

AD A098705

LEVEL II

12

DTIC
ELECTE
MAY 11 1981
S D E



Rockwell International

DTIC FILE COPY

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

81 5 11 020

LEVEL II

12



Rockwell International

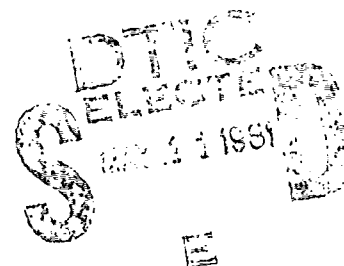
Rocketdyne Division
6633 Canoga Avenue
Canoga Park, California 91304

RI/RD81-140

ANNUAL REPORT
INORGANIC HALOGEN OXIDIZER RESEARCH
(1 March 1980 through 8 February 1981)

21 April 1981

Contract N00014-79-C-0176
G.O. 95067
Office of Naval Research
Power Branch
Code 473



PREPARED BY

K. O. Christe, C. J. Schack,
W. W. Wilson, and R. D. Wilson

APPROVED BY

L. R. Grant
L. R. Grant
Program Manager

Approved for public
release; distribution
unlimited.

Reproduction in whole or in
part is permitted for any
purpose of the United States
Government

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

14. REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RI/RD81-140	2. GOVT ACCESSION NO. AD-A098705	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ANNUAL REPORT, INORGANIC HALOGEN OXIDIZER RESEARCH.	5. TYPE OF REPORT & PERIOD COVERED Annual Report, 1 March 1980 - 28 February 1981	6. PERFORMING ORG. REPORT NUMBER RI/RD81-140
7. AUTHOR(s) K. O. Christie, C. J. Schack, W. W. Wilson, and R. D. Wilson	8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0176	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rocketdyne Division, Rockwell International 6633 Canoga Avenue Canoga Park, California 91304	10. PROGRAM ELEMENT PROJECT, TASK AREA & WORK UNIT NUMBERS OL A 81	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Power Branch Code 473 Arlington, VA 22217	12. REPORT DATE 17 March 1981	13. NUMBER OF PAGES 176
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 169	15. SECURITY CLASS. (of this report) UNCLASSIFIED	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Reproduction in whole or in part is permitted for any purpose of the United States Government DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Synthesis, Oxidizers, Solid-Propellant NF_3/F_2 Gas Generators, Perfluoroammonium Salts, Hypofluorites, Aqueous Fluorination, Chlorine Trifluoride Oxide, Electron Diffraction, Force Field Calculations, High Detonation Pressure Explosives, Sulfur Tetrafluoride, Trifluoromethyl Azide, Perfluoromethylamine, Monofluoroammonium Salts, Perchlorylfluoride, Fluorine Perchlorate, Halogen Oxyfluorides,		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Periodates. A research program was carried out in the area of inorganic high energy oxidizers. Principal areas of investigation included perfluoroammonium salts, halogen fluorides, oxyfluorides, hypofluorites, monofluoramine, aqueous fluorinations, force field calculations, structure determinations, low-temperature matrix isolation studies, and novel energetic anions.		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED 390199
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 473, and the U. S. Army Research Office, with Dr. R. S. Miller of ONR as Scientific Officer. This report covers the period 1 March 1980 through 28 February 1981. The program has been directed by Dr. K. O. Christie. The scientific effort was carried out by Drs. K. O. Christie, C. J. Schack, W. W. Wilson, and Mr. R. D. Wilson.

Accession For		
NTIS GRA&I	☒	
DTIC TAB	☐	
Unannounced	☐	
Justification		
By _____		
Distribution/_____		
Availability Codes		
Dist	Avail and/or	
	Special	
A		

CONTENTS

Foreword.	iii
Introduction	1
Publications and Patents During Past Contract Year	3
Discussion	7
References	11
<u>Appendix A</u>	
Determination of Nitrogen Trifluoride in Perfluoro Ammonium Cation Complex Fluoro Anion Salts	A-1
<u>Appendix B</u>	
Vibrational Spectra of $^{15}\text{NF}_4\text{AsF}_6$ and General Valence Force Field of NF_4^+	B-1
<u>Appendix C</u>	
Synthesis and Characterization of $(\text{NF}_4)_2\text{MnF}_6$	C-1
<u>Appendix D</u>	
United States Patent	D-1
<u>Appendix E</u>	
On The Properties of Azidotrifluoromethane	E-1
<u>Appendix F</u>	
A New Synthesis of Difluoramino Trifluoromethane	F-1
<u>Appendix G</u>	
On The Synthesis and Properties of FOIF_4O , ClOIF_4O , HOIF_4O , and Tetrafluoroperiodates	G-1
<u>Appendix H</u>	
Gas Phase Structure of Chlorine Trifluoride Oxide, ClF_3O	H-1
<u>Appendix I</u>	
Evidence for the Existence of Directional Repulsion Effects by Lone Valence Electron Pairs and π Bonds in Trigonal-Bipyramidal Molecules	I-1
<u>Appendix J</u>	
The General Valence Force Field of Perchloryl Fluoride	J-1
<u>Appendix K</u>	
Das Kraftfeld von SF_4	K-1
<u>Appendix L</u>	
The Formation of the Halogen - Halogen Bond	L-1
<u>Appendix M</u>	
Energetic Materials Research	M-1

INTRODUCTION

This report covers the period from 1 March 1980 through 28 February 1981 and describes Rocketdyne's research efforts in the area of energetic inorganic halogen oxidizers. As in the past years (Ref. 1), our research 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 $\text{NF}_3\text{-F}_2$ 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 made possible.

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

PUBLICATIONS AND PATENTS DURING PAST CONTRACT YEAR

PAPERS PUBLISHED

1. "Simplified Synthesis of $\text{NF}_4^+\text{SbF}_6^-$," by W. W. Wilson and K. O. Christe, J. Fluorine Chem., 15, 83 (1980).
2. "Synthesis and Properties of $\text{NF}_4^+\text{ClO}_4^-$ and $\text{NF}_4^+\text{HF}_2^-\cdot n\text{HF}$ and Some Reaction Chemistry of $\text{NF}_4^+\text{HF}_2^-\cdot n\text{HF}$ Salts," by K. O. Christe, W. W. Wilson and R. D. Wilson, Inorg. Chem., 19 1494 (1980).
3. "Synthesis and Properties of $\text{NF}_4^+\text{SO}_3\text{F}^-$," by K. O. Christe, R. D. Wilson and C. J. Schack, Inorg. Chem., 19, 3046 (1980).
4. "Vibrational Spectra of $^{15}\text{NF}_4\text{AsF}_6$ and General Valence Force Field of NF_4^+ ," by K. O. Christe, Spectrochim Acta, 36A, 921 (1980).
5. "The Force Field of SF_4 ," by W. Sawodny, K. Birk, G. Fogarasi and K. O. Christe, Z. Naturforsch., 35B, 1137 (1980).
6. "Synthesis and Characterization of $(\text{NF}_4)_2\text{MnF}_6$," by K. O. Christe, W. W. Wilson and R. D. Wilson, Inorg. Chem., 19, 3254 (1980).
7. "Evidence for the Existence of Directional Repulsion Effects by Lone Valence Electron Pairs and π Bonds in Trigonal - Bipyramidal Molecules," by K. O. Christe and H. Oberhammer, Inorg. Chem., 20, 296 (1981).

PAPERS IN PRESS

8. "On the Properties of Azidotrifluoromethane," by K. O. Christe and C. J. Schack, Inorg. Chem.
9. "The General Valence Force Field of Perchloryl Fluoride," by K. O. Christe, E. C. Curtis, W. Sawodny, H. Haerthner and G. Fogarasi, Spectrochim Acta.

10. "The Formation of the Halogen - Halogen Bond," by K. O. Christe.
Inorganic Reactions and Methods.
11. "Determination of Nitrogen Trifluoride in Perfluoro Ammonium Cation
Containing Complex Fluoro Anion Salts," by R. Rushworth, C. J. Schack,
W. W. Wilson and K. O. Christe, Anal. Chem.
12. "On the Syntheses and Properties of FOIF_4O , ClOIF_4O , HOIF_4O and Tetra-
fluoroperiodates," by K. O. Christe, R. D. Wilson and C. J. Schack,
Inorg. Chem.
13. "Synthesis and Properties of $\text{NF}_4^+\text{UF}_5\text{O}^-$," by W. W. Wilson, R. D. Wilson, and
K. O. Christe, J. Inorg. Nucl. Chem.
14. "EPR Evidence of Molecular and Electronic Structure of Nitrogen Trifluoride
Radical Cation," by A. M. Maurice, R. L. Belford, K. O. Christe and
I. B. Goldberg, Inorg. Chem.
15. "Gas Phase Structure of Chlorine Trifluoride Oxide, ClF_3O ," by H. Oberhammer
and K. O. Christe, Inorg. Chem.

PAPERS PRESENTED AT MEETINGS

16. "Recent Results in Nitrogen Fluoride Chemistry," by K. O. Christe, C. J.
Schack, W. W. Wilson and R. D. Wilson, 7th European Symposium on Fluorine
Chemistry, Venice, Italy (Sept. 1980).
17. "Synthesis and Properties of $\text{NF}_4\text{UF}_5\text{O}$," by W. W. Wilson, R. D. Wilson and
K. O. Christe, Second Chemical Congress of the North American Continent,
Las Vegas, Nev., (Aug. 1980).
18. "On the Syntheses and Properties of FOIF_4O , ClOIF_4O , HOIF_4O and Tetra-
fluoroperiodates," by K. O. Christe, R. D. Wilson and C. J. Schack,
Fifth Winter Fluorine Conference, Daytona Beach, Florida (February (1981)).

PATENTS ISSUED

19. "High Detonation Pressure Explosives," by K. O. Christe, U.S. 4,207,124
(June 1980).

20. "Peroxonium Salts and Method of Producing Same," by K. O. Christe and W. W. Wilson.
21. "Stable NF_4^+ Salt of High Fluorine Content," by K. O. Christe and W. W. Wilson.
22. "Improved $\text{NF}_3\text{-F}_2$ Gas Generator Compositions," by K. O. Christe and W. W. Wilson.

DISCUSSION

Significant progress has been made in the area of NF_4^+ Chemistry. A number of novel complex fluorotungstate salts have been synthesized and characterized. Most of these salts were found to be stable and are of practical interest as solid propellant WF_6 gas generators. The results of this study are presently being summarized in manuscript form.

Other novel NF_4^+ salts derived from SiF_4 , UF_6 , and BeF_2 have also been successfully synthesized. Characterization of these salts is presently being completed. Some of these salts are attractive because of their potential as ingredients in high NF_3/F_2 yielding solid propellant gas generator formulations.

Analytical procedures for NF_4^+ salts have been refined, and the results are summarized in Appendix A for publication. The vibrational spectra of ^{15}N labeled NF_4AsF_6 , and the general valence force field of NF_4^+ were published in Spectrochimica Acta (see Appendix B).

Thermodynamic data have been determined for NF_4BF_4 , NF_4PF_6 , NF_4AsF_6 , NF_4SbF_6 and NF_4GeF_5 . Measurements on $(\text{NF}_4)_2\text{GeF}_6$ are in progress. This work is being carried out in collaboration with Prof. Peacock of the University of Leicester, U. K. and Dr. Bougon of the French Atomic Energy Commission. The results will be highly useful for theoretical performance calculations and theoretical predictions concerning the possible existence of yet unknown NF_4^+ salts. For example, it was shown that the hypothetical NF_4^+F^- salt, i.e., an ionic NF_5 , cannot exist under normal conditions. This study is expected to be completed during the current year.

The papers on the novel $(\text{NF}_4)_2\text{MnF}_6$ salt was published in Inorganic Chemistry (see Appendix C), and a US patent on the use of NF_4^+ salts in high detonation pressure explosives was issued (see Appendix D). Attempts to synthesize the unknown $(\text{NF}_4)_3\text{AlF}_6$ salt by new methods have so far been unsuccessful.

In addition to the previously mentioned studies on NF_4^+ chemistry, extensive efforts were carried out in several other areas of nitrogen fluorine chemistry. In connection with the interest in a chemical NF laser, the reaction of fluorine atoms with HN_3 was studied by matrix isolation spectroscopy, but no evidence for the existence of an intermediate $\text{F}\cdot\text{HN}_3$ adduct was observed under the given conditions. The compound CF_3N_3 was prepared and characterized (see Appendix E), and it was found that its fluorination provides an improved synthesis of CF_3NF_2 , a compound which is difficult to prepare in good yield and purity according to previous literature methods (see Appendix F). Attempts were made to synthesize the unknown NH_2F molecule by a series of displacement reactions using $\text{NH}_3\text{F}^+\text{CF}_3\text{SO}_3^-$ (Ref. 2) as a starting material (Drs. Grakauskas and Baum from Fluorochem kindly provided the precursor for the preparation of this compound).

Significant progress was also made in the area of halogen fluoride chemistry. The first example of an iodine hypofluorite OIF_4OF was prepared and fully characterized (Appendix G). In connection with this study, numerous interesting reactions of periodates were investigated. In collaboration with Prof. Oberhammer of the University of Tübingen, W. Germany, the molecular structure of ClF_3O was determined by electron diffraction (see Appendix H), and evidence was obtained for the existence of directional repulsion effects by lone valence electron pairs and π -bonds in trigonal-bipyramidal molecules (see Appendix J).

The interesting compound, fluorine perchlorate, recently became readily accessible in high purity through the thermal decomposition of $\text{NF}_4^+\text{ClO}_4^-$ (Ref. 3). Since very little was known about this compound, except for it being highly explosive, a complete characterization was carried out and the results are being summarized in manuscript form. In connection with this study, the knowledge of the General Valence Force Field of FClO_3 was required. Since these data were previously not available, they were determined and are presented in Appendix J in manuscript form. This study was carried out in collaboration with Prof. Sawodny of the University of Ulm, W. Germany, who carried out the Ab Initio Force Field calculations. Similar calculations were also obtained for the closely related SF_4 molecule (see Appendix K). A review chapter on chlorine oxyfluorides was written for the series "Inorganic Reactions and Methods" (see Appendix L).

Aqueous fluorinations of several substrates, such as TeO_4^{--} and CrO_4^{--} , were studied in an attempt to extend the reaction recently discovered by Appelman (Ref. 4) which resulted in the isolation of the first known example of an ionic hypofluorite, FSO_2OF^- . No difficulty was encountered with the duplication of Appelman's work, but so far no evidence for the formation of other analogous hypofluorite anions has been obtained.

REFERENCES

1. Inorganic Halogen Oxidizer Research, ONR Contract N00014-79-C-0176, Annual Report, Rocketdyne, (March 1980).
2. V. Grakauskas, A. H. Remanick, and K. Baum, J. Amer. Chem. Soc., 90, 3839 (1968).
3. K. O. Christe, W. W. Wilson and R. D. Wilson, Inorg, Chem., 19 1494 (1980).
4. E. H. Appelman, L. J. Basile, R. C. Thompson, J. Amer. Chem. Soc., 101, 3384 (1979).

APPENDIX A

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

DETERMINATION OF NITROGEN TRIFLUORIDE IN
PERFLUORO AMMONIUM CATION CONTAINING COMPLEX FLUORO ANION SALTS

R. Rushworth, C. J. Schack, W. W. Wilson and K. O. Christie*

Received November 3, 1980

Brief

The NF_4^+ content of complex fluoro anion salts is determined by quantitative measurement of the NF_3 evolved during hydrolysis using gasometric and chromatographic methods. The use of several quantitative, semiquantitative and qualitative methods for the determination of the anions or for the detection of impurities in the NF_4^+ salts is discussed.

Abstract

The NF_4^+ content of complex fluoro anion salts is determined by quantitative measurement of the NF_3 evolved during hydrolysis of 500-1000 mg size samples using gasometric and chromatographic methods. Analytical data are given for NF_4BF_4 , NF_4SbF_6 , NF_4BiF_6 and NF_4SnF_5 with NF_3 contents ranging from 17 to 40%. These data show a scatter of about ± 2 relative percent for the NF_3 analyses. The use of several quantitative, semiquantitative and qualitative methods for the determination of the anions or for the detection of impurities in the NF_4^+ salts is discussed.

Introduction

Perfluoroammonium salts are unique. In spite of their unusual oxidizing power, they are capable of forming numerous stable salts. Potential applications of NF_4^+ salts include their use in solid propellant $\text{NF}_3\text{-F}_2$ gas generators for chemical HF-DF lasers (1,2) and as a fluorinating agent for aromatic compounds(3). Since generally the elemental analyses of powerful oxidizers are difficult to perform, we would like to report the methods developed in our laboratory for analyzing NF_4^+ salts.

Experimental

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

Apparatus. The hydrolysis reaction of NF_4^+ salts was carried out in a volume calibrated stainless steel vacuum line equipped with Teflon FEP U-traps and bellows seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0-760 mm⁺ 0.01%). The vacuum line was directly interfaced with the gas chromatograph, F and M Model 700, which was equipped with a 1/8" X 20' column packed with PPQ, 80-100 mesh, and was operated at ambient temperature, with 25 mL/min He, and a thermal conductivity detector. Peak area integration was accomplished with a Hewlett-Packard Model 3371 R integrator. Non-volatile materials were handled outside the vacuum system in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line of a Lexel Model 75 Ar ion laser and a Claassen filter (4) for the elimination of plasma lines with sealed glass melting point capillaries as sample containers. Infrared spectra were obtained

using Perkin-Elmer Model 283 or 457 spectrophotometers using a Wilks mini-pellet press for pressing the dry powders between AgCl disks.

Hydrolysis of the NF_4^+ Salt. The sample to be analyzed (500-1000 mg) was transferred in the glove box to a previously evacuated, leak checked, and weighed volume-calibrated Teflon FEP ampoule equipped with a stainless steel valve. After removal from the glove box, the ampoule was reevacuated and reweighed. It was attached to the vacuum line and after cooling to -196° , 2.0 mL of degassed and deionized H_2O was slowly admitted into the sample tube from an inverted bulb. The H_2O addition was carried out in such a manner that the water was frozen at -196° on the upper walls of the tube some distance above the sample. Upon closing the ampoule the frozen water was knocked down onto the sample. The resulting solid mixture was agitated and carefully warmed toward room temperature. As soon as interaction was noticeable, the mixture was chilled in liquid N_2 again to moderate the hydrolysis. Repeating this warming and cooling cycle, two or three times accomplished most of the hydrolysis reaction and at this point the reaction was allowed to go to completion near room temperature.

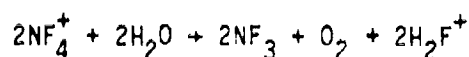
Determination of the $\text{NF}_3\text{-O}_2$ Content by Gas Chromatography. The tip of the ampoule with the resulting hydrolysate was cooled to -78° . Care was taken that all the hydrolysate was in the tip and that it was frozen to avoid distortion of the ensuing pressure measurement by water vapor pressure. With the solution frozen, the ampoule was opened to the calibrated volume of the vacuum line, the gas pressure and temperature were recorded, and the amount of gas was calculated from these PVT measurements. A portion of this gas was analyzed by

GC which had previously been calibrated for NF_3 , O_2 , N_2 , and mixtures thereof. Retention times (in minutes) for the gases were: N_2 (2.4), O_2 (2.55), and NF_3 (4.95). The amount of NF_4^+ , originally present in the sample, was calculated from the total amount of gas evolved and the percentage of NF_3 , as found by GC. Analyses, carried out on pure samples showed that 1 mol NF_4^+ generated 1 mol of NF_3 .

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

Results and Discussion

The analyses of numerous spectroscopically pure NF_4^+ salts of different counterions by the gas chromatographic method have shown (see Table 1) that the hydrolysis of NF_4^+ results in quantitative NF_3 evolution according to:



The solubility of NF_3 in H_2O is very small (5,6) and can therefore be neglected. The hydrolysis reactions must be carefully controlled to avoid violent reactions (7,8) which (i) are dangerous and (ii) can result in the hydrolysis of some NF_3 to nitrogen oxides. The oxygen evolution was found, even under well controlled conditions, to be often less than quantitative due to the formation of some H_2O_2 and HOF (2). In addition, certain oxidizing anions, such as NiF_6^{2-} (7), BiF_6^- (2) or MnF_6^{2-} (8) also produced oxygen on hydrolysis. Consequently, determination of the evolved O_2 should not be used for a quantitative determination of the NF_4^+ content.

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

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

An error analysis of the second method shows that its accuracy is limited by the effectiveness of the $\text{NF}_3\text{-O}_2$ separation. The NF_3 values obtained for high purity NF_4BF_4 standards were found to be highly reproducible, but were always slightly high due to small amounts (0-0.8 mol %) of residual oxygen, as determined by gas chromatographic analyses of the NF_3 trapped at -210°C .

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

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

If the mixture of the salts to be analyzed can contain polyanions, such as $\text{Sb}_2\text{F}_{11}^-$ (2), $\text{Bi}_2\text{F}_{11}^-$ (2), or $\text{Ti}_2\text{F}_{10}^{2-}$ (12), the mole ratio of total cation central atoms to total anion central atoms provides information about the

percentage of polyanions present. The presence of polyanions or of impurities, such as H_3O^+ (13), HF_2^- or solvated HF, can be further confirmed by qualitative spectroscopic techniques, such as infrared and Raman spectroscopy. The question of which cations are combined with which anions can be answered by recording the x-ray powder diffraction patterns of the mixture.

Semi-quantitative methods for the determination of NF_4^+ and MF_x^{n-} include Raman and ^{19}F NMR spectroscopy. In the Raman spectra the symmetric stretching mode of tetrahedral NF_4^+ , for example, occurs at about 850 cm^{-1} (14) and always results in an intense and narrow line outside the frequency range of most anion modes. The relative peak height of this line can therefore be taken as a measure of the NF_4^+ concentration, provided that calibration spectra of analyzed samples recorded under identical instrumental conditions are available and that the relative peak heights of the other complex ions are also known. The advantage of this method is its speed and the small amount of sample required. It is routinely used in our laboratory and gives results within a few percent of those obtained by conventional wet analysis techniques. It should be pointed out, however, that this method is not suitable for the detection of weak Raman scatterers, such as HF.

In the ^{19}F NMR spectra of solutions of NF_4^+ salts in solvents, such as anhydrous HF or BrF_5 , a very narrow well-resolved triplet of equal intensity is observed for NF_4^+ at about 220 ppm downfield from external CFCl_3 with a line width of about 5 Hz and $J_{\text{NF}} = 229\text{ Hz}$ (15, 16). It is well suited for

accurate peak area integration. However, in many cases rapid fluorine exchange between the complex fluoro anions and the HF solvent preempts the simultaneous determination of the anion concentration, thereby limiting the general applicability of this method.

Credit. The authors are indebted to the Office of Naval Research, Power Branch, and the U. S. Army Research Office for financial support of this work.

REFERENCES

- (1) Pilipovich, D. U. S. Pat. 3,963,542 (1976).
- (2) Christe, K. O.; Wilson, R. D.; Schack, C. J.; Inorg. Chem., 1977, 16, 937.
- (3) Schack, C. J.; Christe, K. O.; J. Fluorine Chem., (in press).
- (4) Claassen, H. H.; Selig, H.; Shamir, J.; J. Appl. Spectrosc., 1969, 23, 8.
- (5) Ashton, J. T.; Dawe, R. A.; Miller, K. W.; Smith, E. B.; Stickings, B. J.; J. Chem. Soc. (A), 1968, 1793.
- (6) Dean, C. R. S.; Finch, A.; Gardner, P. J.; J. C. S. Dalton, 1970, 2722.
- (7) Christe, K. O.; Inorg. Chem., 1977, 16, 2238.
- (8) Christe, K. O.; Wilson, W. W.; Wilson, R. D.; Inorg. Chem., 1980, 19, 3254.
- (9) Christe, K. O.; Schack, C. J.; Wilson, R. D.; Inorg. Chem., 1976, 15, 1275.
- (10) Christe, K. O.; Wilson, W. W.; Schack, C. J.; J. Fluorine Chem., 1978, 11, 71.
- (11) a) Peroxide Bomb Apparatus and Methods, Manual No. 121, Parr Instrument Company, Moline, Illinois, 1950.
 b) Oxygen Bomb Calorimetry and Combustion Methods, Technical Manual No. 130, Parr Instrument Co., Moline, Illinois, 1960.
- (12) Christe, K. O.; Schack, C. J.; Inorg. Chem., 1977, 16, 353.
- (13) Christe, K. O.; Schack, C. J.; Wilson, R. D.; Inorg. Chem., 1975, 14, 2224.
- (14) Christe, K. O.; Pilipovich, D.; Inorg. Chem., 1971, 10, 2803.
- (15) Christe, K. O.; Guertin, J. P.; Pavlath, A. E.; Sawodny, W.; Inorg. Chem., 1967, 6, 533.
- (16) Tolberg, W. E.; Rewick, R. T.; Stringham, R. S.; Hill, M. E.; Inorg. Chem., 1967, 6, 1156.

Table 1. The Determination of NF_3 in Various NF_4^+ Salts
by the Gas Chromatographic Method

COMPOUND	THEORETICAL % NF_3	EXPERIMENTAL % NF_3^e
NF_4BF_4 ^a	40.16	40.28
NF_4SbF_6 ^b	21.80	21.69
NF_4SbF_6 ^c	21.80	21.71
NF_4BiF_6 ^b	17.19	16.94
NF_4SnF_5 ^d	23.38	23.60

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

APPENDIX B

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

KARL O. CHRISTE

Rocketdyne, A Division of Rockwell International, Canoga Park, CA 91304, U.S.A.

(Received 3 March 1978; in revised form 6 May 1980)

Abstract—Samples of $^{14}\text{NF}_4\text{AsF}_6$ and $^{15}\text{NF}_4\text{AsF}_6$ were prepared by low-temperature u.v.-photolysis and their vibrational spectra were recorded. The observed spectra are in agreement with space group $P4/n$ for NF_4AsF_6 and site symmetries of S_4 and C_4 for NF_4^+ and AsF_6^- , respectively. The observed ^{14}N – ^{15}N isotopic shifts were used to compute a general valence force field for NF_4^+ .

INTRODUCTION

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

EXPERIMENTAL

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

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

RESULTS AND DISCUSSION

The sample of $^{15}\text{NF}_4\text{AsF}_6$ was of high isotopic purity and its vibrational spectra did not exhibit any detectable bands due to the ^{14}N isotope. To determine the ^{14}N – ^{15}N isotopic shifts, the corresponding ^{14}N salt was prepared and studied by vibrational spectroscopy under identical conditions. Since the ^{15}N salt spectra were identical to those previously published for the ^{14}N salt [15], except for the isotopic shifts observed for ν_3 and ν_4 of NF_4^+ , the

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

Although the assignments given in Table 1 were made for simplicity for tetrahedral NF_4^+ and octahedral AsF_6^- , the observed splittings of the degenerate modes and deviations from the T_d and O_h selection rules indicate that the actual site symmetries of the NF_4^+ and AsF_6^- ions must be lower than T_d and O_h , respectively. Unfortunately, the exact crystal structure of NF_4AsF_6 is unknown, however, based on its reported X-ray powder diffraction data [4], NF_4AsF_6 appears to be isotypic with PCl_4PCl_6 , which belongs to space group $P4/n$ (C_{4h} , No. 85) [29, 30]. In this space group, the NF_4^+ cation would occupy sites of symmetry S_4 . As can be seen from comparison of Tables 1 and 2, the observed NF_4^+ bands agree well with the predictions for S_4 site symmetry, but not with those for D_2 or D_{2d} . Similarly, the deviations from the O_h selection rules, observed for AsF_6^- , are compatible with a site symmetry of C_4 (see Table 3), but not with D_{2d} , D_{2h} , D_2 or S_4 . Based on these results, alternate probable space groups, such as $P4/nmm$, $P4_2/n$, $P4_22_2$, $P4_2/mmc$, $P4/mnc$, $P4_2/mnm$ or $P4/m$, can be ruled out.

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

In solid NF_4AsF_6 the F_2 modes of NF_4^+ are split under S_4 site symmetry into one B and one doubly degenerate E mode. Since the isotopic shifts of both modes are very similar (see Table 2), weighting of the shifts can be neglected and a simple average was used. It should be pointed out however that in certain NF_4^+ salts, such as NF_4BF_4 [31], the ^{14}N – ^{15}N isotopic shifts of the $\nu_3(F_2)$ components can differ by as much as 8 cm^{-1} , thus requiring reliable mode assignments.

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

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

$^{14}\text{NF}_4\text{AsF}_6$		$^{15}\text{NF}_4\text{AsF}_6$		Assignments (point group)*		$\Delta \nu^{14}\text{N}-^{15}\text{N}$
i.r.	Raman	i.r.	Raman	$\text{NF}_4^+(T_d)$	$\text{AsF}_6^-(O_h)$	
2360 vw		2310 vw		$2\nu_3(A_1 + E + F_2)$		
2310 vw		2253 vw				
2012 sh		1984 sh		$\nu_1 + \nu_3(F_2)$		
1997 w		1969 w				
1780 sh						
1763 vw		1732 vw		$\nu_3 + \nu_4(A_1 + E + F_2)$		29.2 + 1.8
1760 sh						
1457 sh		1455 sh		$\nu_1 + \nu_4(F_2)$		2
1453 w		1451 w				
1398 vw		1398 vw			$\nu_1 + \nu_3(F_{1u})$	
1290 vw		1290 vw			$\nu_2 + \nu_3(F_{1u} + F_{2u})$	
1221.9 mw		1218.2 mw		$2\nu_4(A_1 + E + F_2)$		1.85
1165 vs, br	{ 1165.0 (1) 1152.9 (0.6)	1135 vs, br	{ 1136.0 (1) 1123.4 (0.6)	$\nu_3(F_2)$		29.0 } 29.25 ± 0.25
1056 sh		1054 sh		$\nu_2 + \nu_4(F_1 + F_2)$		
1052 vw		1050 vw				
	882 (0+)		882 (0+)	$2\nu_2(A_1 + A_2 + E)$		
	848.2 (7.3)		848.2 (7.3)	$\nu_1(A_1)$		
826 vw		826 vw			$\nu_2 + \nu_6(F_{1u} + F_{2u})$	
710.0 vs, br	704.5 (1.5)	710 vs, br	704.5 (1.5)		$\nu_3(F_{1u})$	
685 sh	685.4 (10)	685 sh	685.4 (10)		$\nu_1(A_{1g})$	
613.3 s	613.3 (2.6)	611.5 s	611.4 (2.6)			1.8, 1.9 } 1.8 ± 0.1
609.0 s	609.0 (5.2)	607.3 s	607.2 (5.2)	$\nu_4(F_2)$	$\nu_2(E_g)$	1.7, 1.8 }
579 w	578.3 (1.2)	579 w	578.3 (1.2)			
	445.0 (1.9)		444.9 (1.9)	$\nu_2(E)$		0 ± 0.1
	441.6 (2.0)		441.5 (2.0)			
395 s		395 s			$\nu_4(F_{1u})$	
	369.6 (3.6)		369.6 (3.6)		$\nu_3(F_{2g})$	

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

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

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

* Spectral activity.

Table 3. Correlation table for the internal vibrations of AsF_6^- in NF_4AsF_6 for space group $\text{P4}_3\text{m}$ and $Z = 2$

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

found to be zero within experimental error. Those of $\nu_1(F_1)$ and $\nu_4(F_2)$ were measured to be 29.25 ± 0.25 and $1.8 \pm 0.1 \text{ cm}^{-1}$, respectively. These values were supported by preliminary measurements on $^{14}\text{NF}_4\text{BF}_4$ and $^{15}\text{NF}_4\text{BF}_4$ [31] which shows very similar averaged isotopic shifts for ν_1 and ν_4 .

For the computation of the general valence force field of NF_4^+ the frequencies and isotopic shifts listed in Table 4 were used. For the F_2 block, the possible ranges of the two diagonal symmetry force constants F_{11} and F_{44} and the ^{14}N - ^{15}N isotopic

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

Since the slopes of the $\Delta\nu_1$ and $\Delta\nu_4$ vs F_{14} plots

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

		$\nu^{14}\text{NF}_4$	$\nu^{15}\text{NF}_4$	$\Delta\nu$	Symmetry force constants	P.E.D.
A_1	ν_1	848.2	848.2	0	$F_{11} = f_r + 3f_{rr} = 8.053$	
E	ν_2	443.3	443.3	0	$F_{22} = f_r - 2f_{rr} + f_{\text{as}} = 0.733$	
F_2	ν_3	1158.95	1129.7	29.25 ± 0.25	$F_{11} = f_r - f_{rr} = 5.52 \pm 0.08$	$96F_{11} + 43F_{44} - 39F_{14}$
	ν_4	611.15	609.35	1.8 ± 0.1	$F_{44} = f_r - f_{\text{as}} = 1.00 \pm 0.02$	$15F_{11} + 67F_{44} + 18F_{14}$
					$F_{14} = \frac{1}{2}(f_{rr} - f_r) = 0.73 \pm 0.03$	
					$f_r = 6.153 \pm 0.1$	
					$f_{rr} = 0.633 \pm 0.03$	

* Stretching, bending and stretch-bend interaction force constants have units of mdyn/Å , mdyn/Å^2 and mdyn/Å radian , respectively.

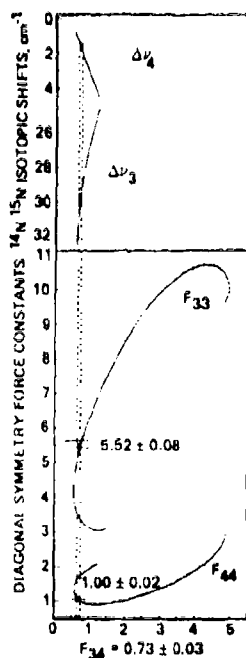


Fig. 1. F_2 block force field (mdyn/Å) of NF_3 . The diagonal symmetry force constants and ^{14}N - ^{15}N isotopic shifts are plotted as a function of the interaction constant F_{34} . The rectangles delineate the observed ^{14}N - ^{15}N isotopic shifts and their uncertainties. The broken vertical and solid horizontal lines indicate the resulting force constant ranges.

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

The general valence force field and the potential energy distribution (PED) of NF_3 are summarized in Table 4. The PED indicates significant mixing of S_1 and S_2 , as expected [32, 36] for a strongly mass coupled system [32, 36]. The close agreement between the general valence force field of this study and the previously reported [5, 7] approximate force field is in line with Pfeiffer's analysis [37] which showed that for similar molecules the method of 'step-wise coupling' gives the best agreement with the general valence force field values. A comparison of the NF stretching force constant of NF_3 (6.15 mdyn/Å with those and the NF bond distances of FNO ($f_s = 2.15\text{ mdyn/Å}$, $r_{\text{NF}} = 1.512\text{ Å}$) and NF_2 ($f_s = 4.31\text{ mdyn/Å}$, $r_{\text{NF}} = 1.365\text{ Å}$) [35] suggests for NF_3 an unusually strong and short ($r = 1.24\text{ Å}$) NF bond.

Acknowledgements—The author is indebted to Drs. L. R. GRANT, E. C. CURTIS, C. J. SCHACK and W. W. WILSON

for useful discussions, to Mr. R. D. WILSON for experimental help, and to Dr. E. PRINZEL for the recording of some of the Raman spectra. This work was in part supported by the Office of Naval Research and the U.S. Army Research Office.

REFERENCES

- [1] K. O. CHRISTE, J. P. GUERTIN and A. E. PAVLADE, *Inorg. Nucl. Chem. Lett.* **2**, 83 (1966).
- [2] W. E. TOLBERG, R. T. REWICK, R. S. STRINGHAM and M. E. HILL, *Inorg. Nucl. Chem. Lett.* **2**, 79 (1966).
- [3] K. O. CHRISTE, J. P. GUERTIN and A. E. PAVLADE, *U.S. Patent* 3 503 719 (1970).
- [4] J. P. GUERTIN, K. O. CHRISTE and A. E. PAVLADE, *Inorg. Chem.* **5**, 1921 (1966).
- [5] K. O. CHRISTE, J. P. GUERTIN, A. E. PAVLADE and W. SAWODNY, *Inorg. Chem.* **6**, 533 (1967).
- [6] W. E. TOLBERG, R. T. REWICK, R. S. STRINGHAM and M. E. HILL, *Inorg. Chem.* **6**, 1156 (1967).
- [7] K. O. CHRISTE and D. PILIPOVICH, *Inorg. Chem.* **10**, 2803 (1971).
- [8] C. T. GOETSCHEL, V. A. CAMPANILE, R. M. CURTIS, K. R. LOOS, D. C. WAGNER and J. N. WILSON, *Inorg. Chem.* **11**, 1696 (1972).
- [9] S. M. SINEL'NIKOV and V. YA. ROSOLOVSKII, *Dokl. Akad. Nauk SSSR* **194**, 1341 (1970).
- [10] V. YA. ROSOLOVSKII, V. I. NEFEDOV and S. M. SINEL'NIKOV, *Izv. Akad. Nauk SSSR, Ser. Khim.* **7**, 1445 (1973).
- [11] S. P. MISHRA, M. C. R. SYMONS, K. O. CHRISTE, R. D. WILSON and R. I. WAGNER, *Inorg. Chem.* **14**, 1103 (1975).
- [12] K. O. CHRISTE, R. D. WILSON and A. E. AXWORTHY, *Inorg. Chem.* **12**, 2478 (1973).
- [13] K. O. CHRISTE and C. J. SCHACK, *Inorg. Chem.* **16**, 353 (1977).
- [14] K. O. CHRISTE, C. J. SCHACK and R. D. WILSON, *Inorg. Chem.* **16**, 849 (1977).
- [15] K. O. CHRISTE, C. J. SCHACK and R. D. WILSON, *Inorg. Chem.* **15**, 1275 (1976).
- [16] K. O. CHRISTE, C. J. SCHACK and R. D. WILSON, *J. Fluorine Chem.* **8**, 541 (1976).
- [17] K. O. CHRISTE, *Inorg. Chem.* **16**, 2238 (1977).
- [18] K. O. CHRISTE, R. D. WILSON and C. J. SCHACK, *Inorg. Chem.* **16**, 937 (1977).
- [19] K. O. CHRISTE, W. W. WILSON and C. J. SCHACK, *J. Fluorine Chem.* **11**, 71 (1978).
- [20] I. J. SOLOMON, J. N. KEITH and A. SNEELSON, *J. Fluorine Chem.* **2**, 129 (1972).
- [21] J. N. KEITH, I. J. SOLOMON, I. SHEFT and H. HYMAN, *J. Inorg. Nucl. Chem. Supplement* **143** (1976).
- [22] K. O. CHRISTE and I. B. GOLDBERG, *Inorg. Chem.* **17**, 759 (1978).
- [23] I. B. GOLDBERG, H. R. CROWE and K. O. CHRISTE, *Inorg. Chem.* **17**, 3189 (1978).
- [24] K. O. CHRISTE, R. D. WILSON and I. B. GOLDBERG, *Inorg. Chem.* **18**, 2578 (1979).
- [25] W. W. WILSON and K. O. CHRISTE, *J. Fluorine Chem.* **15**, 83 (1980).
- [26] W. MAYA, *Inorg. Chem.* **3**, 1063 (1964).
- [27] E. K. PLYLER, A. DANIEL, L. R. BLAINE and E. D. TIDWELL, *J. Res. Nat. Stand.* **64**, 841 (1960).
- [28] *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*, International Union of Pure and Applied Chemistry, Washington Butterworths (1961).
- [29] H. PREISS, *Z. anorg. allgem. Chem.* **380**, 51 (1971).

- [30] D. CLARK, H. M. POWELL and A. F. WELLS, *J. Chem. Soc.* 642 (1942).
- [31] K. O. CHRISTE, unpublished results.
- [32] W. SAWODNY, *J. Mol. Spectry* **30**, 56 (1969).
- [33] A. MUELLER, in: *Vibrational Spectroscopy—Modern Trends* (Edited by A. J. BARNES and W. J. ORVILLE-THOMAS) p. 139. Elsevier, Amsterdam (1977).
- [34] A. ALLAN, J. L. DUNCAN, J. H. HOLLOWAY and D. C. MCKEAN, *J. Mol. Spectry* **31**, 368 (1969).
- [35] W. SAWODNY and P. PULAY, *J. Mol. Spectry* **51**, 135 (1974) and references cited therein.
- [36] S. N. THAKUR and S. N. RAI, *J. Mol. Struct.* **5**, 320 (1970).
- [37] M. PFEIFFER, *J. Mol. Spectry* **31**, 181 (1969).

