INORGANIC HALOGEN OXIDIZERS
ANNUAL REPORT
(1 April 1970 through 31 March 1971)
Inorganic Halogen Oxidizers Annual Report

Abstract

New covalent inorganic perchlorates were prepared from chlorine perchlorate. The compound \( \text{IClO}_4 \) was partially characterized and \( \text{NClO}_4 \) deduced as a primary reaction product. The one-valent iodine perchlorate could not be prepared and the new complex perchlorate, \( \text{CsI(ClO}_4 \) was synthesized. The action of \( \text{CISO}_3 \text{F} \) and \( \text{I}_2 \) produces a variety of iodine fluorosulfates. One partially characterized species is \( \text{OF}_2 \text{SO}_3 \text{F} \). Fluorosulfates of nitrogen could not be made from the reaction of \( \text{NCI}_3 \) and \( \text{CISO}_3 \text{F} \). Neither chlorine perbromate nor chlorine bromate could be isolated from reactions of \( \text{SCl}_2 \text{O}_4 \) with appropriate salts. Based on the nature of the products obtained, a reaction sequence was constructed consistent with the intermediacy of \( \text{CINO}_3 \). The new chlorofluorine of selenium, \( \text{SeF}_2 \text{Cl} \), was prepared from \( \text{CSF}_3 \) and \( \text{CISO}_3 \text{F} \). Extensive data on \( \text{SeF}_2 \text{Cl} \) are reported. The study of the reaction of all the chlorine fluorides and \( \text{HNO}_3 \) was completed. No nitrate derivatives of chlorine other than \( \text{CINO}_3 \) could be formed. Complete vibrational data have been detailed and reported for a number of species, the crystal structure of \( \text{BrF}_4 \text{Sb}_2 \text{F}_{11} \) has been determined.
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The research reported herein was supported by the Office of Naval Research, Power Branch, Code 429, with Mr. Richard L. Hanson as Scientific Officer. This report covers the period 1 April 1970 through 31 March 1971. The program has been directed by Dr. D. Pilipovich, Manager, Exploratory Chemistry. Staff members responsible for the scientific effort were Dr. K. O. Christe, Dr. C. J. Schack, Mr. R. D. Wilson, Dr. E. C. Curtis, Dr. J. F. Hon, and Dr. D. M. Lind. The Program Manager was Dr. E. A. Lawton.
New covalent inorganic perchlorates were prepared from chlorine perchlorate. The compound \( \text{I(CIO}_4\text{)}_3 \) was partially characterized and \( \text{N(CIO}_4\text{)}_3 \) deduced as a primary reaction product. The one-valent iodine perchlorate could not be prepared and the new complex perchlorate, \( \text{CsI(CIO}_4\text{)}_4 \), was synthesized.

The action of \( \text{ClSO}_3\text{F} \) and \( \text{I}_2 \) produces a variety of iodine fluorosulfates. One partially characterized species is \( \text{OIF}_2\text{SO}_3\text{F} \). Fluorosulfates of nitrogen could not be made from the reaction of \( \text{NCl}_3 \) and \( \text{ClSO}_3\text{F} \).

Neither chlorine perbromate nor chlorine bromate could be isolated from reactions of \( \text{Cl}_2\text{O}_4 \) with appropriate salts. Unstable primary reactions products were formed that decomposed to bromine oxides.

The reaction of \( \text{ClSO}_3\text{F} \) and metal periodates gives \( \text{I}_2\text{SO}_3\text{F} \) which is apparently a covalent peroxide. Its decomposition to \( \text{I}_2\text{SO}_3\text{F} \) and \( \text{O}_2 \) was quantitative. Further, the oxygen is quite labile and \( \text{I}_2\text{SO}_3\text{F} \) is an effective oxygenating agent in that perfluoroalkylene oxides could be readily formed from it and fluoroolefins at low temperatures.

Iodyl fluorosulfate and \( \text{F}_2 \) at ambient temperature give \( \text{SO}_3\text{F}_2 \), \( \text{IF}_5\text{O} \), and \( \text{IF}_7 \). The covalent nature of \( \text{I}_2\text{SO}_3\text{F} \) was supported by the formation of \( \text{SO}_3\text{F}_2 \). The use of \( \text{SF}_4 \) as a fluorinating agent toward \( \text{I}_2\text{SO}_3\text{F} \) resulted in the formation of \( \text{IF}_5 \) and \( \text{S}_2\text{O}_5\text{F}_2 \).

The synthesis of \( \text{ClI}_6 \) could not be effected through the reaction of \( \text{Cl}_2\text{O}_4 \) and \( \text{O}_2\text{AsF}_6 \). Based on the nature of the products obtained, a reaction sequence was constructed consistent with the intermediacy of \( \text{ClI}_6 \).
The new chlorofluoride of selenium, SeF$_5$Cl, was prepared from CsSeF$_5$ and ClSO$_3$F. Extensive data on SeF$_5$Cl are reported and include synthesis, vibrational spectrum, force constants, and thermodynamic properties.

The study of the reaction of all the chlorine fluorides and HNO$_3$ was completed. No nitrate derivatives of chlorine other than ClNO$_3$ could be formed.

Complete vibrational data have been detailed and reported for a number of species, including ClO$_2$F$_2^-$, SF$_4$, BrF$_3$, N$_2$F$,^+$, halogen perchlorates, and the group SF$_5^-$, SeF$_5^-$, TeF$_5^-$. In addition, the crystal structure of BrF$_4^+$Sb$_2$F$_{11}^-$ has been determined.
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INTRODUCTION

Traditionally, this program has been primarily involved with a fundamental study in fluorine chemistry. Particular emphasis had been placed on the development of new synthetic techniques and the subsequent application of these techniques in seeking new chemical species. During the past several years, a new dimension was added with the discovery of chlorine perchlorate, Cl$_2$O$_4$. This intermediate arose through our studies involving the reactions of positive chlorine species such as ClF and ClSO$_3$F.

The availability of a novel chemical such as Cl$_2$O$_4$ provided the impetus for studying the syntheses of new perchlorates. Initially, there was demonstrated the formation of new covalent perchlorate derivatives of fluorocarbons. Subsequently, the pursuit of inorganic covalent perchlorates was initiated. A modicum of success was achieved though the synthesis of I(ClO$_4$)$_3$ and its complex ion, I(ClO$_4$)$_4$. Parallel with the study of I(ClO$_4$)$_3$ was the reactions aimed at chemicals such as N(ClO$_4$)$_3$ and N(SO$_3$F)$_3$. In addition, positive halogenation reactions were continued in seeking both covalent perbromates, such as ClOBrO$_3$, and ternary halogen compounds. The latter pursuit is quite a fascinating area and our initial efforts here describe the use of a positive chlorine donor in seeking BrF$_4$Cl.

As in the past, the format of this report contains a section describing work in progress and extensive appendixes of work in manuscript form. These manuscripts, for the most part, involve the structural verification of many of the chemicals utilized in our synthetic studies. An example of how this fits in with the synthetic work can be shown using the ion ClO$_2$F$_2$. Our principal involvement with the chemical CsClO$_2$F$_2$ is to study its use as an intermediate in synthesizing new chlorine oxyfluorides. However, preparatory to this study is the requirement of structural and chemical attributes of the salt so that optimum reactions can be chosen and that a facile interpretation of the results can follow.

The report, we feel, covers a broad spectrum of fundamental activity and perhaps is more reflective of the title than in the past. Indeed our work deals with oxidizing species, certainly inorganic, and extensively with halogen species.
DISCUSSION

REACTION OF CHLORINE PERCHLORATE WITH OTHER HALOGENS

The discovery of chlorine perchlorate was reported in the preceding annual report (Ref. 1). Some of the interesting reactions of CIOC10\textsubscript{3} were also described at that time, notably, its usefulness in forming BrOC10\textsubscript{3} and several fluorocarbon perchlorates. In the case of the BrOC10\textsubscript{3} synthesis, chlorine perchlorate was used to oxidize elemental bromine to the +I oxidation state.

\[ \text{Br}_2 + 2\text{ClOC10}_3 \rightarrow \text{Cl}_2 + 2\text{BrOC10}_3 \]

Stoichiometric amounts of CIOC10\textsubscript{3} were always used and thus no attempt to achieve further oxidation of the Br\textsubscript{2} was made. This has now been done with the goal of preparing Br(OC10\textsubscript{3})\textsubscript{3}. Since related compounds of bromine with electronegative ligands are more stable in the +III oxidation state than in the +I state (e.g., BrF\textsubscript{3} vs BrF), it was hoped that the tris-perchlorate might have enhanced stability relative to the mono substituted material. However, when excess CIOC10\textsubscript{3} was reacted with Br\textsubscript{2} at -45 C, a quantitative yield of BrOC10\textsubscript{3} was obtained. When the reaction temperature was raised to about -20 C, there occurred a gradual decomposition of all bromine species to Br\textsubscript{2}, O\textsubscript{2}, and Cl\textsubscript{2}0\textsubscript{7}. Hence, definite evidence for a trisperchlorate of bromine was not obtained.

Iodine is, of course, more readily oxidized than bromine and CIOC10\textsubscript{3} might be expected to convert I\textsubscript{2} to the +III state despite the failure to do so with bromine. Indeed a facile, quantitative reaction of I\textsubscript{2} and CIOC10\textsubscript{3} was noted, according to the following equation:

\[ \text{I}_2 + 6\text{ClOC10}_3 \rightarrow -45 \text{C} \rightarrow 2\text{I(OC10}_3\text{)}_3 + 3\text{Cl}_2 \]

This novel perchlorate is a pale yellow solid which, unfortunately, gradually decomposes on warming above -45 C. Its covalent nature was established by low temperature Raman spectroscopy. Details concerning its preparation and characterization will be reported in a forthcoming manuscript.

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Attempts were made to prepare a mono perchlorate of iodine by limiting the quantity of ClOClO₃ reacting with I₂. When the stoichiometry of the reaction is changed to 1:1, a white solid, stable at -45 C, is obtained as the sole reaction product. Upon warm up, the product decomposes, resulting in a dark burgundy red, almost black liquid, which solidified upon standing, forming an initially brick red, later slightly colored solid. The volatile material had a low vapor pressure and was a weak infrared absorber. However, upon fluorination with F₂, IF₅ and CIF were formed, indicating the presence of iodine chlorides. The solid, nonvolatile residue exhibited an infrared spectrum similar to that of the I(OCIO₃)₃ decomposition product.

Since complexing is known to stabilize lower, otherwise unstable, oxidation states, we have attempted the synthesis of Cs⁺I(OCIO₃)₂⁻, according to:

\[
\text{CsIBr}_2 + 2\text{ClOClO}_3 \rightarrow \text{CsI(OCIO}_3)_2 + 2\text{BrCl}
\]

Consequently, a sample of CsIBr₂ was prepared and reacted with ClOClO₃. The derived reaction occurred at -45 C as indicated by ClOClO₃ uptake and BrCl liberation. Visually, though, the solid product appeared to be a mixture. This was confirmed by infrared analysis which a portion of the solid showed the characteristic perchlorate absorptions. Thus, some of the perchlorate must have been incorporated in a more highly oxidized iodine species, such as I(OCIO₃)₄⁻, leaving the bottom layers unreacted.

To verify this assumption, it was decided to react CsI directly to CsI(OCIO₃)₄ with excess of ClOClO₃:

\[
\text{CsI} + 4\text{ClOClO}_3 \rightarrow 45 \text{C} \rightarrow \text{CsI(OCIO}_3)_4 + 2\text{Cl}_2
\]

Based on the weight increase of the solid and the consumption of ClOClO₃, better than 90 percent of the CsI was converted to the tetrakis perchlorate. More importantly, the white solid compound is stable at ambient temperature. The composition of this new perchlorate derivative was confirmed by its infrared and low-temperature Raman spectrum. The spectra show the absorption characteristic
for covalently bound perchlorate groups. In addition, the $\text{IO}_4^-$ skeletal modes are very similar to those previously reported for the analogous $\text{I(OSO}_2\text{F)}_4^-$ salts (Ref. 2), suggesting a square planar $\text{IO}_4^-$ configuration. Analysis and characterization of this compound are continuing and the results will be summarized in a forthcoming manuscript.

The general reactivity of $\text{ClOCIO}_3$ suggested the possible synthesis of the novel and highly energetic molecule, nitrogen trisperchlorate. The reaction between $\text{NCIO}_3$ and chlorine perchlorate was studied in Freon 11 solution. The reaction was carried out at low temperature and the following reaction products were observed: $\text{Cl}_2\text{O}_6$, $\text{Cl}_2\text{O}_7$, $\text{NO}_2^+\text{ClO}_4^-$, COFC1, Freon 11, and unreacted $\text{ClOCIO}_3$. The observation of $\text{NO}_2^+\text{ClO}_4$ and $\text{Cl}_2\text{O}_6$ is interesting since it might be interpreted in terms of the formation of an unstable intermediate, $\text{N(OCIO}_3)_3^-$:

$$\text{NCIO}_3 + 3\text{ClOCIO}_3 \rightarrow [\text{N(OCIO}_3)_3^-] + 3\text{Cl}_2$$

$$\text{NO}_2^+\text{ClO}_4^- + \text{Cl}_2\text{O}_6$$

The formation of some COFC1 and $\text{Cl}_2\text{O}_7$ indicates:

$$\text{CFC}_3 + 2\text{ClOCIO}_3 \rightarrow [\text{CFC(OCIO}_3)_2] + 2\text{Cl}_2$$

$$\text{COFC1} + \text{Cl}_2\text{O}_7$$

In order to eliminate the possibility for this side reaction, the experiment was repeated in the perfluorinated solvent, FC78, at -78 C. However, the results were analogous to those obtained in Freon 11 solution, except for the side reaction with Freon 11. It appears that $\text{N(OCIO}_3)_3^-$ is not stable enough to allow its isolation and characterization.
REATIONS OF CHLORINE NITRATE WITH IODINE AND CsNO$_3$

In addition to CIOClO$_3$ and C10SO$_2$F, the behavior of a related ClOX compound, C10NO$_2$, towards iodine was investigated. The expected product was I(ONO$_2$)$_3$. Using excess chloride nitrate, a quantitative synthesis of the trinitrate was obtained at -45 C, based on the amount of produced chlorine and recovered C1ON0$_2$.

\[
I_2 + 6C10NO_2 \rightarrow 2I(ONO_2)_3 + 3Cl_2
\]

Previous preparation of iodine trinitrate had also used C10NO$_2$ as starting material; however, instead of iodine, IC1$_3$ had been employed in the synthesis (Ref. 3). Details regarding the preparation, characterization, and decomposition of the trinitrate will be reported in a forthcoming manuscript.

The C1ON0$_2$ - CsNO$_3$ system was studied in an attempt to prepare the most simple member of the novel class of nitrate chlorates according to:

\[
C1ON0_2 + Cs^+NO_3^- \rightarrow Cs^+[O_2NOClON0_2]^-
\]

After 20 days at -55 C, no complex formation was observed. Increase of the reaction temperature to 25 C and the use of mechanical shaking did not affect the reaction. However, carrying out the reaction at 75 C resulted in a weight increase corresponding to a 12 percent conversion of CsNO$_3$. In view of the low conversion, no characterization of the adduct was undertaken. Instead, attempts were undertaken to increase the conversion. Heating of the starting materials to 85 C for 40 days resulted in a weight increase being 40 percent higher than expected. Inspection of the product revealed the formation of substantial amounts of decomposition products in addition to what we believe to be the desired product based on its infrared spectrum. However, the substitution of the metal reactor by a Pyrex container and stirring of CsNO$_3$ in a large excess of liquid C1ON0$_2$ at ambient temperature for 24 hours did not result in any C1ON0$_2$ uptake.

