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RI/RD80-134

ANNUAL REPORT
INORGANIC HALOGEN OXIDIZER RESEARCH
(1 March 1979 through 29 February 1980)

17 March 1980

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The synthesis and characterization of the following compounds is reported: NF_4ClO_4, NF_4HF_2, NF_4UF_5O, NF_4SO_3F, $FOClO_3$, $FOSO_2F$, OIF_4OF, $H_3O_2SbF_6$, $H_3O_2AsF_6$, D_3OSbF_6, D_3OAsF_6. The kinetics and mechanism of the formation and decomposition of NF_4^+ salts were determined. The structure of ClF_3O was determined by electron diffraction, and vibrational spectra and force fields were obtained for $FOClO_3$ and SF_4.

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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 March 1979 through 29 February 1980. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, W. W. Wilson, and Mr. R. D. Wilson.

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INTRODUCTION

This report covers the period from 1 March 1979 through 29 February 1980 and describes Rocketdyne's research efforts in the area of energetic inorganic halogen oxidizers. As in the past years (Ref. 1), 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. Although the program is directed toward basic research, applications of the results are continuously considered. A typical example of the usefulness of such goal-oriented basic research is the application of NF_4^+ chemistry to solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers.

Only completed pieces of research are included in this report. As in the past (Ref. 1), completed work has been summarized 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 issued. All of these arose from work sponsored under this program.

PUBLICATIONS AND PATENTS DURING PAST CONTRACT YEAR

PAPERS PUBLISHED

1. "Formation and Decomposition Mechanism of NF_4^+ Salts," by K. O. Christe, R. D. Wilson and I. B. Goldberg, Inorg. Chem. 18, 2572 (1979).
2. "Sulfur Tetrafluoride. Assignment of Vibrational Spectra and Force Field," by K. O. Christe, H. Willner, and W. Sawodny, Spectrochim Acta, 35a, 1347 (1979).
3. "Novel Onium Salts. Synthesis and Characterization of the Peroxonium Cation, H_2OOH^+, by K. O. Christe, W. W. Wilson, Inorg. Chem., 18, 2578 (1979).
4. "Cis- and Trans-Iodine (VII) Oxytetrafluoride Hypofluorite, OIF_4OF," by K. O. Christe and R. D. Wilson, Inorg. Nucl. Chem. Letters, 15, 375 (1979).
5. "Reactions of Fluorine Perchlorate with Fluorocarbons and the Polarity of the O-F Bond in Covalent Hypofluorites," by C. J. Schack and K. O. Christe, Inorg. Chem., 18, 2619 (1979).

PAPERS IN PRESS

6. "Synthesis and Properties of $NF_4^+UF_5O^-$," by W. W. Wilson, R. D. Wilson, and K. O. Christe, J. Inorg. Nucl. Chem.
7. "Synthesis and Properties of $NF_4^+SO_3F^-$, by K. O. Christe, R. D. Wilson and C. J. Schack, Inorg. Chem.
8. "The General Valence Force Field of Perchloryl Fluoride," by K. O. Christe and E. C. Curtis, Inorg. Chem.
9. "Synthesis and Properties of $NF_4^+ClO_4^-$ and $NF_4^+HF_2^-$.nHF and Some Reaction Chemistry of NF_4^+ Salts," by K. O. Christe, W. W. Wilson, and R. D. Wilson, Inorg. Chem.
10. "Evidence for the Existence of Directional Repulsion Effects by Lone Valence Electron Pairs and π-Bonds in Trigonal Bipyramidal Molecules," by K. O. Christe and H. Oberhammer, Inorg. Chem.

PAPERS PRESENTED AT MEETINGS

11. "On the Mechanism of the Formation and Decomposition of NF_4^+ Salts," by K. O. Christe, R. D. Wilson and I. B. Goldberg, 4th Winter Fluorine Conference, Daytona Beach, Florida (January 1979).

12. "The Use of Anhydrous HF as a Solvent for the Syntheses of Novel NF_4^+ and Onium Salts," by K. O. Christe, C. J. Schack, W. W. Wilson, and R. D. Wilson, ACS/CSJ Chemical Congress, Honolulu, April 1979.

13. "Fluorine Perchlorate, Synthesis, Properties and Reaction Chemistry," by K. O. Christe, C. J. Schack and E. C. Curtis, ACS/CSJ Congress, Honolulu, April 1979.

14. "Solid Propellant NF_3/F_2 Gas Generators and Other Aspects of Fluorine Chemistry," by K. O. Christe, Materials Research Council Conference, La Jolla, July 1979.

15-16. "Synthesis and Characterization of NF_4ClO_4, NF_4HF_2(uxHF) and cis- and trans-OIF_4OF," by K. O. Christe, W. W. Wilson and R. D. Wilson, 9th International Symposium on Fluorine Chemistry, Avignon, France (September 1979) and 178th National ACS Meeting, Washington D.C., (September 1979).

17. An invited seminar on our research was given at the University of Southern California.

PATENTS ISSUED

18. "Self-Clinkering NF_4^+ Compositions for NF_3-F_2 Gas Generators and Method of Producing Same," by K. O. Christe, C. J. Schack, and R. D. Wilson, U.S. 4,152,406 (May 1979).

19. "Self-Clinkering Burning Rate Modifier for Solid Propellant NF_3-F_2 Gas Generators for Chemical HF-DF Lasers," by K. O. Christe and C. J. Schack, U.S. 4,163,773 (Aug. 1979).

20. "$N_2F_3SbF_6$ and its Preparation," by C. J. Schack and K. O. Christe, US 4,163,774 (Aug. 1979).

21. "Displacement Reaction for Producing NF_4PF_6," by K. O. Christe and C. J. Schack, US 4,172,881 (Oct. 1979).

22. "Self-Clinkering NF_4^+ Compositions for NF_3-F_2 Gas Generators and Method of Producing Same," by K. O. Christe, C. J. Schack and R. D. Wilson, US 4,172,884 (Oct. 1979).

PATENTS PENDING

23. "Novel High Detonation Pressure Explosive," by K. O. Christe.
24. "Peroxonium Salts and Method of Producing Same," by K. C. Christe and W. W. Wilson.

DISCUSSION

The NF_4^+ cation is a unique high energy oxidizer ingredient because it combines high energy with unusual kinetic stability. It was first discovered in 1965 by one of us under ONR contract (Ref. 2) and, over the years, this cation has successfully been combined with counterions of increasing energy content. During the past contract year, efforts were made to better characterize known NF_4^+ salts (Appendix A) and to synthesize novel NF_4^+ salts derived from halogen -fluoride, -oxyfluoride, or -oxide anions. The most energetic salt isolated was $NF_4^+ClO_4^-$ (Appendix B). However, the thermal stability of this salt is insufficient for practical applications. Attempts to prepare salts, such as $NF_4^+NO_3^-$, $NF_4^+ClF_4O^-$, or $NF_4^+BrF_4O^-$ were unsuccessful, but the compound $NF_4^+HF_2^-.nHF$ was isolated and characterized (Appendix B).

During the characterization of $NF_4^+ClO_4^-$ it was found that this salt decomposed to give $FOClO_3$ in essentially quantitative yield, thus providing a novel synthetic method for the production of energetic hypofluorites. The general applicability of this method was tested by the preparation of another novel NF_4^+ salt, $NF_4^+SO_3F^-$, and a study of its decomposition also yielded the corresponding hypofluorite, FSO_2OF (Appendix C). This method was then further extended to the synthesis of novel hypofluorites, such as OIF_4OF (Appendix D) which is the first known example of an iodine hypofluorite. It was thoroughly characterized and found to exist in the form of two isomers, cis and trans. A summary of its properties will be given in the next annual report in manuscript form. The corresponding hypochlorite, OIF_4OCl, was also prepared, but is of very limited thermal stability and, therefore, could not be well characterized.

With the ready availability of hypofluorites by the above method, it was of interest to better characterize fluorine perchlorate, $FOClO_3$. Some of its physical properties were redetermined and its vibrational spectra were thoroughly studied. For an evaluation of its force field, however, the knowledge of the General Valence Force Field of the closely related $FClO_3$ molecule became necessary. Since no reliable literature data were available for this important storable liquid oxidizer, its spectroscopic properties, ^{35}Cl-^{37}Cl isotopic shifts, and Corrolis zeta constants were determined and used for a normal coordinate analysis (Appendix E). Using these data, a normal coordinate analysis of $FOClO_3$ has been started, the results of which will be given in the next annual report in manuscript form.

The reaction chemistry of $FOClO_3$ was also studied. It was found that the compound can be readily added across C=C double bonds, thus yielding fluorocarbon perchlorates. From the direction of this addition, it was concluded that the fluorine in this and similar hypofluorites is not positively polarized, as frequently postulated in the literature. The results of this study are summarized in Appendix F.

A novel method was worked out for the synthesis of new NF_4^+ salts, derived from nonvolatile polymeric Lewis acids which do not possess HF soluble salts and, therefore, cannot be prepared by any presently known method. Using the NF_4HF_2 salt, described in Appendix B, the new salt $NF_4^+UF_5O^-$ was prepared (Appendix G). Our main interest in this salt was to examine whether it could be used as a precursor for the synthesis of UF_5OF. Unfortunately, the thermal stability of $NF_4^+UF_5O^-$ was too high, and no evidence for the formation of UF_5OF was obtained during its vacuum pyrolysis. Attempts to synthesize other uF_5X type compounds, which involved a number of different synthetic approaches, were unsuccessful.

The compatibility of NF_4^+ salts with HMX and TATB in the presence and absence of fluorocarbons was examined. These systems are of interest for high detonation pressure explosives.

In view of the renewed interest in high performance storable liquid oxidizers, we have resumed studies of chlorine oxyfluorides. The molecular structure of ClF_3O was determined by electron diffraction, and evidence for the existence of interesting directional repulsion effects in trigonal bipyramidal molecules was obtained (Appendix H).

We have also continued work in the area of novel onium salts which were discovered under this contract (Ref. 1). A manuscript was published on the peroxonium, H_2OOH^+, cation (Appendix I). Several new D_3O^+ salts were prepared, and a structural study of these salts by neutron diffraction is under progress. The results of this study will be given in the next annual report in manuscript form.

The results of our force field calculations on SF_4 were published in manuscript form (Appendix J) and were confirmed by an ab initio calculation at the University of Ulm, Germany. The results will be given in the next annual report.

Five U.S. patents were issued during the past year covering various aspects of NF_4^+ chemistry and their application to solid propellant NF_3-F_2 gas generators for HF-DF chemical lasers (Appendices K through O).

REFERENCES

1. Inorganic Halogen Oxidizer Research, ONR Contract N00014-70-C-0294, Final Report, Rocketdyne, (February 1979).
2. K. O. Christe, J. P. Guertin, and A. E. Pavlath, U.S. Patent, 3,503,719 (1970).

APPENDIX A

FORMATION AND DECOMPOSITION MECHANISM OF NF_4^+ SALTS

[Reprinted from Inorganic Chemistry, 18, 2572 (1979).]

Contribution from the Rocketdyne Division, Rockwell International, Canoga Park, California 91304,
and the Science Center, Rockwell International, Thousand Oaks, California 91360

Formation and Decomposition Mechanism of NF_4^+ Salts

KARL O. CHRISTE,* RICHARD D. WILSON, and IRA B. GOLDBERG

Received February 12, 1979

The thermal decompositions of NF_4BF_4 and NF_4AsF_6 were studied in a sapphire reactor at different temperatures by total-pressure measurements. It was found that the rates, previously reported by Solomon and co-workers for NF_4AsF_6, significantly differ from those of the present investigation, although both studies result in a $^3/_2$ reaction order. From the temperature dependence of the observed decomposition rates, the following values were obtained for the global activation energies: $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}. The suppression of the decomposition rates by NF_3, F_2, and BF_3 or AsF_5 was measured. A critical evaluation of all experimental data available on the NF_4^+ salt formation and decomposition suggests the following reversible reaction mechanism: $F_2 \rightleftarrows 2\dot{F}$; $\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$; $\dot{N}F_4 + AsF_5 \rightleftarrows \dot{N}F_3^+AsF_6^-$; $\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$. A Born–Haber cycle calculated for NF_4BF_4 shows that the global decomposition activation energy and the heat of the formation reaction are identical within experimental errors and that the second step of the above mechanism is approximately thermochemically neutral. The rate of the thermal formation of NF_4SbF_6 at 250 °C was also studied.

Introduction

The formation and decomposition reactions of NF_4^+ salts are of significant theoretical and practical interest. From a theoretical point of view, the question arises as to whether $\dot{N}F_4$ or NF_5 is produced as an unstable intermediate. This would be highly unusual because second-row elements generally do not form hypervalent molecules. From a practical point of view, a better knowledge of the formation and the decom-

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

Several mechanisms have previously been postulated for the formation of NF_4^+ salts. In 1966, Christe and co-workers suggested in their original reports[1,2] on the synthesis of NF_4AsF_6 by low-temperature glow discharge that either NF_3^+ or F^+ (or F_2^+) is generated in the discharge. These radical cations could then react with either F_2 or NF_3 to yield NF_4^+. In 1972, Solomon and co-workers reported[3] the results from a kinetic study of the thermal decomposition of NF_4AsF_6 in Monel. Based on total pressure measurements, their conclusion was that the decomposition involved the equilibrium dissociation step

$$NF_4AsF_6 \rightleftharpoons NF_5 + AsF_5$$

followed by irreversible decomposition of the unstable NF_5

$$NF_5 \rightarrow NF_3 + F_2$$

The latter step was taken to be a $^1/_2$-order reaction. From the temperature dependence of the kinetic constants, a value of 41 kcal mol^{-1} was obtained for the sum of the overall heat of sublimation and the activation energy for the decomposition of NF_5. In 1973, Christe and co-workers proposed[4] an alternate mechanism for the formation of NF_4^+ salts. This mechanism accounted for the fact that NF_4^+ salts can be synthesized by UV photolysis. It involved the steps

$$F_2 \rightarrow 2\dot{F}$$

$$\dot{F} + AsF_5 \rightleftharpoons \dot{A}sF_6$$

$$\dot{A}sF_6 + NF_3 \rightarrow \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightarrow NF_4^+AsF_6^-$$

Part of this mechanism was later experimentally confirmed by ESR studies[5-7] which showed that the $\dot{N}F_3^+$ radical cation is indeed formed as an intermediate in both the low-temperature UV photosynthesis and the γ-irradiation-induced decomposition of NF_4^+ salts.

Since the observation of $\dot{N}F_3^+$ as an intermediate[5-7] is incompatible with the mechanism proposed[3] by Solomon and since at elevated temperatures metal reactors rapidly absorb F_2-Lewis acid mixtures, a reinvestigation of the thermal decomposition of NF_4AsF_6 in an inert sapphire reactor was undertaken. In particular, a more detailed investigation of the suppression effects of NF_3, F_2, and AsF_5 was expected to yield valuable information. Furthermore, no quantitative data had previously been available on the decomposition rates of NF_4BF_4 and the formation rates of NF_4SbF_6.

Experimental Section

Thermal Decomposition Studies. The samples of NF_4BF_4[8] and NF_4AsF_6[8,9] were prepared as previously described and showed no detectable impurities. All decomposition experiments were carried out in a sapphire reactor (Tyco Co.). The reactor was connected by a Swagelok compression fitting, containing a Teflon front ferrule, to a stainless steel valve and a pressure transducer (Validyne, Model DP7, 0-1000 mm ± 0.5%), the output of which was recorded on a strip chart. The reactor had a volume of 38.7 mL and was heated by immersion into a constant-temperature (±0.05 °C) circulating oil bath. The reactor was passivated at 250 °C with F_2-BF_3 or F_2-AsF_5 mixtures until the pressure remained constant over a period of several days, and weighed amounts of NF_4^+ salts were added in the dry nitrogen atmosphere of a glovebox. After immersion of the reactor into the hot oil bath, the reactor was evacuated, and the pressure change was monitored as a function of time. Control experiments were carried out at the beginning and end of each series of measurements to ascertain that the rates had not significantly changed during each series. The composition of the gaseous decomposition products was shown by chemical analysis, infrared spectroscopy, and gas chromatography to be 1:1:1 mixtures of NF_3, F_2, and the corresponding Lewis acid. For the curve fitting of the kinetic data the method of linear least squares was used with the listed uncertainties being 2σ of the calculated slope.

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

Results and Discussion

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

The results of our measurements on NF_4BF_4 and NF_4AsF_6 are summarized in Tables I and II. In agreement with the previous report[3] on the thermal decomposition of NF_4AsF_6, smooth decomposition curves were obtained. The decomposition rates steadily decreased with increasing pressure in the reactor and the initial rates were restored upon evacuation of the reactor, indicating that the decomposition products suppress the decomposition rates. This was confirmed by studying the influence of different gases on the decomposition rates of NF_4BF_4 and of NF_4AsF_6. The addition of He did not noticeably influence the rates, whereas F_2 and NF_3 resulted in a weak suppression. However, the addition of BF_3 to NF_4BF_4 or of AsF_5 to NF_4AsF_6 resulted in strong rate suppressions (see Tables I and II).

For all decomposition experiments, plots of $P^{1/2}$ vs. time resulted in straight lines (see Figures 1 and 2) indicating a $^1/_2$ reaction order. The resulting global kinetic constants are given in Table III. Arrhenius plots of these constants resulted in straight lines (see Figure 3) and in the global decomposition activation energies $E_{NF_4BF_4} = 36.6 \pm 0.8$ kcal mol^{-1} and $E_{NF_4AsF_6} = 44.7 \pm 4.2$ kcal mol^{-1}, the latter value being in good agreement with that of 41 kcal mol^{-1} previously reported.[3]

The fact that the small mole fraction ranges of sample decomposition studied in these experiments were truly representative for the overall decomposition rates was established by following the decomposition of small samples at somewhat higher temperatures over almost the entire mole fraction (α) range. A typical decomposition curve obtained for NF_4BF_4 at 253 °C (see Figure 4) does not exhibit any sigmoid character, and the $P^{1/2}$ vs. time plot is linear for about the first 25% of α.

Although the results previously reported[3] for the decomposition of NF_4AsF_6 in Monel resulted in a linear $P^{1/2}$ vs. time plot, the reported rates were higher than ours by a factor of

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

	pressure change, mmHg										
				190.8 °C							
time, h	182.2 °C	188.9 °C	190.8 °C	He (500)[c]	F_2 (500)[c]	NF_3 (500)[c]	BF_3 (500)[c]	197.4 °C	204 °C	213.3 °C	215 °C
0	0	0	0	0	0	0	0	0	0	0	0
1	28	40	45	44	38	38	5	64	91	160	180
2	42	66	74	73	64	64	11	103	142	261	285
3	55	86	97	98	84	87	16	134	191	341	367
4	66.5	102	116	117	102	105	21	161	228	409	440
5	77	117	135	136	122	122	26	186	266	468	509
6	86.5	132	152	153	139	138	31	208	300	522	572
7	96	146	168	169	155	152	35	230	336	579	633
8	104	159	183		169	166	39	250		628	689
9	112	171	197		182	180	43	269		675	741
10	120.5	182	210		195	192	47	288		721	791
12	135	204	236		218	217	56	324		806	891
14	149	225	260		238	239	65	355		895	980
16	162	247	280		258	263	73	390			
18		267	300		277		82				
20					295		91				

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

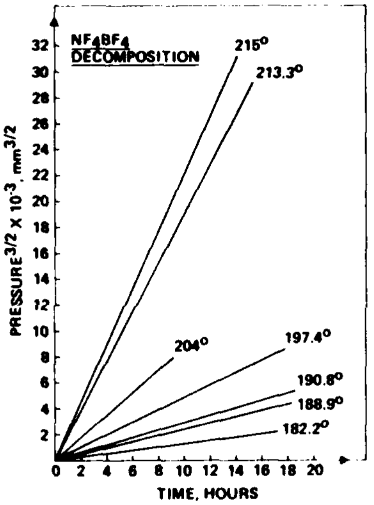


Figure 1. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 2.65 g of NF_4BF_4 at different temperatures (°C).

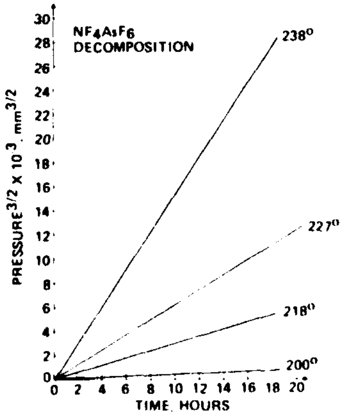


Figure 2. Total pressure ($P^{3/2}$) curves for the thermal decomposition of 1.86 g of NF_4AsF_6 at different temperatures (°C).

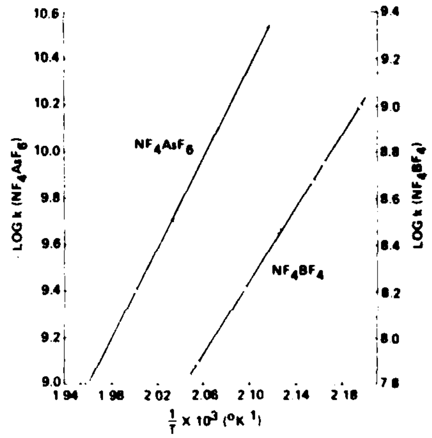


Figure 3. Arrhenius plots for NF_4BF_4 and NF_4AsF_6.

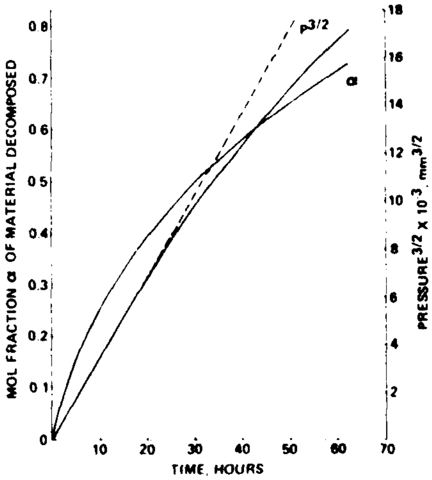


Figure 4. Decomposition curves for 75 mg of NF_4BF_4 at 253 °C. The solid lines are the observed data and the broken line represents the ideal straight line for the $P^{3/2}$ vs. t plot.

about 7. Unfortunately the sample size and the exact reactor volume used in ref 3 were not given. However, the estimated reactor volume (100-cm³ Monel cylinder + Wallace-Tierman FA 145-780 gage) and the reported method of the NF_4AsF_6 synthesis suggest that the previously used sample weight to reactor volume ratios were almost certainly significantly

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

	pressure change, mmHg								
					238 °C				
time, h	200 °C	218 °C	227 °C	238 °C	He (736)[c]	F_2 (197)[c]	NF_3 (567)[c]	AsF_5 (247)[c]	AsF_5 (724)[c]
0	0	0	0	0	0	0	0	0	0
1	2.6	9.9	16	27	28	25	21	5	4
2	4.0	16.0	25	44	45	42	34	8.5	7
3	5.2	20.8	33	58	59	55	44	12	9
4	6.2	25.3	40	71	73	68	54	16.5	11
5	7.2	29.4	46.5	83	85	79	63	20	12
6	8.3	32.2	52.5	93.5	95	90	72	24	13
7	9.2	36.6	57	103.5	105	101	81	28	14
8	10.0	40.0	62	113	115	110	90	32	15.5
9	10.8	43.0	67.5	123	124	120	98	35	17
10	11.6	46.0	72.5	132	133	129	106	38	18
12	13.2	51.4	82	149	151	145	122	45	21
14	14.7	56.6	91	165	166	161	140	52	23
16	16.1	61.4	99.5	181	181	176	160	59	25
18	17.4	66.2	107	197.5	196	190	176	65	
20			115.5	214	213	205	192	72	
25			134				226		
30							252		

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

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

NF_4BF_4		NF_4AsF_6	
temp, °C	10^9k	temp, °C	$10^{10}k$
182.2	0.96 ± 0.01	200	0.284 ± 0.002
188.9	1.74 ± 0.02	218	1.99 ± 0.03
190.8	2.11 ± 0.04	227	4.00 ± 0.02
197.4	3.39 ± 0.05	238	9.69 ± 0.10
204	6.08 ± 0.08	238 (He (736))	9.62 ± 0.08
213.3	12.79 ± 0.22		
215	14.68 ± 0.18	238 (F_2 (197))	9.22 ± 0.05
190.8 (He (500))	2.29 ± 0.03		
		238 (NF_3 (567))	8.60 ± 0.16
190.8 (F_2 (500))	1.86 ± 0.04		
		238 (AsF_5 (247))	1.94 ± 0.12
190.8 (NF_3 (500))	1.92 ± 0.02		
		238 (AsF_5 (724))	0.48 ± 0.08
190.8 (BF_3 (500))	0.314 ± 0.02		

[a] Units mol$^{-1/2}$ L$^{1/2}$ s^{-1}; error limits 2σ.

smaller than those of our experiments. This should have resulted in rates lower than ours. The only possible explanations for the previously reported[3] higher rates are absorption of the suppressing AsF_5 by Monel and/or inaccurate temperature control (heating of the cylinder in a tube furnace).

A large discrepancy of ~10^6 exists between the previously reported[3] results and our kinetic constants (see Table III). Most of this discrepancy (~10^3) appears to be computational.

Furthermore, the previously reported[3] data for the suppression by AsF_5 are inconsistent. Whereas the experimental data in Tables 6 and 7 of ref 3 show strong rate suppression by AsF_5, the kinetic constants given in Table 8 of ref 3 imply only mild suppression by AsF_5. The previously reported[3] strong rate suppression by NF_3 could not be confirmed by the present study. Our data (see Table III) show that NF_3 is only a weak suppressor, comparable to F_2, and that AsF_5 or BF_3 is the only strong suppressor. This is an important observation, because the alleged[3] strong suppression by NF_3 had caused us to propose in a previous publication[4] a mechanism for the formation of NF_4AsF_6 involving the incorrect (see below) steps $F + AsF_5 \rightarrow AsF_6$ and $AsF_6 + NF_3 \rightarrow NF_4^+AsF_6^-$.

Thermal Synthesis of NF_4SbF_6. Whereas the thermal synthesis of NF_4AsF_6 proceeds at too slow a rate for practical kinetic measurements, the rate of formation of NF_4SbF_6 is sufficiently fast. However, SbF_5 tends to form polyantimonates such as $Sb_2F_{11}^-$ or $Sb_3F_{16}^-$ [5,9,11] with SbF_5, which makes a kinetic evaluation of any experimental data very difficult. In view of the importance of the thermal synthesis of NF_4SbF_6 (this compound serves as a starting material for the metathetical syntheses of most other NF_4^+ salts[11-15]) and because of the complete absence of data on its formation rate, nine reactions were carried at 250 °C and at a pressure of

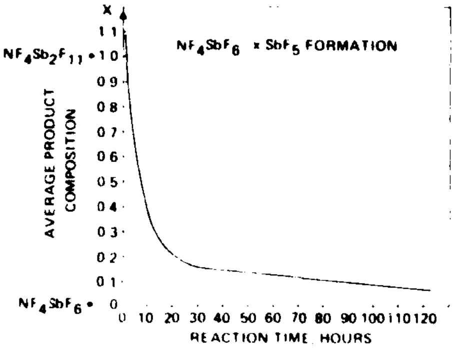


Figure 5. Formation rate of $NF_4SbF_6 \cdot xSbF_5$ from NF_3, F_2, and SbF_5 at 250 °C.

Table IV. Conversion of $NF_3 + F_2 + SbF_5$ to NF_4SbF_6 at 250 °C[a]

reacn time, h	prod compn, $NF_4^+SbF_6^- \cdot xSbF_5$, x	convrsn of SbF_5 to NF_4SbF_6, mol %
1	1.08	48.1
2	0.89	52.9
3	0.78	56.2
6	0.59	62.9
12	0.34	74.6
24	0.17	85.5
50	0.13	88.5
85	0.106	90.4
120	0.064	94.0

[a] Mole ratios of starting materials NF_3:F_2:SbF_5 = 2:2:1. Starting pressure 110 atm; residual pressure calculated for 100% conversion to NF_4SbF_6, 44 atm. The Monel cylinders (95-mL volume) were placed horizontally in the oven, preheated to 250 °C. One hour was required until the cylinders reached 250 °C. This point was taken as zero reaction time.

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

Reaction Mechanism. As pointed out in the Introduction, the formation and decomposition mechanism of NF_4^+ salts is of great interest because it appears to involve an unusual hypervalent species such as $\dot{N}F_4$, $\dot{N}F_5$, $\dot{A}sF_6$, or $\dot{B}F_4$. The following experimental data are known, and the correct mechanism must be compatible with all of these conditions.

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

(2) ESR measurements have shown[5-7] that the $\dot{N}F_3^+$ radical cation is a crucial intermediate in both the low-temperature UV photolytic synthesis and γ-irradiation-induced decomposition of NF_4^+ salts. Furthermore, the fluorination of $\dot{N}F_3^+$ to NF_4^+ appears to require F atoms.

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

(4) Filtered UV radiation[4,8] or heating[9] to 120 °C supply sufficient activation energy for the formation of NF_4^+ salts. This is a strong indication that the first step in the synthesis must be the dissociation of F_2 into two fluorine atoms ($D°(F_2) = 36.8$ kcal mol^{-1}).[16]

(5) The tendency to form NF_4^+ salts by thermal activation strongly decreases with decreasing Lewis acid strength, i.e., $SbF_5 > AsF_5 > PF_5 > BF_3$.[4,8,9] Since the corresponding NF_4^+ salts all possess sufficient thermal stability, a mechanism[3] involving the initial formation of NF_5, followed by its reaction with the corresponding Lewis acid, cannot explain the lack of thermal formation of salts such as NF_4PF_6 or NF_4BF_4. It can be explained, however, by the formation of intermediates of lower thermal stability such as $\dot{N}F_3^+$ salts. For SbF_6^- or AsF_6^-, these NF_3^+ salts were shown to still possess the lifetime required for their efficient conversion to NF_4^+ salts, whereas $NF_3^+BF_4^-$ was found to be of considerably lower thermal stability.[7]

(6) ESR flow-tube experiments[17] gave no indication of interaction between $\dot{F}$ atoms and AsF_5, as expected for the reaction step $AsF_5 + \dot{F} \rightarrow \dot{A}sF_6$.

(7) Infrared matrix isolation studies of the thermal decomposition products from either NF_4AsF_6[3] or $(NF_4)_2NiF_6$[18] gave no evidence for the formation of NF_5.

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

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

Scheme I

$$NF_3 + AsF_5 \rightleftarrows NF_2^+AsF_6^-$$

$$F_2 \rightleftarrows 2\dot{F}$$

$$NF_2^+AsF_6^- + \dot{F} \rightleftarrows \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

Scheme II

$$F_2 \rightleftarrows 2\dot{F}$$

$$\dot{F} + AsF_5 \rightleftarrows \dot{A}sF_6$$

$$\dot{A}sF_6 + NF_3 \rightleftarrows \dot{N}F_3^+AsF_6^-$$

$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

Scheme III

$$F_2 \rightleftarrows 2\dot{F}$$

$$\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$$

$$\dot{N}F_4 + \dot{F} \rightleftarrows NF_5$$

$$NF_5 + AsF_5 \rightleftarrows NF_4^+AsF_6^-$$

Scheme IV

$$F_2 \rightleftarrows 2\dot{F}$$

$$\dot{F} + NF_3 \rightleftarrows \dot{N}F_4$$

$$\dot{N}F_4 + AsF_5 \rightleftarrows \dot{N}F_3^+AsF_6^-$$

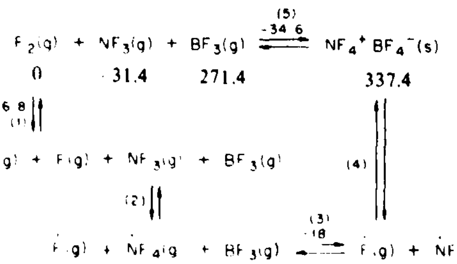
$$\dot{N}F_3^+AsF_6^- + \dot{F} \rightleftarrows NF_4^+AsF_6^-$$

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

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

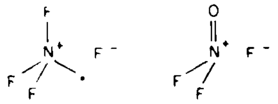
Born–Haber Cycle for NF_4BF_4. It was of interest to examine the thermodynamic soundness of Scheme IV. NF_4BF_4 was chosen for this purpose because it is the only NF_4^+ salt for which the heat of formation has experimentally been determined.[23] The Born–Haber cycle is shown in Scheme V, where all heats of formation or reaction are given in kcal mol^{-1}. From the known heats of reaction of NF_3,[24] BF_3,[24] and NF_4BF_4,[23] the heat of reaction 5 is known to be −34.6 kcal mol^{-1}. Furthermore, the heat of dissociation of F_2, reaction 1, is known[16] to be 36.8 kcal mol^{-1}. A reasonably close estimate for step 3, the heat of formation of solid $\dot{N}F_3^+BF_4^-$ from $\dot{N}F_4$ and BF_3, can be made from the known heat of dissociation of $NF_2O^+BF_4^-$. Since NF_3O and $\dot{N}F_4$ are expected to be quite similar (see below), it is reasonable to assume that step 3 has a heat of reaction similar to that of $NF_3O + BF_3 \rightarrow NF_2O^+BF_4^-$, i.e., −18 kcal mol^{-1}. Consequently, the sum of steps 2 and 4 should be about −53 kcal mol^{-1}. Whereas the heat of reaction of step 2 is difficult to estimate, the heat of

Scheme V

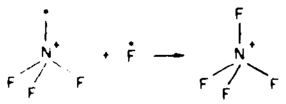


reaction of (4) is easier to estimate because it represents the dissociation energy of the fourth N–F bond in NF_4^+. In NF_3, the heat of dissociation of the third N–F bond is 58 kcal mol^{-1},[1,26,27] and it seems reasonable to assume that the dissociation energy of the fourth N–F bond in NF_4^+ is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

The proposition that steps 2 and 4 should so markedly differ in their heats of reaction, although both involve the formation of one additional N–F bond, is not unreasonable. In step 2 a hypervalent $\dot{N}F_4$ radical is formed which would possess nine valence electrons on the central nitrogen atom. By analogy with the known NF_3O molecule,[28] this energetically unfavorable structure can be circumvented by assuming strong contributions from resonance structures such as



These resonance structures result in a strong polarization, i.e., weakening of all N–F bonds, when compared to those in NF_3. This is demonstrated by the bond lengths of 1.371 and 1.43 Å observed for NF_3[29] and NF_3O,[28] respectively. Thus the energy gained by the formation of a fourth N–F bond in the NF_4 radical is largely compensated by a significant weakening of the remaining N–F bonds. In contrast, the reaction of the $\dot{N}F_3^+$ radical cation with a fluorine atom, i.e.



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

An alternate, attractively simple, and preferable explanation for the above bond weakening effect in NF_4 can be offered if one assumes that, due to the large energy difference between the 2p and 3s nitrogen orbitals, the ninth nitrogen valence electron occupies an antibonding orbital. Experimental evidence for such a model has recently been reported[30] by Nishikida and Williams for the $\dot{N}F_3O^-$ radical anion which is isoelectronic with $\dot{N}F_4$. On the basis of the observed ESR data, $\dot{N}F_3O^-$ possesses a spin density of 0.27 in the nitrogen 2s orbital suggesting that the unpaired electron indeed occupies an antibonding orbital.

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

It should be pointed out that the global activation energy (36.6 ± 0.8 kcal mol^{-1}) of the decomposition of NF_4BF_4 to $NF_3 + F_2 + BF_3$ and the heat of formation of NF_4BF_4 from $NF_3 + F_2 + BF_3$ (-34.6 kcal mol^{-1}) are the same within experimental error. It is difficult to say whether this is coincidental or if it implies that the corresponding forward reactions, i.e., steps 2–4 of the Born–Haber cycle, occur without activation energy. Examples of the latter case are known for the endothermic dissociation of solids such as carbonates.[31] If for NF_4^+ salts the global decomposition activation energies should indeed be identical with the heats of formation from NF_3, F_2, and the corresponding Lewis acid, a value of about -372 kcal mol^{-1} can be predicted for $\Delta H_f^\circ{}_{NF_4AsF_6}$ on the basis of $E_{NF_4AsF_6} = 45$ kcal mol^{-1} and $\Delta H_f^\circ{}_{AsF_5} = 29.55$ kcal mol^{-1}.

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

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APPENDIX B

SYNTHESIS AND PROPERTIES OF $NF_4^+ClO_4^-$ AND $NF_4^+HF_2^- \cdot nHF$ AND SOME REACTION CHEMISTRY OF NF_4^+ SALTS

Karl O. Christe,* William W. Wilson and Richard D. Wilson

Received . . . . .

Abstract

The possibility of synthesizing $NF_4^+XO_4^-$(X= Cl, Br, I) salts by metathesis between NF_4SbF_6 and $CsXO_4$ in anhydrous HF solution at -78° was studied. Of these NF_4XO_4 salts, NF_4ClO_4 was isolated and characterized by vibrational and ^{19}F NMR spectroscopy. It is an unstable white solid decomposing at 25° to give NF_3 and $FOClO_3$ in high yield. The NF_4BrO_4 salt is of marginal stability in HF solution and decomposes to NF_3, O_2 and $FBrO_2$. Attempts to isolate NF_4BrO_4 as a solid resulted in explosions. The NF_4IO_4 salt could not be prepared due to the facile fluorination of IO_4^- to $IF_4O_2^-$ by either HF or BrF_5. Attempts to prepare $NF_4^+XF_4O^-$ (X = Cl, Br) salts by metathesis between NF_4SbF_6 and $CsXF_4O$ in BrF_5 solution at 25° were unsuccessful; with BrF_4O^-, fluoride abstraction occurred resulting in the formation of NF_3, F_2, and BrF_3O, whereas $CsClF_4O$ underwent a displacement reaction with BrF_5 to give $CsBrF_6$ and ClF_3O. The metathetical synthesis of NF_4NO_3 could not be studied in HF due to the reaction of NO_3^- with HF to give NO_2^+, H_2O, and HF_2^-. The metathesis between NF_4SbF_6 and CsF in HF at -78° did not produce $NF_4^+F^-$, but an unstable white solid of the composition $NF_4^+HF_2^- \cdot nHF$. The composition, thermal stability, spectroscopic properties and decomposition products of this solid were studied.