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

APPENDIX C

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

K. O. CHRISTE,* WILLIAM W. WILSON, and RICHARD D. WILSON

Received March 28, 1980

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

Introduction

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

Experimental Section

Materials and Apparatus. The equipment, handling techniques, and spectrometers used in this study have previously been described.^{1,2} A literature method⁴ was used for the synthesis of NF_4SbF_6 . For the synthesis of Cs_2MnF_6 , a previously reported method⁵ was slightly modified. Anhydrous MnCl_2 and dry CsF , in a 1:2 mole ratio, were fluorinated in a Monel cylinder at 400 °C for 36 h by using a $\text{MnCl}_2:\text{F}_2$ mole ratio of 1:10. On the basis of the observed material balance, elemental analysis, X-ray diffraction powder pattern, and vibrational spectra, the resulting yellow solid consisted of high-purity Cs_2MnF_6 .

The Cs_2CuF_6 salt was prepared by high-pressure fluorination of a mixture of CsF and CuCl_2 in a 2:1 mole ratio. The conditions (400 °C, 18 h, 130 atm) were similar to those⁶ previously reported. However, during unsuccessful attempts to prepare Cs_2CuF_6 in a similar manner, it was noticed that very mild fluorination conditions (flow reactor, 200 °C) sufficed to prepare Cs_2CuF_6 . This brick red compound was always formed as the major product, instead of the pale green Cs_3CuF_6 . At the lower fluorination temperatures, the fluorination product also contained CsClF_4 . The infrared spectrum of Cs_2CuF_6 showed major bands at 670, 570, 480, and 430 cm^{-1} . The compatibility of Cs_2CuF_6 with different solvents was studied. In BrF_3 , Cs_2CuF_6 is stable but highly insoluble, whereas in anhydrous HF, it is soluble but undergoes a reaction even at -78 °C, resulting in the formation of a brown solid. When the Cs_2CuF_6 -HF solutions were warmed to room temperature, fluorine evolution was observed, in agreement with a previous report.⁷

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

added at -78 °C on the vacuum line, and the mixture was warmed to 25 °C for 30 min with stirring. The mixture was cooled to -78 °C and pressure filtered at this temperature. The HF solvent was pumped off at 30 °C for 12 h. The white filter cake (14 g; weight calculated for 37.1 mmol of CsSbF_6 = 13.7 g) was shown by Raman spectroscopy to consist mainly of CsSbF_6 . The yellow filtrate residue (6.1 g; weight calculated for 18.5 mmol of $(\text{NF}_4)_2\text{MnF}_6$ = 6.46 g) was shown by elemental analysis to have the following composition (weight %): $(\text{NF}_4)_2\text{MnF}_6$, 91.27; NF_4SbF_6 , 4.27; CsSbF_6 , 4.46. For the elemental analysis, a sample of $(\text{NF}_4)_2\text{MnF}_6$ was hydrolyzed in H_2O , the NF_3 and O_2 evolution was measured by PVT and gas chromatography, and Cs, Sb, and Mn in the hydrolysate were determined by atomic absorption spectroscopy. Anal. Calcd for $[(\text{NF}_4)_2\text{MnF}_6]_{91.27}[\text{NF}_4\text{SbF}_6]_{4.27}[\text{CsSbF}_6]_{4.46}$: NF_3 , 38.07; Mn, 14.37; Sb, 3.07; Cs, 1.61. Found: NF_3 , 37.8; Mn, 14.5; Sb, 3.10; Cs, 1.62.

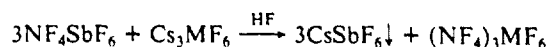
Caution! The reaction of $(\text{NF}_4)_2\text{MnF}_6$ with H_2O is extremely violent, and proper safety precautions must be used.

The CoF_3 - NF_4HF_2 System. A suspension of CoF_3 (231 mg = 2 mmol) in a freshly prepared concentrated NF_4HF_2 -HF solution² (15 mmol of NF_4HF_2) was stirred at -45 °C for 4 h. The tan CoF_3 did not appear to react, and no evidence for the formation of pale blue CoF_6^{3-} was observed. The HF solvent was pumped off while the mixture was allowed to warm slowly toward ambient temperature. At this temperature, the NF_4HF_2 -nHF underwent decomposition and was also pumped off. To ensure complete decomposition of NF_4HF_2 , we warmed the mixture to 45 °C for 4 h under a dynamic vacuum. The tan solid residue (230 mg) was shown by vibrational spectroscopy to be unreacted CoF_3 .

Results and Discussion

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

Attempted Syntheses of $(\text{NF}_4)_3\text{MF}_6$ Salts. In a previous study,⁷ it was shown that the above listed triply charged anions undergo solvolysis in HF. Furthermore, it was found that CuF_6^{3-} decomposed with F_2 evolution and NiF_6^{3-} disproportionated with NiF_6^{2-} formation but that for CoF_6^{3-} the solvolysis to $\text{CoF}_4^- + 2 \text{HF}_2^-$ could be suppressed by the addition of a 10-20-fold excess of fluoride ion to the solution. In view of these results, a simple metathetical reaction of an MF_6^{3-} salt in HF solution according to

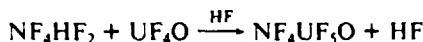


is preempted by the unavoidable solvolysis of MF_6^{3-} . However, the synthesis of a CoF_6^{3-} salt might be possible in the presence of a large excess of fluoride ion, provided the excess of fluoride can be readily removed from the product. Such a method was

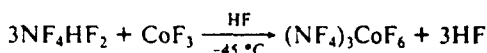
- (1) K. O. Christe, R. D. Wilson, and I. B. Goldberg, *Inorg. Chem.*, **18**, 2572 (1979), and references cited therein.
- (2) K. O. Christe, W. W. Wilson, and R. D. Wilson, *Inorg. Chem.*, **19**, 1494 (1980), and ref 1-18 cited therein.
- (3) K. O. Christe, *Inorg. Chem.*, **16**, 2238 (1977).
- (4) K. O. Christe, C. J. Schack, and R. D. Wilson, *J. Fluorine Chem.*, **8**, 541 (1976).
- (5) K. O. Christe, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **16**, 849 (1977).
- (6) W. Harnischmacher and W. Hoppe, *Angew. Chem., Int. Ed. Engl.*, **12**, 582 (1973).
- (7) T. L. Court, Ph. D. Thesis, University of Nottingham, England, 1971.

- (8) K. O. Christe, W. W. Wilson, and C. J. Schack, *J. Fluorine Chem.*, **11**, 71 (1978).

recently discovered⁹ and successfully applied to the synthesis of $\text{NF}_4\text{UF}_6\text{O}$ according to



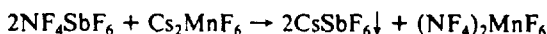
NF_4HF_2 is thermally unstable² and decomposes at 30 °C to NF_3 , F_2 , and HF , which are all gases. Therefore, the HF solvent can be pumped off first at low temperature, followed by decomposition and removal of the excess NF_4HF_2 . Application of this method to the synthesis of $(\text{NF}_4)_3\text{CoF}_6$ according to



was unsuccessful, and no evidence for the formation of a cobalt-containing NF_4^+ salt was obtained. Only unreacted CoF_3 was recovered.

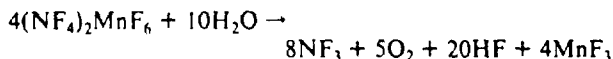
Syntheses of $(\text{NF}_4)_2\text{MF}_6$ Salts. Since the MF_6^{2-} anions contain one negative charge less than the MF_6^{3-} ones, they are less basic and, therefore, are less likely to undergo solvolysis in the strongly acidic solvent HF. The compatibility of TiF_6^{2-} and NiF_6^{2-} with HF has previously been demonstrated^{3,7,10} and led to the successful syntheses of $(\text{NF}_4)_2\text{TiF}_6^{10}$ and $(\text{NF}_4)_2\text{NiF}_6^3$. During this study the compatibility of Cs_2CuF_6 with HF was studied. It was found that Cs_2CuF_6 reacts, even at low temperature, with HF to form a dark brown solid. At room temperature, decomposition with fluorine evolution occurs. The compatibility of Cs_2CoF_6 with HF was not examined since Court had previously shown⁷ that this salt is unstable in HF solution.

In agreement with a previous report,⁷ MnF_6^{2-} was found to be stable in HF solution. Consequently, the metathetical reaction



was carried out which resulted in the isolation of the novel $(\text{NF}_4)_2\text{MnF}_6$ salt. Since the impurities NF_4SbF_6 and CsSbF_6 are well characterized, no attempts were undertaken to purify the compound by well-established⁴ recrystallization techniques.

Properties of $(\text{NF}_4)_2\text{MnF}_6$. The $(\text{NF}_4)_2\text{MnF}_6$ salt is a yellow, crystalline solid which is highly soluble in anhydrous HF. At 24 °C, its solubility exceeds 1.30 g/g of HF. It is stable at room temperature, and, in the absence of fuels, it is not shock sensitive. With water a violent reaction occurs, similar to that previously reported³ for $(\text{NF}_4)_2\text{NiF}_6$. By analogy with the other known NF_4^+ salts, the hydrolysis was found to result in quantitative NF_3 evolution and, therefore, is a useful analytical method. The hydrolysis also produced oxygen in a $\text{NF}_3\text{:O}_2$ mole ratio of 8:5 in excellent agreement with the equation



Thermal Decomposition. At 65 °C, $(\text{NF}_4)_2\text{MnF}_6$ appears to be stable, but at about 100 °C it starts to slowly decompose. Its decomposition rate in a sapphire reactor was monitored by total pressure measurements over the temperature range 100–130 °C. Except for a slightly faster rate during the first 20 min, the decomposition pressures increased approximately linearly with time at 100 °C. At 130 °C, the rates slightly accelerated with increasing time; however, this rate increase was quite small. At 100 °C, 0.17% of the sample decomposed in 17 h, whereas, at 130 °C, 0.66% of the sample decomposed in the same time. The gaseous decomposition products consisted of NF_3 and F_2 in a mole ratio of about 1:2. For identification of the solid residue, a sample of $(\text{NF}_4)_2\text{MnF}_6$

Table I. X-ray Powder Data for $(\text{NF}_4)_2\text{MF}_6$ Salts ($\text{M} = \text{Mn, Ge, Ti, Sn}$)^a

[illegible]

(a) Cu K α radiation and Ni filter, the crystallographic data are summarized in Table II.

Table II. Crystallographic Data of $(\text{NF}_4)_2\text{MF}_6$ Salts ($\text{M} = \text{Ti, Mn, Ni, Ge, Sn}$)^a

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

^a Space group *I*4/*m* (No. 87); *Z* = 2. ^b Data from ref 13.

was completely decomposed under a dynamic vacuum at 240 °C. On the basis of its weight, X-ray powder diffraction pattern,¹¹ and mauve color, this residue was identified as MnF_3 . Consequently, $(\text{NF}_4)_2\text{MnF}_6$ decomposes according to



A comparison with the decomposition data previously published⁷ for $(\text{NF}_4)_2\text{NiF}_6$ shows that the normal stability of $(\text{NF}_4)_2\text{MnF}_6$ is significantly higher than that of $(\text{NF}_4)_2\text{NiF}_6$ which in 6 h at 100 °C exhibited 9% decomposition.

Crystallographic Data. The X-ray powder diffraction pattern of $(\text{NF}_4)_2\text{MnF}_6$ are listed in Table I. The pattern is very similar to those of other $(\text{NF}_4)_2\text{MF}_6$ salts ($\text{M} = \text{Ge, Ti, Sn, Ni}$),^{3,5,10,12,13} indicating that these salts are isotypic. Recent studies on both powdered and single-crystal $(\text{NF}_4)_2\text{NiF}_6$ have shown that this compound crystallizes in a tetragonal form derived from the K_2PtCl_6 structure and belongs to space group $I4/m$. Consequently, the indexing, previously proposed for the $(\text{NF}_4)_2\text{MF}_6$ salts ($\text{M} = \text{Ge, Ti, Sn, Ni}$),^{3,5,10,12} was revised according to ref 13. The revised patterns and the crystallographic data are given in Tables I and II, respectively. Some of the additional lines, previously observed,^{3,4,10,12} were found to be due to small amounts of polyanion salts such as $(\text{NF}_4)_2\text{Ge}_2\text{F}_{10}$ or $(\text{NF}_4)_2\text{Sn}_2\text{F}_{10}$. As expected, the size of the unit cell decrease from $(\text{NF}_4)_2\text{TiF}_6$ to $(\text{NF}_4)_2\text{NiF}_6$ owing to the transition-metal contraction and then increases again when going from Ni to the main-group elements.

NMR Spectrum. The ionic nature of $(\text{NF}_4)_2\text{MnF}_6$ in HF solution was established by its ^{19}F NMR spectrum which was recorded over the temperature range $+20$ to -75°C . It showed at all temperatures a broad resonance at $\delta -218$ (downfield from external CFCl_3), characteristic of NF_4^+ . The lack of observable NF spin-spin coupling, generally seen for

(9) W. W. Wilson and K. O. Christe, *J. Inorg. Nucl. Chem.*, in press.
(10) K. O. Christe and C. J. Schack, *Inorg. Chem.*, **16**, 353 (1977).

- (11) M. A. Hepworth and K. H. Jack, *Acta Crystallogr.*, **10**, 345 (1957); T. C. Ehlerl and M. Hsia, *J. Fluorine Chem.*, **2**, 33 (1972).
- (12) K. O. Christie, C. J. Schack, and R. D. Wilson, *Inorg. Chem.*, **15**, 1275 (1976).
- (13) P. Charpin, M. Lance, T. Bui Huy, and R. Bougon, *J. Fluorine Chem.*, in press.

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

obsd freq, cm^{-1} , and rel intens ^a				assign (point group) ^b	
$(\text{NF}_4)_2\text{MnF}_6$		Cs_2MnF_6		NF_4^+ (T_d)	MnF_6^{2-} (O_h)
IR	Raman	IR	Raman		
2310 vw				$2\nu_1$ ($A_1 + E + F_2$)	
2000 w				$\nu_1 + \nu_1$ (F_2)	
1759 vw				$\nu_1 + \nu_1$ ($A_1 + E + F_2$)	
1466 w				$\nu_1 + \nu_1$ (F_2)	
1221 mw				$2\nu_2$ ($A_1 + E + F_2$)	
		1240 sh			$\left. \begin{array}{l} \nu_1 + \nu_1 \text{ (F}_{1u}\text{)} \\ \nu_2 + \nu_1 \text{ (F}_{1u} + \text{F}_{2u}\text{)} \end{array} \right\}$
		1202 vw			
1160 vs		1155 vw		ν_1 (F_2)	$\left. \begin{array}{l} \nu_2 + \nu_1 \text{ (F}_{1u} + \text{F}_{2u}\text{)} \\ \nu_1 + \nu_1 \text{ (F}_{1u}\text{)} \end{array} \right\}$
1110 sh		1116 w		$\nu_2 + \nu_2$ ($F_1 + F_2$)	
1061 vw				ν_1 (A_1)	$\nu_1 + \nu_1$ (F_{1u})
915 vw		919 vw			$\left. \begin{array}{l} \nu_2 + \nu_2 \text{ (F}_{1u} + \text{F}_{2u}\text{)} \\ \nu_1 \text{ (F}_{1u}\text{)} \end{array} \right\}$
856 vvw	855 m	745 sh		ν_1 (F_2)	
760 sh		732 w			ν_1 (F_{1u})
735 sh		620 vs		ν_2 (F_2)	ν_2 (A_{1g})
620 vs	593 vs	569 vw	590 vs		ν_2 (E_g)
500 vw	505 m		502 m	ν_1 (E)	
450 vw	450 w				
338 s		381 vw			ν_2 (F_{1u})
		338 s			ν_1 (F_{2g})
	304 s		304 s		

^a Uncorrected Raman intensities. ^b By analogy with $(\text{NF}_4)_2\text{NiF}_6$,¹³ the actual site symmetries of NF_4^+ and MnF_6^{2-} are probably S_4 and C_2 , respectively, thus explaining the observed slight deviations from the selection rules for T_d and O_h .

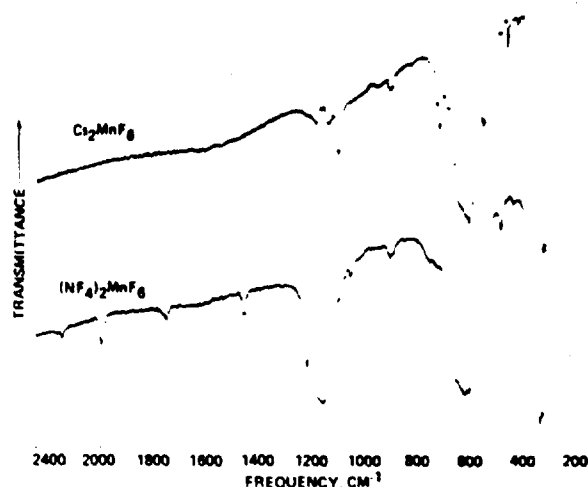


Figure 1. Infrared spectra of solid Cs_2MnF_6 and $(\text{NF}_4)_2\text{MnF}_6$ recorded at 25 °C as dry powders pressed between AgCl disks. The broken lines indicate absorption due to the window material.

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

Vibrational Spectra. The ionic nature of $(\text{NF}_4)_2\text{MnF}_6$ in the solid state was established by its vibrational spectra which exhibit the bands characteristic for NF_4^+ ¹² and MnF_6^{2-} .¹⁶

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

Summary

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

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

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

- (14) K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, *Inorg. Chem.*, **6**, 533 (1967).
 (15) W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, *Inorg. Chem.*, **6**, 1156 (1967).
 (16) S. L. Chodos, A. M. Black, and C. D. Flint, *J. Chem. Phys.*, **65**, 4816 (1976), and references cited therein.

United States Patent [19]

[11]

4,207,124

Christe

[45]

Jun. 10, 1980

[54] HIGH DETONATION PRESSURE
EXPLOSIVES

[75] Inventor: Karl O. Christe, Calabasas, Calif.

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

[21] Appl. No. 902,642

[22] Filed May 4, 1978

[51] Int. Cl.² C06B 25/34

[52] U.S. Cl. 149/92; 149/88;

149/119

[58] Field of Search 149/92, 119, 19.1, 19.9,
149/88

[56] References Cited

U.S. PATENT DOCUMENTS

3,213,610	10/1965	Grigger et al.	60/354
3,245,849	4/1966	Klager	149/19.4
3,325,318	6/1967	Paulukonis	149/109
3,449,179	6/1969	Minakawa et al.	149/92
3,503,719	3/1970	Christe et al.	23/315
3,520,742	7/1970	Witz	149/19.9
3,709,748	1/1973	Roberto	149/109
3,723,202	3/1973	Butler et al.	149/92
3,741,832	6/1973	Spensdel et al.	149/109
3,751,312	8/1973	Wright et al.	149/109
3,752,703	8/1973	Toy et al.	149/19

3,839,106	10/1974	De Prisque et al.	149/92
3,963,542	6/1976	Pilipovich	149/19.3
3,980,509	9/1976	Lubowitz	149/19.3
3,981,756	9/1976	Gotzmer	149/19.3
4,001,136	1/1977	Channell et al.	252/187
4,003,771	1/1977	Lubowitz	149/17

OTHER PUBLICATIONS

Christe et al (I), *Inorganic Chemistry*, 12 (#10)
2478-2481 (1973).Christe, *Inorganic Chemistry*, 16, 2238 (1977).Christe et al II, *Inorganic Chemistry*, 16, 849 (1977).Christe et al III, *Inorganic Chemistry*, 16, 937 (1977).Christe et al IV, *Inorganic Chemistry*, 15, 1275 (1976).Christe et al V, *Inorganic Chemistry*, 16, 353 (1977).Christe et al VI, *J. of Fluorine Chemistry*, 8, 541 (1976).Christe et al VII, *J. of Fluorine Chemistry*, 11, 71 (1978).Schack et al, *J. Inorg. Nucl. Chem.*, Supplement (1976).

Primary Examiner—Edward A. Miller

Attorney, Agent, or Firm—R. S. Sciascia W. Thom

Skeer; Lloyd E. K. Pohl

[57]

ABSTRACT

Insensitive, high performance explosives obtained by combining certain energetic, high density inorganic compounds with insensitive, underoxidized organic nitro compounds.

7 Claims, No Drawings

HIGH DETONATION PRESSURE EXPLOSIVES

BACKGROUND OF THE INVENTION

1. Field of the Invention.

This invention relates to insensitive, high performance explosives.

2. Description of the Prior Art.

The use of organic nitro compounds as explosives is well known. These compounds are self-oxidizing, i.e., the nitro groups provide the oxygen used in oxidation.

The highest detonation pressures achievable with the currently used organic nitro compounds are about 390 kbar. Further, the best performers (those from which detonation pressures approaching 390 Kbar are achievable) are highly sensitive. Thus, the use of the highest performing organic nitro compounds as explosives is risky and impractical. On the other hand, the lower performing explosives which possess acceptable stability are, without exception, underoxidized and generally exhibit low densities. The densities of the stable explosives are generally less than two grams per cm³. These two factors, i.e., the underoxidized nature of the stable organic nitro compounds and their low densities, severely limit their performance.

SUMMARY OF THE INVENTION

It has now been found that the performance of explosives based on commonly used organic nitro compounds can be increased to about 530 kbar by adding certain dense and stable but highly energetic inorganic oxidizers. Among the suitable oxidizers are: (NF₄)₂TiF₆, NF₄BF₄, Ti(ClO₄)₄, (NF₄)₂NiF₆ and other hereinafter named compounds.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Typical examples of performance increases achievable by the use of the inorganic oxidizers of this invention are illustrated in the following table.

TABLE

Examples of Theoretical Performance Improvements		Detonation Pressure (kb)
System	Weight %	
Nitroquandine (NQ)	100	255
NQ + (NF ₄) ₂ TiF ₆	43-57	349
Triaminotrinitrobenzene (TATB)	100	280
TATB + NF ₄ BF ₄	29-71	375
TATB + (NF ₄) ₂ TiF ₆	30-70	408
HMX	100	382
HMX + NF ₄ BF ₄	51-49	449
HMX + Ti(ClO ₄) ₄	70-30	456
HMX + (NF ₄) ₂ TiF ₆	52-48	471
HMX + (NF ₄) ₂ NiF ₆	56-44	527

The detonation pressures set forth in the foregoing table were calculated by means of the Kamlet correlation (*J. Chem. Phys.*, 48, 23 (1968)), a method commonly used for the performance evaluation of explosives. The percentage of oxidizer used was chosen to obtain complete combustion of the organic nitro compound (to CO₂, N₂ and HF in the case of HMX or NQ and to COF₂, N₂ and HF in the case of TATB). As can be seen from the table, the performance of organic nitro explosives is significantly increased by the addition of dense energetic inorganic oxidizers.

Laboratory tests have shown that the oxidizers and explosives are mutually compatible. For example, HMX

and NF₄BF₄ were found to be stable at 150° C. and drop weight tests of the HMX/NF₄BF₄ mixtures showed only a moderate increase in sensitivity over that of pure HMX.

The examples given in the above table are illustrative only and are not intended to limit the scope of the invention. Other commonly used, underoxidized organic nitro compounds of suitable stability could be substituted for the explosives given as examples in the table. Similarly, other inorganic oxidizers could be substituted for those listed in the table.

The primary requirements for suitable oxidizers are high energy content, high density, high thermal stability and low reactivity with the organic nitro compounds. From this point of view, NF₄⁺ containing salts are ideally suited. The NF₄⁺ cation is isoelectronic with the extremely inert CF₄ molecule and, therefore, in spite of its high energy content, a relatively high activation energy is required to cause it to react with other compounds.

The concept of this invention is not limited to fluorine containing oxidizers. As can be seen from the example of Ti(ClO₄)₄ in the table, this fluorine-free oxidizer is equally useful. By analogy with the NF₄⁺ salts, Ti(-ClO₄)₄ possesses all the necessary properties for use as an explosive ingredient.

Although oxygen containing oxidizers will be as effective as fluorine containing oxidizers in most explosives, fluorine containing oxidizers are advantageous in aluminized formulations. The addition of aluminum is known to increase the performance of an explosive, but the Al₂O₃ combustion product formed in a fluorine-free system may not remain for a long enough time in the gas phase. AlF₃, on the other hand, is formed as a combustion product when fluorine containing oxidizers are used. Since AlF₃ (sublimation point 1270° C.) is much more volatile than Al₂O₃ (boiling point 2250° C.), the use of fluorine containing oxidizers offers a distinct advantage for aluminized systems in that efficiencies higher than those obtainable with oxygen containing oxidizers are achieved.

It has been stated above that the oxidizers listed in the table are illustrative only. Examples of other suitable oxidizers are NF₄⁺ salts such as: NF₄Sb₃F₁₆, NF₄SbF₆, NF₄HF₂, NF₄BiF₆, NF₄PF₆, NF₄CeF₅, NF₄AsF₆, NF₄Ti₂F₉, NF₄Ti₃F₁₃, NF₄Ti₆F₂₅, (NF₄)₂SnF₆ and NF₄SnF₅ and other metal perchlorates.

The salts disclosed herein are not soluble in organic nitro compounds so their use in liquid explosives in conjunction with liquid organic compounds is not possible. However, they may be used in plastic bonded (solid) explosives of the type wherein explosive ingredients are bound in a suitable binder (many of which are known in the art) and in slurries where oxidizer particles are suspended in liquid organic nitro compounds.

What is claimed is:

1. An explosive composition comprising an explosive organic nitro compound, and enough of a dense inorganic oxidizer having an NF₄⁺ ion in conjunction with said organic nitro compound to improve detonation pressure.

2. An explosive composition according to claim 1 wherein said NF₄⁺ containing oxidizer is selected from the group consisting of (NF₄)₂TiF₆, NF₄BF₄, (NF₄)₂NiF₆, NF₄Sb₃F₁₆, NF₄SbF₆, NF₄HF₂, NF₄BiF₆, NF₄PF₆, NF₄CeF₅, NF₄AsF₆, NF₄Ti₂F₉, NF₄Ti₃F₁₃, NF₄Ti₆F₂₅, (NF₄)₂SnF₆ and NF₄SnF₅.

3

3. An explosive composition according to claim 1 which is a slurried explosive wherein particles of said dense inorganic oxidizer are suspended in a liquid organic nitro compound.

4. An explosive composition according to claim 1 wherein said organic nitro compound is selected from the group consisting of triaminotrinitrobenzene, nitroguanidine and cyclotetranethylenetetranitramine.

4

5. An explosive composition according to claim 4 wherein said organic nitro compound is nitroguanidine and said dense inorganic oxidizer is $(\text{NF}_4)_2\text{TiF}_6$.

6. An explosive composition according to claim 1 wherein said organic nitro compound is triaminotrinitrobenzene and said dense inorganic oxidizer is selected from the group consisting of NF_4BF_4 and $(\text{NF}_4)_2\text{TiF}_6$.

7. An explosive composition according to claim 1 wherein said organic nitro compound is HMX and said dense inorganic oxidizer is selected from the group consisting of NF_4BF_4 , $(\text{NF}_4)_2\text{TiF}_6$ and $(\text{NF}_4)_2\text{NiF}_6$.

15

20

25

30

35

40

45

50

55

60

65

APPENDIX E

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

ON THE PROPERTIES OF AZIDOTRIFLUOROMETHANE

Karl O. Christe* and Carl J. Schack

Received August 29, 1980

Abstract

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

Introduction

Although the existence of CF_3N_3 has been known for almost two decades¹, very little is known about this interesting molecule. In 1961 Makarov and coworkers mentioned¹ that CF_3N_3 is formed during the chlorination of CF_3NNNH_2 and in 1968 they described its synthesis in more detail². However, the compound was only characterized by elemental analysis, its boiling point, and a statement concerning its explosive properties at elevated temperature.² No further information on CF_3N_3 could be found in the literature. This is not surprising in view of the explosive character, generally exhibited by covalent azides.^{3,4} In view of this paucity of data, a characterization of CF_3N_3 was carried out, the results of which are summarized in this paper.

Experimental

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

Materials and Apparatus. Volatile materials were manipulated in a stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves and a Heise Bourdon tube-type pressure gauge. Gas chromatographic data were obtained using a Varian GC under isothermal conditions with a stainless steel column (1/8" X 10') packed with Poropak PS. Trifluoronitrosomethane (PCR Research Chemicals, Inc.) and hydrazine (Olin-Mathieson) were used as received.

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

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488 nm exciting line of an Ar-ion laser and a Claassen filter⁷ for the elimination of plasma lines. Quartz tubes (4 mm o.d.), closed by a metal valve, were used as sample containers in the transverse-viewing, transverse-excitation technique. A previously described⁸ device was used for recording the low-temperature spectra. Polarization measurements were carried out by method VIII as described by Claassen et al.⁷

The ^{19}F NMR spectra were recorded at 84.6 MHz on a Varian Model EM 390 spectrometer. Chemical shifts were determined relative to the CFCl_3 solvent with positive shifts being downfield from CFCl_3 .⁹

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

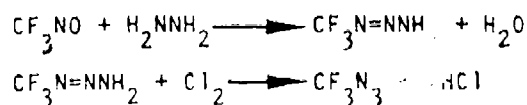
The UV spectra were recorded on Cary Model 14 spectrophotometer using a stainless steel cell of 10 cm pathlength equipped with sapphire windows.

Synthesis of CF_3N_3 . A 200 mL glass ampoule containing a stirring bar was loaded with 78.1 mmol N_2H_4 and 40 mL CH_3OH , stirred and cooled to -78°C .

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

Results and Discussion

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

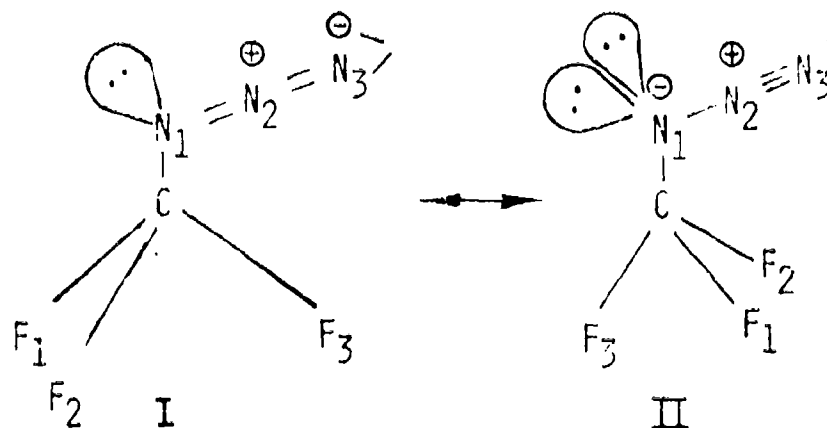


Azidotrifluoromethane is white as a solid and colorless as a liquid and a gas. It melts at -152°C . It is stable at room temperature and can be handled without noticeable decomposition. Vapor pressures were measured over the range -95 to -45°C , and the data were fitted by the method of least squares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

$$\log_{10} P(\text{mm}) = 7.8748 - 1221.7/T(^{\circ}\text{K})$$

with an index of correlation of 0.9998. The extra-polated boiling point is -28.5°C , in good agreement with that of -28.5° at 743 mm, previously reported². Measured vapor pressures at the noted temperatures are $[T(^{\circ}\text{C}), P(\text{mm})]$: -95.2 , 10; -78.6 , 40; -64.6 , 108; -45.5 , 324. The latent heat of vaporization of CF_3N_3 is 5.591 kcal/mol and the derived Trouton constant is 22.9, indicating little association in the liquid phase.

Vibrational Spectra. Figure 1 shows the infrared spectrum of gaseous and the Raman spectrum of liquid CF_3N_3 . The observed frequencies are listed in Table 1. By analogy with the known structures of CH_3N_3 ,^{10,11} CF_3OF ,^{12,13} and ClN_3 ,¹⁴ the CF_3N_3 molecule is expected to possess a structure of symmetry C_s with a planar CN_3 backbone, an approximately linear N_3 group, a staggered CF_3 group, and $r_{\text{N}_1\text{N}_2}$ ($\sim 1.25\text{\AA}$) being significantly longer than $r_{\text{N}_2\text{N}_3}$ ($\sim 1.13\text{\AA}$) due to II being the most important resonance structure.



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

Assuming hindered rotation of the CF_3 group, CF_3N_3 should exhibit 15 fundamental modes of vibration, all active in both the infrared and the Raman spectra. Of these, 10 belong to species a' and can be either polarized or depolarized, while 5 belong to species a'' and should be depolarized in the Raman spectrum. An approximate description of these 15 fundamental vibrations is given in Table 2. Eight of them involve motions of the CF_3 group.

four are due to the N_3 group and three involve the C-N linkage.

Assignments for the four N_3 modes were made by comparison with the known spectra of the covalent azides FN_3 ¹⁶, CIN_3 ^{16,17}, BrN_3 ¹⁶, IN_3 ¹⁸, CH_3N_3 ¹⁹⁻²², CD_3N_3 ^{21,22}, HN_3 ²³⁻²⁷, DN_3 ²³⁻²⁷ and OPF_2N_3 ²⁸ (see Table 2).

Of the four $-N_3$ modes, two are due to stretching motions, one antisymmetric and one symmetric. Since the two NN bonds significantly differ in their bond strength, the higher frequency mode might equally well be described as mainly a stretching of the N_2N_3 bond and the lower one as mainly a stretching of the N_1N_2 bond, however, due to the linear N_3 structure, both modes should be strongly coupled.²² Based on its high frequency and relative intensity, the N_2N_3 stretch is readily assignable to the band at about 2180 cm^{-1} . The N_1N_2 stretch should occur in the frequency range between 1090 and 1270 cm^{-1} and most likely be of higher Raman intensity than the CF_3 stretching modes. It is therefore assigned to the Raman band at about 1150 cm^{-1} . This assignment agrees well with those reported for CIN_3 ¹⁶, BrN_3 ¹⁶ and IN_3 ¹⁸ for which this mode occurs at 1144 , 1160 , and 1176 cm^{-1} , respectively.

The in plane (a'') and out of plane (a''') N_3 deformation modes should occur in the $500-660\text{ cm}^{-1}$ range (see Table 2). Two polarized Raman bands were observed in this range at 580 and 514 cm^{-1} , respectively, and must be due to the in plane N_3 deformation and the antisymmetric a' CF_3 deformation mode. Based on the similarity of the frequencies of the CF_3 modes in CF_3N_3 and CF_3NO ^{29,30} (see Table 2), we prefer to assign the 580 cm^{-1} fundamental to the N_3 a' deformation and the 514 cm^{-1} one to the CF_3 a' deformation mode. A similar choice exists for the two corresponding a'' modes, for which two bands at 594 and 556 cm^{-1} are available for assignment. By comparison with the related compounds listed in Table 2 and based on intensity arguments, we prefer to assign 594 cm^{-1} to $\delta N_3(a'')$ and 556 cm^{-1} to $\delta a_s CF_3(a'')$. Spectra of ^{15}N substituted CF_3N_3 would be required to confirm these assignments.

The assignment of the three fundamental vibrations involving mainly the C-N linkage presents no difficulties because they occur at frequencies outside of the ranges expected for the CF_3 and N_3 modes. Thus, the C-N stretching

mode obviously²² must be assigned to the strongest Raman band at 859 cm^{-1} , and the second strongest Raman band at 179 cm^{-1} must be due to the CNN angle deformation. The latter mode was observed²² at 245 and 231 cm^{-1} for CH_3N_3 and CD_3N_3 , respectively, and the further mass increase of the methyl group in CF_3N_3 can account for the observed additional frequency decrease. The C-N torsional modes in CH_3N_3 and CD_3N_3 have frequencies of 126 and 90 cm^{-1} , respectively¹⁹. Based on the larger mass of the CF_3 group, this mode should show again a frequency decrease for CF_3N_3 and should occur well below 90 cm^{-1} . Due to its low frequency, this mode could not experimentally be observed in the present study.

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

As previously pointed out by Redington,³² the CF_3 modes of molecules of symmetry C_s can be related to those of molecules of symmetry C_{3v} , for which the assignments are well established. Such a correlation is shown in Table 3 for CF_3N_3 , CF_3NO ,^{29,30} CF_3OF ,³³⁻³⁷ CF_3COOH ,³² CF_3CN ,³⁸ CF_3CCH ³⁸ and CF_3H ³⁹. Under C_s symmetry the doubly degenerate e modes of C_{3v} split into one a' and one a'' component. Although the degree of splitting can significantly vary from compound to compound, the average of the a' and the a'' frequency is similar to that of the corresponding degenerate e mode, provided the following secondary effects which can influence the frequencies are kept in mind:

- (i) The covalency, and thereby the bond strength and frequency values, of the C-F bonds in CF_3X increases with increasing electronegativity of X, and
- (ii) coupling between certain modes can result in large frequency shifts.

A typical example for (ii) is the symmetric CF_3 deformation mode. In CF_3CN and CF_3CCH , this mode strongly couples with the stretching modes of the atoms located along the C_{3v} axis. This causes their frequencies to separate and significantly lowers the frequency of S sym CF_3 (see Table 3).

For CF_3N_3 , the following CF_3 modes can be assigned with reasonable confidence. The three CF_3 stretching modes are expected to occur in the $1150 - 1300 \text{ cm}^{-1}$ region and therefore are assigned to the fundamental vibrations at about 1168, 1254 and 1284 cm^{-1} . Since the two higher frequency bands are definitely polarized in the Raman spectrum, the 1168 cm^{-1} band must represent the antisymmetric CF_3 stretch of species a'' . This assignment is in good agreement with previous conclusions^{31,32,40} that $\nu \text{as CF}_3(a'')$ usually exhibits the lowest frequency value of the three CF_3 stretching modes. Based on its higher Raman intensity and a comparison with similar molecules^{31,32,40} the highest frequency fundamental vibrations is assigned to $\nu \text{sym CF}_3(a')$. Based on analogous arguments, the 730 cm^{-1} fundamental vibration must be assigned to the symmetric CF_3 deformation of species a' . Adopting the above assignments for the two N_3 deformation modes, the antisymmetric CF_3 deformation modes are ascribed to the 556 and 513 cm^{-1} bands with the Raman polarization data unambiguously distinguishing the a' from the a'' mode. The CF_3N_3 assignments also suggest that in Redington's³² and Berney's³¹ previous studies the assignments of the $\delta \text{as CF}_3(a')$ $\delta \text{as CF}_3(a'')$ might need to be interchanged. Although intensity arguments were cited against such an exchange, it is supported by Raman polarization data^{31,32}.

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

A normal coordinate analysis was not carried out because of the grossly underdetermined nature of the problem and the strong coupling experienced by

us and others^{30,36} for CF_3X type species. Since the force constants and the resulting potential energy distributions can be varied over a wide range with exact reproduction of the observed frequencies, PED based conclusions concerning the identities of certain fundamental vibrations should be treated with the necessary scepticism.

Numerous overtones and combination bands were observed in the infrared spectrum at higher sample pressures. Almost all of them could be readily assigned (see Tabel 1) and confirm the proposed assignments. The only detectable impurities were possibly traces of C_2F_6 and CF_3NO .

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

Mass Spectrum. The mass spectrum of CF_3N_3 is listed in Table 4. It shows a strong parent ion at $m/e = 111$ and a strong N_3^+ fragment, typical for covalent azides. As expected, the base peak is due to CF_3^+ , but surprisingly, the CF_3N^+ peak at $m/e = 83$ was extremely weak (less than 1%). In contrast to organic azides which generally show RN^+ as base peak. However, the high intensity of the N_2^+ and CF_2N^+ peaks indicate that in CF_3N_3 N_2 elimination is also important, but that CF_3N readily loses a fluorine to form the relatively stable CF_2N radical.⁴¹

UV - Spectrum. The uv absorption spectrum of gaseous CF_3N_3 is shown in Figure 2. The spectrum shows two strong absorptions at 200 and 258 nm, which by analogy to previous assignments for similar covalent azides⁴² might be assigned to the $sp_x \rightarrow \pi_y^*$ and $\pi_y \rightarrow \pi_x^*$ transitions of the azido group, respectively. The previous suggestions,⁴² that the energy difference between these two electronic transitions in a given XN_3 molecule is both a measure for the polarity of the X-N bond and an indication for a negatively polarized chlorine in ClN_3 , appear questionable. If these suggestions were correct, the replacement of the three

hydrogens in CH_3N_3 by three fluorines should result in a closer match of the electronegativities of the methyl and the azido group and hence an increased covalency and a larger energy difference between the two electronic transitions. However, this is clearly not the case. The previously postulated Cl-N_3^+ polarization is also incompatible with the well established⁴ reaction chemistry of ClN_3 which clearly demonstrates the electro-positive character of chlorine in this compound. The principle argument previously presented⁴ for the Cl-N_3^+ polarization in ClN_3 was the relatively high frequency of the N-Hal stretching modes in ClN_3 and BrN_3 . It was suggested that these high frequencies are due to partial N=X double bonding, and that this partial double bond character can only be explained by the following resonance structure invoking a formal negative charge on the halogen atom $\text{IX}=\text{N}^+\text{N}=\text{N}^-$. Obviously, the possibility of the more likely resonance structure $\text{X}^+=\text{N}^-\text{N}=\text{N}^+$ which results also in an X=N double bond but with a positively polarized halogen was overlooked.