In a third experiment, CH$_3$CN was added as a solvent to the C1ON0$_2$-CsNO$_3$ mixture. Upon warming up of the mixture, a violent explosion occurred, terminating the experiment.
As an alternate approach, \( \text{Cl}(\text{ONO}_2)_2^- \) might be formed according to:

\[
\text{Cl}_3^- + 2\text{ClONO}_2 \rightarrow \text{Cl}(\text{ONO}_2)_2^- + 2\text{Cl}_2.
\]

Since Allied had previously reported (Ref. 4) evidence for the formation of \( \text{CsCl}_3^- \) and \( \text{Cs}^+\text{Cl}_2\text{F}^- \), we have attempted to duplicate their experiments. However, no evidence at all could be found for any adduct formation in the \( \text{CsCl}-\text{Cl}_2 \) and the \( \text{CsF}-\text{Cl}_2 \) systems.

**REACTION OF CHLORINE FLUOROSULFATE WITH IODINE AND NC\(_1\text{}_3\)**

In view of the foregoing results for \( \text{I}_2-\text{ClOX} \) oxidation reactions, it would seem likely that the corresponding \( \text{I}_2-\text{ClO}_2\text{S}_2\text{F} \) system would behave the same. Such a conclusion might be further reinforced by the knowledge that iodine does form a stable trisfluorosulfate (Ref. 5) through reaction with \( \text{S}_2\text{O}_5\text{F}_2 \). To confirm this expectation and to parallel the preceding studies, the \( \text{I}_2-\text{ClO}_2\text{S}_2\text{F} \) reaction was examined at -45°C. It was found that complete conversion of the \( \text{I}_2 \) was not accomplished even after several weeks. Increasing the temperature to 0°C resulted in complete consumption of the \( \text{I}_2 \), but it was noted that 10 moles of the \( \text{ClO}_2\text{S}_2\text{F} \) had reacted per mole of \( \text{I}_2 \), liberating 5 moles of \( \text{Cl}_2 \). This direct evidence for the formation of \( ^{+5} \text{I} \) iodine was thought, by analogy to the other \( \text{ClOX} \) oxidations, to be indicative of the generation of \( \text{I}(\text{OSO}_2\text{F})_5 \). However, further examination of the products revealed that appreciable amounts of \( \text{SO}_3 \) were also liberated in the reaction as well as smaller, variable amounts of \( \text{S}_2\text{O}_5\text{F}_2 \).

The liquid iodine fluorosulfate material which remained undistilled after the removal of byproducts was subjected to \( ^{19}\text{F} \) nmr analysis. Samples from two separate preparations gave similar but not identical results. Both samples had only two lines, both rather broad. One of these lines was in the normal fluorosulfate region (Ref. 6) (-41 and -47 ppm relative to \( \text{CFC}_3 \)) for the respective samples and one in the IF region (Ref. 7) (-17 and -19 ppm respectively). In addition to these discrepancies, the area ratios for the resonances in the two samples were widely divergent (e.g., IF:SO\(_3\text{F} \) areas of 5:4 and 2:1, respectively).
Considered all together, the available evidence seems best interpreted in terms of mixture of related moieties being formed in this reaction. The most likely compounds are illustrated by the equation:

\[
\begin{align*}
I_2 + 10 \text{ClOSO}_2F &\rightarrow 5\text{Cl}_2 + 2 [\text{I(OSO}_2F)_5] \\
[\text{I(OSO}_2F)_5] &\rightarrow n\text{SO}_3 + \text{FI(OSO}_2F)_4, \text{F}_2\text{I(OSO}_2F)_3, \text{etc.} \\
[\text{I(OSO}_2F)_5] &\rightarrow \text{S}_2\text{O}_5\text{F}_2 + 0\text{I(OSO}_2F)_3, \text{0}_2\text{IOSO}_2F \\
[\text{I(OSO}_2F)_5] &\rightarrow \text{SO}_3 + \text{S}_2\text{O}_5\text{F}_2 + 0\text{IF}_2(\text{OSO}_2F)
\end{align*}
\]

At least one example of each of the types of products shown is known. Thus, IF\textsubscript{3}(OSO\textsubscript{2}F)\textsubscript{2} (Ref. 8) and I\textsubscript{2}SO\textsubscript{3}F (Ref. 9) have been prepared. The former is a yellow liquid of low volatility not unlike the present product. Furthermore, its nmr spectrum (Ref. 8 and 10) varied somewhat from sample to sample with respect to the relative area of the SO\textsubscript{3}F and IF resonances (the range observed was 1.9 to 2.5:1). The unusual and novel molecule 0IF\textsubscript{2}(OSO\textsubscript{2}F) shown in the last equation was obtained during this study by reacting IF\textsubscript{5} with an excess of SO\textsubscript{3}. Its nmr spectrum also contains two somewhat broad lines at -21 and -44 ppm with the IF:SO\textsubscript{3}F area being 2:1.

Examination of the Raman spectra of these products revealed the presence of the bands characteristic for covalently bound fluorosulfate groups. In addition, they showed varying amounts of SO\textsubscript{3} and a band of strongly varying intensity at about 930 cm\textsuperscript{-1} which we attribute to an I=0 double bond stretching vibration. Hence, it can be concluded that we are dealing with a mixture of at least three different compounds. Their ratio changes not only with the various preparative methods, but also for each product depending upon its work-up conditions. Consequently, more efforts will be required to separate and unequivocally determine the identity and structure of the individual components.
Since nitrogen triperchlorate appeared to be unstable, the following model reaction was carried out in Freon 11 and FC 78 solution:

$$\text{NCl}_3 + 3\text{CIO}_2\text{F} \xrightarrow{45^\circ F} \text{N(0S}_2\text{F)}_3 + 3\text{Cl}_2$$

However, instead of the desired and still unknown nitrogen trisfluorosulfate, only a small amount of HOSO$_2$F could be isolated, which was identified by infrared and mass spectroscopy.

**ATTEMPTED SYNTHESIS OF CHLORINE PERBROMATE**

The successful synthesis of chlorine perchlorate via the interaction of chlorine fluorosulfate and perchlorate salts (Ref. 1) prompted an examination of the analogous reaction with the perbromate salts. Since perbromate compounds have been known only a short time and are difficult to prepare, they are not commercially available. Accordingly, the synthesis of HBrO$_4$ was carried out using the reported procedure (Ref. 11). Perbromic acid is obtained with this method by the oxidation of bromate with fluorine in alkaline solution, followed by acidification. Based on BrO$_3$ used, the yield was 31 percent, which compares very favorably with the 13.5 percent reported in the literature. An aliquot of the resulting 3.8M HBrO$_4$ stock solution was converted to KBrO$_4$ using KOH, recrystallized and the solid KBrO$_4$ was analyzed by pyrolysis.

$$\text{KBrO}_4 \xrightarrow{400^\circ C} \text{KBr} + 2\text{O}_2$$

By volume, the measured $\text{O}_2$ yield was 100.2 percent of theory. By weight loss, the KBrO$_4$ sample had an observed $\text{O}_2$ content of 34.66 percent; theory is 34.97 percent. A sample of CsBrO$_4$ was also prepared. Infrared spectra of both salts agreed with the published data (Ref. 11).

The synthesis of chlorine perbromate was attempted several times with the desired reaction being:

$$\text{MBrO}_4 + \text{CISO}_2\text{F} \rightarrow \text{MSO}_3\text{F} + \text{CIOBrO}_3$$
When either the potassium or cesium salt was used at either -45 or -80 °C, the following similar results were obtained. Complete consumption of the ClSO$_3$F occurred readily, but the product of this reaction was unstable. The instability was indicated by the fact that Cl$_2$ was always present as soon as the ClSO$_3$F reacted, even at -80 °C. Subsequent warming allowed the separation of the volatile products, ClO$_2$ and Cl$_2$O, and finally at 0 °C and above Br$_2$ and oxygen were formed. The presence or absence of excess BrO$_4^-$ salt did not alter this result, and then the product formed from the ClSO$_3$F interaction appeared to be inherently unstable.

From the nature and amount of the decomposition products and their mode of formation, it is reasonably certain that ClOBrO$_3$ was formed as an intermediate. Based on the consistent results of the several attempted preparations of ClOBrO$_3$, the reactions that occurred are:

\[
\begin{align*}
\text{MBrO}_4 + \text{ClSO}_3\text{F} & \rightarrow \text{MSO}_3\text{F} + [\text{ClOBrO}_3] \\
+ [\text{ClBrO}_4] & \rightarrow \text{CIO}^- + (\text{BrO}_3)^x \\
2\text{CIO}^- & \rightarrow \text{ClO}_2 + \frac{1}{2}\text{Cl}_2 \\
2\text{CIO}^- & \rightarrow \text{Cl}_2\text{O} + \frac{1}{2}\text{O}_2 \\
(\text{BrO}_3)^x & \rightarrow \frac{3}{2}\text{O}_2 + \frac{1}{2}\text{Br}_2
\end{align*}
\]

The only significant variation from run to run was the relative amounts of Cl$_2$, Cl$_2$O, and ClO$_2$. This only depends on the course of the ClO$^-$ radical decomposition which might be expected to vary somewhat with changing reaction conditions.

To determine the nature of the Br-O species remaining after the chlorine products were removed, elemental F$_2$ was added at that point. Several hours at ambient temperature were required to achieve significant fluorination. However, perbromyl fluoride, FBrO$_3$ (Ref. 12), was obtained in yields up to 10 percent, indicating the presence of BrO$_3$. Also produced were BrF$_5$ and some SO$_3$F$_2$. The latter was surprising since alkali metal fluorosulfates are not known to be susceptible to
fluorination in this manner. It may be that minor amounts of a species such as 
+ BrO\textsubscript{X}S\textsubscript{X}O\textsubscript{3}F were present and served as the source of the SO\textsubscript{3}F\textsubscript{2}. Control experiments 
were run showing that MBrO\textsubscript{4} salts do not react with F\textsubscript{2} to give FBrO\textsubscript{3} and thus a 
covalent Br-0 compound such as (BrO\textsubscript{3})\textsubscript{X} must have been its precursor. Further proof 
of the formation of (BrO\textsubscript{3})\textsubscript{X} in this reaction was the approximate, Br\textsubscript{2}:O\textsubscript{2} ratio of 
1:3 noted on decomposition of the residues left after the chlorine species had 
been removed.

ATTEMPTED SYNTHESIS OF CHLORINE BROMATES

Stable halogen oxides of the general formula Y-XO\textsubscript{3} are not known except where Y 
is fluorine. In the preceding report on this program (Ref. 1), an unsuccessful 
effort to form chlorine chlorate, Cl-C1\textsubscript{O}\textsubscript{3}, from KC1\textsubscript{O}\textsubscript{3} and ClSO\textsubscript{3}F was described. 
More recently, experiments were carried out aimed at producing Cl-BrO\textsubscript{3}.

\[
\text{MBrO}_{3} + \text{ClSO}_{3}F \rightarrow \text{MSO}_{3}F + \text{Cl-BrO}_{3}
\]

In the case of the bromate, as with the perbromate, reaction of the ClSO\textsubscript{3}F 
ocurred readily at -45 \textdegree C. However, again the product formed was unstable. Free 
Cl\textsubscript{2} was first found and later large quantities of Br\textsubscript{2} and O\textsubscript{2} were liberated. No 
evidence for any stable Br-0 species was obtained.

REACTION OF CHLORINE FLUOROSULFATE WITH PERIODATES

Although a stable, covalent bromine oxide species was not produced by the reaction 
of chlorine fluorosulfate and BrO\textsubscript{X} - salts, the well established superior stability 
of iodine oxide moieties suggested their examination in this respect. Thus, ClSO\textsubscript{3}F 
was reacted with periodate salts, initially with the intention of preparing chlorine 
periodate, C1010\textsubscript{3}.

\[
\text{MIO}_{4} + \text{ClSO}_{3}F \rightarrow \text{MSO}_{3}F + \text{ClO10}_{3} \quad M = \text{Na,K}
\]

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Reactions conducted at -45 C revealed that the C1SO₃F was rapidly taken up, but that at the same time elemental Cl₂ was also rapidly produced. Surprisingly, though, additional warming to ambient temperature did not yield any other volatile product. Examination of the reactor contents showed the presence of a dark red, oily liquid. This material coated the solids present (MSO₃F and unreacted MSO₄) and was pumped away only slowly and incompletely at temperatures to 80 C over long periods of times. Furthermore, it fumed in air, oxidized organic matter, and attacked AgCl infrared windows, leaving primarily an SO₃F⁻ in background (Ref. 13). It also exhibited prominent bands in the I=0 region, 820 cm⁻¹ (Ref. 14) and covalent-SO₃F region (Ref. 2 and 14). These findings were considered to be indicative of a fluorosulfate substituted iodine oxide and most consistent with a compound such as I₀₄SO₃F. In order to test this hypothesis, preparative reactions were conducted using 2 moles of C1SO₃F for each 10₄ in anticipation of the reaction stoichiometry:

\[ \text{MSO}_4 + 2\text{ClSO}_3\text{F} \rightarrow \text{MSO}_3\text{F} + \text{Cl}_2 + \text{I}_4\text{SO}_3\text{F} \]

The evolved Cl₂ approximated this stoichiometry, but was usually only 80 to 85 percent of theoretical, even though no C1SO₃F was left unreacted. Again, only traces of O₂ were formed, thus confirming apparently the integrity of the I₀₄ group. Vacuum separation of the iodine oxide fluorosulfate was still not wholly successful. Efforts to dissolve the red oil in CFC₁₃ or FC-78 fluorocarbons were negative while reaction occurred with CH₃CN, CCl₄, and HF.

Additional experiments designed to elucidate the composition of this liquid oxyfluorosulfate involved its pyrolysis. Upon reaction of the C1SO₃F and removal of the evolved Cl₂, the products were pyrolyzed at 90 to 125 C for several days. The remaining Cl₂ was recovered together with 1 mole of O₂ for each mole of the suspected I₀₄SO₃F.

\[ \text{I}_4\text{SO}_3\text{F} \xrightarrow{\Delta} \text{O}_2 + \text{I}_2\text{SO}_3\text{F} \]

The presence of I₂SO₃F was established gravimetrically and by infrared spectra of the pyrolysis residue which showed only a mixture of MSO₃F and I₂SO₃F.

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In a similar vein, reactions of perfluoropropene, \(C_3F_6\), were employed. These studies were aimed at forming volatile derivatives of the oxyfluorosulfate and thereby assisting in its characterization. Exact reaction stoichiometries were not obtained and a variety of products were formed. The predominant products were perfluoropropene epoxide and one or more fluorosulfate adducts.

\[
\begin{align*}
\text{CF}_3\text{CF}-\text{CF}_2 + "\text{IO}_4\text{SO}_3\text{F}" & \\
\text{CF}_3\text{CF}-\text{CF}_2 & \quad \text{X} \quad \text{OSO}_2\text{F} \\
\text{CF}_3\text{CF}-\text{CF}_2 & \quad (\text{X}=\text{Cl, OSO}_2\text{F})
\end{align*}
\]

The Cl containing adduct probably arose through reaction of impurity ClSO\(_3\)F present. Although a smooth reaction was noted, some oxygenated species were also formed which were the result of C-C bond cleavage. The epoxide and fluorosulfates were identified by comparison of their infrared spectra to authentic samples and also by known derivative reactions (Ref. 15 and 16).

\[
\begin{align*}
\text{CF}_3\text{CF}-\text{CF}_2 & \quad \text{CsF} \quad \Delta \quad \text{CF}_2\text{CF}_2\text{CF} \\
\text{CF}_3\text{CF}-\text{CF}_2 & \quad \text{X} \quad \text{OSO}_2\text{F} \quad \text{CsF} \quad \Delta \quad \text{CF}_3\text{CF}, \text{CF}, \text{CF}, \text{SO}_2\text{F}_2
\end{align*}
\]

While these compounds did not establish precisely the nature of the iodine oxyfluorosulfate, they did emphatically demonstrate that it was a discriminating active oxygen source. The iodine-oxygen bond giving epoxidation and oxygenation reactions could be a terminal, reactive I=O link or it might even be a peroxy-fluorosulfate link, $-\text{I}-\text{OSO}_2\text{F}$. Similar iodine peroxides have been reported to function well as epoxidizing agents (Ref. 17).
Appreciable amounts of unreacted ClSO$_3$F were not recovered from these periodate reactions, but generally some chlorine species were retained with the "IO$_4$SO$_3$F". Therefore, it was decided to investigate whether complete fluorosulfonation had been attained. When increasing ratios of ClSO$_3$F to IO$_4^-$ were used (up to 8:1) essentially all the ClSO$_3$F reacted. Surprisingly though, this reaction still produced Cl$_2$, a little O$_2$, and almost no volatile -SO$_3$F material. All the fluorosulfate values were retained in the red liquid which distilled only with difficulty and with some decomposition. Obviously, one or more very highly fluorosulfonated species are being formed.