The $NF_4^+HF_2^-$ salt is stable in HF solution at 25° and the synthetic usefulness of these solutions for the synthesis of other NF_4^+ salts is briefly discussed. Attempts to prepare NCl_4^+ and NCl_2O^+ salts by F-Cl exchange between BCl_3 and NF_4^+ and NF_2O^+ were unsuccessful.

Introduction

The first reports on the successful syntheses of NF_4^+ salts were published [1,2] in 1966. Since then, numerous NF_4^+ salts have been prepared and characterized which contain as counterions BF_4^- [3-10], XF_5^- (X = Ge, Ti, Sn), [10-12] XF_6^- (X = P, As, Sb, Bi)[1,2,7,8,10,13,14-18], or XF_6^{--} (X = Ge, Sn, Ti, Ni).[10-12,19] All these anions are derived from strong perfluorinated Lewis acids. It was therefore interesting to investigate the possible synthesis of salts derived from either the simplest anion, F^-, or oxygen containing anions. Although in 1968 Tolberg and coworkers found evidence for the existence of unstable NF_4^+ salts probably containing the HF_2^- or the ClO_4^- anion, [4] these salts were not well characterized and no data were published. In this paper, we describe the synthesis and characterization of $NF_4^+HF_2^- \cdot nHF$ and $NF_4^+ClO_4^-$ and the attempted syntheses of $NF_4^+BrO_4^-$, $NF_4^+BrF_4O^-$, $NF_4^+ClF_4O^-$, and $NF_4^+NO_3^-$.[20] Since the existence of a stable $NOCl_2^+SbCl_6^-$ salt has recently been reported, it appeared interesting to study the possiblity of exchanging fluorine for chlorine in either NF_4^+ or NF_2O^+ salts using BCl_3.

Experimental

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[7] NF_2OSbF_6,[21] $CsClF_4O$,[22] and $CsBrF_4O$.[23] The BrF_5 (Matheson) was treated with 35 atm of F_2 at 200°C for 24 hours and then purified by fractional condensation through traps kept at -64° and -95°, with the material retained in the latter being used. Hydrogen fluoride (Matheson) was dried by treatment with 20 atm of F_2 at room temperature, followed by storage over BiF_5 to remove the last traces of H_2O.[18] The CsF (American Potash) was fused in a platinum crucible and ground in the dry box. The $CsClO_4$ (ROC/RIC) was used as received. The $CsNO_3$ was prepared from aqueous Cs_2CO_3 and HNO_3 using a pH-electrode for endpoint detection. It was purified by recrystallization from H_2O and dried in an oven at 100°C for 24 hours. The BCl_3 (Matheson) was treated with Hg and purified by fractional condensation prior to use.

Apparatus. Volatile materials used in this work were handled either in a Monel-Teflon FEP, a stainless steel-Teflon FEP or a Teflon PFA vacuum line. The latter was constructed exclusively from injection molded PFA fittings and valves (Fluoroware, Inc.). The anhydrous HF was preferentially handled in the PFA or Monel line, whereas the halogen fluorides were handled mainly in a steel line. All lines were well passivated with ClF_3 and, if HF was to be used, with HF. Nonvolatile materials were handled in the dry nitrogen atmosphere of a glove box. Metathetical reactions were carried out either in HF or BrF_5 solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter (see Figure 1 of ref. 12). For NMR or low temperature vibrational spectra, the second FEP U-trap, which served as a receiver, was replaced by either a 4mm Teflon FEP or thin-walled Kel-F tube.

Infrared spectra were recorded in the range 4000-200cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Room temperature spectra of solids were obtained using dry powders pressed between AgCl disks. Low temperature spectra were obtained by placing the chilled powder between cold AgCl disks and striking the disks with a hammer. The resulting AgCl sandwich was held in a liquid N_2 cooled sample holder of a low-temperature infrared cell[24] with external CsI windows. Spectra of gases were obtained using a Teflon cell of 5cm pathlength equipped with AgCl windows.

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[25] for the elimination of plasma lines. Sealed quartz, Teflon FEP or Kel-F Tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded using a previously described[26] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[25] Lines due to the Teflon or Kel-F sample tubes were suppressed by the use of a metal mask.

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

Preparation and Properties of $NF_4^+ClO_4^-$. The compatibility of the ClO_4^- anion with HF was established by dissolving $CsClO_4$ in HF and recording the Raman spectra of the solution and of the solid residue recovered after removal of the solvent. Both spectra showed exclusively the bands characteristic for ClO_4^-. In a typical preparation of NF_4ClO_4, NF_4SbF_6 (10.03 mmol) and $CsClO_4$ (10.02 mmol) were placed into the 3/4" o.d. Teflon FEP bottom U-trap of the metathesis apparatus. Anhydrous HF (8.56 g) was added at -196°. The mixture was kept at -78° for 15 hours and then for 2 hours at -45° with agitation. The entire metathesis apparatus was cooled to -78° and inverted to separate the $CsSbF_6$ precipitate from the $NF_4^+ClO_4^-$ solution. Dry N_2 (2 atm) was used to pressurize the solution during this filtration step. The HF solvent was pumped off at -78° and -45° for 7 days. The resulting white solid residue was allowed to warm to ambient temperature and the gaseous decomposition products were separated in a dynamic vacuum by fractional condensation through a series of traps kept at -112°, -186° and -210°. The -210° trap contained 8.0 mmol of NF_3 and the -186° trap had 8.0 mmol of $FOClO_3$ which were identified by infrared, Raman and ^{19}F NMR spectroscopy.[27] The filter cake (3.60 g, weight calcd for 10 mmol of $CsSbF_6$ = 3.69 g) was shown by infrared and Raman spectroscopy to be $CsSbF_6$ and did not contain any detectable impurities. A small amount (80 mg) of a white stable solid residue was left behind after the thermal decomposition of the NF_4ClO_4 which, based on its vibrational spectra, consisted of a mixture of NF_4SbF_6 and $CsSbF_6$. The 20% of NF_4ClO_4 unaccounted for by the above material balance corresponds to the amount of product in the mother liquor typically retained by the $CsSbF_6$ filter cake in similar metathetical reactions. It is decomposed and pumped off during the HF removal step in which the filter cake is allowed to warm to ambient temperature. Based on the above material balance, the NF_4ClO_4 prepared in this manner had a purity of 95 weight percent.

For the spectroscopic identification of NF_4ClO_4 and the determination of its thermal stability, reactions were carried out on a 1-2 mmol scale using 4 mm o.d. Teflon FEP NMR or thin walled Kel-F tubes as receivers. The ^{19}F NMR spectrum of an $NF_4^+ClO_4^-$ solution in anhydrous HF at -40° showed the signals characteristic of NF_4^+ (triplet of equal intensity at ϕ -214.8 with J_{NF} = 229.3 Hz and a linewidth of less than 3 Hz)[10], $FOClO_3$ (singlet at ϕ -219.4)[27], and NF_3 (broad triplet of equal intensity at ϕ -142 with J_{NF} = 150 Hz).[28,29] When the solution was kept at 20° and continuously monitored by NMR, the signal due to NF_4^+ was found to steadily decrease and those due to $FOClO_3$ and NF_3 to correspondingly increase in relative intensity. A solution containing 40 mol% or NF_4^+ and 60 mol% $FOClO_3$ was found to change within 16 hours at 20° to 17 mol% of NF_4^+ and 83 mol% of $FOClO_3$. The decomposition of NF_4ClO_4 in HF solution at ambient temperature was also followed by Raman spectroscopy which showed the bands due to $FOClO_3$[27] to grow with time at the expense of those due to NF_4^+ and ClO_4^-. Due to its low boiling point and low solubility in HF, NF_3 could not be detected in the HF solution by Raman spectroscopy.

The thermal stability of solid $NF_4^+ClO_4^-$ was studied by pumping on a sample at a given temperature for one hour and measuring the amount of NF_3 and $FOClO_3$ evolved. Whereas at -13° NF_4ClO_4 essentially is still stable, slow decomposition was observed at 0° which became rather rapid at 25° giving the sample the appearance of a fluidized sand bath. Caution! Since the thermal decomposition of NF_4ClO_4 yields the very shocksensitive[30] $FOClO_3$ in high yield, appropriate safety precautions should be taken when working with this compound.

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

Reaction of $CsNO_3$ with HF. Cesium nitrate was dissolved in anhydrous HF. The Raman spectrum of the solution did not show the bands characteristic of NO_3^-, but only one band at 1411 cm^{-1} which is characteristic [34] for NO_2^+. The solid residue obtained by pumping the solution to dryness was shown by Raman spectroscopy to consist again of $CsNO_3$.

Reaction of NF_4SbF_6 with $CsBrF_4O$ in BrF_5. A mixture of NF_4SbF_6 (0.536 mmol) and $CsBrF_4O$ (0.449 mmol) was placed in the drybox into a 3/4" o.d. Teflon FEP ampule and BrF_5 (4 ml liquid) was added at -196° using the vacuum line. The contents of the ampule were warmed to 20° and stirred with a magnetic stirring bar for 2.5 hours. The ampule was cooled to -196° and the noncondensible material (0.42 mmol of F_2) was distilled off. The material volatile at -95° was distilled off and consisted of 0.48 mmol of NF_3. The material volatile at 20° was separated by fractional condensation through a series of traps kept at -64°, -78° and -196°. The -64° trap contained BrF_3O (0.43 mmol), in addition to some BrF_5. The two colder traps contained the bulk of the BrF_5. The solid nonvolatile reaction product (205 mg, weight calcd for 0.449 mmol $CsSbF_6$ and 0.087 mmol NF_4SbF_6 = 194 mg) was shown by vibrational spectroscopy to consist mainly of $CsSbF_6$ containing some NF_4SbF_6.

Reaction of $CsClF_4O$ with BrF_5. In a sapphire reactor, $CsClF_4O$ (1.234 mmol) and BrF_5 (15 mmol) were combined at -196°. The mixture was kept at 20° for 12 hours. The volatile products were distilled off and consisted of BrF_5 and ClF_3O(1.2 mmol). The solid residue (405 mg, weight calcd for 1.234 mmol of $CsBrF_6$ = 403 mg) was shown by vibrational spectroscopy to consist of $CsBrF_6$.[35]

Preparation and Properties of $NF_4^+HF_2^- \cdot nHF$. In a typical experiment, NF_4SbF_6 and CsF (10.0 mmol each) were placed into the metathesis apparatus and HF (10 ml) was added at -196°. The mixture was stirred at 20° for 2 hours, then cooled to -78° and filtered. Most of the HF solvent was removed by pumping at -78° for 36 hours, -64° for 12 hours, -57° for 6 hours and -45° for 6 hours. At -45° the residue was still liquid, but when cooled to -78° changed its appearance to that of a wet solid. The pumped off material consisted of HF. The sample was allowed to warm to ambient temperature and the evolved volatile material was pumped off through traps kept at -126°and -210°. The amounts and mole ratios of HF (-126° trap) and NF_3 (-210° trap) were periodically measured while cooling the sample back to -45°. Several hours of warming to ambient temperature and to 40° were required to achieve complete decomposition of the salt. A total of 8.32 mmol of NF_3 and 19.63 mmol of HF were collected with the HF:NF_3 mole ratio ranging from 10.1 at the start to 1.54 towards the end of the decomposition. A small amount (80 mg) of a stable white solid residue was left behind after completion of the decomposition which consisted mainly of NF_4SbF_6 and some $CsSbF_6$. The filter cake (3.5 g, weight calcd for 10.0 mmol of $CsSbF_6$ = 3.687 g) consisted of $CsSbF_6$. The 15% of NF_4^+ value unaccounted for by the above material balance is in line with the amount of material in the mother liquor generally retained by the $CsSbF_6$ filter cake in similar reactions (see NF_4ClO_4 preparation.)

Based on the above material balance, the purity of $NF_4HF_2 \cdot nHF$ obtained in this manner is about 97 mol% with the $CsSbF_6$ and NF_4SbF_6 impurities being caused by the slight solubility of $CsSbF_6$ in HF and a small excess of one reagent. During the above described ambient-temperature decomposition of $NF_4HF_2 \cdot nHF$, the originally liquid sample first turned milky and pasty, then after recooling it to -45° had the appearance of a white dry solid which melted very slowly when warmed again to 20°. On melting it started to bubble and foam.

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

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

Reactions of NF_4SbF_6 and NF_2OSbF_6 with BCl_3. A sample of NF_4SbF_6 (1.85 mmol) was treated in a Teflon FEP ampule with a tenfold excess of BCl_3 for three hours at 20°. The volatile products were separated by fractional condensation and shown to consist of NF_3 and mixed BF_xCl_{3-x} type compounds. A small amount of solid residue (60 mg) was identified by vibrational spectroscopy as $NO^+SbCl_6^-$.

A sample of NF_2OSbF_6 was similarly treated with BCl_3. The volatile products consisted again of mixed BF_xCl_{3-x} type compounds, but $NO^+SbF_6^-$ was formed in almost quantitative yield as a nonvolatile residue.

Results and Discussion

The general usefulness of the metathetical reaction

$$NF_4^+SbF_6^- + Cs^+X^- \xrightarrow[-78^o]{HF} Cs^+SbF_6^-\downarrow + NF_4^+X^-$$

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

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

$$NF_4SbF_6 + CsClO_4 \xrightarrow[-78^o]{HF} CsSbF_6\downarrow + NF_4ClO_4$$

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

$$NF_4ClO_4 \longrightarrow NF_3 + FOClO_3$$

In HF solution the rate of decomposition is slower, but follows the same path. The essentially quantitative formation of $FOClO_3$ is noteworthy and represents a new and convenient synthesis of $FOClO_3$.

Based on the observed material balance, the yield of NF_4ClO_4 is high and the only significant loss of material is due to the amount of mother liquor retained by the $CsSbF_6$ filter cake. The purity of the NF_4ClO_4 product is also high and the impurities present are $CsSbF_6$, in an amount corresponding to its solubility in HF at -78°, and any slight excess of starting material used in the reaction.

The ionic composition of NF_4ClO_4, both in HF solution and the solid state, was established by vibrational and ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum of $NF_4^+ClO_4^-$ in HF solution showed the signal characteristic[13,14] for tetrahedral NF_4^+. The Raman spectra of this solution confirmed the presence of tetrahedral NF_4^+ (1170 w, br, 855 vs, p, 612 m, 448 mw)[10] and ClO_4^- (940s, p, 620w, 460w)[34]. The infrared and Raman spectra of solid $NF_4^+ClO_4^-$ are given in Figure 1. The observed frequencies and their assignments in point group T_d are summarized in Table 1. As expected for a solid, splittings of bands into their degenerate components and crystal splittings are observed. In addition $\nu_1(A_1)$ and $\nu_2(E)$ which ideally are infrared inactive were some observed in the infrared spectrum as extremely weak bands. The pronounced Christiansen effect[36] observed for the infrared spectrum is due to the experimental difficulties in obtaining good pressing of AgCl windows at low temperature. The pressing was achieved by striking the sample sandwiched between the AgCl plates with a hammer. The sample did not detonate under these conditions indicating that NF_4ClO_4 is considerably less sensitive than its decomposition product $FOClO_3$.[30]

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

$$NF_4SbF_6 + CsBrO_4 \xrightarrow[-78^\circ]{HF} CsSbF_6\downarrow + NF_4BrO_4$$

to be carried out.

The presence of tetrahedral NF_4^+ [10,13,14] and BrO_4^- [31] in the resulting HF solution was demonstrated by ^{19}F NMR and Raman spectroscopy. By analogy with NF_4ClO_4, slow decomposition of the NF_4BrO_4 solution occurred at room temperature. However, instead of the yet unknown $FOBrO_3$, only its expected[37] decomposition products, $FBrO_2$ and O_2, were obtained in addition to NF_3.

$$NF_4BrO_4 \longrightarrow NF_3 + [FOBrO_3]$$

$$[FOBrO_3] \longrightarrow FBrO_2 + O_2$$

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

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

$$IO_4^- + 4HF \longrightarrow IF_4O_2^- \text{ (cis and trans isomer)} + 2H_2O$$

$$IF_4O_2^- + 2HF \longrightarrow HF_2^- + HOIF_4O$$

$$IO_4^- + 2BrF_5 \longrightarrow IF_4O_2^- \text{ (trans isomer mainly)} + 2BrF_3O$$

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

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

$$CsBrF_4O + HF \longrightarrow CsHF_2 + BrF_3O$$

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

$$CsBrF_4O + NF_4SbF_6 \xrightarrow[25^o]{BrF_5} CsSbF_6 + BrF_3O + F_2 + NF_3$$

The formation of these products indicates that the salt $NF_4^+BrF_4O^-$ is not stable under these conditions and that, contrary to the $NF_4^+ClO_4^-$ and $NF_4^+IF_4O_2^-$ reactions, fluoride abstraction from BrF_4O^- is preferred over the fluorination of BrF_4O^- to either BrF_4OF or BrF_5O. A similar fluoride abstraction has previously been observed[4] for BrF_6^-

$$NF_4SbF_6 + CsBrF_6 \xrightarrow[25^o]{BrF_5} CsSbF_6 + NF_3 + F_2 + BrF_5$$

but not for BrF_4^- which was fluorinated[4] to BrF_5

$$NF_4SbF_6 + KBrF_4 \xrightarrow[25^o]{BrF_5} KSbF_6 + NF_3 + BrF_5$$

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

$$CsClF_4O + BrF_5 \longrightarrow CsBrF_6 + ClF_3O$$

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

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

These results imply an equilibrium, such as

$$NO_3^- + 4HF \overset{HF}{\rightleftharpoons} NO_2^+ + H_2O + 2\ HF_2^-$$

which has previously been postulated[40] for these solutions. In view of the absence of NO_3^- in HF solution, no metathetical reactions between $CsNO_3$ and NF_4SbF_6 were attempted.

Preparation and Properties of $NF_4HF_2 \cdot nHF$. The $NF_4^+F^-$ salt, which has an active fluorine content in excess of 90 weight percent, would be of extreme interest. However, previous attempts to prepare a stable salt from NF_3 and F_2 at -196° by either bremsstrahlung[3] or uv-photolysis[10] were unsuccessful indicating that the salt is unstable with regard to its decomposition to NF_3 and F_2. Since most of the metathetical reactions for the production of NF_4^+ salts are carried out in anhydrous HF, which is an acid, it was of interest to define the nature and stability of a possible $NF_4^+HF_2^-$ salt. A previous unpublished study[4] of the LiF - NF_4SbF_6 system in HF at ambient temperature had provided evidence that after removal of the precipitated $LiSbF_6$ a stable solution was obtained containing the NF_4^+ cation. All attempts to isolate a salt at temperatures of -44° and above from this solution resulted in decomposition to NF_3, F_2 and HF. Removal of the solvent at -78° resulted in a wet solid which was not characterized.

Since our previous studies[18] had shown that a low-temperature metathesis using a cesium salt is superior to a lithium salt based process, the following system was studied

$$NF_4SbF_6 + CsHF_2 \xrightarrow[-78^\circ]{HF} CsSbF_6\downarrow + NF_4HF_2$$

Based on the observed material balance, the soluble product consisted of about 97 mole% NF_4HF_2 with the remainder being $CsSbF_6$ and excess of either starting material. In agreement with the previous observation[4], NF_4HF_2 is stable in HF solution at ambient temperature and shows in the ^{19}F NMR spectrum the characteristic[13,14] NF_4^+ signal. The presence of the NF_4^+ cation and the virtual absence of anions other than those due to solvated F^- was also demonstrated by Raman spectroscopy of solutions at different concentrations. As shown by trace A of Figure 2, these solutions exhibited only the four bands characteristic[10] of tetrahedral NF_4^+. The difficulty in observing bands due to solvated HF_2^- is not surprising in view of HF being a weak scatterer and the expected broadness of the lines of HF_2^- undergoing rapid exchange with the solvent HF.

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

$$NF_4HF_2 \cdot nHF \longrightarrow NF_3 + F_2 + (n+1)HF$$

It was found that the mole ratio of NF_3:HF was about 10.1 at the beginning and 1.54 towards the end of this decomposition. These results demonstrate that complete removal of solvated HF from NF_4HF_2 is extremely difficult and is accompanied by decomposition of most of the NF_4^+ salt itself. The presence of a solvated $HF_2^- \cdot nHF$ anion was also demonstrated by Raman spectroscopy (see trace B of Figure 2) which shows the presence of broad complex bands in the vicinity of the symmetric (600 cm^{-1}) and the antisymmetric (1455 cm^{-1}) stretching mode[34] of HF_2^-. Upon removal of most of the solvated HF, these bands lost intensity, resulting in a spectrum consisting exclusively of the NF_4^+ bands (see trace C of Figure 2).

It is also noteworthy that with decreasing HF content, the melting point of $NF_4^+HF_2^- \cdot nHF$ increases and approaches room temperature for n approaching zero. The decomposition of $NF_4HF_2 \cdot nHF$ becomes rather slow for decreasing n, particularly in the presence of other stable fluorides. It appears that such fluorides can assume the function of stabilizing the HF_2^- anion. A typical example for such a fluoride is AlF_3 or AlF_4^-.[27] A careful analysis of such systems is therefore necessary to avoid the interpretation of such $(NF_4HF_2)_nMF_x$ in terms of $(NF_4)_nMF_{x+n}$ salts.

The possibility of preparing stable HF solutions of NF_4HF_2 renders them a very useful intermediate. By addition of a stronger or less volatile Lewis acid, the HF_2^- anion can be displaced and NF_4HF_2 can be converted into other NF_4^+ salts. This was first demonstrated[4] by reacting NF_4HF_2 solutions with BF_3 to form NF_4BF_4, and has recently been extended[41] to the formation of other salts, which due to the low solubility of their cesium salts are not amenable to direct metathetical reactions.

Halogen Exchange in NF_4^+ and NF_2O^+. In view of the existence of a stable $NCl_2O^+SbCl_6^-$ salt[20], it was of interest to study the possibility of halogen exchange in either NF_4^+ or NF_2O^+ with BCl_3. For both salts, the observation of mixed BF_xCl_{3-x} products indicated that halogen exchange took place. For NF_4^+ the main product was gaseous NF_3 suggesting that the likely NF_3Cl^+ intermediate might be unstable towards decomposition under the given conditions. For $NF_2O^+SbF_6^-$, the main product was $NO^+SbF_6^-$ which could arise again from breaking of the rather weak N-Cl bonds in an NCl_2O^+ intermediate.

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Diagram Captions

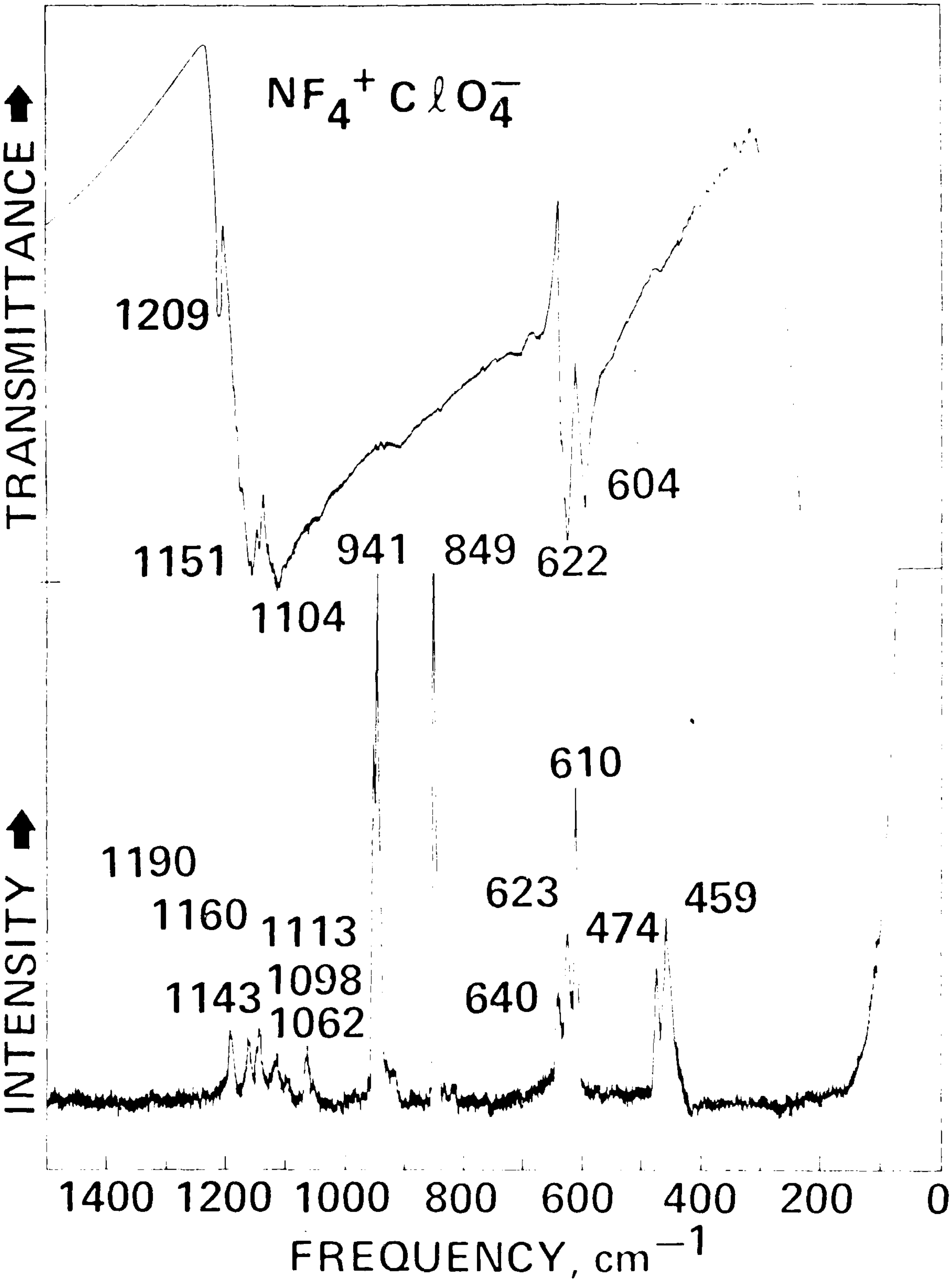
Figure 1. Low-temperature vibrational spectra of solid $NF_4^+ClO_4^-$. The infrared spectrum was recorded as a dry powder between AgCl disks at -196°. The broken line indicates absorption due to the AgCl window material. The Raman spectrum was recorded at -110° with a spectral slit width of 6 cm^{-1}.

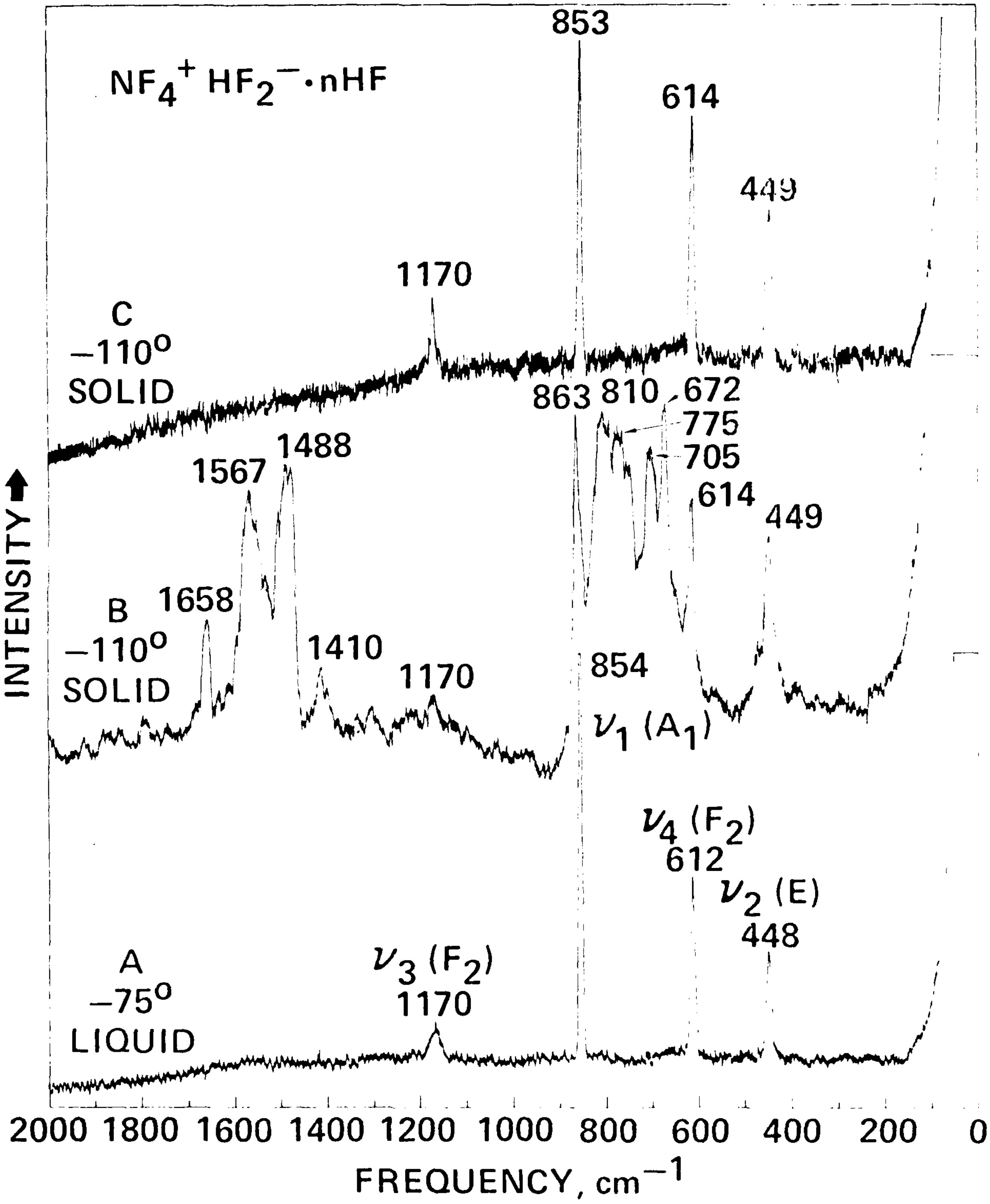
Figure 2. Raman spectra of liquid and solid $NF_4^+HF_2^-\cdot nHF$ in a Kel-F capillary. Trace A, spectrum of a concentrated HF solution at -75°. The given assignments are for tetrahedral NF_4^+. Trace B, sample of trace A cooled to -110°. In addition to the NF_4^+ bands, the spectrum shows bands attributed to $HF_2^-\cdot nHF$. Trace C, spectrum of the solid at -110° containing only a small excess of HF. The sample of trace B was used after pumping off most of the HF and decomposing most of the sample at about -20°. All spectra were recorded with a spectral slit width of 8 cm^{-1}.

TABLE I. VIBRATIONAL SPECTRA OF SOLID NF_4ClO_4

Obsd freq, cm^{-1}, and rel intens[a]		Assignment (point group)	
IR	Raman	$NF_4^+(T_d)$	$ClO_4^-(T_d)$
1209 w		$2\nu_4(A_1+E+F_2)$	
	1190 (1.3)		
1151 s	1160 (1)	$\nu_3(F_2)$	
	1143 (1.2)		
1104 vs	1113 (0.8)		
	1098 (0.3)		$\nu_3(F_2)$
	1062 (1)		
	950 (6)		$\nu_1(A_1)$
	941 (10)		
	849 (10)	$\nu_1(A_1)$	
	640 (2)		
622 s	623 (3)		$\nu_4(F_2)$
604 s	610 (6)	$\nu_4(F_2)$	
	474 (2.5)		$\nu_2(E)$
	459 (3.5)	$\nu_2(E)$	

(a) Uncorrected Raman intensities


$NF_4^+ Cl O_4^-$
TRANSMITTANCE
INTENSITY
1209
1151
1104
941
849
622
604
610
1190
1160
1113
1098
1143
1062
623
640
474
459
1400
1200
1000
800
600
400
200
0
FREQUENCY, cm^{-1}


NF$_4^+$ HF$_2^-$·nHF
853
614
449
1170
C
−110°
SOLID
863
810
672
775
705
1567
1488
614
449
B
1658
−110°
SOLID
1410
1170
854
ν_1 (A$_1$)
ν_4 (F$_2$)
612
ν_2 (E)
448
A
−75°
LIQUID
ν_3 (F$_2$)
1170
INTENSITY
2000
1800
1600
1400
1200
1000
800
600
400
200
0
FREQUENCY, cm^{-1}

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

APPENDIX C

SYNTHESIS AND PROPERTIES OF $NF_4^+SO_3F^-$

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

Received.......

Abstract

The novel salt $NF_4^+SO_3F^-$ was prepared by metathesis between NF_4SbF_6 and $CsSO_3F$ in anhydrous HF solution at -78°. In HF solution, it is stable at room temperature. Removal of the solvent produces a white solid which is stable at 0°, but slowly decomposes at +10° to produce $FOSO_2F$ and NF_3 in high yield. The ionic nature of the compound, both in the solid state and in HF solution, was established by Raman and ^{19}F NMR spectroscopy. Cesium sulfate was found to react with anhydrous HF producing $CsSO_3F$ as the major product. Similarly, $CsPO_2F_2$, the Raman spectrum of which is reported, was found to react with HF to give $CsPF_6$ in quantitative yield.

Introduction

Among oxidizers, the NF_4^+ cation is unique. In spite of being one of the most powerful oxidizers known, it possesses high kinetic stability,[1] thereby permitting its combination with a surprisingly large number of anions to form stable or metastable salts. Anions capable of NF_4^+ salt formation include BF_4^- [2-9] XF_5^- (X=Ge,Ti,Sn)[9-11] XF_6^- (X=P,As,Sb,Bi) [6,7,9,12-19] XF_6^{2-} (X=Ge,Sn,Ti, Ni,Mn),[9-11,20,21] ClO_4^-,[22] HF_2^- [22] and several perfluoro polyanions. [6,10,11,19] Recent studies have shown that NF_4^+ salts of oxygen containing anions are of particular interest because hypofluorites, such as OIF_4OF[23] or $FOClO_3$,[22] can be formed during their thermal decomposition.

In this paper we would like to report results on the possible synthesis of salts derived from sulfur or phosphorous oxyfluorides. We are aware of only one unpublished study[3] in this area, in which the evolution of some $FOSO_2F$ from either an NF_4SbF_6-$HOSO_2F$ solution at -78° or a supposedly dry mixture of NF_4SbF_6 and $LiSO_3F$ at room temperature was interpreted[3] as evidence that NF_4SO_3F, if it exists, is unstable even at -78°. In view of the relative stability of NF_4ClO_4[22] and the similarity between ClO_4^- and isoelectronic SO_3F^- and $PO_2F_2^-$, the isolation of NF_4SO_3F and $NF_4PO_2F_2$ seemed possible.

Experimental

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.[22] Literature methods were used for the synthesis of NF_4SbF_6,[6] $ClOSO_2F$[24] and $HOPOF_2$[25]. The $CsPO_2F_2$ was prepared by the addition of Cs_2CO_3 to a 10% excess of $HOPOF_2$ frozen at -196°. The mixture was allowed to react at room temperature with agitation, and the volatile products and excess $HOPOF_2$ were pumped off at 40° for 12. hours. Based on the observed material balance and vibrational spectra, the solid residue consisted of $CsPO_2F_2$ of high purity. The Cs_2SO_4 was obtained from aqueous Cs_2CO_3 and H_2SO_4 using a pH-electrode for endpoint (pH of 3.86) detection. The solution was taken to dryness and dried in an oven at 100° for 24 hours. The $CsSO_3F$ was prepared by allowing CsCl (10.3 mmol) and $ClOSO_2F$ (15.5 mmol) to react in a 10 ml stainless steel cylinder at ambient temperature for several days. All volatile material was removed from the cylinder, and the solid product was pumped on overnight. The weight of the solid (2.43 g vs. 2.40 g theoretical) together with its infrared and Raman spectra confirmed the completeness of the reaction and the identity of the product.

Preparation and Properties of $NF_4^+SO_3F^-$. The compatibility of the SO_3F^- anion with HF was established by dissolving $CsSO_3F$ in dry HF and recording the Raman spectra of the starting material, the HF solution, and of the solid residue recovered after removal of the solvent. All spectra showed the bands characteristic[26] for SO_3F^-. The ^{19}F NMR spectrum of the HF solution was also recorded and consisted of a singlet at ϕ -33.8 (downfield from external $CFCl_3$) for SO_3F^- and a relatively narrow HF solvent peak at ϕ 191.

In a typical preparation of NF_4SO_3F, NF_4SbF_6 (3.145 mmol) and $CsSO_3F$ (3.146 mmol) were combined in a previously described[22] Teflon metathesis apparatus. Dry HF[22] (3 ml liquid) was added and the resulting mixture was stirred at ambient temperature for 3 hours with a magnetic stirring bar, followed by cooling to -78° and filtration at this temperature. The HF solvent was pumped off from the filtrate at -30° for 3 hours leaving behind a white solid residue. The thermal stability of this residue was established by incremental warm up of the solid in a dynamic vacuum and by trapping, measuring (PVT) and identifying (infrared spectroscopy) the volatile decomposition products. Up to 0°, only HF and small amounts of NF_3 were collected indicating the possible presence of small amounts of unstable $NF_4HF_2 \cdot nHF$[22] in the product. At temperatures of 9° or higher, significant decomposition of the solid was observed, producing equimolar amounts of NF_3 and $FOSO_2F$. Allowing for about 20% of the product solution being retained, as generally seems to be the case with similar metathetical reactions,[22] by the filter cake and being lost during solvent pump-off, the yield of NF_3 and $FOSO_2F$ was essentially quantitative. The filtercake (1.0 g, weight calcd for 3.15 mmol of $CsSbF_6$ = 1.16 g) was shown by vibrational spectroscopy to be $CsSbF_6$[28] and did not show any detectable impurities.

