF_2[29]	SO[30]	ClF_3O_2[17]	$FClO_3$[31]	ClF_3O[32]	$FClO_2$[33]	ClF_3[34]	FClO[35]
$f_{X=O}$		11.99	11.63	10.61		11.22	10.42		8.12	9.23	9.4	9.37	9.07	6.85	4.19
f_r(eq)	5.26	5.68	5.29		5.51	4.07		4.78		3.35	3.9	3.16	2.53	2.59	2.70
f_R(ax)		3.54			3.30					2.70		2.34			
f_{rr}	0.34	0.27	0.26		0.25	0.35		0.39							
$f_{RR'}$		0.28			0 19					−0.04		0.26			0.35

Table 5. Thermodynamic properties of SF_4O

T, K	$Cp°$, cal/mol	$H°-H_0°$, kcal/mol	$-(F° - h_0°)/T$, cal/(mol deg)	$S°$, cal/(mol deg)
0	0	0	0	0
100	10.185	0.861	50.332	58.946
200	15.546	2.138	56.890	67.580
298.15	20.314	3.910	61.611	74.726
300	20.388	3.948	61.692	74.852
400	23.683	6.163	65.794	81.202
500	25.849	8.647	69.442	86.736
600	27.301	11.309	72.737	91.585
700	28.303	14.092	75.742	95.873
800	29.016	16.960	78.502	99.702
900	29.538	19.889	81.052	103.151
1000	29.929	22.863	83.421	106.285
1100	30.229	25.872	85.632	109.152
1200	30.463	28.907	87.703	111.792
1300	30.650	31.963	89.651	114.238
1400	30.800	35.036	91.490	116.516
1500	30.923	38.122	93.230	118.645
1600	31.025	41.220	94.882	120.644
1700	31.110	44.327	96.453	122.527
1800	31.182	47.441	97.951	124.308
1900	31.243	50.563	99.383	125.995
2000	31.296	53.690	100.754	127.599
2100	31.341	56.821	102.069	129.127
2200	31.381	59.958	103.333	130.586
2300	31.415	63.097	104.548	131.982
2400	31.446	66.241	105.719	133.320
2500	31.473	69.386	106.849	134.604
2600	31.497	72.535	107.941	135.839
2700	31.518	75.686	108.996	137.028
2800	31.538	78.839	110.018	138.174
2900	31.555	81.993	111.008	139.281
3000	31.571	85.150	111.968	140.351
3100	31.585	88.307	112.901	141.387
3200	31.598	91.466	113.807	142.390
3300	31.609	94.627	114.688	143.362
3400	31.620	97.788	115.545	144.306
3500	31.630	100.951	116.380	145.223
3600	31.639	104.114	117.193	146.114
3700	31.647	107.279	117.987	146.981
3800	31.655	110.444	118.761	147.825
3900	31.662	113.609	119.517	148.647
4000	31.669	116.776	120.255	149.449
4100	31.675	119.943	120.977	150.231
4200	31.680	123.111	121.682	150.995
4300	31.686	126.279	122.373	151.740
4400	31.691	129.448	123.049	152.469
4500	31.695	132.617	123.710	153.181
4600	31.699	135.787	124.359	153.878
4700	31.704	138.957	124.994	154.559
4800	31.707	142.128	125.617	155.227
4900	31.711	145.299	126.228	155.881
5000	31.714	148.470	126.827	156.521
5100	31.717	151.642	127.416	157.149
5200	31.720	154.813	127.993	157.765
5300	31.723	157.986	128.561	158.370
5400	31.726	161.158	129 118	158.963
5500	31.728	164.331	129.666	159545
5600	31.731	167.504	130.205	160.116
5700	31.733	170.677	130.735	160.678
5800	21.735	173.850	131.256	161.230
5900	31.737	177.024	131.768	161.772
6000	31.739	180.198	132.273	162.306

by the following model. The bonding of the three equatorial ligands, ignoring the second bond of the S=O double bond, is mainly due to an sp^2 hybrid, whereas the bonding of the two axial SF bonds involves one delocalized p-electron pair of the sulfur atom for the formation of a semi-ionic three-center four-electron $p\sigma$ bond [36–38]. The incorrectness of the assignments previously made [9] by Cleveland and coworkers is also reflected by their force field which resulted in significantly stronger axial ($f_R = 5.54$ mdyn/Å) than equatorial (f_r = 4.40 mdyn/Å) SF bonds, contrary to the electron diffraction data [3–5].