The complicated nature of this system was further attested to when distilled and undistilled samples of this highly fluorosulfonated material were subjected to $^{19}$F nmr analysis. The undistilled sample showed two types of fluorines with lines at -41 ppm, clearly an SO$_3$F resonance (Ref. 6), and -17 ppm, outside the SO$_3$F region but readily assignable to IF (Ref. 7). The area ratio for the two resonances was 5SO$_3$F:3IF. The distilled sample, however, contained only one type of fluorine (-39 ppm) due to SO$_3$F. Since in all other respects these compounds appeared the same, it appears that the IF groups reacted on distillation. More noteworthy, than the loss of these groups is their formation from ClSO$_3$F. Just as found in the I$_2$-ClSO$_3$F system, here also the ClSO$_3$F functions in part as a fluorinating agent. No other examples of this type of behavior have been published.

Investigation of the IO$_4^-$-ClSO$_3$F reaction is continuing. The complimentary studies on these iodine-fluorosulfate systems have given some insight into the compositions obtainable and their properties. Additional work should resolve the problem.

REACTION OF CHLORINE FLUOROSULFATE WITH IODATES

The reaction of KIO$_3$ with ClSO$_3$F was investigated to determine whether it paralleled the periodate case. At ambient temperature, an equimolar mixture of the two readily produced O$_2$ and Cl$_2$ in agreement with the basic reaction path:

\[
\text{KIO}_3 + 2\text{ClSO}_3\text{F} \rightarrow \text{KS0}_3\text{F} + \text{IO}_2\text{SO}_3\text{F} + \text{Cl}_2 + 1/2\text{O}_2
\]
The X-ray powder pattern for the resultant IC$_2$SO$_3$F was given (Ref. 9), but no other spectroscopic data. A synthesis was carried out and good agreement with the original synthetic data (Ref. 9) was obtained. In addition, I$_2$O$_5$ was reacted with CISO$_3$F since this compound was the source of the SO$_3$F group in the present iodine oxide studies. The observed reaction was:

$$\text{I}_2\text{O}_5 + 2\text{CISO}_3\text{F} \rightarrow 2\text{IO}_2\text{SO}_3\text{F} + \text{Cl}_2 + \frac{1}{2}\text{O}_2$$

The iodyl fluorosulfate from either reaction carried out in our laboratory was a pale yellow solid having identical infrared spectra and X-ray powder patterns. However, our observed powder pattern was different than that reported (Ref. 9). It seems likely that the original data may be in error, perhaps due to some hydrolytic decomposition.

The infrared spectra of these authentic samples of IO$_2$SO$_3$F were used to confirm the presence of this compound in other systems. This use is aided by the fact that the fluorosulfate absorbances for this compound are unusual. Strong bands attributable to either ionic or covalent SO$_3$F are lacking and are replaced by bonds of intermediate wavelength. This is illustrated in Table 1.

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
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<tbody>
<tr>
<td>COMPARISON OF THE INFRARED BANDS OF VARIOUS FLUOROSULFATES</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M$^+$SO$_3$F$^-$ cm$^{-1}$ Relative Intensity</th>
<th>IO$_2$SO$_3$F cm$^{-1}$ Relative Intensity</th>
<th>CISO$_3$F (Ref. 18) cm$^{-1}$ Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1285 vs</td>
<td>1345 vs</td>
<td>1481 vs</td>
</tr>
<tr>
<td>1080 s</td>
<td>1185 vs</td>
<td>1248 vs</td>
</tr>
<tr>
<td>1025 s</td>
<td>875 s</td>
<td>855 vs</td>
</tr>
<tr>
<td>780 s</td>
<td>840 s</td>
<td>830 ms</td>
</tr>
<tr>
<td>585 s, complex</td>
<td>575 m, complex</td>
<td>570 ms</td>
</tr>
</tbody>
</table>

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The observed bands closely resemble those of SnCl$_2$(SO$_3$F)$_2$ (1385, s; 1130, vs; 1087, s; 864 s, 628 m; 586 cm$^{-1}$, s) which are attributed to a bidentate SO$_3$F bridges (Ref. 19). A more complete study of the vibrational spectrum of I$_2$SO$_3$F will be made.

REATIONS OF IODYL FLOROSULFATE

Attempts were made to fluorinate I$_2$SO$_3$F to form any of several possible iodine oxyfluorides; e.g., FIO$_2$, F$_3$I$_2$, F$_3$I$_0$, etc. To limit the tendency of fluorine to simply replace oxygen, the first experiments were restricted to low temperature conditions, -45 and -78 C, at up to 33 atm F$_2$ pressure. However, even prolonged reaction periods (several weeks) failed to produce any detectable reactions. Ambient temperature was then tried and it was found that moderate F$_2$ pressures (~5 atm) caused complete reaction of the I$_2$SO$_3$F according to:

\[
\text{I$_2$SO$_3$F} + x\text{SSF$_2$} \rightarrow \text{SO$_3$F$_2$} + \text{IF}_50/\text{IF}_7 + \text{O}_2
\]

Use of increasing fluorine pressures increased the relative amount of IF$_7$ to IF$_50$, and at the lowest pressures, essentially all the iodine was converted to IF$_50$. The formation of SO$_3$F$_2$ indicates the non-ionic nature of the SO$_3$F group in this compound since ionic fluorosulfates do not yield SO$_3$F$_2$ in this manner. A sample of chloryl fluorosulfate was also prepared and fluorinated as indicated by the equations:

\[
2\text{ClO$_2$} + S_2O_6F_2 \rightarrow 2\text{ClO$_2$SO$_3$F} \quad \text{(Ref. 20)}
\]

\[
\text{ClO$_2$SO$_3$F} + \text{F$_2$} \rightarrow \text{FCIO$_2$} + \text{SO$_3$F$_2$}
\]

Virtually, a quantitative yield of each product was realized in the fluorination reaction. Again, the formation of SO$_3$F$_2$ points to a non-ionic SO$_3$F group in the starting material.
Sulfur tetrafluoride was also used to fluorinate iodyl fluorosulfate hoping for partial oxygen-fluorine exchange under relative mild conditions. A vigorous reaction occurred at room temperature, resulting in complete oxygen exchange, giving IF$_5$ as the exclusive iodine product according to:

$$2\text{IO}_2\text{SO}_3\text{F} + 5\text{SF}_4 \rightarrow 2\text{IF}_5 + \text{S}_2\text{O}_5\text{F}_2 + 5\text{SOF}_2$$

Thus no new iodine oxyfluorides were obtained from IO$_2$SO$_3$F.

**REACTIONS OF CHLORINE PERCHLORATE WITH OXIDIZING COMPLEXES**

A displacement of a cation from a complex salt employed the dioxygenyl species, O$_2^+$AsF$_6^-$ (Ref. 21). It was hoped that the O$_2^+$ cation would facilitate the reaction by eliminating the interfering fluorination reaction.

$$\text{O}_2^+\text{AsF}_6^- + \text{ClO}_3^- \rightarrow 0.2\text{ClO}_4^- + \text{ClF} + \text{AsF}_5$$

A 3 week reaction period at -45 C showed incomplete but substantial reaction of the ClOClO$_3$ (75 percent). Surprisingly, nearly 1 mole of FC10$_2$ was formed for each ClOClO$_3$ reacted. Oxygen and Cl$_2$ were also noted. The yields of these materials suggested the following reaction sequence:

$$\text{O}_2^+\text{AsF}_6^- + \text{ClOClO}_3 \rightarrow [0.2\text{ClO}_4] + [\text{ClAsF}_6]$$
$$[0.2\text{ClO}_4] \rightarrow 3/2\text{O}_2 + \cdot\text{ClO}_3$$
$$\cdot\text{ClO}_3 + [\text{ClAsF}_6] \rightarrow \text{FC1O}_3 + 1/2\text{Cl}_2 + \text{AsF}_5$$

Not all the AsF$_5$ was observed as such. Some was consumed in forming the minor product, ClO$_2$AsF$_6^-$, and some remained undetected. The only other product was a small amount of Cl$_2$OF$_7^-$. Since all the chlorine and oxygen were accounted for, no O$_2$ClO$_4$ could have remained.

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Because ClSO₃F was very effective in functioning as a chlorinating agent; e.g., in chlorinating the ClO₄⁻ ion to ClOClO₃, it was investigated further for this activity. This led to the following reaction:

\[ \text{CsSeF}_5 + \text{ClSO}_3\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{SeF}_5\text{Cl} \]

Previous to this, both SF₅Cl and TeF₅Cl were known but not the selenium analog. The preparation and characterization of this new compound are described in Appendix A and B.

Later it was found that SeF₅Cl could be also obtained directly from Se or SeF₄ and ClF or ClF₃, but in lower yields. Optimally then it seemed possible that the reaction of equimolar quantities of Se and ClF₅ might furnish SeF₅Cl. When tried, however, the observed reaction was:

\[ 2\text{Se} + 2\text{ClF}_5 \rightarrow \text{SeF}_4 + \text{SeF}_6 + \text{Cl}_2 \]

Fluorination occurred to the complete exclusion of chlorination.

**ATTEMPTED PREPARATION OF THE NCl₄⁺ CATION**

The successful preparation of NF₄⁺ from

\[ \text{NF}_3 + \text{F}_2 + \text{AsF}_5 \rightarrow \text{NF}_4^+\text{AsF}_6^- \] (Ref. 23)

suggests the possibility of a similar reaction in the chlorine system:

\[ \text{NCl}_3 + \text{Cl}_2 + \text{SbCl}_5 \rightarrow \text{NCl}_4^+\text{SbCl}_6^- \]
Samples of NC\textsubscript{3} (which is unstable towards light and shock-sensitive) were prepared and reacted with SbCl\textsubscript{5} and Cl\textsubscript{2} in CCl\textsubscript{4} solution. A small amount of solid residue, insoluble in CCl\textsubscript{4}, was obtained. However, no evidence for attributable to either NC\textsubscript{4}\textsuperscript{+} or SbCl\textsubscript{6}\textsuperscript{-} could be obtained by vibrational spectroscopy.

Since the ClF bond is already polarized in the direction Cl-F, its heterolytic fission according to

\[
\text{NC}_3 + \text{ClF} + \text{AsF}_5 \rightarrow \text{NC}_4\textsuperscript{+}\text{AsF}_6\textsuperscript{-}
\]

might be more facile than that of Cl\textsubscript{2} in the NC\textsubscript{3}-Cl\textsubscript{2}-SbCl\textsubscript{5} system. The NC\textsubscript{3}-ClF-AsF\textsubscript{5} system was investigated in different solvents (Freon 11 and FC-78), the desired reaction being:

\[
\text{NC}_3 + \text{ClF} + \text{AsF}_5 \rightarrow \text{NC}_4\textsuperscript{+}\text{AsF}_6\textsuperscript{-}
\]

A solid product was obtained in low yields. Its infrared spectrum shows it to be an AsF\textsubscript{6}\textsuperscript{-} salt. Further characterization by Raman spectroscopy revealed, however, that the solid was Cl\textsubscript{10}\textsuperscript{+}\text{AsF}_6\textsuperscript{-}, (Ref. 22). Thus, no evidence for the existence of a stable NC\textsubscript{4}\textsuperscript{+} salt could be obtained.

**ATTEMPTED SYNTHESIS OF THE BrF\textsubscript{6}\textsuperscript{+} AND CIF\textsubscript{6}\textsuperscript{+} CATIONS**

A number of new approaches were studied which might lead to the novel cations CIF\textsubscript{6}\textsuperscript{+} and BrF\textsubscript{6}\textsuperscript{+}. These attempts included the use of uv photolysis, of PtF\textsubscript{6} and IrF\textsubscript{6} as fluorinating agents, and of XeF\textsuperscript{+} or NF\textsubscript{4}\textsuperscript{+} salts as starting materials. Since the existence of NF\textsubscript{4}\textsuperscript{+} salts is well established (Ref. 23), the following model reaction was investigated:

\[
\text{NF}_3 + \text{F}_2 + \text{AsF}_5 \xrightarrow{\text{uv}} \text{NF}_4\textsuperscript{+}\text{AsF}_6\textsuperscript{-}
\]

A small amount of white solid was obtained when a mixture of NF\textsubscript{3}, F\textsubscript{2}, and AsF\textsubscript{5}, contained in a quartz bulb, was exposed to sunlight. It was identified by infrared and Raman spectroscopy as O\textsubscript{2}\textsuperscript{+}\text{AsF}_6\textsuperscript{-}. The small amount of O\textsubscript{2} might have been present as impurity in the fluorine or might have resulted from interaction between
the starting materials and the glass. A second approach encompassed uv activation in a stainless steel sapphire cell. Exposure of the mixture to uv irradiation for 8 days did not result in the formation of detectable amounts of $\text{NF}_4^+\text{AsF}_6^-$. 

In another approach, $\text{NF}_4^+\text{AsF}_6^-$, prepared by the known pressure-temperature method, was heated in the presence of $\text{BrF}_5$ for several days to 90°C, 165°C, and 185°C, the desired reaction being:

$$\text{NF}_4^+\text{AsF}_6^- + \text{BrF}_5 \rightarrow ? \rightarrow \text{BrF}_6^+\text{AsF}_6^- + \text{NF}_3$$

At each temperature, only a small amount of $\text{NF}_3$ was detected in the volatile products, but no $\text{BrF}_5$ was consumed. This indicates that the $\text{NF}_3$ evolution was due to attack of $\text{NF}_4^+\text{AsF}_6^-$ on the metal cylinder and not due to $\text{BrF}_6^+$ formation.

Since the previous (Ref. 24) Raman studies of $\text{NF}_4^+$ were carried out before a Laser Raman spectrometer was available, the observed Raman spectrum had been of poor quality. We have now repeated this study with a laser instrument. The improved Raman frequencies and corrected force constants will be reported in a future paper. We have also attempted to synthesize the $\text{BrF}_6^+$ cation using $\text{XeF}^+\text{AsF}_6^-$ as the oxidizing species:

$$\text{XeF}^+\text{AsF}_6^- + \text{BrF}_5 \rightarrow \text{BrF}_6^+\text{AsF}_6^- + \text{Xe}$$

Two reactions were carried out at 75°C and 130°C. In both experiments, no $\text{BrF}_6^+\text{AsF}_6^-$ was formed. The only reaction taking place was a slow attack of the metal container resulting in the evolution of Xe.

The XeF$_2$ used in the above experiment was synthesized from Xe and F$_2$ by uv photolysis. Replacing F$_2$ by ClF resulted only in a small amount of XeF$_2$ with most of the ClF being converted to Cl$_2$ and ClF$_3$. No evidence for a new compound, such as XeFCl, was obtained.
Several experiments were carried out using the powerful fluorinating agents, PtF$_6$ and IrF$_6$, in conjunction with CsBrF$_6$. We reasoned that the "anionic" forms of halogen fluorides would be more readily oxidized due to (1) the availability of labile electrons for the primary oxidation step, and (2) the presence of an additional F ligand which, in essence, corresponds to a half way point as far as coordination is concerned. Part of the rationale is based on the ease of oxidation of Cl(III) to Cl(V). Starting from the species ClF$_2^+$, ClF$_3^-$, and ClF$_4^-$ we have shown ClF$_2^+$ not to be oxidized at all, ClF$_3^-$ with difficulty and ClF$_4^-$ quite readily.

Our experiments involved the action of PtF$_6$ on CsBrF$_6$.

$$2\text{PtF}_6 + \text{Cs}^+\text{BrF}_6^- \rightarrow \text{Cs}^+\text{PtF}_6^- + \text{BrF}_6^-\text{PtF}_6^-$$

However, several experiments showed that the weight increase after the reaction was minimal and that no detectable amounts of BrF$_6^-\text{PtF}_6^-$ were formed in this reaction.