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

Acknowledgement. The authors gratefully acknowledge financial support of this work from the Office of Naval Research, Power Branch, and the U. S. Army Research Office.

Table 1. Vibrational Spectra of CF_3N_3

Obsd freq, cm^{-1} , and intens ^a		Assignment in point group C_s
Infrared (gas)	Raman (liquid)	
3465 w		$\nu_1 + \nu_2 = 3466(a^1)$
3436 sh		$\nu_1 + \nu_3 = 3436(a^1)$
3327 w		$\nu_1 + \nu_4 = 3332(a^1)$
3039 w		$\nu_1 + \nu_5 = 3041(a^1)$
2755 vw		$\nu_1 + \nu_7 = 2762(a^1)$
2567 w		$2\nu_2 = 2568(a^1)$
2510 w		$2\nu_3 = 2508(a^1)$
2440 mw		$\nu_2 + \nu_4 = 2434(a^1)$
2410 sh		$\nu_3 + \nu_4 = 2404(a^1)$
2354 vw		$\nu_1 + \nu_{10} = 2361(a^1)$
2302 vw		$2\nu_4 = 2300(a^1)$
2270 vw		
2183 s	2182(1.1)p	$\nu_1(a^1)$
2140 m	2137(0.1)	$\nu_2 + \nu_5 = 2143(a^1)$
2018 mw		$\nu_2 + \nu_6 = 2014(a^1)$
1856 vw		$\nu_2 + \nu_7 = 1864(a^1)$
1798 w		$\nu_2 + \nu_8 = 1797(a^1)$
1713 vw		$2\nu_5 = 1718(a^1)$
1625 mw }		impurity?
1613 mw }		
1590 w		$\nu_5 + \nu_6 = 1589(a^1)$ or $\text{CF}_3\text{NO?}$
1455 w		$2\nu_6 = 1460(a^1)$
1427 mw		$\nu_3 + \nu_{10} = 1432(a^1)$
1370 mw	1370(0.1)	$\nu_5 + \nu_8 = 1372(a^1)$
1316 m		$\nu_6 + \nu_7 = 1310(a^1)$
1284 vs	1280(0.2)p	$\nu_2(a^1)$
1255 ms	1253(0.2)p	$\nu_3(a^1)$
1223 mw		C_2F_6 impurity?
1169 vs	1165 sh, dp	$\nu_{11}(a^1)$
1152 sh	1149(0.5)p	$\nu_4(a^1)$
1110 sh	1110(0+)	C_2F_6 impurity or $2\nu_{13} = 1112(a^1)?$
1034 vw		$\nu_5 + \nu_{10} = 1038(a^1)$
1009 vw		
859 mw, PQR	859(10)p	$\nu_5(a^1)$
751 w, PQR	814(0+) 751(0+)	? $\nu_7 + \nu_{10} = 759(a^1)$
731 m, PQR	730(3.8)p	$\nu_6(a^1)$
687 vw	685(0+)	$\nu_8 + \nu_{10} = 692(a^1)$
594 mw	594(0.2)dp	$\nu_{12}(a^{11})$
582 sh	580(1.1)p	$\nu_7(a^1)$
557 w	555 sh	$\nu_{13}(a^{11})$
513 mw, PQR	514(1.7)p	$\nu_8(a^1)$
450 vw		$\nu_{14}(a^{11})$
402 w, PQR	403(1.6)p	$\nu_9(a^1)$
	179(4.3)p	$\nu_{10}(a^1)$

(a) Uncorrected Raman Intensities representing relative peak height.

RI/RD81-140

E-10

Table 2. Assignment of the 15 fundamental vibrations of CF_3N_3 compared to those of closely related molecules.

related molecules.

		obsd frequency, cm ⁻¹													
Assignment	Approx description of mode for CF ₃ N ₃	CF ₃ N ₃	CF ₃ NO ^a	CF ₃ COOH ^b	CF ₃ OF ^c	FN ₃ ^d	ClN ₃ ^d	BrN ₃ ^d	IN ₃ ^e	CH ₃ N ₃ ^f	CD ₃ N ₃ ^f	HN ₃ ^g	DN ₃ ^g	OPF ₂ N ₃ ^h	
a ¹ ν ₁	ν _{asym} N ₃ or νN ₂ N ₃	2182	--	--	--	2034	2066	2062	2058	2106	2118	2140	2112	2175	
ν ₂	ν _{sym} CF ₃	1284	1291	1254	1294										
ν ₃	ν _{asym} CF ₃	1254	1230	1211	1258										
ν ₄	ν _{sym} N ₃ or νN ₁ N ₂	1150	--	--	--	1086	1144	1160	1176	1272	1285	1151	1184	1265	
ν ₅	νC-N	859	809	--	--					910	830				
ν ₆	δsCF ₃	730	730	781	679										
ν ₇	δN ₃ in plane	580	--	--	--	503	520	530	578	666	640	534	492		
ν ₈	δas CF ₃	513	533	508	584										
ν ₉	δrock CF ₃	402	428		434										
ν ₁₀	δCNN	179	296	--	250					245	231				
a ¹¹ ν ₁₁	ν _{asym} CF ₃	1168	1175	1189	1223										
ν ₁₂	δN ₃ out of plane	594	--	--	--					560	560	607	588		
ν ₁₃	δas CF ₃	556	551	591	608										
ν ₁₄	δrock CF ₃	450	428												
ν ₁₅	τ		[50] ⁱ	144						126	90				

RI/RD81-140

(a) Data from ref 29, 30 with some revised assignments.

(u) Data from ref 27.

(b) Data from ref 32.

(e) Data from ref 18.

(h) Data from ref 28.

(c) Data from ref 33 - 37 with some revised assignments.

(f) Data from ref 12-22

(i) Estimated value from ref. 29.

Table 3. Spectral correlation between the fundamental vibrations of the CF_3 group in molecules of symmetry C_{3v} and those of symmetry C_{3v} .

Class	Description of mode	C_{3v}		C_s		Class	Description of mode
		obsd freq, cm^{-1}	obsd freq, cm^{-1}	obsd freq, cm^{-1}	obsd freq, cm^{-1}		
		CF_3CN^a	CF_3CCH^a	CF_3H^b	CF_3COOH^c	$CF_3N_3^d$	CF_3OF^e
a_1	$\nu_{sym} CF_3$	1227	1253	1117	1254	1284	1294
	$\delta_{sym} CF_3$ (umbrella)	522 ^f	536 ^f	700	781	730p	679
					1189	1254	1263
e	$\nu_{asym} CF_3$	1214	1179	1152	1189	1211	1243
					1189	1168dp	1223
					591	556	608
	$\nu_{asym} CF_3$ (scissor)	618	612	507	549	542	596
					508	533	584
	$\delta_{rock} CF_3$	463	453		434	450	434
						402p	

(a) Data from ref 38.

(b) Data from ref 39.

(c) Data from ref 32.

(d) p and d indicates polarization in the Raman spectra. In C_s symmetry, a' modes cannot be polarized.

(e) Data from ref 33-37.

(f) strongly coupled modes (see text)

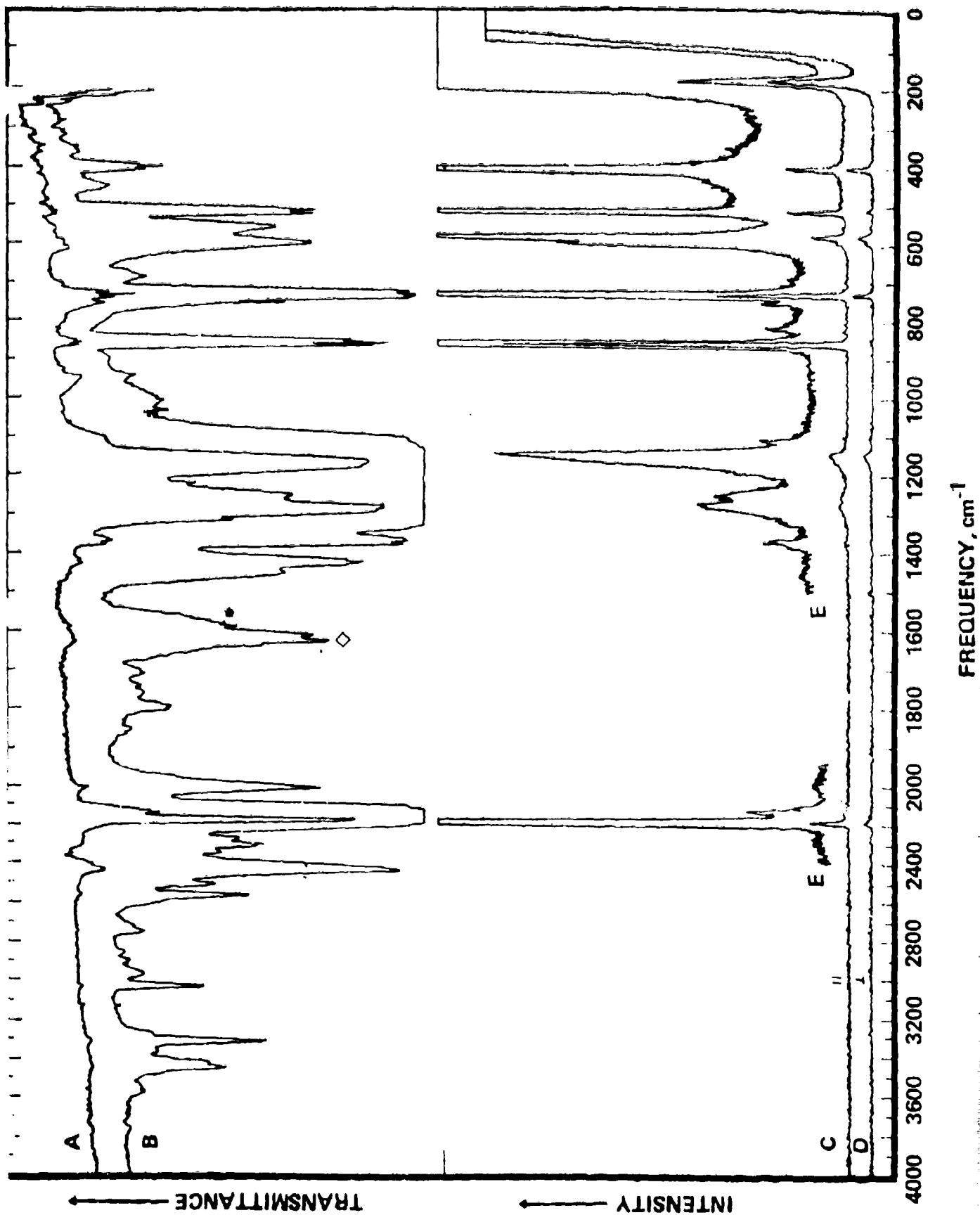
Table 4. Mass Spectrum of CF_3N_3

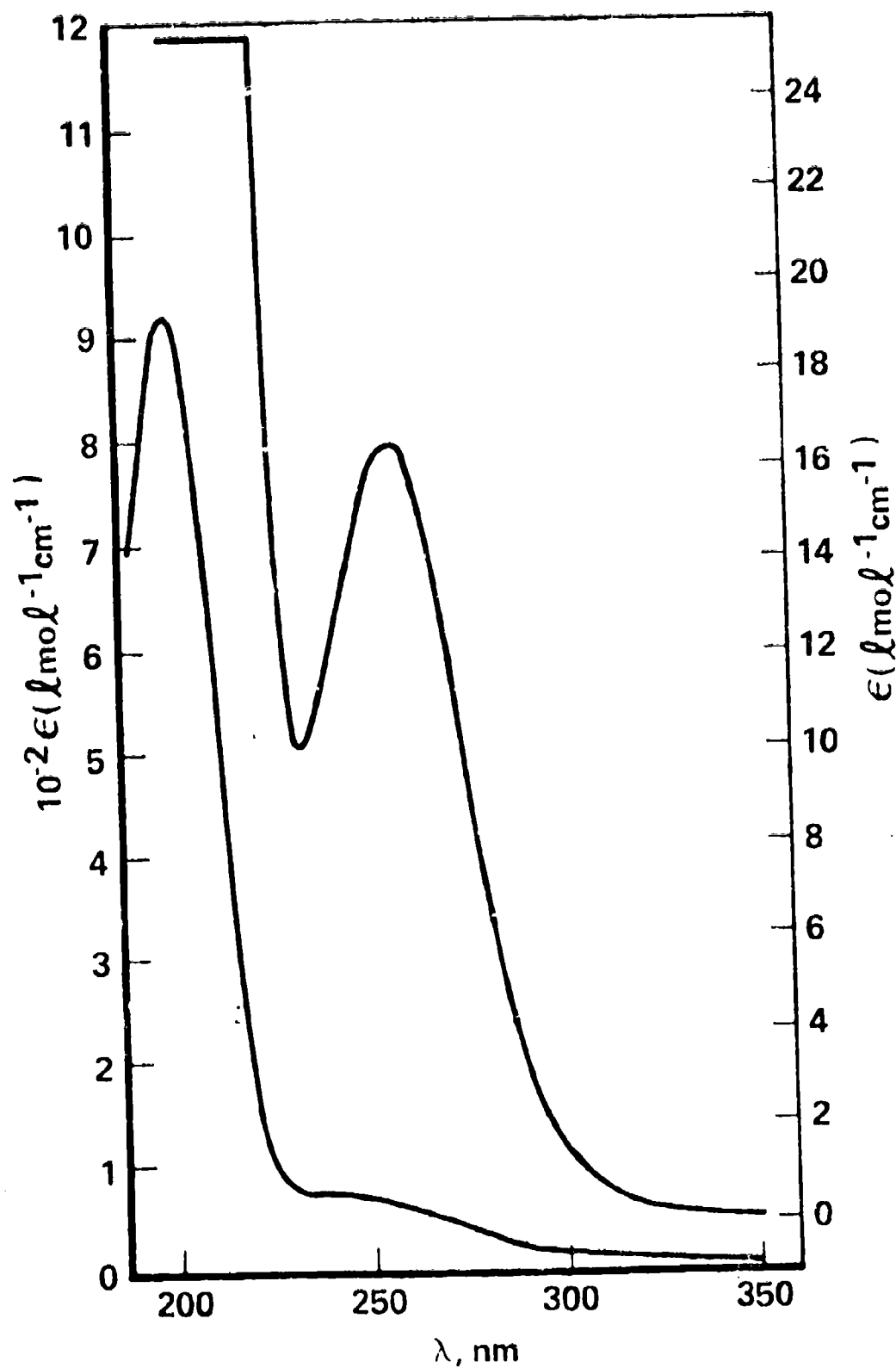
m/e	Rel. Intensity	Assignment
28	90	N_2
31	68	CF
42	27	N_3
45	37	CFN
50	39	CF_2
64	52	CF_2N
69	100	CF_3
92	31	CF_2N_3
111	79	CF_3N_3

Diagram Captions

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

Figure 2. uv - absorption spectrum of gaseous CF_3N_3 .





RI/RD81-140

E-16

REFERENCES

- [1] Makarov, S. P.; Yakubovich, A. Ya.; Ginsburg, V. A.; Filatov, A. S.; Englin, M. A.; Privezentseva, N. F.; Nikiforova, T. Ya. Doklady Akad. Nauk SSSR, 1961, 141, 357.
- [2] Makarov, S. P.; Yakubovich, A. Ya.; Filatov, A. S.; Englin, M. A.; Nikiforova, T. Ya. Zh. Obshch. Khim., 1968, 38, 709.
- [3] Patai, S. Edit., "The Chemistry of the Azido Group"; Interscience Publishers, John Wiley & Sons, New York, 1971.
- [4] Dehnicke, K. Angew. Chem. Internat. Edit. Engl. 1967, 6, 240.
- [5] Plyler, E. K.; Danti, A.; Blaine, L. R.; Tidwell, E. D. J. Res. Natl. Bur. Stand., Sect. A, 1960, 64, 841.
- [6] International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, Washington, D. C., 1961.
- [7] Claassen, H. H.; Selig, H.; Shamir, J. Appl. Spectrosc., 1969, 23, 8.
- [8] Miller, F. A.; Harney, B. M. Appl. Spectrosc., 1970, 24, 271.
- [9] Pure Appl. Chem. 1972, 11, 1215.
- [10] Livingston, R. L.; Rao C. N. R. J. Phys. Chem., 1960, 64, 756.
- [11] Salathiel, W. M.; Curl, Jr. R. F., J. Chem. Phys., 1966, 44, 1288.
- [12] Buckley, P.; Weber, J. P. Can. J. Chem. 1974, 52, 942.
- [13] Diodati, F. P.; Bartell, L. S. J. Mol. Struct., 1971, 8, 395.
- [14] Cook, R. L.; Gerry, M. C. L. J. Chem. Phys., 1970, 53, 2525.
- [15] Davis, M. I.; Boggs, J. E.; Coffey, Jr. D.; Hanson, H. P., Phys. Chem., 1965, 69, 3727; Turner, H. P.; Cox, P. A. Chem. Phys. Lett., 1976, 19, 585.
- [16] Milligan, D. E.; Jacox, M. E. J. Chem. Phys., 1964, 40, 2461.
- [17] Clark, T. C.; Cyne, M. A. A. Trans-Faraday Soc., 1969, 65, 2994.
- [18] Dehnicke, K. Angew. Chem. 1976, 88, 612.
- [19] Fateley, W. G.; Miller, F. A. Spectrochim. Acta, 1961, 17, 857.
- [20] Manica, E.; Zerbi, G. Gazz. Chem. Ital., 1960, 90, 53.
- [21] Miller, F. A.; Bassi, D. Spectrochim. Acta, 1963, 19, 565.
- [22] Thompson, W. T.; Fletcher, W. H. Spectrochim. Acta, 1966, 22, 1907.

- [23] Dows, D. A.; Pimentel, G. C. J. Chem. Phys., 1955, 23, 1258.
- [24] Pimentel, G. C.; Charles, S. W.; Rosengren, K. J. J. Chem. Phys., 1966, 44, 3029.
- [25] Moore, G. B.; Rosengren, K. J. J. Chem. Phys., 1966, 44, 4108.
- [26] Levine, D. M.; Dows, D. A. J. Chem. Phys., 1967, 46, 1168.
- [27] Shimanouchi, T. J. Phys. Chem. Ref. Data, 1972, 1, 202.
- [28] O'Neill, S. R.; Shreeve, J. M. Inorg. Chem., 1972, 11, 1629.
- [29] Shurvell, H. F.; Dass, S. C.; Gordon, R. D. Can. J. Chem., 1974, 52, 3149.
- [30] Demuth, R.; Bürger, H.; Pawelke, G.; Willner, H. Spectrochim. Acta, Part A, 1978, 34A, 113.
- [31] Berney, C. V. Spectrochim. Acta, Part A, 1971, 27A, 663.
- [32] Redington, R. L. Spectrochim. Acta, Part A, 1975, 31A, 1699.
- [33] Wilt, P. M. Dissertation, Vanderbilt University, 1967.
- [34] Wilt, P. M.; Jones, E. A. J. Inorg. Nucl. Chem., 1967, 29, 2108.
- [35] Smardzewski, R. R.; Fox, W. B. J. Fluor. Chem., 1975, 6, 417; J. Phys. Chem., 1975, 79, 219.
- [36] Kuo, J. C.; DesMarteau, D. D.; Fateley, W. G.; Hammaker, R. M.; Marsden, C. J.; Witt, J. D. J. Raman Spectrosc., 1980, 9, 230.
- [37] Hammaker, R. M.; Fateley, W. G.; Manocha, A. S.; DesMarteau, D. D.; Streusand, B. J.; Durig, J. R. J. Raman Spectrosc., 1980, 9, 181.
- [38] Shimanouchi, T. J. Phys. Chem. Ref. Data, 1973, 2, 247 and 250.
- [39] Shimanouchi, T. J. Phys. Chem. Ref. Data, 1972, 1, 54.
- [40] Christie, K. O.; Naumann, D. Spectrochim. Acta, Part A, 1973, 29A, 2017.
- [41] Ogden, P. A.; Mitsch, R. A. J. Am. Chem. Soc., 1967, 89, 3868.
- [42] Dehnicke, K.; Ruschke, P. Z. Naturforsch. 1978, 33b, 750.

APPENDIX F

A NEW SYNTHESIS OF DIFLUORAMINO TRIFLUOROMETHANE

CARL J. SCHACK

Rocketdyne, a Division of Rockwell International
Canoga Park, California 93104

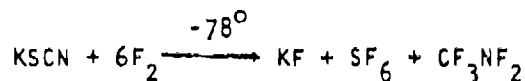
To Professor William T. Miller on his 70th Birthday

ABSTRACT

Fluorination of azidotrifluoromethane furnishes difluoramino trifluoromethane in a direct, reproducible, and high yield reaction. A maximum rate of conversion with minimum degradation was obtained at 70-80°. Enhancement of the rate of reaction was realized with added KF as a catalyst.

INTRODUCTION

Numerous methods have been reported^[1,2] for the synthesis of difluoramino trifluoromethane, CF_3NF_2 , including fluorination of amines, nitriles, metal cyanides, and metal thiocyanides. Fluorinating agents employed are NF_3 , N_2F_4 , transition metal fluorides, and fluorine. Nearly all these processes suffer from low yields of the desired CF_3NF_2 , poor reproducibility, and/or the presence of difficultly separable by-products. For example, many of the methods produce coproduct C_2F_6 whose b.p. is the same as that of CF_3NF_2 and thus it is very tedious to effect their separation. Ruff has reported [3] an excellent yield of CF_3NF_2 by the reaction shown.



However, half of the fluorine consumed goes to by-products and the small difference in the b.p.'s of SF_6 and CF_3NF_2 , 14°, requires chromatographic purification techniques.

It has now been discovered that a direct, reproducible, high yield synthesis of CF_3NF_2 is possible according to:



Minimal side reactions were encountered.

EXPERIMENTAL

Volatile materials were manipulated in a stainless-steel vacuum line equipped with Teflon FEP U traps and 316 stainless-steel bellows seal valves and a Heise Bourdon-Tube type gauge. Gas chromatographic data were obtained using a Varian GC under isothermal conditions with a stainless-steel column (1/8" X 10') packed with Poropak PS. Fluorine (Air Products) was scrubbed with AsF_5 immediately before it was used. Trifluoromethyl azide was prepared by a previously described procedure [4,5].

Synthesis of CF_3NF_2 . A 30 ml stainless-steel Hoke cylinder was loaded with CF_3N_3 (1.68 mmol) and F_2 (6.70 mmol) at -196°C . The cooling bath was removed and as soon as the cylinder was free of frost, it was placed in an oven preheated to 70°C . After 24 hours the reactor was cooled to -196°C and all volatile material, consisting mainly of the excess F_2 and by-product N_2 , was pumped away. The condensable material (1.69 mmol) was shown by infrared spectroscopy and GC analysis at 65°C to be 51% unreacted CF_3N_3 and 49% CF_3NF_2 with a trace of CF_4 . When fluorinated for an additional 24 hour period at 70°C , the yield of CF_3NF_2 was 84% and about 15% CF_3N_3 was still recovered. Further fluorination consumed the azide and produced CF_3NF_2 (92%), CF_4 (6%) and C_2F_6 (1-2%). A similar 70°C fluorination reaction in which the reactor contained 18 mmol of anhydrous KF powder, gave a 68% yield of CF_3NF_2 after 1 day. After 2 days this yield had increased to 73% and was accompanied by a 6.4% yield of the degradation product CF_4 .

RESULTS AND DISCUSSION

Azidotrifluoromethane and difluoroamino trifluoromethane are potentially hazardous and should be handled with caution. The existence of CF_3N_3 has been known for some time [4], but its chemistry remained unexplored. In covalent azides, X-N-N-N , the N-N bond adjacent to the X group is longer and weaker than the other N-N bond [6]. In a fluorination reaction this is a

likely fragmentation point and if controllable could be expected to lead to X-N-F derivatives. For CF_3N_3 this was expected to produce CF_3NF_2 . It was found that little or no reaction occurred with F_2 at $\leq 20^\circ$. Increasing the temperature, however, gave reproducible amounts of CF_3NF_2 . Percent conversions after 24 hours at various temperatures are shown in Figure 1.

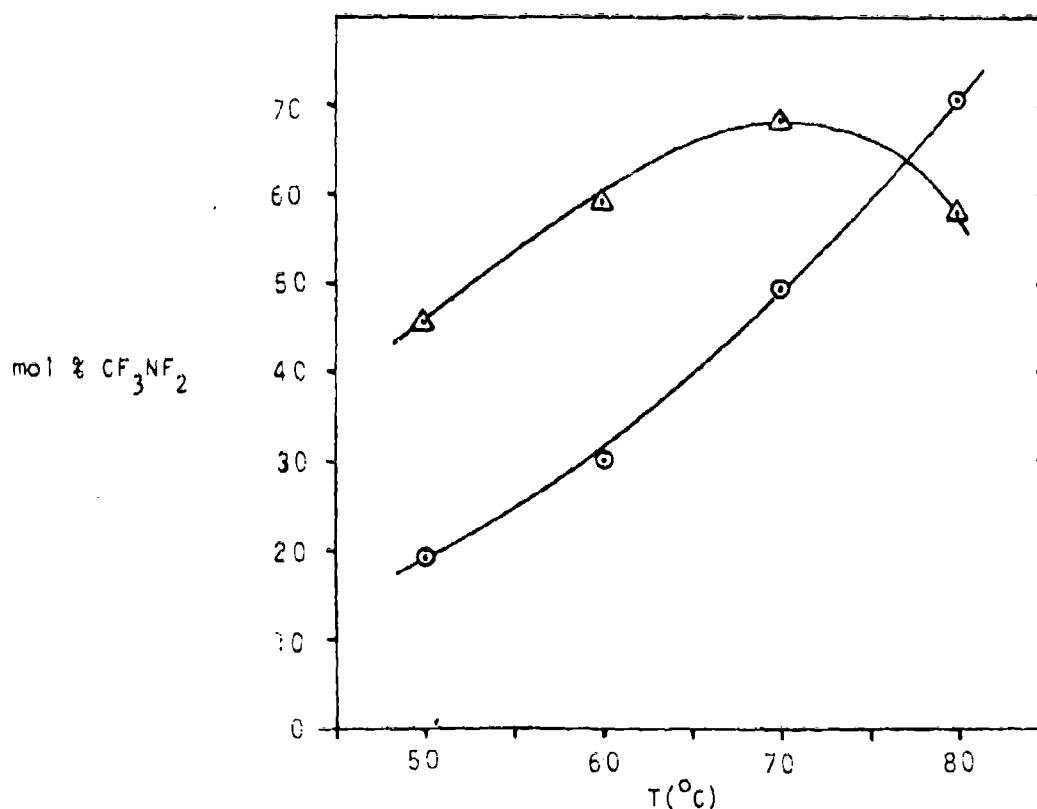
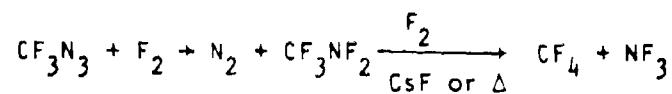


Figure 1. Yield % CF_3NF_2 after 24 hours without (○) and with added KF (Δ) as a catalyst.

Enhancement of the rate of reaction was realized with added KF, while CsF at 20°C or higher temperature lead to further fluorination as shown in the equation.



The maximum yield of CF_3NF_2 observed in both catalyzed and uncatalyzed reactions for 1 day was about 70%. After slightly longer reaction times yields are in the 90-95% range. In addition to the by-products CF_4 and NF_3 which are easily separated, there was also some C_2F_6 formed (~1%) when all the CF_3N_3 had reacted. Although not a very fast reaction, this synthesis has the advantages of high-yield, easy product purification, and reproducibility.

ACKNOWLEDGEMENT

The author gratefully acknowledges support for this work by the Office of Naval Research, Power Branch. Helpful discussions with Drs. K. O. Christe and L. R. Grant are also appreciated.

REFERENCES

- 1 J. K. Ruff, Chem. Rev., 67, 665 (1967).
- 2 J. P. Freeman, Adv. Fluorine Chem., 6, 287 (1970).
- 3 J. K. Ruff, J. Org. Chem., 32, 1675 (1967).
- 4 S. P. Makarov, A. Ya Yakubovich, A. S. Filatov, M. A. Englin, and T. Ya. NikiForova, Zh. Obshch. Khim., 38, 709 (1968).
- 5 K. O. Christe and C. J. Schack, Inorg. Chem., in press.
- 6 K. Jones in "Comprehensive Inorganic Chemistry," Vol. 2, J. C. Bailar et al Eds., Pergamon Press (1973) p. 281.

APPENDIX G

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

ON THE SYNTHESSES AND PROPERTIES OF FOIF₄O, ClOIF₄O, HOIF₄O, AND TETRAFLUOROPERIODATES

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

Received October 16, 1980

Abstract

Mixtures of cis- and trans- CsIF₄O₂ were prepared by the interaction of CsIO₄ with either anhydrous HF, BrF₅, ClF₃, ClF₅ or F₂. The vibrational spectra of these mixtures were recorded and partial assignments are given for cis- and trans- IF₄O₂⁻. The assignment for trans- IF₄O₂⁻ were supported by a normal coordinate analysis. The CsIF₄O₂ salt dissolves in CH₃CN with the formation of IF₄O₂⁻ anions, but undergoes solvolysis in anhydrous HF with formation of HOIF₄O. An improved synthesis of HOIF₄O from CsIF₄O₂ and BiF₅ in anhydrous HF is reported, and its Raman and ¹⁹F NMR spectra were recorded. The interaction of CsIF₄O₂ with NF₄SbF₆ in anhydrous HF results in solutions containing NF₄⁺, HF₂⁻, and HOIF₄O. On standing or when pumped to dryness, these mixtures decompose to yield NF₃ and the new compound FOIF₄O in high yield. The latter compound, the first known example of an iodine hypofluorite, was thoroughly characterized and shown by vibrational and NMR spectroscopy to be a mixture of the cis- and the trans-isomer. For comparison, the vibrational spectra of IF₅O have also been recorded. The reaction of CsIF₄O₂ with ClOSO₂F was shown to yield the novel compound ClOIF₄O. The fluorination reactions of CsIO₄, CsIF₄O₂, IF₅O and HOIF₄O with elementary fluorine were also studied.

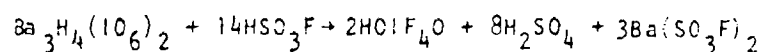
Introduction

The number of elements known to form stable hypofluorites is very limited.¹ Thus stable hypofluorites are known only for carbon, nitrogen, sulfur, selenium, fluorine, and chlorine containing compounds. In addition, the unstable hypofluorous acid, HOF, has been prepared.² Since recent work in our laboratory had shown that the thermal decomposition of certain NF₄⁺ salts of oxyanions,

such as NF_4ClO_4 ³ and $\text{NF}_4\text{SO}_3\text{F}$ ⁴, produces the corresponding hypofluorites in high yield, it was interesting to apply this method to the synthesis of novel hypofluorites. Preliminary results⁵ showed that FOIF_4O , the first known example of an iodine hypofluorite, can be prepared in this manner. In this paper, detailed information is given on the synthesis, properties and reaction chemistry of this interesting compound and of related iodine oxyfluoride derivatives, such as ClOIF_4O , HOIF_4O and the IF_4O_2^- anion.

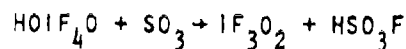
The literature on the synthesis and properties of salts containing the IF_4O_2^- anion is scant. The first report on the existence of IF_4O_2^- salts was published in 1971 by Engelbrecht and coworkers,⁶ but was limited to a one sentence statement that HOIF_4O interacts with either alkali metal fluorides or trifluoroacetates to yield the corresponding salts. In a subsequent paper,⁷ this statement was repeated, but again no data were given. In 1975, Aubke and coworkers reported⁸ that CsF combines with an excess of IF_3O_2 to give $\text{Cs}^+\text{IF}_4\text{O}_2^-$. A melting point, elemental analysis and incomplete vibrational spectra were given which were incorrectly interpreted in terms of a cis-isomer. In 1976, Selig and Elgad reported⁹ that partial hydrolysis of IF_7 produces IF_5O , HOIF_4O , and, with increased water addition, the IF_4O_2^- anion which was identified by ^{19}F NMR and vibrational spectroscopy as the cis isomer. Although Selig and Elgad reported only solution data, their vibrational spectra strongly disagreed with those reported by Aubke for solid $\text{Cs}^+\text{IF}_4\text{O}_2^-$. In 1977, Gillespie and Krasznai published¹⁰ that solutions of KIO_4 in IF_5 contain a mixture of IO_2F , IOF_3 and cis and trans IF_4O_2^- . On cooling solutions of KIO_4 dissolved in boiling IF_5 , they isolated a $\text{KIF}_4\text{O}_2 \cdot 2\text{IF}_5$ adduct which can be converted into KIF_4O_2 . Both compounds were shown by ^{19}F NMR and Raman spectroscopy to contain in the solid state and in CH_3CN solution trans IF_4O_2^- . In IF_5 solution, however, IF_4O_2^- was shown to exist in a cis-trans equilibrium, with the cis isomer being favored.

The tetrafluoroorthoperiodic acid, HOIF_4O , was first prepared by Engelbrecht and coworkers¹¹ according to

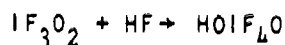


Since HOIF_4O could not be separated from HSO_3F by distillation, it was

converted into the more volatile IF_3O_2 ,



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



The acid was characterized^{6,11} by its physical constants and mass and NMR spectra which showed the compound to be a mixture of the cis and the trans isomer, with the cis isomer being more abundant. Selig and Elgud found⁹ that solutions of NaIO_4 in anhydrous HF contain HOIF_4O , as well as other unidentified fluorine species, and reported the ^{19}F NMR spectra of both isomers in HF solution. Gillespie and Krasznai¹⁰ also listed chemical shifts for cis and trans HOIF_4O , but did not specify the solvent, and gave a coupling constant of 21 Hz for the cis isomer, which disagrees with the values of about 220 Hz reported by others^{6,9,11}.

Experimental

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

Materials. Literature methods were used for the syntheses of NF_4SbF_6 ,¹² IF_5O ,^{13,14} and ClOSO_2F .¹⁵ The CsIO_4 was prepared by slowly combining with stirring, stoichiometric amounts of concentrated aqueous solutions of CsCl and NaIO_4 . The mixture was cooled to 0°C , and the CsIO_4 precipitate was filtered off, washed three times with ice water and dried for 16 hours in an oven at 110°C . Its vibrational spectra showed no detectable impurities. Bismuth pentafluoride (Ozark Mahoning Co.) was used as received. 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°C , with the material retained in the latter being used. Hydrogen fluoride (Matheson) was dried by treatment with 20 atm of F_2 at room temperature, followed by storage over BiF_5 to remove the last traces of H_2O .¹⁶ The ClF_3 (Matheson) and ClF_5 (Rocketdyne) were purified by fractional condensation prior to their use.

Apparatus. Volatile materials used in this work were handled 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 in HF solution using an apparatus consisting of two FEP U-traps interconnected through a coupling containing a porous Teflon filter (see Figure 1 of ref. 17). For NMR or low temperature vibrational spectra, the second FEP U-trap, which served as a receiver, was replaced by either a 4 mm Teflon FEP or thin-walled Kel-F tube.

Infrared spectra were recorded in the range $4000\text{--}200\text{cm}^{-1}$ on a Perkin-Elmer Model 283 spectrophotometer. Room temperature spectra of solids were obtained using dry powders pressed between AgCl disks. Spectra of gases were obtained using a Teflon cell of 5 cm pathlength equipped with AgCl windows. The spectra of matrix-isolated FOIF_4O and IF_5O were obtained at 6°K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research grade Ne (Matheson) was used as a matrix material in a mole ratio of 1000:1. The spectrometer was calibrated by comparison with standard gas calibration points^{18,19}, and the reported frequencies are believed to be accurate to $\pm 2\text{ cm}^{-1}$.

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

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

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

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

A total of eight preparations were carried out in a similar manner, using shorter reaction times, slightly higher reaction temperatures (~50°C), and rapid HF removal at elevated temperature. The conversion of CsIO_4 to CsIF_4O_2 after the first HF treatment was generally in the range of 75-90%, and the Raman spectra showed the presence of some unreacted CsIO_4 . This unreacted CsIO_4 was readily converted to CsIF_4O_2 by repeated treatment with anhydrous HF, however in most cases, repeated HF treatments resulted in a slight weight decrease and the appearance of bands due to HF_2^- (infrared: 1435 cm^{-1} , s, br; 1228 cm^{-1} ms. Raman: complex band at 790-740 cm^{-1} with maximum at 759 cm^{-1}). This is caused by the solvolysis of CsIF_4O_2 in anhydrous HF and the volatility of the resulting HIOF_4O (see below). The ratio between the cis- and the trans- isomer of CsIF_4O_2 varied somewhat for the different preparations, with the trans isomer being slightly favored at the lower and the cis isomer being somewhat favored at the higher reaction temperatures.

The CsIO₄-BrF₅ System. Cesium periodate (2.453 mmol) was placed in a passivated sapphire reactor equipped with a stainless steel valve and a magnetic stirring bar. Bromine pentafluoride (14.99 mmol) was added at -196°C, and the mixture was allowed to react during warm up to room temperature. A fast reaction with gas evolution occurred which was moderated by intermittent cooling with liquid N₂. After completion of the warm up cycles, the mixture was stirred at 20°C for 24 hours, resulting in a clear, pale yellow solution. The Raman spectrum of this solution showed the presence of BrF₅, BrF₃O, and of IF₄O₂⁻ (mainly trans with a small amount of cis-isomer). The solution was kept at 22°C for 4 days, then cooled to -196°C. The materials, volatile at -196°C, consisted of 1.92 mmol of oxygen. The materials volatile at 22°C were separated by fractional condensation and identified by Raman spectroscopy. They consisted of unreacted BrF₅ (9.9 mmol) and a mixture of BrF₃ and BrF₃O (found 682 mg, calcd. for 3.84 mmol BrF₃ + 1.06 mmol BrF₃O = 688 mg). The solid residue (804 mg, weight calcd for 2.453 mmol of CsIF₄O₂ = 787 mg) was shown by Raman spectroscopy to consist mainly of trans CsIF₄O₂, CsBrF₄ and smaller amounts of cis CsIF₄O₂, and possibly some solvated BrF₃O. Vacuum pyrolysis at 90°C resulted in a solid residue consisting again of trans CsIF₄O₂, CsBrF₄ and a small amount of cis CsIF₄O₂ and in the evolution of some IF₅ (~8 weight %).

The CsIO₄-ClF₃ System. A well passivated (with ClF₃) sapphire tube equipped with a stainless steel valve and containing a Teflon coated stirring bar was loaded with CsIO₄ (1.14 mmol), followed by ClF₃ (10.6 mmol). The liquid ClF₃ and solid periodate were stirred magnetically overnight at 0-20°C. This resulted in a clear, very pale yellow solution. Upon removal of the volatile material and pumping for several hours at ambient temperature, a white powder (0.493 g) remained in the tube which was identified by vibrational spectroscopy as a mixture of CsF·3IF₅ and CsClF₄ (weight calculated for the conversion of 1.14 mmol of CsIO₄ to 0.38 mmol CsF·3IF₅ and 0.76 mmol CsClF₄ was 0.497 g). The volatile materials consisted of ClF, FClO₂, and unreacted ClF₃.