The S—O stretching force constant increases with both increasing oxidation state of the central atom and increasing fluorine substitution. The equatorial S—F stretching force constants also tend to increase for the same sulfur oxidation state with increasing fluorine substitution, except for $SF_4O \rightarrow SF_6$. Provided the given force constants differences are meaningful, the latter effect might be explained by the higher s-character of the equatorial SF bonds in SF_4O (sp^2) when compared to those in SF_6 (sp^3d^2). Comparison between the stretching force constants of SF_4O and SF_4 shows good agreement, the slight increase from SF_4 to SF_4O being attributable to the increase of the sulfur oxidation state.

Thermodynamic properties. In view of the absence of thermodynamic data for SF_4O in the literature and of their interest for chemical lasers, we have computed thermodynamic properties for SF_4O (see Table 5). The molecular geometry and frequencies from the above force field computation were adopted assuming $\nu_6 = 475$ cm^{-1} and an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation [39]. It should be kept in mind, however, that the frequencies of two fundamentals (ν_4 and ν_6) are uncertain and that the sum of the frequencies may therefore be in error by as much as 200 cm^{-1}.

SUMMARY

The vibrational spectra of pure SF_4O have been recorded. Out of the 12 fundamentals expected for symmetry C_{2v}, 10 have been observed and the previous assignments [9] were revised for 8 of the fundamentals. As for SF_4, the assignments for the A_1 equatorial SF_2 scissoring and the A_2 torsional mode present difficulties. A systematic study of the vibrational spectra of the presently known pseudo-trigonal bipyramidal fluorides and oxyfluorides is desirable to support the assignments for the deformation modes. The results of a normal coordinate analysis indicate that the proposed assignments for SF_4O are plausible. The stretching force constants of SF_4O are in good agreement with those found for SF_4 and similar molecules. The large differences in the values of the equatorial and the axial SF stretching force constants indicates that model [illegible] (or possible C) of GUNDERSEN and HEDBERG [illegible] are more probable than their preferred [illegible].

Acknowledgment—The authors are indebted to [illegible] Grant for helpful discussions and to the Office of [illegible] Research, Power Branch for financial support.

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Fig. 4. Definition of internal coordinates.

Journal of Fluorine Chemistry, 8 (1976) 541 544
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Received: July 22, 1976

SHORT COMMUNICATION

Improved Syntheses of NF_4BF_4 and NF_4SbF_6

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In view of the importance of NF_4^+ salts for solid propellant NF_3-F_2 gas generators [1], improved syntheses of NF_4BF_4 and NF_4SbF_6 were required.

Two methods have previously been reported for the synthesis of $NF_4SbF_6 \cdot xSbF_5$ involving the use of either high pressure and temperature [2,3] or uv-irradiation [4]. Of these, the thermal method is more convenient for larger scale production. According to Tolberg et al. [2,3] the most favorable reaction conditions are:

$$NF_3 + F_2 + SbF_5 \xrightarrow[\substack{100\text{-}125^\circ \\ 2\ \text{days}}]{3000\ \text{psi}} NF_4Sb_3F_{16}$$

$$NF_4Sb_3F_{16} \xrightarrow[\substack{200^\circ \\ 2\text{-}3\ \text{days}}]{\text{vacuum}} NF_4SbF_6 + 2SbF_5$$

The resulting product contained an appreciable amount of Monel salts and was removed from the reactor by cutting it open with a hacksaw and scraping out the hard clinkered product. Based on recent work done in our laboratory [1], temperatures (250-260°), higher than those reported by Tolberg, are required for the vacuum pyrolysis of $NF_4SbF_6 \cdot xSbF_5$ to NF_4SbF_6 within a reasonable time period.