**ATTEMPTED PREPARATION OF ClO$_2$F$_2$ AND ClO$_2$F$_3$**

Recently, the existence of the salt Cs$^+\text{ClO}_2\text{F}_2^-$ has been reported (Ref. 25). Since it was previously shown (Ref. 26) that ClF$_4^-$ can readily be fluorinated to form ClF$_5^-$ (Ref. 26), we hoped the fluorination of ClO$_2\text{F}_2^-$ might be possible, yielding the novel oxyfluoride, ClO$_2$F$_3^-$. Therefore, a sample of Cs$^+\text{ClO}_2\text{F}_2^-$ was prepared and characterized since no structural data had previously been given (Ref. 26) for this interesting compound. The structural data on ClO$_2\text{F}_2^-$ have been summarized in Appendix C.

Four fluorination reactions of Cs$^+\text{ClO}_2\text{F}_2^-$ using F$_2$ were carried out at -55 C, 25 C, 75 C, and 125 C using F$_2$. At the low temperatures no reaction occurred, whereas at 125 C most of the CsClO$_2\text{F}_2^-$ (82 percent) had decomposed into CsF and ClO$_2$F. No evidence for a new chlorine oxyfluoride was obtained. When PtF$_6$ was tried as a fluorinating agent again no evidence for ClO$_2$F$_3^-$ could be obtained.

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REACTION OF CHLORINE FLUORIDES WITH ACTIVE HYDROXYL GROUPS

A series of reactions were investigated to complete a systematic study on the reactivity of chlorine fluorides towards hydroxyl groups. The following stoichiometries were established by quantitative synthesis:

\[
\begin{align*}
\text{ClF (excess)} + \text{HONO}_2 & : \\
\text{ClF} + \text{HONO}_2 & \rightarrow \text{HF} + \text{ClONO}_2 \\
\text{ClF}_3 (\text{excess}) + \text{HONO}_2 & : \\
2\text{ClF}_3 + 2\text{HONO}_2 & \rightarrow 2\text{HF} + \text{ClO}_2\text{F} + \text{ClF} + 2\text{NO}_2\text{F} \\
\text{ClF}_3 + \text{HONO}_2 (\text{excess}) & : \\
3\text{ClF}_3 + 9\text{HONO}_2 & \rightarrow 9\text{HF} + 2\text{ClO}_2 + \text{ClONO}_2 + 4\text{N}_2\text{O}_5 \\
\text{ClF}_5 (\text{excess}) + \text{HONO}_2 & : \\
\text{ClF}_5 + 2\text{HONO}_2 & \rightarrow 2\text{HF} + \text{ClO}_2\text{F} + 2\text{NO}_2\text{F} \\
\text{ClF}_5 + \text{HONO}_2 (\text{excess}) & : \\
\text{ClF}_5 + 5\text{HONO}_2 & \rightarrow 5\text{HF} + 2\text{N}_2\text{O}_5 + [0_2\text{ClONO}_2] \\
\text{ClF}_5 + \text{HOH} (\text{excess}) & : \\
2\text{ClF}_5 + 5\text{HOH} & \rightarrow 10\text{HF} + 2\text{ClO}_2 + 1/2\text{O}_2 \\
\text{ClO}_2\text{F} + \text{HONO}_2 (\text{excess}) & : \\
2\text{ClO}_2\text{F} + 2\text{HONO}_2 & \rightarrow 2\text{HF} + 2\text{ClO}_2 + \text{N}_2\text{O}_5 + 1/2\text{O}_2
\end{align*}
\]
No stable novel compounds, such as chlorine trinitrate, mixed chlorine fluoride nitrates, or chloryl nitrate were observed. A manuscript discussing the above reactions in more detail will be written.

PREPARATION AND CHARACTERIZATION OF ALKALI METAL FLUORIDE·2IF₅ SALTS

With the exception of the Cl₂F⁺ cation (Ref. 27), no mixed halogen fluoride chlorides are known; i.e., where the ligands consist of both chlorine and fluorine. In a recent paper (Ref. 28), Meinert speculated on the formation of IF₄Cl as an intermediate in the CsCl-IF₅ reaction. This intermediate, however, supposedly attacked glass rapidly and, hence, could not be isolated or identified. We have studied the CsCl-IF₅ system in a metal-Teflon vacuum system. In the first experiment, CsCl was allowed to react with a large excess of IF₅ in a metal U-tube at 20°C for 30 minutes. In the reaction products, all the chlorine could be accounted for in terms of Cl₂ (48 percent) and unreacted CsCl (52 percent). The solid nonvolatile residue was shown to consist of a mixture of 52-percent CsCl and 48-percent CsIF₆·2IF₅. Vacuum pyrolysis of the product at 100°C resulted in the evolution of two moles of IF₅ per mole of CsIF₆·2IF₅. A second experiment between CsCl and IF₅ was carried out in a Teflon U-trap at 0°C. Under these conditions, almost no conversion of CsCl to Cl₂ occurred. This is most likely due to the high melting point (+9°C) of IF₅.

Whereas the desired IF₄Cl could not be isolated, the results of one experiment suggest the solution to the mystery previously encountered in the structural study of the IF₆⁻ anion. Four independent groups, Argonne National Laboratory, University of Glasgow, University of Berlin, and Rocketdyne had obtained different spectroscopic data on the CsF·IF₅ adduct (Ref. 29 through 31). The infrared and Raman spectra obtained now for CsIF₆ and CsIF₆·2IF₅ indicate the discrepancies of the spectra were due to the presence of various amounts of CsIF₆·2IF₅ in the CsIF₆ samples.
The structure of the IF$_6^-$ is of particular interest because it is isoelectronic with XeF$_6$. The structure and bonding of both XeF$_6$ and IF$_6^-$ have not yet been clearly established in spite of numerous efforts. Consequently, we have started a more systematic study of the various IF$_6^-$ salts. We have synthesized five different alkali metal fluoride -IF$_5$ salts and established their composition by quantitative synthesis and vacuum pyrolysis as: CsIF$_6$ (97 percent) + CsF (3 percent); RbIF$_6$ (73 percent) + RbF (27 percent); KIF$_6$ (95 percent) + KF (5 percent); CsF·3IF$_5$ (97 percent) + CsF (3 percent); and RbI·3IF$_5$ (50 percent) + RbIF$_6$ (23 percent) + RbF (27 percent). Attempts to prepare an NaF·IF$_5$ adduct were unsuccessful. A structural study of these five adducts has been completed. The crystal structures of KIF$_6$, RbIF$_6$, and CsIF$_6$ are analogous according to X-ray diffraction data. All three adducts are hexagonal with unit cell dimensions ranging from 15.72 to 16.52 Å for a and from 11.00 to 11.89 Å for c. Density measurements (by displacement method) indicate 18 molecules per unit cell (KIF$_6$: d(exp) = 3.55, d(clcd) = 3.55; CsIF$_6$: d(exp) = 4.06, d(clcd) = 3.98 g/ml). The average volume per F atom was found to be 17.4 Å$^3$. This value is very close to those found for similar complex fluorides. The thermal decomposition of the adducts was studied by differential scanning calorimetry (DSC). No evidence for a stepwise decomposition of the 3:1 adducts was obtained indicating the nonexistence of a 2:1 adduct as an intermediate. The results will be written up in manuscript form.

ALKALI METAL FLUORIDE ADDUCTS OF Cl$_2$O

The existence of alkali metal fluoride adducts of Cl$_2$O has previously been suggested (Ref. 1), but no clear cut stoichiometry could be established at that time. In order to verify the previous findings, the complex formation between Cl$_2$O and CsF was studied. Six reactions, carried out under varying conditions, did not provide any positive evidence for an adduct. Similarly, previous reports on the formation of an adduct between the NF$_2$O$^+$ cation and hexafluoroacetone could not be confirmed. Carbonyl fluoride also was shown not to interact with NOF$_2^+$. 

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MATRIX ISOLATION STUDIES

A number of reactive oxidizers were studied by infrared spectroscopy at 3 to 10 K in various matrices. Manuscripts reporting the results obtained for BrF₃, C10C10₁₃, and BrOC10₃ are included as Appendix E and G.

VIBRATIONAL SPECTROSCOPY AND FORCE CONSTANT CALCULATIONS

The structure and bonding of several interesting compounds have been determined by vibrational spectroscopy and force constant computations. These compounds included Cs⁺SF₅⁻, Cs⁺SF₅⁻₀⁻, Cs⁺SeF₅⁻, SeF₅⁻Cl, N₂⁺AsF₆⁻, N₂⁺SbF₆⁻, SF₄, BrF₃, C1F₅, BrOC10₃, C10C10₅, and Cs⁺ClO₂F₂. Most of the results are given in Appendix B, C, H, and J in manuscript form. The remaining data are still being evaluated and will be written up as manuscripts. Most of the above listed compounds are either novel compounds for which vibrational analysis was required to establish their identity or are known compounds which are structurally related to yet unknown compounds of interest.

SINGLE CRYSTAL X-RAY STUDIES

A single crystal structural study of the BrF₅⁻2SbF₅ adduct was completed in cooperation with Dr. Lind of the NR Science Center. In spite of great experimental difficulties, we succeeded in establishing its structure as being predominantly ionic, i.e., BrF₄⁺Sb₂F₁₁⁻, with weak cis fluorine bridges resulting in long zig-zag chains. The results of this study are given in Appendix I.
EXPERIMENTAL

REACTION OF IODINE AND CHLORINE FLUOROSULFATE

Sublimed I$_2$ (2.30 mmol) was placed in a prepassivated 30 milliliter, stainless steel cylinder. The closed cylinder was cooled to -196 C before evacuating to avoid loss of I$_2$. While at -196 C, CISO$_3$F (26.8 mmol) was added. The reactor was then warmed to room temperature for 4 days, whereupon it was recooled to -196 C. No noncondensable gas was observed. While gradually warming to ambient temperature over 4 hours, the cylinder was pumped out, passing the evolved gases through successive U-traps cooled to -78 C, -95 C, -112 C, and -196 C. The separated, measured, and analyzed gases were 11.7 mmol Cl$_2$, 3.48 mmol CISO$_3$F, and -0.5 mmol S$_2$OF. The -78 C fraction contained SO and approximately half the remaining liquid product. This product and the undistilled material were yellow colored. The latter was analyzed by nmr. The observed I$_2$:Cl$_2$ ratio for the reaction was 1.00:5.09.

ATTEMPTED SYNTHESIS OF CHLORINE PERBROMATE

Typical of the reactions of BrO$_4^-$ salts and CISO$_3$F used to seek ClOBrO$_3$ is the following experiment. A prepassivated 30 milliliter, 316 stainless steel cylinder was loaded with 4.48 mmol KBrO$_4$, followed by 4.51 mm CISO$_3$F. The reaction was allowed to proceed at -45 C for 6 days. On recooling to -196 C, only a trace of noncondensible gases were found. While warming to 0 C, the volatile products present were pumped out and separated by passing through a series of traps cooled to -95 C, -112 C, and -196 C. These products were Cl$_2$, Cl$_2$O, and ClO$_2$, as identified by infrared and GC analysis. The closed reactor was re-examined after standing overnight at ambient temperature. It was found to contain 2.20 mmol Br$_2$, 6.74 mmol O$_2$, and minor amounts of ClO$_2$ and Cl$_2$. In all the recovered Cl$_2$ (1.04 mmol), Cl$_2$O (0.87 mmol), and ClO$_2$ (0.60 mmol) accounted for all the charged CISO$_3$F, none of which was recovered. The ratio of Cl:Br:O in these materials was 1.00:1.01:4.02, and thus, quite in keeping with complete conversion toward decomposition of ClOBrO$_3$. 

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ATTEMPTED SYNTHESIS OF CHLORINE BROMATE

Potassium bromate (5.63 mmol) and ClSO$_3$F (3.11 mmol) were reacted in a 30 milliliter cylinder for several weeks at -45 C. When examined at -45 C, it was found that 0.27 mmol O$_2$ was present, together with 1.44 mmol Cl$_2$, contaminated with a small amount of BrCl. Subsequent warming to ambient temperature for several hours resulted in the formation of O$_2$ (2.19 mmol) and Br$_2$ (1.28 mmol). Since most (86 percent) of the chlorine and bromine from any possible new species was already accounted for, the products were not examined further.

REACTIONS OF PERIODATES AND CHLORINE FLUOROSULFATE

Dry, commercial Na or K periodate was loaded into a reactor in the dry box, followed by a measured amount of ClSO$_3$F which had been freshly fractionated. The reaction was allowed to proceed at -45 C or ambient temperature. When carried out in Teflon or glass reactors, the dark red liquid product was much in evidence in less than 1 hour. After reacting for 2 days to several weeks, volatile products were pumped out, separated, and analyzed by normal vacuum line methods, supplemented by infrared and gas chromatograph. Some typical results are shown in Table 2.

<table>
<thead>
<tr>
<th>MIO$_4^+$ mmol</th>
<th>ClSO$_3$F mmol</th>
<th>Temperature, °C</th>
<th>Time, days</th>
<th>O$_2$, mmol</th>
<th>Cl$_2$, mmol</th>
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</thead>
<tbody>
<tr>
<td>5.05</td>
<td>4.01</td>
<td>-45</td>
<td>35</td>
<td>0.1</td>
<td>1.87</td>
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<td>0.1</td>
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<tr>
<td>1.14</td>
<td>9.58</td>
<td>25</td>
<td>10</td>
<td>0.25</td>
<td>4.26</td>
</tr>
</tbody>
</table>

Generally, small amounts of ClSO$_3$F (~1 percent) were also found, together with variable, but quite small yields of S$_2$O$_5$F and Cl$_2$/FCl$_2$. The potassium salt gave rise to more O$_2$ on reaction at ambient temperature than did the sodium salt.
In the case where $\text{I}_2\text{SO}_3\text{F}$ was pyrolyzed, the experiment was carried out according to the preceding general procedure. A 2.57 mmol sample of Na$\text{IO}_4$ was reacted with 5.32 mmol C$\text{ISO}_3\text{F}$ at ambient temperature for 2 weeks. At that time, 2.24 mmol Cl$_2$ and 0.35 mmol O$_2$ were recovered. The nonvolatile products were pyrolyzed in the reaction cylinder for 1 week at 125°C, thereby producing additional O$_2$ and Cl$_2$, along with a small amount of S$_2\text{O}_5\text{F}_2$ and Cl$_2$. In all, 2.57 mmol O$_2$ was obtained, 2.82 mmol Cl$_2$. An off-white solid (0.934 g), which was identified as a mixture of Na$\text{SO}_3\text{F}$ and $\text{I}_2\text{SO}_3\text{F}$ by its infrared spectrum remained in the reactor. The theoretical weight of these products was 0.976 g.

**REACTION OF IODATE AND CHLORINE FLUOROSULFATE**

Potassium iodate (2.62 mmol) and C$\text{ISO}_3\text{F}$ (2.62 mmol) were placed in a 30 milliliter stainless steel cylinder. On warming to room temperature, the reactor was mechanically shaken for 2 days. Recooling to -196°C showed 0.31 mmol of noncondensable gas was present. Fractional condensation of the condensable products yielded 1.13 mmol Cl$_2$ and 0.38 mmol ClO$_2$. The solid product was examined in the glove box, weighed (0.79 g), and its infrared spectrum was taken. These observations indicated only unreacted K$\text{IO}_3$ and product K$\text{SO}_3\text{F}$ and $\text{I}_2\text{SO}_3\text{F}$ to be present. The calculated weight for the theoretical proportion of solid products is 0.80 g.