The $\text{CsIO}_4\text{-ClF}_5$ System. When CsIO_4 was allowed to interact with a large excess of ClF_5 in a stainless steel reactor at room temperature, the composition of the solid reaction product depended on the reaction time. After short reaction times (about several hours) the solid consisted, based on its weight change and Raman spectra, mainly of unreacted CsIO_4 and smaller amounts of trans CsIF_4O_2 . After longer reaction times (in excess of 1 month), the solid consisted mainly of CsIF_8 and trans CsIF_4O_2 and some CsIF_4O .

The $\text{CsIO}_4\text{-F}_2$ System. The fluorination of CsIO_4 with elemental fluorine in a static system at temperatures up to 60°C resulted in a solid product which, based on its vibrational spectra, was a mixture of mainly CsIF_8 , CsIF_6 , and CsIO_4 containing smaller amounts of CsIF_4O and cis and trans CsIF_4O_2 .

Synthesis of HOIF_4O . In a typical experiment, CsIF_4O_2 (2.0 mmol) and BiF_5 (2.0 mmol) were placed in a passivated Teflon FEP U-trap containing a magnetic stirring bar. One arm of the trap was closed off by the stainless steel valve, while the other one was connected through a porous Teflon filter to a second Teflon U-trap which was capped off by another valve. Anhydrous HF (5mL liquid) was condensed into the U-trap, and the CsIF_4O_2 , BiF_5 , HF mixture was stirred at 25°C for 1 hour. The double U-trap assembly was cooled to -78°C , inverted and the HOIF_4O containing HF solution was separated from the CsBiF_6 precipitate by pressure filtration. The HF solvent was pumped off at -45 and -13°C . The residue was allowed to warm to ambient temperature and the material volatile at 25°C was collected at -78°C in a 4 mm o.d. external Teflon U-trap. This trap was shown to contain HOIF_4O (~2 mmol) which was identified by its Raman and ^{19}F NMR spectra. The filter cake (0.9 g) was identified by its Raman spectrum as CsBiF_6 .

Synthesis of FOIF_4O . In a typical experiment, CsIF_4O_2 (5.0 mmol) and NF_4SbF_6 (5.0 mmol) were placed in the Teflon-FEP metathesis apparatus (see above) and anhydrous HF (5 mL liquid) was condensed in at -78°C . The mixture was stirred for 1 hour at room temperature. The apparatus was cooled to -78°C , inverted and the white precipitate was separated from the solution by pressure filtration. Most of the HF solvent was pumped off over several hours at temperatures ranging from -64 to -30°C . The resulting white solid residue was allowed to decompose during slow warm-up from -30°C to ambient. The volatile products

were passed through a Teflon U-trap containing passivated NaF pellets, followed by a series of cold traps kept at -78°C , -95°C , -112°C and -210°C . The -78°C trap contained a small amount of unidentified material which was discarded, the -95°C fraction consisted of pure FOIF_4O (2.36 mmol), the -112°C trap had 1.69 mmol of FOIF_4O containing a small amount of IF_5O as impurity, and the contents of the -210°C trap consisted of NF_3 (4.0 mmol). A small amount of white solid residue, which was left behind after the thermal decomposition of the filtrate, was shown by vibrational spectroscopy to consist mainly of trans- CsIF_4O_2 . The filter cake (1.8 g) was identified by Raman spectroscopy as CsSbF_6 . The -95°C fraction was used for the characterization of FOIF_4O and was shown by vibrational and ^{19}F NMR analysis to be free of IF_5O .

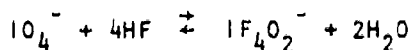
For the elemental analysis, 278.7 mg of the material was condensed at -196°C into an ampule containing 12 mL of frozen 1N NaOH. The mixture was warmed to ambient temperature for 12 hours and then analyzed for total iodine by energy dispersive X-ray fluorescence spectrometry, for IO_4^- by iodometric titration, for base consumption by back titration with 0.1N HCl using a pH electrode and for fluoride by titration using $\text{La}(\text{NO}_3)_3$ and an Orion specific ion electrode. Anal. Calcd for FOIF_4O : I, 49.98; F, 37.42; OH^- consumed, 6.0 equiv/mol; iodometric titration, 8.0 equiv/mol, assuming the following hydrolysis reaction: $\text{FOIF}_4\text{O} + 6\text{OH}^- \rightarrow \text{IO}_4^- + 5\text{F}^- + 0.5\text{O}_2(\text{g}) + 3\text{H}_2\text{O}$. Found: I, 50.0; F, 36.0; OH^- consumed, 6.1 equiv/mol; iodometric titration, 7.8 equiv/mol.

Synthesis of ClOIF_4O . A 30 mL stainless steel cylinder was loaded with 2.32 mmol CsIF_4O_2 , and 2.12 mmol ClSO_3F was added at -196°C . After keeping the cylinder for 5 days at -78°C , the volatile products were removed from the cylinder. The solid residue was identified by vibrational spectroscopy as CsSO_3F . The volatiles were fractionated through traps cooled to -45°C , -78°C , and -196°C . The lowest temperature fraction (0.77 mmol) was mainly Cl_2 together with some FCIO_2 , while the -45°C trap contained a white solid which melted above 0°C and which was identified by its infrared spectra as IF_5 . The -78°C trap contained a yellow-orange solid, which on slight warming

melted to an orange liquid. Its gas phase infrared spectrum was recorded at 25°C and showed the following bands (cm⁻¹, rel. intens., assignment): 912 m, I=O stretch; 763 mw, O-Cl stretch; 678 vs, 635 s, 532 mw IF and I=O stretching. The compound was found to be thermally unstable and very difficult to handle. It readily decomposed to IF₅ and its synthesis required careful temperature control. When the synthesis was carried out for example at -45°C, only decomposition products were obtained. Attempts to isolate fluorocarbon derivatives of ClOIF₄O by adding it across the C=C double bond of C₂F₄ resulted at -78°C in no reaction and at room temperature in the oxygenation, fluorination and decomposition products COF₂, CF₃COF, ClCF₂COF, C₂F₅Cl, and IF₅.

Results and Discussion

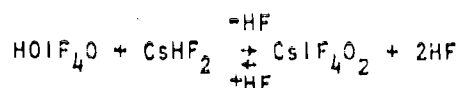
Synthesis of CsIO₂F₄. In our work the known⁹ equilibrium



was utilized for a convenient synthesis of CsIF₄O₂. To shift this equilibrium to the right, a large excess of HF must be used and the HF treatment must be repeated at least once. The resulting CsIF₄O₂ consists of a mixture of the cis and the trans isomer, as shown by ¹⁹F NMR and vibrational spectroscopy (see below). The ratio of cis to trans isomer varies somewhat with the reaction conditions used, but the formation of the cis isomer appears to be slightly favored. The ¹⁹F NMR and Raman spectra were recorded for solutions of CsIF₄O₂ in anhydrous HF and CH₃CN. Whereas the CH₃CN solution spectra show the presence of the IF₄O₂⁻ anion, the spectra of the HF solutions are characteristic (see below) for those of HOIF₄O. This finding is in excellent agreement with the previous report by Selig and Elgud⁹ that solutions of NaIO₄ in anhydrous HF contain HOIF₄O and the report by Engelbrecht and co-workers^{6,7} that HOIF₄O interacts with alkali metal fluorides to form IF₄O₂⁻ salts. Consequently, the above equilibrium reaction involves at least two reactions



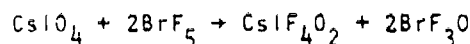
and upon HF and H₂O removal



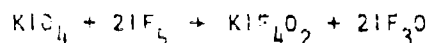
The intermediate formation and the slight volatility of HOIF_4O also explain why in some of our CsIF_4O_2 preparations, when the HF was rapidly pumped off at elevated temperature, a weight loss accompanied by some CsHF_2 formation was observed.

The above synthesis of CsIF_4O_2 from CsIO_4 and HF appears more convenient than the previously reported methods involving either the difficult to obtain IF_3O_2 as a starting material or the isolation and recrystallization of $\text{MIF}_4\text{O}_2 \cdot 2\text{IF}_5$ from IF_5 , followed by its pyrolysis. However, the latter method produces almost exclusively the trans isomer and might be the preferred method if pure trans IF_4O_2 is desired. The fact that the cis-trans isomer ratio strongly depends on the nature of the reactants suggests that this ratio is kinetically and not thermodynamically controlled. This conclusion is in excellent agreement with those reached by Toetsch and Sladky for the closely related $\text{Tef}_4(\text{OH})_2$ system. ^{21a}

An alternate method for the formation of CsIF_4O_2 involves the reaction of CsIO_4 with BrF_5 . The main reaction can be described by

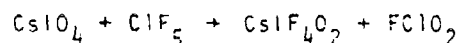


This reaction is analogous to that ¹⁰ previously reported for $\text{KIO}_4 + \text{IF}_5$, i.e.



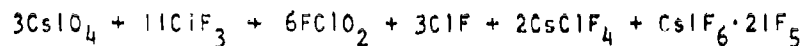
and produces almost entirely the trans isomer. Compared to the IF_5 reaction, the BrF_5 reaction offers the advantage that the BrF_3O and BrF_3 by-products are volatile and can easily be pumped off. However, the resulting product was contaminated by nonvolatile CsBrF_4 which could not be readily separated from the CsIF_4O_2 .

The reactions of CsIO_4 with chlorine fluorides were also briefly studied. With ClF_5 , trans CsIF_4O_2 was formed in low conversion according to:

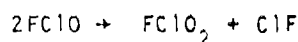


Attempts to achieve higher conversions by the use of longer reaction times failed due to the formation of CsIF_5 as the main product and of CsIF_4O as a minor product.

When ClF_5 was replaced by the more reactive ClF_3 , complete conversion of the CsIO_4 was obtained, however all the oxygens in IO_4^- were exchanged for fluorine and the solid product consisted of a mixture of $\text{CsIF}_6 \cdot 2\text{IF}_5$ ²² and CsClF_4 ²³. Based on the observed material balance, the following reaction occurred:



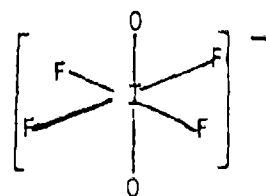
The formation of ClF and of half of the FCIO_2 can be readily explained by the well known²⁴ disproportionation of the expected unstable FCIO intermediate:



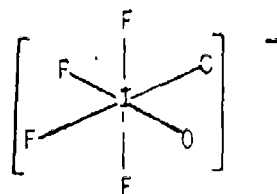
The fluorination of CsIO_4 by elemental fluorine at temperatures up to 60°C in a static system was also studied. The main products were CsIF_8 and CsIF_6 , with CsIF_4O and cis and trans CsIF_4O_2 as minor products.

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

Vibrational Spectra of CsIF_4O_2 . The vibrational spectra of solid CsIF_4O_2 were recorded for samples which differed in their cis and trans isomer content. The observed spectra are given in Figures 1 and 2 and the observed frequencies and their assignments in point group D_{4h} and C_{2v}



D_{4h} , trans



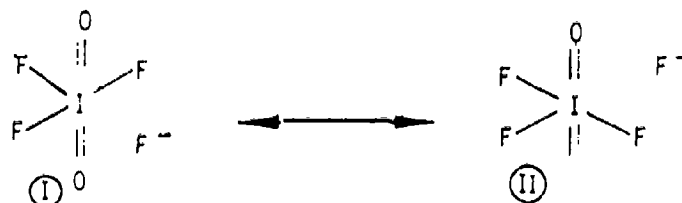
C_{2v} , cis

are summarized in Tables I and II, respectively. The bands belonging to the trans isomer could be readily distinguished from those of the cis isomer due to the fact that only the trans isomer has a center of symmetry which causes the infrared and Raman bands to be mutually exclusive. Furthermore,

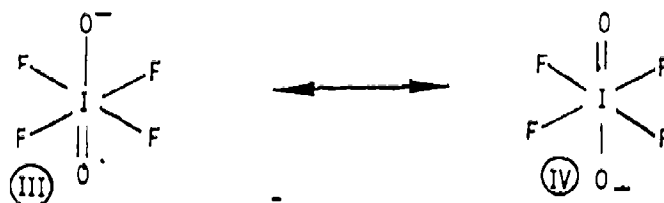
the ^{19}F NMR spectrum (see below) clearly distinguished the trans from the cis isomer and established which isomer was more abundant in a given sample.

Assignments and Normal Coordinate Analysis for trans IF_4O_2^- . The trans IF_4O_2^- anion of symmetry D_{4h} should possess 11 fundamental modes classified as $2A_{1g} + 2A_{2u} + B_{1g} + B_{2g} + B_{2u} + E_g + 3E_u$. Of these, the A_{1g} , B_{1g} , B_{2g} and E_g modes should be Raman active only, the A_{2u} and E_u modes should be infrared active only, whereas the B_{2u} mode should be inactive in both spectra. Of the 10 active modes, all five Raman active modes and three out of the five infrared active modes have been observed and can be readily assigned based on their activity, polarization data and by comparison with the closely related species IF_4^- ,²⁵ IF_4O^- ,²⁶ IF_5 ,^{27,28} and IF_5O .^{14,29} (see Table I). The correctness of these assignments was confirmed by a normal coordinate analysis, using the symmetry coordinates and G matrix elements previously published³⁰ by Beattie and coworkers. The bond distances were estimated to be $r_{\text{IF}} = 1.92 \text{ \AA}$ and $d_{\text{IO}} = 1.72 \text{ \AA}$, based on the known structures and stretching frequencies of the related IF_5O .^{14,29,31} and IF_5 .^{27,28,32} molecules and the IF_4O^- anion.^{26,33} The force constants of the B_{1g} , B_{2g} and E_g species are uniquely determined. In the A_{1g} block, the G_{12} element is zero and therefore F_{12} can be ignored. For the A_{2u} block, the extremal solution,³⁴ $F_{44} = \text{Min}$, was used which has previously been shown²⁵ for the closely related IF_4^- anion to be an excellent approximation to a general valence forcefield for these weakly coupled systems. For the E_u block, only the frequency value of the stretching mode is experimentally known. A comparison with the force field of the related IF_4^- anion²⁵ showed that, due to the heavy iodine central atom, the approximation $F_{99} = \lambda_g/G_{99}$ yields an almost exact value for the stretching force constant in the E_u block, and was therefore used for IF_4O_2^- . The resulting force field is listed in Table III and strongly supports our assignments. Table IV gives a comparison of the internal stretching force constants of trans IF_4O_2^- with those of the closely related species IF_4^- ,²⁵ IF_4O^- ,²⁶ IF_5 ,³⁵ IF_5O and IF_6^+ .³⁶ As previously discussed³⁷ for chlorine oxyfluorides, the IF stretching force constants increase in the sequence anions < neutral molecules < cations, and within a given group with increasing oxidation state of the iodine

central atom. The 10 stretching force constants are in the range expected for I = O double bonds and demonstrate that, even in the anions, the formal negative charge is located mainly on the more electronegative fluorine ligands rather than on the oxygen ligand. Consequently, contributions from resonance structures, such as I and II,



are more important than those from III and IV



to explain the bonding in IF_4O_2^- . Resonance structures, such as I and II, also account for the decrease of the IF stretching force constants with increasing formal negative charges and also with decreasing oxidation state of the central atom. Both effects increase the $\hat{\text{I}}^+ - \hat{\text{F}}^-$ polarity of the IF bonds, hereby causing the bonds to become more ionic, longer and therefore weaker. This weakening of the IF bonds can be very significant as is demonstrated by the low value of f_r in IF_4^- which is only 41% of that in IF_6^+ . The fact that the 10 stretching force constant drops from IF_4O^- (6.56 mdyn/Å) towards IF_4O_2^- (6.15 mdyn/Å), in spite of an increase in the oxidation state of the iodine atom, is interesting and parallels the trends previously noted³⁷ for chlorine oxyfluorides, i.e., the electron releasing effect of oxygen ligands in highly electronegative compounds.

Assignments for cis IF_4O_2^- . Our assignments for cis IF_4O_2^- have been limited to the stretching modes because only 10 of the 15 fundamentals, expected for point group C_{2v} , have been observed and because no reliable assignments have been published for similar XF_4O_2 species. The assignment

of the two 10_2 stretching modes is straight forward based on their high frequencies, relative intensities and the previously published ^{18}O spectra.⁹ The symmetric $1F_2$ axial and the symmetric $1F_2$ equatorial stretch must belong to the two intense polarized Raman bands at 540 and 609 cm^{-1} , respectively, with the axial mode resulting in a weak and the equatorial mode resulting in a strong infrared counterpart. The antisymmetric axial and the antisymmetric equatorial $1F_2$ stretch should both be very intense in the infrared spectrum and therefore are assumed to coincide at about 600 cm^{-1} , resulting in a very strong, broad band.

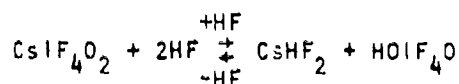
Comparison with Previous $1F_4O_2^-$ Assignments. Disregarding some solvent induced shifts, the above assignments for cis $1F_4O_2^-$ agree well with those previously reported⁹ by Sellig and Elgud for an aqueous solution. The only minor discrepancy is the assignment of the antisymmetric axial $1F_2$ stretch. For trans $1F_4O_2^-$, the assignments proposed by Gillespie and Krasznai for six of the modes have been revised for three of them. The vibrational spectra reported by Carter et al.⁸ show that their sample contained mainly trans $1F_4O_2^-$, but was incorrectly interpreted in terms of the cis isomer.

^{19}F NMR Spectra of $1F_4O_2^-$ and $HO1F_4O$. The presence and the relative amounts of cis and of trans $1F_4O_2^-$ in the above samples were verified by ^{19}F NMR spectroscopy. The spectra were recorded in CH_3CN solution at $-70^\circ C$ and showed a narrow singlet at $\delta 65.1$ for the trans isomer and a broader A_2B_2 pattern at $\delta 66.0$ and 112.8 with $J_{FF} = 204\text{ Hz}$ for the cis isomer. The observed shifts and coupling constant are in fair agreement with the value previously reported for solutions in CH_3CN (trans: $\delta 62.0$),¹⁰ $1F_5$ (cis: $\delta 68.5$, 102.1 ; $J_{FF} = 202\text{ Hz}$. trans: $\delta 70.6$),¹⁰ and aqueous HF (cis: $\delta 64$, 105 ; $J_{FF} = 196\text{ Hz}$).⁵

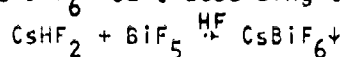
Solutions of $Cs1F_4O_2$ in anhydrous HF at $-75^\circ C$ resulted in a sharp singlet at $\delta 62.0$ and a broadened A_2B_2 pattern at $\delta 61.8$ and 85.9 with $J_{FF} = 220\text{ Hz}$. At room temperature, the A_2B_2 pattern was broadened to the extent that it could barely be detected. Although these spectra are

similar to those of IF_4O_2^- , it was conclusively shown (see below) by Raman spectroscopy that they are due to cis and trans HOF_4O and not to IF_4O_2^- . This finding is in excellent agreement with the conclusion⁹ reached by Selig and Elgud that their signals (1) and (2) observed for solutions of NaIO_4 in HF are due to cis and trans HOF_4O . The observed chemical shifts and coupling constant are in fair agreement with previous reports^{6,7,9,10} considering the different solvents and conditions used for recording the spectra. The coupling constant of 21 Hz, previously reported by Gillespie and Krasznai,¹⁰ appears to be a typographical error.

Synthesis and Properties of HOF_4O . The above described experiments involving CsIF_4O_2 in HF solutions indicate the existence of the following equilibrium



which, in the presence of a large excess of HF, is shifted all the way to the right side. In view of the lack of a convenient synthesis of HOF_4O ,^{6,7} this reaction was utilized to prepare HOF_4O . Since during HF removal the above equilibrium is shifted back to the left, the CsHF_2 was converted into an insoluble BiF_6^- salt according to



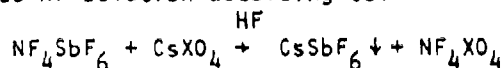
which can be filtered off at -78°C . The resulting mixture of HOF_4O and HF can be easily separated by fractional condensation or distillation.

The ^{19}F NMR spectrum of HOF_4O in HF solution was recorded at -75°C and was identical to that obtained by dissolving CsIF_4O_2 in HF (see above). The ratio of cis to trans isomer in the HOF_4O sample appeared to be similar to that in the CsIF_4O_2 starting material. It should be pointed out that at room temperature the signal due to the cis isomer can be so broad that it is difficult to detect, thereby giving the false impression of dealing with samples containing exclusively the trans isomer.

The Raman spectra of liquid HOF_4O showed some variation. Freshly prepared samples and HF solutions exhibited spectra similar to that of

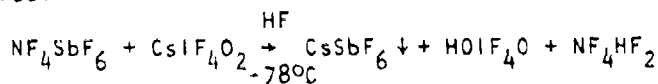
trace A of Figure 3. On standing, the 872 cm^{-1} band decreased in intensity and bands at 828 and 799 cm^{-1} started to grow in. In addition the bands in the $600\text{--}700\text{ cm}^{-1}$ region became broader and shifted to slightly lower frequencies, as shown by trace B of Figure 3. Based on its ^{19}F NMR spectrum, a sample of HOIF_4O in HF solution which showed a Raman spectrum very similar to that of trace A of Figure 3 consisted mainly of the cis isomer. Whether the change from Raman spectrum A to spectrum B involves a change in the isomer ratio or is caused by association effects was not clearly established.

Synthesis of FOIF_4O . Previous studies have shown that unstable NF_4^+ salts containing oxyanions, such as ClO_4^- or SO_3F^- , can be prepared by metathesis in anhydrous HF solution according to:

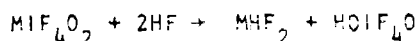


Thermal decomposition of these NF_4^+ salts provided a new high yield synthetic route to hypofluorites.^{3,4} Since no examples of iodine hypofluorites had previously been known, it was interesting to examine the applicability of this method to periodates.

Since the IO_4^- anion is fluorinated to IF_4O_2^- in anhydrous HF, as shown by the above studies and the previous report by Selig and Elgad,⁹ the metathetical reaction of IO_4^- itself could not be studied. However, when IO_4^- was replaced by IF_4O_2^- , the following metathetical reaction occurred:



The CsSbF_6 precipitate could be easily filtered off at -78°C and Raman and ^{19}F NMR spectroscopy of the filtrate showed the presence of NF_4^+ ³⁸ and HOIF_4O (see above) with no evidence for the IF_4O_2^- anion. This is in agreement with the above results for CsIF_4O_2 which demonstrated that MIF_4O_2 salts undergo solvolysis in anhydrous HF according to:



Raman and ^{19}F NMR spectra showed that these NF_4HF_2 - HOIF_4O containing HF

solutions are unstable at room temperature and slowly decompose to NF_3 ^{39,40} and a new compound identified (see below) as a mixture of cis and trans FOIF_4O . At the same time, the relative intensities of the NF_4^+ and HOIF_4O signals decreased accordingly. When the HF solvent was pumped off at -30°C from a freshly prepared NF_4HF_2 - HOIF_4O solution, a white solid residue was obtained. The low-temperature Raman spectrum of this solid showed the presence of the NF_4^+ cation, but the remaining bands were too broad to permit a positive distinction between IF_4O_2^- , HOIF_4O and possibly some $\text{HF}_2^- \cdot n\text{HF}$.³ The new compound FOIF_4O was obtained in high yield by decomposing at room temperature this thermally unstable solid, with the by-product being NF_3 . Since the same products were obtained from HF solutions which, based on their ^{19}F NMR and Raman spectra, contained only HOIF_4O but not IF_4O_2^- , it appears that FOIF_4O is formed by fluorination of HOIF_4O by either NF_4^+ or nascent fluorine formed during the thermal decomposition of the marginally stable $\text{NF}_4^+ \text{HF}_2^- \cdot n\text{HF}$.³ Consequently, it was interesting to investigate whether FOIF_4O could also be obtained by the fluorination of HOIF_4O with elementary fluorine. However, fluorination reactions carried out at 25°C using either neat or HF solutions of HOIF_4O , 2 atm of F_2 pressure and a shaker for agitation, did not result in any fluorination of HOIF_4O and only unchanged starting materials were recovered.

Since the fluorination reactions of alkali metal salts, such as CsSF_5O , CsCF_3O , CsClO_4 , or KNO_3 with elementary fluorine yield the corresponding hypofluorites,¹ it was interesting to study the analogous fluorination reaction of CsIF_4O_2 . In static systems up to 60°C slow reactions between CsIF_4O_2 and F_2 were observed producing IF_5O in low yield as the only volatile product. Since IF_5O is the primary decomposition product of FOIF_4O (see below) the intermediate formation of some FOIF_4O in this reaction cannot be ruled out. Similarly, the fluorination of CsIO_4 with F_2 under comparable conditions produced small amounts of IF_5O as the only volatile product. The Raman spectra of the solid residues from both reaction systems showed the presence of CsIF_8 ,⁴¹ CsIF_6 ,²² cis and trans CsIF_4O_2 , and CsIF_4O .²⁶ The low reactivity of the $\text{I}=\text{O}$ double bond in IF_5O was further demonstrated by separate experiments showing that F_2 is not added across the $\text{I}=\text{O}$

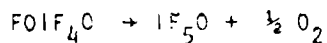
double bond, even in the presence of CsF as a catalyst, at temperatures between -196 and 25°C using an excess of F₂.

Properties of FOIF₄O. As shown by NMR and vibrational spectroscopy (see below), FOIF₄O exists in the form of two isomers, one in which the two oxygens are cis and one in which they are trans to each other. Attempts were unsuccessful to separate the two isomers by gas chromatography at 25° using a 30 foot, 3/16 inch o.d., stainless steel column containing 50-percent Halocarbon oil No. 4-11V on Ke1-F 300 (70-80 mesh).⁴² Consequently, the physical properties could only be determined for a mixture of both isomers. Based on their ¹⁹F NMR peak areas, the ratio of cis to trans isomer in the sample used for the physical property measurements was 1.92:1. FOIF₄O is colorless as a gas, pale yellow as a liquid, and white in the solid state. The given sample melted at -33.1°C. Vapor pressures were fitted by the method of least squares to the equation

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

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

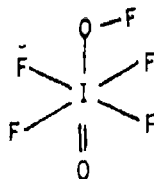
FOIF₄O is marginally stable at room temperature and can be handled in well passivated metal and Teflon equipment without rapid decomposition. The fact that IF₅O was frequently observed as an impurity in the vibrational and NMR spectra suggests the following primary decomposition mode



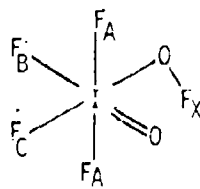
when a sample of FOIF₄O has heated in a stainless steel cylinder to 120°C

for 388 hours decomposition to IF_5 and O_2 was observed. This is not surprising in view of a previous report¹³ that IF_5O readily decomposed to IF_5 and O_2 . As expected for a hexacoordinated iodine species, FOIF_4O is neither a good fluoride ion acceptor nor a donor. Thus, it does not form stable adducts at room temperature with either the strong Lewis acid SbF_5 or the strong Lewis base CsF . Attempts to add FOIF_4O across the $\text{C}=\text{C}$ double bond in C_2F_4 were unsuccessful. Fluorination and oxygenation of C_2F_4 occurred with COF_2 , CF_3CFO and C_2F_6 being the principal reaction products.

^{19}F NMR Spectra of FOIF_4O . The ^{19}F NMR spectra of FOIF_4O were recorded for the neat material and HF solutions and were essentially identical. The spectra of the neat liquid and solid are shown in Figure 4, together with the observed chemical shifts and coupling constants. Peak area measurements showed that the 202 and 67 ppm signals belong to an AX_4 and the 176, 175 and 77 ppm signals to an A_2BCX system. The AX_4 system is readily assigned to the trans isomer



The chemical shift of 66.8 ppm of the four equatorial fluorines is almost identical to that in IF_5O (68.5 ppm for neat IF_5O at -20°C) and that of 202.5 ppm of the fluorine on oxygen is similar to those of other hypofluorites, such as O_3ClOF (219 ppm)⁴³, SF_5OF (189 ppm),⁴⁴ or trans - $\text{SeF}_4(\text{OF})_2$ (179 ppm).⁴⁵ The fluorine-fluorine coupling constant, $J_{\text{FF}} = 34$ Hz, is in good agreement with the value of 27 Hz, previously reported for the coupling constant of the four equatorial fluorines to the two hypofluorite fluorines in trans - $\text{SeF}_4(\text{OF})_2$.⁴⁵ The broadened fluorine on iodine resonance and the lack of observable fine structure in FOIF_4O is attributed to unresolved ^{19}F coupling ($1_I = 5/2$) due to decreased quadrupole relaxation caused by the approximately spherically symmetric electric field about the iodine.⁶ The A_2BCX system is assigned to the cis-isomer



RI/RD81-140

G-19

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

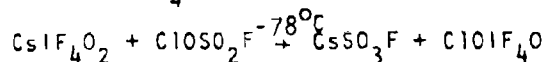
Vibrational Spectra of FOIF₄O and IF₅O. The infrared spectra of the gas and of the Neon matrix isolated solid and the Raman spectra of liquid and solid FOIF₄O were recorded (see Figures 5 to 7), and the observed frequencies are summarized in Table V. The studied samples were mixtures of cis and trans FOIF₄O with a cis:trans ratio of about 1.9 based on the NMR spectra and, in the matrix study, also contained a small amount of IF₅O, formed during manipulation of the sample. Since the vibrational spectra of cis and trans FOIF₄O and of IF₅O are all very similar, the gas phase infrared spectra are only of limited value for distinguishing the three compounds. However, the Raman spectra of the liquid and solid and particularly the infrared spectra of the matrix isolated samples definitely confirm the presence of the two FOIF₄O isomers established by the ¹⁹F NMR study. Some distinction of the cis from the trans isomer bands was possible from a comparison of spectra of samples having different cis to trans ratios (see for example traces D and E of Figure 5).

Tentative assignments for the stretching modes of cis and trans FOIF₄O are given in Table V and were made by comparison with those established for IF₅O^{14,29} and IF₄O₂⁻ (see above), relying mainly on the observed relative infrared and Raman intensities.

The vibrational spectra observed for IF_5O are in excellent agreement with those previously reported,^{14,29} except for the fact that our spectra do not show a strong infrared band at 640 cm^{-1} . As previously suggested,²⁹ this band is due to IF_5 , the principal decomposition product of IF_5O .

Mass Spectra. The recording of the mass spectrum of FOIF_4O presented difficulties due to reaction of the compound with the inlet system, resulting in the formation of some IF_5O . Further, I_2 has almost the same mass (253.8) as the parent FOIF_4O (253.9), thus making a distinction of the two molecules difficult. These problems were overcome by recording the spectra of pure IF_5O under the same conditions and subtracting the IF_5O pattern from that of the FOIF_4O containing sample. The interference from I_2 was eliminated by recording spectra of 1:1 mixtures of ClF_3 and FOIF_4O . The ClF_3 oxidized I_2 rapidly to iodine fluorides, but did not appear to interact with FOIF_4O . The mass cracking pattern obtained in this manner for FOIF_4O is listed in Table VI and agrees with the expectations⁴⁶ for a hypofluorite. The I-OF single bond is readily broken to yield an intense IF_4O^+ fragment which can undergo additional oxygen and/or fluorine loss.

Synthesis of ClOIF_4O . Since FOIF_4O was found to be stable, the synthesis of the analogous hypochlorite, ClOIF_4O appeared feasible. Using CsIF_4O_2 and ClOSO_2F , a generally useful reagent for the syntheses of hypochlorites,⁴⁷ the synthesis of ClOIF_4O was accomplished according to:



The resulting ClOIF_4O appears to be highly reactive, difficult to handle and thermally unstable. Consequently, the compound could not be well characterized. The main evidence for its existence is the infrared spectrum of the gas which exhibits a spectrum similar to that of FOIF_4O , but with the O-F stretch being replaced by a band at 763 cm^{-1} , characteristic of an O-Cl stretch,⁴⁷ and with the I=O, IF, and I-O stretching modes being shifted to slightly lower frequencies. The compound decomposes to IF_5 , and attempts to add it across the C=C double bond of C_2F_4 did not result in stable adducts.

Conclusion: Although the isolation of NF_4^+ salts of either IO_4^- or IF_4O_2^- was not possible, solutions containing NF_4^+ and HIOF_4O were found to decompose to produce FOIF_4O in high yield. This is in marked contrast to the similar syntheses of FOClO_3 and FOSO_2F where the corresponding $\text{NF}_4^+\text{ClO}_4^{3-}$ and $\text{NF}_4^+\text{SO}_3\text{F}^{4-}$ salts were shown to be the actual intermediates. FOIF_4O is the first known example of an iodine hypofluorite and exists as a cis and a trans isomer. It is a stable compound and was thoroughly characterized. The analogous hypochlorite, ClOIF_4O , was also prepared for the first time, but, as expected, is considerably less stable than FOIF_4O . The reaction of CsIO_4 with HF was found to be a convenient synthesis of CsIF_4O_2 which, by reaction with BiF_5 in HF , can readily be converted into HIOIF_4O , thus providing easy access to tetrafluoroperiodates. The bonding in trans IF_4O_2^- was studied by vibrational spectroscopy, and the results of a normal coordinate analysis are in excellent agreement with the trends previously established³⁷ for chlorineoxyfluorides.

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

REFERENCES

- [1] Lustig, M., Shreeve, J. M. Adv. Fluor. Chem. 1973, 7, 175.
- [2] Appelman, E. H. Acc. Chem. Res. 1973, 6, 113.
- [3] Christe, K. O.; Wilson, W. W.; Wilson, R. D. Inorg. Chem. 1980, 19, 1494.
- [4] Christe, K. O.; Wilson, R. D.; Schack, C. J. Inorg. Chem. 1980, 19, 3046.
- [5] Christe, K. O.; Wilson, R. D. Inorg. Nucl. Chem. Letters 1979, 15, 375.
- [6] Engelbrecht, A.; Peterfy, P.; Schandara, E. Z. Anorg. Allgem. Chem. 1971, 384, 202.
- [7] Engelbrecht, A.; Mayr, O.; Ziller, G.; Schandara, E. Mh. Chem. 1974, 105, 796.
- [8] Carter, H.A.; Ruddick, J. M.; Sams, J. R.; Aubke, F. Inorg. Nucl. Chem. Lett. 1975, 11, 29.
- [9] Selig, H.; Elgad, U. J. inorg. nucl. Chem. Supplement 1976, 91.
- [10] Gillespie, R. J.; Krasznai, J. P. Inorg. Chem. 1977, 16, 1384.
- [11] Engelbrecht, A.; Peterfy, P. Angew. Chem. Internat. Edit. 1969, 8, 768.
- [12] Christe, K. O.; Schack, C. J.; Wilson, R. D. J. Fluorine Chem. 1976, 8, 541.
- [13] Schack, C. J.; Pilipovich, D.; Cohz, S. N.; Sheehan D. F. J. Phys. Chem. 1968, 72, 4697.
- [14] Holloway, J. H.; Selig H.; Claassen, H. H. J. Chem. Phys. 1971, 54, 4305.
- [15] Schack, C. J.; Wilson, R. D. Inorg. Chem. 1970, 9, 311.
- [16] Christe, K. O.; Wilson, W. W.; Schack, C. J. J. Fluorine Chem. 1978, 11, 71.
- [17] Christe, K. O.; Schack, C. J.; Wilson, R. D. Inorg. Chem. 1977, 16, 849.
- [18] Plyler, E. K.; Danti, A.; Blaine, L.R.; Tidwell, E. D. J. Res. Natl. Bur. Stand., Sect. A, 1960, 64, 841.
- [19] International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, Washington, D. C., 1961.

- [20] Claassen, H. H.; Selig, H.; Shamir, J. Appl. Spectrosc., 1969, 23, 8.
- [21] Pure Appl. Chem. 1972, 29, 627.
- [21a] Toetsch, W.; Sladky, F. Paper I 11, 7th European Symposium on Fluorine Chemistry, Venice, Italy. Sept. 1980.
- [22] Christe, K. O. Inorg. Chem. 1972, 11, 1215.
- [23] Christe, K. O.; Sawodny, W. Z. Anorg. Allgem. Chem. 1970, 374, 306.
- [24] Cooper, T. D.; Dost, F. N.; Wang, C. H. J. Inorg. Nucl. Chem. 1972, 34, 3564.
- [25] Christe, K. O.; Naumann, D. inorg. Chem. 1973, 12, 59.
- [26] Christe, K. O.; Wilson, R. D.; Curtis, E. C.; Sawodny, W.; Kuhlmann, W., Inorg. Chem. 1978, 17, 533.
- [27] Begun, G. M.; Fletcher, W. H.; Smith, D. F. J. Chem. Phys. 1965, 42, 2236.
- [28] Selig, H.; Holzman, A. Isr. J. Chem. 1969, 7, 417.
- [29] Smith, D. F.; Begun, G. M. J. Chem. Phys. 1965, 43, 2001.
- [30] Beattie, I. R.; Webster, M.; Chantry, G. W. J. Chem. Soc. A. 1964, 6172.
- [31] Pierce, S. B.; Cornwell, C. D. J. Chem. Phys. 1967, 47, 1731.
- [32] Robiette, A. G.; Bradley, R. H.; Brier, P. N. Chem. Commun. 1971, 1567.
- [33] Ryan, R. R.; Asprey, L. B. Acta Crystallogr., Sect. B 1972, 28, 979.
- [34] Sawodny, W. J. Mol. Spectrosc. 1969, 30, 56.
- [35] Christe, K. O.; Curtis, E. C.; Wilson, R. D. J. inorg. nucl. Chem., Supplem. 1976, 437.
- [36] Christe, K. O.; Sawodny, W. Inorg. Chem. 1967, 6, 1783.
- [37] Christe, K. O.; Schnack, C. J. Adv. Inorg. Chem. Radiochem. 1976, 18, 331.
- [38] Christe, K. O.; Guertin, J. P.; Pavlath, A. E.; Sawodny, W. Inorg. Chem. 1967, 6, 533.
- [39] Rose, W. B.; Nebgen, J. W.; Metz, F. I. Rev. Sci. Instr. 1966, 37, 238.
- [40] Shamir, J.; Hyman, H. H. Spectrochim. Acta, Part A, 1967, 23, 1891.
- [41] Adams, C. J. Inorg. Nucl. Chem. Lett. 1974, 10, 831.
- [42] Dayan, V. H.; Neale, C. B. Adv. Chem. 1966, 54, 223.

- [43] Christe, K. O. unpublished results.
- [44] Harris, R. K.; Packer, K. J. J. Chem. Soc. 1962, 3077.
- [45] Smith, J. E.; Cady, G. H. Inorg. Chem. 1970, 9, 1293.
- [46] Huston, J. L.; Studier, M. H. J. Fluor. Chem. 1979, 13,235.
- [47] Schack, C. J.; Christe, K. O. Isr. J. Chem. 1978, 17, 20.

Table 1. Vibrational Spectra of trans IF_4O_2 and their Assignment in Point Group D_{2h}
Compared to those of Closely Related Molecules

obsd freq. cm^{-1} and rel. intens.										Assignments for IF_4O_2 in D_{2h}										Approximate Description of mode																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																								
$\text{trans-ClIF}_4\text{O}_2$					$\text{IF}_4\text{O}^{\text{c}}$					IF_4^{d}					IF_5^{e}																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
solid					solid					solid					gas																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
IR					IR					IR					IR																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
Raman					Raman					Raman					Raman																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
569(5.5)	824(10)	885 s	349 s	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)						555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	555(2)	5

Table II. Vibrational Spectra of cis IF_4O_2

Obsd freq, cm^{-1} , and rel intens ^a		Assignment for point group C_{2v}	Approx. description of mode
IR	Raman		
875 vs	875	$\nu_{12} (\text{B}_2)$	$\nu_{\text{asym}} \text{IO}_2$
855 vs	856(10)	$\nu_1 (\text{A}_1)$	$\nu_{\text{sym}} \text{IO}_2$
600 vs, br		$\nu_9 (\text{B}_1)$	$\nu_{\text{asym}} \text{IF}_2 \text{ax}, \nu_{\text{as}} \text{IF}_2 \text{eq}$
600 vs, br	605(9.8)	$\nu_2 (\text{A}_1)$	$\nu_{\text{sym}} \text{IF}_2 \text{eq}$
550 mw	552 sh	$\nu_3 (\text{A}_1)$	$\nu_{\text{sym}} \text{IF}_2 \text{ax}$
395 sh	394 (3.4)	$\nu_4 (\text{A}_1)$	$\delta \text{sciss IO}_2$
364 s	365 sh		
328 mw	332(6.5)		
	235 (0.2)		
	210 (0.5)		

(a) Uncorrected Raman intensities (peak height).