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

For the spectroscopic identification of NF_4SO_3F, reactions were carried out on a 1 mmol scale in a previously described[22] manner. The ^{19}F NMR spectrum of a solution of $NF_4^+SO_3F^-$ in HF at -30° showed the signals characteristic for NF_4^+ (triplet of equal intensity at ϕ -215 with J_{NF} = 226 Hz and a linewidth of less than 3 Hz),[9] SO_3F^- (singlet at ϕ -33.5), and HF (broad singlet at ϕ 193). No evidence for the presence of $FOSO_2F$[27] was observed. The Raman spectra of the HF solution at 25° and of solid NF_4SO_3F at -100° were also recorded and are shown in Figure 1. The spectra showed the presence of only small amounts of $CsSbF_6$[28] indicating a purity of NF_4SO_3F in excess of 90 weight percent, in agreement with the observed material balance. Raman and ^{19}F NMR spectra of HF solutions of NF_4SO_3F, which were kept at 25° for several days, showed no evidence of $FOSO_2F$ formation.

<u>Reaction of Cs_2SO_4 with HF</u>. The Cs_2SO_4 salt was found to be highly soluble in HF. Raman spectra of these solutions and of the solid residue obtained after the solvent removal, showed the complete absence of the SO_4^{--} anion[28] and the presence of the SO_3F^- anion[26]. The presence of the SO_3F^- anion in the HF solution was confirmed by ^{19}F NMR spectroscopy which showed a strong singlet at ϕ -33.8, characteristic for SO_3F^-.

<u>Reaction of $CsPO_2F_2$ with HF.</u> A sample of $CsPO_2F_2$ (2.1 mmol) was treated with anhydrous HF (3 ml liquid) for 12 hours at 25°. The white solid residue, left behind after removal of the solvent, was identified by its infrared and Raman spectrum as $CsPF_6$[28] (2.1 mmol) and did not contain detectable amounts of $PO_2F_2^-$.[31-33]

Results and Discussion

The novel salt $NF_4^+SO_3F^-$ was prepared from NF_4SbF_6 and $CsSO_3F$ by low-temperature metathesis in anhydrous HF solution according to:

$$NF_4SbF_6 + CsSO_3F \xrightarrow[-78^\circ]{HF} CsSbF_6\downarrow + NF_4SO_3F$$

The NF_4SO_3F salt can be isolated as a white solid which is stable at 0°, but slowly decomposes at +10° to produce NF_3 and $FOSO_2F$ in high yield according to

$$NF_4SO_3F \longrightarrow NF_3 + FOSO_2F$$

Its HF solution appears to be stable at ambient temperature. The thermal stability of NF_4SO_3F is very similar to that[22] of NF_4ClO_4. This is not surprising since SO_3F^- and ClO_4^- are isoelectronic and chemically very similar. This chemical similarity is also demonstrated by their decomposition modes, which in both cases produce the corresponding hypofluorites in high yield.

The decomposition of $NF_4^+SO_3F^-$ represents a new, high yield, convenient synthesis of $FOSO_2F$. The previously reported methods for the preparation of $FOSO_2F$ involved either the fluorination of SO_3[34,35] or $S_2O_6F_2$[36]. NF_4SO_3F is the third known example of an NF_4^+ salt of an oxy-anion producing on thermal decomposition the corresponding hypofluorite. The other two known examples are NF_4ClO_4[22] and

$NF_4IF_4O_2$.[23] This indicates that the thermal decomposition of unstable NF_4^+ salts of oxy-anions may be a general method for the synthesis of hypofluorites.

The ionic nature of NF_4SO_3F, both in the solid state and in HF solution, was verified by Raman and ^{19}F NMR spectroscopy. The Raman spectra are shown in Figure 1 and demonstrate the presence of the bands characteristic for NF_4^+ [9,22] and SO_3F^-.[26] The observed frequencies and their assignments are summarized in Table I. The SO_3F^- bands in NF_4SO_3F are very similar to those observed for $CsSO_3F$ (see Figure 1). The minor frequency shift observed for the SF stretching mode is not surprising in view of a previous infrared study of the alkali metal salts which showed that the frequency of this fundamental strongly depends on the nature of the cation and varied from 812 cm^{-1} in $LiSO_3F$ to 715 cm^{-1} in $CsSO_3F$.[26] The observed splitting of some of the modes of both the NF_4^+ cation and the SO_3F^- anion into their degenerate components is easily explained by solid state effects and has also been observed for $NF_4^+ClO_4^-$.[22]

The ^{19}F NMR spectrum of $NF_4^+SO_3F^-$ in HF solution showed a triplet of equal intensity at ϕ-215 with J_{NF} = 226 Hz and a linewidth of less than 3Hz, characteristic for NF_4^+, a singlet at ϕ-33.5, characteristic[9] for SO_3F^-, and the characteristic HF signal at ϕ 193. The assignment of the ϕ-33 signal to SO_3F^- was verified by recording the spectrum of $CsSO_3F$ in HF under the same conditions.

In view of the above mentioned usefulness of NF_4^+ salts of oxy-anions for the preparation of novel hypofluorites, it appeared interesting to attempt the syntheses of $(NF_4)_2SO_4$ and $NF_4PO_2F_2$. The thermal decomposition of these two hypothetical salts would offer an opportunity to prepare the yet unknown hypofluorites, $SO_2(OF)_2$ and $POF_2(OF)$. However, both the SO_4^{--} and $PO_2F_2^-$ anion were found to interact with anhydrous HF according to:

$$SO_4^{--} + 3HF \longrightarrow SO_3F^- + H_2O + HF_2^-$$

and

$$PO_2F_2^- + 4HF \longrightarrow PF_6^- + 2H_2O$$

Attempts to prepare $POF_2(OF)$ by fluorination of $HOPOF_2$ with atomic fluorine, generated by the controlled decomposition of $NF_4HF_2 \cdot nHF$,[22] were also unsuccessful. The main products were NF_4PF_6[9] and an unidentified nonvolatile phosphorous oxyfluoride.

Although vibrational spectra have been reported[31-33] for the $PO_2F_2^-$ anion, the previous assignment of several fundamentals is open to question. Figure 2 and Table 2 summarize the vibrational spectra of $CsPO_2F_2$, obtained in our study. The given assignment was made by analogy with that of isoelectronic SO_2F_2 which is well established.[37-39] Whereas, the splitting of $\nu_8(B_2)$ can easily be explained by Fermi resonance with $\nu_4+\nu_9(B_2)$,the reason for the observed splitting of ν_4 is less obvious. The possibility of one of the components assigned to ν_4 actually being due to the $\nu_5(A_2)$ torsional mode cannot be ruled out, but is unlikely due to the facts that this mode should be infrared inactive under C_{2v} selection rules and usually is of such low intensity in the Raman spectra that it is very difficult to observe.

In summary, the present study shows that within the isoelectronic series, ClO_4^-, SO_3F^-, $PO_2F_2^-$, SO_4^{--}, the first two anions are capable of forming NF_4^+ salts of moderate stability which can decompose to NF_3 and the corresponding hypofluorites. The syntheses of $NF_4PO_2F_2$ and $(NF_4)_2SO_4$ by metathesis in HF was prevented by the reaction of $PO_2F_2^-$ and SO_4^{--} with the solvent to yield PF_6^- and SO_3F^-, respectively.

Acknowledgement. The authors thank Drs. L. R. Grant and W. W. Wilson for helpful discussions and to the Office of Naval Research, Power Branch, and the Army Research Office for financial support of this work.

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Diagram Captions

Figure 1. Raman spectra of $NF_4^+SO_3F^-$. Upper trace, HF solution at 25°, middle trace, neat solid at -100°. Weak bands due to the sample tubes and small amounts of $CsSbF_6$ were subtracted from the spectra. Bottom trace, solid $CsSO_3F$ at 25°. The spectra were recorded with spectral slitwidths of 8, 6 and 4 cm^{-1}, respectively.

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

Table I. Raman Spectra of NF_4SO_3F and $CsSO_3F$

Obsd freq, cm^{-1}, and rel intens[a]			Assignment (point group)	
NF_4SO_3F		$CsSO_3F$		
HF solution	solid	solid	$NF_4^+(T_d)$	$SO_3F^-(C_{3v})$
	1277 (0.7)	1278 (0.7)		$\nu_4(E)$
	1267 (0.4)			
1165 (0.4)	1166 (1.3)		$\nu_3(F_2)$	
	1152 (1.8)			
1087 (6.7)p	1083 (10)	1076 (10)		$\nu_1(A_1)$
853 (10)p	850 (9.5)		$\nu_1(A_1)$	
	749 (1.1)	719 (1.2)		$\nu_2(A_1)$
	738 (0.8)			
612 (3)	612 (6)		$\nu_4(F_2)$	
575 (1.2)	584 (1.7)	582 (2)		$\nu_5(E)$
	563 (2.5)	560 (2.2)		$\nu_3(A_1)$
446 (2.8)	450 (4)		$\nu_2(E)$	
400 (1)	415 (2.5)	406 (3.8)		$\nu_6(E)$
	404 (2.3)	396 (3.5)		

(a) uncorrected Raman intensities

Table II. Vibrational Spectra of Solid $CsPO_2F_2$ and Their Assignment Compared to Those of SO_2F_2

Obsd freq, cm^{-1} and rel intens

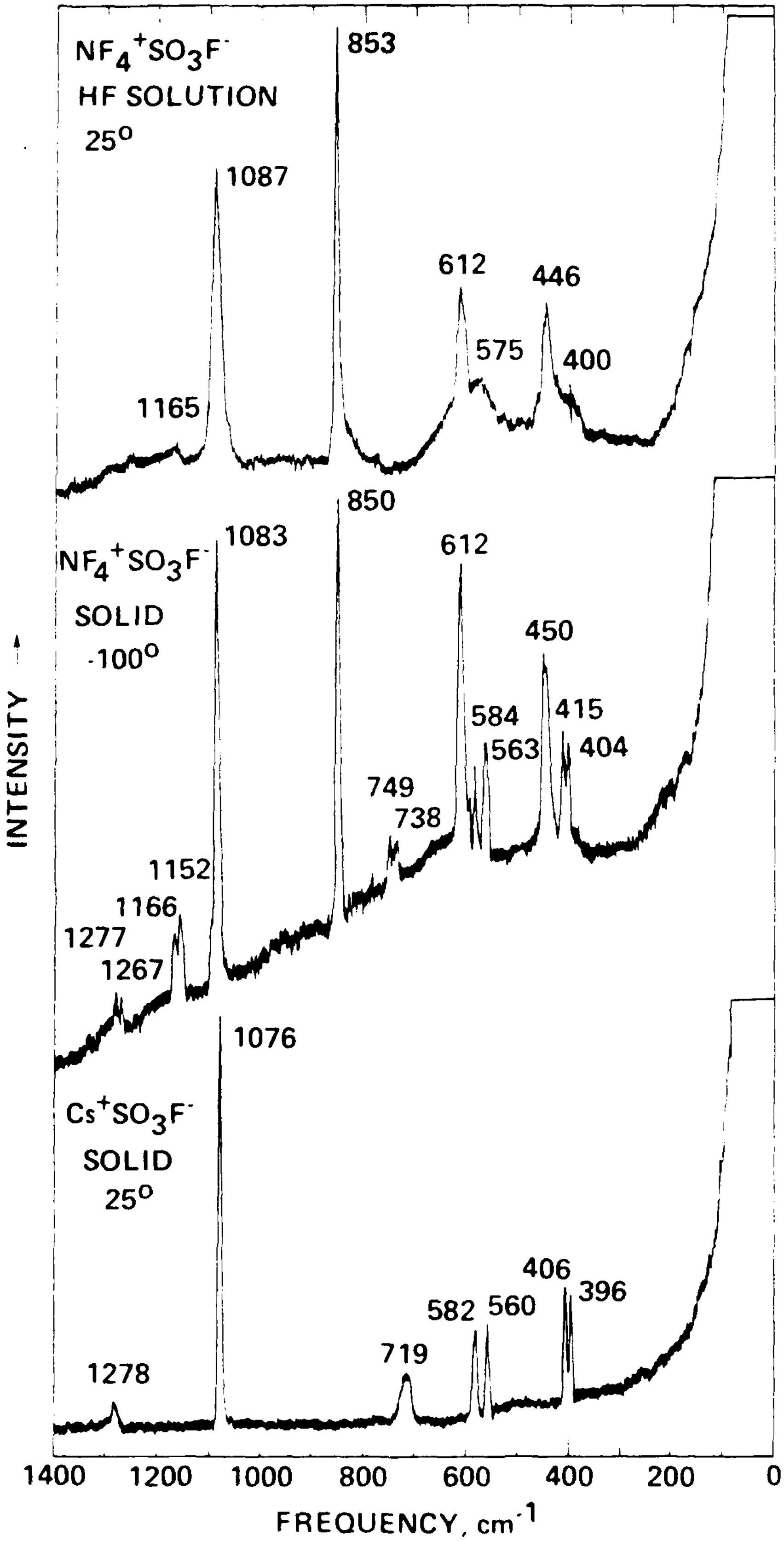
$CsPO_2F_2$ [a]		SO_2F_2 [b]		Assignment (point group C_{2v})		Approximate description of mode
Raman	IR	Raman	IR			
1143 (10)	1142 vs	1270 vs	1270 vs	A_1	ν_1	sym. PO_2 stretch
813 (3.7)	825 vs	848 vs	848 vs		ν_2	sym. PF_2 stretch
512 (6)	520 sh	552 m	553 s		ν_3	δ scissoring PO_2
370 sh	370 mw }	384 m	384 vw		ν_4	δ scissoring PF_2
353 (5.7)	351 mw }					
--	--	$[384 \pm 15]^c$		A_2	ν_5	τ
1318(0+)	1325 vs	1504 w	1503 vs	B_1	ν_6	asym. PO_2 stretch
501 (2)	494 s	539 m	540 s		ν_7	δ rock PF_2
851 (0.7)	850 sh }	888 w	886 vs	B_2	ν_8	asym. PF_2 stretch[d]
830 (1.2)	825 vs }					
501 (2)	508 s	544 m	544 s		ν_9	δ rock PO_2

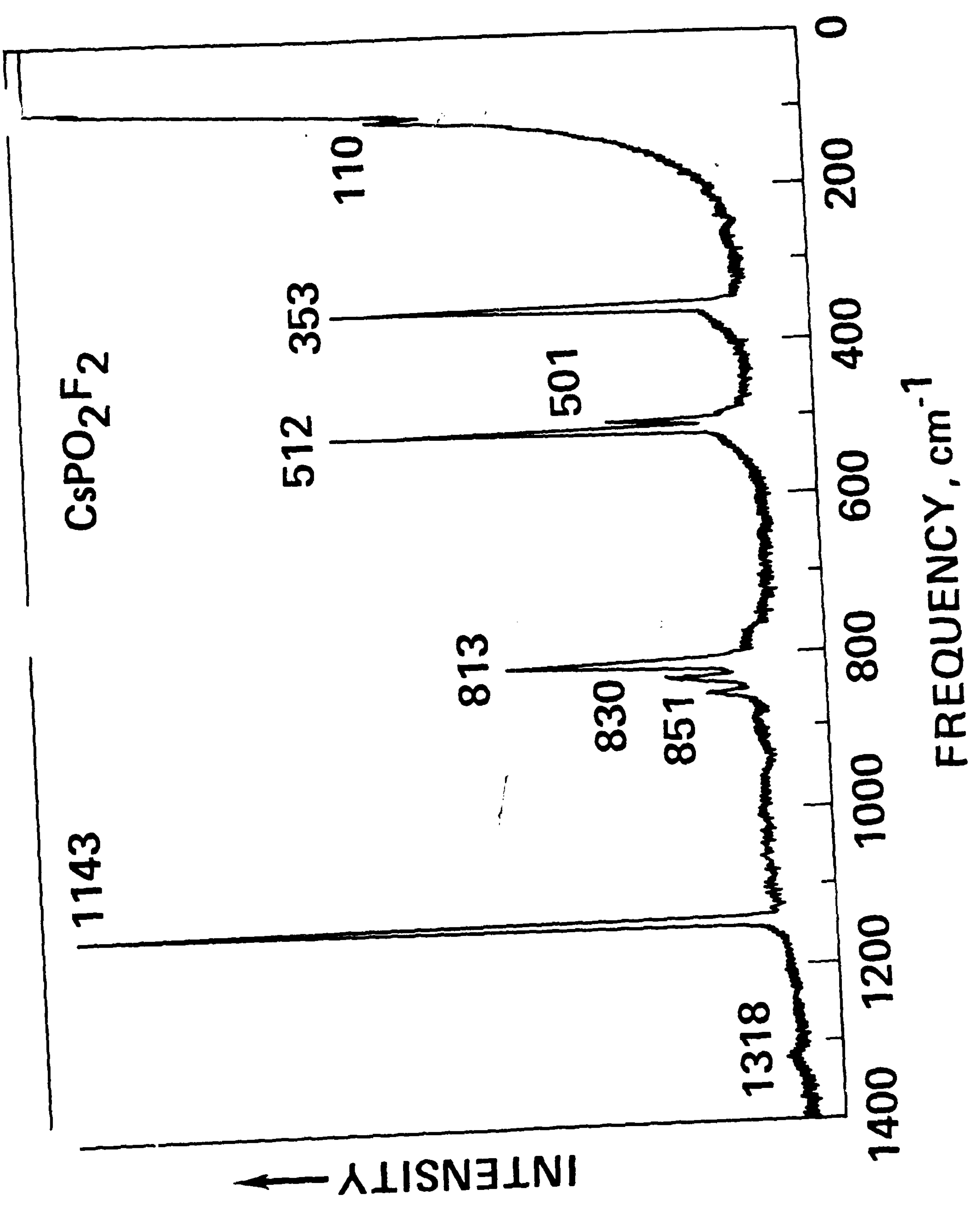
(a) data from this study; uncorrected Raman intensities; since ν_7 and ν_9 have very similar frequencies and intensities, their assignments are tentative.

(b) data from ref. 36-38

(c) from microwave data, ref. 36

(d) in Fermi resonance with $\nu_4+\nu_9(B_2) = 854\ cm^{-1}$


NF$_4$$^+SO_3F^-$
HF SOLUTION
25°
853
1087
1165
612
575
446
400
NF$_4$$^+SO_3F^-$
SOLID
-100°
850
1083
612
450
584
563
415
404
749
738
1152
1166
1277
1267
Cs$^+$SO$_3$F$^-$
SOLID
25°
1076
1278
719
582
560
406
396
INTENSITY →
1400
1200
1000
800
600
400
200
0
FREQUENCY, cm^{-1}


$CsPO_2F_2$
110
353
501
512
813
830
851
1143
1318
0
200
400
600
800
1000
1200
1400
FREQUENCY, cm^{-1}
INTENSITY

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

APPENDIX D

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

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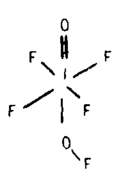
(*Received 22 June* 1979)

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

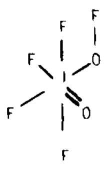
Metathetical reactions between NF_4SbF_6 and $CsXO_4$ were carried out in anhydrous HF solution as previously described (5). The solutions were cooled to -78°C and the insoluble $CsSbF_6$ precipitate was separated from the solution by filtration. The HF solvent was pumped off at -30°C and the residue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

$$IO_4^- + 4HF \longrightarrow IF_4O_2^- + 2H_2O$$

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



trans



cis

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

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

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APPENDIX E

THE GENERAL VALENCE FORCE FIELD OF PERCHLORYL FLUORIDE

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Received . . . .

Abstract

The infrared spectra of $FClO_3$ in Ne, N_2, and Ar matrices were recorded and the ^{35}Cl - ^{37}Cl isotopic shifts were measured. The Coriolis constants of the E-species vibrations were redetermined and together with the isotopic data used for the computation of a general valence force field. The A_1 block, for which only isotopic frequencies are available, remains underdetermined, but it was possible to place narrow limits on four force constants while the other two are in accord with orbital following arguments. It is shown that ν_2 and ν_3 are best described as an antisymmetric and a symmetric combination, respectively, of the ClF stretching and the ClO_3 bending motions. Comparison with 13 previously published force fields demonstrates the inadequacy of underdetermined force fields for strongly coupled systems, such as $FClO_3$. The ClO and ClF stretching force constants were found to be 9.75 and 3.51 mdyn/Å, respectively, in good agreement with those expected for a mainly covalent Cl-F single and Cl=O double bonds.

Introduction

During a normal coordinate analysis of the fluorine perchlorate, $FOClO_3$, molecule[1] we became interested in the force field of the closely related perchloryl fluoride, $FClO_3$, molecule. Although $FClO_3$ is a well known and important molecule, and at least 13 force fields[2-14] have previously been published for it, comparison of the literature data revealed large discrepancies. Furthermore, for most of these computations estimated structural parameters had been used. Since the structure of $FClO_3$ has been well established by electron diffraction data[6] and since for similar molecules a combination of isotopic frequencies and Coriolis constants have been shown to result in well defined general valence force fields,[15-17] it was interesting to apply this approach to $FClO_3$. Further interest was added to the problem by the fact that in several studies[2,3,8,9,11] $FClO_3$ had been used as a model compound to test the quality of approximate force fields. An evaluation of the merits of the different approximating methods, however, requires the knowledge of a reliable general valence force field. Finally, based on the results of a normal coordinate analysis, Gans pointed out[9] that two possible assignments (715 and 549 cm^{-1}) exist in the A_1 block for the Cl-F stretching mode and that, as a result, ν_2 and ν_3 might be mixtures of Cl-F stretching and angle deformations. The purpose of this study was to clarify some of these aspects and to obtain a better understanding of the force field of this interesting molecule.

Experimental

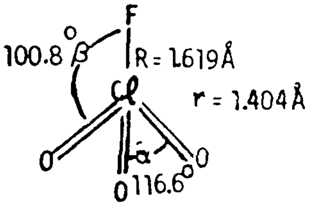
Perchloryl fluoride (Pennsalt) was handled in a passivated stainless steel - Teflon FEP vacuum system and purified prior to use by fractional condensation. Infrared spectra of the gas were recorded using a 5 cm path-length Teflon cell with CsI windows. The infrared spectra of matrix-isolated $FClO_3$ were obtained at 6°K with an Air Products Model DE 202 S helium refrigerator equipped with CsI windows. Research grade Ne, N_2 and Ar (Matheson) were used as matrix materials in a mole ratio of 1000:1. The infrared spectra were recorded on a Perkin Elmer Model 283 spectrophotometer calibrated by comparison with standard gas calibration points.[18,19] The reported frequencies and isotopic shifts are believed to be accurate to $\pm$ 2 and $\pm$ 0.1 cm^{-1}, respectively.

Results and Discussion

Since the infrared and Raman spectra and the assignments of $FClO_3$ are well established,[10,20-25] only the infrared matrix isolation spectra were recorded for the determination of the ^{35}Cl-^{37}Cl isotopic shifts. These spectra were obtained at 6°K using three different matrix materials, Ne, N_2, and Ar, at a MR of 1000. The observed spectra, frequencies and assignments are shown in Figure 1. By analogy with the similar halogen fluorides, BrF_3,[26] BrF_3O[27] and $FBrO_2$[28], neon matrices exhibited the least matrix site effect splittings and showed frequencies closest to those of the gas phase values.

The additioned splittings observed for the N_2 and the Ar matrices are attributed to matrix site effects.

A general valence force field was computed for $FClO_3$ using a previously described machine method[29]. The frequency values were taken from previous gas phase measurements[10,21,22,24,25] and are summarized in Table 1. The ^{35}Cl-^{37}Cl isotopic shifts were taken from the present matrix work except for ν_3 and ν_5 which were more accurately determined[22] by a previous high resolution gas phase infrared study (see Tabel 1). Anharmonic frequencies were used for the force field computations because sufficient experimental data for anharmoniicity corrections were not available. Since the relative signs of the symmetry coordinates are critical for the computation of the Coriolis constants, the symmetry coordinates have been summarized in Table II. The following internal coordinates and the geometry, determined by an electron diffraction study,[6] were used:



As expected for a five atomic molecule of symmetry C_{3v}, $FClO_3$ exhibits a total of 6 fundamental vibrations classified as $3A_1+3E$.

E-Block Force Field. The ^{37}Cl isotope can provide only two new independent frequencies, due to the product rule. Consequently, the fact that the isotopic splitting for ν_6 could not be measured, is unimportant. Similarly, the Coriolis constants can provide two additional independent data points since they are related by the sum rule, $\zeta_4+\zeta_5+\zeta_6=2B/A$. Again, the fact that one Coriolis constant could not be measured, does not decrease the number of available independent data points. Thus, there were a total of seven pieces of independent data available to determine six force constants. The least squares computer code, used for our force field computations, did not converge when the observed frequencies and the previously reported Coriolis ζ constant values[5,10] were used as input data. Consequently, this code was used to compute five symmetry force constants and the Coriolis constants as a function of the sixth constant, F_{45}, requiring an exact fit of the five observed frequencies. The resulting range of solutions is shown in Figure 2.

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

The other set of Coriolis constants was calculated[5] from infrared gas-phase band contours. For the determination of ζ_5 the accurately known Q branch spacing of ν_5 (0.1581 cm^{-1})[22] was used according to $\zeta_5 = 1 - \frac{B}{A} - \frac{0.1581}{2A}$ where A and B are the reduced moments of inertia. At the time of the original computation[5] of ζ_5, an experimental value was available[22,30] only for B, but A had to be estimated. Reevaluation of ζ_5 with A and B values of 0.1846 and 0.1764 cm^{-1}, respectively, deduced from the electron diffraction structural data,[6] resulted in a revised value for ζ_5 of -0.384 ± 0.008, assuming one percent uncertainties for both the value of A and the value of the Q branch spacing. The values of A and B computed from the published electron diffraction data[6] are considered to be more precise than ± one percent in view of the 0.64% deviation between our value of B (0.1764 cm^{-1}=5292 Mc/sec) and that of 5258.682 ± 0.005 Mc/sec obtained [30] by microwave spectroscopy.

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

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

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

This E block force field appears entirely plausible. All the off-diagonal symmetry force constants have relatively small values, and the potential energy distribution (see Table 1) shows the fundamentals to be highly characteristic (70-98%). They are well described as an antisymmetric ClO_3 stretch, an antisymmetric ClO_3 deformation and a ClO_3 rocking mode. Figure 2 also demonstrates that the general valence force field is approximately an extremal solution with F_{44} being a maximum and F_{55} and F_{66} being close to their minima.

<u>A_1-Block Force Field</u>. For the A_1 block, the product rule reduces the six vibrational frequencies to five independent pieces of data. Therefore, a unique force field cannot be determined. However, as done for the E-block, five symmetry force constants were computed as a function of the sixth one, requiring again an exact (±0.05 cm^{-1}) fit of the observed frequencies and chlorine isotopic shifts. The range of possible force constants can then be restricted by limiting the off-diagonal symmetry force constants to a plausible range. The results from these computations are displayed in Figures 3 and 4 which show the force field plots as a function of F_{13} and F_{23}, respectively. Both figures represent the same results, except that Figure 4 covers a much wider range because small changes in F_{23} cause very large changes in F_{12} and F_{13}. Furthermore, Figure 4 also displays the upper and lower sections of each force constant ellipsis, thus demonstrating the effect of reversing the

assignments of ν_2 and ν_3. This effect has previously been demonstrated[9] by the model computations of Gans and will be discussed below in more detail.

Inspection of Figures 3 and 4 allows the following conclusions: (i) Assuming plausible values for F_{12} and F_{13}, i.e. values not exceeding about +0.8 or -0.8 mdyn/Å and mdyn/rad, respectively, the values of F_{11}, F_{22}, F_{33} and F_{23} are fixed already within rather narrow limits, $F_{11}=9.84\pm 0.06$, $F_{22}=3.55\pm 0.06$, $F_{33}=2.60\pm 0.04$, $F_{23}=0.62\pm 0.05$. (ii) The values of F_{12} and F_{13} are poorly determined, but exhibit an approximately linear relationship, i.e. $F_{12}\sim 1.3F_{13}$ with F_{12} and F_{13} always having the same sign. (iii) F_{23} must be positive and must have a value of at least 0.57 mdyn/rad. (iv) In Figure 4, the upper halves of the force constants ellipses of F_{11}, F_{33}, F_{12} and F_{13} correspond to the lower half of F_{22} and vice versa. The first case corresponds to the assignment $\nu_2 > \nu_3$, whereas the latter case corresponds to the reversed assignment. The crossover between these two assignments occurs at about extremal values of not only $F_{23}\cong$ Min, but also of $F_{11}\cong$ Max and $F_{22}\cong$ Min, and where F_{12} and $F_{13}\approx 0$. This is demonstrated by the potential energy distributions and eigenvectors listed in Table IV. (v) As expected on the basis of (iv), ν_2 and ν_3 are strongly mixed and in the vicinity of the assignment cross-over are about equal mixtures of Cl-F stretching and symmetric ClO_3 deformation. As can be seen from the eigenvectors given in Tables I and IV, ν_2 is an antisymmetric and ν_3 is a symmetric combination of the symmetry coordinates S_2 and S_3. In view of this, any argument about which of these two fundamentals is the stretching and which one is the deformation mode, is rather meaningless, particularly in the proximity of the preferred (see below) force field.

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

Although, as pointed out above, F_{12} and F_{13} are not well determined by the observed isotopic shifts, arguments can be advanced in favor of a force field being close to the extremal value of F_{23}=Min. The Hybrid Orbital Force Field constraints[35] $F_{46}=-F_{56}$ and $F_{13}=(F_{46}-F_{56})/2\sqrt{2}$ (in our symmetry coordinates) have been shown[16] to also be valid for the similar C_{3v} molecule CHF_3. The first condition ($F_{46}= -F_{56}$) is approximately fullfilled for $FClO_3$ and, therefore, the second condition is expected to be also applicable and to result in a reasonable estimate for F_{13}. The value of -0.21 mdyn/rad thus calculated for F_{13} of $FClO_3$ corresponds very closely to the force field with F_{23}= Min. Consequently, we prefer for the A_1 block of $FClO_3$ a force field with $F_{13}= -0.2$ which is listed in Table 1.

Comparison with Previous Force Fields. Table V gives a comparison of our force field with those previously reported. In most cases, an exact comparison of the bend-bend and stretch-bend force constants is difficult because for most of the previous force fields all force constants were given in units of mdyn/Å and the authors were not specific which bondlengths (r, R or possible combinations) were used for their normalization procedures. For a comparison with our force field, approximate values of the previously reported all mdyn/Å force fields can be obtained by multiplying F_{33} and F_{66} by rR, F_{13} by R or $\sqrt{rR}$, F_{23} and F_{45} by r or $\sqrt{rR}$, F_{55} by r^2 or rR, F_{46} by $\sqrt{rR}$, and F_{56} by rR or $r^{3/2}R^{1/2}$. Furthermore, most of the previously published force fields were computed with estimated geometries or inaccurate Coriolis constants. Consequently, an objective evaluation of the merits of the individual approximating methods is difficult and was not undertaken.

General Comments. We would like to point out the wide range of force constant values previously published for $FClO_3$ which fully supports the previous critical statements[9] by Gans concerning the questionable value of force constant calculations from insufficient or inaccurate data. In such cases, the computation of wide solution ranges is important to determine the range of possible plausible solutions.

The values of 9.75 and 3.51 mdyn/Å obtained for the Cl=O and the Cl-F stretching force constant, respectively, of $FClO_3$ are in excellent agreement with our expectations[37] for highly covalent Cl=O double and Cl-F single bonds. Higher Cl=O force constants have only been observed for the cations ($ClF_2O_2^+$ (12.1 mdyn/Å)[38] and ClF_2O^+ (11.2 mdyn/Å)[39] and are caused by their formal positive charge.[37] Similarly, $ClF_2O_2^+$ is the only chlorine oxyfluoride species which exhibits a higher (4.46 mdyn/Å) ClF stretching force constant. This can be attributed to the high oxidation state of chlorine (+VII) and the energetically favorable pseudo-tetrahedral structure of $FClO_3$.

The results of the present study are of particular interest because they demonstrate that arguments concerning the assignment of certain modes, capable of undergoing coupling, can be rather meaningless. This has recently been demonstrated[36] for the axial and the equatorial SF_2 scissoring modes in SF_4 and is now further substantiated for $FClO_3$. Rather than resulting in highly characteristic fundamentals, their symmetry coordinates are strongly mixed and the fundamentals correspond to an antisymmetric and a symmetric combination of the corresponding symmetry coordinates

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Diagram Captions

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

Figure 2. E block symmetry force constants and Coriolis constants of $FClO_3$ plotted as a function of F_{45}. The units of the force constants are given in Table 1. The observed Coriolis constants are marked by + and their uncertainties are given by rectangles. The solid and the two broken lines represent the general valence force field and its uncertainties, respectively, derived from the corresponding ζ_5 values. values.

Figure 3. A_1 - block symmetry force constants of $FClO_3$ plotted as a function of F_{13}.

Figure 4. A_1 - block symmetry force constants of $FClO_3$ plotted as a function of F_{23}.

TABLE 1. Frequencies[a] of $F^{35}C\ell O_3$ and ^{35}C - $^{37}C\ell$ Isotopic Shifts[b], Assignment, Symmetry Force Constants[c], Potential Energy Distribution[d] and Eigenvectors of $FC\ell O_3$

Assignment in point-group C_{3v}		Approximate description of mode	$F^{35}C\ell O_3$ freq, cm^{-1}	$^{35}C\ell$ - $^{37}C\ell$ isotopic shifts, cm^{-1}	symmetry force constants		PED	eigenvectors		
								S_1	S_2	S_3
A_1	ν_1	$\nu sym\ C\ell O_3$	1063	3.05	$F_{11} = f_r + 2f_{rr}$	9.88	$0.95F_{11}$	0.25	-0.08	0.09
	ν_2	asym combin. of $\nu_{C\ell F}$ and $\delta_{sC\ell O_3}$	717	10.0	$F_{22} = f_R$	3.51	$0.68F_{22} + 0.49F_{33} + 0.22F_{23} + 0.05F_{11}$	-0.04	-0.24	0.24
	ν_3	sym combin. of $\nu_{C\ell F}$ and $\delta_{sC\ell O_3}$	550	0.89	$F_{33} = 0.72f_\beta + 0.28f_\alpha + 1.45f_{\beta\beta} + 0.55f_{\alpha\alpha} - 1.79f_{\alpha\beta} - 0.89f_{\alpha\beta'}$	2.56	$0.52F_{33} + 0.33F_{22} + 0.16F_{23}$	0.01	0.13	0.19
					$F_{12} = \sqrt{3}\ f_{rR}$	-0.26				
					$F_{13} = 0.85f_{r\beta} + 1.70f_{r\beta'} - 1.05f_{r\alpha} - 0.53f_{r\alpha'}$	-0.2				
					$F_{23} = 1.47f_{R\beta} - 0.91f_{R\alpha}$	0.574		S_4	S_5	S_6
E	ν_4	$\nu asym\ C\ell O_3$	1315	15.8	$F_{44} = f_r - f_{rr}$	9.69	$0.98F_{44}$	0.32	0.17	0.11
	ν_5	$\delta asym\ C\ell O_3$	591	3.09	$F_{55} = f_\alpha - f_{\alpha\alpha}$	1.53	$0.73F_{55} + 0.11F_{66} + 0.10F_{56}$	-0.02	0.31	0.13
	ν_6	$\delta rock\ C\ell O_3$	405	$\lvert 0.17 \rvert$[e]	$F_{66} = f_\beta - f_{\beta\beta}$	1.49	$0.90F_{66} + 0.26F_{55} - 0.17F_{56}$	0	-0.13	0.24
					$F_{45} = f_{r\alpha} - f_{r\alpha'}$	-0.29				
					$F_{46} = f_{r\beta} - f_{r\beta'}$	-0.33				
					$F_{56} = f_{\alpha\beta} - f_{\alpha\beta'}$	0.26				

(a) Frequencies were taken from the gas phase values of refs 10, 21, 22, 24, 25

(b) Taken from this study, except for $\Delta\nu_3$ and $\Delta\nu_5$

(e) Calculated value. Splitting was too small to be experimentally observable.

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

(d) Percent contributions. Contributions of less than 5% to the PED are not listed.