**PREPARATION OF IODYL FLUOROSULFATE**

Iodine pentoxide (6.11 mmol) that had been dried in the oven was placed in a 30 milliliter stainless steel cylinder and 12.9 mmol C$\text{ISO}_3\text{F}$ added. After 6 days at ambient temperature on the shaker, the cylinder was cooled to -196°C. Oxygen was present (2.08 mmol) and identified by its vapor pressure. After pumping away the O$_2$, the reactor was warmed to ambient temperature and the evolved materials were separated by fractional condensation. These consisted of 6.22 mmol Cl$_2$, and 0.36 mmol of a mixture of C$\text{ISO}_3\text{F}$ and S$_2\text{O}_5\text{F}_2$. Prolonged pumping at ambient temperature was necessary to remove the last traces of these volatile products from the solid. The solid left in the reactor was pale yellow, hygroscopic, and identical to $\text{I}_2\text{SO}_3\text{F}$ prepared via S$_2\text{O}_6\text{F}_2$. Powder diffraction data for $\text{I}_2\text{SO}_3\text{F}$ are shown in Table 3.

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FLUORINATION OF IODYL FLUOROSULFATE

A 2.15 mmol sample of \( \text{I}_2\text{SO}_3\text{F} \) was reacted with approximately 22 mmol \( \text{F}_2 \) in a 30 milliliter cylinder at ambient temperature for 10 days. The material not condensable at -196 C (\( \text{F}_2 \) and \( \text{O}_2 \)) was pumped out and the other volatile products were fractionally separated while warming back to ambient temperature. These products were 1.09 mmol \( \text{IF}_5 \), 1.07 mmol \( \text{IF}_7 \), 1.91 mmol \( \text{SO}_3\text{F}_2 \), and 0.13 mmol \( \text{S}_2\text{O}_6\text{F}_2 \). Thus, all the \( \text{I}_2\text{SO}_3\text{F} \) had reacted.

A 2.05 mmol sample of \( \text{I}_2\text{SO}_3\text{F} \) was reacted with 3.28 mmol \( \text{SF}_4 \) at ambient temperature in a 10 milliliter cylinder. No -196 C noncondensable gases were found, and the other products were separated in U-traps cooled at -80 C, -112 C, and -196 C. These were identified by their infrared spectra as \( \text{IF}_5 \), \( \text{S}_2\text{O}_5\text{F}_2 \), \( \text{SO}_2 \), and \( \text{SOF}_2 \). No unreacted \( \text{SF}_4 \) was recovered.
REACTION OF IODINE AND CHLORINE PERCHLORATE

Sublimed I₂ (0.545 mmol) was placed in an FEP Teflon tube fitted with a stainless steel valve. Freshly fractionated C10C10₃ (4.02 mmol) was condensed into the tube at -196 C and the reaction allowed to proceed by raising the temperature to -45 C. After a week, the materials volatile at -45 C were pumped out and separated by fractional condensation. No noncondensable gas was present. Some chlorine perchlorate was recovered (0.73 mmol), together with Cl₂ (1.72 mmol), which was contaminated with a small amount of FC10₃ and CO₂. Based on 1 mole of I₂ reacting with 6 moles of C10C10₃ to give I(OClO₃)₃ and Cl₂, the yield of Cl₂ was 102 percent. The product was a pale yellow solid.

Thermal decomposition of the I(OClO₃)₃ was noted on warming to 0 C. Pumping on the solid at that temperature for several days while trapping the evolved gases at -196 C showed that Cl₂O₇ was the primary volatile decomposition product, but other highly colored chlorine oxides such as ClO₂ and probably Cl₂O₆ were also given off. The decomposed I(OClO₃)₃ was dark red at 0 C, but became nearly white when warmed to ambient temperature for the final stage of the decomposition. At this point, the measured weight loss corresponded to the removal of 1.1 mmol of Cl₂O₇ from each I(OClO₃)₃.

REACTION OF IODINE AND CHLORINE NITRATE

In the same manner as the above I₂-C10C10₃ reaction, 1.005 mmol I₂ and 8.20 mmol C10NO₂ were reacted at -45 C. After 1 week, the materials volatile at -45 C were removed and separated. These were unreacted C10NO₂ (2.23 mmol) and Cl₂ (3.01 mmol). Based on 3Cl₂ from each I₂ reacting to give I(ONO₂)₃, the Cl₂ yield was 99.8-percent. The product I(ONO₂)₃ was a fluffy light yellow colored solid at -45 C. Thermal decomposition of the I(ONO₂)₃ was accomplished by the same method used for the trisperchlorate compound. An excellent yield of N₂O₅ (2.05 mmol) was obtained based on one N₂O₅ from each I(ONO₂)₃. The resulting solid was tan colored. Gradually over the next week, additional decomposition was evident since the typical brown colored fumes of NO₂ became visible in the tube. An infrared spectrum of the solid at that time showed no N=O absorption.
APPENDIX A

SELENIUM CHLORIDE PENTAFLUORIDE
REFERENCES

1. R-8234, Final Report, Inorganic Halogen Oxidizers, Nonr 4428(00), Rocketdyne, A Division of North American Rockwell, Canoga Park, California, 31 May 1971, CONFIDENTIAL.


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SELENIUM CHLORIDE PENTAFLUORIDE

By C. J. Schack, R. D. Wilson, and J. F. Hon

The existence of SF₅Cl has been known¹ for some time, while TeF₅Cl has been reported² more recently. However, no report concerning the preparation of the intermediate member of the S-Se-Te triad, SeF₅Cl, has appeared. Since the best synthetic routes³ to SF₅Cl involve chlorination of sulfur fluoride substrates, and since this reaction had been found to be enhanced by added alkali metal fluorides⁴, this technique was applied to the formation of SeF₅Cl. We wish now to report the synthesis and characterization of this new compound.

Experimental

Apparatus and Materials

The equipment used in this work has been described⁵ and was supplemented with a Perkin-Elmer Model 457 Infracord and a 10 cm., stainless steel, infrared cell fitted with AgBr windows. Details concerning the preparation or treatment of ClF, Cl₂SO₃F, and CsF have been given.⁵ Additional materials were purchased and used as received.

SeF₄. - Selenium tetrafluoride was first prepared from Se powder and ClF according to Pitts and Jache.⁶ Later it was determined that ClF₃ performed equally well in this reaction, thereby circumventing the need to prepare ClF. Typically, a prepassivated 30 ml stainless steel cylinder was loaded with Se powder (14.2 mmol) in the dry box. Chlorine trifluoride (20.3 mmol) was added at -196⁰ from a vacuum line and the cylinder allowed to warm slowly to ambient temperature where it was maintained for a day or until needed. Vacuum fractionation through U-traps cooled to -30, -78, and -196⁰ furnished SeF₄ (12.3 mmol) in the highest temperature trap. The purity and identity of the...
SeF₄ was verified by its vapor pressure and infrared spectrum. Based on the equation

\[ 3 \text{Se} + 4 \text{ClF}_3 \rightarrow 3 \text{SeF}_4 + 2 \text{Cl}_2 \]

the yield was 87%, a value comparable to that found for ClF reactions.

SeF₅Cl. - Selenium chloride pentafluoride was prepared by first forming the solid complex, CsSeF₅, from CsF and SeF₄. Weighed samples of the complex were placed in prepassivated cylinders and ClSO₃F added at -196°C. After warming to room temperature for several hours or more, the volatile products were separated by fractional condensation at -95, -112, and -196°C. Unreacted ClSO₃F was retained at -95°C while by-products and impurities such as ClIF, FC1O₂, and Cl₂ passed into the trap cooled to -196°C. Pure SeF₅Cl was found in the -112°C fraction. From 4.50 mmol CsSeF₅, 4.13 mmol SeF₅Cl was obtained, corresponding to a yield of 91.7% for the equation.

\[ \text{CsSeF}_5 + \text{ClSO}_3\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{SeF}_5\text{Cl} \]

The presence of uncomplexed CsF in the salt does not inhibit the formation of SeF₅Cl directly, but does result in the loss of some ClSO₃F by reaction to form ClIF.

Because the system CsF/SF₄/ClF was very effective in producing SF₅Cl, it was expected that CsF/SeF₄/ClF would behave similarly. Such was not the case and unreacted ClF was always fully recoverable after one day or several weeks in contact with CsSeF₅. However, in the course of preparing SeF₄ from Se and ClF or ClF₃, it was found that excesses of the chlorine fluorides gave detectable yields of SeF₅Cl. To determine the extent of this reaction, 4.19 mmol SeF₄ and 4.21 mmol ClF were placed in a 10 ml stainless steel cylinder and kept at ambient temperature for eight days. Separation of the products by fractional condensation led to the recovery of unreacted SeF₄ and ClF (1.45 mmol each), as well as trace amounts of SeF₆ and Cl₂. The main product was SeF₅Cl (2.62 mmol), representing a 95% yield based on the SeF₄ that had reacted. With ClF₃, up to 10% yields of SeF₅Cl were obtained, but always accompanied by much greater amounts of SeF₆. Thus the direct reaction of SeF₄ and ClF affords an alternate, albeit less efficient, route to SeF₅Cl.
Properties of SeF₅Cl. - Selenium chloride pentafluoride is colorless as a gas, liquid or solid. It is stable at ambient temperature when stored in clean, dry, passivated stainless steel cylinders. However, contact with glass always resulted in significant decomposition. Even glassware suitably dry and otherwise prepared for the manipulation of ClF₃ did not serve for handling SeF₅Cl. It seems likely that this property hindered the earlier discovery of this compound.

Analysis. - A 0.2001 g sample of SeF₅Cl was hydrolyzed with excess standardized NaOH solution in a glass ampoule fitted with a Teflon Fischer-Porter valve. Fluoride, selenium, and base consumption were determined as reported by Smith and Cady. Fluoride was also determined by the usual thorium nitrate titration. The amount of base consumed was calculated, assuming the hydrolysis equation

\[ \text{SeF}_5\text{Cl} + 8\text{OH}^- \rightarrow \text{SeO}_4^{2-} + 4\text{H}_2\text{O} + 5\text{F}^- + \text{Cl}^- . \]

Anal. Calcd for SeF₅Cl: Se, 37.71; F, 45.37; OH⁻ consumed, 8.00 equiv/mol. Found: Se, 37.98; F, 45.18; OH⁻ consumed, 7.82 equiv/mol.

Molecular Weight. - The molecular weight of the compound as determined by vapor density, assuming ideal gas behavior was 208 (calcd. 209.5).

Vapor Pressure, Boiling Point, and Melting Point. - The vapor (sublimation) pressure of SeF₅Cl over the temperature range -79 to 3°C is \( P(\text{mm}) \): 

-78.7; 6; -64.4; 19; -45.3; 66; -32.2; 142; -23.0; 220; 0.0; 630; 3.5; 729.

The pressure-temperature relationship is described by the equation \( \log P_{\text{mm}} = 7.779 - 1360/T^\circ\text{K} \). The normal boiling point calculated from the equation is 4.5°C; with a heat of vaporization of 6.22 kcal/mole and a Trouton constant of 22.4. Under its own vapor, the compound melts at -19°C. Since part of the pressure-temperature data given is below the melting point, it is actually a sublimation pressure and not a vapor pressure. However, pressure values obtained above and below the melting point were nearly on the same line, indicating little difference in the heats of sublimation and vaporization, and consequently a very low heat of fusion.

Infrared Spectrum. - The infrared spectrum of SeF₅Cl in the range 4000 - 250 cm⁻¹ shows several absorptions with the most prominent ones occurring at 745 (v, vs).
440 (vs), 420 (s), 385 (w), and 335 cm\(^{-1}\) (m). The two highest frequencies and the strongest bands noted are comparable to bands of similar intensity and position in related hexacoordinate selenium fluorides. Thus, the two strongest bands for SeF\(_6\)^10 occur at 780 and 430 cm\(^{-1}\) and for SeF\(_5\)OF\(^11\) at 750 and 422 cm\(^{-1}\). That these bands are typical of the SeF\(_5\) group is shown by their presence in a series of substituted SeF\(_5\) compounds.\(^1\) A detailed analysis of the vibrational spectrum of SeF\(_5\)Cl is in progress.\(^1\)2

**Nuclear Magnetic Resonance Spectrum.** - The \(^{19}\)F nmr spectrum of SeF\(_5\)Cl is shown in Figure 1. It is an AB\(_4\) spectrum and resembles that of SF\(_5\)Cl\(^13\) so closely as to be virtually identical. The reported chemical shifts for SF\(_5\)Cl when converted to a CFCl\(_3\) reference point are -62.3 and -125.8 ppm, respectively, for the axial and equatorial fluorines. For SeF\(_5\)Cl, the corresponding values taken from Figure 1 are -71.3 and -132.0 ppm. The only part of the spectrum of SeF\(_5\)Cl not identical with the SF\(_5\)Cl example is the appearance of the small satellite lines due to \(^{77}\)Se-\(^{19}\)F coupling. The observed coupling constant of 629 Hz is furthermore comparable to selenium-fluorine coupling in compounds which contain a chlorine bonded to the selenium central atom as in SeOfCl, where a value of 647 Hz was reported.\(^1\)4

**Acknowledgment**

The authors gratefully acknowledge support for this work by the Office of Naval Research, Power Branch. We are also indebted to Drs. D. Pilipovich and K O. Christie for helpful discussion.
References

Figure 1. $^{19}\text{F nmr}$ Spectrum of SeF$_5$Cl

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A-8
APPENDIX B

SELENIUM PENTAFLUORIDE CHLORIDE VIBRATIONAL SPECTRUM,
FORCE CONSTANTS, AND THERMODYNAMIC PROPERTIES

R-8725
B-1/B-2
Contribution from Rocketdyne, a Division of North American Rockwell, Canoga Park, California 91304

SELENIUM PENTAFLUORIDE CHLORIDE, SeF$_5$Cl. VIBRATIONAL SPECTRUM, FORCE CONSTANTS, AND THERMODYNAMIC PROPERTIES

By K. O. Christie, C. J. Schack, and E. C. Curtis

Received ...

Abstract

The infrared spectrum of gaseous and the Raman spectrum of liquid SeF$_5$Cl is reported. The observed spectrum is consistent with symmetry $C_4v$. The structure of SeF$_5$Cl can be derived from an octahedron with one chlorine and five fluorine atoms occupying the six corners. A modified valence force field and thermodynamic properties in the range 0 - 2000$^\circ$K were computed for SeF$_5$Cl.

Introduction

The existence of the novel selenium fluoride chloride, SeF$_5$Cl, has recently been discovered. In this paper, we wish to report its vibrational spectrum, force constants, and thermodynamic properties.

Experimental

The preparation, purification, physical properties, and handling of SeF$_5$Cl will be described elsewhere. The infrared spectra were recorded on a Perkin Elmer Model 457 spectrophotometer in the range of 4000 - 250 cm$^{-1}$. The instrument was calibrated by comparison with standard calibration points. Stainless steel cells of 5 or 10 cm path-length fitted with AgCl or AgBr windows were used as sample containers. The Raman spectrum of liquid SeF$_5$Cl was recorded using a R-8725...
Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ~-25°C and a d.c. ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. Clear Kel-F tubes (~2 mm i.d.) were used as sample containers in the transverse viewing-transverse excitation technique.

Results and Discussion

Vibrational Spectrum. - Figures 1 and 2 show the infrared spectrum of gaseous and the Raman spectrum of liquid SeF$_5$Cl, respectively. The observed frequencies are listed in Table I.

Since SeF$_5$Cl can be considered as a mono-substituted derivative of octahedral SeF$_6$, it should belong to point group C$_{4v}$. The eleven normal modes of SeF$_5$Cl of symmetry C$_{4v}$ can be classified as 4a$_1$ + 2b$_1$ + 2b$_2$ + 4e. Of these, all eleven modes will be Raman active, whereas only the a$_1$ and e modes will be infrared active. Of the Raman lines, the four a$_1$ modes should be polarized, the rest being depolarized. The assignment of the observed bands to individual modes (Table I) is based on the following arguments. There are four clearly polarized Raman lines at 721, 656, 443, and 385 cm$^{-1}$. As predicted by theory, these have counterparts in the infrared spectrum. Hence, these four bands must belong to species a$_1$. The two higher frequency lines are within the range expected for stretching modes of mainly covalent Se–F bonds. They are assigned, respectively, to the SeF and the symmetric SeF$_4$ stretching vibrations on the basis of their relative Raman intensities. Similarly, the SeCl stretching mode should be of higher Raman intensity than the SeF$_4$ umbrella deformation. Therefore, the 443 cm$^{-1}$ band is assigned to the SeF$_4$ deformation. This assignment is further supported by the fact that in the infrared spectra of both, SeF$_4$(OF)$_2$ and SeF$_5$OF, very strong infrared bands were observed at about 430 cm$^{-1}$.