Table III. Symmetry Force Constants^a of trans IF₄O₂

A _{1g}	ν ₁	569	$F_{11} = f_r + 2f_{rr} + f_{rr}^{\prime}$	3.623
	ν ₂	824	$F_{22} = f_{\alpha} + f_{\alpha\alpha}$	6.400
A _{2u}	ν ₃	885	$F_{33} = f_d - f_{dd}$	5.903
	ν ₄	349	$F_{44} = f_{\beta} + 2f_{\beta\beta} + f_{\beta\beta}^{\prime} - f_{\beta\beta}^{\prime\prime} - 2f_{\beta\beta}^{\circ} - f_{\beta\beta}^{\dagger}$	1.700
			$F_{34} = 2f_{d\beta} - 2f_{d\beta}^{\prime}$	-0.036
B _{1g}	ν ₅	555	$F_{55} = f_r - 2f_{rr} + f_{rr}^{\prime}$	3.447
B _{2g}	ν ₆	255	$F_{66} = f_{\gamma} - 2f_{\gamma\gamma} + f_{\gamma\gamma}^{\prime}$	0.671
B _{2u}	ν ₇	--	$F_{77} = f_{\beta} - 2f_{\beta\beta} + f_{\beta\beta}^{\prime} - f_{\beta\beta}^{\prime\prime} + 2f_{\beta\beta}^{\circ} - f_{\beta\beta}^{\dagger}$	--
E _g	ν ₈	380	$F_{88} = f_{\beta} - f_{\beta\beta}^{\prime} - f_{\beta\beta}^{\prime\prime} + f_{\beta\beta}^{\dagger}$	1.201
E _u	ν ₉	590	$F_{99} = f_r - f_{rr}^{\prime}$	2.998

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

Table IV. Stretching Force Constants (mdyn/Å) of trans IF_4O_2^- Compared to Those of Similar Molecules and Ions

(oxidation state)	$\text{IF}_4^- (+III)^a$	$\text{IF}_4\text{O}^- (+V)^b$	$\text{IF}_4\text{O}_2^- (+VII)$	$\text{IF}_5 (+V)^c$	$\text{IF}_5\text{O} (+VII)^d$	$\text{IF}_6^+ (+VII)^e$
$f_r (\text{IF})$	2.22	2.46	3.27	3.77	4.42	5.42
f_{rr}	0.18	0.16	0.04	0.04	0.00	-0.07
$f_{rr'}$	0.47	0.45	0.27	0.38	0.18	0.19
$f_d (IO)$	--	6.56	6.15	--	6.99	--
f_{dd}	--	--	0.25	--	--	--
	Anions			Molecules		Cation

(a) Data from ref 25.

(b) Data from ref 26.

(c) Data from ref 35.

(d) Data from ref 29.

(e) Data from ref 36.

Table V. Vibrational Spectra of FOIF₂O^a

obsd freq, cm ⁻¹ , and rel intens ^b				tentative assignments to cis and trans isomer
IR		Raman		
gas	Ne Matrix	liquid -20°C	solid -80°C	
1375vw				2x688
1315 w				2x655
	930.5 m	926 (2.9)p	924 (1.7)	ν ₁ =0 trans
916 s	920.2 ms	916 (4)p	914 (3.6)	ν ₁ =0 cis
	914 mw	890 (0.6)p	891 (0.4)	ν ₀ F trans
900 sh	901.2 m			ν ₀ F cis
701 sh	703.9 m			
	698.6 s			
693 vs	695.2 vs	695 sh	690 sh	vas IF ₄ trans
	692.3 m			vas IF ₂ ax cis
688 vs	688.6 vs	680 (3.9)p	679 (3.3)	ν ₁ -0 trans
	686 sh			
	657.9 m			
653 s	656.3 ms	654 (4.5)p	652 (2.9)	ν ₁ -0 cis
		631 (6)p	630 (5)	ν _{sym} IF ₂ ax cis
		624 (9.2)p	622 (6.8)	ν _{sym} IF ₄ trans
584 ms	590.9 ms	585 (10)p	586 (10)	ν _{sym} IF ₂ eq cis
	583.0 mw	575 sh	577 (4)	and
	574.3 w			
	410.1 mw			
			570 sh	vas IF ₂ eq cis
	363.7 ms			
	359.4 m	360 sh	358 (1)	
	353.5 sh			
	351.5 ms			
	341.2 m	340 sh		
335 s	336.5 vs			
	334.2 sh	334 (5.4)p	333 (4)	
	315.7 mw			
	308.5 m	311 (0.4)p	311 (0.4)	
	295.5 mw			
		291 (0.7)	291 (1)	
		264 (1)p	263 (0.8)	
		205 (0.1)	203 (0+)	
		182 (0.9)p	183 (0.6)	

(a) Mixture of cis and trans isomer.
based on trace E of Figure 5.

(b) Uncorrected Raman intensities

RI/RD81-140

G-30

Table VI. Mass Spectrum^a of a Mixture of cis and trans FOIF₄O

m/e	rel intens	ion
219	72	IF ₄ O ⁺
203	100	IF ₄ ⁺
200	32	IF ₃ O ⁺
184	18	IF ₃ ⁺
181	73	IF ₂ O ⁺
178	1	IO ₂ F ⁺
165	18	IF ₂ ⁺
162	38	IOF ⁺
146	15	IF ⁺
143	7	IO ⁺
127	38	I ⁺

(a)

Recorded with an ionization potential of 70 eV, using a 1:1 mixture of FOIF₄O and ClF₃. Peaks due to ClF₃ and IF₅O have been subtracted from the pattern.

Diagram Captions

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

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

Figure 3. Raman spectra of liquid HOIF_4O , recorded in Teflon FEP tubes at room temperature.

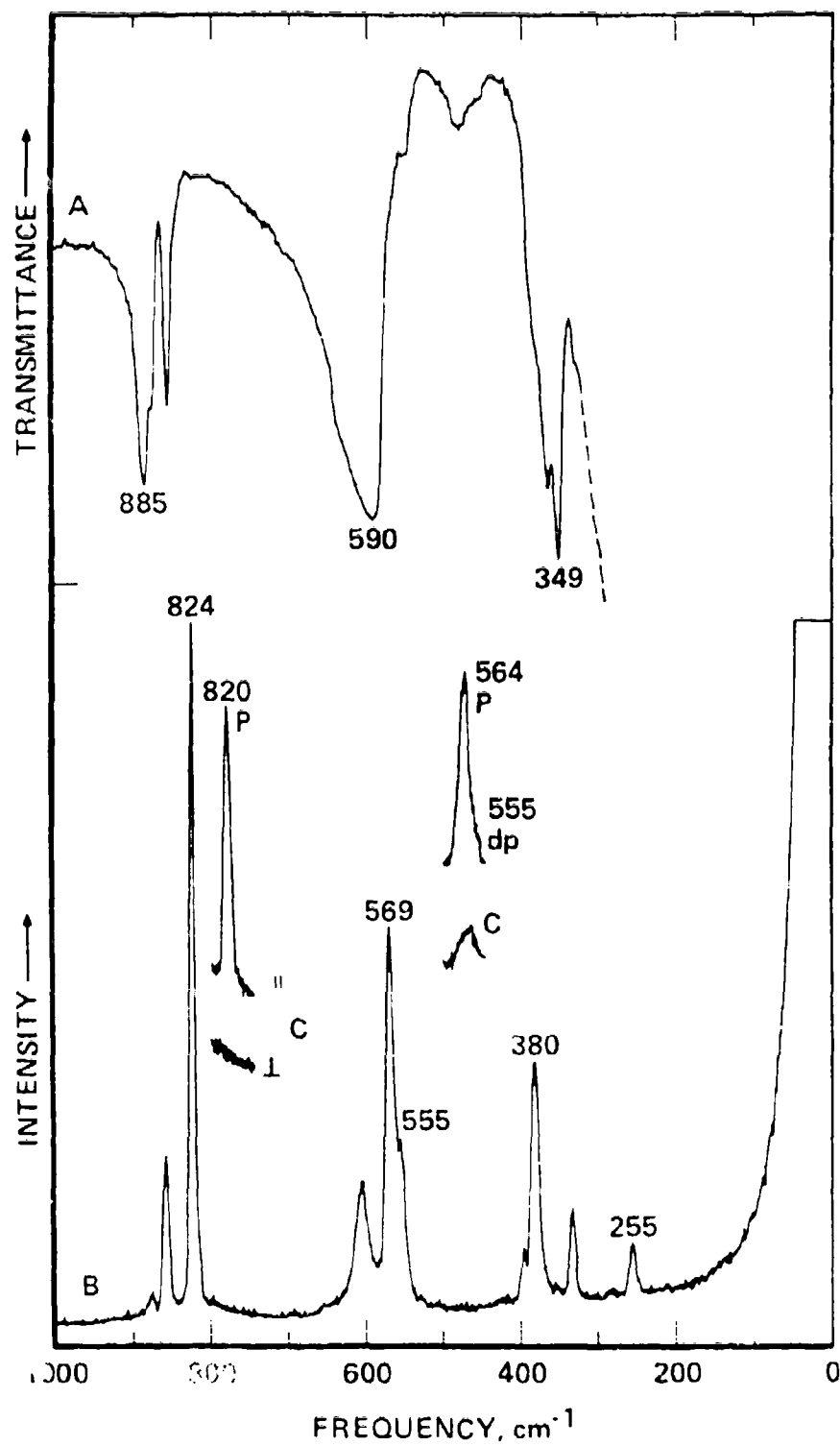
Figure 4. ^{19}F NMR spectra of cis and trans FOIF_4O recorded at different temperatures. The signals due to the O-F fluorines are given at a ten times wider scale than those due to fluorines on iodine. Positive shifts are downfield from the external CFCl_3 standard.

Figure 5. Vibrational spectra of a mixture of cis and trans FOIF_4O in a ratio of about 1.9:1. Traces A and B, infrared spectra of the gas recorded at pressures of 10 and 95 mm, respectively, in a 5 cm path length cell equipped with AgCl windows. Most of the absorption below 400 cm^{-1} is due to the window material. Trace C, infrared spectrum of FOIF_4O isolated in a Neon matrix (MR 1000:1) and recorded at 6°K. Traces D, E and F, Raman spectra of liquid FOIF_4O recorded in 4 mm o.d. quartz tubes at -20°C for 2 samples containing somewhat different ratios of cis (c): trans (t) isomer with the incident polarization parallel and perpendicular.

Figure 6. Infrared spectra of IF_5O and FOIF_4O in Ne matrix (MR 1000:1) at 6°K recorded at 20 fold scale expansion. The bands due to IF_5O in the FOIF_4O spectrum are marked by an asterisk.

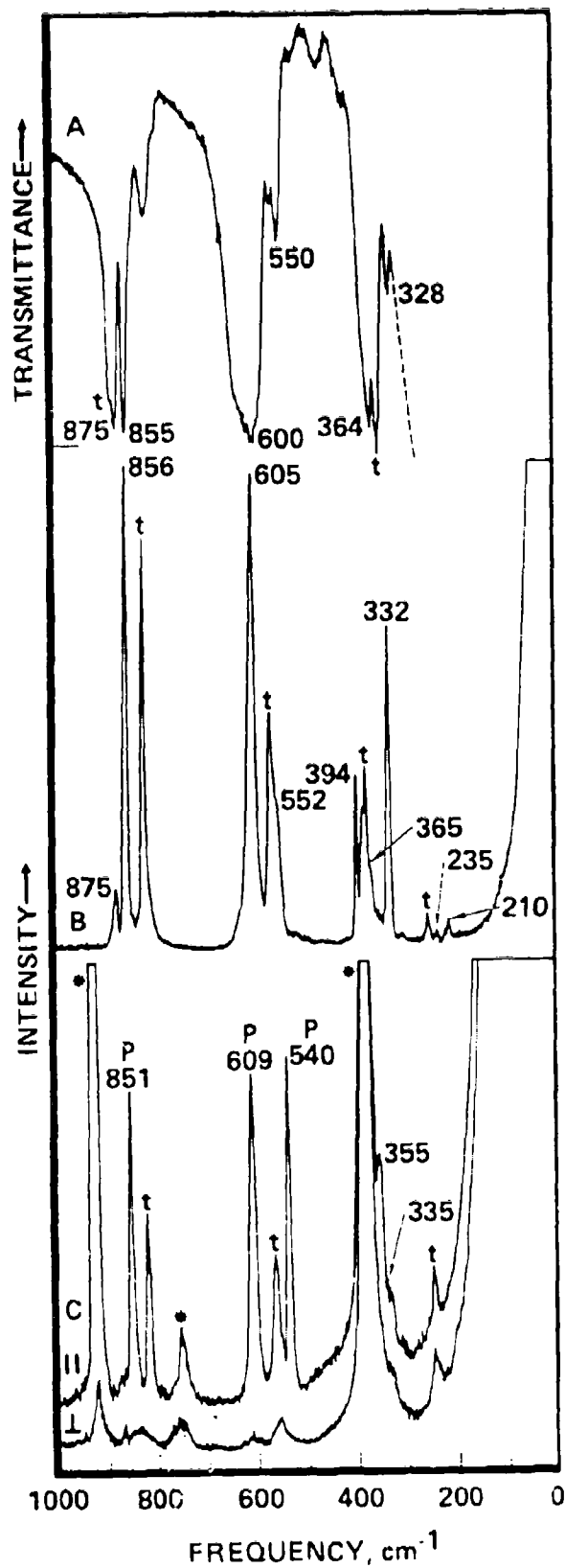
Figure 7. Infrared spectra of IF_5O and FOIF_4O in Ne matrix (MR 1000:1).

Figure 8. Vibrational spectra of IF_5O . Trace A, Infrared spectra of the gas, trace B, infrared spectrum in Ne matrix, trace C, Raman spectrum of the liquid, all recorded under conditions identical to those of Figure 5.



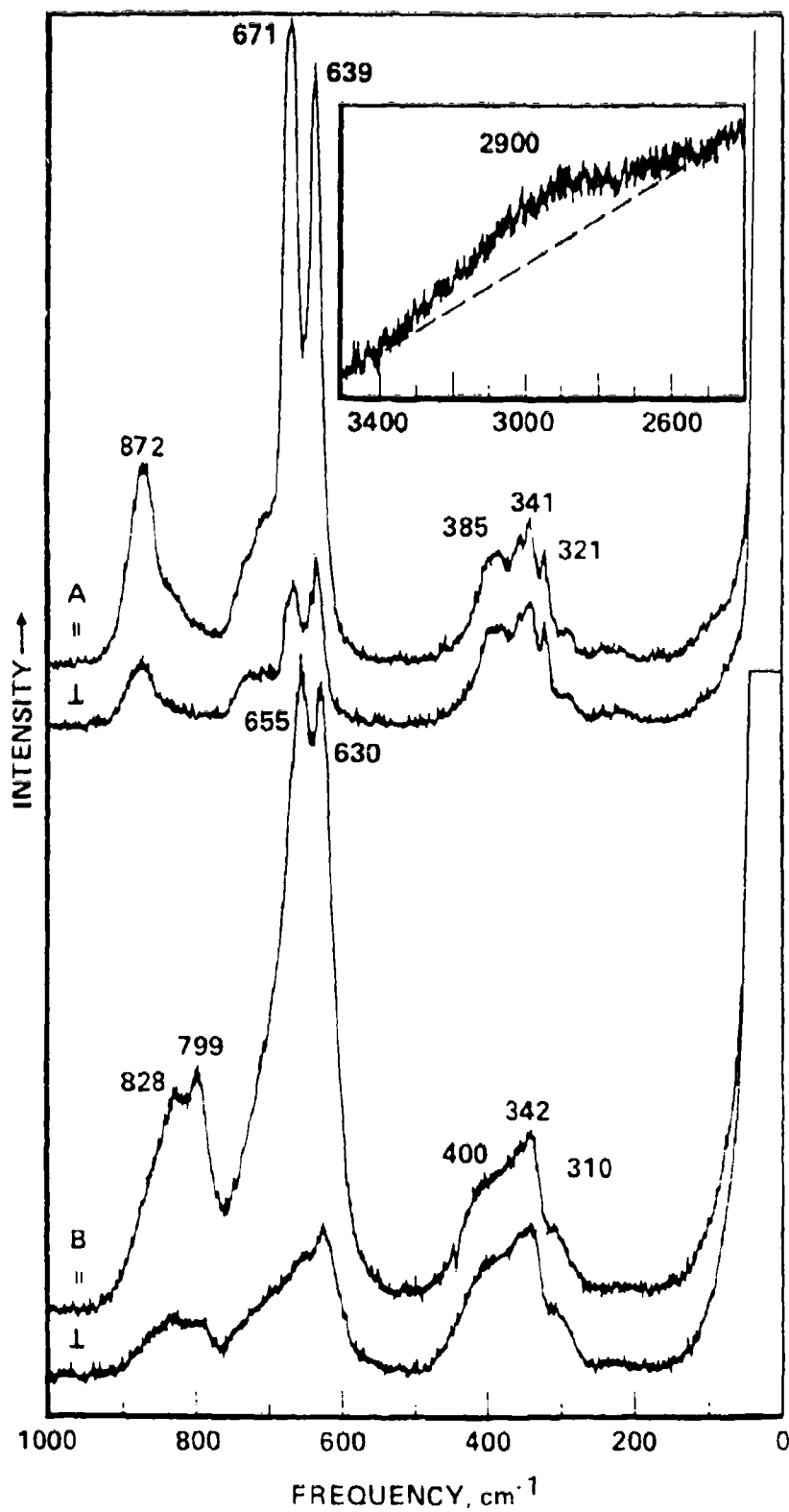
RI/RD81-140

G-34



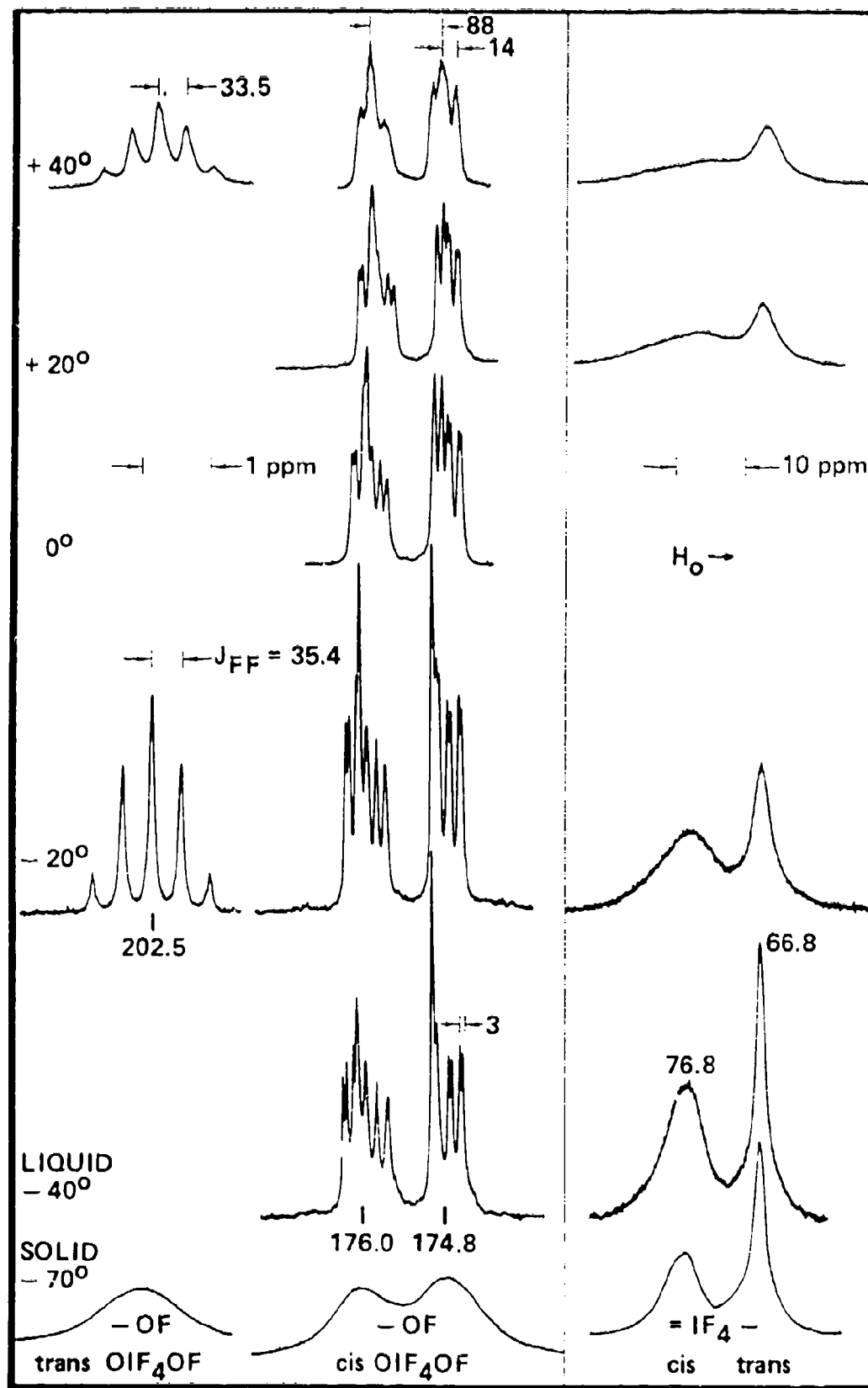
RI/KD81-140

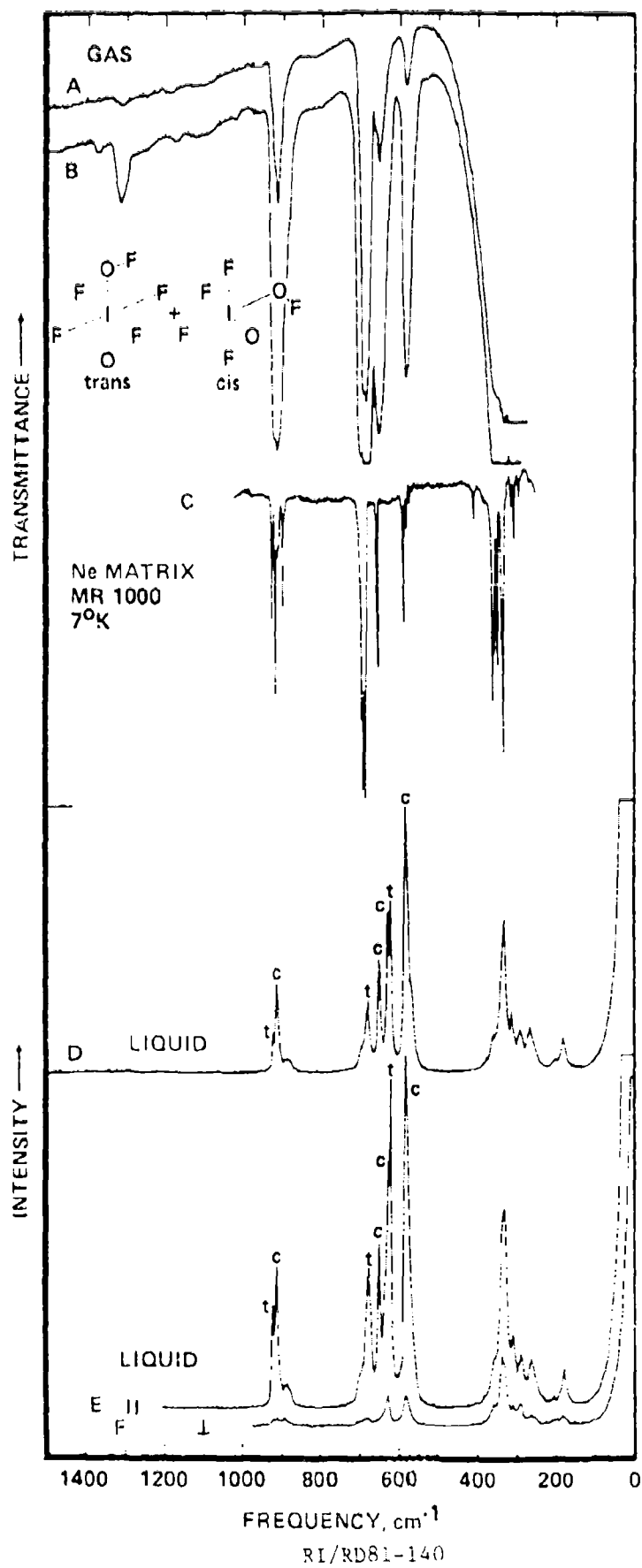
G-35

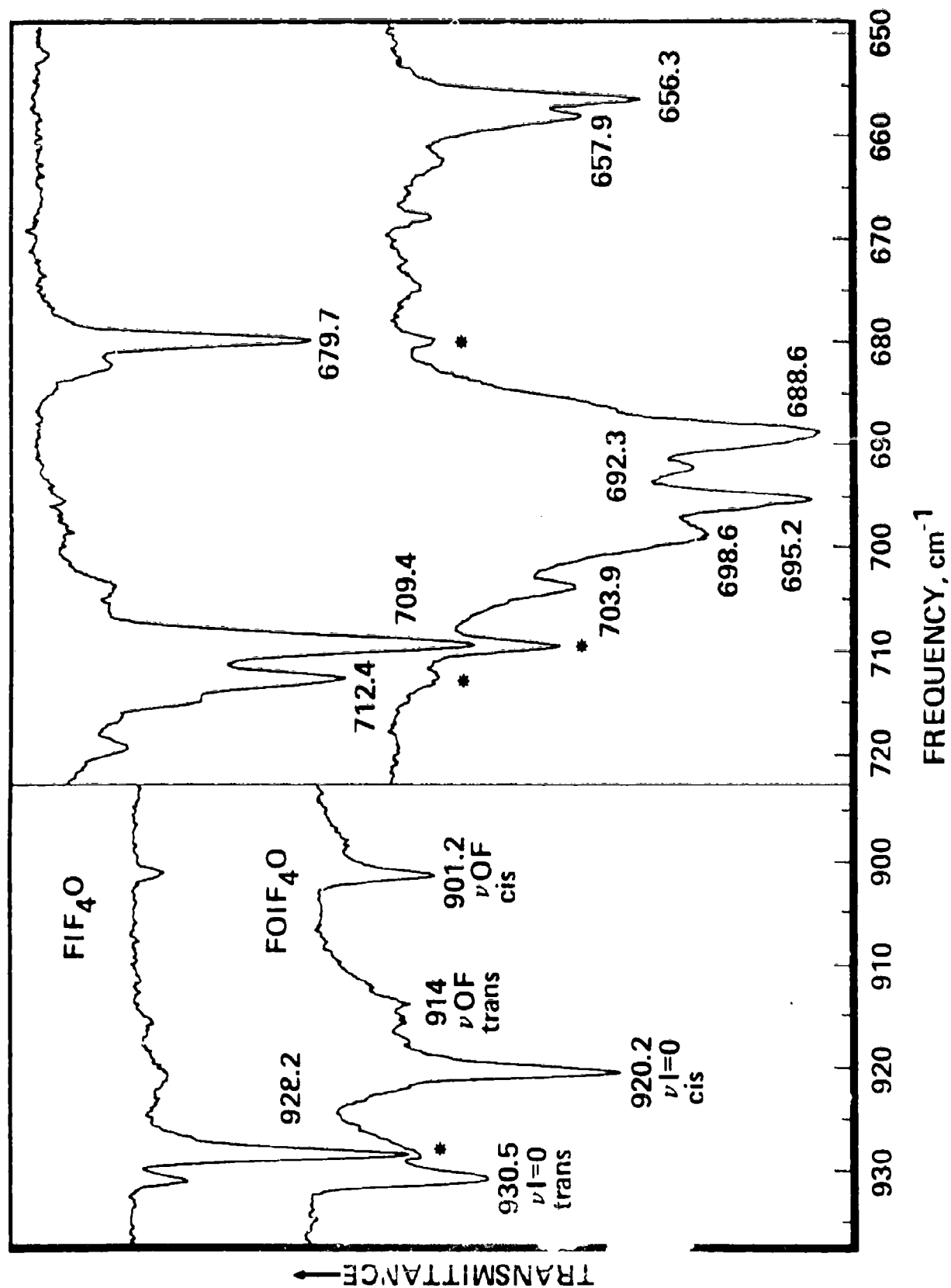


RI/RD81-140

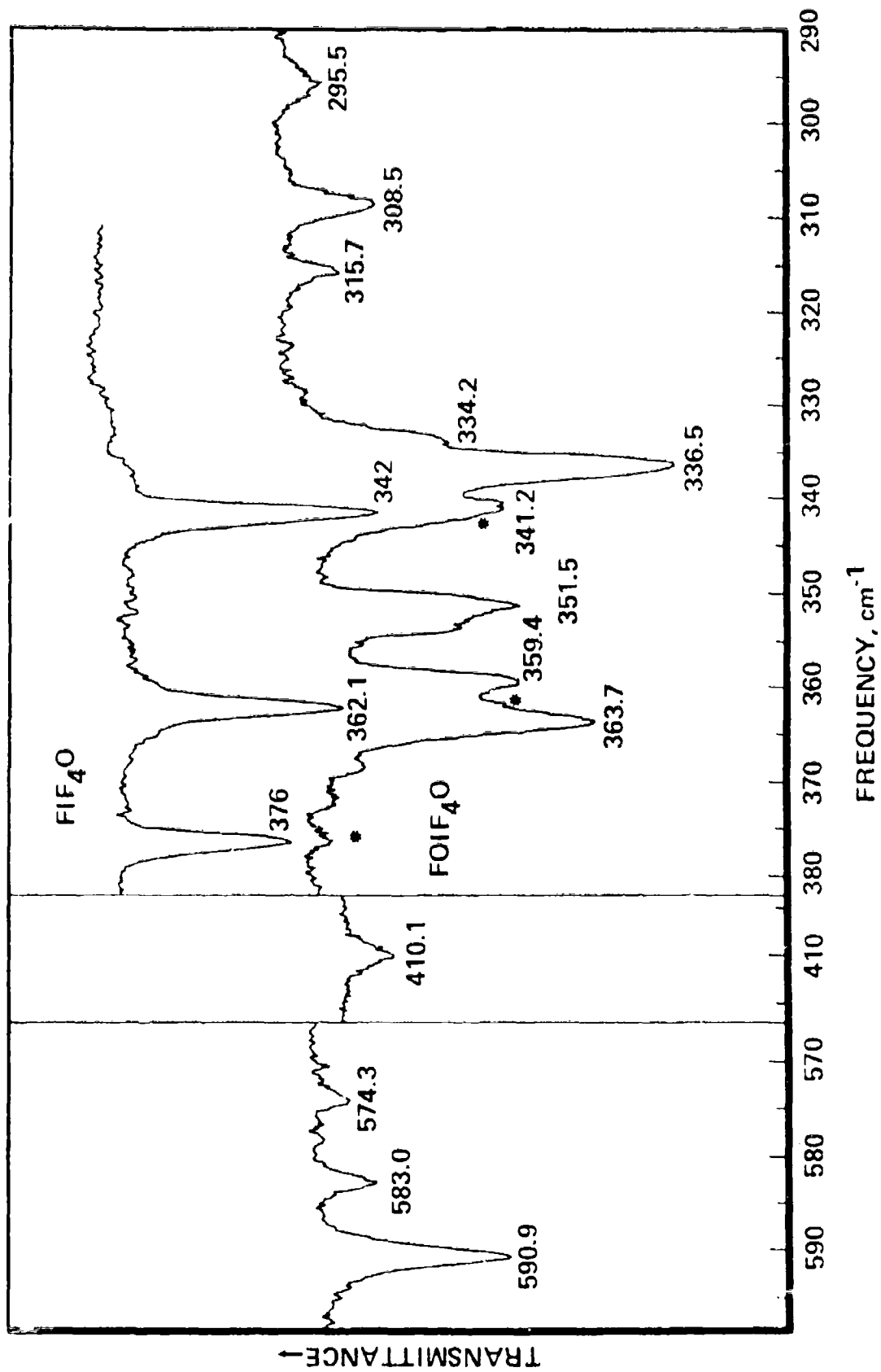
G-36





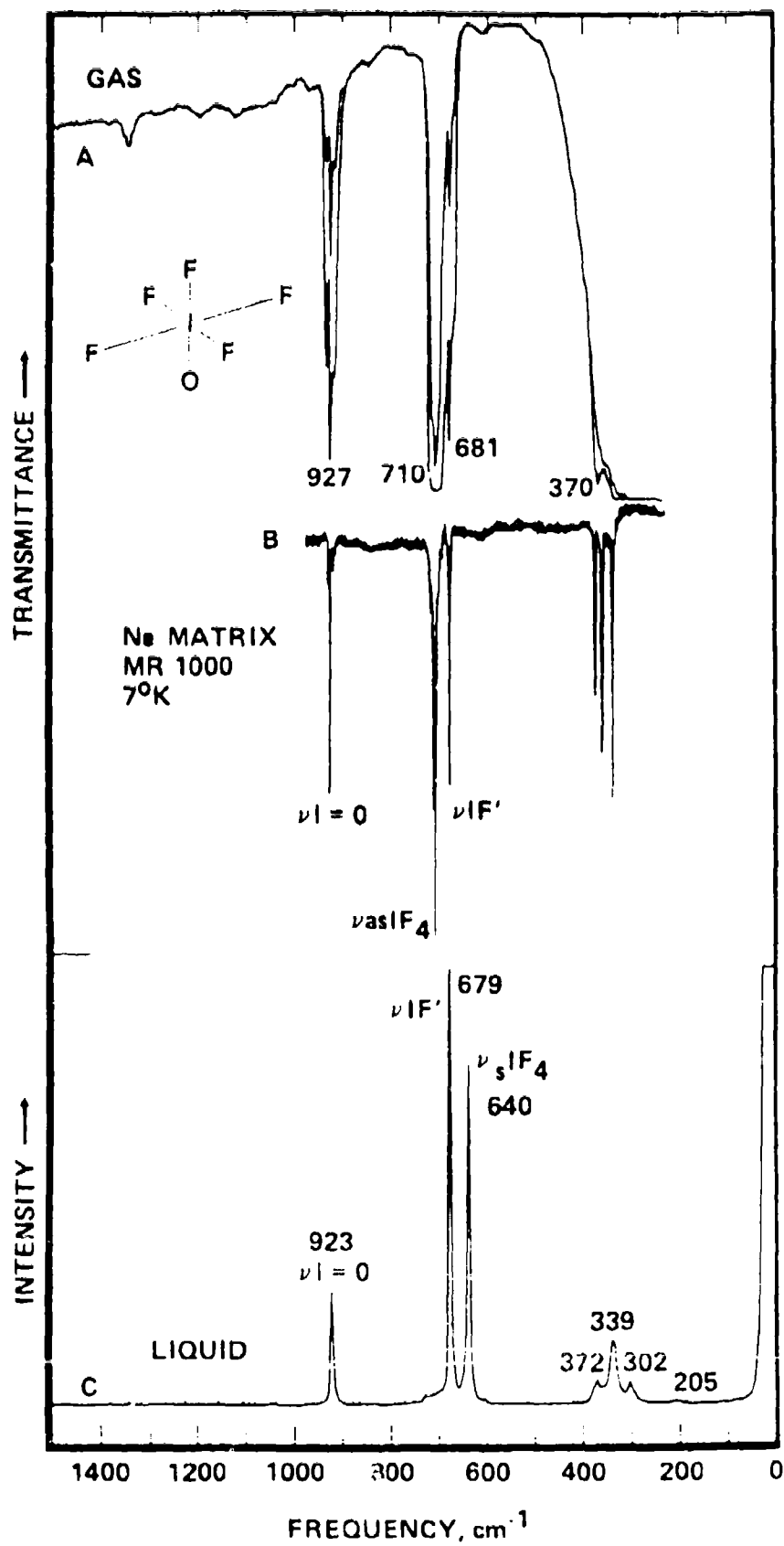


RI/RD81-140



RI/RD81-140

G-40



RI/RD81-140

G-41/G-42

APPENDIX H

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

GAS PHASE STRUCTURE OF CHLORINE TRIFLUORIDE OXIDE, ClF_3O

Heinz Oberhammer and Karl O. Christe

Received . . .

Abstract

The molecular structure of ClF_3O has been studied by gas electron diffraction. A distorted trigonal bipyramid with the following geometric parameters (r_α values) was obtained: $\text{Cl} = \text{O}$ 1.405 (3) Å, $\text{Cl}-\text{F}_e = 1.603$ (4) Å, $\text{Cl}-\text{F}_a = 1.713$ (3) Å, $\angle \text{F}_e \text{ClO} = 108.9^\circ$ (0.9), $\angle \text{F}_a \text{ClF}_e = 87.9^\circ$ (1.2) and $\angle \text{F}_a \text{ClO} = 94.7^\circ$ (2.0). Steric repulsion effects in equatorial and axial directions for the double bond and the lone electron pair of chlorine are discussed. The position of the lone pair was derived from ab initio calculations.

Introduction

Chlorine trifluoride oxide was independently discovered in 1965 at Rocketdyne¹ and 1970 at Saclay². No structural data have been published for this interesting compound, except for its vibrational^{2,3} and ^{19}F ^{1,4} and ^{17}O ⁵ NMR spectra which were in agreement with a pseudotrigonal bipyramidal structure of symmetry C_s . In this structure, two fluorines occupy the axial and one fluorine, one oxygen and one sterically active free valence electron pair occupy the equatorial positions. It was recently proposed⁶ that free valence electron pairs and π bonds can result in directional repulsion effects for trigonal bipyramidal molecules. Since ClF_3O possesses both a free valence electron pair and a π bond, a knowledge of its exact molecular structure was of great interest. In this paper, the results of a structure determination of ClF_3O by gas phase electron diffraction are given in support of the previously proposed⁶ directional repulsion effects.

Experimental

The sample of ClF_3O used for this study was prepared by low-temperature fluorination of ClONO_2 using a previously described method.¹ The sample was purified by fractional condensation, followed by complexing with KF and controlled vacuum pyrolysis of the resulting KClF_4O adduct.⁷ The product showed no impurities detectable by vibrational and NMR spectroscopy¹⁻⁴ and was handled exclusively in well passivated (with ClF_3) Teflon-stainless steel equipment.

The electron diffraction intensities were recorded with a Balzer Diffractograph KD-G2⁸ at two camera distances (50 and 25 cm) and an accelerating voltage of about 60 kV. The nozzle temperature was 10°C and the sample was kept at -35°C . The camera pressure never exceeded 1.10^{-5} Torr during the experiment. (Throughout this paper $1 \text{ \AA} = 100 \text{ pm}$, $1 \text{ Torr} = 101.325/760 \text{ kPa}$). The electron wavelength was determined from ZnO diffraction patterns. An s - range ($s = (4\pi/\lambda) \sin \theta/2$, λ ..electron wavelength, θ ..scattering angle) of $1.4 - 17 \text{ \AA}^{-1}$ and $8 - 35 \text{ \AA}^{-1}$, for the two camera distances, was covered in the experiment. For each camera distance two plates were selected and the intensity data were evaluated in the usual way⁹. The averaged molecular intensities were measured in steps of $\Delta s = 0.2 \text{ \AA}^{-1}$.

Results and Discussion

Structure Analysis. The observed molecular intensities are given in Figure 1. A preliminary geometric model was derived from the radial distribution function (Figure 2) and then refined by a least squares analysis based on the molecular intensities. A diagonal weight matrix was used⁹ and theoretical intensities were calculated with the scattering amplitudes and phases of J. Haase¹⁰. The only geometric constraint was an assumed C_s symmetry. The ratios between the vibrational amplitudes of the bonded distances and of some non-bonded distances were constrained to the spectroscopic values (see Table 1). Parallel vibrational amplitudes and harmonic vibrational corrections $\Delta r = r_a - r_\alpha$ (Table 1) were calculated from the force field of Reference 3 with the program NORCOR¹¹. Two correlation coefficients had values larger than 0.5: $[\langle F_a \text{ClF}_e \rangle / \langle F_a \text{ClO} \rangle] = 0.88$ and $[1(\text{bonded}) / 1(F_a \dots F_a)] = 0.61$. The results

of the least squares analysis are summarized in Table 1. Estimated uncertainties are 3σ values and a possible scale error of 0.1% is included for bonded distances.