We have now found that most of the drawbacks of the above procedure can be avoided by directly synthesizing NF_4SbF_6. For this purpose, NF_3, F_2, and SbF_5 in a 2:2:1 mol ratio are heated in a Monel cylinder to 250° for 72 hours. The size of the cylinder is chosen in such manner that at the completion of the reaction the autogenous pressure is about 70 atm. The excess of NF_3 and F_2 is removed under vacuum at room temperature and the desired NF_4SbF_6

product is extracted from the Monel cylinder with anhydrous HF using about 50 ml of liquid HF per 100 g of NF_4SbF_6. Since, contrary to a previous report [3], the formed Monel salt impurities (about 5%) are quite insoluble in anhydrous HF, they can be easily removed from the product by incorporating a porous Teflon filter (Pall Corporation) into the HF solution transfer line. Based on elemental and spectroscopic analyses and the observed material balances, the resulting product was shown to be essentially pure NF_4SbF_6.

Several methods have previously been reported for the synthesis of NF_4BF_4. This salt can be prepared either directly from NF_3, F_2, and BF_3 using glow discharge [5,6], bremsstrahlung [7] or ultraviolet radiation [4,8], or indirectly from NF_4SbF_6 using a metathetical process [3,9]. Of these, the metathetical process is most amenable to the larger scale production of NF_4BF_4 utilizing existing technology. The original metathetical NF_4BF_4 process [3] involved the following steps:

$$CsF + HF \xrightarrow{HF} CsHF_2$$

$$NF_4SbF_6 + CsHF_2 \xrightarrow{HF} CsSbF_6\downarrow + NF_4HF_2$$

$$NF_4HF_2 + BF_3 \xrightarrow{HF} NF_4BF_4 + HF$$

Since the crude product, thus obtained, contained much $CsSbF_6$, its NF_4BF_4 content was increased by extraction with BrF_5. The use of BrF_5 resulted in the following side reaction:

$$NF_4BF_4 + CsSbF_6 \xrightarrow{BrF_5} CsBF_4\downarrow + NF_4SbF_6$$

The composition of the final product was reported [3] to be: 91.5% NF_4BF_4 and 8.5% NF_4SbF_6. In addition to the requirement of BrF_5 as a recrystallization solvent, this process suffers from the following disadvantage. Highly concentrated solutions of NF_4HF_2 in HF are unstable decomposing to NF_3, F_2, and HF. This can cause a pressure build up in the metathesis apparatus which in turn can render filtration steps more difficult.

This process was somewhat improved upon [9] by substituting CsF by AgF. This modification eliminated the BrF_5 extraction step and resulted in a product of the composition (mol %): NF_4BF_4 (89), $NF_4Sb_2F_{11}$ (7.9), $AgBF_4$ (3.1). However, the process still involved the handling of concentrated NF_4HF_2 solutions. Furthermore, the cost of silver salts is rather high and therefore requires their recycling in high yields.

We have now found that NF_4BF_4 of at least 97 mol % purity can be prepared by a simpler process using anhydrous HF at different temperatures as the only solvent. Furthermore, we have shown that the purity of the NF_4BF_4

can be raised to above 99 mol % by a single recrystallization from BrF_5. The cesium content in both products was shown to be less than 0.1 mol %, the principal impurity being NF_4SbF_6.

Our improved process consists of the following steps:

$$CsBF_4 + 1.1\ NF_4SbF_6 \xrightarrow[-78^\circ \text{ filtr.}]{HF} CsSbF_6\downarrow + NF_4BF_4 + 0.1\ NF_4SbF_6$$

$$NF_4BF_4 + 0.1\ NF_4SbF_6 \xrightarrow[25^\circ]{\text{recryst. from HF}} \underset{(97\text{ m }\%)}{NF_4BF_4\downarrow} + \text{mother liquor}$$

$$NF_4BF_4 \xrightarrow[25^\circ]{\text{recryst. from } BrF_5} \underset{(99+\text{ m }\%)}{NF_4BF_4\downarrow} + \text{mother liquor}$$

The important features of our process are:

(i) The use of $CsBF_4$ instead of $CsHF_2$ eliminates one step and avoids the complications caused by NF_4HF_2.

(ii) The use of a 10 mol % excess of NF_4SbF_6 decreases the solubility of $CsSbF_6$ by the common ion effect.

(iii) Carrying out the $CsSbF_6$ filtration step at -78° decreases the SbF_6^- concentration since the solubilities of SbF_6^- salts in anhydrous HF decrease with decreasing temperature much more rapidly than those of BF_4^- salts. Furthermore, the amount of NF_4BF_4, retained in the $CsSbF_6$ filter cake by absorption of a certain volume of mother liquor, is minimized owing to the decreased solubilities.