Table II. Symmetry Coordinates of $FClO_3$

A_1	$S_1 =$	$(r_1+r_2+_3)/\sqrt{3}$
	$S_2 =$	R
	$S_3 =$	$0.4912\ (\beta_1+\beta_2+\beta_3) - 0.3034(\alpha_1+\alpha_2+\alpha_3)$
	$S* =$	$0.3034\ (\beta_1+\beta_2+\beta_3) + 0.4912(\alpha_1+\alpha_2+\alpha_3)$
E	$S_{4a} =$	$(r_2+r_3-2r_1)/\sqrt{6}$
	$S_{4b} =$	$(r_3-r_2)/\sqrt{2}$
	$S_{5a} =$	$(\alpha_2+\alpha_3-2\alpha_1)/\sqrt{6}$
	$S_{5b} =$	$(-\alpha_3-\alpha_1)/\sqrt{2}$
	$S_{6a} =$	$(2\beta_1-\beta_2-\beta_3)/\sqrt{6}$
	$S_{6b} =$	$(\beta_2-\beta_3)/\sqrt{2}$

* redundant coordinate

TABLE III. Coriolis Constants of $FC\ell O_3$

	ref. 5[a]	ref. 10[a]	ref. 3[b]	this work[a]
ζ_4	0.45 ± 0.10	0.38 ± 0.04	0.52	0.54 ± 0.05
ζ_5	-0.25 ± 0.02	-0.29 ± 0.04	-0.60	-0.384 ± 0.008
ζ_6	0.23 ± 0.10	0.36 ± 0.04	0.49	0.32 ± 0.05
$\zeta_4 + \zeta_5 + \zeta_6$	0.43	0.45	0.41	0.477 ± 0.005[c]

(a) experimentally determined values

(b) values computed from the approximate force field of ref. 3

(c) calculated from $I_A/2I_B$ assuming a one percent uncertainty in the ratio of the moments of inertia obtained from the structure determination of ref. 6

Table IV. Potential Energy Distribution[a] and Eigenvectors of Three Sets of A_1 - Block Force Constants of $FClO_3$

symmetry force constants[b]						PED			Eigenvectors		
F_{11}	F_{22}	F_{33}	F_{12}	F_{13}	F_{23}	Q_1	Q_2	Q_3	Q_1	Q_2	Q_3
9.28	3.93	2.92	1.71	1.4	1.02	$0.83F_{11}+0.13F_{13}+0.07F_{33}$	$0.90F_{22}+0.49F_{33}-0.40F_{23}$	$0.59F_{33}+0.26F_{22}+0.30F_{11}-0.16F_{12}-0.23F_{13}+0.24F_{23}$	$0.24S_1-0.02S_2+0.12S_3$	$-0.01S_1-0.26S_2+0.22S_3$	$-0.08S_1+0.11S_2+0.19S_3$
9.88	3.51	2.56	-0.26	-0.2	0.574	$0.95F_{11}$	$0.68F_{22}+0.49F_{33}-0.22F_{23}-0.05F_{11}$	$0.52F_{33}+0.33F_{22}+0.16F_{23}$	$0.25S_1-0.08S_2+0.09S_3$	$-0.04S_1-0.24S_2+0.24S_3$	$0.01S_1+0.13S_2-0.19S_3$
9.41	3.95	2.72	-1.59	-1.2	0.80	$0.84F_{11}+0.14F_{12}+0.08F_{22}-0.06F_{13}$	$0.65F_{22}+0.58F_{33}-0.30F_{23}-0.12F_{12}+0.09F_{11}+0.11F_{13}$	$0.50F_{33}+0.38F_{22}+0.19F_{11}+0.21F_{23}-0.15F_{13}-0.14F_{12}$	$0.24S_1-0.12S_2+0.06S_3$	$-0.05S_1-0.22S_2+0.25S_3$	$0.06S_1+0.13S_2+0.18S_3$

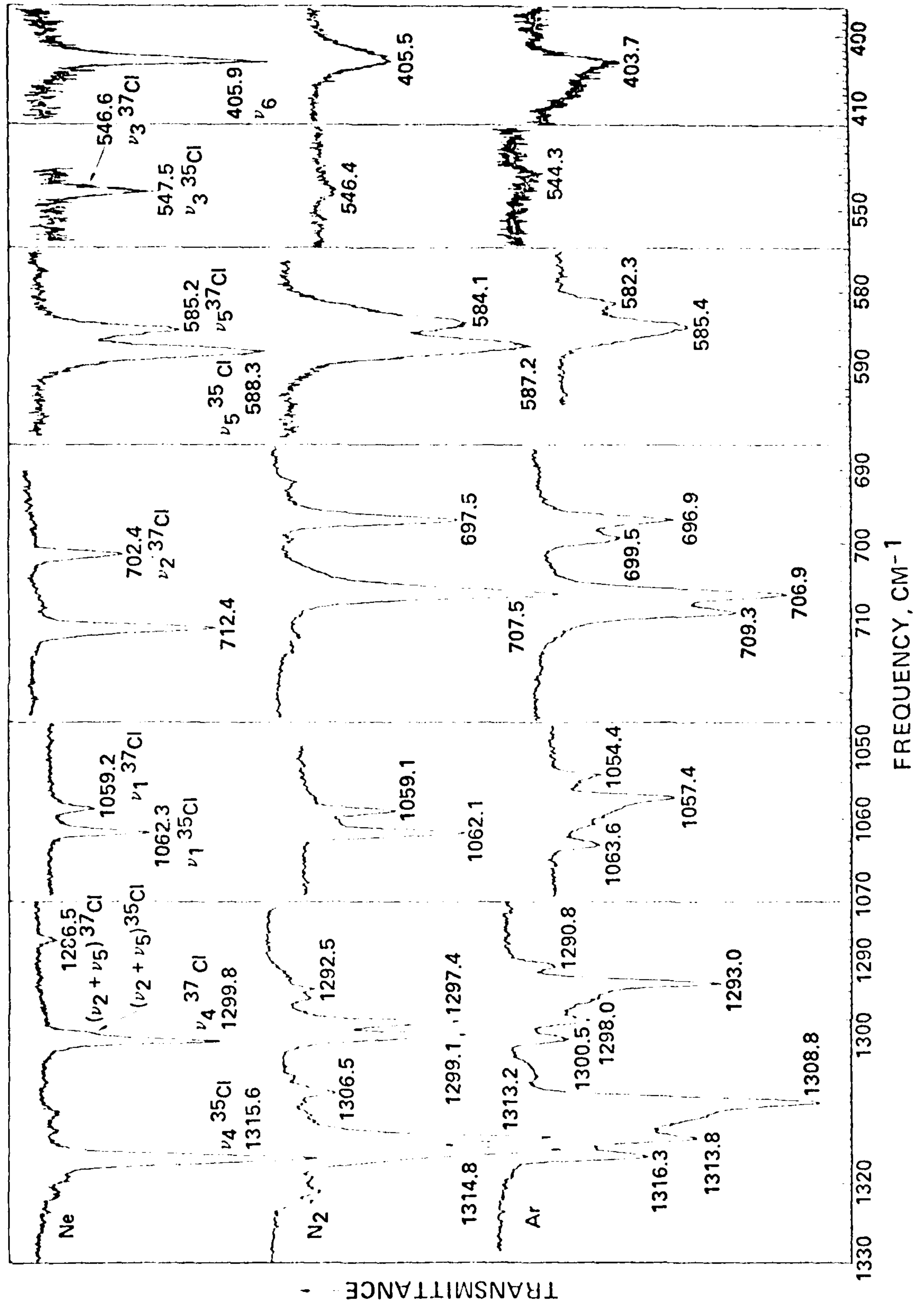
(a) Percent contribution. Contributions of less than 5% to the PED are not listed.

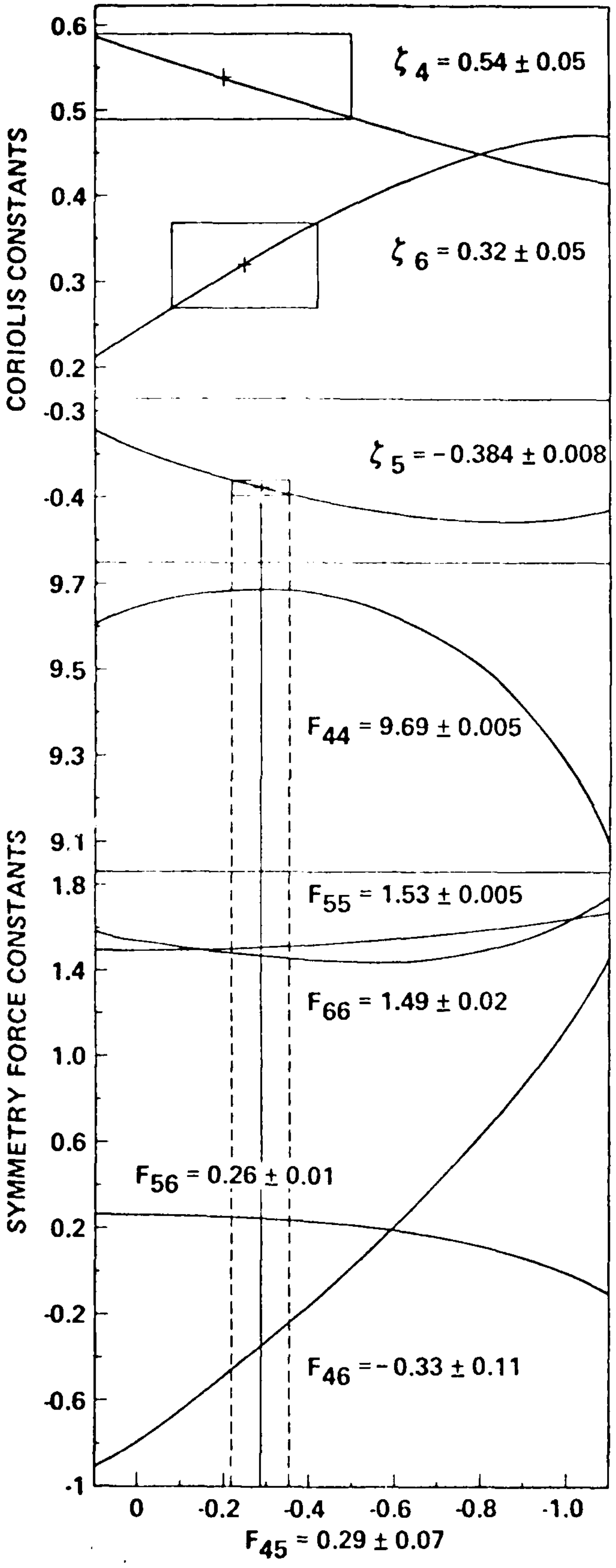
(b) For units see footnote c of Table 1.

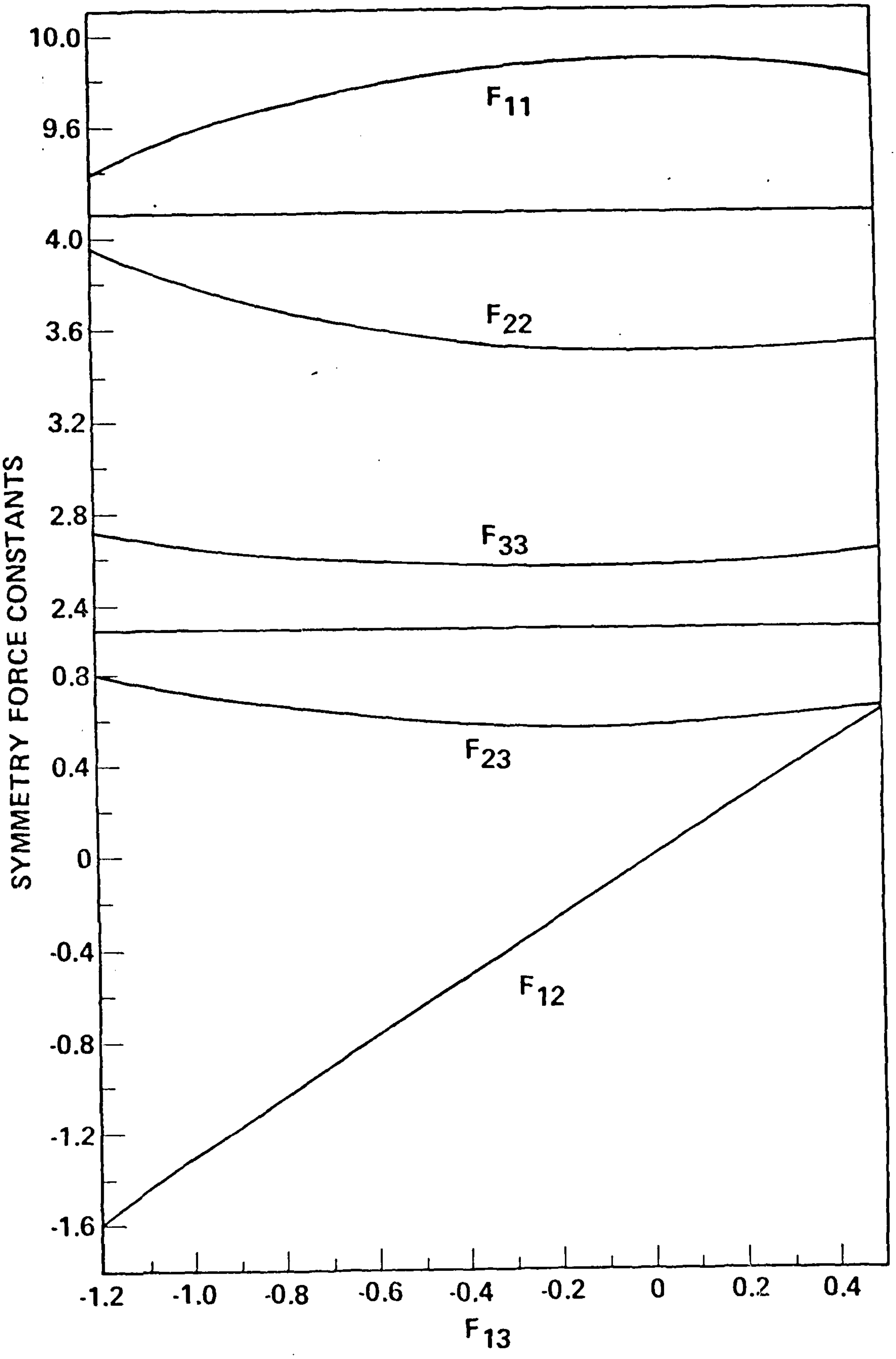
Table V. Comparison of the Different Force Field of $FClO_3$

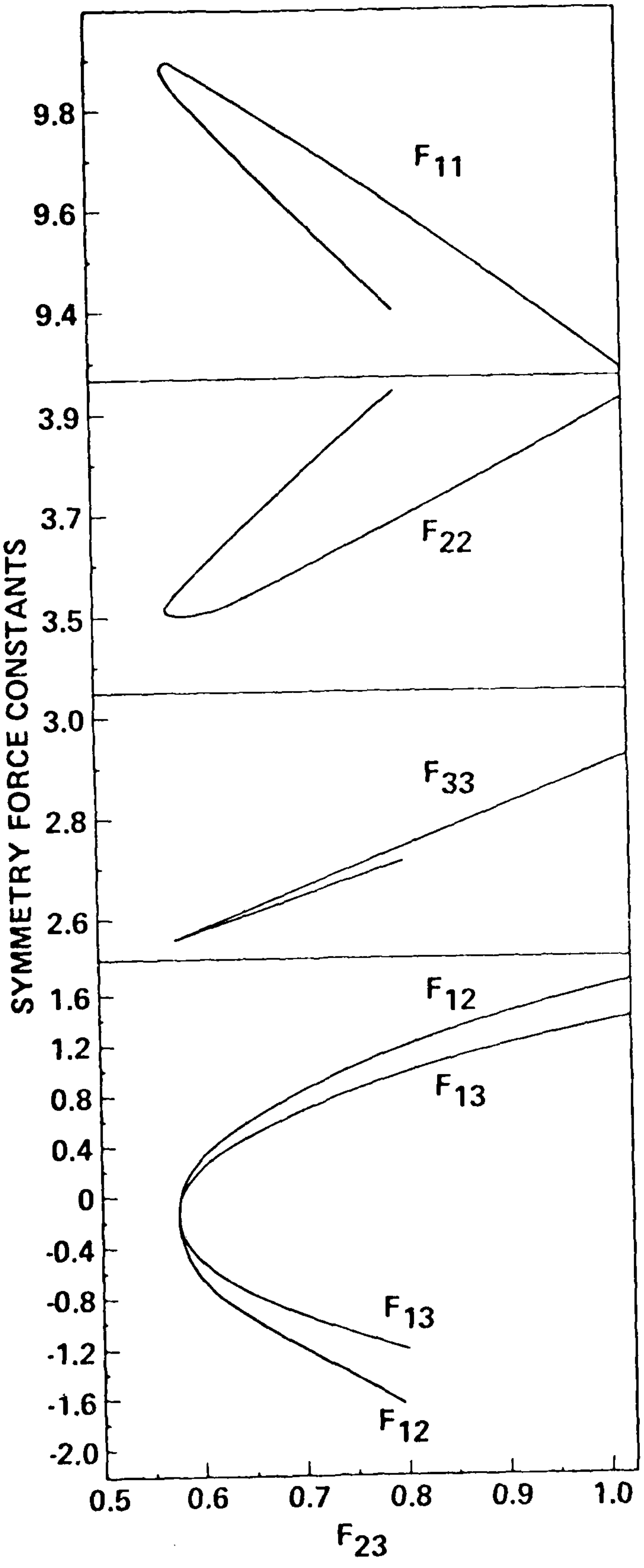
		this work[a]	ref. 2[b]	ref 3[b]	ref 4[b]	ref 5[b]	ref 6[a]	ref 7[b]	ref 8[b]	ref 9[a]	ref 10[b]	ref 11[b]	ref 12[b]	ref 13	ref 14[a]
A_1	F_{11}	9.88	8.64	8.64									9.49		
	F_{22}	3.51	3.91	3.92									3.69		
	F_{33}	2.56	1.82	0.85									2.98		
	F_{12}	-0.26	-0.03	-0.04									-0.19		
	F_{13}	-0.2	0.13	0.09									-0.07		
	F_{23}	0.574	-0.44	-.030						<-0.4			0.725		
E	F_{44}	9.69	9.80	9.82		9.30				9.26	10.91	10.24	9.59		
	F_{55}	1.53	1.03	1.04		0.81				1.75	0.93	0.9-1.0	1.50		
	F_{66}	1.49	0.62	0.53		0.96				1.31	0.66	0.68	1.08		
	F_{45}	-0.29	-0.09	-0.09		-0.68				0	-0.49	-0.37	-0.12		
	F_{46}	-0.33	0.04	0.04		-0.67				0	0.73		0.06		
	F_{56}	0.26	0	0		-0.20				0	-0.13	-0.17	0		
	f_r	9.75	9.41	9.43	9.37		9.30	9.75		9.5±0.1			9.56	9.36-9.55	9.42
	f_R	3.51	3.91	3.92	3.93		4.35	3.69	4.10	3.5±0.5			3.69	3.72-4.10	3.47
	f_{rr}	0.063	-0.39	-0.39			--	0.62					-0.03		0.24
	f_{rR}	-0.15	-0.02	-0.02			-0.25	0.53					-0.11		
	f_α						1.95	1.03							1.75
	f_β						1.60	0.82							1.84
	$f_{R\beta}$						0.55	--							0.39
	$f_{\beta\beta}$														0.53

(a) Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian^2, and stretch-bend interaction constants in mdyn/radian.
(b) All force constants in mdyn/Å. For comments on conversion into units of (a) see text.


Ne
N$_2$
Ar
TRANSMITTANCE
FREQUENCY, CM-1
1330
1320
1300
1290
1070
1060
1050
710
700
690
590
580
550
410
400
ν_4 ^{35}Cl 1315.6
ν_4 ^{37}Cl 1299.8
$(\nu_2+\nu_5)^{35}$Cl
1286.5 $(\nu_2+\nu_5)^{37}$Cl
1062.3 ν_1 ^{35}Cl
1059.2 ν_1 ^{37}Cl
712.4
702.4 ν_2 ^{37}Cl
ν_5 ^{35}Cl 588.3
585.2 ν_5 ^{37}Cl
547.5 ν_3 ^{35}Cl
546.6 ν_3 ^{37}Cl
405.9 ν_6
1314.8
1306.5
1299.1, 1297.4
1292.5
1062.1
1059.1
707.5
697.5
587.2
584.1
546.4
405.5
1316.3
1313.8
1313.2
1308.8
1300.5
1298.0
1293.0
1290.8
1063.6
1057.4
1054.4
709.3
706.9
699.5
696.9
585.4
582.3
544.3
403.7


CORIOLIS CONSTANTS
SYMMETRY FORCE CONSTANTS
0.6
0.5
0.4
0.3
0.2
-0.3
-0.4
9.7
9.5
9.3
9.1
1.8
1.4
1.0
0.6
0.2
-0.2
-0.6
-1
$\zeta_4 = 0.54 \pm 0.05$
$\zeta_6 = 0.32 \pm 0.05$
$\zeta_5 = -0.384 \pm 0.008$
$F_{44} = 9.69 \pm 0.005$
$F_{55} = 1.53 \pm 0.005$
$F_{66} = 1.49 \pm 0.02$
$F_{56} = 0.26 \pm 0.01$
$F_{46} = -0.33 \pm 0.11$
0
-0.2
-0.4
-0.6
-0.8
-1.0
$F_{45} = 0.29 \pm 0.07$


10.0
9.6
4.0
3.6
3.2
2.8
2.4
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
SYMMETRY FORCE CONSTANTS
F_{11}
F_{22}
F_{33}
F_{23}
F_{12}
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
F_{13}



9.8
9.6
9.4
F_{11}
3.9
3.7
3.5
F_{22}
3.0
2.8
2.6
F_{33}
1.6
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
-1.6
-2.0
F_{12}
F_{13}
F_{13}
F_{12}
SYMMETRY FORCE CONSTANTS
0.5
0.6
0.7
0.8
0.9
1.0
F_{23}

APPENDIX F

[Reprinted from Inorganic Chemistry, 18, 2619 (1979).]

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

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

Carl J. Schack* and Karl O. Christe

Received March 9, 1979

Although $FOClO_3$ has been known for decades,[1,2] its reaction chemistry has remained virtually unexplored and is limited to references to unpublished work, cited in a review.[3] This lack of data is attributed to the previous report[2] that $FOClO_3$ consistently exploded during attempted freezing. During a study[4] of NF_4ClO_4, it was found that very pure $FOClO_3$ could be obtained in high yield by the thermal decomposition of NF_4ClO_4. The $FOClO_3$, prepared in this manner, could be manipulated and repeatedly frozen without explosions, thus allowing us to study some of its properties[5] and reaction chemistry.

Of particular interest to us were the reactions of $FOClO_3$ with fluorocarbons. Previous work[6] in our laboratory had demonstrated that $ClOClO_3$ and $BrOClO_3$ add readily to fluorocarbon double bonds, resulting in covalent fluorocarbon perchlorates. Consequently, one would expect fluorine perchlorate to undergo a similar reaction. However, a literature citation[3] suggested that $FOClO_3$ does not add across the double bond in $Cl_2C{=}CF_2$. Furthermore, reactions of covalent hypofluorites, such as CF_3OF, are commonly interpreted in terms of a highly unusual $CF_3O^{\delta-}$–$F^{\delta+}$ type polarization of the O–F bond ("positive fluorine"). If the O–F bond in CF_3OF is indeed polarized in this direction, the fluorine in $FOClO_3$ should be even more positive because of the higher electronegativity of the perchlorato group. Since the direction of the addition of a hypohalite across an unsymmetrical olefinic double bond strongly depends on the direction and the degree of polarization of the O–Hal bond,[7] a study of the O_3ClOF–$CF_3CF{=}CF_2$ reaction system offered an ideal opportunity to experimentally test the validity of the "positive fluorine" concept.

Experimental Section

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

Apparatus and Materials. Volatile materials were manipulated in a well-passivated (with ClF_3) 304 stainless steel vacuum line equipped with Teflon-FEP U-traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube type gage (0–1500 mm, ±0.1%). Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (CS Laboratory Supplies) and $CFCl_3$ as an internal standard. Hexafluoropropylene and CF_3I were purchased while $CF_2{=}CF_2$ was prepared by pyrolyzing Teflon. Fluorine perchlorate was obtained from the decomposition of NF_4ClO_4.[10]

Reaction with Hexafluoropropylene. A 30-mL stainless steel cylinder was loaded at −196 °C with $FOClO_3$ (1.59 mmol) and C_3F_6 (2.08 mmol). The closed cylinder was warmed to −45 °C and kept at that temperature overnight. Separation of the products was achieved by vacuum fractionation in U traps cooled at −78, −95, and −196 °C. The coldest trap contained unreacted C_3F_6 together with $FClO_3$, CF_3CFO, and a small amount of $(CF_3)_2CO$. In the other traps only the colorless liquid $C_3F_7OClO_3$ was found (1.18 mmol, 74% yield based on $FOClO_3$). The following temperature–vapor pressure data were measured (°C, mm): −46.6, 4; −22.7, 17; −9.3, 36; 0.0, 59; 10.6, 99; 22.0, 161. The vapor pressure–temperature relation is described by the equation $\log P = 7.5257 - (1571.94/T)$ (pressure in mmHg and temperature in K) with a calculated normal boiling point of 65.2 °C and a heat of vaporization of 7.19 kcal/mol. A vapor density of 265 g/mol was measured compared to a calculated value of 268.5 g/mol for $C_3F_7ClO_4$. Strong mass spectral peaks were found for the ions $C_2F_4ClO_4^+$, $C_3F_7^+$, $CF_2ClO_4^+$, $C_3F_5O^+$, $C_3F_5^+$, $C_2F_5^+$, $C_2F_4O^+$, $C_2F_4^+$, $C_2F_3O^+$, ClO_3^+, $C_2F_2O^+$, CF_3^+ (base peak), ClO_2^+, COF_2^+, ClO^+, CF_2^+, and COF^+. The following infrared bands were observed (cm^{-1}, intensity): 1340 (sh), 1325 (sh), 1290 (vs), 1250 (sh), 1235 (vs), 1200 (m), 1171 (w), 1153 (m), 1119 (ms), 1088 (m), 1026 (s), 988 (s), 968 (m–s), 784 (w), 746 (m), 723 (w), 676 (m), 641 (m–s), 614 (s), 530 (w).

Reaction with Tetrafluoroethylene. Fluorine perchlorate (0.61 mmol) and C_2F_4 (0.62 mmol) were combined at −196 °C in a 10-mL stainless steel cylinder. By evaporation of the liquid nitrogen from a liquid nitrogen–dry ice slush used to cool the reaction cylinder, the temperature was allowed to slowly rise to −78 °C and finally over several days by loss of solid CO_2 to about −45 °C. Fractional condensation of the products at −112 and −196 °C permitted the isolation of $C_2F_5OClO_3$ (0.42 mmol, 68% yield) which was identified by its known vibrational, NMR, and mass spectra.[8] Smaller amounts of CF_3CFO, C_2F_6, Cl_2, and O_2 were observed as byproducts.

Reaction with Trifluoromethyl Iodide. Into a cold (−196 °C) 30-mL stainless steel cylinder CF_3I (0.66 mmol) and then $FOClO_3$ (1.40 mmol) were condensed. Warm-up to about −45 °C was accomplished slowly as noted in the preceding example. After several days at −45 °C the reactor was recooled to −196 °C, and the presence of a considerable amount of noncondensable gas (oxygen) was noted. Fractionation of the condensable products showed a mixture of COF_2, CF_4, Cl_2, I_2, IF_5, and a solid iodine oxide to be the principal species present. However, a small amount of CF_3OClO_3 (0.05 mmol, 8% yield) was also found and identified by comparison with reported data.[8]

Results and Discussion

Under carefully controlled reaction conditions, similar to those previously used for the polar additions of $ClOClO_3$ and $BrOClO_3$,[7] fluorine perchlorate was found to add across olefinic double bonds in high yield. With tetrafluoroethylene the following reaction occurred:

$$CF_2{=}CF_2 + FOClO_3 \xrightarrow{-45\ ^\circ C} CF_3CF_2OClO_3$$

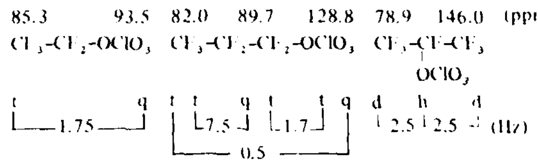
With the unsymmetrical olefin perfluoropropylene a mixture of two isomers was found:

$$CF_3CF{=}CF_2 + FOClO_3 \xrightarrow{-45\ ^\circ C} \underset{68\%}{CF_3CF_2CF_2OClO_3} + \underset{32\%}{CF_3CF(OClO_3)CF_3}$$

These two perfluoropropyl perchlorates are novel compounds which were identified by vapor density measurements and spectroscopic data. The presence of the covalent $-OClO_3$ group was demonstrated by infrared spectroscopy which showed the intense bands typical of this group[8] at 1290 ($\nu_{as}(ClO_3)$), 1026 ($\nu_s(ClO_3)$), and 614 cm^{-1} ($\nu(Cl{-}O)$). Additional support for the covalent perchlorate structure was obtained from the mass spectrum which showed strong peaks for the ions, ClO_3^+, ClO_2^+, and ClO^+ but not for ClO_4^+, as is generally the case for fluorocarbon perchlorates. A parent ion was not observed, and the highest m/e was $C_2F_4ClO_4^+$, i.e., the parent minus a CF_3 group.

Gas chromatography of the product revealed a slight asymmetry for the $C_3F_7ClO_4$ peak, thereby indicating the presence of isomers. This was confirmed by ^{19}F NMR spectroscopy, showing that both possible adducts were formed. The observed chemical shifts and coupling constants, together

Chart I



with higher resolution data than previously *reported*[8] *for* $C_2F_5OClO_3$, are summarized in Chart I (d = doublet, t = triplet, q = quartet, h = heptet). The resonances of fluorines geminal to a perchlorato group were broadened due to chlorine quadrupole relaxation. On the basis of their relative peak areas, the ratio of the two isomers was *n* 68% and iso 32%.

The fact that in the reaction of $FOClO_3$ with $CF_3CF{=}CF_2$ both isomers are formed significantly differs from the previously reported[6] $ClOClO_3$ and $BrOClO_3$ reactions where exclusive Markownikoff type additions occurred. The latter produced 100% of $CF_3CFXCF_2OClO_3$, as expected for a polar addition of the positively polarized terminal halogen to the carbon with the highest electron density.[7]

$$CF_3CF{=}CF_2 + Cl^{\delta+}\ O^{\delta}ClO_3 \rightarrow CF_3CFClCF_2OClO_3$$

The formation of both isomers (*n* and iso) in the corresponding $FOClO_3$ reaction suggests that the F O bond in $FOClO_3$ is not strongly polarized in either direction. This is not surprising in view of the known very small dipole moment (0.023 D) of the closely related $FClO_3$ molecule[9] and the expected similar electronegativities of a ClO_3 and an $OClO_3$ group. The fact that the percentage of *n* isomer was somewhat higher than that of the iso isomer can be explained by steric effects (bulky CF_3 group) and is insufficient reason to postulate a strongly positive fluorine in $FOClO_3$. The occurrence of a free-radical mechanism is unlikely in view of the high yield of the products (74%), the mild (45 °C) and well-controlled reaction conditions, and the absence of detectable amounts of C_3F_8 and $C_3F_6(OClO_3)_2$ in the reaction products.

In contrast to the olefin addition reactions, the reaction of $FOClO_3$ with CF_3I was more difficult to control. The primary reaction path appears to have involved oxidation of the iodine followed by degradation to oxygenated and fluorinated species. Nevertheless, a modest yield (8%) of the desired perchlorate, CF_3OClO_3, was realized. By comparison, the $ClOClO_3$–CF_3I reaction is also vigorous but can be controlled to give a nearly quantitative yield of CF_3OClO_3.[8]

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

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

Registry No. $FOClO_3$, 10049-03-3; $CF_3CF_2CF_2OClO_3$, 70749-47-2; $CF_3CF(OClO_3)CF_3$, 70749-48-3; $C_2F_5OClO_3$, 22675-67-8; CF_3OClO_3, 52003-45-9; C_3F_6, 116-15-4; C_2F_4, 116-14-3; CF_3I, 359-37-5.

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

APPENDIX G

SYNTHESIS AND PROPERTIES OF $NF_4^+UF_5O^-$

William W. Wilson, Richard D. Wilson and Karl O. Christe*

Received . . . . .

Abstract

A new method for the synthesis of NF_4^+ salts is reported. It permits the synthesis of otherwise inaccessible salts derived from nonvolatile Lewis acids which do not possess HF - soluble cesium salts. The method was successfully applied to the synthesis of the novel salt $NF_4^+UF_5O^-$. This compound is a yellow solid, stable at room temperature. It was characterized by analysis and vibrational spectroscopy.

Introduction

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

$$NF_3 + F_2 + XF_n \xrightarrow{\Delta E} NF_4^+ XF_{n+1}^-$$

If the Lewis acid is polymeric and nonvolatile, its NF_4^+ salt can usually be prepared by an indirect metathetical process [3,4], provided a compatible solvent is available in which the starting materials are soluble and one of the products is insoluble. This metathetical approach has been demonstrated for several NF_4^+ salts [3 - 7]. A typical example is the synthesis of $(NF_4)_2NiF_6$ in anhydrous HF solution [7] using the cesium salts. The latter salts are preferred because they exhibit the most favorable solubility products for a metathesis in HF[4]:

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

However, in cases where the corresponding cesium salt starting material or both products are insoluble in the solvent and the Lewis acid is nonvolatile, neither one of the above approaches can be used. In this paper a method which circumvents these problems is described and is applied to the synthesis of the novel salt $NF_4^+UF_5O^-$.

Experimental

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described [8]. Literature methods were used for the syntheses of UF_4O[9], KUF_5O[10], and NF_4SbF_6[3]. The CsF (American Potash) was fused in a platinum crucible and ground in the dry box. The HF (Matheson) was dried by treatment with F_2, followed by storage over BiF_5 to remove last traces of water [4].

Preparation and Properties of $NF_4^+UF_5O^-$. In a typical experiment, a solution of NF_4HF_2 (12.5 mmol) in anhydrous HF (12.5g) was prepared from NF_4SbF_6 and CsF at -78^o, as previously described [8], and added to UOF_4 (6.18 mmol). The resulting mixture was kept at -78^o for 40 hours, then warmed to -31^o for 6 hours with stirring, followed by removal of all volatile products in vacuo by slowly raising the temperature from -31^o to 20^oC. A yellow solid residue (2.70 g, weight calcd for 6.18 mmol of NF_4UF_5O=2.71 g) was obtained. This compound was stable at ambient temperature and of low solubility in HF. It was identified by elemental analysis and vibrational spectroscopy as $NF_4^+UF_5O^-$. For the elemental analysis, a weighed amount of sample was hydrolyzed in H_2O and the NF_3 evolution was measured [12]. The hydrolysate was analyzed for Cs and Sb by atomic absorption spectroscopy, and for U gravimetrically as U_3O_8. Based on this analysis, the compostion (weight %) of the yellow solid was: NF_4UF_5O, 96.8; NF_4SbF_6, 1.7; $CsSbF_6$, 1.4.

The thermal decomposition of $NF_4^+UF_5O^-$ was studied in a sapphire reactor, equipped with a pressure transducer. The onset and rate of decomposition was determined by total pressure measurements [13] in a closed system over the temperature range $40\text{-}60^oC$. For the determination of the decomposition products, a sample of NF_4UF_5O (2 mmol) was rapidly heated to 150°C in a dynamic vacuum, and the volatile products were collected in traps, cooled to -126° and -210°C, and were identified by their infrared spectra. The -126°C trap contained 1.1 mmol of UF_6, and the contents of the -210°C trap consisted of 1.5 mmol of NF_3 and a small amount of OF_2. The infrared spectrum of the pale yellow solid residue (350 mg) showed strong bands characteristic for UF_4O [9], UO_2F_2[14], NF_4^+ [2 - 8], and two broad bands at 520 and 410 cm^{-1}, probably due to UF_n vibrations. In addition, the spectrum indicated the presence of a small amount of UF_5O^- [10,11].

Results and Discussion

Synthesis. The metathetical synthesis of NF_4UF_5O according to

$$NF_4SbF_6 + MUF_5O \xrightarrow{HF} MSbF_6\downarrow + NF_4UF_5O$$

was not possible because both the MUF_5O (M = alkali metal) and NF_4UF_5O salts possess very low solubilities in anhydrous HF. Furthermore, in agreement with a previous report [10], we could not prepare a well defined $CsUF_5O$ salt by the reaction of CsF with UF_4O in anhydrous HF solution. The product always contained a large amount of unreacted UF_4O. Attempts to obtain reasonably pure NF_4UF_5O by a metathetical reaction using stoichiometric amounts of UF_4O, CsF, and NF_4SbF_6 in HF as starting materials, were also unsuccessful due to the unfavorable solubilities. However, preparation of an HF solution of NF_4HF_2 [8] according to

$$NF_4SbF_6 + CsHF_2 \xrightarrow[-78^{\circ}]{HF} NF_4HF_2 + CsSbF_6\downarrow$$

followed by removal of the insoluble $CsSbF_6$ by filtration at -78° and addition of this solution to UF_4O, resulted in NF_4UF_5O of about 97% purity.

$$NF_4HF_2 + UF_4O \xrightarrow{HF} NF_4UF_5O + HF$$

A twofold excess of NF_4HF_2 was used to ensure complete conversion of UF_4O to UF_5O^-. After solvent removal, the excess of unreacted NF_4HF_2 was decomposed [8] at 40°C to NF_3, F_2 and HF which were pumped off.

Properties. NF_4UF_5O is a yellow, crystallinic solid, stable up to about 50°C. Its composition was established by elemental analysis. The ionic nature of the salt was demonstrated by vibrational spectroscopy which showed the presence of the NF_4^+ cation and UF_5O^- anion. For comparison, a sample of KUF_5O was prepared from KF and UF_4O in HF, as previously reported [10] and its spectra were also recorded. The infrared spectra of NF_4UF_5O and KUF_5O are shown in Figure 1, and the observed infrared and Raman frequencies are summarized in Table 1. Whereas the infrared spectrum of KUF_5O is in good agreement with those [10,11] previously reported, the recording of a Raman spectrum with the available exciting line (4880Å) was very difficult due to fluorescence, strong color and poor scattering. For NF_4UF_5O, a similar, but not quite as severe, problem existed. Based on some of the Raman bands, observed for UF_5O^- in NF_4UF_5O, and by comparison with the well defined infrared bands, it appears that some of the Raman bands previously reported [10] for KUF_5O are open to question.