Of the remaining six depolarized Raman bands, the 745, 424, and 336 cm$^{-1}$ lines have counterparts in the infrared and, consequently, belong to species e. The very intense infrared band at 745 cm$^{-1}$ obviously represents the antisymmetric
TABLE II

Vibrational Spectrum of SeF₆Cl

<table>
<thead>
<tr>
<th>Infrared, gas</th>
<th>Raman, liquid</th>
<th>assignment for point</th>
</tr>
</thead>
<tbody>
<tr>
<td>1449 vw</td>
<td></td>
<td>2ν₁ = 1442 (A₁)</td>
</tr>
<tr>
<td>1380 w</td>
<td></td>
<td>ν₅ + ν₈ = 1381 (E)</td>
</tr>
<tr>
<td>865 vw</td>
<td></td>
<td>ν₃ + ν₉ = 861 (E)</td>
</tr>
<tr>
<td>821 w</td>
<td></td>
<td>ν₃ + ν₄ = 824 (A₁)</td>
</tr>
<tr>
<td>745 vvs</td>
<td>745 (0.3) dp</td>
<td>ν₈ (e)</td>
</tr>
<tr>
<td>729 ms, sh</td>
<td>721 (1.8) p</td>
<td>ν₁ (a₁)</td>
</tr>
<tr>
<td>654 w</td>
<td>656 (10) p</td>
<td>ν₂ (a₁)</td>
</tr>
<tr>
<td></td>
<td>636 (0.6) dp</td>
<td>ν₅ (b₁)</td>
</tr>
<tr>
<td>587 vw</td>
<td></td>
<td>ν₇ + ν₁₁ = 593 (E)</td>
</tr>
<tr>
<td>529 w</td>
<td></td>
<td>ν₈ - ν₁₁ = 532 (A₁ + A₂ + B₁ + B₂)</td>
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<tr>
<td>468 w, sh</td>
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<tr>
<td>440 vs</td>
<td>443 (2.2) p</td>
<td>ν₃ (a₁)</td>
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<td>421 s</td>
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<td>ν₉ (e)</td>
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<td>385 (8.5) p</td>
<td>ν₄ (a₁) Cl₃</td>
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<td></td>
<td>380 dp</td>
<td>ν₇ (b₂) + ν₄ (a₁) Cl₃</td>
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<td>334 m</td>
<td>336 (1.2) dp</td>
<td>ν₁₀ (e)</td>
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<tr>
<td></td>
<td>213 (1.4) dp</td>
<td>ν₁₁ (e)</td>
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R-8725
B-5
TABLE II

Fundamental Frequencies of SeF$_5$Cl and SF$_5$Cl$^a$

<table>
<thead>
<tr>
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<td>$\nu_1$</td>
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<tr>
<td>$\nu_2$</td>
<td>$v_{\text{sym}XF_4}$</td>
<td>707</td>
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<td>$\nu_3$</td>
<td>$\delta_{\text{sym}XF_4}$ out of plane</td>
<td>602</td>
</tr>
<tr>
<td>$\nu_4$</td>
<td>$v_{XCl}$</td>
<td>402</td>
</tr>
<tr>
<td>$\nu_5$</td>
<td>$v_{\text{sym}XF_4}$ out of phase</td>
<td>625</td>
</tr>
<tr>
<td>$\nu_6$</td>
<td>$\delta_{\text{aa}XF_4}$ out of plane</td>
<td>--</td>
</tr>
<tr>
<td>$\nu_7$</td>
<td>$\delta_{\text{sym}XF_4}$ in plane</td>
<td>505</td>
</tr>
<tr>
<td>$\nu_8$</td>
<td>$v_{\text{aa}XF_4}$</td>
<td>909</td>
</tr>
<tr>
<td>$\nu_9$</td>
<td>$\delta_{XF_4}$</td>
<td>579</td>
</tr>
<tr>
<td>$\nu_{10}$</td>
<td>$\delta_{\text{aa}XF_4}$ in plane</td>
<td>441</td>
</tr>
<tr>
<td>$\nu_{11}$</td>
<td>$\delta_{\text{Cl}XF_4}$</td>
<td>287</td>
</tr>
</tbody>
</table>

(a) Frequency values taken from Reference 3
SeF$_4$ stretching vibration. For SeF$_4$(OF)$_2$ and SeF$_5$OF, this mode was observed$^4$ at 743 and 750 cm$^{-1}$, respectively. By analogy with the known spectrum$^3,5$ of the SF$_5$Cl molecule, one might expect the F-SeF$_4$ wagging to have the highest and the ClSeF$_4$ wagging mode to have the lowest frequency of the three remaining e modes, with the antisymmetric in plane SeF$_4$ deformation being intermediate. Consequently, the bands at 424 and 336 cm$^{-1}$ are assigned to the F-SeF$_4$ wagging and the antisymmetric in plane SeF$_4$ deformation modes, respectively. Since the infrared spectrum was not recorded below 250 cm$^{-1}$, it is not known if the 213 cm$^{-1}$ Raman band has indeed a counterpart in the infrared spectrum. However, the assignment of the 213 cm$^{-1}$ Raman line to the fourth e mode, the Cl-SeF$_4$ wagging mode, appears very plausible for the following reasons. The SeCl stretching mode, $\nu_4$, occurs at a frequency (385 cm$^{-1}$), considerably lower than those of the three SeF$_4$ stretching modes. Hence, the Cl-SeF$_4$ deformation frequency should be lower than 300 cm$^{-1}$ and must be assigned to 213 and not to 380 cm$^{-1}$, the only remaining alternative.

For the assignment of the remaining three (2b$_1$ and 1b$_2$) modes, we are left with only two Raman lines. The unobserved Raman line is assumed to be the antisymmetric out of plane SeF$_4$ deformation mode, $\nu_6$. The fact that this mode has not been observed is not surprising. For the structurally similar halogen pentafluorides (ClF$_5$, BrF$_5$, and IF$_5$) and for SF$_5^-$ and TeF$_5^-$, all belonging to point group C$_{4v}$, this mode was not observed. Of the two available Raman lines (636 and 380 cm$^{-1}$), the higher frequency value obviously belongs to the symmetric out of phase SeF$_4$ stretching mode, leaving the 380 cm$^{-1}$ band to be assigned to the SeF$_4$ scissoring mode.

In the infrared spectrum of the gas, several bands of very low relative intensity were observed which cannot be attributed to fundamental vibrations. Most of them can satisfactorily be assigned to overtones and combination bands (see Table I).

The above given assignments rest mainly on the Raman lines, the polarization measurements, relative intensities, and the presence or absence of counterparts in the infrared spectrum. It appears interesting to examine to what extent the infrared band contours agree with theoretical predictions. It should be kept in mind, however, that band contours are sometimes subject to unpredictable
changes and, hence, do not always agree with the predictions. Ideally, the \( \text{a}_1 \) modes should show PQR structure as expected for parallel bands of a symmetric top molecule with \( I_A \) and \( I_B \) being similar to \( I_C \). Indeed, \( \nu_3 \) and \( \nu_4 \) show the expected band shape. The band shape of \( \nu_1 \) is not clear-cut; however, its band shape may have been influenced by Coriolis interaction with \( \nu_3(e) \), which occurs at almost the same frequency. The band contour of \( \nu_2 \) does not show a sharp PQR structure. This was also the case for \( \nu_2 \) of SF\(_5\)Cl.\(^3\),\(^6\) The band contour of \( \nu_9(e) \) agrees with that expected for a perpendicular band, but that of \( \nu_{10} \) closely resembles that of the parallel bands. It is interesting to note that \( \nu_{10}(e) \) of SF\(_5\)Cl\(^3\) and the corresponding \( \nu_9(e) \) mode of ClF\(_5\)\(^6\) also showed a PQR structure different from those of the remaining perpendicular bands in species \( e \).

The fact that the band contour of the lowest perpendicular band resembles those of the parallel bands has been observed for a number of symmetric top molecules and can be attributed to first order Coriolis perturbations.\(^8\) In summary, the band contours of SeF\(_5\)Cl agree well with those observed for SF\(_5\)Cl, even though differing somewhat from those predicted on the basis of the rigid rotor, harmonic oscillator approximation.

Comparison between the vibrational spectra of SF\(_5\)Cl\(^3\),\(^5\) and SeF\(_5\)Cl shows good agreement. However, the SeF\(_5\)Cl data and results from force constant calculations\(^9\) indicate that for SF\(_5\)Cl, the original assignment of the S-Cl wagging mode, \( \nu_{11}(e) \), to the 287 cm\(^{-1}\) band by Cross \textit{et al.}\(^5\) should be retained. The revision of this assignment by Griffiths\(^3\) was based on the fact that he observed an infrared counterpart for the 396 cm\(^{-1}\) Raman band. The latter, however, might equally well be interpreted as the Cl\(^{37}\) isotope band of the S-Cl stretching mode, \( \nu_4 \), at 402 cm\(^{-1}\) the splitting and relative intensity being in good agreement with predictions. Furthermore, the infrared spectrum of SF\(_5\)Cl showed\(^3\) a broad band at about 280 cm\(^{-1}\) which might represent the counterpart to the Raman band at 271 cm\(^{-1}\). Hence, the original assignment\(^5\) for \( \nu_{11} \) does not violate the selection rules and results in a more reasonable frequency value.

The high relative intensity of the 306 cm\(^{-1}\) band in the Raman spectrum of SF\(_5\)Cl and its infrared activity also argue against its proposed assignment\(^5\) to \( \nu_6 \) since for all the remaining related molecules, it has either not been observed or has been of very low intensity. Consequently, we propose that for SF\(_5\)Cl, \( \nu_6 \) has either not been observed or is hidden underneath the intense \( \nu_4 \) band.

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In summary, the vibrational spectrum of SeF$_5$Cl is consistent with symmetry $C_{4v}$. Ten out of eleven fundamentals were observed and assigned in agreement with the selection rules for $C_{4v}$.

**Force Constants.** A normal coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method$^9$, assuming the following geometry and coordinate definitions:

- $R_{SeF}$ = 1.68 Å,
- $D_{SeCl}$ = 2.14 Å,
- $r_{SeF}$ = 1.68 Å,
- $\alpha = \angle FSeF$ = 90°,
- $\beta = \angle FSeF$ = 90°,
- and $\delta = \angle ClSeF$ = 90°, where $F$ refers to the axial (unique) fluorine ligand.

The deformation coordinates were weighted by unit (1Å) distance. The bond lengths were estimated using the Schomaker-Stevenson rule.$^{10}$

The force constants were calculated by trial and error with the aid of a time-sharing computer to get exact agreement between the observed and computed frequencies using the simplest possible modified valence force field. Unique force constants could not be computed since the general valance field has 38 constants and there are only ten observed frequencies. However, numerical experiments showed that some of the principal force constants are quite independent of the chosen interaction constants and, hence, should approach those of a general valence force field. The computed values are

- $f_R = 4.42$ mdyn/Å,
- $f_D = 2.75$ mdyn/Å,
- $f_R = 4.31$ mdyn/Å,
- $f_{rr} = 0.07$ mdyn/Å rad$^2$,
- $f_{rr}' = 0.35$ mdyn/Å,
- $f_{\alpha} = 1.26$ mdyn/Å,
- $f_{\beta} = 1.92$ mdyn/Å,
- $f_\delta = 1.16$ mdyn/Å,
- $f_{\delta} = 0.30$ mdyn/Å,
- $f_{55}' = 0.18$ mdyn/Å,
- and $f_{D\delta} = 0.28$ mdyn/Å.

The two interactions, $f_{RR}$ and $f_{RR}'$, were determined from only one symmetry force constant value making the assumption $f_{RR}/f_{55} = f_{RR}'/f_{55}'$.

The values of the stretching force constants, $f_R$ and $f_D$, of SeF$_5$Cl are identical within their uncertainty limits, indicating similar bonding for both the axial and the equatorial fluorine ligands. Furthermore, their magnitude (4.3 to 4.4 mdyn/Å) approximates those obtained for other mainly covalent, hexavalent selenium compounds such as SeF$_6$ (5.01 mdyn/Å)$^{11}$ Se$_2$F$_2$ (4.44 mdyn/Å)$^{12}$, or Se$_6$F$^-$ (4.23 mdyn/Å)$^{12}$ with bond orders$^{12,13,14}$ close to one. The slight decrease of the stretching force constant values from SeF$_6$ towards SeF$_5$Cl parallels that found for the analogous pair, SF$_6$ and SF$_5$Cl$^{12}$ (see Table III). It can be explained by the substitution of one fluorine atom in XF$_6$ by a less electronegative

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ligand, such as Cl. This causes an increased polarity \( \frac{\delta^+}{\delta^-} \) of the remaining SF bonds. Since stretching force constants reflect only the contributions from covalent bonding,\(^{12,14}\) their value should correspondingly decrease.

<table>
<thead>
<tr>
<th></th>
<th>SeF(_6)</th>
<th>SeF(_5)Cl(^{b})</th>
<th>SeF(_6)</th>
<th>SeF(_5)Cl</th>
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<tr>
<td>( f_R )</td>
<td>4.83</td>
<td>4.42</td>
<td>5.01</td>
<td>4.31</td>
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<tr>
<td>( f_r )</td>
<td>5.26</td>
<td>5.01</td>
<td></td>
<td></td>
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</tbody>
</table>

(a) Reference 15
(b) Reference 12
(c) Reference 11

The interaction constants are in accord with our experience with similar molecules.\(^7\) The value given for \( f_{D6} \) was determined from \( V(\delta_{D6} - \delta_{D8}) = 0.4 \), which was required to fit \( \nu_3 \) and \( \nu_4 \). This is not too surprising considering the mixing of the two modes (see Table IV). No evidence was found for the similar terms, \( f_{D8} \), \( f_{D8} \), and \( f_{D8} \), being non-zero, although this cannot be ruled out and might be expected from our experience with similar molecules\(^7\) or from orbital following arguments.

Coriolis coupling coefficients were computed for SeF\(_5\)Cl hoping that the e-block band contours could support the assignment. The computed values using the above given force constants were \( \zeta_3 = 0.5 \), \( \zeta_9 = 0.5 \), \( \zeta_{10} = 0.4 \) and \( \zeta_{11} = 0.7 \). However, the values of the moments of inertia are such that these values for \( \zeta \) do not result in very distinctive band shapes.\(^8\) The band shapes are further complicated by the natural chlorine and selenium isotopes and by hot bands. Although the
observed band shapes are not inconsistent with those predicted, the contours could not be used to verify the computed $\zeta$'s.

The potential energy distribution was computed using the above force constants and is shown in Table IV. The assignment listed in Table I is supported by these values. The mixing of $v_3$ and $v_4$ is large, so that strictly, one is not a stretching and one a deformational mode, but rather a symmetric and antisymmetric combination of the two motions.

**Thermodynamic Properties.** - The thermodynamic properties were computed for this molecule using the rigid-rotor-harmonic-oscillator\(^16\) approximation. The results are given in Table V. The frequencies used were those of Table II, assuming a computed value of 336 cm\(^{-1}\) for $v_6$. The moments of inertia used were $I_x = I_y = 312$ and $I_z = 214$ amu \(\text{A}^2\) computed from the geometry assumed above, with a symmetry factor of 4.

**Acknowledgment.** - We are indebted to Dr. D. Pilipovich for continuous encouragement and to Dr. J. Cape for the use of the Raman spectrometer. This work was supported by the Office of Naval Research, Power Branch.
TABLE IV

Potential Energy Distribution for SeF₅Cl.

Contributions of less than 0.10 are not listed.