(iv) Since NF_4BF_4 and NF_4SbF_6 have comparable solubilities in HF at room temperature, the 10% excess of NF_4SbF_6 used in the $CsSbF_6$ precipitation step can be removed as mother liquor by recrystallization from HF at room temperature. Unfortunately, the solubilities in HF at room temperature are so high that a significant percentage of the mother liquor is retained by the NF_4BF_4 precipitate. This problem can be minimized by using for this recrystallization a solvent in which these NF_4^+ salts are less souble. Thus, a single recrystallization from BrF_5 raised the product purity above the 99 mol % level. Other suitable solvents could be used to replace BrF_5 in this step. The mother liquors of the recrystallization steps can be easily recycled into the $CsSbF_6$ precipitation step, thus avoiding the loss of any NF_4^+ values.

In summary, the combination of the two improved processes for the syntheses of NF_4SbF_6 and NF_4BF_4, respectively, results in a relatively simple and economical process for the production of NF_4BF_4 in a purity of about 97 mol %. Furthermore, it was demonstrated for the first time that high purity (99+ mol %) NF_4BF_4 can be prepared by metathesis.

We are indebted to Drs. L. R. Grant and R. I. Wagner for helpful discussions. This work was in part supported by the Office of Naval Research, Power Branch.

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IGNITION TEST - GASEOUS F_2-NF_3 ON MAGNETIC RECORDING TAPE

A sample of standard 1" wide, 6" long, 1-mil thick polyester magnetic recording tape (Ampex Catalog No. 787-57G11A-GS FSN5835-168-9522 per specification WT001553) was subjected to a short burst of gaseous F_2/NF_3 to determine the hypergolicity (ignition) characteristics of the system. The reaction was spontaneous and rapid with the tape bursting into flame immediately. The tape sample was placed in a windowed combustion chamber (as shown in Fig. 1). The F_2/NF_3 gases were those generated from burning NF_4BF_4/KF/Mg grains and contained in a 1-gallon Hoke cylinder at approximately 500 psi. The actual gas composition is presented in Table I. The test system was plumbed as shown in Fig. 1 using 1/2" diameter stainless steel lines and air-operated 1/2" diameter Worthington Model 9420 control valves with GN_2 operators. Test procedure was as follows:

1) Tape sample was inserted into the window bomb and held in place with a standard strand sample holder.

2) After closing the bomb assembly and checking for leaks with GN_2 (by backfilling thru the vent valve) the vent valve was closed.

3) The hand valve on the Hoke cylinder was opened and the test cell closed.

4) The fill valve was remotely opened while viewing the window bomb thru the test cell window. The fill valve was cycled on and off as quickly as possible. Immediately after opening the fill valve, visible flames were apparent in the window bomb.

5) Visible flame died out in a few seconds and the vent valve was opened, initiating more visible flame in the window bomb as gaseous flow out of the window bomb occurred. These flames soon died out.

6) The vent valve was closed and the fill valve again cycled quickly on and off. Visible flame was again spontaneous and immediate, only this time the gasket (Teflon) on the window also burned, causing visible flame to spew out around the window.

7) The vent valve was opened and left open to permit venting of the bomb to ambient pressure.

8) After approximately one hour, the hand valve on the Hoke cylinder was closed and the top of the window bomb was removed. The tape sample was completely consumed. The window gasket was badly burned, ruining the gasket and the window. (Replacements are available.)

Surprisingly enough, a magnesium-Teflon ignition pellet placed in a nickel crucible in the bottom of the window bomb was not burned during these tests. The pellet was removed from the bomb after the test, slightly scorched, but it obviously did not ignite.

No pressure measuring device was utilized in these tests. However, the estimated pressure in the window bomb was less than 100 psi since the fill valve was open a very short time and pressure equilibrium with the Hoke cylinder reservoir almost certainly did not occur.

This test data indicates that utilization of gases generated from NF_4BF_4 containing grains is a viable method of rapidly destroying magnetic tape and probably almost any other stored data housed in a suitable container so that gas flow across the material is ensured.

TABLE I. GAS ANALYSIS OF GASES IN HOKE CYLINDER

Gas	Mole %
NF_3	47.3
F_2	38.3
He	8.3*
N_2	2.8
BF_3	2.1
HF	0.4
CF_4	0.2
CF_3OF	0.3
COF_2	0.1
O_2	0.1
Unknown	0.1

*The He value is probably too high as a result of the gas sampling procedure.