The assignments of the bands due to NF_4^+ are well established [2-8] and require no further discussion. For the UF_5O^- anion, only the stretching vibrations can be assigned with some confidence. The band in the 810-835 cm^{-1} region occurs at too high a frequency for a U-F stretching mode and, therefore, is assigned to the UO stretch. The intensity and band width of the 580-600 cm^{-1} band in both the infrared and Raman spectra are comparable to those of the UO stretch and is therefore, assigned to the unique UF stretching mode. The broad intense infrared band at about 490 cm^{-1} should represent the antisymmetric UF_4 stretch, and the strong Raman band at about 490 cm^{-1} is assigned to the symmetric in-phase UF_4 stretching mode. The weak infrared band at about 430 cm^{-1} could be due to either the symmetric out-of-phase UF_4 stretching mode $\nu_5(B_1)$, (assuming that for the solid the site symmetry of UF_5O^- is lower than C_{4v}), or the OUF_4 deformation mode ν_9 (E). However, for the latter assignment, the frequency appears somewhat high and is shifted in the wrong direction when going from KUF_5O to NF_4UF_5O. Due to the stronger anion-cation interaction in KUF_5O, the stretching modes are expected to be shifted to lower and the deformation modes to higher frequencies.

The thermal decomposition of NF_4UF_5O was studied in more detail since the decomposition of NF_4^+ salts containing oxyanions has been shown [8, 15, 16] to be a useful synthetic route to hypofluorites. The NF_4UF_5O salt is stable up to about 50°C, but started to decompose in a sapphire reactor at 60°C at an approximately linear rate, resulting in a pressure build-up of about 4.6 mm Hg per hour for a 2 mmol sample in a 38.7 cc volume. The nature of the decomposition products was established by rapid pyrolysis at 150°C in a dynamic vacuum. The main decomposition products, condensible at -210°C, were NF_3, UF_6, and a small amount of OF_2. The pale yellow solid residue contained UF_4O and UO_2F_2 as the major products. The formation of UF_4O, UF_6 and UO_2F_2 as main decomposition products can be readily explained by assuming

$$NF_4UF_5O \rightarrow NF_3 + F_2 + UF_4O$$

as the primary decomposition step, followed by the well established [9, 17] decomposition of UF_4O

$$2UF_4O \rightarrow UF_6 + UO_2F_2$$

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

Conclusion. The results of this study show that NF_4^+ salts which are derived from nonvolatile polymeric Lewis acids and are insoluble in HF, are accessible by treating the corresponding Lewis acid with an excess of NF_4HF_2 in HF solution. Although this approach has so far been demonstrated only for UF_4O, it might be of general use.

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Diagram Caption

Figure 1. Infrared spectra of KUF_5O and NF_4UF_5O recorded as dry powders pressed between AgCl disks. The broken lines represent absorption due to the AgCl window material.

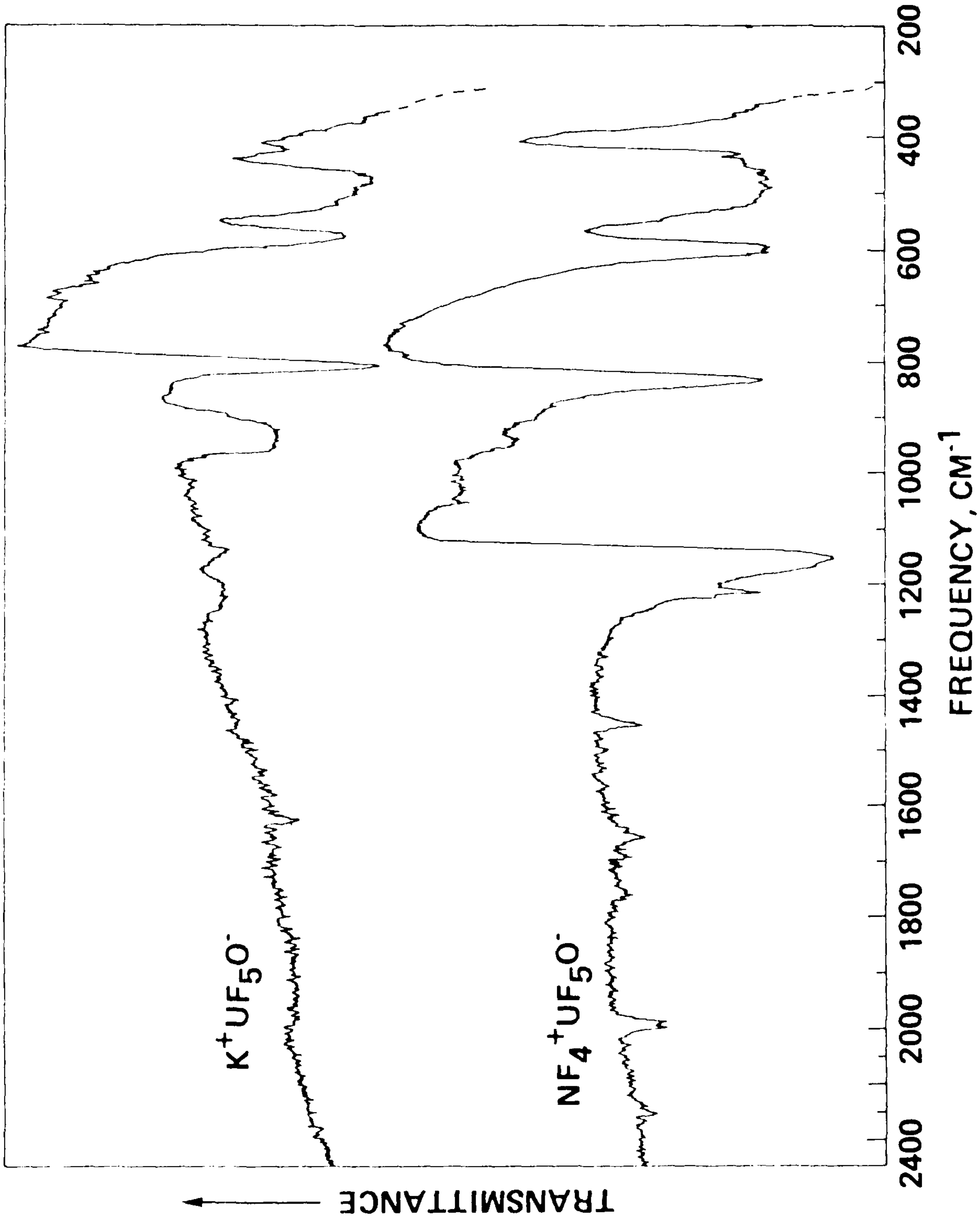

$K^+UF_5O^-$
$NF_4^+UF_5O^-$
FREQUENCY, CM^{-1}
200
400
600
800
1000
1200
1400
1600
1800
2000
2400
TRANSMITTANCE

Table I. Vibrational Spectra of NF[illegible] and KUF_5O and their Assignment

Obsd freq, cm^{-1} and rel. intens[a]				Assignment (point group)	
KUF_5O		NF_4UF_5O		NF_4^+ (T_d)	UF_5O^- (C_{4v})
IR	Ra	IR	Ra[b]		
		2310vw		$2\nu_3(A_1+E+F_2)$	
		2000w		$\nu_1+\nu_3(F_2)$	
		1765vw		$\nu_3+\nu_4(A_1+E+F_2)$	
1630vw		1660vw			$2\nu_1(A_1)$
		1459w		$\nu_1+\nu_4(F_2)$	
1230vw		1250sh			ν_1+430 c
		1215mw		$2\nu_4(A_1+E+F_2)$	
		1155vs	1165vw	$\nu_3(F_2)$	
1150vw					$2\nu_2(A_1)$
		1050vw		$\nu_2+\nu_4(F_1+F_2)$	
940m		945mw			ν_2+360 c, d
			850 sh	$\nu_1(A_1)$	
812vs	815s	834vs	837vs		$\nu_1(A_1)$
			610 sh	$\nu_4(F_2)$	
582vs		600vs	601s		$\nu_2(A_1)$
			492 m		$\nu_3(A_1)$
475vs,br		490vs,br			$\nu_8(E)$
425w		431w			$\nu_9(E)$ or $\nu_5(B_1)$ c
370sh		360sh			$\nu_{10}(E)$ or $\nu_9(E)$ c

(a) uncorrected Raman intensities

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

(c) tentative assignments

(d) this band has previously also been reported [10] for KUF_5O, however, its relative intensity appears much too high for a combination band and therefore the band might be due to some UO_2^{2+}.

APPENDIX H

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

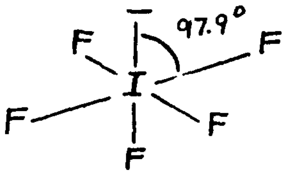
Sir:

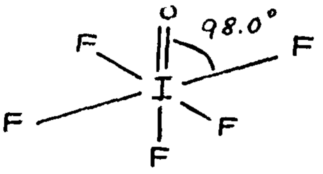
The Gillespie-Nyholm valence shell electron pair repulsion (VSEPR) theory[1,2] is very useful for explaining the basic structural features of many classes of inorganic compounds. The theory assumes that the geometry around a given central atom is determined by the number of electron pairs in its valence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

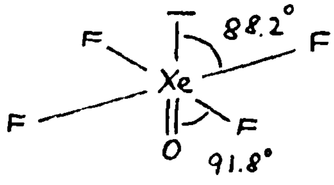
Contrary to the ligands in a tetrahedron or octahedron, those in a trigonal bipyramidal molecule, when arranged as equidistant points on a sphere, are not equivalent. The two axial ligands have a greater (ideally by a factor of $\sqrt{2}$) central atom-ligand bond length than the three equatorial ligands. Consequently, an equatorial ligand possesses two nonequivalent pairs of neighbors, one axial one of greater bond length and ideally at 90° angles, and one equatorial one of shorter bond length and ideally at 120° angles.

In this paper, two cases are presented which are strong evidence for the existence of directional repulsion effects in trigonal bipyramidal molecules. These two cases are (i) a comparison of the structures of SF_4[3,4] and $X{=}SF_4$ (where X is O or CH_2),[5-10] and (ii) the structure of ClF_3O.[11] In the first case, the relative repulsion of the axial and of the equatorial fluorine ligands by either the Π-bonds of a double bond or a free valence electron pair is compared, whereas in the second case, the combined effect of a lone pair and of a doubly bonded oxygen is described.

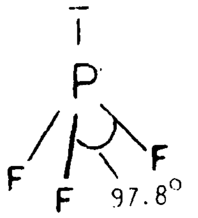
For a meaningful comparison, we must first establish the relative replulsive strength of a lone valence electron pair and of a doubly bonded oxygen in the absence of directional effects. Inspection of the known structures of IF_5[12] and IF_5O[13] and of $XeOF_4$[14]

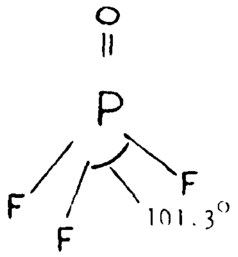






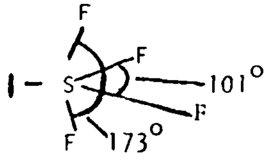
shows that in these pseudo-octahedral molecules the repulsive strengths of a lone valence elctron pair and of a doubly bonded oxygen are very similar, and that, as demonstrated for $XeOF_4$, the oxygen can be even slightly more repulsive than a free valence electron pair. In the pseudo-tetrahedral modecules PF_3 and PF_3O,[2] the free valence electron pair appears to be somewhat more repulsive than oxygen.

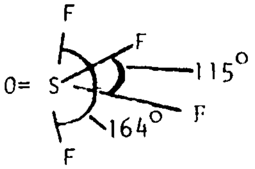


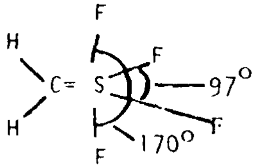


The above examples show that, for practical purposes, the nondirectional repulsive strengths of a free valence electron pair and of a doubly bonded oxygen are comparable. For a more precise comparison, effects such as changes in the oxidation state of the central atom or in the hybridization of the orbitals,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

Returning to the less symmetric case of trigonal bipyramidal molecules let us consider the structures of SF_4, $O=SF_4$ and $H_2C=SF_4$.







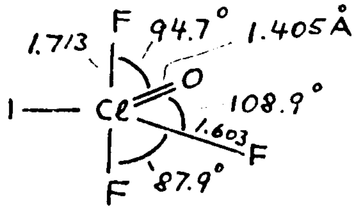
As recently pointed out by Oberhammer and Boggs,[6] the FSF bond angles are surprisingly different in these molecules, but could be well duplicated by ab initio MO calculations. These calculations showed that the observed differences in the structures of $O=SF_4$ and $H_2C=SF_4$ can be satisfactorily explained by the different population of the X=S Π-bond orbitals in the equatorial and the axial plane (OSF_4, Π_{eq}=0.17a.u., Π_{ax}=0.12a.u., $H_2C=SF_4$, Π_{eq}=0.23a.u., Π_{ax}=0.02a.u.).

The comparatively small $F_{eq}SF_{eq}$ bond angle of SF_4 can be rationalized in the following manner. A lone electron pair can be delocalized rather easily, as shown by a comparison of BrF_6^-[15] and IF_6^-.[16] Although in both ions, the central atom possesses a lone valence electron pair, the seize of bromine permits only a maximum coordination number of six (toward fluorine) and the lone pair in BrF_6^- is sterically inactive and centrosymmetric. In IF_6^-, the larger central atom can readily accept seven or eight ligands, as demonstrated by the existence of IF_7 and IF_8^-,[17,18] and, therefore, the lone valence electron pair becomes sterically active and is localized. Due to its ease of delocalization, a free valence electron pair can then be expected to compress in a trigonal bipyramidal arrangement preferentially that FSF angle, which is more easily compressed. Since in an ideal trigonal bipyramid the equatorial FSF angle is 120°, it should be compressed more easily than the two axial fluorine which must be compressed against the fluorine containing equatorial plane which is at a 90° angle.

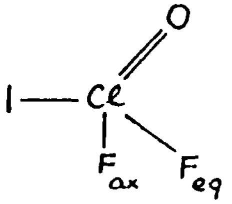
On the other hand, the Π-orbitals of an S=X double bond are more localized and concentrated between the sulfur and the X atom in the equatorial and the axial plane of the molecule. Depending on the relative population of these orbitals, preferential repulsion of either the axial or the equatorial fluorines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

In view of these directional repulsion effects, the change in a single bond angle is not a good measure for the overall repulsive strength of a ligand or a free valence electron pair. Since the repulsion of all the other ligands must be considered, the average quadruple angle[10] should be used for such a comparison. In SF_4, OSF_4 and H_2CSF_4, these average quadruple angles are 111.5, 110.3 and 113.3°, respectively, indicating that the overall repulsive strengths of a free valence electron pair and of a S=X Π-bond are, within experimental error, quite similar, but that they strongly differ in their directions.

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



SIDE VIEW



TOP VIEW

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

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

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APPENDIX I

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

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Received March 5, 1979

The synthesis and properties of $H_3O_2{}^+Sb_2F_{11}{}^-$, $H_3O_2{}^+SbF_6{}^-$, and $H_3O_2{}^+AsF_6{}^-$, the first known examples of peroxonium salts, are reported. These salts were prepared by protonation of H_2O_2 in anhydrous HF solutions of the corresponding Lewis acids. They were isolated as metastable solids which underwent decomposition to the corresponding H_3O^+ salts and O_2 in the temperature range 20–50 °C. The $H_3O_2{}^+$ salts were characterized by vibrational and NMR spectroscopy. Modified valence force fields were computed for the isoelectronic series H_2OOH^+, H_2NOH, and H_2NNH^-. The similarity of their observed spectra and computed force fields suggests that the ions are isostructural with H_2NOH which possesses C_s symmetry with the unique hydrogen being trans to the other two hydrogens. The influence of protonation on the stretching frequency of the two central atoms is discussed for the series HOO^-, HOOH, H_2OOH^+, H_2NNH^-, H_2NNH_2, $H_3NNH_2{}^+$, and $H_3NNH_3{}^{2+}$. Attempts to protonate both oxygen atoms in H_2O_2 to form $H_4O_2{}^{2+}(SbF_6{}^-)_2$ resulted in $H_3O_2{}^+Sb_2F_{11}{}^-$ as the only product. The strongly oxidizing Lewis acid BiF_5 underwent a redox reaction with H_2O_2 in HF, resulting in quantitative reduction of BiF_5 to BiF_3, accompanied by O_2 evolution. When a 2:1 excess of BiF_5 was used, an adduct formed having the approximate composition $BiF_3 \cdot BiF_5$. Heating a mixture of solid $H_3O_2{}^+Sb_2F_{11}{}^-$ with a strongly fluorinating agent, such as BiF_5 or Cs_2NiF_6, resulted in a green chemiluminescence band centered at 5150 Å.

Introduction

Anhydrous HF–Lewis acid solutions are ideally suited to protonate less acidic substrates. This technique has successfully been applied to the isolation of novel salts containing the H_3O^+,[1-4] H_3S^+,[5,6] $NH_2F_2{}^+$,[7] and $AsH_4{}^+$[6] cations. Since all these cations contain a single central atom, it appeared interesting to extend this method to a substrate containing two central atoms, such as H_2O_2. In such a case, both single and double protonation are possible, and the influence of protonation on the strength of the bond between the two central atoms can be studied. Such effects are well-known[8] for the related hydrazine molecule. Although the $HO_2{}^-$ anion is known,[9,10] to our knowledge the corresponding cations derived from H_2O_2 have only been postulated,[11] but not characterized or isolated as salts.

Further interest was added to this study by the fact that H_2O_2 is a starting material for the generation of excited molecular oxygen which in turn is of great interest for a near resonant energy-transfer iodine laser. Therefore, the combination of an $H_3O_2{}^+$ cation with a strongly oxidizing anion in the form of a stable salt could provide a suitable solid-propellant gas generator for excited oxygen.

Experimental Section

Materials and Apparatus. Volatile materials used in this work were manipulated in well-passivated (with ClF_3 and HF) vacuum lines constructed either entirely from Monel Teflon-FEP or entirely from Teflon-PFA with injection-molded fittings and valves (Fluoroware Inc.). Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Hydrogen fluoride was dried by treatment with F_2, followed by storage over BiF_5 to remove last traces of H_2O.[3] Antimony pentafluoride and AsF_5 (Ozark Mahoning Co.) were purified by distillation and fractional condensation, respectively. Bismuth pentafluoride (Ozark Mahoning Co.) was used as received. Hydrogen peroxide (90%, FMC Corp.) was purified by repeated fractional crystallization,[12] and material of 99.95% purity, as analyzed by titration with $KMnO_4$ solution, was obtainable by this method. All equipment, used for handling H_2O_2, was washed with 12 N H_2SO_4, thoroughly rinsed with distilled H_2O and dried in an oven prior to use. For the hazards and necessary precautions of handling concentrated H_2O_2 see ref 12. The synthesis of Cs_2NiF_6 has previously been described.[13]

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

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[15] for the elimination of plasma lines. Sealed quartz or Teflon-FEP tubes were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature spectra were recorded with a previously described[16] device. Polarization measurements were carried out according to method VIII listed by Claassen et al.[15]

Debye–Scherrer powder patterns were taken with a GE Model XRD-6 diffractometer. Samples were sealed in quartz capillaries (~0.5-mm o.d.).

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

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

For the chemiluminescence experiments, $H_3O_2Sb_2F_{11}$ was mixed with either solid BiF_5 or Cs_2NiF_6 and placed into the bottom of a Pyrex glass tube which was equipped with a stopcock. The tube was connected to a vacuum manifold and heated in a dynamic vacuum by a stream of hot air until gas evolution and chemiluminescence were observed. The emitted light was analyzed with a 0.5-m McKee-Pederson monochromator over the range 2000–10 000 Å using a spectral slit width of 25 Å.

Preparation of $H_3O_2{}^+AsF_6{}^-$. In a typical experiment, AsF_5 (15.39 mmol) and anhydrous HF (50.76 mmol) were combined at −196 °C is a passivated Teflon-FEP ampule equipped with a valve. The mixture was allowed to melt and homogenize. The ampule was then taken to the drybox, and H_2O_2 of 99.95% purity (15.29 mmol) was syringed in at −196 °C. The ampule was transferred back to the vacuum line and evacuated at −196 °C; it was then kept at −78 °C for 2 days to allow reaction. After this period, no evidence was found for material noncondensable at −196 °C, i.e., no O_2 evolution. The mixture was warmed to −45 °C, and a clear solution resulted. Material volatile at −45 °C was removed by pumping for 10 h and was collected at −196 °C. A white solid residue resulted which was of marginal stability at ambient temperature. On the basis of the observed material balance (weight of 15.29 mmol $H_3O_2AsF_6$: calcd, 3.423 g; found, 3.47 g), the conversion of H_2O_2 to $H_3O_2AsF_6$ was complete within experimental error. The compound was shown by infrared and Raman spectroscopy to contain the $H_3O_2{}^+$ cation and $AsF_6{}^-$ anion.[1,7,17-20]

Thermal Decomposition of $H_3O_2{}^+AsF_6{}^-$. A sample of $H_3O_2AsF_6$ (28.93 mmol) was allowed to decompose at ambient temperature. An exothermic reaction occurred, generating 14.6 mmol of O_2 and a white solid residue which was identified by vibrational spectroscopy as $H_3O^+AsF_6{}^-$.[1]

Preparation of $H_3O_2{}^+SbF_6$. Antimony pentafluoride (27.96 mmol) was added in the drybox to a passivated Teflon-FEP U-tube equipped with two valves and a Teflon-coated magnetic stirring bar. Anhydrous HF (522.9 mmol) was added on the vacuum line at −196 °C, and the mixture was homogenized by stirring at 20 °C. In the drybox hydrogen peroxide (27.97 mmol) was syringed into the U-tube at −196

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°C. The cold tube was transferred back to the vacuum line and was evacuated. The tube was warmed from −196 to −78 °C for 1 h with agitation which resulted in the formation of a finely divided white solid, suspended in the liquid HF. When the mixture was warmed to 20 °C, the white solid completely dissolved. No gas evolution was observed during the entire warm-up operation, and no noncondensable material could be detected when the mixture was cooled again to −196 °C. The HF solvent was pumped off at −22 °C for 3 h resulting in 7.566 g of a white solid (weight calculated for 27.96 mmol of $H_3O_2SbF_6$ = 7.570 g), stable at 20 °C. The compound was shown by vibrational spectroscopy to be composed of $H_3O_2^+$ cations and SbF_6^- anions.[1,5,7,18,19] Additional support for the composition of the product was obtained by allowing a sample of $H_3O_2SbF_6$ to thermally decompose at about 45 °C. This decomposition produced O_2 and the known H_3OSbF_6 salt[1] in almost quantitative yield.

Preparation of $H_3O_2Sb_2F_{11}$. The synthesis of this compound was carried out in a manner identical with that described above for the preparation of $H_3O_2SbF_6$, except for using an excess of SbF_5. Thus, the combination of SbF_5 (14.83 mmol), HF (407 mmol), and H_2O_2 (6.83 mmol) produced 3.581 g of a white solid (weight calculated for 6.83 mmol of $H_3O_2SbF_6 \cdot 1.17SbF_5$ = 3.581 g), stable up to about 50 °C. The compound was shown by vibrational and NMR spectroscopy to contain the $H_3O_2^+$ cation and $Sb_2F_{11}^-$ as the principal anion.

The H_2O_2–HF–BiF_5 System. Bismuth pentafluoride (10.68 mmol), HF (394 mmol), and H_2O_2 (10.15 mmol) were combined in a passivated Teflon ampule in a manner analogous to that described for the preparation of $H_3O_2SbF_6$. The mixture was warmed from −196 °C to ambient temperature. During the warm-up operation gas evolution was observed which was accompanied by the formation of a copious white precipitate which showed little solubility in HF at ambient temperature. Bands due to either BiF_6^-[3] or BiF_5[21,22] (both are strong Raman scatterers) could not be detected in the Raman spectra of either the liquid or the solid phase. The evolved gas was removed from the ampule at −196 °C and consisted of 10.1 mmol of O_2. The material volatile at 20 °C was pumped off, leaving behind 2.897 g of a white solid which was identified by vibrational spectroscopy as BiF_3[3,23] (weight calculated for 10.68 mmol BiF_3 = 2.841 g).

When BiF_5 and H_2O_2 in a mole ratio of 2:1 were combined in a similar manner in anhydrous HF solution, the weight of the resulting white stable solid product closely corresponded to that expected for $BiF_3 \cdot BiF_5$. The product was characterized by vibrational spectroscopy which showed it to be an adduct and not a simple physical mixture of BiF_3 and BiF_5.

Results and Discussion

Synthesis. On the basis of the observed material balances, H_2O_2 is protonated in HF–MF_5 (M = As, Sb) solutions according to

$$H_2O_2 + HF + MF_5 \rightarrow H_3O_2^+MF_6^-$$

No evidence was found for double protonation, i.e., $H_4O_2^{2+}$ formation, even when SbF_5 was used in a twofold excess. Instead, the polyanion $Sb_2F_{11}^-$ was formed according to

$$H_2O_2 + HF + 2SbF_5 \rightarrow H_3O_2^+Sb_2F_{11}^-$$

It is interesting to compare these results with those previously reported[24] for the N_2H_4–HF–TaF_5 system for which double protonation, i.e., $N_2H_6^{2+}(TaF_6^-)_2$ and $N_2H_6^{2+}TaF_7^{2-}$ formation, has been observed. Although other effects, such as the relative solubilities of the possible products, are certainly important, the predominant reason for the exclusive single protonation of H_2O_2 appears to be its decreased basicity. Whereas N_2H_4 is a weak base in aqueous solution (pK_b = 5.77), H_2O_2 is a weak acid (pK_a = 11.6). With increasing protonation, the basicity of the resulting cations further decreases, and $N_2H_5^+$ (pK_a = 6.1) becomes a weak and $N_2H_6^{2+}$ (pK_a = −1) a strong acid.[24,25] Whereas $N_2H_5^+$ has an acidity comparable to that of H_2S (pK_a = 7) which is known[5,6] to form stable H_3S^+ salts, $H_3O_2^+$ is too acidic to undergo further protonation to $H_4O_2^{2+}$.

Attempts to prepare $H_3O_2^+$ salts derived from BiF_5 were unsuccessful. The latter is a relatively strong oxidizer and is readily reduced by H_2O_2 in HF solution according to

$$BiF_5 + H_2O_2 \rightarrow BiF_3 + 2HF + O_2$$

When a twofold excess of BiF_5 was used, the following reaction was observed:

$$2BiF_5 + H_2O_2 \rightarrow BiF_3 \cdot BiF_5 + 2HF + O_2$$

The resulting $BiF_3 \cdot BiF_5$ product was shown by vibrational spectroscopy [Raman: 591 (10), 583 (4.6), 538 (1.5), 521 (0.1), 496 (0.6), 475 (sh), 232 (0.5, br), 120 (0.2, br) cm^{-1}. IR: 708 (w), 615 (s), 606 (sh), 575 (s), 550 (sh), 535 (vs), 400–500 (m, vbr) cm^{-1}] not to be a physical mixture of BiF_3[3,23] and BiF_5.[21,22] By analogy with the known BiF_3–SbF_5 and SbF_3–SbF_5 systems,[26-28] a $BiF_3 \cdot BiF_5$-type adduct appears most plausible. However, in view of the complexity of the products formed in the SbF_3–SbF_5 system,[27,28] a detailed characterization of this $BiF_3 \cdot BiF_5$ adduct was beyond the scope of this study.

Properties. The $H_3O_2^+SbF_6^-$, $H_3O_2^+Sb_2F_{11}^-$, and $H_3O_2^+AsF_6^-$ salts are white crystalline solids. X-ray powder patterns were taken for $H_3O_2^+Sb_2F_{11}^-$ but contained too many lines to allow indexing. All these $H_3O_2^+$ salts are of marginal thermal stability and were shown to undergo exothermic decomposition to the well-known[1] H_3O^+ salts according to

$$H_3O_2^+MF_6^- \rightarrow H_3O^+MF_6^- + {}^1/{}_2O_2$$

Of the above $H_3O_2^+$ salts, the AsF_6^- salt is the least stable and easily decomposes at room temperature. The $H_3O_2Sb_2F_{11}$ salt was found to be most stable. On the basis of DSC data, its decomposition starts with a small endotherm at 51 °C, followed by a large exotherm. In a sealed melting point capillary, decomposition accompanied by foaming was observed at about 65 °C. The thermal stability of $H_3O_2SbF_6$ is intermediate between those of $H_3O_2AsF_6$ and $H_3O_2Sb_2F_{11}$. It should be pointed out that the thermal stability of these $H_3O_2^+$ salts appears to decrease in the presence of free H_2O_2. Probably, the highly acidic $H_3O_2^+$ salt catalyzes the exothermic decomposition of H_2O_2, with the evolved heat promoting the decomposition of the $H_3O_2^+$ salt itself.

The reaction of $H_3O_2^+$ salts with fluorinating agents appeared interesting as a potential method for the generation of excited molecular oxygen (O_2*). Antimony pentafluoride or SbF_6^- were not strong enough oxidizers to fluorinate $H_3O_2^+$, and BiF_6^- reacted at too low a temperature with H_2O_2 to permit isolation of the desired $H_3O_2BiF_6$ salt. Therefore, the concept could not be directly tested to produce O_2* by the simple thermal decomposition of a salt composed of $H_3O_2^+$ and an oxidizing anion. However, when solid $H_3O_2Sb_2F_{11}$ was mixed at room temperature with a solid oxidizer, such as BiF_5 or Cs_2NiF_6, and when this mixture was heated to about 80 °C, a reaction occurred which was accompanied by green (5150-Å) chemiluminescence. This 5150-Å band did not exhibit detectable fine structure, and no additional bands were observed over the range 2000–10 000 Å. Consequently, the 5150-Å emission is not attributed to either vibrationally excited HF[29] or O_2.[30]

Nuclear Magnetic Resonance Spectra. The ^{19}F NMR spectrum of $H_3O_2SbF_6 \cdot 1.17SbF_5$ was recorded for a SO_2 solution at −90 °C. It showed resonances (ϕ 91, multiplet; 111, doublet of doublets; 133, quintet) characteristic[31] for $Sb_2F_{11}^-$. In addition, a weaker doublet at ϕ 102 was observed which is characteristic[31,32] for $SbF_5 \cdot SO_2$. The quintet part of this species could not be directly observed since it exhibits a chemical shift similar to that of the quintet of $Sb_2F_{11}^-$. The observation of some $SbF_5 \cdot SO_2$ is in excellent agreement with a previous report[31] that the highest polyanion observed for $SbF_6^- \cdot nSbF_5$ in SO_2 solution is $Sb_2F_{11}^-$, with any remaining SbF_5 being converted to $SbF_5 \cdot SO_2$. In addition to the signals due to $Sb_2F_{11}^-$ and $SbF_5 \cdot SO_2$ a weak unresolved signal was

Table I. Vibrational Spectra of $H_3O_2AsF_6$, $H_3O_2SbF_6$, and $H_3O_2Sb_2F_{11}$ and Their Assignments

obsd freq, cm^{-1} (rel intens)^a								
$H_3O_2AsF_6$		$H_3O_2SbF_6$			$H_3O_2Sb_2F_{11}$		assignt (pt group)	
IR (−196 °C)	Raman (−100 °C)	IR (−196 °C)	Raman (−110 °C)	Raman (25 °C)	IR (25 °C)	Raman (25 °C)	$HOOH_2^+$ (C_s)	SbF_6^- (O_h)^b
3440 sh	3440 (0.8)	3440 sh		3440 (0+)	3447 s	3435 (0+)	ν_1 (A′)	
3400–3150 vs		3400–3150 vs			3400 } vs, vbr		ν_7 (A″)	
3228 vs	3230 (0+) br	3230 vs			2600		ν_2 (A′)	
					2178 w			
1535 w	1547 (0.4)			1539 (0+)	1531 m	1530 (0+)	ν_3 (A′)	
1425 mw	1417 (1)	1421 mw		1426 (0+)	1420 ms	1419 (0+)	ν_4 (A′)	
		1280 w						
					1228 mw	1227 (0+)	ν_8 (A″)	
1115 m		1126 mw		1130 (0+) br	1137 s	1135 (0+)	ν_5 (A′)	
1100 } m, vbr		1065 sh						
900		965 sh						
		915 w						
870 m	873 (10)	876 mw	879 (8.6)	880 (5.4)		878 (1.5) }		
					869 m	868 (3)	ν_6 (A′)	
						771 (0.2)		
728 vs	734 (39)		689 (5)		730 }	688 (10)		
	711 (1.5)		677 (10)	667 (10)	vs, br	664 (0.5)		ν_1 (A_{1g})
665 vs	673 (9.5)	666 vs	642 (7)		640	649 (5.4)		
635 sh		615 s						
585 m		571 ms			594 mw			
	559 (2.4)		560 (2)					
550 ms		514 m		555 (0.7) br	565 m	576 (0.7)		ν_2 (E_g)
	528 (1.4)		530 (0.5)					
470 m		375 mw			508 m			
	400 (0+)		326 (1)			301 (2.5)		
388 vs		309 ms						
	370 (5.0)		283 (5)	282 (4)		280 (1)		ν_5 (F_{2g})
348 ms			263 (0.9)					
	316 (1.2)		226 (0.5)	226 (0+)		236 (2)		
	202 (2.5)		200 (1.5)					
	189 sh		174 (3.2)	167 (0+)		167 sh		
	149 sh		126 (2.4)	122 (0+)		144 (0.6)		
	129 (3.2)					112 sh		

[a] Uncorrected Raman intensities. [b] The assignments given for SbF_6^- are for the room-temperature Raman spectrum of $H_3O_2SbF_6$ in which SbF_6^- appears to be octahedral due to rotational averaging. In the low-temperature spectra the symmetry of the MF_6^- anion is much lower than O_h (see text).

observed at ϕ 106, in agreement with previous observations[31] on the t-BuF·3.8SbF_5 system. This signal is tentatively assigned to some SbF_5·H_2O- or SbF_5·H_2O·SbF_5-type species.[33]

Attempts to observe the characteristic SbF_6^- signal in the ^{19}F NMR spectra of $H_3O_2SbF_6$ in different solvents were unsuccessful. In SO_2ClF the compound was insoluble. In either HF or HF acidified with AsF_5 only a single peak was observed due to rapid exchange between all fluorine-containing species. In SO_2 at −85 °C only two unresolved signals were observed at ϕ 107 and 127 with an area ratio of 4:1 indicating the possible presence of some $(SbF_5)_n$·H_2O-type species.[33] The failure to observe SbF_6^- for $H_3O_2SbF_6$ in SO_2 parallels the previous report[31] by Bacon and co-workers who found that, unlike $CsSb_2F_{11}$, the $CsSbF_6$ salt is rather insoluble in SO_2 and $Sb_2F_{11}^-$ is the only observable anion in this solvent.

The ^1H NMR spectrum of $H_3O_2Sb_2F_{11}$ in CH_3SOCH_3 solution showed a single broad asymmetric peak. Its line width and chemical shift were temperature dependent. At 20 °C its line width at half-height was 81 Hz, and δ was 11.80 relative to external Me_4Si with a shoulder on the upfield side. At 0 °C the line narrowed to 36 Hz and broadened again at −60 °C to 72 Hz. With decreasing temperature the line became more symmetric and shifted downfield (δ 12.20 at −60 °C). The failure to observe two different types of protons and the variation of the observed line widths indicate rapid proton exchange for $H_3O_2^+$. The assignment of the observed signal to $H_3O_2^+$ is supported by its large downfield shift. For comparison, 99% pure H_2O_2 exhibits between 20 and −30 °C a chemical shift of δ 10.3 relative to external Me_4Si. On protonation, this signal is expected to be shifted further downfield, as has previously been demonstrated[34] for numerous other species. The signal assigned to $H_3O_2^+$ also occurs significantly downfield from those previously reported for H_3O^+ [1,34,35] and SbF_5·H_2O[33] and therefore cannot be due mainly to these species.

In HF–AsF_5 solution at −80 °C, only a single broad signal at δ 11.06 was observed for $H_3O_2Sb_2F_{11}$ indicating rapid proton exchange between $H_3O_2^+$ and the HF solvent. In SO_2 solutions of $H_3O_2Sb_2F_{11}$, two lines at δ 9.94 and 11.84, respectively, were observed at −80 °C. The relative intensity of the δ 9.94 signal varied from sample to sample and also as a function of temperature. With decreasing temperature the peak area of the δ 9.94 signal decreased more rapidly than that of the δ 11.84 signal. These observations suggest that the two signals cannot belong to the same species. By comparison with previous reports,[1,34,35] the δ 9.94 signal is assigned to H_3O^+, and the more intense δ 11.84 signal is attributed to $H_3O_2^+$, in good agreement with our observations for the CH_3SOCH_3 solution. The line width of the δ 11.84 signal was temperature dependent and showed a minimum (~7 Hz) at about −60 °C, but no splittings could be observed. With increasing temperature, the δ 9.94 and 11.84 signals moved closer together, indicating the onset of chemical exchange between the two species.

The observations of H_3O^+ in the proton spectrum and possibly of a small amount of an $(SbF_5)_n$·H_2O adduct in the fluorine spectrum suggest that $H_3O_2Sb_2F_{11}$ may undergo either a redox reaction or decomposition in SO_2 solution.