Ab initio Calculations: The molecular wave function at the experimental geometry was calculated with the program TEXAS¹². For second row atoms, 4-21 basis sets¹³ and for chlorine a 3-3-21 basis set¹⁴, supplemented by d functions¹², was used. The position of the chlorine lone electron pair (Figure 3) was obtained by transformation to localized orbitals, using Boys' criterion¹⁵. Atomic net charges and overlap populations (Table 2) were derived by a Mulliken population analysis¹⁶.

Molecular Structure of ClF₃O: Chlorine trifluoride oxide is a distorted trigonal bipyramidal molecule with three different ligands in the equatorial plane: a single bond, a double bond and a lone valence electron pair. The angles (Figure 3) between the axial bonds and the double bond are larger (by about 7°) than the angles between the axial bonds and the single bond or the lone electron pair, i.e. the axial fluorine atoms are bent away from the double bond into the sector between the single bond and the lone electron pair. This demonstrates that in the axial direction the steric repulsion of the double bond is larger than the repulsion from either the lone pair or the single bond. The angles in the equatorial plane, however, indicate that in the equatorial direction the repulsion by the lone pair is largest, followed by the double bond, with the single bond being smallest. This directional repulsion effect of double bonds which has been pointed out previously⁶, correlates well with the different population of the π bond orbitals in the axial and the equatorial plane¹⁷. For ClF₃O, these populations (Table 2) are almost equal.

The observed bond distances (Cl = O 1.405 Å, Cl-F_e 1.603 Å, Cl-F_{ax} 1.713 Å) agree well with previous estimates (Cl = O 1.42 Å, Cl-F_e 1.62 Å, Cl-F_{ax} 1.72 Å)³ derived from the observed vibrational spectra and a comparison with related molecules. They confirm the conclusions, previously reached from the results of a normal coordinate analysis,³ that the chlorine-oxygen bond has double bond character and that the axial Cl-F bond is significantly weaker than the equatorial one. These results support a previously outlined bonding scheme assuming mainly sp² hybridization for the bonding of the three equatorial ligands (ClF, ClO σ bond, and free valence electron pair) and the use of a chlorine p orbital for

the bonding of the two axial fluorines by means of a semi-ionic three center-4 electron bond pair.^{3,7,18}

A comparison of the bond lengths in ClF_3O with those in closely related molecules (see Table 3) also correlates well with the conclusions previously derived from force field computations.^{3,7,18} These computations had shown that, if the bonds are separated according to the two possible types (i.e. mainly covalent and mainly semi-ionic 3c-4e), the bond strength within each type increases with increasing formal oxidation state of the central atom and decreases with increasing oxygen substitution. The first effect is due to an increase in the effective electronegativity of the central atom with increasing oxidation state. This increase causes the electronegativities of the central atom and the ligands to become more similar and therefore the bonds to become more covalent. The second effect is caused by oxygen being less electronegative than fluorine thereby releasing electron density to the molecule and increasing the ionicity of the Cl-F bonds.^{7,18} Although the previous force field computations clearly reflected these trends, the uncertainties in force constants, obtained from an underdetermined force field, were rather large and certainly are not as precise as the more reliable bond length measurements from this study.

Acknowledgement. H. O. would like to express his appreciation to NATO for a research grant, and K.O.C. to the Office of Naval Research and the Army Research Office for financial support.

Reference

- [1] Pilipovich, D.; Lindahl, C. B.; Schack, C. J.; Wilson, R. D.; Christe, K. O. *Inorg. Chem.*, 1972, 11, 2189.
- [2] Bougon, R.; Isabey, J.; Plurien, P. C. R. Acad. Sci., Ser. C, 1970, 271, 1366.
- [3] Christe, K. O.; Curtis, E. C. *Inorg. Chem.*, 1972, 11, 2196.
- [4] Alexandre, M.; Rigny, P. *Can. J. Chem.*, 1974, 52, 3676.
- [5] Virlet, J.; Tantot, G. *Chem. Phys. Lett.*, 1976, 44, 296.
- [6] Christe, K. O.; Oberhammer, H. *Inorg. Chem.*, 1981, 20, 296.
- [7] Christe, K. O.; Schack, C. J., *Adv. Inorg. Chem. Radiochem.*, 1976, 18, 319.
- [8] Oberhammer, H. in Sim, G. A., and Sutton, L. E. (eds.), *Molecular Structures by Diffraction Methods*, The Chemical Society, London, 1976, 4, 24.
- [9] Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.*, 1981, 70, 273.
- [10] Haase, J. A. *Naturforsch.*, 1970, 25A, 936.
- [11] Christen, D. *J. Mol. Struct.*, 1978, 48, 101.
- [12] Pulay, P. *Theor. Chim. Acta*, 1979, 50, 299.
- [13] Pulay, P.; Fogarasi, G.; Pang, F.; Bogg, J. E. *J. Am. Chem. Soc.*, 1979, 101, 2550.
- [14] Oberhammer, H.; Bogg, J. E. *J. Mol. Struct.*, 1979, 55, 283.
- [15] Boys, S. F. *Quantum Theory of Atoms, Molecules and Solid State*, Löwdin, P. O. Ed., Academic Press, New York, 1966.
- [16] Mulliken, R. S. *J. Chem. Phys.*, 1955, 23, 1833.
- [17] Oberhammer, H.; Bogg, J. E. *J. Mol. Struct.*, 1979, 56, 107.
- [18] Christe, K. O. XXIVth Int. Congr. Pure Appl. Chem., 1974, IV, 115.
- [19] Gilbert, D. A.; Roberts, A.; Griswold, P. A., *Phys. Rev.* 1949, 76, 1726 L.
- [20] Smith, D. F., *J. Chem. Phys.* 1953, 21, 609.
- [21] Altman, A. B.; Miakshin, I. N.; Sukhoverklov, V. F.; Romanov, G. V.; Spiridonov, V. P. *Dokl. Akad. Nauk SSR.* 1978, 241, 360.
- [22] Parent, C. R.; Gerry, M. C. L. *J. Mol. Spectr.* 1974, 49, 343.

- [23] Clark, A. H.; Beagley, B. Cruickshank, D. W. J. J. Chem. Soc. (A) 1970, 872.
- [24] Clark, A. H.; Beagley, B. J. Chem. Soc. (A) 1970, 46.

Table 1: Results of electron diffraction experiment and spectroscopic calculations.

a) geometric parameters (r_a values) in Å and degrees. See text for estimated uncertainties.

Cl=O	1.405 (3)	$\angle F_a Cl F_e$	87.9 (1.2)
Cl-F _e	1.603 (4)	$\angle F_a Cl O$	94.7 (2.0)
Cl-F _a	1.713 (3)	$\angle F_a Cl F_a^a$	170.5 (4.1)
$\angle F_e Cl O$	108.9 (0.9)		

b) vibrational amplitudes from electron diffraction and spectroscopic data and harmonic vibrational corrections in Å.

	vibrational amplitudes		$r_a - r_\alpha$
	e.d.	spectr.	
Cl=O	0.032 (7) ^b	0.036	0.0010
Cl-F _e	0.041 (7) ^b	0.047	0.0001
Cl-F _a	0.048 (7) ^b	0.053	0.0010
F _e ..O	0.066 (6) ^c	0.065	-0.0008
F _a ..O	0.073 (6) ^c	0.072	0.0000
F _a ..F _e	0.079 (6) ^c	0.078	-0.0007
F _a ..F _a	0.061 (10)	0.067	-0.0010

c) Agreement factors for both camera distances.

$$R_{50} = 5.2 \%$$

$$R_{25} = 7.0 \%$$

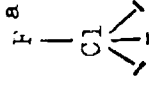
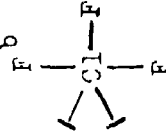
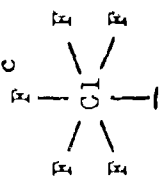
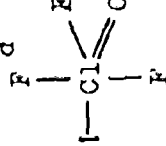
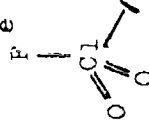
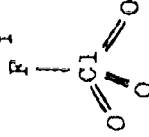
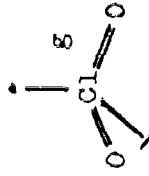
^a dependent parameter. ^{b,c} ratio constrained to spectroscopic value.

Table 2: Atomic net charges (a.u.), dipole moment (D) and overlap populations (a.u.) for ClF_3O .

net charge		overlap population	
Cl	+ 1.76	Cl-F _e	0.092
F _e	- 0.31	Cl-F _a	0.070
F _a	- 0.46	Cl=O π_{eq}	0.103
O	- 0.53	π_{ax}	0.091
μ^a	1.74		

^a see Fig. 3 for direction of dipole moment.

Table 3: Geometric parameters of some chlorine-fluorine-oxygen compounds.

RI/RD81-140							
Cl-F	1.628	1.598 (5)	1.571 (14)	1.603 (4)	1.697 (3)	1.619 (4)	---
Cl-F _a	---	1.698 (5)	1.669 (15)	1.713 (3)	---	---	---
Cl=O	---	---	---	1.405 (3)	1.418 (2)	1.404 (2)	1.475 (3)
$\angle F_e Cl F_a$	---	87.5 (5)	86.0 (15)	87.9 (12)	---	---	---
$\angle F_a Cl F_a$	---	175.0 (7)	---	170.5 (4) ^h 108.9 (9) ^h 94.7 (20) ⁱ	---	---	---
$\angle O Cl F$	---	---	---	---	101.7 (1)	100.8 (8)	---
$\angle O Cl O$	---	---	---	---	115.2 (1)	116.6 (5)	117.7 (17)

^a r_e values from Ref. 19. ^b r_o values from Ref. 20. ^c r_a values from Ref. 21.

^d r_a values from this work. ^e r_o values from Ref. 22. ^f r_a values from Ref. 23.

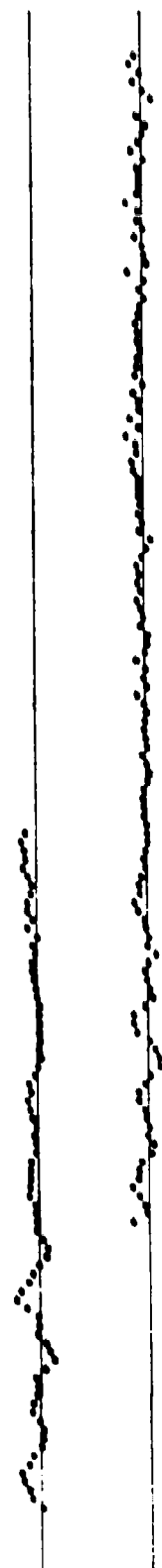
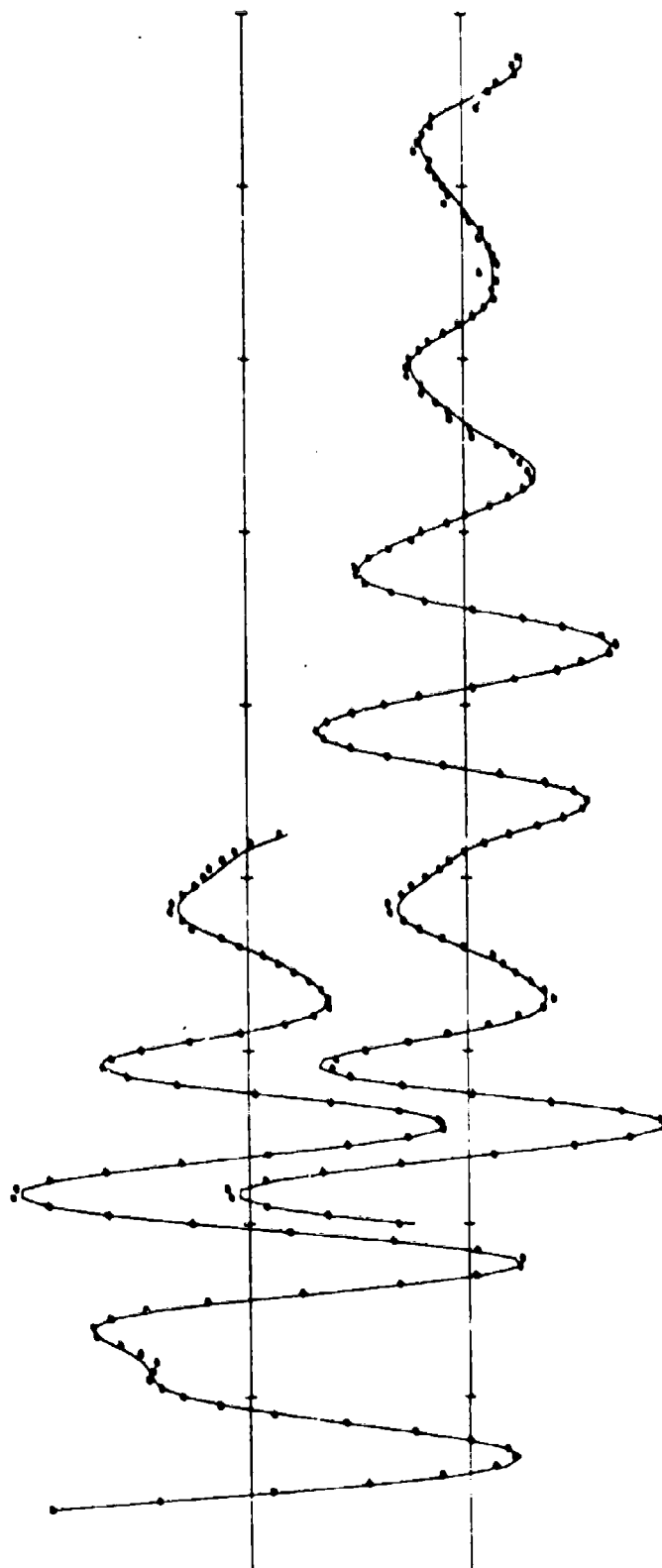
^g r_a values from Ref. 24. ^h $\angle O=Cl-F_e$. ⁱ $\angle O=Cl-F_a$.

Diagram Captions

Fig. 1: Experimental (ooo) and calculated (—) molecular intensities and differences.

Fig. 2: Experimental radial distribution function and difference curve.

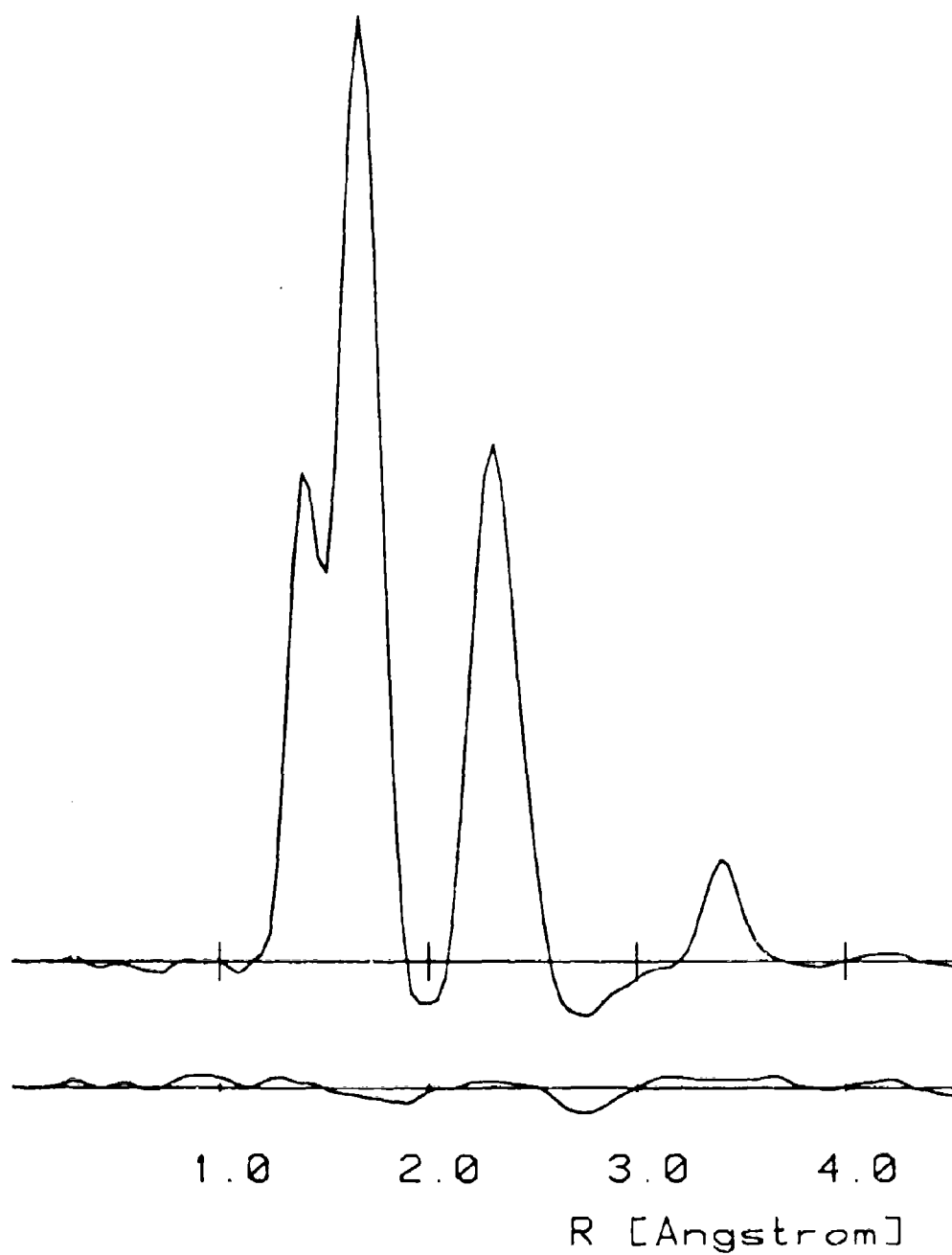
Fig. 3: Bond angles in axial (a) and equatorial (b) directions.



4.0 8.0 12.0 16.0 20.0 24.0 28.0 32.0
S [1/Ang.]

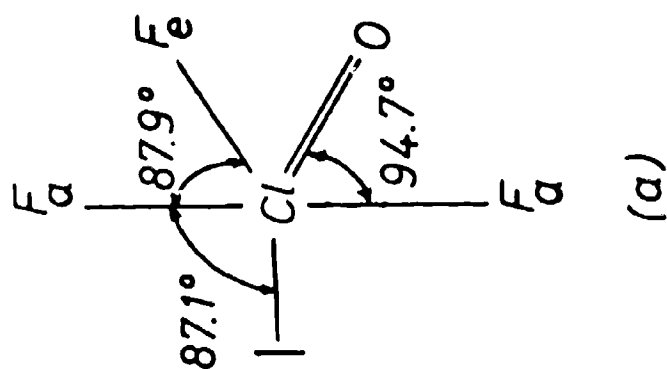
RI/RD81-140

H-11

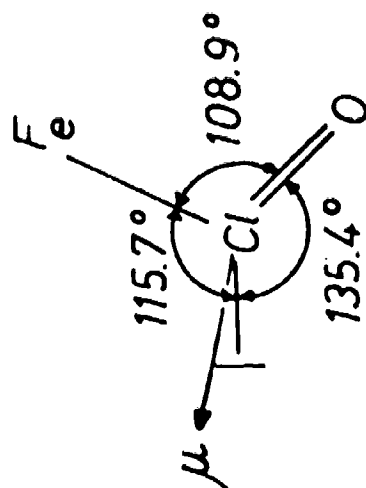


RI/RD81-140

H-12



(a)



(b)

APPENDIX I

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

Sir:

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

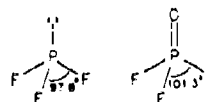
Contrary to the ligands in a tetrahedron or octahedron, those in a trigonal-bipyramidal molecule, when arranged as being equidistant from each other, are no longer on the surface of a sphere and become nonequivalent. The two axial ligands have a greater (ideally by a factor of $2^{1/2}$) central atom-ligand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

In this correspondence, two cases are presented which are strong evidence for the existence of directional repulsion effects in trigonal-bipyramidal molecules. These two cases are (i) a comparison of the structures of SF_4 ^{3,4} and $\text{X}=\text{SF}_4$ (where X is O or CH_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 repulsive strength of a lone valence electron pair and of a doubly bonded oxygen in the absence of directional effects. Inspection of the known structures of IF_3 ,¹² and IF_3O ¹³ and of XeOF_4 ¹⁴

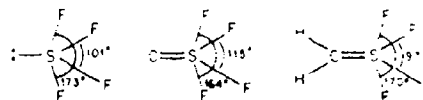


shows that in these pseudooctahedral molecules the repulsive strengths of a lone valence electron pair and of a doubly bonded oxygen are very similar and that, as demonstrated for XeOF_4 , the oxygen can be even slightly more repulsive than a free valence electron pair. In the pseudotetrahedral molecules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



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

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



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

The comparatively small $\text{F}_{eq}\text{SF}_{eq}$ bond angle of SF_4 can be rationalized in the following manner. A lone electron pair can be delocalized rather easily, as shown, for example, by the structure of BrF_5 ¹⁵ as opposed to that of IF_6 .¹⁶ Although

- (1) R. J. Gillespie and R. S. Nyholm, *Q. Revs., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963), **47**, 18 (1970).
- (2) R. J. Gillespie, "Molecular Geometry", Van Nostrand-Reinhold, London, 1972.
- (3) W. M. Tolles and W. D. C. Conn, *J. Chem. Phys.*, **36**, 1119 (1962).
- (4) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963).
- (5) G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969).
- (6) H. Oberhammer and J. E. Boggs, *J. Mol. Struct.*, **56**, 107 (1979); H. Bock, J. E. Boggs, G. Kleemann, D. Leniz, H. Oberhammer, E. M. Peters, K. Seppelt, A. Simon, and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, **18**, 944 (1979).
- (7) K. S. R. Murty and A. K. Mohanty, *Ind. J. Phys.*, **45**, 535 (1971); K. S. R. Murty, *Bull. Nat. Inst. Ind.*, **30**, 73 (1965).
- (8) J. D. Graybeal, Sixth Austin Symposium on Gas Phase Molecular Structure, Austin, Texas, 1976.
- (9) K. O. Christe, C. J. Schack, and E. C. Curtis, *Spectrochim. Acta, Part A*, **33A**, 323 (1977).
- (10) I. Hargittai, *J. Mol. Struct.*, **56**, 301 (1979).
- (11) H. Oberhammer, unpublished results.

RI/RD81-140

I-1

- (12) A. G. Robiette, R. H. Bradley, and P. N. Brier, *J. Chem. Soc. D*, 1567 (1971); R. K. Heenan and A. G. Robiette, *J. Mol. Struct.*, **55**, 191 (1979).
- (13) L. S. Bartell, F. B. Clippard, and E. J. Jacob, *Inorg. Chem.*, **15**, 3009 (1976).
- (14) J. F. Martins and E. B. Wilson, *J. Mol. Spectrosc.*, **26**, 410 (1968).
- (15) R. Bougon, P. Charpin, and J. Sorano, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **272**, 565 (1971).

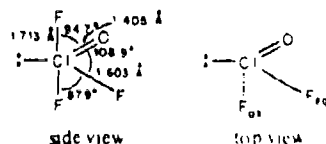
in both ions the central atom possesses a lone valence electron pair, the size of bromine permits only a maximum coordination number of 6 (toward fluorine) and the lone pair in BrF_6^- is sterically inactive and centrosymmetric. In IF_6^- , the larger central atom can readily accept seven or eight ligands,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

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

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

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

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



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

In summary, in trigonal-bipyramidal molecules, cylindrically nonsymmetric valence electron pairs can result in directional repulsion effects. These effects can be rather pronounced and cannot be accounted for by simple VSEPR theory.¹²

Acknowledgment. K.O.C. is indebted to the Office of Naval Research, Power Branch, for financial support.

Rocketdyne
A Division of Rockwell International
Canoga Park, California 91304

K. O. Christie*

Department of Chemistry
University of Tübingen
7400 Tübingen 1, West Germany

H. Oberhammer

*16: K. O. Christie, *Inorg. Chem.*, **11**, 1215 (1972).

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

*18: F. Seel and M. Pimpl, *J. Fluorine Chem.*, **10**, 413 (1977).

Received February 14, 1980

APPENDIX J

Contribution from Rocketdyne, a Division of
Rockwell International Corporation, Canoga Park, California 91304,
the Department of Inorganic Chemistry of the University of Ulm,
West-Germany and the Department of General and Inorganic Chemistry,
Eötvös Lorand University Budapest, Hungary

THE GENERAL VALENCE FORCE FIELD OF PERCHLORYL FLUORIDE

Karl O. Christe*, E. C. Curtis, W. Sawodny,
H. Härtner and G. Fogarasi

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, was fixed with the help of ab initio force constant calculations. It is shown that ν_2 and ν_3 are best described as an antisymmetric and a symmetric combination, respectively, of the ClF stretching and the ClO_3 bending motions. Comparison with 13 previously published force fields demonstrates the inadequacy of underdetermined force fields for strongly coupled systems, such as FClO_3 . The ClO and ClF stretching force constants were found to be 9.76 and 3.49 $\text{mdyn}/\text{\AA}$, 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 , molecule¹ 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 fields²⁻¹⁴ 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 data⁶ 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 out⁹ 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

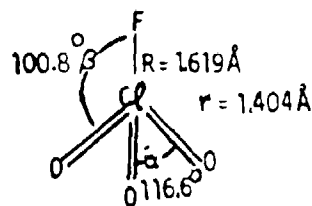
Perchloryl fluoride (Pennsalt) was handled in a passivated stainless steel - Teflon FEP vacuum system and purified prior to use by fractional condensation. Infrared spectra of the gas were recorded using a 5 cm path-length Teflon cell with CsI windows. The infrared spectra of matrix-isolated FClO_3 were 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 ± 2 and $\pm 0.1\text{ cm}^{-1}$, 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 and Table 1. As expected for a five atomic molecule of symmetry C_{3v} , FClO_3 exhibits a total of 6 fundamental vibrations classified as $3\text{A}_1 + 3\text{E}$. By analogy with the similar halogen fluorides, BrF_3 ²⁶, BrF_3O ²⁷ and FBrO_2 ²⁸, neon matrices exhibited the least matrix site effect splittings and showed frequencies closest to those of the gas phase values. The additional splittings observed for the N_2 and the Ar matrices are attributed to matrix site effects.

A general valence force field was computed for FClO_3 using a previously described machine method²⁹. 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 determined²² by a previous high resolution gas phase infrared study (see Table 1). Anharmonic frequencies were used for the force field computations because sufficient experimental data for anharmonicity corrections were not available. Since the relative signs of the symmetry coordinates are critical for the computation of the Coriolis constants, the symmetry coordinates have been summarized in Table II. The following internal coordinates and the geometry, determined by an electron diffraction study,⁶ were used:



As it was clear from the beginning, that the measured isotopic splittings would not suffice to determine the A_1 block force constants unequivocally, ab initio force constant calculations were performed too, using the force method³⁰, a 4-21G basis set³¹ for F and O and a 3-3-21 basis set³² for the chlorine atom, which was augmented by one d function with exponent 0.6³³.

when it was realized, that the pure basis did not reproduce the geometrical data properly. With the augmented basis set for Cl, the calculated geometry ($r_{\text{ClF}} 1.628 \text{ \AA}$, $r_{\text{ClO}} 1.437 \text{ \AA}$, $\angle \text{ClO}_2 116.57^\circ$, $\angle \text{ClOF} 100.8^\circ$) is in good agreement with the experimental values. Table III shows the results of the ab initio force constant calculations (set I). The usual³⁴⁻³⁸ deviation of the diagonal force constants was remedied by a subsequent iteration using the measured frequencies (set II in Table III).

E-Block Force Field. The³⁷ 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 IV) 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 calculated⁵ 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 computation⁵ 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 data⁶ are considered to be more precise than $\pm$ 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 $\pm$ 0.005 Mc/sec obtained³⁰ by microwave spectroscopy.

The previously reported⁵ 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 Mann²¹. 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 reported³¹⁻³⁴ 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 ³⁵Cl and ³⁷Cl 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 IV). 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 Tables III and V and Figure 2 with uncertainties derived from the uncertainty limit of ζ_5 .

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

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 III) 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.

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

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

between F_{12} (0.154 mdy/ $\text{\AA}$) and F_{13} (0.0 mdy/rad) is too large), they may be used to fix the force field within narrow limits, provided their sign and order of magnitude is correct, which was proven for many examples (e.g. ³⁴⁻³⁸). Thus, the ab initio value of F_{12} may be regarded as an upper limit, the value of F_{13} as a lower one, while F_{23} is close to the minimum value. F_{13} exhibits the largest uncertainty. Its lower limit is given by the ab initio value (0) and its upper limit by the value for F_{12} . The force field derived in this way with an optimal adaption to the experimental data is given in Table III as set III.

The strong mixing of the symmetry coordinates S_2 and S_3 in v_2 and v_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 molecule is linear, the F-Cl and Cl-X stretching motions should be strongly coupled and, therefore, result in an antisymmetric and a symmetric F-Cl-X stretch.

Comparison with Previous Force Fields. Table 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 mdy/ $\text{\AA}$ 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 mdy 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 FCIO_3 which fully supports the previous critical statements⁹ by Gans concerning the questionable value of force constant calculations from insufficient or inaccurate data. In such cases, the computation of wide solution ranges is important to determine the range of possible plausible solutions.

The values of 9.76 and 3.49 mdyne/Å obtained for the Cl=O and the Cl-F stretching force constant, respectively, of FClO_3 are in excellent agreement with our expectations⁴⁵ 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 mdyne/Å)⁴⁶ and ClF_2O^+ (11.2 mdyne/Å)⁴⁷ and are caused by their formal positive charge.⁴⁵ Similarly, ClF_2O_2^+ is the only chlorine oxyfluoride species which exhibits a higher (4.46 mdyne/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 demonstrated⁴⁴ 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.

Acknowledgement. One of the authors (K. O. Christe) is grateful to the Office of Naval Research, Power Branch, for financial support, and one of us (W. Sawodny) wishes to acknowledge the help of Dr. Ruoff.

References

- (1) Christe, K. O., Curtis, E. C., to be published.
- (2) Sawodny, W., Fadini, A., Ballein, K. *Spectrochim. Acta*, 1965, 21, 995.
- (3) Mueller, A., Krebs, B., Fadini, A., Glemser, O., Cyvin, S. J., Brunvoll, J., Cyvin, B. N., Elvebredd, I., Hagen, G., Vizi, B. 2. *Naturforsch.*, 1968, 23a, 1656.
- (4) Goubeau, J., Kilcioglu, E., Jacob, E. *Z. anorg. allgem. Chem.*, 1968, 357, 190.
- (5) Hoskins, L. C. *J. Chem. Phys.*, 1969, 50, 1130.
- (6) Clark, A. H., Beagley, B., Cruickshank, D. W. J., Hewitt, T. G. *J. Chem. Soc. (A)*, 1970, 872.
- (7) Nagarajan, G., Redmon, M. J. *Mh. Chem.*, 1972, 103, 1406.
- (8) So, S. P., Chau, F. T. *Z. Phys. Chem. (Frankfurt)*, 1973, 85, 69.
- (9) Gans, P. *J. Mol. Struct.*, 1972, 12, 411.
- (10) Clark, R. J. H., Rippon, D. M. *Mol. Phys.*, 1974, 28, 305.
- (11) Mueller, A., Rai, S. N. *J. Mol. Struct.*, 1975, 24, 59.
- (12) Karelin, A. I., Ionov, S. P., Ionova, G. V. *Zh. Strukt. Khim.*, 1970, 11, 454.
- (13) Kharitonov, Yu. Ya., Karelin, A. I., Rosolovskii, V. Ya. *J. Mol. Struct.*, 1973, 19, 545.
- (14) Sunder, S., McClung, R. E. *Can. J. Phys.*, 1974, 52, 2299.
- (15) McDowell, R. S., Goldblatt, M. *Inorg. Chem.*, 1971, 10, 625.
- (16) Kirk, R. W., Wilt, P. M. *J. Mol. Spectrosc.*, 1975, 58, 102.
- (17) Mohan, N., Mueller, A., Nakamoto, K. *Adv. Infrared Raman Spectrosc.*, 1975, 1, 173.
- (18) Plyler, E. K., Danti, A., Blaine, L. R., Tidwell, J. *Res. Natl. Bur. Stand., Sect., A*, 1960, 64, 841.
- (19) International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworths, Washington, D. C., 1961.
- (20) Engelbrecht, A., Atzwanger, H. *J. Inorg. Nucl. Chem.*, 1956, 2, 348.
- (21) Lide, D. R. Jr., Mann, D. E. *J. Chem. Phys.*, 1956, 25, 1128.
- (22) Madden, R. P., Benedict, W. S. *J. Chem. Phys.*, 1956, 25, 594.
- (23) Powell, F. X., Lippincott, E. R. *J. Chem. Phys.*, 1960, 32, 1883.
- (24) Claassen, H. H., Appelman, E. H. *Inorg. Chem.*, 1970, 9, 622.
- (25) Murphy, W. F., Sunder, S., Katz, H. *J. Raman Spectroscop.*, 1978, 7, 76.

- (26) Frey, R. A., Redington, R. L., Aljibury, A. L. K. J. Chem. Phys., 1971, 54, 344.
- (27) Christe, K. O., Curtis, E. C., Bougon, R. Inorg. Chem., 1978, 17, 1533.
- (28) Christe, K. O., Curtis, E. C., Jacob, E. Inorg. Chem., 1978, 17, 2744.
- (29) Curtis, E. C. Spectrochim. Acta, Part A, 1971, 27a, 931.
- (30) Pulay, P. Mol. Phys., 1969, 17, 197 and in H. Schaefer III (ed.): Modern Theoretical Chemistry, Vol. 4, p. 153, Plenum Press, New York 1977
- (31) Pulay, P., Fogarasi, G., Pang, F. Boggs, J. E. J. Am. Chem. Soc., 1979, 101, 2550.
- (32) Oberhammer, H., Boggs, J.E., J. Mol. Struct., 1980, 62, 259.
- (33) Fogarasi, G. to be published
- (34) Sawodny, W., Pulay, P., J. Mol. Spectry, 1974, 51, 135.
- (35) Pulay, P., Ruoff, A., Sawodny, W., Mol. Phys., 1975, 30, 1123.
- (36) Molt, K., Sawodny, W., Pulay, P., Fogarasi, G., Mol. Phys., 1976, 32, 169.
- (37) Fogarasi, G., Pulay, P., Molt, K., Sawodny, W., Mol. Phys., 1977, 33, 1565.
- (38) Sawodny, W., Birk, K., Fogarasi, G., Christe, K.O., Z. Naturforsch., 1980, 356, 1137.
- (39) Lide, D. R. Jr. J. Chem. Phys., 1965, 43, 3767.
- (40) Edgell, W. F., Moynihan, R. E. J. Chem. Phys., 1966, 45, 1205.
- (41) Moynihan, R. E., "Studies in Molecular Spectroscopy: The Influence of Coriolis Coupling on the Infrared Band Shapes," Ph.D thesis, Purdue University, 1954.
- (42) Valentine, R. W., "Studies of Molecular Spectroscopy: The Influence of Coriolis Coupling on the Infrared Band Shapes of Prolate Symmetric Rotors," Ph.D. thesis, Purdue University, 1957.
- (43) Hoskins, L. C. J. Chem. Phys., 1966, 45, 4594.
- (44) Christe, K. O., Willner, H., Sawodny, W. Spectrochim. Acta, Part A, 1979, 35a, 1347.
- (45) Christe, K. O., Schack, C. J. Adv. Inorg. Chem. Radiochem., 1976, 18, 319.
- (46) Christe, K. O., Wilson, R. D., Curtis, E. C., Inorg. Chem., 1973, 12, 1358.
- (47) Christe, K. O., Curtis, E. C., Schack, C. J., Inorg. Chem., 1972, 11, 2212.

Diagram Captions

- Figure 1. Infrared matrix isolation spectra of FCIO_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 FCIO_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.
- Figure 3. A_1 - block symmetry force constants of FCIO_3 plotted as a function of F_{23} .