IGNITION TEST - GASEOUS F_2-NF_3 ON MAGNETIC RECORDING TAPE

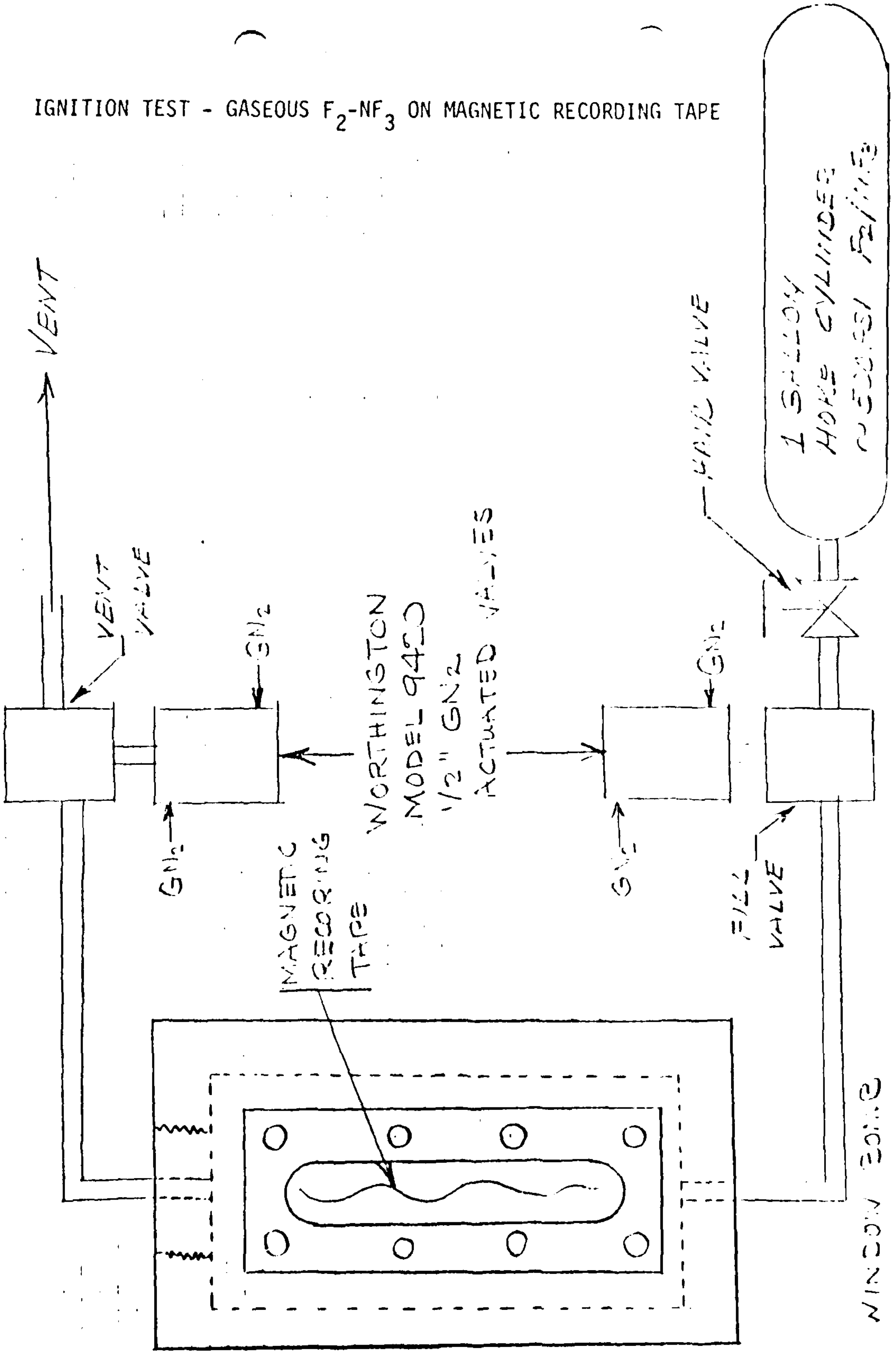

FIGURE 1: TEST SETUP FOR IGNITION TEST