Vibrational Spectra. The infrared and Raman spectra of $H_3O_2AsF_6$, $H_3O_2SbF_6$, and $H_3O_2Sb_2F_{11}$ are shown in Figures

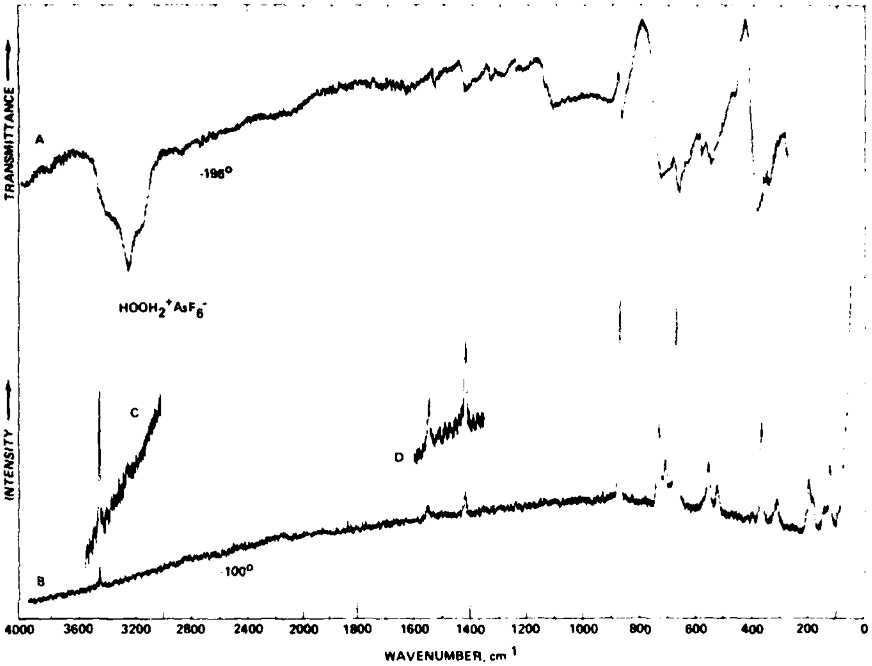


Figure 1. Vibrational spectra of $H_3O_2^+AsF_6^-$: trace A, infrared spectrum of the solid as a dry powder between CsI disks recorded at −196 °C; trace B, Raman spectrum of the solid in a glass tube recorded at −100 °C with a spectral slit width of 8 cm^{-1} and a sensitivity of 100 000; inserts C and D were recorded with a spectral slit width of 10 cm^{-1} at sensitivities of 380 000 and 250 000, respectively.

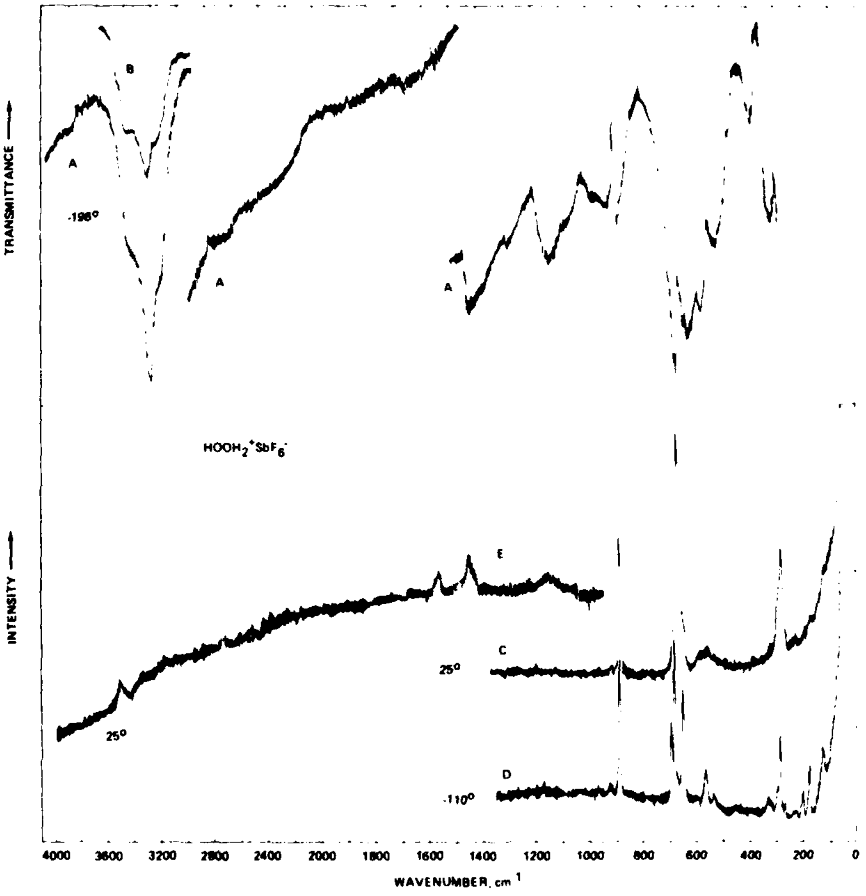


Figure 2. Vibrational spectra of $H_3O_2^+SbF_6^-$: traces A and B, infrared spectra of the solid recorded at −196 °C at two different sample concentrations; traces C and E, Raman spectra of the solid recorded at 25 °C with spectral slit widths of 5 and 10 cm^{-1}, respectively; trace D, Raman spectrum of the solid recorded at −110 °C.

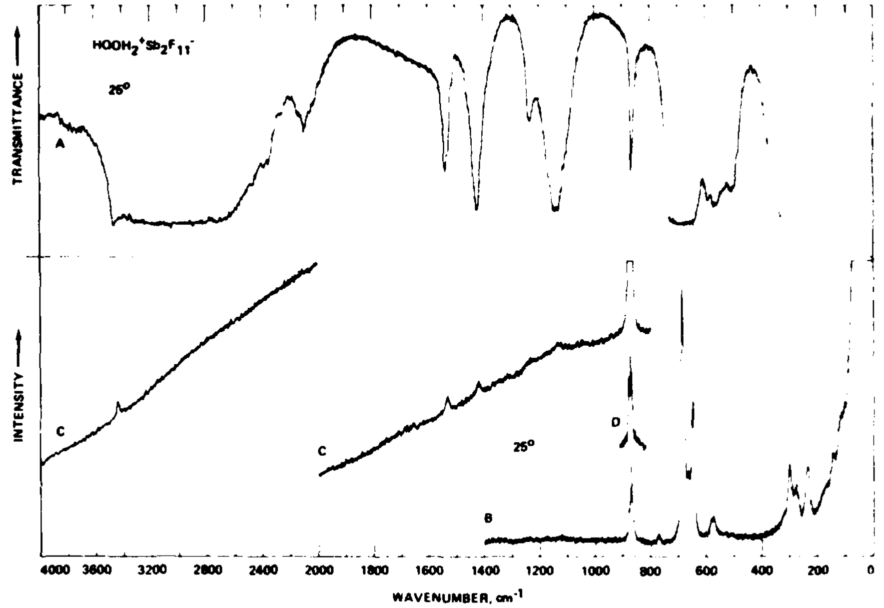


Figure 3. Vibrational spectra of $H_3O_2^+Sb_2F_{11}^-$: trace A, infrared spectrum of the solid as a dry powder between pressed AgCl disks; traces B, C, and D, Raman spectra of the solid recorded at 25 °C with spectral slit widths of 5, 10, and 2.5 cm^{-1}, respectively.

1, 2, and 3, respectively, and the observed frequencies are summarized in Table I. For the thermally more stable antimonate salts, spectra could be obtained at ambient temperature without the samples undergoing significant decomposition to the corresponding H_3O^+ salts. For $H_3O_2AsF_6$, only low-temperature spectra could be obtained.

The vibrational spectra of $H_3O_2SbF_6$ (see Figure 2) showed a pronounced temperature dependence. At room temperature, the Raman spectrum (traces C and E) exhibited three bands at 667, 555, and 282 cm^{-1}, respectively, characteristic for octahedral SbF_6^-.[1,5,7,18,19] When the sample temperature was lowered, the number of bands due to SbF_6^- significantly increased, indicating that the symmetry of SbF_6^- became lower than O_h. This transition was found to be reversible and to occur close to room temperature. Similar transitions have previously been observed for the corresponding H_3O^+,[1] D_3O^+,[36] and O_2^+[37] salts. They can be attributed to rapid motions of the ions in the crystal lattice at room temperature, causing rotational averaging. With decreasing temperature, these motions are frozen out, causing the observed effects of symmetry lowering of the anions. Since the symmetry of the corresponding cations is low (no degeneracies), their vibrational spectra are much less affected.

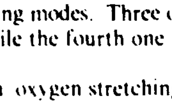
Assignments for the $H_3O_2^+$ Cation. The assignments for $H_3O_2^+$ were made on the basis of the following arguments. With the exception of the O–O torsional mode, which by comparison with the known frequency[38] of the corresponding N–O torsion in the isoelectronic H_2NOH molecule is expected to occur below 400 cm^{-1}, all of the fundamental vibrations of $H_3O_2^+$ should have frequencies higher than those of the anions. The bands due to the anions can be further identified by comparison with the ambient and low-temperature spectra previously reported for the corresponding H_3O^+[1] and $NH_3F_2^+$[7] salts. In view of the complexity of the low-temperature anion spectra, in Table I only the room-temperature Raman spectrum of rotationally averaged SbF_6^- has been assigned. Keeping in mind that $Sb_2F_{11}^-$ spectra strongly depend on the nature of the countercation, the room-temperature spectrum of $Sb_2F_{11}^-$ in $H_3O_2Sb_2F_{11}$ is in fair agreement with those previously observed for this anion in numerous other salts.[39-43]

Thus, the intense bands occurring above 800 cm^{-1} should belong to $H_3O_2^+$. By comparison with the known trans structure of isoelectronic H_2NOH,[44] this cation should have the following structure of symmetry C_s

Table II. Comparison of the Vibrational Spectrum of $H_3O_2^+$ with Those of Isoelectronic H_2NOH and H_4N_2

assignt for H_2XYH in pt group C_s		approx descript of mode	obsd freq, cm^{-1}		
			H_2-OOH^+	H_2-NOH^b	H_2-NNH^- ^{c}
A′	ν_1	$\nu(YH)$	3440	3656	3202
	ν_2	$\nu_{svm}(XH_2)$	3229	3297	3100
	ν_3	$\delta_{sciss}(XH_2)$	1536	1605	1599
	ν_4	$\delta(XYH)$ in plane	1421	1357	1330
	ν_5	$\delta_{wag}(XH_2)$	1136	1115	1103
	ν_6	$\nu(XY)$	875	895	847
A″	ν_7	$\nu_{asym}(XH_2)$	3275	3350	3155
	ν_8	$\tau(XH_2)$	1228	1297	1232
	ν_9	$\tau(XY)$	[386]^a	386	[386]^a

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



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

The three hydrogen–oxygen stretching modes should occur above 2500 cm^{-1}. Their assignment, however, is somewhat complicated. By comparison with the known spectra of related molecules, such as CH_3NH_2,[45] H_2NOH,[38,46] H_2O, CH_3OH, and $>CH_2$ group containing molecules,[47] we would expect the H_2O– group to exhibit two intense infrared bands in the OH stretching region. Of these two, the antisymmetric stretching mode should have a frequency 50–100 cm^{-1} higher than that of the symmetric stretching mode. In the Raman spectrum the symmetric stretching mode should be much more intense than the antisymmetric one. The unique –OH stretching mode should be of considerably lower infrared intensity than the two –OH_2 stretching modes.

Inspection of the Raman spectrum of $H_3O_2AsF_6$ shows a very narrow Raman line at 3440 cm^{-1} and a barely detectable broad line at 3230 cm^{-1}. Since the 3440-cm^{-1} Raman line shows only a rather weak infrared counterpart while the 3230-cm^{-1} one exhibits a very intense infrared counterpart and since no intense infrared band occurs above 3440 cm^{-1}, the 3440-cm^{-1} band is assigned to the unique –OH stretch and the 3230-cm^{-1} band to the symmetric –OH_2 stretch of H_2OOH^+. The 3228-cm^{-1} infrared band exhibits a shoulder on both its high- and its low-frequency side. Instead of assigning these two shoulders to two separate bands, one might equally well attribute them to a single broad band onto which the sharper 3228-cm^{-1} band is superimposed. Such a broad band might be expected for the antisymmetric –OH_2 stretching mode, and its center (3275 cm^{-1}) results in a frequency value which agrees well with the above predicted frequency difference between the symmetric and the antisymmetric –OH_2 stretching mode. In the spectrum of $H_3O_2SbF_6$ the situation is almost identical. For $H_3O_2Sb_2F_{11}$, the infrared counterpart to the 3435-cm^{-1} Raman band is also rather narrow and occurs at the very edge of the intense and extremely broad infrared band. These observations seem to support our assignments, although it is not obvious why the Raman line for the unique –OH stretch should be so much sharper than that for the symmetric –OH_2 stretch. If the –OH stretch and the symmetric –OH_2 stretch would have comparable Raman line widths, the latter should have a greater peak height than the –OH stretch and should be easily observed.

Whereas the modes involving mainly O–H bonds should be of low Raman and of high infrared intensity, the O–O stretching mode should be quite intense in the Raman spectrum and occur in the frequency range 800–1000 cm^{-1}. It is therefore assigned to the strong Raman line occurring in all samples between 868 and 880 cm^{-1}. As expected, this band shows a counterpart of medium intensity in the infrared spectra. In the spectra of $H_3O_2SbF_6\cdot 1.17SbF_5$ ("$H_3O_2Sb_2F_{11}$") this band shows a splitting into two components, separated by about 10 cm^{-1}. This splitting might be due to the sample not having an exact 1:2 stoichiometry and therefore containing a mixture of different polyantimonates. For the two well-defined 1:1 adducts $H_3O_2AsF_6$ and $H_3O_2SbF_6$, no splittings of this band could be detected.

Of the five deformation modes expected for $H_3O_2^+$ of symmetry C_s, four involve the O–H bonds and should occur in the frequency range 1000–1700 cm^{-1}. Indeed, four infrared bands were observed in this frequency range for $H_3O_2SbF_6$, with counterparts in the Raman spectrum. Their assignment to the individual modes (see Table II) was made by analogy to those known[47] for related molecules, such as H_2O, CH_3OH, CH_3NH_2, and CH_3X.

The –OH_2 scissoring mode should have the highest frequency and occur between 1500 and 1600 cm^{-1}. It is therefore assigned to the band observed in most spectra at about 1535 cm^{-1}. The –NH_2 in-plane deformation mode is usually very intense in the infrared spectrum and occurs for H_2NOCH_3[38] and H_2NOH[38,46] at 1150 and 1115 cm^{-1}, respectively. For H_2OOH^+ it is therefore assigned to the strong infrared band at about 1130 cm^{-1}. The –NH_2 twisting mode is usually very weak and occurs in H_2NNH_2, H_2NOH,[38] and H_2NNH^-[48] at 1260, 1297, and 1232 cm^{-1}, respectively. It is therefore assigned to the medium weak band observed for $H_3O_2SbF_6$ at 1228 cm^{-1}. There is only one frequency (~1420 cm^{-1}) left for assignment to the –OOH in-plane deformation mode. This assignment is in fair agreement with the value of 1345 cm^{-1} attributed to the corresponding –COH deformation in CH_3OH.[47]

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

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

[a] Bond distances in Å and angles in degrees.

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

In summary, with the exception of the O–O torsional mode, all fundamentals of H_2OOH^+ have been observed and assigned. The assignments are summarized in Table III and are compared to those of isoelectronic H_2NOH[38,46] and H_2NNH^-.[48] The similarity of the vibrational spectra of H_2OOH^+, H_2NOH, and H_2NNH^- suggests that the two ions are isostructural with NH_2OH for which a trans structure of symmetry C_s was established[44] by microwave spectroscopy and confirmed[49] by ab initio molecular orbital theory. As expected for salts containing cations with hydrogen ligands and anions with fluorine ligands, strong cation–anion interactions were observed. These result in a lowering of the oxygen–hydrogen stretching frequencies and cause splittings of the anion bands in the spectra at low temperature at which rotational-averaging processes are frozen out.

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

For the computation of the force fields, the vibrational frequencies and assignments of Table II were used. The required potential and kinetic energy metrics were computed by a machine method[50] using the geometries given in Table III. Since the frequency of the X–Y torsion mode ν_9 (A″) is unknown for both H_2OOH^+ and H_2NNH^- and since, on the basis of its expected low frequency, coupling with other modes should be negligible, this fundamental was omitted from the normal-coordinate analyses. For H_2OOH^+ and H_2NNH^-, the bond angles were assumed to be identical with those known[44] for H_2NOH, and the bond lengths were estimated by comparison with those known for the similar H_2O_2 and N_2H_4 molecules. The bending coordinates were weighted by unit (1 Å) distance.

The force constants of these H_2XYH-type species were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. Since in the A′ block the X–Y stretching force constant F_{66} was found to strongly depend on the values of the stretch–bend interaction constants F_{46} and F_{56}, the diagonal-symmetry force constants were computed as a function of F_{46} and F_{56}. As can be seen from Figures 4 and 5, the values of YH (F_{11}) and XH_2 (F_{22}) stretching force constants are unaffected by the choice of F_{46} and F_{56}, but the X–Y stretch (F_{66}) depends strongly on the choice of F_{46} and F_{56}. In the absence of additional ex-

Table IV. Anharmonic Symmetry Force Constants[a] and Potential Energy Distribution[b] of H_2OOH^+, H_2NOH, and H_2NNH^- [c]

	symmetry force constants				PED		
		H_2OOH^+	H_2NOH	H_2NNH^-		H_2OOH^+	H_2NOH	H_2NNH^-
A′	$F_{11} = f_R$	6.607	7.46	5.675	F_{11}	100	100	100
	$F_{22} = f_r + f_{rr}$	5.92	6.13	5.42	F_{22}	100	100	100
	$F_{33} = f_\alpha$	0.628	0.733	0.748	F_{33}	95	99	99
	$F_{44} = f_\beta$	1.054	0.902	0.977	F_{44}	94	98	98
	$F_{55} = f_\gamma + f_{\gamma\gamma}$	0.715	0.72	0.728	F_{55}	95	97	96
	$F_{66} = f_D$	3.93	3.87	3.15	F_{66}	101	99	103
	$F_{35} = 2^{1/2} f_{\alpha\gamma}$	0.1	0.1	0.1				
	$F_{46} = f_{D\beta}$	0.2	0.2	0.2				
	$F_{56} = 2^{1/2} f_{D\gamma}$	0.3	0.3	0.3				
A″	$F_{77} = f_r - f_{rr}$	5.884	6.089	5.401	F_{77}	100	100	100
	$F_{88} = f_\gamma - f_{\gamma\gamma}$	0.782	0.922	0.850	F_{88}	100	100	100

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

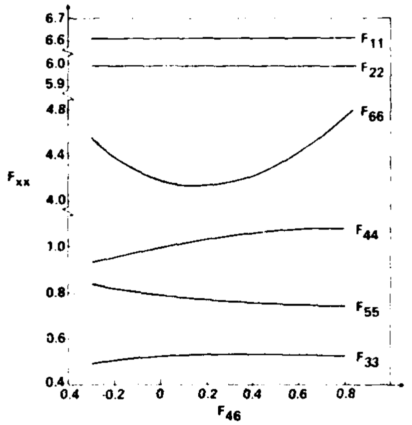


Figure 4. Diagonal symmetry force constants (stretching constants F_{11}, F_{22}, and F_{66} in mdyn/Å and deformation constants F_{33}, F_{44}, and F_{55} in mdyn Å/rad²) of the A′ block of H_2OOH^+ as a function of the stretch-bend interaction constant F_{46} (in mdyn/rad). All the remaining off-diagonal symmetry force constants were assumed to be zero.

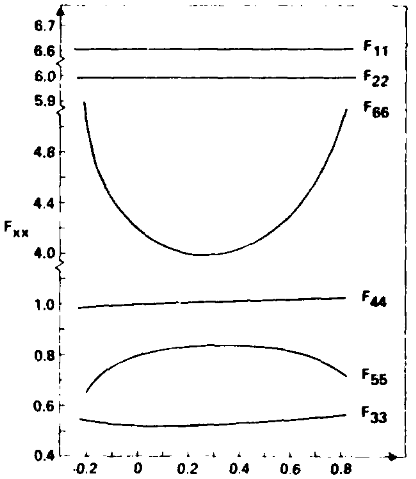


Figure 5. Diagonal symmetry force constants of the A′ block of H_2OOH^+ as a function of F_{56}.

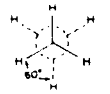
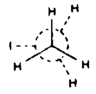
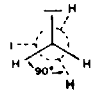
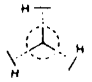
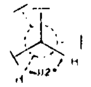
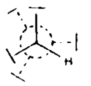
perimental data, such as oxygen isotopic shifts, the uncertainty in the value of F_{66} obtained by underdetermined force fields must therefore be considered to be substantial. In the absence of such additional data, we have chosen for the isoelectronic H_2XYH series a force field which resulted in a highly characteristic potential energy distribution (PED) for all fundamentals (see Table IV). The X-Y stretching force constants obtained in such a manner represent minimal values but could be higher by as much as 0.4 mdyn/Å if larger positive values are assumed for F_{46} and F_{56}. A moderate size value was found necessary for F_{35} to obtain a characteristic PED for ν_3 and ν_5.

In a recent paper, Botschwina and co-workers have reported[51] a partial ab initio harmonic force field for H_2NOH. Since this type of computation can yield valuable information about the off-diagonal force constants, a comparison with the results of Table IV appeared interesting. Botschwina et al. report a value of 0.629 mdyn/rad for F_{46} (using the force constant designation of Table IV of our work) and predict values of 8.1 ± 0.1 mdyn/Å and 0.9 ± 0.05 mdyn Å/rad² for F_{11} and F_{33}, respectively. The latter two values and the positive sign of F_{46} are in fair agreement with the anharmonic force field of Table IV, although the value computed[51] for F_{46} appears to be high. A calculation of a force field with $F_{46} = 0.63$ and $F_{56} = 0$ resulted in ν_5 and ν_6 becoming almost equal mixtures of F_{55} and F_{66} and an unacceptably high value of about 5 mdyn/Å for F_{66}. Assuming a positive value for F_{56} resulted in even less acceptable force constants.

A comparison of the results of Table IV shows that the force fields of isoelectronic H_2OOH^+, H_2NOH, and H_2NNH^- are indeed very similar and suggests that all members of this series are isostructural. The small deviations observed within the series (higher values of F_{11}, F_{22}, and F_{77} for H_2NOH) can be readily explained. For H_2NOH, gas-phase frequencies of the isolated molecule were used, whereas in the H_2OOH^+ and H_2NNH^- salts the anion cation interactions lower the stretching frequencies somewhat (see above).

The question whether ν_6, the fundamental vibration assigned to the stretching mode of the two central atoms, is highly characteristic or not also needed to be answered. The fact that ν_6 is of very high Raman intensity, whereas ν_5 is barely observable, and the known high polarizabilities of the central atoms relative to those of the hydrogen ligands argue strongly in favor of ν_6 being predominately the O–O stretching mode. Furthermore, the value of the O–O stretching force constant F_{66} (3.93 mdyn/Å) and the highly characteristic nature of ν_6 (101% F_{66}) of H_2OOH^+ are in excellent agreement with the previously reported[52] findings for gaseous HOOH (F_{O-O} = 3.776 mdyn/Å; ν_{O-O} = 105% of F_{O-O}). For solid HOOH, a value (F_{O-O} = 3.999 mdyn/Å) was found[53] which is slightly higher than that in H_2OOH^+. A further argument in favor of highly characteristic X-Y stretching frequencies in these and closely related molecules is based on the vibrational spectra observed for deuterated molecules, such as DOOD.[52,53] If the fundamental assigned to the O-O stretch in HOOH would contain strong contributions from X-H bending modes, its frequency should significantly decrease on deuteration.

Table V. Preferred Rotational Isomers, Number of Vicinal Ligand Repulsions (R), and Attractions (A), and Frequencies (cm^{-1}) of the Stretching Mode of the Two Central Atoms of $H_3NNH_3^{2+}$,[a] $H_3NNH_2^+$,[b] H_2NNH_2,[c] H_2NNH^-,[d] H_2OOH^+,[d] HOOH,[e] and HOO^- [f]

					
3R	2R-1A	1R-2A	3A	2A-1R	1A-2R
$H_3NNH_3^{2+}$ 1048[g]	$H_3NNH_2^+$ 949[h]-968[i]	H_2NNH_2 850-938[j]	H_2NNH^- 847[k]		
			H_2OOH^+ 875[l]	HOOH 864-881[m]	HOO^- 836[n]

[a] Geometry of preferred rotational isomer is based on that of isoelectronic C_2H_6.[55] [b] Geometry assumed to be analogous to that of isoelectronic CH_3NH_2.[56] [c] Reference 57. [d] Geometry is based on that of isoelectronic H_2NOH.[44] [e] Reference 58. [f] For HOO^-, a preferred rotational isomer does not exist. The structure is given exclusively for didactic purposes. [g] From Raman spectrum of $N_2H_6F_2$ in anhydrous HF solution (B. Friec and H. H. Hyman, *Inorg. Chem.*, 6, 2233 (1967)). [h] From infrared spectrum of solid $(N_2H_5)TaF_7$.[24] [i] From Raman spectrum of N_2H_5Cl in aqueous HCl solution (J. T. Edsall, *J. Chem. Phys.*, 5, 225 (1937)); see also J. C. Decius and D. P. Pearson, *J. Am. Chem. Soc.*, 75, 2436 (1953). [j] The assignments for the N–N stretching mode in N_2H_4 are not well established and significantly differ for the gas and condensed phases (see example ref 48 and J. R. Durig, S. F. Bush, and E. E. Mercer, *J. Chem. Phys.*, 44, 4238 (1966)). The latter authors assigned the N–N stretch in N_2H_4 to bands in the 1087–1126-cm^{-1} frequency region which does not fit the general trends listed in this table. [k] From infrared spectrum of solid NaN_2H_3.[48] [l] This work. [m] Reference 12. [n] Reference 10.

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

Influence of Progressive Protonation on the Bond Strength of the Two Central Atoms. It seemed interesting to examine how in an H_mXYH_n-type species the replacement of a free valence electron pair of a central atom by a hydrogen ligand influences the strength of the X–Y bond. Further interest was added to this problem by the fact that these X–Y bonds are single bonds, thus resulting in hindered rotation and rotational conformers. In the literature,[8,54] the concept has been advanced that in a singly bonded X–Y system the replacement of a free valence electron pair on X or Y by a bonded ligand will diminish the overall ligand or electron-pair repulsions, thereby strengthening the X–Y bond. The results of the present study combined with previous literature data offered an excellent opportunity to examine the validity of this simple repulsion concept for the progressively protonated series HOO^-, HOOH, and H_2OOH^+, which is isoelectronic with H_2NNH^-, followed by H_2NNH_2, $H_3NNH_2^+$, and $H_3NNH_3^{2+}$.

For this series the energetically most favored rotational isomers and the stretching frequencies of the two central atoms are summarized in Table V. Stretching frequencies are preferred over force constants because for HOOH,[53] H_2OOH^+, and H_2NNH^- these frequencies are highly characteristic and because of the lack of reliable fully determined force fields for most of these species. In Table V, frequency ranges are given for HOOH, $H_3NNH_2^+$, and N_2H_4. For the first two, these ranges are caused by the fact that the frequencies vary somewhat for different phases. For N_2H_4, the large given range is mainly due to the uncertainty in the assignment of the N–N stretching mode (see footnote *k* of Table V). In spite of these limitations, inspection of the listed frequencies reveals not only that there is a definite X–Y stretching frequency increase with progressive protonation but also that the increase of the O–O stretching frequency from HOO^- to H_2OOH^+ (30 cm^{-1}) is much smaller than that (201 cm^{-1}) encountered for the H_2NNH^- to $H_3NNH_3^{2+}$ part of the series.

This marked difference is difficult to explain by the simple free valence electron pair repulsion concept[8,54] which should result in a more uniform trend and cannot account for the eclipsed structure of H_2NOH. A better explanation for the observed trends can be given on the basis of the following considerations. (i) The preferred rotational isomers (see Table V) indicate that in an H_mXYH_n-type species, in which the X and Y central atoms possess free valence electron pairs, attractive forces exist between a free valence electron pair on one central atom and a hydrogen ligand bonded to the other central atom. In terms of molecular orbital theory, this effect can be considered to be the result of both dipolar attraction and back-donation from lone-pair orbitals of one central atom into antibonding orbitals of the other.[49] On the other hand, free valence electron pairs on X are repelled by free pairs on Y, and the same holds for vicinal hydrogen ligands. These effects explain the eclipsed configuration of H_2NOH,[44] the staggered one of C_2H_6,[55] and the gauche ones[56-58] of the remaining species. (ii) When going from HOO^- to $H_3NNH_3^{2+}$, one observes that the number of repulsions between vicinal ligands (including the free valence electron pairs) decreases from two for HOO^- to zero for H_2OOH^+ and H_2NNH^- and then increases again to three for $H_3NNH_3^{2+}$. (iii) It is known that for peroxides a weakening of the oxygen–ligand bonds results in a strengthening of the O–O bond (FOOF, ν_{O-O} 1257 cm^{-1}; HOOH, ν_{O-O} 864 cm^{-1})[59,12] and vice versa. Furthermore, it is known[8] that the $^{\delta-}X-H^{\delta+}$ polarity of an X–H bond increases by the addition of a second H^+ to X. This increase in bond polarity upon progressive protonation weakens the X–H bonds and therefore should strengthen the X–X bond. In addition, protonation is expected to shift more s character to the orbital involved in the X–X bond, thereby strengthening this bond. In our opinion, these two effects are the major reasons for the observed increase of the X–X stretching frequency within this series.

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

The above analysis indicates that the replacement of a free valence electron pair on one of the two central atoms by a hydrogen ligand could either decrease *or* increase the vicinal ligand (or electron pair) repulsion. The direction of the effect depends on whether the two central atoms possess less than three or three and more hydrogen ligands. With less than three hydrogen ligands, a free pair–free pair repulsion is replaced by a free pair–XH bond attraction, whereas with three or more hydrogen ligands an attraction is replaced by a vicinal hydrogen–hydrogen ligand repulsion. The importance of the attractive forces in this type of molecule is in agreement with the results from molecular orbital calculations.[49,61]

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

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

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Registry No. $H_3O_2^+Sb_2F_{11}^-$, 70850-27-0; $H_3O_2^+SbF_6^-$, 70850-28-1; $H_3O_2^+AsF_6^-$, 70850-29-2; H_2NNH , 25415-88-7; H_2NOH, 7803-49-8; AsF_5, 7784-36-3; SbF_5, 7783-70-2; BiF_5, 7787-62-4; H_2O_2, 7722-84-1; HF, 7664-39-3; $BiF_3 \cdot BiF_5$, 70850-25-8.

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APPENDIX J

Sulfur tetrafluoride. Assignment of vibrational spectra and force field

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

INTRODUCTION

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

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

EXPERIMENTAL

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

RESULTS AND DISCUSSION

Infared spectra

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

In agreement with previous experience [6, 13, 15, 16], neon matrices produced the best spectra and exhibited frequencies closest to those of the gas phase values. Because accurate anharmonicity corrections were not possible, all observed isotopic shifts were corrected by a factor of 1.01, a value close to those previously used for similar molecules [13, 16, 17]. The observed isotopic shifts are in fair agreement with the values previously reported [11] for some of these bands in an N_2 matrix.

For some of the bands, matrix splittings were observed. The use of ^{34}S enriched samples facilitated distinction between isotopic and matrix splittings. For the $353\,cm^{-1}$ fundamental, the splitting observed in a N_2 matrix had previously been interpreted [11] in terms of a coincidence of the two fundamentals ν_3 and ν_9. Although varying degrees of splitting were observed during the present study for the $353\,cm^{-1}$ fundamental in Ar and Ne matrices (see Fig. 1), these splittings are identical for both $^{32}SF_4$ and $^{34}SF_4$. Since it appears unlikely that ν_3 and ν_9 should exhibit identical sulfur isotopic shifts, these splittings are attributed to matrix splittings of a single fundamental. This conclusion is supported by the normal coordinate analysis, given below, which shows that the large isotopic shift observed for the $532\,cm^{-1}$ deformation mode can be explained only by assigning this frequency to ν_3. Similar matrix splittings were observed and identified for several other bands and are denoted in Table 1.

Normal coordinate analysis and assignments

A listing of the nine fundamentals of SF_4 and their assignment in point group C_{2v} is given in Table 2, together with an approximate description of these modes. Based on the previous studies [1–12], the assignments for ν_1, ν_2 and ν_4 in the A_1 block, ν_6 in the B_1 block, and ν_8 in the B_2 block are well established. The remaining four modes are all deformation modes. Assuming no coincidences, three fundamentals at 532, 475 and $353\,cm^{-1}$ are available for assigment to these four modes. Based on relative intensity considerations and the fact that all three fundamentals are i.r. active, the missing fundamental should be the torsional mode ν_5 (A_2)

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

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

*Corrected for anharmonicity.
†These bands showed matrix splittings.

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

The assignment of the 532, 475 and 353 cm^{-1} fundamentals was established in the following manner. The 353 cm^{-1} band has previously been assigned [5, 6, 8, 10, 11] to ν_9 (B_2), and this assignment has recently been supported by microwave spectroscopy [1]. Since the ^{32}S–^{34}S isotopic shifts of ν_8 and of the 353 cm^{-1} fundamental are now both known, a force field computation can be used to test the correctness of this assignment. If the assignment is correct, both observed isotopic shifts must result in an identical force field. As can be seen from Fig. 2, the isotopic shifts observed for the 867 and the 353 cm^{-1} fundamental result in the same force field, thus establishing the 353 cm^{-1} fundamental as ν_9 (B_2).

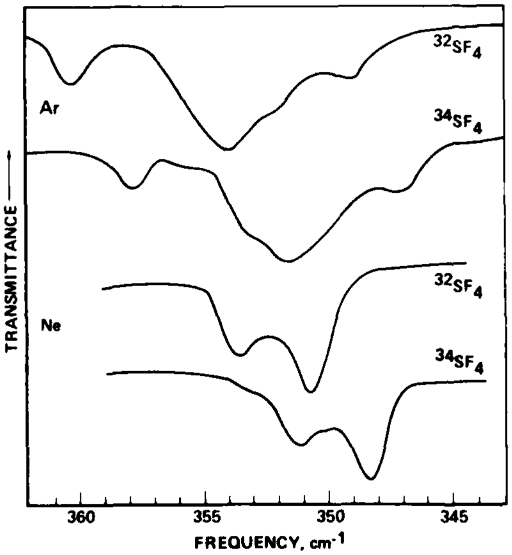


Fig. 1. Infrared spectra of $^{32}SF_4$ and $^{34}SF_4$ in argon and neon matrices. The observed splittings are attributed to matrix effects.

A distinction between the two possible assignments (532 and 475 cm^{-1}) for ν_7 (B_1) can be made in a similar manner, since the sulfur isotopic shifts of ν_6 (B_1) and of the 532 cm^{-1} deformation mode (4.05) cm^{-1} are known. From a computation of the B_1 force field (see Fig. 3) it becomes obvious that the sulfur isotopic shift of ν_7 has to be less than 1 cm^{-1} in order to agree with the force field obtained from the isotopic frequencies of ν_6. Since the isotopic shift of 4.05 cm^{-1}, observed for the 532 cm^{-1} band, is much too large for ν_7, the 532 cm^{-1} fundamental must be ν_3 (A_1) and the 475 cm^{-1} one must be ν_7 (B_1). Additional support for this assignment was obtained from the computation of the A_1 block force field (See Table 3). No difficulty was encountered to duplicate the isotopic shifts observed for ν_1, ν_2 and ν_3.

The missing frequency of ν_5 (A_2) was calculated to be 437 cm^{-1} assuming $F_{55} = F_{77}$. This assumption seemed most plausible because of the three possible $f_{\alpha\alpha}$ interaction constants, the one which involves two angles sharing a common equatorial fluorine ligand, i.e. $f''_{\alpha\alpha}$, should have the largest value and because in F_{55} and F_{77} $f''_{\alpha\alpha}$ has the same sign.

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

Table 2. Assignment of normal modes of SF_4

Species	Approximate description of mode	Frequency (cm^{-1})
A_1 ν_1	ν sym XF_2 eq	892
ν_2	ν sym XF_2ax	558
ν_3	δ sciss XF_2eq and ax, sym comb	532
ν_4	δ sciss XF_2ax and eq, asym comb	228
A_2 ν_5	XF_2 twist	[437]*
B_1 ν_6	ν asym XF_2ax	730
ν_7	XF_2eq wagging	475
B_2 ν_8	ν asym XF_2eq	867
ν_9	δ sciss XF_2ax out of plane	353

*Value calculated from $F_{55} = F_{77}$

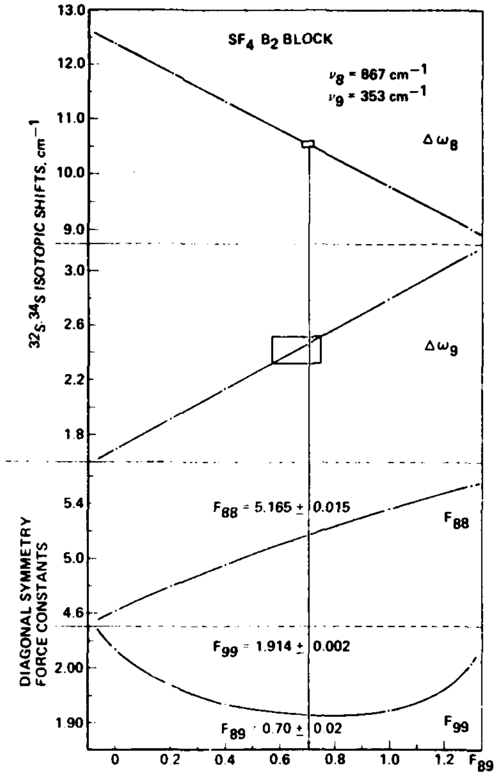
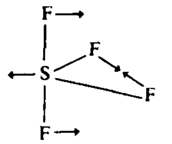


Fig. 2. Solution range of force constants and computed sulfur isotopic shifts for the B_2 block of SF$_4$. The rectangles indicate the uncertanities of the observed anharmonicity corrected isotopic shifts and the vertical line the resulting general valence force field. The units are cm^{-1} for the isotopic shifts and mdyn Å^{-1}, mdyn Å rad^{-2} and mdyn rad^{-1} for F_{88}, F_{99} and F_{89}, respectively.