TABLE I Frequencies^a and ³⁵Cl-³⁷Cl Isotopic Shifts^b of F³⁵ClO₃

Species	mode	F ³⁵ ClO ₃ frequency (cm ⁻¹)	³⁵ Cl- ³⁷ Cl isotopic shift (cm ⁻¹)
A ₁	ν ₁	1063	3.05
	ν ₂	717	10.0
	ν ₃	550	0.89
E	ν ₄	1315	15.8
	ν ₅	591	3.09
	ν ₆	405	[0.17] ^c

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

(b) Taken from this study, except for Δν₃ and Δν₅ (from ref. 22)

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

TABLE II Symmetry Coordinates and Symmetry Force Constants for FCIO_3

$$\begin{aligned}
 A_1 \quad & S_1 = (r_1 + r_2 + r_3) / \sqrt{3} \\
 & S_2 = R \\
 & S_3 = 0.4912 (B_1 + B_2 + B_3) - 0.3034 (\alpha_1 + \alpha_2 + \alpha_3) \\
 & S_4 = 0.3034 (B_1 + B_2 + B_3) + 0.4912 (\alpha_1 + \alpha_2 + \alpha_3) \\
 \\
 E \quad & S_{4a} = (r_2 + r_3 - 2r_1) / \sqrt{6} \\
 & S_{4b} = (r_3 - r_2) / \sqrt{2} \\
 & S_{5a} = (\alpha_2 + \alpha_3 - 2\alpha_1) / \sqrt{6} \\
 & S_{5b} = (\alpha_3 - \alpha_2) / \sqrt{2} \\
 & S_{6a} = (2B_1 - B_2 - B_3) / \sqrt{6} \\
 & S_{6b} = (B_2 - B_3) / \sqrt{2}
 \end{aligned}$$

* redundant coordinate

$$F_{11} = f_r + 2f_{rr}$$

$$F_{22} = f_R$$

$$F_{33} = 0.72f_B + 0.28f_{\alpha} + 1.45f_{BB} + 0.55f_{\alpha\alpha} - 1.79f_{\alpha B} - 0.89f_{\alpha\alpha}$$

$$F_{12} = \sqrt{3} f_{rR}$$

$$F_{13} = 0.85f_{rB} + 1.70f_{r\alpha} - 1.05f_{rR} - 0.53f_{r\alpha}$$

$$F_{23} = 1.47f_{RB} - 0.91f_{R\alpha}$$

$$F_{44} = f_r - f_{rr}$$

$$F_{55} = f_{\alpha} - f_{\alpha\alpha}$$

$$F_{66} = f_B - f_{BB}$$

$$F_{45} = f_{r\alpha} - f_{\alpha r}$$

$$F_{46} = f_{rB} - f_{Br}$$

$$F_{56} = f_{\alpha B} - f_{B\alpha}$$

Table III - Force constants calculated for FeO_3 ^a

	I	II	II	final set ^b	eigenvectors
	ab initio calc. diagonal terms adapted to frequencies	ab initio calc. diagonal terms adapted to frequencies	final set ^b		S_1 S_2 S_3
$A_1: F_{11}$	8.563	9.951	9.90 [±] 0.05		0.25 -0.08 0.09
F_{22}	4.857	3.267	3.49 [±] 0.07		-0.04 -0.24 0.24
F_{33}	2.754	2.673	2.58 [±] 0.05		0.01 0.13 0.19
F_{12}	0.154	0.154	0.13 [±] 0.03		S_4 S_5 S_6
F_{13}	0.0	0.0	0.07 [±] 0.07		0.12 0.17 0.11
F_{23}	0.481	0.481	0.58 [±] 0.01		-0.02 0.31 0.13
$E: F_{44}$	8.590	9.675	9.69 [±] 0.01		0
F_{55}	1.403	1.520	1.53 [±] 0.01		
F_{66}	1.640	1.506	1.49 [±] 0.02		
F_{45}	-0.267	-0.267	-0.29 [±] 0.01		
F_{46}	-0.345	-0.345	-0.33 [±] 0.11		
F_{56}	0.271	0.271	0.26 [±] 0.07		
$\nu_1(\Delta\nu_1)$	1001.6(15.25)	1062.46(2.78)	1062.93(2.96)	0.95F ₁₁	
$\nu_2(\Delta\nu_2)$	830.08(8.13)	725.95(10.72)	717.15(9.95)	$0.68F_{22} + 0.40F_{33} - 0.22F_{35} + 0.05F_{11}$	
$\nu_3(\Delta\nu_3)$	578.35(11.72)	540.39(0.32)	549.97(0.76)	$0.57F_{33} + 0.33F_{22} + 0.16F_{23}$	
$\nu_4(\Delta\nu_4)$	1239.29(15.09)	1314.96(15.85)	1315.05(15.80)	0.98 F ₄₄	
$\nu_5(\Delta\nu_5)$	578.08(3.09)	590.96(3.09)	590.97(3.09)	0.73 F ₅₅ + 0.11 F ₆₆ + 0.10 F ₅₆	
$\nu_6(\Delta\nu_6)$	414.63(0.06)	404.77(0.16)	404.87(0.17)	0.90 F ₆₆ + 0.26 F ₅₅ - 0.17 F ₅₆	
ζ_4	0.54	0.53	0.54		
ζ_5	-0.30	-0.38	-0.38		
ζ_6	0.24	0.32	0.32		

- (a) Stretching constants in $\text{mdyn}/\text{\AA}$ to 2nm^{-1} ; deformation constants in mdyn/rad^2 ad; stretch-bend interaction constants in $\text{mdyn}/\text{rad}=10\text{ nN}$
 (b) A block: optimal addition to experimental data with minimum deviation from ab initio values; for off-diagonal force constants
 E block: calculated from experimental data
 (c) Percent contributions; contributions of less than 5% to the PED are not listed

TABLE IV . Coriolis Constants of FC20₃

	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

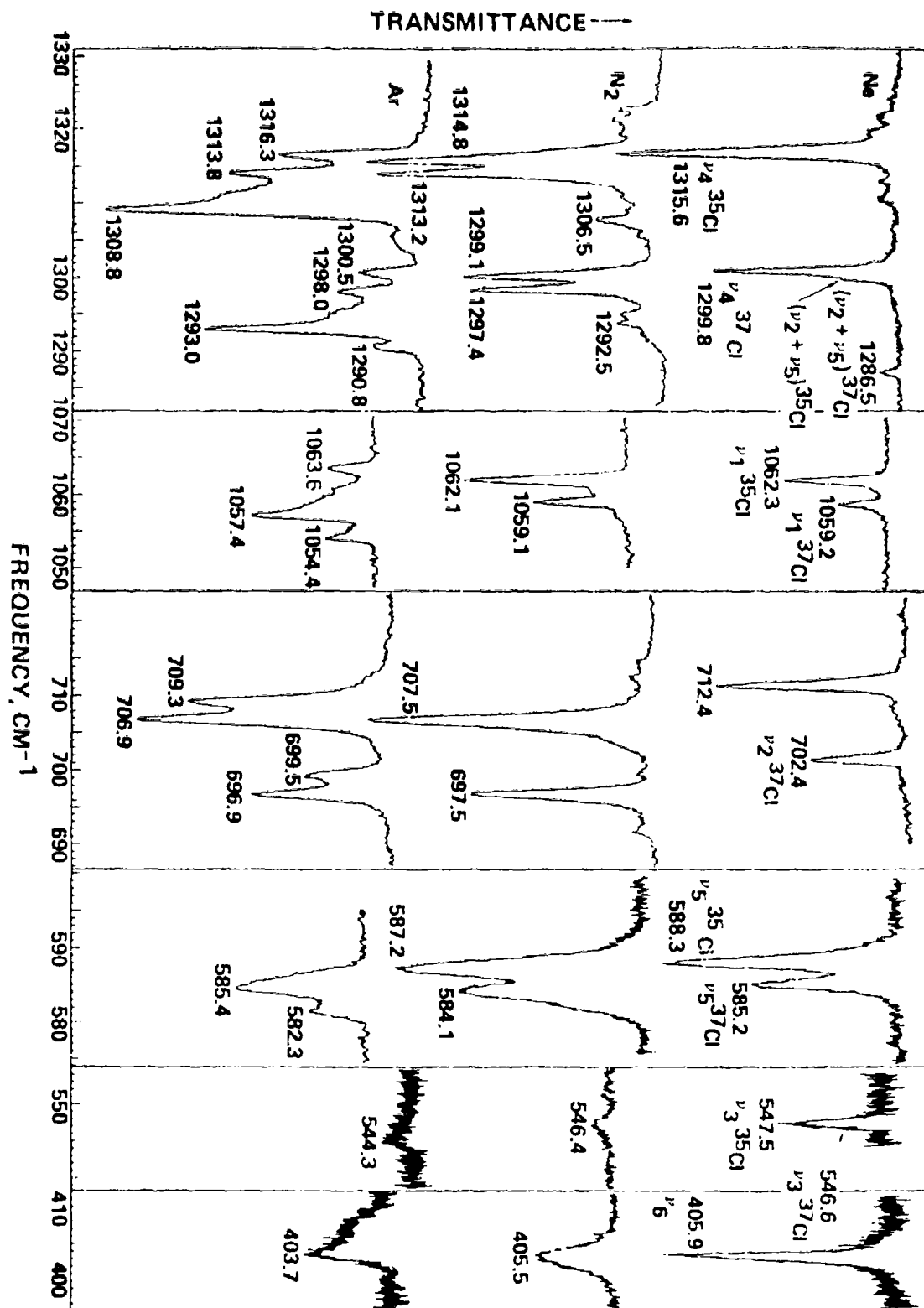
(b) values computed from the approximate force field of ref. 3

(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

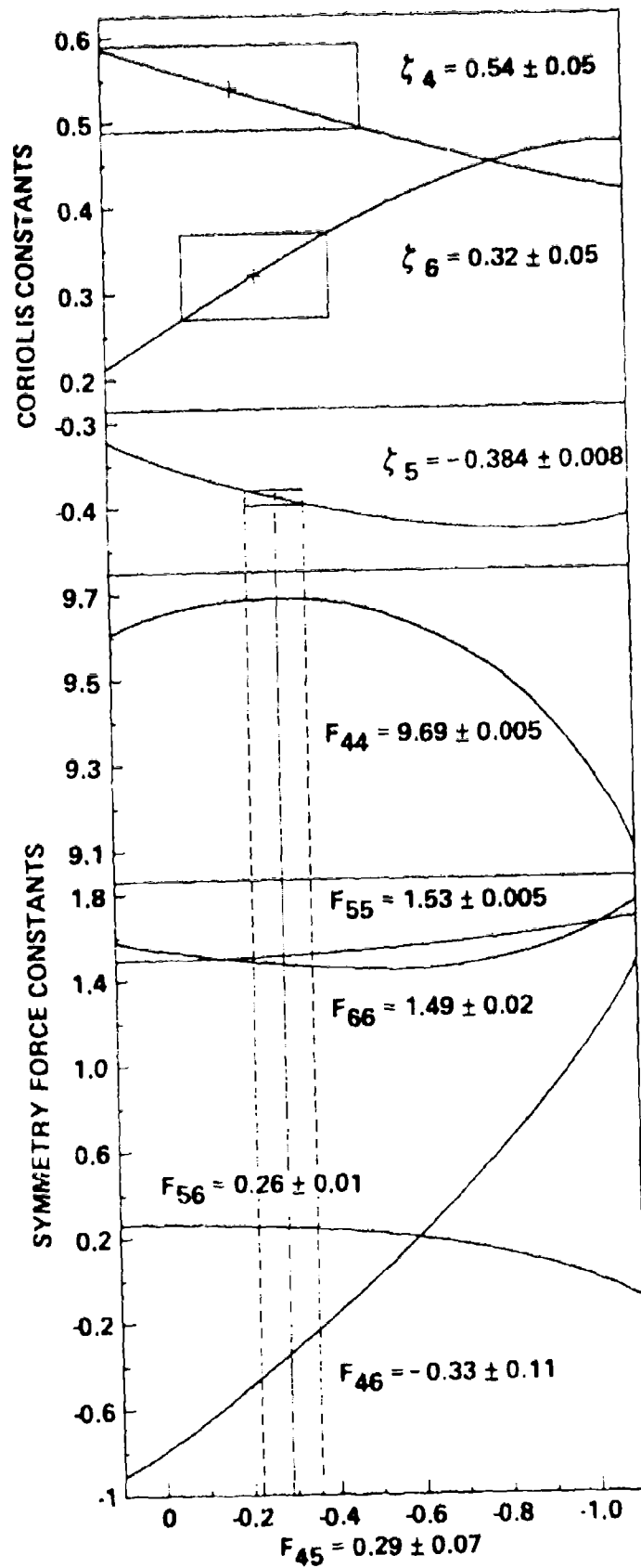
Table V. Comparison of the Different Force Field of FCI(1)

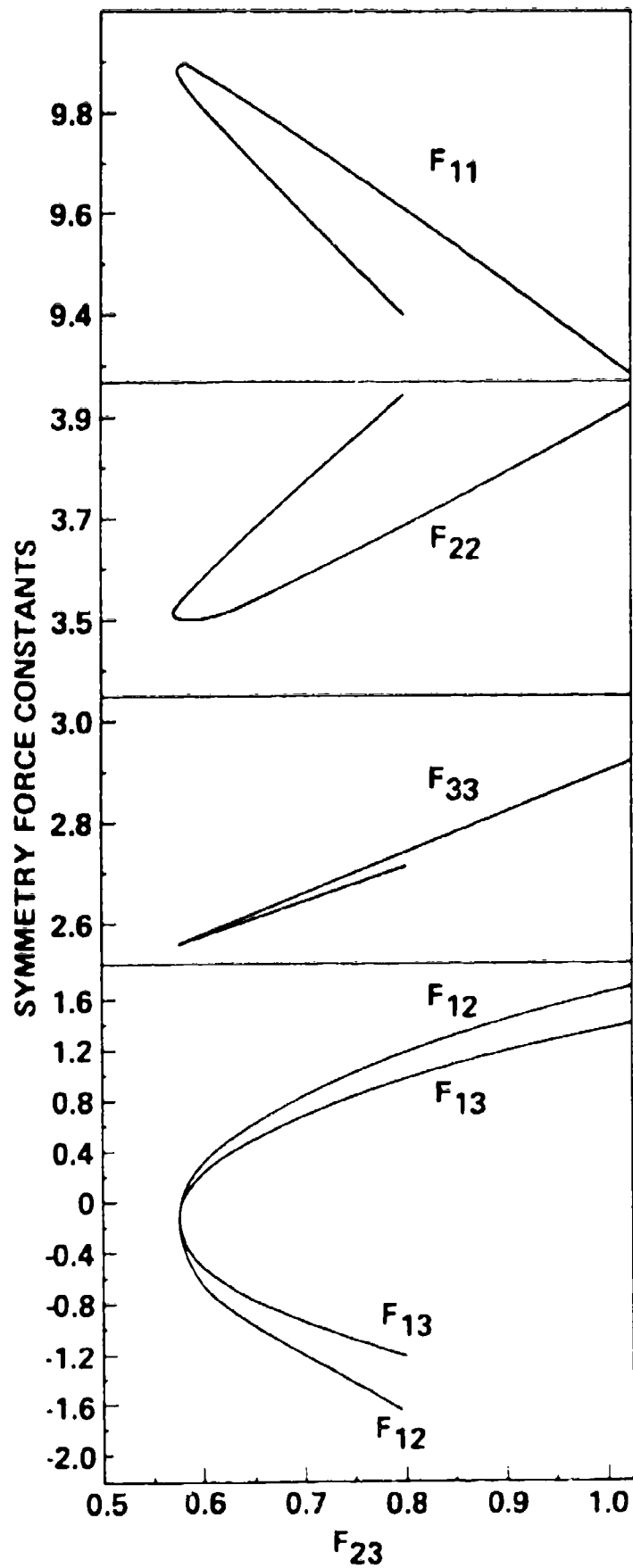
	this work ^a	ref. 1 ^b	ref 3 ^b	ref 4 ^b	ref 5 ^b	ref 6 ^a	ref 7 ^b	ref 8 ^b	ref 9 ^a	ref 10 ^b	ref 11 ^b	ref 12 ^b	ref 13	ref 14 ^b
A ₁ F ₁₁	9.90	8.64	8.64									9.49		
F ₂₂	3.49	3.91	3.92									3.69		
F ₃₃	2.58	1.82	0.85									2.98		
F ₁₂	0.13	-0.03	-0.04									-0.19		
F ₁₃	0.07	0.13	0.09									-0.07		
F ₂₃	0.58 ₅	-0.44	-0.50						<-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	9.76	9.41	9.43	9.37		9.30	9.75		9.5-0.1			9.56	9.36-9.55	9.42
f _R	3.49	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}	0.07	-0.39	-0.39			--	0.62					-0.03		0.24
f _{rr}	0.08	-0.02	-0.02			-0.25	0.53					-0.11		
f _{rr}						1.95	1.03							1.75
f _{rr}						1.60	0.82							1.84
f _{rr}						0.55	--							0.39
f _{rr}														0.53

(a) Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian² 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.



RI/RD81-140





RI/RD81-140

J-19/J-20

Das Kraftfeld von SF₄The Force Field of SF₄

Wolfgang Sawodny* und Karl Birk

Abteilung für Anorganische Chemie der Universität Ulm, Oberer Eselsberg, D-7900 Ulm

Geza Fogarasi

Department für Allgemeine und Anorganische Chemie, Eötvös-Lorand-Universität,
H-1088 Budapest, Ungarn

Karl O. Christe

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

*Herrn Prof. Dr.-Ing. Fritz Seel zum 65. Geburtstag gewidmet*Z. Naturforsch. **85b**, 1137–1142 (1980); eingegangen am 9. Mai 1980

Force Constants

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

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

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

Das Kraftfeld aus experimentellen Daten

Die Normalschwingungen des SF₄ teilen sich nach 4 A₁ + 1 A₂ + 2 B₁ + 2 B₂ auf die Schwingungsrassen auf. Die Symmetrie-Koordinaten wurden wie in [11] gewählt, die F- und G-Matrizen nach der Wilsonschen Methode abgeleitet. Als experimentelle Größen standen die Schwingungsfrequenzen nach [13] (Werte der IR-Gasspektren; ³²S–³⁴S-Isotopenverschiebungen aus Spektren in Ne-Matrix), 5 Zentrifugaldehnungskonstanten [12] und die mittleren Schwingungsamplituden [14] zur Verfügung, letztere wurden allerdings nicht in die Iteration einbezogen, sondern nachträglich berechnet.

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

* Sonderdruckanforderungen an Dr. W. Sawodny.
0340-5087/80/0900-1137/\$ 01.00/0

Tab. I. Kraftfeld für SF₄ aus experimentellen Daten (Valenzkraftkonstanten mdyn/Å = 10³ Nm⁻¹, Deformationskonstanten mdyn Å = aJ, Valenz/Deformations-Wechselwirkungskonstanten mdyn = 10 nN).

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

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

sich auch in einer unzureichenden Wiedergabe von Δν₃ äußern.

ab-initio-Berechnung der Kraftkonstanten für SF₄

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

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

Basissatz S: F:		3-3-21 G 4-21 G exp. Geom.	3-3-21 G 4-21 G theor. Geom.	3-3-21 + 1d G 4-21 G exp. Geom.
Ort:				
A ₁ : F ₁₁		9,212	6,059	7,580
F ₂₂		6,049	4,523	4,886
F ₃₃		1,104	0,739	1,309
F ₄₄		1,125	1,033	1,233
F ₁₂		0,698	0,584	0,756
F ₁₃		0,041	—0,104	0,073
F ₁₄		0,433	0,438	0,422
F ₂₃		0,065	0,155	—0,034
F ₂₄		—0,176	—0,033	—0,051
F ₃₄		0,488	0,498	0,513
A ₂ : F ₅₅		1,950	1,966	2,099
B ₁ : F ₆₆		5,028	3,888	4,073
F ₇₇		2,237	2,268	2,413
F ₆₇		0,658	0,679	0,784
B ₂ : F ₈₈		9,133	6,136	7,320
F ₉₉		3,273	2,147	3,008
F ₈₉		0,541	0,625	0,624
ν_1 ($\Delta\nu_1$)	892 (11,33)	1124,90 (13,08)	850,72 (10,36)	1033,31 (13,03)
ν_2 ($\Delta\nu_2$)	558 (0)	727,11 (0,0)	708,71 (1,94)	648,29 (0,03)
ν_3 ($\Delta\nu_3$)	532 (4,09)	547,26 (5,12)	477,71 (2,91)	569,31 (4,72)
ν_4 ($\Delta\nu_4$)	228 (—)	223,72 (0,01)	153,88 (0,0)	248,50 (0,01)
ν_5 ($\Delta\nu_5$)	[437] (—)	472,23 (0,0)	461,34 (0,0)	489,94 (0,0)
ν_6 ($\Delta\nu_6$)	730 (13,13)	982,52 (17,18)	850,70 (14,67)	874,61 (15,68)
ν_7 ($\Delta\nu_7$)	475 (—)	550,80 (1,30)	515,14 (1,19)	571,11 (1,08)
ν_8 ($\Delta\nu_8$)	867 (10,52)	1184,66 (15,59)	976,78 (12,84)	1054,18 (13,79)
ν_9 ($\Delta\nu_9$)	353 (2,42)	458,68 (2,76)	372,86 (2,14)	440,62 (2,68)
mit obigen Basissätzen berechnet:				
r (Å)	1,545		1,628	1,559
R (Å)	1,646		1,694	1,631
β (°)	101,6°		110,0°	102,2°
γ (°)	173,1°		161,4°	169,7°

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

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

die Richtigkeit der Zuordnung, die ja lange Zeit in der Literatur kontrovers war [1–13], prüfen. Die aus der *ab initio*-Rechnung erhaltenen Frequenzwerte stützen eindeutig die Zuordnung aller Valenzschwingungen und der Deformationen ν_4 und ν_9 nach [6, 10, 13], die Besonderheit einer sehr hohen Deformationsschwingung in A₁ (ν_3 , nur knapp unterhalb der Valenzfrequenz ν_2) wird bestätigt. Die Alternative mit $\nu_3 = 350 \text{ cm}^{-1}$ [11] kann man damit endgültig ausschließen. Lediglich die Zuschreibung der Schwingungen bei 475 und 532 cm^{-1} zu ν_3 (A₁) und ν_7 (B₁) ([6, 10] einerseits, [13] andererseits) läßt sich nicht entscheiden, die Berechnung ergibt hier identische Frequenzwerte. Jedoch wird die Zuordnung $\nu_3 = 532 \text{ cm}^{-1}$, $\nu_7 = 475 \text{ cm}^{-1}$ (wie in [13]) durch die Isotopenverschiebungen (die *ab initio* alle etwas zu hoch erhalten werden) gestützt. Wir haben diese Zuordnung darüber hinaus durch

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

	nachiteriertes <i>ab initio</i> -Feld	Modifizierungen:			
		a	b	c	d
F ₁₁	5,533 ± 0,099	5,535	5,522	5,505	5,626
F ₃₂	3,724 ± 0,056	3,683	3,698	3,684	3,662
F ₃₃	1,448 ± 0,229	1,458	1,456	1,465	1,447
F ₄₄	0,891 ± 0,138	0,876	0,879	0,880	0,873
F ₁₂	0,756	0,68	0,70	0,68	0,65
F ₁₃	0,073	0,12	0,11	0,10	0,13
F ₁₄	0,422	0,36	0,37	0,36	0,40
F ₂₃	−0,034	−0,034	−0,05	−0,034	−0,034
F ₂₄	−0,051	−0,051	−0,07	−0,051	−0,051
F ₃₄	0,513	0,513	0,513	0,518	0,505
ν_1 ($\Delta\nu_1$)	890,60 (11,64)	891,07 (11,82)	891,15 (11,82)	890,96 (11,93)	891,03 (11,56)
ν_2 ($\Delta\nu_2$)	557,95 (0,21)	557,88 (0,11)	557,82 (0,04)	557,90 (0,15)	557,81 (0,02)
ν_3 ($\Delta\nu_3$)	535,41 (3,81)	533,53 (3,80)	533,45 (3,86)	534,11 (3,69)	533,76 (4,03)
ν_4 ($\Delta\nu_4$)	227,56 (0,11)	227,77 (0,10)	227,78 (0,10)	227,71 (0,10)	227,75 (0,10)
τ_{xxxx}	−11,5	−11,5	−11,5	−11,6	−11,2
τ_{yyyy}	−5,5	−5,6	−5,6	−5,6	−5,6
τ_{zzzz}	−2,1	−2,1	−2,1	−2,1	−2,1
τ_{xxyy}	+ 0,28	−0,04	−0,001	−0,02	−0,02
τ_{xxzz}	−1,9	−1,9	−1,9	−1,9	−1,9
τ_{yyzz}	−0,8	−0,8	−0,8	−0,8	−0,8
T ₁	−12,6	−12,9	−12,9	−12,9	−12,9
T ₂	−2,1	−2,1	−2,1	−2,1	−2,1

eine Messung der Polarisationsgrade der Linien bei 558 und 532 cm^{−1} (die Linien bei 475 und 350 cm^{−1} waren so schwach, daß ihr Polarisationsgrad nicht festgestellt werden konnte) im Raman-Gasspektrum bestätigt: beide Linien sind im Gegensatz zu früheren Angaben [5] polarisiert. Für die inaktive ν_5 (A₂) läßt sich aus der *ab initio*-Rechnung ein Bereich von 400–450 cm^{−1} abschätzen, so daß die Annahme $\nu_5 = 437$ cm^{−1} [13] durchaus plausibel ist.

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

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

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

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

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

Betrachtet man die Wiedergabe der experimentellen Daten durch das nachiterierte *ab initio*-Feld für A_1 (in Kombination mit den experimentell ermittelten Kraftkonstanten für B_1 und B_2), so werden die Isotopenverschiebungen gut reproduziert, die τ -Werte zeigen hingegen noch größere Diskrepanzen als bei der Iteration nach ν , $\Delta\nu$ und τ gemeinsam. Da aber die τ 's wegen anharmonischer Effekte weniger zuverlässig sind und zudem noch im Gegensatz zu den Isotopenverschiebungen eine wesentlich geringere Meßgenauigkeit aufweisen, erscheint dies aber tragbar, ja man muß sogar vermuten, daß das völlig andere Kraftfeld bei der Iteration nach allen experimentellen Daten gerade durch das Bemühen um eine Angleichung der τ -Werte, die aber trotzdem nur bei τ_{xxxx} und T_1 innerhalb der angegebenen [12] Fehlergrenze erreicht wird, verursacht ist. Beim *ab initio*-Feld werden für alle τ 's zu niedrige Werte erhalten, T_1 könnte aber durch eine Erniedrigung von ν_3 (A_2) angeglichen werden (für $\nu_3 = 400 \text{ cm}^{-1}$: $T_1 = -14,8 \text{ MHz}$). Jedoch zeigt sich bei ihm für das ebenfalls im Summenausdruck T_1 verborgenen τ_{xxyy} sogar ein positiver Wert, was nicht möglich ist. Es ist also zumindest erforderlich, die Nichtdiagonalglieder des *ab initio*-Feldes so zu variieren,

daß τ_{xxyy} negativ wird. Bei der Untersuchung, welchen Einfluß die Nichtdiagonalglieder einzeln auf die Meßdaten haben, zeigte sich, daß dieser bei F_{23} und F_{24} außerordentlich gering ist, für F_{34} hingegen extrem stark: schon eine Änderung unter $0,01 \text{ mdyn}$. A verschiebt τ_{xxyy} erheblich, jedoch werden gleichzeitig ν_3 , $\Delta\nu_3$ und $\Delta\nu_1$ so sehr in negativem Sinne beeinflusst, daß dieser Effekt kaum genutzt werden kann. Eine Verkleinerung von F_{12} , F_{14} und eine Vergrößerung von F_{13} wirken bezüglich τ_{xxyy} in der gewünschten Richtung, wenn auch nicht stark. Sie wurden daher alle drei gemeinsam geändert, um sich nicht mit einer Größe allzuweit vom *ab initio*-Wert zu entfernen. Tab. III zeigt 4 solche Kraftfelder (Modifizierungen a-d), bei denen die Nichtdiagonalglieder gemäß dieser Erfahrungen festgelegt wurden. Sie reproduzieren alle Daten etwa gleich gut. Auf die Diagonalkraftkonstanten haben diese Änderungen kaum Einfluß, und man kann wohl davon ausgehen, daß die korrekte Lösung für die Rasse A_1 des SF₄ tatsächlich in diesem eng umschriebenen Bereich liegen wird. Daraus ergeben sich für SF₄ folgende Valenzkraftkonstanten $f_r(S-F_{eq}) = 5,36 \text{ mdyn/Å}$ ($f_{rr} 0,19 \text{ mdyn/Å}$); $f_R(S-F_{ax}) = 3,25 \text{ mdyn/Å}$ ($f_{RR} 0,43 \text{ mdyn/Å}$). Die mittleren Schwingungsamplituden bei 298°K für all diese Lösungen betragen (in Å, in Klammern experimentelle Werte [14]): SF_{ax} : $0,048$ ($0,047 \pm 0,005$); SF_{eq} : $0,041$ ($0,041 \pm 0,005$); $F_{eq}F_{eq}$: $0,074$ ($0,068 \pm 0,01$); $F_{ax}F_{eq}$: $0,069$ ($0,067 \pm 0,005$); $F_{ax}F_{ax}$: $0,060$ ($0,059 \pm 0,01$) und entsprechen so den Werten, die auch mit dem Kraftfeld in [13] erhalten wurden. Auch Eigenvektoren und Potentialenergieverteilung stimmen weitgehend mit den Ergebnissen von [13] überein, insbesondere was die völlige Mischung der Symmetriekoordinaten S_3 und S_4 in den Schwingungen ν_3 und ν_4 anbetrifft.

- [1] R. E. Dodd, L. A. Woodward und H. L. Roberts, Trans. Farad. Soc. **52**, 1052 (1956).
- [2] R. L. Redington und C. V. Berney, J. Chem. Phys. **43**, 2020 (1965).
- [3] I. W. Levin und C. V. Berney, J. Chem. Phys. **44**, 2557 (1966).
- [4] S. J. Cyvin, Acta Chem. Scand. **23**, 576 (1969).
- [5] K. O. Christe und W. Sawodny, J. Chem. Phys. **52**, 6320 (1970).
- [6] R. A. Frey, R. L. Redington und A. L. K. Aljibury, J. Chem. Phys. **54**, 344 (1971).
- [7] I. W. Levin und W. C. Harris, J. Chem. Phys. **55**, 3048 (1971).
- [8] I. W. Levin, J. Chem. Phys. **55**, 5393 (1971).
- [9] C. V. Berney, J. Mol. Struct. **12**, 87 (1972).
- [10] K. O. Christe, W. Sawodny und P. Pulay, J. Mol. Struct. **21**, 158 (1974).
- [11] K. O. Christe, E. C. Curtis, C. J. Schack, S. J. Cyvin, J. Brunvoll und W. Sawodny, Spectrochim. Acta **32A**, 1141 (1976).
- [12] H. Inoue, A. Naruse und E. Hirota, Bull. Chem. Soc. Jpn. **49**, 1260 (1976).
- [13] K. O. Christe, H. Willner und W. Sawodny, Spectrochim. Acta **35A**, 1347 (1979).
- [14] K. Kimura und S. H. Bauer, J. Chem. Phys. **39**, 3172 (1963).

- [15] W. J. Hehre und W. A. Lathan, J. Chem. Phys. **56**, 5265 (1972).
[16] P. Skancko, G. Fogarasi und J. E. Boggs, J. Mol. Struct., im Druck.
[17] P. Pulay, G. Fogarasi, F. Pang und J. E. Boggs, J. Am. Chem. Soc. **101**, 2550 (1979).
[18] P. Pulay, Mol. Phys. **17**, 197 (1969) und in H. F. Schofer III (Herausg.): Modern Theoretical Chemistry Vol. 4, S. 153, Plenum Press, New York 1977.
[19] P. Pulay, Theor. Chim. Acta **50**, 299 (1979).
[20] H. Oberhammer und J. E. Boggs, J. Mol. Struct. **56**, 107 (1979).
[21] W. M. Tolles und W. D. Gwinn, J. Chem. Phys. **36**, 1119 (1962).
[22] W. Sawodny und P. Pulay, J. Mol. Spectr. **51**, 135 (1974).
[23] P. Pulay, A. Ruoff und W. Sawodny, Mol. Phys. **30**, 1123 (1975).
[24] K. Molt, W. Sawodny, P. Pulay und G. Fogarasi, Mol. Phys. **32**, 169 (1976).
[25] G. Fogarasi, F. Pulay, K. Molt und W. Sawodny, Mol. Phys. **33**, 1565 (1977).

Contribution to: Inorganic Reactions
and Methods

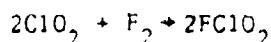
2.2 The Formation of the Halogen - Halogen Bond

2.2.7 Preparation of Halogen Oxyfluorides

Halogen oxyfluorides can be prepared by reactions involving the formation of either halogen-fluorine or halogen-oxygen bonds. Since this chapter deals exclusively with the formation of the halogen-halogen bond, preparative methods for halogen oxyfluorides based on the formation of halogen-oxygen bonds are not included in the following discussion.

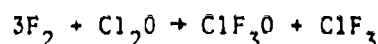
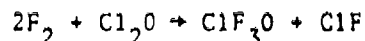
2.1.7.1 By Reaction of Halogen Oxides with Elemental Fluorine

The interaction of F_2 with chlorine oxides, such as ClO_2 [1-5], Cl_2O_6 [6-7] or Cl_2O_7 [8], produces $FClO_2$. Essentially quantitative yields of $FClO_2$ are obtained with ClO_2 as a starting material and moderated reaction conditions. Particularly, the use of inert solvents, such as $CFCI_3$, or diluents, such as air or N_2 , are recommended to avoid hazards due to the explosive nature of the chlorine oxides. In the case of the higher chlorine oxides, the use of elevated temperature and the decreased yields of $FClO_2$ suggest that the primary step in these reactions involves the thermal decomposition of these chlorine oxides to ClO_2 which is then fluorinated. Therefore, all of the above reactions are likely to involve the step:



In view of the shock sensitivity of chlorine oxides, none of the above methods is recommended for the large scale production of $FClO_2$, and necessary safety precautions must be used. The recommended method for the preparation of $FClO_2$ is the reaction of $NaClO_3$ with ClF_3 (see section 2.2.7.6).

The low temperature ($-78^\circ C$) fluorination of Cl_2O with elemental fluorine [9] produces ClF_3O as the main product. Depending on the reaction conditions, the by-products can be either ClF or ClF_5 :



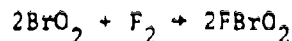
When no catalyst is used or if KF and NaF are present as catalysts, ClF is the main by-product. When the more basic alkali metal fluorides, RbF and CsF, are used, ClF₃ is the favored coproduct. The formation of ClF₃ rather than ClF is presumably associated with the more ready formation of ClF₂⁻ intermediates with RbF and CsF. Yields of ClF₃O from Cl₂O are rather variable and may be affected by the particular alkali fluoride present. Yields of over 40% have been consistently obtained and have reached over 80% using either NaF or CsF. Since NaF does not form an adduct with ClF₃O^[10], stabilization of the product by complex formation does not seem to influence the ClF₃O yields strongly.

Owing to unpredictable explosions experienced with liquid Cl₂O, attempts were made to circumvent the Cl₂O isolation step. For this purpose, the crude Cl₂O, still absorbed on the mercuric salts, was directly fluorinated. Again, ClF₃O was formed, but its yield was too low to make this synthetic route attractive.

The fluorination of solid Cl₂O to ClF₃O proceeded at temperatures as low as -196°C provided the fluorine was suitably activated by methods such as glow discharge. Unactivated fluorine did not interact with Cl₂O at -196°C. The relatively low yield of ClF₃O (1-2%) makes this modification impractical.

Due to the shocksensitivity of Cl₂O, its fluorination reaction is not the preferred method for the preparation of ClF₃O. Replacement of Cl₂O by the more stable ClONO₂ results in a safer process (see Section 2.2.7.5).

By analogy with ClO₂, BrO₂ is readily fluorinated by elemental F₂ to give FBrO₂ in high yield:^[11]

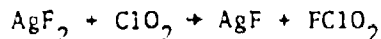


However, direct reaction with F_2 is not practical because, even at -78°C , the reaction is exceedingly vigorous resulting in spontaneous decomposition of the BrO_2 and explosions. Liquid Cl_2 or perfluoropentane have successfully been used as a diluent to moderate the reaction. BrO_2 is not soluble in these solvents and must be suspended. Again, this method is not recommended for larger scale preparations of FBrO_2 and appropriate safety precautions must be taken.

The fluorination of I_2O_5 with elemental fluorine in anhydrous HF was reported^[12] to result in the formation of FIO_2 . This claim, however, was refuted by a subsequent study^[13] which showed that anhydrous HF quantitatively converts I_2O_5 or FIO_2 to IF_5 .

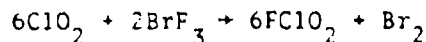
2.2.7.2 By Reaction of Halogen Oxides with Fluorinating Agents other than F_2

In the FCIO_2 synthesis from ClO_2 and F_2 , the latter can be replaced by other fluorinating agents. Thus, the passage of ClO_2 , diluted by N_2 , over AgF_2 ^[14] or CoF_3 ^[12] at room temperature produced pure FCIO_2 in high yield.



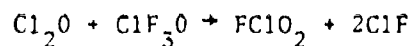
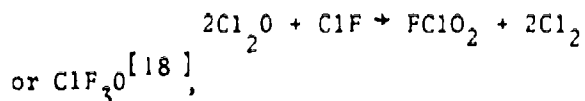
The consumption of the AgF_2 can be readily followed by the color change of AgF_2 (dark brown) to AgF (yellow).

Halogen fluorides can also be used to fluorinate ClO_2 to FCIO_2 . Thus, the passage of ClO_2 through liquid BrF_3 at 30°C has been reported^[14] to proceed according to



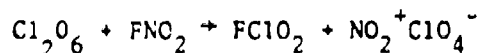
The risk of explosions in the ClO_2 - AgF_2 reaction is somewhat reduced

when ClO_2 is replaced by the less dangerous Cl_2O . The yield of FClO_2 was 35% [15-16]. Similarly, Cl_2O can be fluorinated at -78°C with either ClF [17],

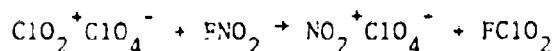


In these two reactions, the unstable FClO molecule is probably formed as an intermediate which can readily disproportionate to yield FClO_2 and ClF (see Section 2.2.7.4).

The fluorination of Cl_2O_6 with a variety of fluorinating agents was also studied and yields FClO_2 as the principal product. Fluorinating agents used with Cl_2O_6 include BrF_3 or BrF_5 , [19] HF [20], and FNO_2 [14]. The latter reaction was carried out in CFCl_3 solution at 0°C and proceeded according to:

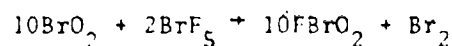


These reactions of Cl_2O_6 were carried out at low temperatures at which decomposition of Cl_2O_6 to $2\text{ClO}_2 + \text{O}_2$ can be excluded. However, they can be rationalized in terms of the easy polarization of Cl_2O_6 to $\text{ClO}_2^+ \text{ClO}_4^-$ [12].

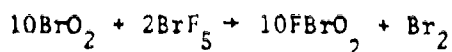


The ionic structure of ClO_6 in the solid state has been established by vibrational spectroscopy [21].

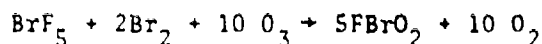
Fluorination of BrO_2 to FBrO_2 is readily achieved by the use of BrF_5 as a fluorinating agent [12,22].



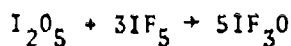
The reaction is carried out at -55°C in liquid BrF_5 , and the FBrO_2 is separated from the Br_2 by-product and excess of BrF_5 by vacuum fractionation. This reaction can be further simplified by preparing the BrO_2 in situ by passing O_3 through a solution of Br_2 in BrF_5 [12,22,23].



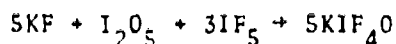
The reaction is carried out at -55°C in liquid BrF_5 , and the FBrO_2 is separated from the Br_2 by-product and excess of BrF_5 by vacuum fractionation. This reaction can be further simplified by preparing the BrO_2 in situ by passing O_3 through a solution of Br_2 in BrF_5 [12,22,23].



When I_2O_5 is dissolved in boiling IF_5 , white hygroscopic needles of IF_3O separate on cooling of the solution [24].

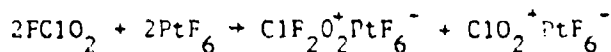


A modification of this reaction was used to [25] prepare KIF_4O according to:

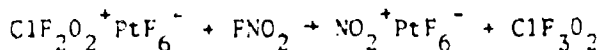


2.2.7.3 By Reaction of Halogen Oxyfluorides with Fluorinating Agents

The fluorination of a chlorine oxyfluoride to one of higher oxidation state is a difficult task due to the scarcity of stable low (+III) and high (+VII) oxidation state oxyfluorides. Thus, there is only one case known, [26,27] where FCIO_2 is fluorinated by the very strong oxidizer PtF_6 according to:

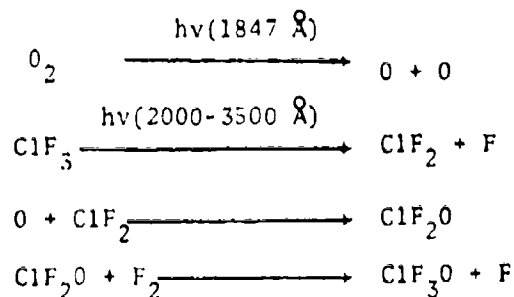


Several side reactions compete with this reaction and the yield of ClF_2O_2^+ varies greatly with slight changes in the reaction conditions. The $\text{ClF}_2\text{O}_2^+\text{PtF}_6^-$ can be converted to ClF_3O_2 by a displacement reaction using FNO_2 :



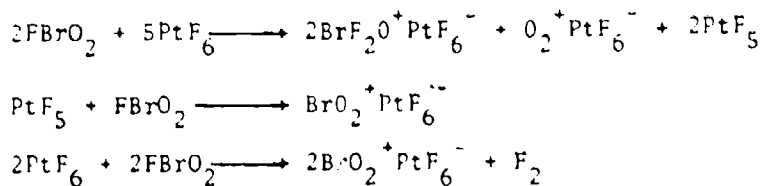
A scrambling of oxygen and fluorine ligands was achieved in the synthesis of ClF_3O from various mixtures of chlorine, fluorine and oxygen containing starting materials using uv-photolysis [28-30]. The claim [30] for the formation of ClF_5O in the uv-photolysis of the $\text{ClF}_5\text{-OF}_2$ system could not be confirmed by work in other laboratories [31].

A detailed kinetic study of the photolyses of the $\text{ClF}_3 - \text{O}_2$ and of the $\text{Cl}_2 - \text{F}_2 - \text{O}_2$ systems was carried out^[32]. Contrary to the original report^[28], the rate of ClF_3O formation was demonstrated to be the same for both systems, to increase with O_2 concentration, and to be independent of irradiation time. Furthermore, the rate of ClF_3O formation was shown to be proportional to the intensity of the 1847 Å band of the Hg spectrum indicating that the dissociation of O_2 to two ground-state, ^3p , oxygen atoms is the primary photochemical process. The following mechanism was proposed which requires the photochemical dissociation of ClF_3 as well:

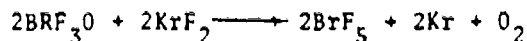
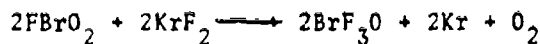


The photolysis of ClF_3 was investigated under similar conditions. A photochemical steady state was quickly achieved, where $[\text{F}_2] = [\text{ClF}] = \alpha[\text{ClF}_3]$, and α has a value of about 1 at low and of about 3 at high pressures. These results together with the known photochemical decomposition of OF_2 ^[33] explain why ClF_3O can be readily generated by the photolysis of so many different starting materials, including the halogen oxyfluorides FClO_2 , FClO_3 and IF_5O .