<table>
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<tr>
<th>a₁ v₁</th>
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<th>0.88 fᵦ</th>
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<td>v₂</td>
<td>654</td>
<td>0.90 fᵦ</td>
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<tr>
<td>v₃</td>
<td>440</td>
<td>0.41 fᵦ + 0.36fᵦ + 0.21 f₈ + 0.11 fᵦ</td>
</tr>
<tr>
<td>v₄</td>
<td>384</td>
<td>0.58 fᵦ + 0.15fᵦ + 0.15f₈</td>
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<tr>
<td>b₁ v₅</td>
<td>636</td>
<td>0.95 fᵦ</td>
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<tr>
<td>v₆</td>
<td>(336)</td>
<td>0.54 fᵦ + 0.33 f₈</td>
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<td>b₂ v₇</td>
<td>380</td>
<td>1.10 fₐ - 0.10 fₐₐ′</td>
</tr>
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<td>e v₈</td>
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<td>1.00 fᵦ</td>
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<td>1.02 f₆ - 0.16 f₆₆′</td>
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R-8725
B-12
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(a) Units for $C_p^0$, $S^0$, and $F^0$ are g calories, g moles, and degrees Kelvin and for $H_0^0$, kilocalories, and moles.
REFERENCES

1. C. J. Schack and R. D. Wilson, to be published.


Diagram Captions

Figure 1. - Infrared spectrum of gaseous SeF$_5$Cl at 434 (A), 40 (B), 10 (C), 2 (D), and 1.5 mm (E) pressure in 10 cm cell; window material AgBr.

Figure 2. - Raman spectrum of liquid SeF$_5$Cl. Traces A, B, and D incident polarization perpendicular; traces C and E incident polarization parallel. Traces A and B were recorded at different recorder voltages, traces D and E under higher resolution. Experimental conditions were identical for A and C and for D and E, except for change of direction of polarization. F indicates spectral slit width.
Figure 2.
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B-17/B-18
APPENDIX C

DIFLUOROCHLORATE (V) ANION, C\textsubscript{10}F\textsubscript{2}\textsuperscript{–} VIBRATIONAL SPECTRUM AND FORCE CONSTANTS
Contribution from Rocketdyne, a Division of North American Rockwell
Canoga Park, California 91304

The Difluorochlorate (V) Anion, ClO2-F2-
Vibrational Spectrum and Force Constants
By Karl O. Christe and E. C. Curtis
Received ... 1971

Abstract
The infrared and the Raman spectrum of solid CsF·ClO2-F2 have been recorded. They are consistent with a ClO2-F2- anion of symmetry C2v. The structure can be derived from a trigonal bipyramid, where the two F atoms occupy the axial and the two O atoms and the lone electron pair occupy the equatorial positions. A modified valence force field has been computed for ClO2-F2-, indicating double bond character for the ClO bonds and rather weak ClF bonds with high ionic contributions.

Introduction
Huggins and Fox have recently reported the existence of CsClO2-F2. However, they did not succeed in obtaining any spectroscopic or structural data on this interesting compound. In this paper, we wish to report the vibrational spectrum and a modified valence force field for CsClO2-F2.

Experimental Section

Materials and Apparatus. — The materials used in this work were manipulated in a well-passivated (with ClF3) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 1F4Y). Pressures were measured with a Heise, Bourdon tube-type gauge (0–1500 mm + 0.1%). Chloryl fluoride (prepared in this laboratory from KClO3 and F2)2

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C-3
was purified by fractional condensation. Its purity was determined by measuring its vapor pressure and infrared spectrum. Cesium fluoride was fused in a platinum crucible and powdered in a dry box prior to use. Because of their hygroscopicity, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000–250 cm\(^{-1}\). The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to \(\sim -25^\circ\), and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses, pyrex or clear Kel-F capillaries were used as sample containers. For the capillaries, the transverse viewing-transverse excitation technique and for the conical tube the axial viewing-transverse excitation technique was used.

**Preparation of CsClO\(_2\)F.** – Dry CsF (7.64 mmol) was placed into a 10 ml prepassivated (with ClF\(_3\)) 316 stainless steel cylinder and ClO\(_2\)F (22.50 mmol) was added at \(-196^\circ\). The cylinder was kept at \(-25^\circ\) for 24 hours and subsequently placed on a mechanical shaker for 24 hours at 25\(^\circ\). Unreacted ClO\(_2\)F (16.89 mmol) was removed in vacuo at 25\(^\circ\), indicating that 73.4% of the CsF had been converted to CsClO\(_2\)F\(_2\).

**Results and Discussion**

**Synthesis and Properties.** – The synthesis and properties of CsClO\(_2\)F\(_2\) were in good agreement with those previously reported. The hydrolysis of CsClO\(_2\)F\(_2\) was...
studied by exposing a sample of CsClO$_2$F$_2$ between AgCl plates to atmospheric moisture and by monitoring the changes in its infrared spectrum. It was shown that the decrease of the relative intensity of the bands characteristic for ClO$_2$F$^-$ (see below) was accompanied by the appearance of the bands characteristic$^{3,4}$ for the ClO$_3^-$ and HF$_2^-$ anions. This indicates the following hydrolysis reaction:

$$\text{ClO}_2\text{F}_2^- + \text{H}_2\text{O} \rightarrow \text{ClO}_3^- + 2\text{HF}$$

**Vibrational Spectra.** - Figures 1 and 2 show the infrared and Raman spectra, respectively, of solid CsClO$_2$F$_2$. Weak absorptions owing to ClO$_3^-$ and HF$_2^-$ were almost always observed in the infrared spectrum and are omitted in Figure 1. The appearance of the ClO$_3^-$ and HF$_2^-$ bands in the infrared spectrum is due to the pronounced hygroscopicity of CsClO$_2$F$_2$ and to the small sample size used for infrared spectroscopy. The observed frequencies are listed in Table I, together with their assignment.

Numerous structural models can be written for ClO$_2$F$_2^-$. However, their number can be restricted since the chlorine central atom possesses a free electron pair which should be sterically active. Consequently, this chlorine atom should be penta coordinated, thus resulting in a pseudo trigonal bipyramidal structure for ClO$_2$F$_2^-$. For this structural type, five different arrangements of the ligands are possible. Comparison with the known structures of related molecules, such as substituted phosphorous pentafluorides$^{5-10}$, XeOF$_2$, or PO$_2$F$_2$ shows that the two axial positions are always occupied by the two most electronegative ligands.$^{11}$ Theoretical explanations for this behavior have previously been given.$^{13-16}$ Therefore, the most plausible structure for ClO$_2$F$_2^-$ is

$$\begin{bmatrix}
    F & \text{C} & 0 \\
    \text{C} & \text{C} & 0 \\
    \text{F} & \text{F} & \text{F}
\end{bmatrix}$$

This type of structure has also been suggested$^{11}$ for XeOF$_2$, which is isoelectronic with ClO$_2$F$_2^-$. The correctness of the proposed model can be tested by inspection of the observed vibrational spectrum. Spectroscopically, this model should contain the elements.
of the ClO$_2^+$ cation and the ClF$_2^-$ anion, both of which have recently been characterized.\textsuperscript{17-20} The ClO$_2^+$ cation is preferred over the ClO$_2^-$ radical and ClO$_2^-$ anion because ClO$_2^+$ and ClO$_2F_2^-$ contain a chlorine of the same oxidation state (+V). Furthermore, in ClO$_2F_2^-$, the electron withdrawing effect of the two highly electronegative fluorine ligands is expected to partially compensate the bond weakening influence of the formal negative charge.\textsuperscript{21} On the other hand, one should expect the two ClF bonds to be rather weak for the following reasons. Generally, in chlorine fluorides, replacement of two fluorine atoms by one doubly bonded oxygen atom significantly weakens the remaining ClF bond.\textsuperscript{22} Furthermore, the formal negative charge in anions always decreases the Cl-F bond strength by increasing the ionic contribution to these bonds. This can be easily understood since the formal negative charge will not be concentrated at the central atom but will be distributed mainly over the highly electronegative fluorine ligands. Since ClO$_2F_2^-$ contains two doubly bonded oxygen atoms and a formal negative charge, the ClF bonds in ClO$_2F_2^-$ should be at least as weak or weaker than in ClF$_2^-$. A closer inspection of Table I immediately reveals that the above predictions are indeed correct. The three fundamentals involving only a motion of the ClO$_2$ part of the ion exhibit frequencies very close to those of ClO$_2^+$\textsuperscript{17} and ClO$_2F^-$.\textsuperscript{22} The bands assignable to the three corresponding ClF$_2$ motions show frequencies somewhat lower than those\textsuperscript{20} observed for ClF$_2^-$. All nine fundamentals expected for XeO$_2F_2$ of symmetry C$_{2v}$ (these are classified as $4A_1 + A_2 + 2B_1 + 2B_2$) were observed if a coincidence of $v_7(B_1)$ and $v_9(B_2)$ at 337 cm$^{-1}$ is assumed. This double coincidence might account for the surprisingly high relative intensity of the 337 cm$^{-1}$ Raman band and has also been observed\textsuperscript{11} for isoelectronic XeO$_2$. The assignment of the observed bands to the individual modes is straightforward and was made by comparison with the known spectra of the related molecules listed in Table I. Comparison between the corresponding X-F modes in XeO$_2F_2$\textsuperscript{11} and ClO$_2F_2^-$ shows that the deformational modes have similar frequencies but that the XeF stretching frequencies are considerably higher than the ClF ones. This is not surprising since Cl and Xe do not belong to the same period of the periodic system. Generally, by going to the next higher period, the electronegativity of the central atom decreases and its size increases, thus resulting in an increase of the X-F stretching and a decrease of the X-F deformation force constants, respectively. This effect causes the stretching and deformation frequencies to move further apart with increasing mass number and has been observed for several series of related molecules and
ions, such as ClF$_5$, BrF$_5$, IF$_5$, SF$_5^-$, SeF$_5^-$, TeF$_5^-$, ClF$_2^+$, BrF$_2^+$, or ClF$_4^-$, BrF$_4^-$. The assignment of the weak and broad Raman band at 480 cm$^{-1}$ to $v_6(A_2)$ should be considered tentative. This band may contain some contribution from $v_6(B_1)$; however, its band center at 480 cm$^{-1}$ differs by 30 cm$^{-1}$ from the band center observed for $v_6$ in the infrared spectrum (510 cm$^{-1}$) and, hence, should belong to a different mode. In addition to the bands assigned to fundamental vibrations, a weak band was observed at 855 cm$^{-1}$ in the infrared spectrum of Cl$_2$F$_2^-$. This band cannot be due to a fundamental vibration and, hence, is assigned to the combination band, $v_3 + v_6(B_1)$. The splitting of $v_1(A_1)$ into three components in the Raman spectrum and of $v_8(B_2)$ into two components in the infrared spectrum is too large to be due to the two different chlorine isotopes. One would expect the isotope splittings in Cl$_2$F$_2^-$ to be similar to those found for ClO$_2^+$ and ClO$_2$.$^{22}$ Since the Cl$_2$F$_2^-$ spectra were recorded for crystalline samples, other effects, such as site symmetry splittings, are possible.

In summary, the observed number of bands, their frequencies and relative intensities in both the infrared and Raman spectrum are consistent with the predicted pseudo trigonal bipyramidal structure of symmetry $C_{2v}$. The agreement between the spectrum of Cl$_2$F$_2^-$ and those of related molecules is excellent.

**Force constants.** - A normal coordinate analysis was carried out to aid in the spectral assignment. The kinetic and potential energy metrics were computed by a machine method,$^{27}$ assuming the following geometry: $r_{ClF} = 1.79\text{Å}$, $r_{ClO} = 1.43\text{Å}$, $\alpha = \gamma_{OClO} = 120^\circ$, $\beta = \gamma_{OCIF} = 90^\circ$, and $\gamma_{FClF} = 180^\circ$. The ClF distance was taken as somewhat larger than those$^{28}$ of the two longer bonds in ClF$_3$ due to the uncommonly low stretching frequencies in Cl$_2$F$_2^-$. The ClO distance was estimated from the bond length–frequency correlation of Robinson.$^{29}$ The bond angles were assumed to be those of an ideal trigonal bipyramid, although they might be slightly reduced due to repulsion by the lone pair in accord with the Gillespie–Nyholm theory.$^{30}$

The force constants were calculated by trial and error with the aid of a time-sharing computer to get exact agreement between the observed and the computed frequencies using the simplest possible modified valence force field.

R-8725
C-7
Owing to the undetermined nature of the problem (17 force constants from 9 vibrational frequencies), unique force constants could not be computed. However, numerical experiments established that some of the principal force constants are quite independent of the chosen interaction constants and, hence, should approach those of a general valence force field. The computed values are

\[ f_R = 8.3, \quad f_{RR} = 0.1, \quad f_r = 1.6, \quad \text{and} \quad f_{rr} = -0.1 \text{ mdyne/Å}; \quad f_\theta = 1.95, \quad f_\phi = 1.2, \]

\[ f^{'}_\theta = 0.57, \quad \text{and} \quad f^{'}_\phi = 0.1 \text{ mdyne/Å rad}^2; \quad \text{and} \quad f_{r\theta}^{'} f_{r\phi}^{'} = 0.3. \]

The deformation coordinates were weighted by unit (1Å) distance.

The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength of the various bonds. Comparison with the values obtained for a number of related molecules and ions (see Table II) indicates for ClO\(_2\)F\(_2\) double bond character for the two chlorine oxygen bonds and unusually weak ClF bonds. The value of the Cl=O stretching force constant, \( f_R \), is slightly lower than those in ClO\(_2\) and ClO\(_2\)F\(_2\). This slight decrease might be explained by factors, such as the influence of the formal negative charge, change in hybridization due to the altered coordination number of the central atom, and different physical states (solid versus gas). Hence, no attempt will be made to evaluate the relative contributions from each effect.

Whereas the ClO bonds in ClO\(_2\)F\(_2\) exhibit double bond character, the value of the ClF stretching force constant, \( f_r \), of 1.6 mdyne/Å is unusually low. In addition to the reasons discussed above, i.e., oxygen substitution and formal negative charge, weak ClF bonds might be expected since ClO\(_2\)F\(_2\) has a pseudo trigonal bipyramidal structure. As pointed out previously\(^3\), this type of structure appears to be energetically unfavorable as also indicated by the low thermal stability of the CsF·ClO\(_2\)F adduct.

The small negative value of the ClF stretch-stretch interaction constant, \( f_{rr}^{'} \), is comparable to that found for KrF\(_2\) for which an explanation was given by Coulson\(^3\). The values found for the OCIF and OCIO deformation constants are as expected. The large values found for the interaction constant \( f_{BB}^{'} \), and the stretch-bend interaction term, \( f_{RB} \), are in accord with those obtained for the halogen pentafluoride molecules\(^3\).

R-8725
C-8
From the above discussion of the stretching force constants, it became obvious that the Cl = 0 bonds are predominantly covalent, whereas the Cl-F bonds contain strong contributions from ionic bonds. This finding confirms the previous predictions postulating the following bond model for a trigonal bipyramid type moiety with a free electron pair on the central atom. The two most electronegative ligands, i.e., fluorine atoms, occupy the axial positions and the two oxygen atoms and the free electron pair the three equatorial positions of the trigonal bipyramid. The equatorial bonds should have mainly sp² character (ignoring the double bond contributions), whereas the axial bonds involve mainly a delocalized p-electron pair of the chlorine central atom for the formation of a semi-ionic three-center four-electron p-σ bond pair. For an ideal semi-ionic 3c4e bond, one should therefore expect f to have a value about half that of a covalent Cl-F bond. The low value of 1.6 mdy/n/A obtained for C10F₂ obviously fulfills these requirements (covalent Cl-F bonds show stretching force constants ranging from about 3.5 to 4.7 mdy/n/A) and supports the above given bond model.

Acknowledgement. - The authors wish to express their gratitude to Drs. D. Pilipovich and C. J. Schack of Rocketdyne for helpful discussions and to Dr. I. Silversa of the Science Center of North American Rockwell for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch.
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<td>1221(0.8)</td>
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<td>902W</td>
<td>844</td>
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<td>1191</td>
<td>vs</td>
<td>1076(10)</td>
<td>1064</td>
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<td>845vs</td>
</tr>
<tr>
<td>855vw</td>
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<td>328s</td>
<td>333ms</td>
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<td>510vs,br</td>
<td></td>
<td>585vs</td>
<td>575W</td>
<td>702</td>
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<td>330–370m</td>
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<td>363(10)</td>
<td>324s</td>
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<td>198(0.7)</td>
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(a) Reference 11.