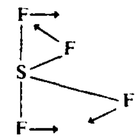
it becomes necessary, however, to exchange the assignments of ν_1 (A_1) and ν_6 (B_1) for SF$_4$O.

The force field of SF$_4$ is summarized in Table 3. The B_1 and B_2 block values represent a general valence force field. The A_1 block is still underdetermined (ten symmetry force constants and seven frequency values), but is expected to be a good approximation to a general valence force field in view of the good agreement between the observed and calculated isotopic shifts. The off-diagonal symmetry force constants listed in Table 3 were required in order to be able to duplicate the observed sulfur isotopic shifts. The value of F_{23} is necessary to make $\Delta\nu_2$ close to zero. The relatively large isotopic shift of ν_1 can only be achieved by the use of an F_{11} value which concentrates the isotopic shifts of ν_1 and ν_3 almost exclusively in ν_1 and by the use of F_{13} and F_{14} which transfer some of the isotopic shift from ν_1 to ν_3. Since ν_3 is an almost equal mixture of F_{33} and F_{44} (see PED of Table 3), the isotopic shift balance between ν_1 and ν_3 can be equally well achieved by either F_{13} or F_{14}, as long as their sum equals to about 0.6 mdyn rad^{-1}. Therefore the chosen ratio between F_{13} and F_{14} is somewhat arbitrary, and their values were made about equal for cosmetic reasons.

The potential energy distribution (PED) is given in Table 3 and shows that all fundamentals are highly characteristic, with the exception of ν_3 and ν_4. The latter are almost equal mixtures of F_{33} and F_{44}. As previously discussed in detail [10, 11] and shown by their eigenvectors (see Table 3), ν_3 is a symmetric and ν_4 is an antisymmetric combination of the symmetry coordinates S$_3$ and S$_4$, i.e.



ν_3, symmetric combination of axial and equatorial bending



ν_4, antisymmetric combination of axial and equatorial bending.

In view of thse facts, a discussion is rather meaninglesss whether ν_3 or ν_4 is mainly axial or equatorial bending. Furthermore, it shows that ν_4 is

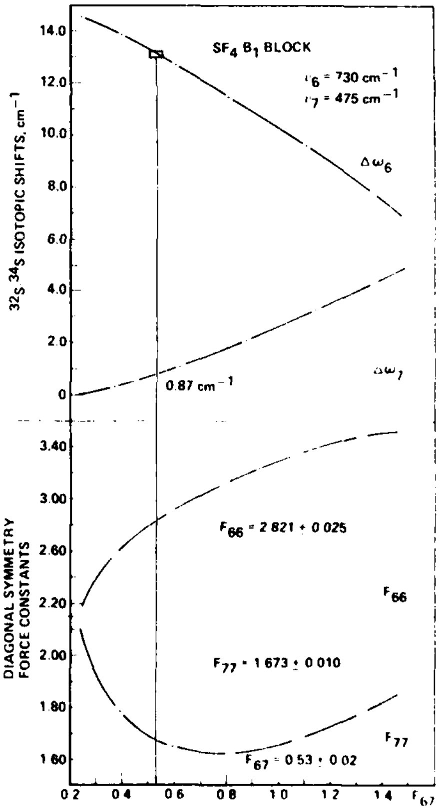


Fig. 3. Solution range of force constants and computed sulfur isotopic shifts for the B_1 block of SF$_4$. For further explanations see caption of Fig. 2

Table 3. Force field*, computed and observed harmonic sulfur isotopic shifts†, potential energy distribution‡ and eigenvectors of SF_4

			$\Delta\omega$ comp	$\Delta\omega$ observed	PED	Eigenvectors S_1	 S_2	 S_3	 S_4
A_1	$F_{11} = f_r + f_{rr}$	5.884	11.37	11.35 ± 0.05	$95F_{11}$	−0.275	−0.014	0.123	0.194
	$F_{22} = f_R + f_{RR}$	3.476	0.07	0	$99F_{22}$	−0.010	0.229	0.014	−0.028
	$F_{33} = 0.99\ f_\beta + 0.01 f_\gamma - 0.15 f_{\beta\gamma}$	1.414	4.14	4.09 ± 0.05	$30F_{33} + 29F_{44} + 26F_{34}$	0.045	0.018	0.187	0.238
	$F_{44} = 0.004\ f_\beta + 0.71 f_\gamma + 0.29\ (f_\alpha + f_{\alpha\alpha} + f'_{\alpha\alpha} + f''_{\alpha\alpha}) + 0.13\ f_{\alpha\beta} + 1.80 f_{\alpha\gamma} + 0.11\ f_{\beta\gamma}$	0.863	0.08		$91F_{33} + 89F_{44} - 80F_{34}$	0	−0.005	0.141	−0.178
	F_{13}	0.320							
	F_{14}	0.300							
	F_{23}	0.100							
	F_{34}	0.4913							
A_2	$F_{55} = f_\alpha - f_{\alpha\alpha} - f'_{\alpha\alpha} + f''_{\alpha\alpha}$	1.673	0			S_6	S_7		
B_1	$F_{66} = f_R - f_{RR}$	2.821	13.14	13.13 ± 0.05	$101F_{66} + 22F_{77} - 23F_{67}$	0.335	−0.203		
	$F_{77} = f_\alpha + f_{\alpha\alpha} - f'_{\alpha\alpha} - f''_{\alpha\alpha}$	1.673	0.87		$84F_{77} + 10F_{67}$	0.050	0.259		
	$F_{67} = \sqrt{2}(f_{R\alpha} - f'_{R\alpha})$	0.530				S_8	S_9		
B_2	$F_{88} = f_r - f_{rr}$	5.165	10.53	10.52 ± 0.05	$105F_{88} - 9F_{89}$	0.297	−0.096		
	$F_{99} = f_\alpha - f_{\alpha\alpha} + f'_{\alpha\alpha} - f''_{\alpha\alpha}$	1.914	2.48	2.42 ± 0.1	$101F_{99}$	−0.003	0.196		
	$F_{89} = \sqrt{2}(f_{r\alpha} - f'_{r\alpha})$	0.700							
	f_r	5.525							
	f_R	3.149							
	f_{rr}	0.360							
	f_{RR}	0.328							

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

†In cm $^{-1}$.

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

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

Additional experimental data which could be used as a constraint for the SF_4 assignment and force field, are centrifugal distortion constants [12] and mean amplitudes of vibration [20]. Since the observed centrifugal distortion constants "are not well determined" and have been shown [12] to be insensitive towards changes in the assignment of the deformation modes, they are not a useful constraint. Mean amplitudes of vibration have previously been reported [10] for SF_4 using five different assignments and force fields. These data showed that only $\langle q^2\rangle^{1/2}$ $F_3 \ldots F_4$ and $\langle q^2\rangle^{1/2}$ $F_3 \ldots F_3$ are sufficiently sensitive to variation of the assignment of the deformation modes in question. As can be seen from Table 4, the revised force field given in Table 3 results in mean amplitudes of vibration which are in excellent agreement with the observed values, thus lending additional support to our assignment. It should be pointed out that both the centrifugal distortion constants and the mean amplitudes of vibration, although useful for the detection of gross errors in the assignments, are not sensitive enough to be useful constraints for the force field of SF_4.

Table 4. Computed* (298 K) and observed [20] mean amplitudes (in Å) of vibration of SF_4

$S\text{–}F_{eq}$	0.041	0.041 ± 0.005
$S\text{–}F_{ax}$	0.048	0.047 ± 0.005
$F_{eq}\text{–}F_{eq}$	0.073	0.068 ± 0.010
$F_{eq}\text{–}F_{ax}$	0.069	0.067 ± 0.005
$F_{ax}\text{–}F_{ax}$	0.061	0.059 ± 0.010

*Using the force field of Table 3.

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APPENDIX K

United States Patent [19]

Christe et al.

[11] **4,152,406**

[45] **May 1, 1979**

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[54] SELF-CLINKERING NF_4^+ COMPOSITIONS FOR NF_3-F_2 GAS GENERATORS AND METHOD OF PRODUCING SAME

[75] Inventors: **Karl O. Christe**, Calabasas; **Carl J. Schack**, Chatsworth; **Richard D. Wilson**, Canoga Park, all of Calif.

[73] Assignee: **Rockwell International Corporation**, El Segundo, Calif.

[21] Appl. No.: **734,153**

[22] Filed: **Oct. 20, 1976**

[51] Int. Cl.² **C01G 21/52**; C01G 23/02

[52] U.S. Cl. **423/351**; 149/119; 149/109.4; 423/472

[58] **Field of Search** 149/119, 19.3, 109.4; 423/351, 472

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Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

Improved NF_4^+ compositions for solid propellant NF_3-F_2 gas generators are described which produce NF_3 and F_2 free of gaseous Lewis acids and do not require clinker forming additives for their complexing. The novel self-clinkering compositions $(NF_4)_2SnF_6$, NF_4SnF_5, $(NF_4)_2TiF_6$, $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$ and processes for their production are disclosed.

8 Claims, No Drawings

SELF-CLINKERING NF_4^+ COMPOSITIONS FOR NF_3-F_2 GAS GENERATORS AND METHOD OF PRODUCING SAME

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions of matter and methods of producing the same and is particularly directed to improved solid propellant NF_3-F_2 gas generators derived from self-clinkering NF_4^+ salts, together with methods for producing such gas generators.

2. Description of the Prior Art

NF_4^+ salts are the key ingredients for solid propellant NF_3-F_2 gas generators, as shown by D. Pilipovich in U.S. Pat. No. 3,963,542. These propellants consist of a highly over-oxidized grain using NF_4^+ salts as the oxidizer. Burning these propellants with a small amount of fuel, such as aluminum powder, generates sufficient heat to thermally dissociate the bulk of the oxidizer. This is shown for NF_4BF_4 in the following equation:

$$NF_4BF_4 \rightarrow NF_3 + F_2 + BF_3$$

As can be seen from the equation the gaseous combustion products contain the volatile Lewis acid BF_3. This disadvantage of a volatile Lewis acid byproduct is shared by all the previously known NF_4^+ compositions. These volatile Lewis acids possess a relatively high molecular weight and a low γ value $\left(\gamma \doteq \frac{C_{pl}}{C_{vl}}\right)$, relative to the preferred diluent helium and frequently act as a deactivator for the chemical HF-DF laser. Consequently, these volatile Lewis acids must be removed from the generated gas prior to its use in an efficient chemical laser. Based on the state of the art, heretofore, this would be achieved by adding a clinker forming agent, such as KF, to the solid propellant formulation. The function of this additive served to convert the volatile Lewis acid, such as BF_3, to a non-volatile salt as shown by the following equation:

$$KF + BF_3 \rightarrow KBF_4$$

The principal disadvantges of this approach are that, even if an excess of KF is used, complete clinkering cannot always be guaranteed, and that the addition of the KF severly degrades the yield of NF_3-F_2 obtainable per pound of formulation. This problem could be solved by using NF_4^+ containing compositions derived from non-volatile Lewis acids. However, the synthesis of such compositions has previously been unknown, since highly stable and non-volatile Lewis acids are polymeric and contain coordination-wise saturated central atoms. Consequently, these compounds possess very little or no acidity, which renders the synthesis of such salts very difficult.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

The above described problem of obtaining a Lewis acid free NF_3-F_2 gas stream from NF_4^+ compositions without clinker forming additives is overcome by the present invention. We have found that NF_4^+ salts, derived from the polymeric non-volatile Lewis acids SnF_4 (subliming at 704° C.) and TiF_4 (1 atm vapor pressure at 284° C.) can be prepared. The lack of acidity of SnF_4 at temperatures, at which NF_4^{30} salts can be formed and exist, was demonstrated. It was shown that mixtures of NF_3, F_2, and SnF_4, when heated to temperatures of up to 300° C. at autogenous pressures of about 150 atm, did not show any eevidence for NF_4^+ formation.

Since a direct synthesis of an NF_4^+ salt derived from SnF_4 was not possible, we have studied metathetical and displacement reactions. Because SnF_6^{--} salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. The following methathetical reaction

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

was carried out. It resulted in the precipitation of the rather insoluble salt $CsSbF_6$, while the soluble $(NF_4)_2SnF_6$ remained in solution. The two products were separated by a simple filtration step. The composition (in mol%) of the crude product was: $(NF_4)_2SnF_6$, 83; NF_4SbF_6, 13; $CsSbF_6$, 4. The purity of this product can be easily increased by following the procedures outlined for NF_4BF_4 in our co-pending application Ser. No. 731,198 filed Oct. 12, 1976, and now U.S. Pat. No. 4,107,275.

Another NF_4^+ salt derived from SnF_4 was obtained by the following quantitative displacement reaction in anhydrous HF as a solvent.

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

For TiF_4, the direct synthesis of an NF_4^+ salt from NF_3, F_2, and TiF_4 is still possible, since TiF_4 possesses already some vapor pressure at temperatures where NF_4^+ salts can be formed. However, the product thus obtained is very rich in TiF_4, as shown by the following equation:

$$NF_3 + F_2 + 6TiF_4 \xrightarrow[\text{160 atm}]{\text{190° C., 50 days}} NF_4Ti_6F_{25}$$

The NF_4^+ content of this salt could not be significantly increased by any changes in the reaction conditions.

Displacement reactions between NF_4BF_4 and TiF_4, either in HF solution or in the absence of a solvent, produced NF_4^+ salts according to

$$NF_4BF_4 + n\ TiF_4 \rightarrow NF_4TiF_5.(n-1)TiF_4 + BF_3$$

where, depending on the exact reaction conditions, n equals either 3 or 2.

A further increase in the NF_4^+ content was possible by the following metathetical reaction which yielded $(NF_4)_2TiF_6$:

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

The separation and purification procedure for this product is analogous to that outlined above for $(NF_4)_2SnF_6$.

The advantages of the above disclosed concept of using these novel self-clinkering NF_4^+ composition for NF_3-F_2 gas generators become obvious from a comparison of their theoretical performance data. In Table I, the theoretical yields of usable fluorine, expressed in weight percent, of $(NF_4)_2SnF_6$ and $(NF_4)_2TiF_6$ are compared to that of KF clinkered NF$_4$BF$_4$, the highest performing presently known system. The novel self-clinkering compositions clearly outperform KF clinkered NF$_4$BF$_4$. Furthermore, the risk of incomplete clinkering which always exists for a clinkered formulation is avoided.

TABLE I

A Comparison of the Theoretical Performance of Self-clinkering (NF$_4$)$_2$SnF$_6$ and (NF$_4$)$_2$TiF$_6$ with KF-clinkered NF$_4$BF$_4$

System	Performance (Weight % Usable F)
NF$_4$BF$_4$. 1.2KF	38.5
(NF$_4$)$_2$SnF$_6$	46.0
(NF$_4$)$_2$TiF$_6$	55.6

Accordingly, it is an object of the present invention to provide higher performing solid propellant NF$_3$-F$_2$ gas generator compositions.

Another object of the present invention is to provide self-clinkering NF$_4^+$ compositions capable of generating Lewis acid free NF$_3$ and F$_2$.

Another object of the present invention is to provide processes for the production of self-clinkering NF$_4^+$ compositions.

These and other objects and features of the present invention will be apparent from the following examples. It is understood, however, that these examples are merely illustrative of the invention and should not be considered as limiting the invention in any sense.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLE I

Metathetical reactions were carried out in an apparatus consisting of three Teflon FEP U-traps interconnected by Monel unions and closed off at each end by a Monel valve. The union between trap II and trap III contained a Teflon filter and was held in place by a press fit. The passivated apparatus was taken to the dry box and Cs$_2$SnF$_6$ and NF$_4$SbF$_6$ (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$_2$SnF$_6$ solution to run into trap II containing the NF$_4$SbF$_6$ solution. Upon contact of the two solutions, copious amounts of a white precipitate (CsSbF$_6$) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to −80° C. After completion of the filtration step, trap III was warmed to ambient temperature and the HF solvent was pumped off. The solid residue on top of the filter consisted mainly of CsSbF$_6$, whereas the solid collected in trap III was mainly the desired (NF$_4$)$_2$SnF$_6$.

The following example gives a typical product distribution obtainable with the above procedure and apparatus. Starting materials: NF$_4$SbF$_6$ (9.72 mmol), Cs$_2$SnF$_6$ (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$_4$)$_2$SnF$_6$ = 2.01 g). Elemental analysis for solid from trap III. Found: NF$_3$, 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3. Calculated analysis for a mixture (mol %) of 82.8 (NF$_4$)$_2$SnF$_6$, 12.9 NF$_4$SbF$_6$, and 4.3 CsSbF$_6$: NF$_3$, 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43.

(NF$_4$)$_2$SnF$_6$ is a white, crystalline, hygroscopic solid, stable at room temperature but decomposing at 240° C. Its characteristic x-ray powder pattern is listed in Table II. Its ionic composition, i. e. the presence of discrete NF$_4^+$ cations and SnF$_6^{--}$ anions was established by ^{19}F nmr, infrared and Raman spectroscopy.

The ^{19}F nmr spectrum, recorded for a BrF$_5$ solution, showed in addition to the solvent lines a triplet of equal intensity with $\phi = -220$, $J_{NF} \approx 229.6$ Hz, and a line width at half height of about 5 Hz, which is characteristic of tetrahedral NF$_4^+$. In addition, a narrow singlet at $\phi = 149$ was observed with the appropriate 117/119Sn satellites (average $J_{SnF} = 1549$ Hz), characteristic of octahedral SnF$_6^{--}$. The vibrational spectra of (NF$_4$)$_2$SnF$_6$ and their assignments are summarized in Table III.

EXAMPLE II

A mixture of NF$_4$BF$_4$ and SnF$_4$ (9.82 mmol each) was placed into a passivated Teflon-FEP ampoule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10 ml liquid) was added at −78° C., and the resulting suspension was stirred at 25° C. for 2 hours. The volatile material was pumped off at 35° C. leaving behind a white stable solid which, on the basis of its weight (3.094 g) and Raman spectrum, consisted of 83 mol percent NF$_4$SnF$_5$ and 17 mol percent unreacted starting materials. The HF treatment was repeated (again for 2 hours) and the non-volatile residue (2.980 g, weight calcd for 9.82 mmol of NF$_4$SnF$_5$ = 2.982 g) was shown by infrared, Raman, and ^{19}F nmr spectroscopy to be essentially pure NF$_4$SnF$_5$. Anal. Calcd for NF$_4$SnF$_5$: NF$_3$, 23.38; Sn, 39.08. Found: NF$_3$, 23.6; Sn, 38.7.

TABLE II

X-RAY POWDER DATE FOR (NF$_4$)$_2$SnF$_6$[a]

d obsd	d calcd	Int	h k l
6.27	6.36	w	1 1 1
5.67	5.70	vs	0 0 2
4.99	5.04	vw	1 0 2
3.67	3.69	w	2 1 2
3.55	3.59	s	1 0 3
3.42	3.42	s	3 1 0
2.990	2.990	s	2 1 3
2.851	2.851	ms	0 0 4
2.492	2.490	m	3 3 1
2.347	2.356	w	3 2 3
2.230	2.228	s	4 2 2
2.120	2.123	mw	5 1 0
2.023	2.024	mw	5 0 2
1.961	1.963	w	4 0 4
1.917	1.914	m	4 4 0
1.882	1.881	mw	5 0 3
1.834	1.832	w	5 3 1
1.813	1.814	mw	4 4 2
1.763	1.765	vw	5 3 2
1.712	1.712	w	6 2 0
1.686	1.686	m	5 4 0,3 0 6
1.662	1.662	m	3 1 6
1.616	1.614	mw	6 3 0
1.570	1.570	mw	5 0 5
1.500	1.501	mw	6 4 0
1.397	1.396	mw	6 4 3
1.387	1.386	w	6 5 0
1.359	1.359	mw	7 0 6,5 4 5
1.331		mw	
1.314		mw	
1.263		w	
1.231		w	
1.212		mw	
1.192		w	
1.177		mw	

[a]tetragonal a = 10.828Å c = 11.406Å Cu K$_\alpha$ radiation Ni filter

TABLE III

VIBRATIONAL SPECTRA OF SOLID $(NF_4)_2SnF_6$

Obsd Freq (cm^{-1}) and Rel Inten		Assignments (Point Group)	
IR	Raman	NF_4^+ (T_d)	SnF_6^{--} (O_h)
1224 mw		$2\nu_4(A_1 + E + F_2)$	
1160 vs.	1158 (1.5)	$\nu_3 (F_2)$	
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)	$\nu_1 (A_1)$	
613 mw	613 (5.0)		
605 mw	607 (1.5)	$\nu_4 (F_2)$	
	579 (8.3)		$\nu_1 (A_{1g})$
550 vs			$\nu_3 (F_{1u})$
	470 (0+) br		$\nu_2 (E_g)$
	449 (3.1)		
	442 (2.9)	$\nu_2 (E)$	
	251 (3.3)		$\nu_5 (F_{2g})$
	84 (0.3)	Lattice Vibration	

NF_4SnF_5 is a white, crystalline, hygroscopy solid, stable at room temperature and decomposing above 200° C. Its characteristic x-ray powder pattern is listed in Table IV.

TABLE IV

X-RAY POWDER DATA FOR NF_4SnF_5

d obsd	Int	d obsd	Int
7.72	mw	2.571	mw
6.32	vs	2.519	vw
5.69	w	2.276	w
5.29	w	2.146	w
4.51	m	2.064	ms
4.19	m	1.965	mw
3.80	vs	1.929	w
3.46	m	1.820	m
3.32	m	1.780	mw
3.17	mw	1.757	mw
2.868	w	1.732	mw
2.802	w	1.700	mw
2.743	m	1.661	vw
2.683	w	1.639	w
		1.615	w

its ionic structure, i.e., presence of NF_4^+ cations, was established by its ^{19}F nmr spectrum in BrF_5 solution. In addition to the solvent lines, it showed the triplet (see above) at $\phi = -220$, characteristic of NF_4^+. Two resonances were observed for SnF_5^- at $\phi = 145.4$ and 162.4, respectively, with an area ratio of 1:4. At −20° C. the resonances consisted of broad lines, but at lower temperatures the $\phi = 162.4$ signal showed splittings. Based on a more detailed analysis of these data, the SnF_5^- anion appears to have a diameric or polymeric structure. The vibrational spectrum of NF_4SnF_5 is listed in Table V and again establishes the presence of discrete NF_4^+ cations.

EXAMPLE III

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

EXAMPLE IV

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 described in Example I 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° C. and filtered. The volatile materials were pumped off at 50° C. for 1 hour. The filter cake (3.85 g) was shown by its x-ray powder diffraction pattern and vibrational spectroscopy to be mainly $CsSbF_6$ containing, due to the hold up of some mother liquor, a small amount of $(NF_4)_2TiF_6$. 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, 36.2; 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, 36.43; Ti, 12.29; Sb, 4.06; Cs, 4.43. Based on the observed Raman spectrum, the composition of the filtrate residue was estimated to be 90 $(NF_4)_2TiF_6$ and 10 $CsSbF_6$, in good agreement with the above elemental analysis.

$(NF_4)_2TiF_6$ is a white, crystalline, hygroscopic solid, stable at room temperature, but decomposing above 200° C. *Its characteristic x-ray powder pattern is listed* in Table VI.

TABLE V

VIBRATIONAL SPECTRA OF SOLID NF_4SnF_5

Obsd Freq (cm^{-1}) and Rel Intens NF_4SnF_5		Assignments (Point Group)
IR	Raman	NF_4^+ (T_d)
1222 mw		$2\nu_4 (A_1 + E + F_2)$
	1168 (0.4)	
1165 vs	1159 (0.8)	$\nu_3 (F_2)$
	1150 sh	
1134 w,sh		
1061 w		
		$\nu_2 + \nu_4 (F_1 + F_2)$.
1048 w		
	811 (0.2)	$2\nu_2 (A_1 + A_2 + E)$
850 wv	851 (10)	$\nu_1 (A_1)$
635 vs		
	622 (9.2)	
605 mw	606 (3.3)	$\nu_4 (F_2)$
575 vs		
	574 (0.5)	
559 w, sh	558 (2.0)	
490 m	490 (0+)	
458 m		
	448 (2.5)	
		$\nu_2 (E)$
	440 (2.3)	
	272 (0.6)	
	247 (1.4)	
	222 (1.1)	
	197 (0.6)	
	154 (0+)	
	135 (0.2)	

TABLE VI

X-RAY POWDER DATE 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

TABLE VI-continued

X-RAY POWDER DATE FOR $(NF_4)_2TiF_6$[a]			
d obsd	d calcd	Int	h k l
2.465	2.463	w	3 3 1
2.315	2.318	mw	3 2 3
2.201	2.200	s	4 2 2
2.100	2.101	w	5 1 0
1.990	1.990	vw	5 2 0,5 0 2
1.892	1.894	m	4 4 0
1.789	1.789	mw	6 0 0,4 4 2
1.663	1.664	mw	2 2 6
1.641	1.644	mw	3 0 6

[a] tetragonal, a = 10.715A, c = 11.114A, Cu Kα radiation Ni filter

Its ionic structure, i.e. the presence of discrete NF_4^+ cations and TiF_6^{--} anions was established by ^{19}F nmr and vibrational spectroscopy. The ^{19}F nmr spectrum showed the triplet at $\phi = -220$, characteristic for NF_4^+ as shown above, and the characteristic TiF_6^{--} signal at $\phi = -81.7$. The vibrational spectra are listed in Table VII.

TABLE VII

VIBRATIONAL SPECTRA OF SOLID $(NF_4)_2TiF_6$			
Obsd Freq (cm^{-1}) and Rel Intens		Assignments (Point Group)	
IR	Raman	$NF_4^+ (T_d)$	$TiF_6^{--} (O_h)$
1219 mw		$2\nu_4(A_1 + E + F_2)$	
1160 vs	1158 (1.4)		
1132 sh,vw		$\nu_3(F_2)$	
1060 vw		$\nu_2 + \nu_4(F_1 + F_2)$	
1021 w			
910 vw			$\nu_1 + \nu_4(F_{1u})$
	883 (0.1)	$2\nu_2(A_1 + A_2 + E)$	
850 sh,vw	853 (10)	$\nu_1(A_1)$	
804 w			
611 mw	612 (5)	$\nu_4(F_2)$	
	607 sh		
	601 (8.0)		$\nu_1(A_{1g})$
563 vs			$\nu_3(F_{1u})$
452 vw	450 (3.3)		
	442 (2.6)	$\nu_2(E)$	
	289 (8.2)		$\nu_5(F_{2g})$
	107 (0+)		
	86 (2)	Lattice Vibrations	

EXAMPLE V

TiF_4 (11.3 mmol), NF_3 (200 mmol), and F_2 (200 mmol) were heated in a passivated 90 ml Monel cylinder to various temperatures for different time periods. After each heating cycle, the volatile products were temporarily removed and the progress of the reaction was followed by determining the weight gain of the solid and recording its vibrational spectra. Heating to 200° C. for 3 days resulted in a weight gain of 8 mg and the vibrational spectra showed mainly unreacted TiF_4 in addition to a small amount of NF_4^+ and a polyperfluorotitanate (IV) anion (probably $Ti_6F_{25}^-$) having its strongest Raman line at 784 cm^{-1}. During the next two heating cycles (190°-195° C. for 14 days and 180° C. for 35 days) the solid gained 149 and 41 mg, respectively, in weight. The vibrational spectra did not show any evidence of unreacted TiF_4, and the relative intensities of the bands due to NF_4^+ had significantly increased. Furthermore, the 784 cm^{-1} Raman line had become by far the most intense Raman line. Additional heating to 230° C. for 3 days did not result in significant changes in either the weight or the vibrational spectra of the solid. Based on the observed weight increase and on the lack of spectroscopic evidence for the presence of lower polyperfluorotitanate (IV) anions, the solid product appears to have the approximate composition $NF_4Ti_6F_{25}$ (calcd weight increase, 205 mg; obsd weight increase 198 mg).

EXAMPLE VI

Displacement reactions were carried out either in HF solution at room temperature or by heating the starting materials in the absence of a solvent in a Monel cylinder. For the HF solution reactions, the solid starting materials (6 mmol of NF_4BF_4 in each experiment) were placed in a passivated Teflon FEP ampoule and 15 ml of liquid anhydrous HF was added. The mixture was stirred with a Teflon coated magnetic stirring bar at room temperature for a given time period. The volatile products were pumped off at 50° C. for 3 hours and the composition of the solid residue was determined by elemental and spectroscopic analyses and from the observed material balances.

The thermal displacement reactions were carried out in a prepassivated 90 ml Monel cylinder which was heated in an electric oven for a specified time period. The volatile products were separated by fractional condensation in a vacuum line, measured by PVT, and identified by infrared spectroscopy. The solid residues were weighed and characterized by elemental and spectroscopic analyses. The results of these experiments are summarized in Table VIII.

TABLE VIII

Results from the Displacement Reactions between NF_4BF_4 and TiF_4		
Reactants (mol)	Reaction Conditions	Products (mol)
NF_4BF_4(6), untreated TiF_4(6)	HF, 24° C., 18h	$NF_4Ti_2F_9$(4), NF_4BF_4(4)
NF_4BF_4(6), untreated TiF_4(12)	HF, 24° C., 72h	$NF_4Ti_2F_9$(6)
NF_4BF_4(6), prefluor. TiF_4(6)	HF, 24° C., 138h	$HF_4Ti_3F_{13}$(~2), NF_4BF_4(~4), small amount of $NF_4TI_2F_9$
NF_4BF_4(6), prefluor. TiF_4(12)	HF, 24° C., 96h	$NF_4Ti_3F_{13}$(4), NF_4BF_4(2),
NF_4BF_4(6), untreated TiF_4(6)	190° C., 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° C., 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° C., 20h	$NF_4Ti_2F_9$(3), NF_4BF_4(3), BF_3(3)
NF_4BF_4(6), prefluor. TiF_4(12)	170° C., 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° C., 192h	$NF_4Ti_2F_9$(6), BF_3(6)

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

We claim:

1. A compound for use in an improved NF_3—F_2 gas generator, said compound having the general composition $(NF_4^+)_nA^{n-}$, wherein A^{n-} is derived from TiF_4 and is self-clinkering.

2. A compound for use in an improved NF_3—F_2 gas generator, said compound having the general composition $(NF_4^+)_nA^{n-}$, wherein A^{n-} is TiF_6^{--} and is self-clinkering.

3. A compound for use in an improved NF_3—F_2 gas generator, said compound having the general composition $(NF_4^+)_nA^{n-}$, wherein A^{n-} is $Ti_2F_9^-$ and is self-clinkering.

4. A compound for use in an improved NF_3—F_2 gas generator, said compound having the general composition $(NF_4^+)_nA^{n-}$, wherein A^{n-} is $Ti_3F_{13}^-$ and is self-clinkering.

5. A compound for use in an improved NF_3-F_2 gas generator, said compound having the general composition $(NF_4)_n^+A^{n-}$, wherein A^{n-} is $Ti_6F_{25}^-$ and is self-clinkering.

6. A process for the production of $NF_4^+TiF_5^- \cdot nTiF_4$, comprising the steps of treating NF_4BF_4 with TiF_4 in anhydrous HF solution at room temperature.

7. A process for the production of $NF_4^+TiF_5 \cdot nTiF_4$, comprising the step of treating NF_4BF_4 with TiF_4 at temperatures ranging from 150° to 200° C.

8. A process for the production of $NF_4Ti_6F_{25}$, comprising the step of heating a mixture of NF_3, F_2 and TiF_4 to 170° C. to 200° C. at elevated pressure.

* * * * *

APPENDIX L

United States Patent [19] [11] **4,163,773**

Christe et al. [45] **Aug. 7, 1979**

[54] **SELF-CLINKERING BURNING RATE MODIFIER FOR SOLID PROPELLANT NF_3-F_2 GAS GENERATORS FOR CHEMICAL HF-DF LASERS**

[75] Inventors: **Karl O. Christe**, Calabasas; **Carl J. Schack**, Chattsworth, both of Calif.

[73] Assignee: **The United States of America as represented by the Secretary of the** Navy, Washington, D.C.

[21] Appl. No.: **970,775**

[22] Filed: **Dec. 18, 1978**

[51] **Int. Cl.**^{2} **C01B 21/18**

[52] **U.S. Cl.** **423/351; 423/462;** 149/119

[58] **Field of Search** 423/351, 462, 466; 149/19.3, 119

[56] **References Cited**

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3,980,509	9/1976	Lubowitz et al.	423/462
3,981,756	9/1976	Gotzmer, Jr.	423/462
4,001,136	1/1977	Channell et al.	252/187

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Christe et al., Novel and Known NF_4^+ Salts, Inorg. Chem., vol. 15, No. 6, 1976, pp. 1275-1282.

Christe et al., Synthesis and Characterization of NF_4BiF_6 and Properties of NF_4SbF_6, Inorg. Chem. vol. 16, No. 4, pp. 937-940, 1977.

Christe, Synthesis and Characterization of $(NF_4)_2NiF_6$, Inorg. Chem. vol. 16, No. 9, 1977, pp. 2238-2241.

Primary Examiner—O. R. Vertiz
Assistant Examiner—Thomas W. Ray
Attorney, Agent, or Firm—R. S. Sciascia; W. Thom Skeer; L.E.K. Pohl

[57] **ABSTRACT**

$N_2F_3SnF_5$ is formed by reacting $N_2F_3SbF_6$ and Cs_2SnF_6 in the presence of HF. $N_2F_3SnF_5$ is useful as a component of NF_3-F_2 gas generating compositions.

2 Claims, No Drawings

SELF-CLINKERING BURNING RATE MODIFIER FOR SOLID PROPELLANT NF_3-F_2 GAS GENERATORS FOR CHEMICAL HF-DF LASERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a composition of matter which is useful in NF_3-F_2 gas generator formulations.

2. Description of the Prior Art

In the recent past, certain new self-clinkering NF_4^+ salts have been synthesized. Among these are $(NF_4)_2SnF_6$, NF_4SnF_5, $(NF_4)_2TiF_6$, NF_4TiF_9, $NF_4Ti_3F_{13}$, $NF_4Ti_6F_{25}$ and $(NF_4)_2NiF_6$. When such self-clinkering salts are utilized as oxidizers and combined with a fuel such as aluminum, NF_3 gas, F_2 gas and solids are produced when the combination is burned. The gases are useful as lasing materials. The fact that solids or "clinkers" are produced is important in that it overcomes a disadvantage present when, for example NF_4BF_4 is used as the oxidizer. When NF_4BF_4 is used, NF_3, F_2 and another gas, BF_3, are produced. The gaseous BF_3 is not useful as a laser material and acts to deactivate the laser. By producing a solid or "clinker" instead of gases other than NF_3 and F_2, the self-clinkering salts overcome this problem.

Frequently, formulations containing NF_4^+ salts require burning rate modifiers. Typically, $N_2F_3^+$ salts which are more reactive than NF_4^+ salts can be used. However, insofar as is known from the prior art, no self-clinkering $N_2F_3^+$ salts are available.

SUMMARY OF THE INVENTION

According to this invention, a self-clinkering $N_2F_3^+$ salt which is useful as a burning rate modifier has been prepared. The salt has the formula $N_2F_3SnF_5$. Synthesis is accomplished by means of a reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 in HF. Insofar as is known by the inventors, the salt of this invention is the first self-clinkering $N_2F_3^+$ salt ever produced.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The salt, $N_2F_3SbF_6$, may be prepared according to the procedure set forth in the following example

EXAMPLE I

Synthesis of $N_2F_3SbF_6$. A Teflon amplule, containing a Teflon coated magnetic stirring bar and equipped with a stainless steel valve, was loaded with 14.4 mmol of SbF_5 in a glovebox. The ampule was then attached to a vacuum line and 2 ml of anhydrous HF was condensed into the ampule at −78° C. while stirring and warming to ambient temperature. The system was then pressurized with N_2F_4 (1 atm). A gradual decrease in the pressure was noted due to uptake of N_2F_4. Periodic cycling to below 0° C. seemed to increase the rate of N_2F_4 uptake. After several hours the unreacted N_2F_4 and HF solvent were pumped off at 40° C. until constant weight was achieved. The observed weight gain corresponded to the reaction of 12.1 mmol of N_2F_4. When the reaction was repeated on a larger scale with 8 ml HF for 3 days, it was found that 74.0 mmol of SbF_5 reacted with 73.5 mmol of N_2F_4 to give 23.66 g of $N_2F_3SbF_6$ (weight calcd for 74.0 mmol of $N_2F_3SbF_6$ 23.74 g), which was characterized by ^{19}F NMR and vibrational spectroscopy.

To produce the salt of this invention, $N_2F_3SnF_5$, one utilizes $N_2F_3SbF_6$ obtained from Example 1 and Cs_2SnF_6 and carries out the procedure set forth in the following example.

EXAMPLE II

Solid $N_2F_3SbF_6$ (6.43 mmol) and Cs_2SnF_6 (3.24 mmol) were placed in a well passivated (with ClF_3) Monel vacuum line equipped with Teflon-FEP U traps and diaphragm values. Approximately 2 ml of anhyrous HF was added. After stirring and shaking vigorously for 30 minutes at room temperature, some of the HF was removed under vacuum and the mixture was cooled to −78° C. The solid and liquid phases were separated by pressure filtration and the volatile products were removed by pumping at 25° C. for 15 hours. The volatile material was separated by fractional consideration and consisted of the HF solvent and N_2F_4 (3.2 mmol). The filtrate residue (0.3 g) was analyzed by means of vibrational and NMR spectroscopy and shown to be $N_2F_3SnF_5$.