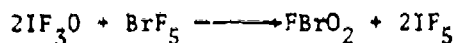
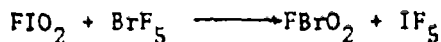
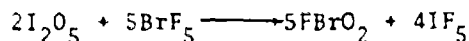
For bromine oxyfluorides, fluorinations with the powerful oxidizers PtF_6 and KrF_2 have been studied. With PtF_6 the following reactions were observed^[34],



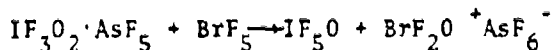
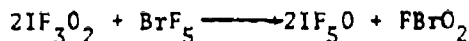
but no evidence for the formation of BrO_2F_2^+ was obtained. Similarly, the reactions of KrF_2 with either FBrO_2 , BrF_3O or FBrO_3 [35-36] did not produce any novel bromine + VII compounds, but proceeded according to



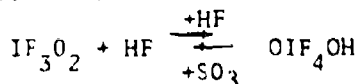
Iodine (+V) oxyfluorides or oxide are fluorinated by BrF_5 to yield FBrO_2 and IF_5 ,



but heptavalent IF_5O_2 or its AsF_5 or SbF_5 adducts are fluorinated to give IF_5O [36]



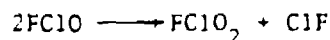
The addition of HF to IF_3O_2 results in the formation of OIF_4OH [37]. This reaction is reversible



and represents an example for the addition of HF across a $\text{X}=\text{O}$ double bond with formation of a new $\text{X}-\text{F}$ bond.

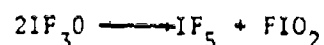
2.2.7.4 By Disproportionation of Halogen Oxyfluorides

The thermally unstable compound FCIO is known [31,38] to readily disproportionate at room temperature according to

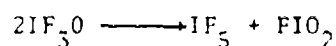


This reaction explains the formation of FCIO_2 and CIF in reactions where FCIO would be the expected reaction product (see Section 2.2.7.2).

Iodine trifluoride oxide is stable at room temperature, but at 100°C undergoes a reversible change into IF₅ and FIO₂^[24].

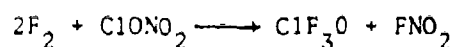


This reaction is also involved in the thermal and photochemical decomposition of IF₃O₂^[37] according to



2.2.7.5 By Reaction of Positive Halogen Compounds with Fluorinating Agents

For the synthesis of ClF₃O the fluorination of ClONO₂ with F₂ at -35°C^[9] is most attractive.

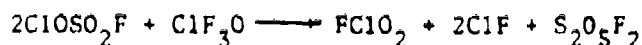


Contrary to chlorine oxides, ClONO₂ has the advantage of not being shock sensitive. Other advantages include (a) less fluorine is required than in the fluorination reactions of Cl₂O which yield ClF₃ as a coproduct, (b) the great difference in the volatilities of the products FNO₂ and ClF₃O (ΔT_{bp} ~ 100°C) permits an easy separation by fractional condensation, (c) ClONO₂ can be prepared more conveniently, and (d) yields of ClF₃O are somewhat higher.

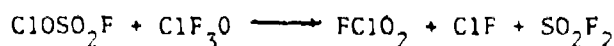
In the fluorination of ClONO₂, side reactions compete with the actual fluorination step. These are caused by thermal decomposition of the starting material due to inefficient removal of the heat of reaction. Hence, the rate of the competing reactions is markedly affected by the reaction temperature. At reaction temperatures near or above ambient, the decomposition of the hypochlorite appears to be favored and little or no ClF₃O is formed, resulting in rapid, rather uncontrolled reactions. Apparently, thermal decomposition

preceding the fluorination step yields only intermediates incapable of producing ClF_3O . Thus, in order to maximize the desired fluorination reaction, long reaction times at low temperature ($T < 0^\circ\text{C}$) are indicated.

Similarly, ClOSO_2F interacts with ClF_3O ^[18]



and



These reactions can be rationalized in terms of a reduction of ClF_3O to the unstable FClO which readily decomposes to FClO_2 and ClF (see Section 2.2.7.4)

2.2.7.6 By Reaction of Halogen Oxyacids and their Salts with Fluorinating Agents

Whereas the fluorination of halogen oxyacids generally results in the formation of the corresponding fluorooxy compounds^[39],



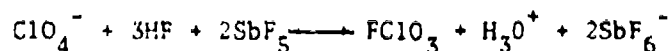
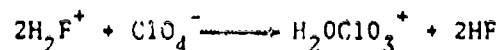
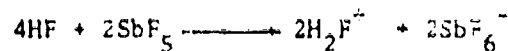
the fluorination of the salts of these halogen oxyacids is a more useful method for the synthesis of halogen oxyfluorides. The nature of the halogen oxyfluoride product depends on the starting material and on the reaction conditions chosen. Thus the fluorination of perchlorates can be used as a high yield synthesis of perchloryl fluoride. Heating of KClO_4 to $70^\circ - 120^\circ\text{C}$ in an excess of SbF_5 produces FClO_3 in 50% yield^[40]. The yield of FClO_3 can be increased to 90% and the reaction temperature can be lowered to $20^\circ - 50^\circ\text{C}$, when a mixture of $\text{HF} - \text{SbF}_5$ is used^[41]. Slightly lower yields were obtained when the HF solvent was replaced by AsF_5 , IF_5 , or BrF_5 .

Most of the commercial processes are based on the use of HOSO_2F ^[42]. Evolution of FClO_3 starts at 50°C and goes to completion at $85^\circ - 110^\circ\text{C}$. The yields of FClO_3 vary from 50 to 80%^[5,42-44] and, if necessary, the

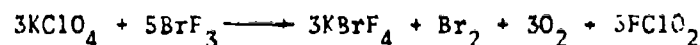
HOSO_2F can be regenerated^[43]. If desired, the reaction can be carried out in glass apparatus. The influence of certain additives on the yield of FClO_3 was studied^[45]. The addition of 5 to 25% of SbF_3 to the HOSO_2F increases the yield of FClO_3 to 90% and higher but hinders the regeneration of HOSO_2F . The addition of $\text{HF} - \text{BF}_3$ increases the FClO_3 yield to 85% but requires elevated pressure. Zinc, aluminum, silver, and lead fluorides were found to decrease the yield of FClO_3 .

The highest yield of perchloryl fluoride (97%) was achieved with a mixture of fluorosulfonic acid and SbF_5 as fluorinating medium. Potassium, sodium, lithium, magnesium, barium, calcium, and silver perchlorates and perchloric acid itself undergo the reaction. Commercial reagents are used and their additional purification is not necessary; unlike all the previous methods the preparation of perchloryl fluoride by this method can be carried out at room temperature. At high temperature ($100^\circ - 135^\circ\text{C}$) the reaction time is 1 — 10 min in all, which allows the process to be carried out continuously in a packed column. The purity of product obtained after the usual purification reaches 98% and over; air and carbon dioxide are present as trace impurities^[46].

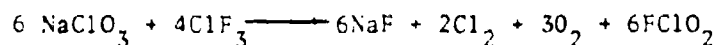
The exact mechanism of the reaction between ClO_4^- and superacids has as yet not been established, although numerous comments on it were published [12,41,47-50]. Based on the present understanding of superacid chemistry [51-53] and of the complex formation of FClO_3 , a mechanism involving ClO_3^+ as an intermediate is very unlikely. Furthermore, the high yields of FClO_3 (up to 97%) would be surprising in view of the expected instability of ClO_3^+ . Other mechanisms, such as the one shown, involving protonated perchloric acid^[54] are more plausible:



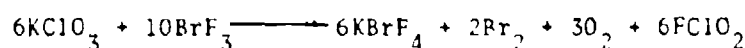
Other methods for the synthesis of FClO_3 from metal perchlorates include the electrolysis of a saturated solution of NaClO_4 in anhydrous HF with a current efficiency of 10%^[55] and the fluorination of NO_2ClO_4 by ClF_3 at room temperature which results in the formation of FClO_3 and smaller amounts of FClO_2 , ClO_2 and ClNO_2 ^[56]. The corresponding reaction of KClO_4 with BrF_3 was reported^[57] to yield FClO_2 in 97% yield.



If the MClO_4 starting material is replaced by MClO_3 , the main fluorination product is generally FClO_2 . For example, the reaction of NaClO_3 with an equimolar amount of ClF_3 produces FClO_2 in high yield^[57]. This method is based on previous reports^[55-58] that gaseous ClF_3 reacts with KClO_3 to give FClO_2 in high yield. The substitution of KClO_3 by NaClO_3 is significant since the product NaF does not form an adduct with ClF_3 , whereas KF does. This decreases by 60% the amount of ClF_3 required for the reaction. By analogy with the $\text{KClO}_3 + \text{BrF}_3$ reaction^[59], the idealized stoichiometry of the above reaction is



The use of a slight excess of ClF_3 is recommended to avoid the possible formation of shock-sensitive chlorine oxides. The $\text{KClO}_3 + \text{BrF}_3$ reaction^[59]

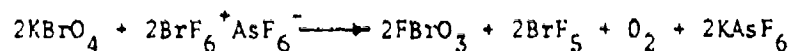
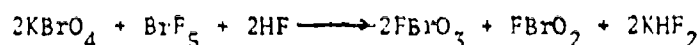
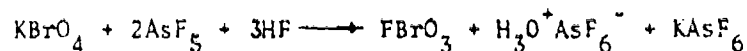


also produces FClO_2 in high yield, but it is difficult to obtain pure colorless FClO_2 by this method.

The fluorination of KClO_3 with elemental fluorine has also been studied [55 60-62], but is not synthetically useful for preparing FClO_2 due to the large amounts of FClO_3 always formed.

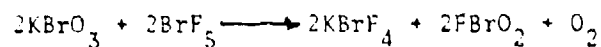
The low temperature fluorination of NaClO_2 with F_2 produces FClO_2 as the main product, however, small amounts of ClF_3O were also obtained in addition to ClF_3 , ClF and Cl_2 [9].

The fluorination of alkali metal perbromates with HF and Lewis acids is analogous to that of the perchlorates and produces FBrO_3 as the main product in high yield. The reactions were carried out in HF solution using SbF_5 , AsF_5 , BrF_5 or $\text{BrF}_6^+ \text{AsF}_6^-$.

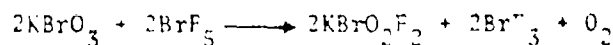


In the absence of HF, CsBrO_4 was found [25] to react with BrF_5 and F_2 at room temperature to produce CsBrF_4O as the solid and FBrO_3 and FBrO_2 as the volatile products. Potassium perbromate was less reactive than the cesium salt and required prolonged heating to 80°C to achieve a substantial conversion to KBrF_4O . In the absence of F_2 , the conversion of CsBrO_4 to CsBrF_4O was very low, even at 80°C , and was not catalyzed by HF.

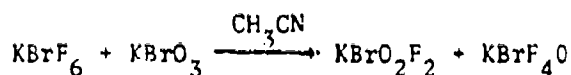
The reaction of KBrO_3 with BrF_5 is rather complex. According to the original report, [22] KBrO_3 reacts with BrF_5 at -50°C according to



Subsequent work [65] showed that the reaction of KBrO_3 with equimolar amounts of BrF_5 at room temperature proceeds according to



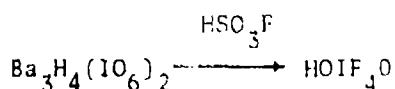
and that the reaction is rather slow when a large excess of BrF_5 is used. It was also reported^[66] that KBrO_3 and BrF_5 at a mole ratio of 1:2.5 did not react appreciably at room temperature, but that a rapid reaction occurred when catalytic amounts of HF were added. The solid product of this reaction consisted of KBrO_2F_2 and KBrF_4O , and FBrO_2 was produced as the volatile product. The possible formation of KBrF_4O in this system was established^[61] by showing that the use of a large excess of BrF_5 and F_2 at 80°C can result in quantitative formation of KBrF_4O . This reaction, however, can be difficult to duplicate and can easily result in the formation of KBrF_4 ^[25]. The $\text{KBrO}_3 + \text{BrF}_5$ reaction was further modified⁶⁶ by reacting KBrF_6 with KBrO_3 in CH_3CN solution.



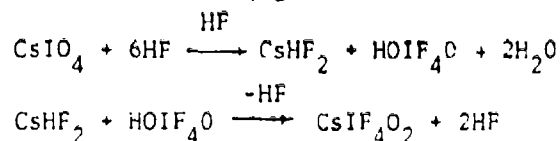
The KBrF_4O produced is slightly soluble in CH_3CN , whereas KBrO_2F_2 is not. Therefore, the two products can be separated by extraction with CH_3CN .

From a mechanistic point of view, the reactions of BrF_5 with BrO_3^- or BrO_4^- are very interesting since they involve an oxygen-fluorine exchange. On the basis of the observed quantitative yields of BrF_4O^- , a free radical mechanism involving the addition of oxygen atoms to bromine fluorides is extremely unlikely. A mechanism involving the addition of BrF_5 or BrF_6^- across a $\text{Br}=\text{O}$ double bond of BrO_4^- or BrO_3^- , followed by FBrO_3 or FBrO_2 elimination with BrF_4O^- formation, appears plausible, but requires further experimental support.

The fluorination of periodates has also been studied in detail. For example, $\text{Ba}_3\text{H}_4(\text{IO}_6)_2$ is fluorinated by HSO_3F to tetrafluoro orthoperiodic acid^[37].



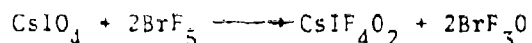
The same compound is also formed from solutions of HIO_3 or NaIO_4 in anhydrous HF. [68] When CsIO_4 is repeatedly treated with anhydrous HF and the solvent is pumped off, the less volatile acid HOIF_4O displaces HF from the CsHF_2 with quantitative formation of CsIF_4O_2 (cis:trans $\approx$ 2:1). [69] This reaction represents a convenient synthesis for IF_4O_2^- salts.



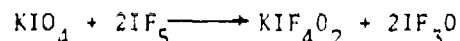
With elemental fluorine at 60°C , CsIO_4 was converted [69] to mainly CsIF_8 and CsIF_6 , but the product also contained lesser amounts of CsIF_4O and cis- and trans- CsIF_4O_2 . With a large excess of ClF_5 at room temperature, CsIO_4 was slowly converted to CsIF_8 , trans CsIF_4O_2 and some CsIF_4O . With the more reactive fluorinating agent ClF_3 , complete conversion of CsIO_4 was obtained at ambient temperature according to:



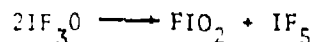
With BrF_5 the main reaction can be described by



This reaction is analogous to that reported [70] for KIO_4 and IF_5 , i.e.



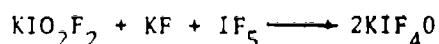
and produces almost entirely trans IF_4O_2^- . Under the experimental conditions (120°C , vacuum) used for the removal of the excess IF_5 , the IF_3O disproportionates according to



resulting in FIO_2 and KIF_4O_2 as the final products. Compared to the IF_5 reaction, the BrF_5 reaction offers the advantage that the BrF_3O and BrF_5 by-

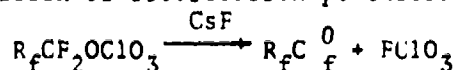
products are volatile and can easily be pumped off. However, the resulting solid product is contaminated with CsBrF_4 .

The fluorination of iodates has also been studied. Whereas the fluorination of HIO_3 in aqueous HF results in the formation of the IO_2F_2^- anion [71], solutions of NaIO_3 in anhydrous HF contain IF_5 [13]. With IF_5 as a fluorinating agent, MIO_3 or KIO_2F_2 produced the corresponding IF_4O^- salts [72].

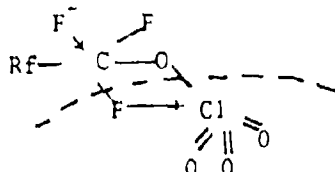


2.2.7.7 By Elimination Reactions

Very little is known on reactions involving the elimination of halogen oxyfluorides. The only reaction reported in the literature is the CsF catalyzed FCIO_3 elimination of fluorocarbon perchlorates [73].



This reaction proceeds at 60°C in nearly quantitative yield and probably involves the attack of the CF_2 carbon atom by the fluoride anion, followed by an internal nucleophilic displacement reaction and FCIO_3 elimination.



The reactions of BrF_5 with BrO_3^- or BrO_4^- (see Section 2.2.7.6) may also involve similar intermediates which decompose with FBrO_2 or FBrO_3 elimination. However, these intermediates have as yet not been isolated.

REFERENCES

- [1] H. Schmitz and H. J. Schumacher, Z. Anorg. Allg. Chem., 249, 238 (1942).
- [2] P. J. Aymonino, J. E. Sicre, and H. J. Schumacher, J. Chem. Phys., 22, 756 (1954).
- [3] J. E. Sicre and H. J. Schumacher, Z. Anorg. Allg. Chem., 286, 232 (1956).
- [4] M. Schmeisser and F. L. Ebenhöch, Angew. Chem., 66, 230 (1954).
- [5] W. Kwasnick in "Handbook of Preparative Inorganic Chemistry" (G. Brauer, ed.), 2nd ed., Vol. 1, p 1-5, Academic Press, New York, 1963.
- [6] A. J. Arvia and P. J. Aymonino, Spectrochim. Acta, 19, 1449 (1963).
- [7] A. J. Arvia, W. H. Basualdo, and H. J. Schumacher, Z. Anorg. Allg. Chem., 286, 58 (1956).
- [8] R. V. Figini, E. Goloccia, and H. J. Schumacher, Z. Phys. Chem. (Frankfurt am Main) [N.S] 14, 32 (1958).
- [9] D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, Inorg. Chem., 11, 2189 (1972).
- [10] K. O. Christe, C. J. Schack, and D. Pilipovich, Inorg. Chem., 11, 2205 (1972).
- [11] M. Schmeisser and E. Pammer, Angew. Chem., 67, 156 (1955).
- [12] M. Schmeisser and K. Brändle, Adv. Inorg. Chem. Radiochem., 5, 41 (1963).
- [13] H. Selig and U. El-Gad, J. Inorg. Nucl. Chem., 35, 3517 (1973).
- [14] M. Schmeisser and K. Fink, Angew. Chem., 69, 780 (1957).
- [15] Y. Macheteau and J. Gillardeau, Bull. Soc. Chim. Fr., 4075 (1967).
- [16] J. Gillardeau and Y. Macheteau, French Patent 1,527,112 (1968).
- [17] K. O. Christe, Inorg. Chem., 11, 1220 (1972).
- [18] C. J. Schack, C. B. Lindahl, D. Pilipovich and K. O. Christe, Inorg. Chem., 11, 2201 (1972).
- [19] R. Weiss, Ph.D. Thesis, Techn. University, Aachen, Germany (1959).
- [20] M. Schmeisser, Angew. Chem., 67, 493 (1955).
- [21] A. C. Pavia, J. L. Pascal and A. Potier, C. R. Acad. Sci., Ser. C 272, 1495 (1971).

- [22] M. Schmeisser and E. Pammer, *Angew. Chem.*, 69, 781 (1957).
- [23] M. Schmeisser and L. Taglinger, *Chem. Ber.*, 94, 1533 (1961).
- [24] E. E. Aynsley, R. Nichols and P. L. Robinson, *J. Chem. Soc.* 623 (1953);
E. E. Aynsley, *J. Chem. Soc.*, 2425 (1958); E. E. Aynsley and M. L. Hair,
J. Chem. Soc., 3747 (1958).
- [25] K. O. Christe, R. D. Wilson, E. C. Curtis, W. Kuhlmann and W. Sawodny,
Inorg. Chem., 17, 533 (1978).
- [26] K. O. Christe, *Inorg. Chem.*, 12, 1580 (1973).
- [27] K. O. Christe and R. D. Wilson, *Inorg. Chem.*, 12, 1356 (1973).
- [28] D. Pilipovich, H. H. Rogers and R. D. Wilson, *Inorg. Chem.*, 11, 2192
(1972).
- [29] R. Bougon, J. Isabey and P. Plurien, *C. R. Acad. Sci., Ser. C* 271, 1366
(1970).
- [30] K. Züchner and O. Glemser, *Angew. Chem.*, 84, 1147 (1972).
- [31] K. O. Christe and C. J. Schack, *Adv. Inorg. Chem. Radiochem.*, 18, 319
(1976).
- [32] A. E. Axworthy, K. H. Mueller, and R. D. Wilson, "Photochemistry of
Interest as Rocket Propellants," Final Report on Contract No. AFOSR-
TR-73-2183 (1973).
- [33] R. Gatti, E. Stavicco, J. E. Sicre and H. J. Schumacher, *Z. Phys. Chem.*
(Frankfurt am Main) N.S. 23, 164 (1960).
- [34] M. Adelhelm and E. Jacob, *Angew. Chem., Intern. Ed. Engl.*, 16, 461 (1977).
- [35] R. J. Gillespie and P. Spekkens, *J. Chem. Soc. Dalton Trans.*, 1539 (1977).
- [36] R. J. Gillespie and P. H. Spekkens, *Israel J. Chem.*, 17, 11 (1978);
R. Bougon, T. Bui Huy, P. Charpin, R. J. Gillespie, and P. H. Spekkens,
J. Chem. Soc. Dalton, 6 (1979).
- [37] A. Engelbrecht and P. Peterfy, *Angew. Chem., Internat. Edit. Engl.*,
8, 768 (1969); A. Engelbrecht, P. Peterfy and E. Schandara, *Z. Anorg.*
Allg. Chem., 384, 202 (1971).
- [38] T. D. Cooper, F. N. Dost and C. H. Wang, *J. Inorg. Nucl. Chem.*, 34,
3564 (1972).
- [39] G. H. Rohrback and G. H. Cady, *J. Amer. Chem. Soc.*, 69, 677 (1947).
- [40] A. Engelbrecht, U. S. Patent, 2,942,947 (1960).

- [41] C. A. Wamser, W. B. Fox, D. Gould, and B. Sukornick, Inorg. Chem., 7, 1933 (1968); C. A. Wamser, B. Sukornick, W. B. Fox and D. Gould, Inorg. Syn., 14, 29 (1973).
- [42] G. Barth - Wehrenalp, J. Inorg. Nucl. Chem., 2, 266 (1956).
- [43] G. Barth - Wehrenalp, U. S. Pat., 2,942,948 (1960).
- [44] W. Lalande, U. S. Pat., 2,982,617 (1961).
- [45] H. Dess, U. S. Pat., 2,982,618 (1961).
- [46] G. Barth - Wehrenalp and H. Mandell, U. S. Pat., 2,942,949 (1960).
- [47] J. Barr, R. J. Gillespie, and R. C. Thompson, Inorg. Chem., 3, 1149 (1964).
- [48] G. Barth - Wehrenalp, J. Inorg. Nucl. Chem., 4, 374 (1957).
- [49] K. Lang, Ph.D. Thesis, University of Munich, Germany (1956).
- [50] A. A. Woolf, J. Inorg. Nucl. Chem., 3, 250 (1956).
- [51] K. O. Christe, C. J. Schack, and R. D. Wilson, Inorg. Chem., 14, 2224 (1975).
- [52] R. J. Gillespie, Accounts Chem. Res., 1, 202 (1968).
- [53] G. A. Olah, A. M. White and D. H. O'Brien, Chem. Rev., 70, 561 (1970).
- [54] K. Lang, Diploma Thesis, University of Munich, Germany (1955).
- [55] A. Engelbrecht and H. Atzwanger, Monatsh. Chem., 83, 1087 (1952); J. Inorg. Nucl. Chem., 2, 348 (1956).
- [56] A. W. Beardell and C. J. Grelecki, U. S. Pat. 3,404,958 (1968).
- [57] K. O. Christe, R. D. Wilson and C. J. Schack, Inorg. Nucl. Chem. Lett., 11, 161 (1975).
- [58] D. F. Smith, G. M. Begun and W. H. Fletcher, Spectrochim. Acta, 20, 1763 (1964).
- [59] A. A. Woolf, J. Chem. Soc., 4113 (1954).
- [60] H. Bode and E. Klesper, Angew. Chem., 66, 605 (1954).
- [61] A. Engelbrecht, Angew. Chem., 66, 442 (1954).

- [62] J. E. Sicre and H. J. Schumacher, *Angew. Chem.*, 69, 226 (1957).
- [63] E. H. Appelman and M. H. Studier, *J. Am. Chem. Soc.*, 91, 4561 (1969).
- [64] P. Spekkens, Ph.D. Thesis, McMaster University, Hamilton, Ontario, Canada, 1977.
- [65] R. Bougon and G. Tantot, *C. R. Acad. Sci., Ser. C*, 281, 271 (1975).
- [66] R. J. Gillespie and P. Spekkens, *J. Chem. Soc. Dalton Trans.*, 2391 (1976).
- [67] R. Bougon, T. Bui Huy, P. Charpin and G. Tantot, *C. R. Acad. Sci., Ser. C* 283, 71 (1976).
- [68] H. Selig and U. Elgad, *J. Inorg. Nucl. Chem. Suppl.* 91 (1976).
- [69] K. O. Christe, R. D. Wilson and C. J. Schack, *Inorg. Chem.*, in press.
- [70] R. J. Gillespie and J. P. Krasznai, *Inorg. Chem.*, 16, 1384 (1977).
- [71] J. B. Milne and D. Moffett, *Inorg. Chem.*, 14, 1077 (1975).
- [72] J. B. Milne and D. M. Moffett, *Inorg. Chem.*, 15, 2165 (1976).
- [73] C. J. Schack, D. Pilipovich and J. F. Hon, *Inorg. Chem.*, 12, 897 (1973).

Compound Index Entries

2.2.7.1

Empirical

Linearized Structural

Context

Formulas

Formulas



Reaction with F_2



Reaction with F_2



Reaction with F_2



Formation



Reaction with F_2



Formation



Formation



Formation



Reaction with F_2



Formation



Reaction with F_2



Formation



Reaction with HF



Formation

2.2.7.2



Reaction with AbF_2



Reaction with CoF_3



Formation



Reaction with BrF_3



Reaction with AgF_2



Reaction with ClF



Reaction with ClF_3O

ClFO	FCIO	Formation
Cl ₂ O ₆	Cl ₂ O ₆	Reaction with BrF ₃
Cl ₂ O ₆	Cl ₂ O ₆	Reaction with BrF ₅
Cl ₂ O ₆	Cl ₂ O ₆	Reaction with HF
Cl ₂ O ₆	Cl ₂ O ₆	Reaction with FNO ₂
ClNO ₆	NO ₂ ClO ₄	Formation
BrO ₂	BrO ₂	Reaction with BrF ₅
BrFO ₂	FBrO ₂	Formation
I ₂ O ₅	I ₂ O ₅	Reaction with IF ₅
F ₃ IO	IF ₃ O	Formation
F ₄ IKO	KIF ₄ O	Formation

2.2.7.3

ClFO ₂	FCIO ₂	Reaction with PtF ₆
ClF ₈ O ₂ Pt	ClF ₂ O ₂ PtF ₆	Formation
ClF ₈ O ₂ Pt	ClF ₂ O ₂ PtF ₆	Reaction with FNO ₂
ClF ₃ O ₂	ClF ₃ O ₂	Formation
ClF ₃ O	ClF ₃ O	Formation
ClF ₃	ClF ₃	Reaction with OF ₂
ClF ₅	ClF ₅	Reaction with OF ₂
ClF ₅ O	ClF ₅ O	Formation
ClF ₃	ClF ₃	Photolysis in presence of O ₂
ClF ₃ O	ClF ₃ O	Kinetics of formation
F ₅ IO	IF ₅ O	Formation of ClF ₃ O
ClFO ₃	FCIO ₃	Formation of ClF ₃ O
BrFO ₂	FBrO ₂	Reaction with KrF ₂

BrFO₂
 BrF₈O_{Pt}
 BrF₆O₂Pt
 BrF₂O₂⁺
 BrFO₂
 BrF₃O
 BrFO₃
 BrF₃O
 BrF₅
 I₂O₅
 FIO₂
 F₃IO
 F₃IO₂
 F₅IO
 AsF₈IO₂
 AsBrF₈O
 F₃IO₂
 F₄HIO₂

2.2.7.4

ClFO
 ClFO₂
 ClF
 F₃IO
 F₅I
 FIO₂

FBrO₂
 BrF₂O_{PtF}₆
 BrO₂PtF₆
 BrF₂O₂⁺
 FBrO₂
 BrF₃O
 FBrO₃
 BrF₃O
 BrF₅
 I₂O₅
 FIO₂
 IF₃O
 IF₃O₂
 IF₅O
 IF₃O₂·AsF₅
 BrF₂OAsF₆
 IF₃O₂
 OIF₄OH

FCIO

FCIO₂
 ClF
 IF₃O
 IF₅
 FIO₂

Reaction with PtF₆
 Formation
 Formation
 Formation
 Reaction with KrF₂
 Reaction with KrF₂
 Reaction with KrF₂
 Formation
 Formation
 Reaction with BrF₅
 Reaction with BrF₅
 Reaction with BrF₅
 Reaction with BrF₅
 Formation
 Reaction with BrF₅
 Formation
 Reaction with HF
 Formation

Disproportionation

Formation

Formation

Disproportionation

Formation

Formation

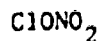


Disproportionation

2.2.7.5



Formation



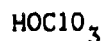
Reaction with F_2



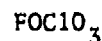
Reaction with ClOSO_2F



Formation



Reaction with F_2



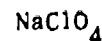
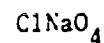
Formation



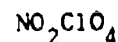
Formation



Fluorination of



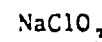
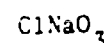
Electrolysis in HF



Reaction with ClF_3



Reaction with BrF_3



Reaction with ClF_3



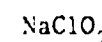
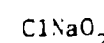
Reaction with ClF_3



Reaction with BrF_3



Reaction with F_2



Reaction with F_2



Formation



Formation



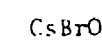
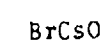
Reaction with BrF_5



Reaction with AsF_5



Reaction with BrF_6AsF_6



Reaction with BrF_5 and F_2

BrCsF_4O	CsBrF_4O	Formation
BrFO_3	FBrO_3	Formation
BrFO_2	FBrO_2	Formation
BrKO_4	KBrO_4	Reaction with BrF_5 and F_2
BrKO_3	KBrO_3	Reaction with BrF_5
BrF_2KO_2	KBrO_2F_2	Formation
BrF_4KO	KBrF_4O	Formation
BrKO_3	KBrO_3	Reaction with KBrF_6
$\text{Ba}_3\text{H}_4\text{I}_{12}\text{O}_{12}$	$\text{Ba}_3\text{H}_4(\text{IO}_6)_2$	Reaction with HSO_5F
F_4HIO_2	HOIF_4O	Formation
INaO_4	NaIO_4	Reaction with HF
HIO_4	HOIO_3	Reaction with HF
CsIO_4	CsIO_4	Reaction with HF
CsF_4IO_2	CsIF_4O_2	Formation
CsIO_4	CsIO_4	Reaction with F_2
CsF_4IO	CsIF_4O	Formation
CsIO_4	CsIO_4	Reaction with ClF_5
CsIO_4	CsIO_4	Reaction with ClF_3
CsIO_4	CsIO_4	Reaction with BrF_5
BrF_3O	BrF_3O	Formation
IKO_4	KIO_4	Reaction with IF_5
F_3IO	IF_3O	Formation
F_4IKO_2	KIF_4O_2	Formation
F_3IO	IF_3O	Disproportionation
FIO_2	FIO_2	Formation

HIO_3	HIO_3	Reaction with HF
INaO_3	NaIO_3	Reaction with HF
IKO_3	KIO_3	Reaction with IF_5
CsIO_3	CsIO_3	Reaction with IF_5
F_2IKO_2	KIF_2O_2	Reaction with IF_5
CsF_4IO	CsIF_4O	Formation
F_4IKO	KIF_4O	Formation
2.2.7.7		
ClFO_3	FCIO_3	Formation
ClFO_3	FCIO_3	Elimination reactions
BrFO_3	FBrO_3	Elimination reactions
BrFO_2	FBrO_2	Elimination reactions

APPENDIX M
Energetic Materials Research

DISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Code 473 Arlington, VA 22217 Attn: Dr. R. Miller	10	Office of Naval Research San Francisco Area Office 760 Market Street Room 447 San Francisco, CA 94102 Attn: Dr. P. A. Miller	1
Office of Naval Research Western Office 1030 East Green Street Pasadena, CA 91106 Attn: Dr. T. Hall	1	Dr. H. G. Adolph Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910	1
Office of Naval Research Eastern/ Central Regional Office 495 Summer Street Boston, MA 02210 Attn: Dr. L. Pebbles Dr. A. Wood	2	Dr. R. Bernecker Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910	1
Defense Documentation Center Bldg 5 Cameron Station Alexandria, VA 22314	12	Dr. J. W. Enig Naval Surface Weapons Center Code R10 White Oak, Silver Spring, MD 20910	1
Dr. William Tolles Dean of Research Naval Postgraduate school Monterey, CA 93940	1	Dr. M. J. Kamlet Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910	1
Dr. J. Schnur Naval Research Lab. Code 6510 Washington, D.C. 20375	1	Dr. D. J. Pastine Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910	1
Naval Air Systems Command Code 330D Washington, D.C. 20360 Attn: Mr. R. Heitkotter	1	Dr. E. Zimet Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910	1
Naval Air Systems Command Code 10C Washington, D.C. 20360 Attn: Dr. H. Mueller Dr. H. Rosenwasser	1	Mr. G. L. MacKenzie Naval Surface Weapons Center Code R101 Indian Head, MD 20640	1
Naval Sea Systems Command Washington, D.C. 20362 Attn: Mr. J. Murrin, Code 62R2 Mr. W. Blaine, Code 62R Mr. G. Edwards, Code 62R3	1	Mr. H. Haiss Naval Surface Weapons Center Code R22 Indian Head, MD 20640	1
		Dr. K. F. Mueller Naval Surface Weapons Center Code R11 Indian Head, MD 20640	1

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. T. D. Austin	1	Naval Weapons Center	1
Naval Surface Weapons Center		China Lake, CA 93555	
Code R22		Attn: Dr. W. Norris, Code 385	
Indian Head, Md 20640			
Naval Surface Weapons Center		Commander	1
White Oak		Army Msl Rsch & Dev Comd	
Silver Spring, MD 20910		Attn: Dr. R. G. Rhoades,	
Attn: Mr. L. Roslund, Code R12		Code DRMDI-TK	
		Redstone Arsenal, AL 35809	
Naval Surface Weapons Center	1	HQ US Army Mat Dev-Readiness Com	1
White Oak		Attn: Mr. S. R. Matos,	
Silver Spring, MD 20910		Code DRCDE-DW	
Attn: Mr. M. Stosz, Code R12		5011 Eisenhower Ave. Rm 8N42	
		Alexandria, VA 22333	
Naval Sea Systems Command	1	Commander	1
Washington, D.C. 20362		ATSC	
Attn: Mr. R. Beabregard SEA 64E		Attn: Mr. Richard Smith,	
Naval Ordnance Station	1	Code DLFP	
Code 5034		Andrews AFB	
Indian Head, MD 20640		Washington, D.C. 20334	
Attn: Mr. S. Mitchell			
Naval Weapons Center	1	Commander	1
China Lake, CA 93555		AFRPL	
Attn: Dr. L. Smith, Code 3205		Attn: Dr. R. R. Weiss, Code CA	
		Edwards AFB, CA 93523	
Naval Weapons Center	2	Code AFRPL MKPA	3
China Lake, CA 93555		Edwards Air Force Base, CA 93523	
Attn: Dr. C. Thelen, Code 3205		Attn: Dr. F. Roberto	
Naval Weapons Center	3	Dr. C. Merrill	
China Lake, CA 93555		Lt. S. Clift	
Attn: Dr. A. Amster, Code 385		Mr. R. Geisler	
Naval Weapons Center	3	U.S. Army Research Office	1
China Lake, CA 93555		Chemistry Division.	
Attn: D. R. Derr, Code 388		P.O. Box 12211	
		Research Triangle Park, NC 27709	
Naval Weapons Center	1	Johns Hopkins University APL	1
China Lake, CA 93555		Chemical Propulsion Inform.	
Attn: Dr. R. Reed Jr., Code 388		Agency	
Naval Weapons Center	1	John Hopkins Road	
China Lake, CA 93555		Laurel, MD 20810	
Attn: Dr. A. Nielsen, Code 385		Attn: Mr. Theodore M. Gilliland	
Naval Weapons Center		Air Force of Scientific Research	1
China Lake, CA 93555		Directorate of Chemical Sciences	
Attn: Mr. H. Richter, Code 3858		Bolling Air Force Base	
		Washington, D.C. 20332	

	<u>No. Copies</u>		<u>No. Copies</u>
Air Force Office of Scientific Research Directorate of Aerospace Sciences Bolling Air Force Base Washington, D.C. 20332	1	Hercules Inc. Eglin AFATL/DLDEL Attn: Dr. Ronald L. Simmons Eglin, AFB, FL 32542	1
Commander Army Ballistic Rsch Labs Attn: Mr. L. A. Watermeier, Code DRDAR-BLP Aberdeen Proving Ground, MD 21005	1	Hercules In. Magna Bacchus Works Attn: Mr. E. H. DeButts P.O. Box 98 Magna, UT 94044	1
Commander Army Ballistic Rsch Labs Attn: Dr. Ingo W. May Code DRDAR-BLP Aberdeen Proving Ground, MD 21005	1	Hercules Magna Bacchus Wor Attn: Dr. James H. Thacher P.O. Box 98 Magna, UT 84044	1
Commander AFATL Attn: Dr. Otto K. Heiney Eglin AFB, FL 32542	1	Lockheed Msl & Space Co. Inc. Attn: Dr. H. P. Marshall Dept. 52-35 3251 Hanover St. Palo Alto, CA 94304	1
Atlantic Research Corp. Attn: Dr. C. B. Henderson 5390 Cherokee Ave. Alexandria, VA 22314	1	Thiokol Chem Corp. Brigham City Wasatch Div. Attn: Dr. G. Thompson Brigham City, UT 84302	1
Commander Armament Rsch & Dev Com Attn: Dr. R. Walker Dover, NJ 07801	3	Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. J. Kury	1
Commander Ballistic Msl Def Adv Technology Ctr Attn: Dr. David C. Sayles P.O. Box 1500 Huntsville, AL 35807	1	Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. R. McGuire	1
Hercules Inc. Cumberland Aerospace Div Allegany Ballistics Lab Attn: Dr. Rocco Musso P.O. Box 210 Cumberland, MD 21502	2	Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. R. Rogers, WX-2	1
Army Research Office P.O. Box 1011 Research Triangle Park, N.C. 27700 Attn: Dr. S. Spielvogel Chemical Division	20	Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. B. Craig, M Division	1

	<u>No. Copies</u>		<u>No. Copies</u>
Rohm and Haas Company 723-A Arcadia Circle Huntsville, AL 35801 Attn: Dr. H. Shuey	1	University of Massachusetts Department of Chemistry Amherst, MA 03003 Attn: Professor J. C. Chien	1
Strategic Systems Project Office Department of the Navy Room 901 Washington, D.C. 20376 Attn: Dr. J. F. Kincaid	1	Univ. of Illinois at Chicago Circle Department of Chemistry Box 4348 Chicago, IL 60680 Attn: Professor J. H. Boyer	1
Strategic Systems Project Office Department of the Navy Room 1048 Washington, D.C. 20376 Attn: Mr. E. L. Throckmorton	1	Fluorechem, Inc. 680 South Ayon Avenue Azusa, CA 91702 Attn: Dr. Kurt Baum	1
Anal-Syn Lab Inc. P.O. Box 547 Paoli, PA 19301 Attn: Dr. V. J. Keenan	1	Polysciences, Inc. Paul Valley Industrial Park Harrington, PA 18976 Attn: Dr. B. David Halpern	1
Rockwell International Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91304 Attn: Dr. Karl O. Christe	1	Office of Naval Research 800 N. Quincy Street Arlington, VA 22217 Attn: Dr. G. Neece Code 472	1
Rockwell International Rocketdyne Division 6633 Canoga Avenue Canoga Park, CA 91304 Attn: Dr. M. B. Frankel	1	University of Massachusetts Department of Chemistry Amherst, MA 03003 Attn: Professor P. Lillya	1
SRI International 333 Ravenswood Avenue Menlo Park, CA 94025 Attn: Dr. D. L. Ross	1	Naval Weapons Support Center Code 5042 Crane, IN 47522 Attn: Dr. B. Dowda	1
		Johns Hopkins University Department of Chemistry Baltimore, MD 21218 Attn: Dr. Joyce J. Kaufman	1