When $N_2F_3SnF_5$ is combined with a fuel such as aluminum and burned NF_3 gas, F_2 gas, N_2 gas and a solid are obtained. (Since N_2 is normally used as an inert diluent its formation does not degrade the performance of a laser.) Thus $N_2F_3SnF_5$ is self-clinkering. That is, a non-gaseous product (the solid or "clinker") rather than a gaseous product (such as the BF_3 produced when NF_4BF_4 is burned) results upon burning of $N_2F_3SnF_5$. In addition, the useful gases NF_3 and F_2 (and N_2) are produced. Insofar as is known by the inventors, $N_2F_3SnF_5$ is the only self-clinkering $N_2F_3^+$ salt that has ever been produced to date.

What is claimed is:

1. $N_2F_3SnF_5$.

2. A method for preparing $N_2F_3SnF_5$ comprising the steps of:

forming a solution of $N_2F_3SbF_6$ salt and Cs_2SnF_6 salt in HF,

allowing the salts to react.

* * * * *

APPENDIX M

United States Patent [19]
Schack et al.

[11] **4,163,774**
[45] **Aug. 7, 1979**

[54] $N_2F_3SBF_6$ AND ITS PREPARATION

[75] Inventors: **Carl J. Schack**, Chattsworth; **Karl O. Christe**, Calabasas, both of Calif.

[73] Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, D.C.

[21] Appl. No.: **964,025**

[22] Filed: **Nov. 27, 1978**

[51] **Int. Cl.**^{2} **C01B 21/18**
[52] **U.S. Cl.** **423/351**; 423/462; 149/119
[58] **Field of Search** 423/351, 462, 466; 149/19.3, 119

[56] **References Cited**

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3,981,756	9/1976	Gotzmer, Jr.	423/462
4,001,136	1/1977	Channell et al.	252/187

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Christe et al., Synthesis & Characterization of NF_4BiF_6 and Properties of NF_4SbF_6, Inorg. Chem. vol. 16, No. 4, 1977, pp. 937-940.

Christe, Synthesis and Characterization of $(NF_4)_2NiF_6$, Inorg. Chem. Vol. 16, No. 9, 1977, pp. 2238-2241.

Primary Examiner—O. R. Vertiz
Assistant Examiner—Thomas W. Roy
Attorney, Agent, or Firm—R. S. Sciascia; W. Thom Skeer; L. E. K. Pohl

[57] **ABSTRACT**

N_2F_4 and SbF_5 react in anhydrous HF to produce $N_2F_3SbF_6$. The salt is useful as a burn rate modifier in NF_3-F_2 gas generators.

3 Claims, No Drawings

$N_2F_3SBF_6$ AND ITS PREPARATION

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the salt $N_2F_3SbF_6$ and to its preparation.

2. Description of the Prior Art

The use of solid compositions to produce fluorine and NF_3 for chemical lasers is known. For example, Pilipovich in U.S. Pat. No. 3,963,542, describes such a composition. The need for burn rate modifiers for solid gas generating compositions is also well known.

SUMMARY OF THE INVENTION

According to this invention, a salt that is useful as a burn rate modiifier for NF_3-F_2 gas generators is provided. The salt is a fluorine containing salt having the formula $N_2F_3SbF_6$ and is prepared by reacting N_2F_4 and SbF_5 in anhydrous HF. Insofar as is known by the inventors, $N_2F_3SbF_6$ has not been previously synthesized.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The preparation of the salt of this invention is illustrated by the following example.

EXAMPLE

Synthesis of $N_2F_3SbF_6$. A Teflon ampule, containing a Teflon coated magnetic stirring bar and equipped with a stainless steel valve, was loaded with 14.4 mmol of SbF_5 in a glovebox. The ampule was then attached to a vacuum line and 2 ml of anhydrous HF was condensed into the ampule at −78° C. while stirring and warming to ambient temperature. The system was then pressurized with N_2F_4 (1 atm). A gradual decrease in the pressure was noted due to uptake of N_2F_4. Periodic cycling to below 0° C. seemed to increase the rate of N_2F_4 uptake. After several hours the unreacted N_2F_4 and HF solvent were pumped off at 40° C. until constant weight was achieved. The observed weight gain corresponded to the reaction of 12.1 mmol of N_2F_4. When the reaction was repeated on a larger scale with 8 ml HF for 3 days, it was found that 74.0 mmol of SbF_5 reacted with 73.5 mmol of N_2F_4 to give 23.66 g of $N_2F_3SbF_6$ (weight calcd for 74.0 mmol of $N_2F_3SbF_6$ 23.74 g), which was characterized by ^{19}F NMR and vibrational spectroscopy.

Tests in which small amounts of $N_2F_3SbF_6$ were incorporated into aluminized NF_3-F_2 gas generator compositions showed that the salt was effective as a burn rate modifier.

What is claimed is:

1. The salt having the formula:

$N_2F_3SbF_6$.

2. A method for preparing the salt having the formula $N_2F_3SbF_6$ comprising the steps of:

forming a solution of N_2F_4 and SbF_5 in anhydrous HF; and

reacting the N_2F_4 and SbF_5 at room temperature.

3. A method according to claim 2 wherein the HF solvent is removed by distillation.

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United States Patent [19]

Christe et al.

[11] **4,172,881**

[45] **Oct. 30, 1979**

[54] **DISPLACEMENT REACTION FOR PRODUCING NF_4PF_6**

[75] Inventors: **Karl O. Christe**, Calabasas; **Carl J. Schack**, Chatsworth, both of Calif.

[73] Assignee: **Rockwell International Corporation**, El Segundo, Calif.

[21] Appl. No.: **849,377**

[22] Filed: **Nov. 7, 1977**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 732,275, Oct. 14, 1976, abandoned.

[51] **Int. Cl.**^{2} **C01B 25/10**

[52] **U.S. Cl.** **423/301**; 423/351; 149/119

[58] **Field of Search** 423/301, 293, 351; 149/119

[56] **References Cited**

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Christe et al., Annual Report-Inorganic Halogen Oxidizer Research, 1/26/76, pp. A-1 to A-4, A-10 to A-13, A-25, Cover Page.

Primary Examiner—O. R. Vertiz

Assistant Examiner—Thomas W. Roy

Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

A method of producing NF_4PF_6 by a displacement reaction between NF_4BF_4 and PF_5.

1 Claim, No Drawings

DISPLACEMENT REACTION FOR PRODUCING NF_4PF_6

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of Ser. No. 732,275 filed Oct. 14, 1976, and abandoned Dec. 5, 1977, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to methods of producing compositions and is particularly directed to a method of producing NF_4PF_6 by a displacement reaction between NF_4BF_4 and PF_5.

2. Description of the Prior Art

$NF_4{}^+$ salts are the key ingredients for solid propellant $NF_3—F_2$ gas generators, such as that disclosed by D. Pilipovich in U.S. Pat. No. 3,963,542, for chemical HF-DF lasers. Whereas NF_4SbF_6 and NF_4AsF_6 can be prepared with relative ease, according to the methods taught by W. E. Tolberg et al, in U.S. Pat. No. 3,708,570, and K. O. Christe et al, in U.S. Pat. No. 3,503,719, these compounds suffer from the disadvantage of containing a relatively heavy anion, thus decreasing their performance in an $NF_3—F_2$ gas generator. This disadvantage can be overcome by replacing the $SbF_6{}^-$ or $AsF_6{}^-$ anion by the lighter $PF_6{}^-$ anion. The existence of this salt has previously been claimed by Tolbert et al in U. S. Pat. No. 3,708,570, but their production process was so inefficient that they could not isolate an amount of material sufficient for its isolation, identification and characterization.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

This problem of synthesizing NF_4PF_6 is overcome by the present invention. The method of the present invention involves a displacement reaction between the readily available NF_4BF_4 and PF_5 according to:

$$NF_4BF_4 + PF_5 \rightarrow NF_4PF_6 + BF_3$$

Applicants have found that the displacement reaction can be carried out at any temperature above the melting point of PF_5 (−94° C.) and below the decomposition temperature of NF_4PF_6 (above 245° C.). Moreover, the pressure is not essential and is given by the reaction temperature (that is, the vapor pressure of PF_5).

This method provides NF_4PF_6 of high purity.

Accordingly, it is an object of the present invention to provide an improved process for the production of NF_4PF_6.

This and other objects and features of the present invention will be apparent from the following examples.

DETAILED DESCRIPTION OF THE INVENTION

In a typical experiment, pure NF_4BF_4 (2.07 mmol) was combined at −196° C. with an excess of PF_5 (40.01 mmol) in a 10-ml 316 stainless steel cylinder. The mixture was kept at 25° C. for 64 h. The volatile materials were removed in vacuo and separated by fractional condensation. They consisted of BF_3 (2.05 mmol) and unreacted PF_5 (37.93 mmol). The white solid residue had gained 120 mg in weight. Based on the above material balance, the conversion of NF_4BF_4 to NF_4PF_6 was essentially complete. This was further confirmed by vibrational spectroscopy which showed the solid to be NF_4PF_6 containing no detectable amounts of NF_4BF_4.

The salt NF_4PF_6 is a white, crystalline, hydroscopic solid, stable at room temperature, but rapidly decomposing at 245° C. Its characteristic x-ray diffraction powder pattern is listed in Table I. Its vibrational spectrum is listed in Table II and establishes the ionic nature of the salt, i.e. the presence of discrete $NF_4{}^+$ cations and $PF_6{}^-$ anions. This was further confirmed by ^{19}F nmr spectroscopy in HF solution which showed the triplet ($J_{NF}=230$ Hz at $\phi=-217$) characteristic for $NF_4{}^+$.

TABLE I

X-RAY POWDER DATA FOR $NF_4PF_6{}^a$

d obsd	d calcd	Int	h k l
5.40	5.36	ms	1 1 0
4.55	4.53	s	1 0 1
3.91	3.89	vs	1 1 1
3.79	3.79	s	2 0 0
2.91	2.91	ms	211
2.65	2.65	m	1 0 2
2.40	2.40	vw	3 1 0
2.307	2.305	m	3 0 1
2.204	2.205	vw	3 1 1
2.171	2.171	mw	2 1 2
1.882	1.883	ms	3 0 2,0 0 3
1.825	1.827	vw	3 1 2,1 0 3
1.784	1.785	w	3 3 0
1.747	1.747	mw	4 1 1
1.685	1.685	w	3 2 2,2 0 3
1.646	1.646	w	2 1 3
1.622	1.622	w	4 2 1
1.536	1.540	vw	4 1 2
1.485	1.486	vw	5 1 0
1.464	1.463	vw	5 0 1
1.437	1.437	w	5 1 1
1.408	1.407	vw	5 2 0
1.365	1.365	vw	5 2 1,1 1 4
1.333	1.335	w	5 0 2
1.318	1.319	vw	4 4 0
1.302	1.304	vw	2 1 4
1.259	1.259	w	4 2 3
1.214	1.216	w	6 1 1

[a] Tetragonal, a = 7 577, c = 5 653A, Cu K_α radiation Ni filter

TABLE II

VIBRATIONAL SPECTRUM OF NF_4PF_6

Obsd Frequency (cm^{-1}) Ir	Raman	Assignments for $NF_4{}^+(T_d)$
2380 vw 2320 w		$2\nu_3(A_1 + E + F_2) \approx 2320$
2005 w		$\nu_1 + \nu_3(F_2) = 2008$
1765 w		$\nu_3 + \nu_4(A_1 + E + F_2) = 1769$
1457 w		$\nu_1 + \nu_4(F_2) = 1457$
1221 mw		$2\nu_4(A_1 + E + F_2) \approx 1218$
1166 vs	1168(1.5) 1150(0.8)	$\nu_3(F_2)$
1135 vw		
1056 vw		$\nu_2 + \nu_4(F_1 + F_2) \approx 1049$
	880(0.2)	$2\nu_2(A_1 + A_2 + E) \approx 880$
	849(8.2)	$\nu_1(A_1)$
611 m	609(7.4)	$\nu_4(F_2)$
608 m	441(2.9)	$\nu_2(E)$

TABLE II-continued

VIBRATIONAL SPECTRUM OF NF_4PF_6

		Assignments for PF_6^- (O_h)
1590 w		$\nu_1 + \nu_3(F_{1u}) = 1590$
1414 w		$\nu_2 + \nu_3(F_{1u} + F_{2u}) = 1413$
1308 vw		$\nu_1 + \nu_4(F_{1u}) = 1307$
842 vs 789 w	838(1.5)	$\nu_3(F_{1u})$
749 w	748(10)	$\nu_1(A_{1g})$
	571(0.8)	$\nu_2(E_g)$
559 s		$\nu_4(F_{1u})$
474 vw	469(1.2)	$\nu_5(F_{2g})$

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the form of the present invention described above is illustrative only and is not intended to limit the scope of the present invention.

We claim:

1. A process for the production of NF_4PF_6 characterized by combining NF_4BF_4 with an excess of PF_5 at above about $-196°$ C., reacting the reactants while warming the reaction system to a temperature less than about 25° C. and removing the volatile reaction products by pumping.

* * * * *

United States Patent [19]

Christe et al.

[11] **4,172,884**

[45] **Oct. 30, 1979**

[54] **SELF-CLINKERING NF_4+ COMPOSITIONS FOR NF_3-F_2 GAS GENERATORS AND METHOD OF PRODUCING SAME**

[75] Inventors: **Karl O. Christe**, Calabasas; **Carl J. Schack**, Chatsworth; **Richard D. Wilson**, Canoga Park, all of Calif.

[73] Assignee: **Rockwell International Corporation**, El Segundo, Calif.

[21] Appl. No.: **927,713**

[22] Filed: **Jul. 24, 1978**

Related U.S. Application Data

[62] Division of Ser. No. 734,153, Oct. 20, 1976, Pat. No. 4,152,406.

[51] **Int. Cl.**^{2} **C01G 19/00**

[52] **U.S. Cl.** **423/351**; 149/19.3; 149/119

[58] **Field of Search** 423/351; 149/19.3, 119

[56] **References Cited**

U.S. PATENT DOCUMENTS

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3,980,509	9/1976	Lubowitz	149/19.3
4,001,136	1/1977	Channell et al.	149/119
4,107,275	8/1978	Christe et al.	149/119
4,108,965	8/1978	Christe	423/351

Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

Improved NF_4+ compositions for solid propellant NF_3-F_2 gas generators are described which produce NF_3 and F_2 free of gaseous Lewis acids and do not require clinker forming additives for their complexing. The novel self-clinkering compositions $(NF_4)_2SnF_6$, NF_4SnF_5, $(NF_4)_2TiF_6$, $NF_4Ti_2F_9$, $NF_4Ti_3F_{13}$, and $NF_4Ti_6F_{25}$ and processes for their production are disclosed.

5 Claims, No Drawings

SELF-CLINKERING NF_4^+ COMPOSITIONS FOR NF_3-F_2 GAS GENERATORS AND METHOD OF PRODUCING SAME

The invention herein described was made in the course of or under a contract or subcontract thereunder, (or grant) with the United States Navy.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of Ser. No. 734,153 filed Oct. 20, 1976, and now U.S. Pat. No. 4,152,406.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions of matter and methods of producing the same and is particularly directed to improved solid propellant NF_3—F_2 gas generators derived from self-clinkering NF_4^+ salts, together with methods for producing such gas generators.

2. Description of the Prior Art

NF_4^+ salts are the key ingredients for solid propellant NF_3—F_2 gas generators, as shown by D. Pilipovich in U.S. Pat. No. 3,963,542. These propellants consist of a highly over-oxidized grain using NF_4^+ salts as the oxidizer. Burning these propellants with a small amount of fuel, such as aluminum powder, generates sufficient heat to thermally dissociate the bulk of the oxidizer. This is shown for NF_4BF_4 in the following equation:

$$NF_4BF_4 \rightarrow NF_3 + F_2 + BF_3$$

As can be seen from the equation the gaseous combustion products contain the volatile Lewis acid BF_3. This disadvantage of a volatile Lewis acid byproduct is shared by all the previously known NF_4^+ compositions. These volatile Lewis acids possess a relatively high molecular weight and a low γ value ($\gamma = C_{pi}/C_{vi}$), relative to the preferred diluent helium and frequently act as a deactivator for the chemical HF-DF laser. Consequently, these volatile Lewis acids must be removed from the generated gas prior to its use in an efficient chemical laser. Based on the state of the art, heretofore, this would be achieved by adding a clinker forming agent, such as KF, to the solid propellant formulation. The function of this additive served to convert the volatile Lewis acid, such as BF_3, to a non-volatile salt as shown by the following equation:

$$KF + BF_3 \rightarrow KBF_4$$

The principal disadvantages of this approach are that, even if an excess of KF is used, complete clinkering cannot always be guaranteed, and that the addition of the KF severely degrades the yield of NF_3—F_2 obtainable per pound of formulation. This problem could be solved by using NF_4^+ containing compositions derived from non-volatile Lewis acids. However, the synthesis of such compositions has previously been unknown, since highly stable and non-volatile Lewis acids are polymeric and contain coordination-wise saturated central atoms. Consequently, these compounds possess very little or no acidity, which renders the synthesis of such salts very difficult.

BRIEF SUMMARY AND OBJECTS OF THE INVENTION

The above described problem of obtaining a Lewis acid free NF_3—F_2 gas stream from NF_4^+ compositions without clinker forming additives is overcome by the present invention. We have found that NF_4^+ salts, derived from the polymeric non-volatile Lewis acids SnF_4 (subliming at 704° C.) and TiF_4 (1 atm vapor pressure at 284° C.) can be prepared. The lack of acidity of SnF_4 at temperatures, at which NF_4^+ salts can be formed and exist, was demonstrated. It was shown that mixtures of NF_3, F_2, and SnF_4, when heated to temperatures of up to 300° C. at autogenous pressures of about 150 atm, did not show any evidence for NF_4^+ formation.

Since a direct synthesis of an NF_4^+ salt derived from SnF_4 was not possible, we have studied metathetical and displacement reactions. Because SnF_6^{--} salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. The following methathetical reaction

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

was carried out. It resulted in the precipitation of the rather insoluble salt $CsSbF_6$, while the soluble $(NF_4)_2SnF_6$ remained in solution. The two products were separated by a simple filtration step. The composition (in mol%) of the crude product was: $(NF_4)_2SnF_6$, 83; NF_4SbF_6, 13; $CsSbF_6$, 4. The purity of this product can be easily increased by following the procedures outlined for NF_4BF_4 in our co-pending application Serial No.   , filed

Another NF_4^+ salt derived from SnF_4 was obtained by the following quantitative displacement reaction in anhydrous HF as a solvent.

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

For TiF_4, the direct synthesis of an NF_4^+ salt from NF_3, F_2, and TiF_4 is still possible, since TiF_4 possesses already some vapor pressure at temperatures where NF_4^+ salts can be formed. However, the product thus obtained is very rich in TiF_4, as shown by the following equation:

$$NF_3 + F_2 + 6TiF_4 \xrightarrow[\text{160 atm}]{\text{190° C., 50 days}} NF_4Ti_6F_{25}$$

The NF_4^+ content of this salt could not be significantly increased by any changes in the reaction conditions.

Displacement reactions between NF_4BF_4 and TiF_4, either in HF solution or in the absence of a solvent, produced NF_4^+ salts according to

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

where, depending on the exact reaction conditions, n equals either 3 or 2.

A further increase in the NF_4^+ content was possible by the following metathetical reaction which yielded $(NF_4)_2TiF_6$:

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

The separation and purification procedure for this product is analogous to that outlined above for $(NF_4)_2SnF_6$.

The advantages of the above disclosed concept of using these novel self-clinkering NF_4^+ composition for NF_3—F_2 gas generators become obvious from a comparison of their theoretical performance data. In Table I, the theoretical yields of usable fluorine, expressed in weight percent, of $(NF_4)_2SnF_6$ and $(NF_4)_2TiF_6$ are compared to that of KF clinkered NF_4BF_4, the highest performing presently known system. The novel self-clinkering compositions clearly outperform KF clinkered NF_4BF_4. Furthermore, the risk of incomplete clinkering which always exists for a clinkered formulation is avoided.

TABLE I

A COMPARISON OF THE THEORETICAL PERFORMANCE OF SELF-CLINKERING $(NF_4)_2SnF_6$ AND $(NF_4)_2TiF_6$ WITH KF-CLINKERED NF_4BF_4

System	Performance (Weight % Usable F)
$NF_4BF_4 . 1.2KF$	38.5
$(NF_4)_2SnF_6$	46.0
$(NF_4)_2TiF_6$	55.6

Accordingly, it is an object of the present invention to provide higher performing solid propellant NF_3—F_2 gas generator compositions.

Another object of the present invention is to provide self-clinkering NF_4^+ compositions capable of generating Lewis acid free NF_3 and F_2.

Another object of the present invention is to provide processes for the production of self-clinkering NF_4^+ compositions.

These and other objects and features of the present invention will be apparent from the following examples. It is understood, however, that these examples are merely illustrative of the invention and should not be considered as limiting the invention in any sense.

DETAILED DESCRIPTION OF THE INVENTION

EXAMPLE I

Metathetical reactions were carried out in an apparatus consisting of three Teflon FEP U-traps interconnected by Monel unions and closed off at each end by a Monel valve. The union between trap II and trap III contained a Teflon filter and was held in place by a press fit. The passivated apparatus was taken to the dry box and Cs_2SnF_6 and NF_4SbF_6 (in a 1:2 mole ratio) were placed into traps I and II, respectively. The apparatus was connected to the vacuum line through flexible corrugated Teflon FEP tubing. Anhydrous HF, in an amount sufficient to just dissolve the starting materials, was added to traps I and II. Trap I was flexed to allow the Cs_2SnF_6 solution to run into trap II containing the NF_4SbF_6 solution. Upon contact of the two solutions, copious amounts of a white precipitate ($CsSbF_6$) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to −80° C. After completion of the filtration step, trap III was warmed to ambient temperature and the HF solvent was pumped off. The solid residue on top of the filter consisted mainly of $CsSbF_6$, whereas the solid collected in trap II 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. Calculated analysis 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.

$(NF_4)_2SnF_6$ is a white, crystalline, hygroscopic solid, stable at room temperature but decomposing at 240° C. Its characteristic x-ray powder pattern is listed in Table II. Its ionic composition, i.e. the presence of discrete NF_4^+ cations and SnF_6^{--} anions was established by ^{19}F nmr, infrared and Raman spectroscopy.

The ^{19}F nmr spectrum, recorded for a BrF_5 solution, showed in addition to the solvent lines a triplet of equal intensity with $\phi = -220$, $J_{NF} = 229.6$ Hz, and a line width at half height of about 5 Hz, which is characteristic of tetrahedral NF_4^+. In addition, a narrow singlet at $\phi = 149$ was observed with the appropriate $^{117/119}Sn$ satellites (average $J_{SnF} = 1549$ Hz), characteristic of octahedral SnF_6^{--}. The vibrational spectra of $(NF_4)_2SnF_6$ and their assignments are summarized in Table III.

EXAMPLE II

A mixture of NF_4BF_4 and SnF_4 (9.82 mmol each) was placed into a passivated Teflon-FEP ampoule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10 ml liquid) was added at −78° C., and the resulting suspension was stirred at 25° C. for 2 hours. The volatile material was pumped off at 35° C. leaving behind a white stable solid which, on the basis of its weight (3.094 g) and Raman spectrum, consisted of 83 mol percent NF_4SnF_5 and 17 mol percent unreacted starting materials. The HF treatment was repeated (again for 2 hours) and the non-volatile residue (2.980 g, weight calcd for 9.82 mmol of NF_4SnF_5 = 2.982 g) was shown by infrared, Raman, and ^{19}F nmr spectroscopy to be essentially pure NF_4SnF_5. Anal. Calcd for NF_4SnF_5:NF_3, 23.38; Sn, 39.08. Found: NF_3, 23.6; Sn, 38.7.

TABLE II

X-RAY POWDER DATE FOR $(NF_4)_2SnF_6^a$

d obsd	d calcd	Int	h k l
6.27	6.36	w	1 1 1
5.67	5.70	vs	0 0 2
4.99	5.04	vw	1 0 2
3.67	3.69	w	2 1 2
3.55	3.59	s	1 0 3
3.42	3.42	s	3 1 0
2.990	2.990	s	2 1 3
2.851	2.851	ms	0 0 4
2.492	2.490	m	3 3 1
2.347	2.356	w	3 2 3
2.230	2.228	s	4 2 2
2.120	2.123	mw	5 1 0
2.023	2.024	mw	5 0 2
1.961	1.963	w	4 0 4
1.917	1.914	m	4 4 0
1.882	1.881	mw	5 0 3
1.834	1.832	w	5 3 1
1.813	1.814	mw	4 4 2
1.763	1.765	vw	5 3 2
1.712	1.712	w	6 2 0
1.686	1.686	m	5 4 0,3 0 6
1.662	1.662	m	3 1 6
1.616	1.614	mw	6 3 0
1.570	1.570	mw	5 0 5
1.500	1.501	mw	6 4 0
1.397	1.396	mw	6 4 3

TABLE II-continued

X-RAY POWDER DATE FOR $(NF_4)_2SnF_6$[a]			
d obsd	d calcd	Int	h k l
1.387	1.386	w	6 5 0
1.359	1.359	mw	7 0 6,5 4 5
1.331		mw	
1.314		mw	
1.263		w	
1.231		w	
1.212		mw	
1.192		w	
1.177		mw	

[a] tetragonal, a = 10.828Å, c = 11.406Å, Cu K_α radiation Ni filter

TABLE III

Vibrational Spectra of Solid $(NF_4)_2SnF_6$			
Obsd Freq (cm^{-1}) and Rel Inten		Assignments (Point Group)	
IR	Raman	NF_4^+ (T_d)	SnF_6—(O_h)
1224 mw		$2\nu_4 (A_1 + E + F_2$	
1160 vs	1158 (1.5)	$\nu_3 (F_2)$	
1132 sh,vw			$\nu_1 + \nu_3 (F_{1\mu})$
1059 vw		$\nu_2 + \nu_4 (F_1 + F_2)$	
1026 vw			$\nu_2 + \nu_3 (F_{1u} + F_{2u})$
	811 (0.1)	$2\nu_2(A_1 + A_2 + E)$	
854 vvw	853 (10)	$\nu_1 (A_1)$	
613 mw	613 (5.0)		
605 mw	607 (1.5)	$\nu_4 (F_2)$	
	579 (8.3)		$\nu_1 (A_{1g})$
550 vs			$\nu_3 (F_{1u})$
	470 (0+) br		$\nu_2 (E_g)$
	449 (3.1)		
	442 (2.9)	$\nu_2 (E)$	
	251 (3.3)		$\nu_5 (F_{2g})$
	84 (0.3)	Lattice Vibration	

NF_4SnF_5 is a white, crystalline, hygroscopy solid, stable at room temperature and decomposing above 200° C. Its characteristic x-ray powder pattern is listed in Table IV.

TABLE IV

X-RAY POWDER DATA FOR NF_4SnF_5			
d obsd	Int	d obsd	Int
7.72	mw	2.571	mw
6.32	vs	2.519	vw
5.69	w	2.276	w
5.29	w	2.146	w
4.51	m	2.064	ms
4.19	m	1.965	mw
3.80	vs	1.929	w
3.46	m	1.820	m
3.32	m	1.780	mw
3.17	mw	1.757	mw
2.868	w	1.732	mw
2.802	w	1.700	mw
2.743	m	1.661	vw
2.683	w	1.639	w
		1.615	w

Its ionic structure, i.e., presence of NF_4^+ cations, was established by its ^{19}F *nmr spectrum in* BrF_5 solution. *In* addition to the solvent lines, it showed the triplet (see above) at $\phi = -220$, characteristic of NF_4^+. Two resonances were observed for SnF_5 at $\phi = 145.4$ and 162.4, respectively, with an area ratio of 1:4. At −20° C. the resonances consisted of broad lines, but at lower temperatures the $\phi = 162.4$ signal showed splittings. Based on a more detailed analysis of these data, the SnF_5^- anion appears to have a diameric or polymeric structure. The vibrational spectrum of NF_4SnF_5 is listed in *Table V and again establishes the presence of discrete* NF_4^+ cations.

EXAMPLE III

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

EXAMPLE IV

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 described in Example I 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° C. and filtered. The volatile materials were pumped off at 50° C. for 1 hour. The filter cake (3.85 g) was shown by its x-ray powder diffraction pattern and vibrational spectroscopy to be mainly $CsSbF_6$ containing, due to the hold up of some mother liquor, a small amount of $(NF_4)_2TiF_6$. 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, 36.2; 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, 36.43; Ti, 12.29; Sb, 4.06; Cs, 4.43. Based on the observed Raman spectrum, the composition of the filtrate residue was estimated to be 90 $(NF_4)_2TiF_6$ and 10 $CsSbF_6$, in good agreement with the above elemental analysis.

$(NF_4)_2TiF_6$ is a white, crystalline, hygroscopic solid, stable at room temperature, but decomposing above 200° C. Its characteristic x-ray powder pattern is listed in Table VI.

TABLE V

Vibrational Spectra of Solid NF_4SnF_5		
Obsd Freq (cm^{-1}) and Rel Intens NF_4SnF_5		Assignments (Point Group)
IR	Raman	NF_4^+ (T_d)
1222 mw		$2\nu_4 (A_1 + F + F_2)$
	1168 (0.4)	
1165 vs	1159 (0.8)	$\nu_3 (F_2)$
	1150 sh	
1134 w,sh		

TABLE V-continued

Vibrational Spectra of Solid NF_4SnF_5

Obsd Freq (cm^{-1}) and Rel Intens NF_4SnF_5		Assignments (Point Group)
IR	Raman	NF_4^+ (T_d)
1061 w		$\nu_2 + \nu_4 (F_1 + F_2)$
1048 w		
	881 (0.2)	$2\nu_2 (A_1 + A_2 + E)$
850 vw	851 (10)	$\nu_1 (A_1)$
635 vs		
	622 (9.2)	
605 mw	606 (3.3)	$\nu_4 (F_2)$
575 vs		
	574 (0.5)	
559 w, sh	558 (2.0)	
490 m	490 (0+)	
458 m		
	448 (2.5)	$\nu_2 (E)$
	440 (2.3)	
	272 (0.6)	
	247 (1.4)	
	222 (1.1)	
	197 (0.6)	
	154 (0+)	
	135 (0.2)	

TABLE VI

X-RAY POWDER DATE 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 = 10.715A, c = 11.114A, Cu K_α radiation Ni filter

Its ionic structure, i.e. the presence of discrete NF_4^+ cations and TiF_6^{--} anions was established by ^{19}F nmr and vibrational spectroscopy. The ^{19}F nmr spectrum showed the triplet at $\phi = -220$, characteristic for NF_4^+ as shown above, and the characteristic TiF_6^{--} signal at $\phi = -81.7$. The vibrational spectra are listed in Table VII.

TABLE VII

VIBRATIONAL SPECTRA OF SOLID $(NF_4)_2TiF_6$

Obsd Freq (cm^{-1}) and Rel Intens		Assignments (Point Group)	
IR	Raman	$NF_4^+ (T_d)$	$TiF_6^{--} (O_h)$
1219 mw		$2\nu_4(A_1 + E + F_2)$	
1160 vs	1158 (1 4)		
1132 sh,vw		$\nu_3 (F_2)$	
1060 vw		$\nu_2 + \nu_4(F_1 + F_2)$	
1021 w			
910 vw			$\nu_1 + \nu_4(F_{1\mu})$
	883 (0.1)	$2\nu_2(A_1 + A_2 + E)$	
850 sh,vw	853 (10)	$\nu_1 (A_1)$	
804 w			
611 mw	612 (5)	$\nu_4 (F_2)$	
	607 sh		

TABLE VII-continued

VIBRATIONAL SPECTRA OF SOLID $(NF_4)_2TiF_6$

Obsd Freq (cm^{-1}) and Rel Intens		Assignments (Point Group)	
IR	Raman	$NF_4^+ (T_d)$	$TiF_6^{--} (O_h)$
	601 (8.0)		$\nu_1(A_{1g})$
563 vs			$\nu_3(F_{1\mu})$
452 vw	450 (3.3)		
	442 (2.6)	$\nu_2 (E)$	
	289 (8.2)		$\nu_5(F_{2g})$
	107 (0+)		
	86 (2)	Lattice Vibrations	

EXAMPLE V

TiF_4 (11.3 mmol), NF_3 (200 mmol), and F_2 (200 mmol) were heated in a passivated 90 ml Monel cylinder to various temperatures for different time periods. After each heating cycle, the volatile products were temporarily removed and the progress of the reaction was followed by determining the weight gain of the solid and recording its vibrational spectra. Heating to 200° C. for 3 days resulted in a weight gain of 8 mg and the vibrational spectra showed mainly unreacted TiF_4 in addition to a small amount of NF_4^+ and a polyperfluorotitanate (IV) anion (probably $Ti_6F_{25}^-$) having its strongest Raman line at 784 cm^{-1}. During the next two heating cycles (190°-195° C. for 14 days and 180° C. for 35 days) the solid gained 149 and 41 mg, respectively, in weight. The vibrational spectra did not show any evidence of unreacted TiF_4, and the relative intensities of the bands due to NF_4^+ had significantly increased. Furthermore, the 784 cm^{-1} Raman line had become by far the most intense Raman line. Additional heating to 230° C. for 3 days did not result in significant changes in either the weight or the vibrational spectra of the solid. Based on the observed weight increase and on the lack of spectroscopic evidence for the presence of lower polyperfluorotitanate (IV) anions, the solid product appears to have the approximate composition $NF_4Ti_6F_{25}$ (calcd weight increase, 205 mg; obsd weight increase 198 mg).

EXAMPLE VI

Displacement reactions were carried out either in HF solution at room temperature or by heating the starting materials in the absence of a solvent in a Monel cylinder. For the HF solution reactions, the solid starting materials (6 mmol of NF_4BF_4 in each experiment) were placed in a passivated Teflon FEP ampoule and 15 ml of liquid anhydrous HF was added. The mixture was stirred with a Teflon coated magnetic stirring bar at room temperature for a given time period. The volatile products were pumped off at 50° C. for 3 hours and the composition of the solid residue was determined by elemental and spectroscopic analyses and from the observed material balances.

The thermal displacement reactions were carried out in a prepassivated 90 ml Monel cylinder which was heated in an electric oven for a specified time period. The volatile products were separated by fractional condensation in a vacuum line, measured by PVT, and identified by infrared spectroscopy. The solid residues were weighed and characterized by elemental and spectroscopic analyses. The results of these experiments are summarized in Table VIII.

TABLE VIII

RESULTS FROM THE DISPLACEMENT REACTIONS BETWEEN NF_4BF_4 AND TiF_4

Reactants (mol)	Reaction Conditions	Products (mol)
$NF_4BF_4(6)$, untreated $TiF_4(6)$	HF, 24° C., 18h	$NF_4Ti_2F_9(4)$, $NF_4BF_4(4)$
$NF_4BF_4(6)$, untreated $TiF_4(12)$	HF, 24° C., 72h	$NF_4Ti_2F_9(6)$
$NF_4BF_4(6)$, prefluor. $TiF_4(6)$	HF, 24° C., 138h	$HF_4Ti_3F_{13}(\sim 2)$, $NF_4BF_4(\sim 4)$, small amount of $NF_4Ti_2F_9$
$NF_4BF_4(6)$, prefluor. $TiF_4(12)$	HF, 24° C., 96h	$NF_4Ti_3F_{13}(4)$, $NF_4BF_4(2)$,
$NF_4BF_4(6)$, untreated $TiF_4(6)$	190° C., 18h	$NF_4Ti_2F_9(\sim 3)$, $NF_3(\sim 3)$, $BF_3(\sim 6)$, small amounts of NF_4BF_4 and $NF_4Ti_3F_{13}$
$NF_4BF_4(6)$, untreated $TiF_4(6)$	160° C., 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° C., 20h	$NF_4Ti_2F_9(3)$ $NF_4BF_4(3)$ $BF_3(3)$
NF_4 $BF_4(6)$, prefluor. $TiF_4(12)$	170° C., 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° C., 192h	$NF_4Ti_2F_9(6)$, $BF_3(6)$

Obviously, numerous variations and modifications may be made without departing from the present invention. Accordingly, it should be clearly understood that the forms of the present invention described above are illustrative only and are not intended to limit the scope of the present invention.

We claim:

1. A compound for use in an improved NF_3—2 gas generator, said compound having the general composition $(NF_4^+)nA^{n-}$, wherein A^{n-} is derived from SnF_4 and is self-clinkering.

2. A compound for use in an improved NF_3—F_2 gas generator, said compound having the general composition $(NF_4^+)nA^{n-}$, wherein A^{n-} is SnF_6^{--} and is self-clinkering.

3. A compound for use in an improved NF_3—F_2 gas generator, said compound having the general composition $(NF_4^+)nA^{n-}$, wherein A^{n-} is SnF_5^- and is self-clinkering.

4. A process for the poduction of $(NF_4^+)_2SnF_6^{--}$, comprising the steps of combining a soluble $NF_4^+X^-$ salt with a soluble alkali metal salt of SnF_6^{--} in a suitable solvent to produce an insoluble alkali metal X salt, and filtering off the precipitated insoluble alkali metal X salt from the solution containing the soluble $(NF_4^+)_2SnF_6^{--}$ salt.

5. A process for the production of NF_4SnF_5, comprising the steps of treating NF_4BF_4 in an anhydrous HF solution with an equimolar amount of SnF_4 and removing all products volatile at room temperature.

* * * * *

APPENDIX P

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