(c) Reference 17.

(d) Reference 22.


(f) Reference 20.
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<tr>
<td>(f_r)</td>
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(a) Reference 17.
(d) Reference 22.
(e) Reference 20.
(h) Reference 25.
REFERENCES

Diagram Captions

Figure 1. - Infrared spectrum of solid Cs\textsuperscript{+}ClO\textsubscript{2}F\textsubscript{2} as dry powder in an AgBr disk.

Figure 2. - Raman spectrum of solid Cs\textsuperscript{+}ClO\textsubscript{2}F\textsubscript{2}. Sample container, glass capillary. C indicates spectral slit width.
Vibrational Assignment of $\text{SF}_4$

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(Received .... 1971)

In a previous paper$^1$ we reported the Raman spectrum of gaseous $\text{SF}_4$. The Raman data suggested the need of revising all assignments for the deformational modes except for $\nu_7 (B_1)$. For the four stretching modes, the previous assignment,$^2-4$ made on the basis of infrared band contours, was adopted and force constants and mean amplitudes of vibration were computed.$^1$ In a recent paper,$^5$ Frey, Redington, and Aljibury proposed a reversed assignment for the two antisymmetric stretching modes, $\nu_6 (B_2)$ and $\nu_8 (B_2)$, based on a comparison with the spectra of the structurally related molecules $\text{BrF}_3$ and $\text{ClF}_3$. Since the observed infrared band contours might be used as an argument against the revised$^5$ assignment, we have recomputed the force constants and mean amplitudes of vibration for $\text{SF}_4$, using the previously described$^1$ methods. It was hoped that the results from these computations might allow discrimination between the two possible assignments.

The results from these computations are listed in Tables I and II. The symmetry force constants for the $A_1$ block are identical to those previously reported.$^1$ Two sets of force constants are given. For the computation of set I, the previous assignment$^1-4$ (i.e., $\nu_6 > \nu_8$) was chosen, whereas set II is based on $\nu_8 > \nu_6$ as recently suggested.$^5$ As can be seen from Table II,
Table I. Force Constants of SF₆. Valence Force Constants in mdyneÅ⁻¹, Deformation Constants in mdyneÅ⁻¹, and Stretching-Deformation Coupling Terms in mdyne. Set I: ν₆ > ν₅; Set II: ν₆ > ν₅⁺.

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<td>B₁</td>
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<td>F₆₇</td>
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<tr>
<td></td>
<td>F₇₇</td>
<td>2.20</td>
</tr>
<tr>
<td>B₂</td>
<td>F₈₈</td>
<td>3.33</td>
</tr>
<tr>
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<td>F₈₉</td>
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<td>F₉₉</td>
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<tr>
<td>f₋</td>
<td>3.57</td>
<td>3.07</td>
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<tr>
<td>f₄'</td>
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<tr>
<td>f₉'</td>
<td>1.21</td>
<td>0.49</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>r</td>
<td>1.545 ± 0.003d</td>
<td>1.56 ± 0.02e</td>
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(a) Ref. 7
(b) Ref. 8
(c) Ref. 5
(d) Ref. 9
(e) Ref. 10

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D-4
Table II. Mean-Square Amplitudes of \( SF_4 \) (in 1).

<table>
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<th>(&lt; q^2 &gt; \text{ obs}^{1/2} &gt;</th>
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<tr>
<td></td>
<td>( S-F_1 )</td>
<td>( S-F_3 )</td>
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<tr>
<td></td>
<td>0.050</td>
<td>0.044</td>
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<tr>
<td></td>
<td>0.049</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>0.049</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>0.047 ( \pm 0.005 )</td>
<td>0.041 ( \pm 0.005 )</td>
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<tr>
<td></td>
<td>0.074</td>
<td>0.073</td>
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<tr>
<td></td>
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</table>

R-8725
D-5
the mean amplitudes of vibration are similar for both sets and, hence, not very useful for discriminating between the two possible assignments, although the agreement with the experimental data is slightly better for set II. It should be noted that the values reported in our previous paper for \( f^{22}_1 \) are incorrect due to a computational error. The revised values are in agreement with the experimental data if \( v_{12} \) is assumed to be larger than 500 cm\(^{-1}\). In the Raman spectra of the gas and the liquid, there was evidence indicating a frequency of about 400 cm\(^{-1}\) for this mode. For this frequency value, \( f^{22}_1 \) would be just outside the uncertainty limit given for the experimental data. This discrepancy might be eliminated by reversing the assignment of \( \delta_{SF}(\text{eq.}) \) and \( \delta_{SF}(\text{ax.}) \) in species A. This reduces all \( f^{22}_1 \) values by 0.005 A, but increases the value of \( f^{22}_3 \) to 0.004 A (set III, Table II). However, the latter value is clearly outside of the experimentally found range of 0.068 ± 0.01 A. Consequently, it appears that for \( SF_4 \), \( \delta_{SF}(\text{eq.}) \) is higher than \( \delta_{SF}(\text{ax.}) \), contrary to the findings for \( SF_5 \) and the assignments made by Bartell for related trigonal-bipyramidal molecules. The remaining slight discrepancy (0.005 A) for \( f^{22}_3 \) between set II and the observed values might be due to the fact that for the \( A_1 \) block, the interaction force constants were chosen to be as small as possible, implying little mixing between the various modes. However, for similar trigonal bipyramidal molecules, a computed potential energy distribution indicates considerable mixing of the different modes. Set III of Table II indicates that some mixing between \( v_3 \) and \( v_4 \), i.e. the introduction of a larger value for the interaction force constant \( F_34 \), might increase the value of \( f^{22}_3 \) and decrease that of \( f^{22}_1 \). This would improve the agreement between the computed and observed mean amplitudes of vibration and would also decrease the otherwise unexpectedly large difference between the two deformation force constants, \( f_\alpha \) and \( f_\beta \).

Whereas the mean amplitudes of vibration are not very useful for discriminating between set I and set II, the force constants (see Table I) offer the following arguments in favor of set II: (1) Generally, the stretch-stretch interaction
constant is relatively small whenever two bonds form an angle close to 90°. For set I, the equatorial fluorine atoms ($\angle F-S-F = 103.8^\circ$) exhibit for $f'_R$ an unreasonably high value of 1.21 mdyne/Å compared to 0.49 mdyne/Å for set II; (2) The value of the second stretch-stretch interaction constant, $f'_R$, shows only for set II a value similar to those observed for the related species, SF$_5^-$, ClF$_3^-$, and BrF$_5^-$; (3) The bond length of the equatorial S-F bonds in SF$_4$ (1.545 $\pm$ 0.003 Å) is similar to that in SF$_6$ (1.56 $\pm$ 0.02 Å). Since bond lengths are usually closely related to the stretching force constants, one might expect $f'_R$ of SF$_4$ to approach the SF$_6$ value of 5.26 mdyne/Å. This is true only for set II; (4) The relatively large difference in the length of the equatorial and the axial bonds of SF$_4$ (0.10 Å) favors set II which shows the larger difference between $f'_R$ and $f'_R$; (5) Set II is in better agreement with the values found for SF$_5^-$ if the general decrease in the force constant values owing to the formal negative charge is taken into account.

In summary, the proposed reassignment of $v_6(B_1)$ and $v_8(B_2)$ results in a more satisfactory set of force constants for SF$_4$, although it remains difficult to rationalize the observed infrared band contours. Table III lists the preferred assignment and set of force constants which can be derived from the presently available experimental data.

Acknowledgments

We thank Dr. E. C. Curtis and D. Pilipovich, Rocketdyne, for many helpful discussions. This work was in part supported by the U. S. Office of Naval Research, Power Branch.

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D-7
Table III. Preferred Assignment and Symmetry Force Constants of SF₄

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<td>A₁ F₁₁ 3.48</td>
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<td>ν₂ 558</td>
<td>ν sym SF₂ ax.</td>
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<td>ν₃ 475</td>
<td>δ sciss SF₂ eq.</td>
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<td>ν₄ 226</td>
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<td>F₁₄ 0.01</td>
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<td>A₂ ν₅ 414</td>
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<td>δ rock</td>
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R-8725
D-8
References

APPENDIX E

VIBRATIONAL SPECTRUM OF BROMINE TRIFLUORIDE

R-8725
E-1/E-2
Abstract - The infrared spectrum of matrix isolated BrF_3 has been recorded. All six fundamental vibrations expected for a T-shaped molecule of symmetry C_2v were observed. A modified valence force field and some thermodynamic properties have been computed for BrF_3.

Recently, Selig and coworkers [1] have reported the complete vibrational spectrum of gaseous BrF_3. It is difficult to obtain the vibrational spectrum of monomeric BrF_3 owing to its low vapor pressure at ambient temperature, its tendency to disproportionate at elevated temperature, its association in the liquid phase, and its corrosiveness. In this note, we wish to report the results of an independent study of the vibrational spectrum of solid BrF_3. In our study these difficulties were circumvented by the use of low-temperature, matrix-isolation techniques.

Experimental

The apparatus used for the low-temperature, matrix-isolation studies was similar to that previously described [2]. Bromine trifluoride (from The Matheson Company) was purified by fractional condensation, the material retained at -23°C being used. It was handled in a passivated (with CIF_3 and BrF_3) stainless steel/Teflon FEP vacuum system connected directly to the sample inlet system. The BrF_3-Ar mixtures were prepared by standard manometric techniques.
using research grade Ar (99.9995% min. from The Matheson Company). The infrared spectra were recorded at 40° K on a Perkin Elmer Model 457 spectrophotometer in the range 4000-230 cm⁻¹. The instrument was calibrated by comparison with standard calibration points [3]. The Raman spectrum of liquid BrF₃ was recorded using a Coherent Radiation Laboratories Model 52 Ar ion laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to approximately -250 ° and a d.c. ammeter. Polarization measurements were carried out using a Model 310 polarization rotator from Spectra-Physics. A stainless steel cell having Teflon O-rings and sapphire windows was used as sample container. The design of this cell was similar to that of Gasner and Claassen [4].

Results and Discussion

Figure 1 depicts the infrared spectrum of BrF₃ in argon matrix at 40° K. Since BrF₃ even in the gas phase shows a tendency to associate [5], the spectrum was recorded at the following argon to BrF₃ mole ratios (MR): 100, 200, 400, 800 and 1600. The relative intensity of some of the bands decreased with increasing MR. Therefore, the spectra of only the two samples with the lowest and highest MR value are shown in Figure 1.

In all spectra the two characteristic absorptions of SiF₄, i.e. \( \nu_3 \) and \( \nu_4 \) at about 1030 and 390 cm⁻¹, respectively [6], were observed. The formation of SiF₄ was due to interaction of BrF₃ with sections of the metal vacuum line, and extensive passivation of the line with ClF₃ and BrF₃ was required to keep
the SiF$_4$ concentration at an acceptably low level. At high SiF$_4$ levels, an additional band at 660 cm$^{-1}$ appeared in some of the spectra. Based on its relative intensity in different spectra, this band does not appear to be related to any other band. Hence, it is assigned to the diatomic molecule BrF for which a frequency of about 670 cm$^{-1}$ was reported based on band spectra [7] and low resolution infrared spectra of Br$_2$-BrF$_3$ mixtures [8]. Thus, it appears that small amounts of silicon, present in the steel, can reduce BrF$_3$ to BrF with SiF$_4$ being the by-product.

The Raman spectrum of liquid BrF$_3$ (which always shows a yellow color) has been redetermined with the green 5145 Å argon line. This avoids the problems associated with the use of the blue mercury lines. It agrees well with that previously reported [9] and hence is not depicted. This indicates that the broad, unresolved absorption between 400 and 600 cm$^{-1}$ is likely to be due to association in the liquid phase.

The frequencies observed for matrix isolated BrF$_3$ are listed in Table 1 together with those recently reported [1] for the gas. The agreement between the two sets of data is excellent. The six fundamentals expected for a T-shaped BrF$_3$ molecule of symmetry C$_2v$ [10] were assigned as previously suggested [1, 9]. The coincidence of $\nu_3(A_1)$ and $\nu_6 (B_2)$ at 242 cm$^{-1}$ in the gas phase is confirmed by the observation of two bands in the spectrum of the matrix isolated solid. In addition to $\nu_4$ of SiF$_4$ at 385 cm$^{-1}$, there are two bands of variable relative intensity at 578 and 502 cm$^{-1}$. Since their relative intensity decreases with increasing MR, they cannot be due to BrF$_3$ itself and
are tentatively assigned to di-or polymeric species. This tendency of \( \text{BrF}_3 \) to associate is also demonstrated by the Raman spectrum of the liquid. It shows a strong, polarized band at 673 cm\(^{-1} \) which is in good agreement with the values observed for \( \gamma_1 (A_1) \) in the gas and the matrix-isolated solid. Furthermore, it exhibits three weak bands at 337, 268, and 233 cm\(^{-1} \), respectively, having frequencies similar to those assigned to the three deformational modes. The fact that the symmetric F-Br-F stretching mode, \( \gamma_2 (A_1) \), is the most intense band in the Raman spectrum of \( \text{BrF}_3 \) gas\(^{[1]} \) but does not appear as a strong, distinct band in the Raman spectrum of the liquid, indicates strong association in the liquid phase through formation of fluorine bridges involving the two axial and not the equatorial fluorine atom (the terms axial and equatorial refer to a trigonal bipyramidal structure assuming the two localized free electron pairs of the bromine atom to occupy two equatorial positions).

In the infrared spectrum of matrix-isolated \( \text{BrF}_3 \), a number of weak bands were observed above 700 cm\(^{-1} \) (see Table I) which obviously cannot be attributed to fundamental vibrations. Most of them can be assigned to overtones and combination bands of \( \text{BrF}_3 \), thus lending additional support to the given assignment.

The infrared spectrum of non-matrix-isolated, solid \( \text{BrF}_3 \) has previously been reported \(^{[11, 12]} \). Two different spectra were obtained depending on whether the solid had a glassy or crystalline appearance \(^{[12]} \). Both types of spectra showed two prominent absorptions at about 670 and 600 cm\(^{-1} \) but showed additional strong absorptions in the range 400 to 500 cm\(^{-1} \), indicating association similar to that in the liquid phase. In addition, the infrared spectrum of crystalline \( \text{BrF}_3 \) showed a decrease in the relative intensity of the 600 cm\(^{-1} \)
## Table 1

VIBRATIONAL SPECTRUM OF BrF₃

<table>
<thead>
<tr>
<th>RA Gas</th>
<th>IR</th>
<th>Matrix Isolated Solid</th>
<th>Assignment in Pointgroup C₂ᵥ</th>
</tr>
</thead>
</table>
| 675 s, p | 675 s | 672 s | $\nu$_1 (A₁) $\nu_{\text{Br-F'}}$
| 612 vw | 614 vs | 592 vs | $\nu$_4 (B₁) $\nu_{\text{as F-Br-F}}$
| 552 vs, p | 552 w | 545 mw | $\nu$_2 (A₂) $\nu_{\text{a F-Br-F}}$
| 350 vw | 346 mw | 346 mw | $\nu$_5 (B₁) δas in plane
| 242 s | 250 m | 250 m | $\nu$_6 (B₂) δ out of plane
| 242 s | 235 mw | 235 mw | $\nu_{3}$ (A₁) δs in plane
| 1340 vw | 1345 vw | 1345 vw | $2\nu_{3} = 1344$
| 1287 vw | 1265 mw | 1265 mw | $\nu_{1} + \nu_{4} = 1264$
| 1327 w | | | $\nu_{2} + \nu_{4} = 1217$
| 1170 mw | | | $2\nu_{2} = 1184$
| 1138 mw | | | $\nu_{2} + \nu_{6} = 1137$
| 1062 mw | | | $
u_{4}$
| 977 mw | | | $
u_{1} + \nu_{6} = 922$, $\nu_{1} + \nu_{5} = 905$
| 920 | 920 w, br | 920 w, br | $\nu_{2} + \nu_{5} = 891$
| 895 | 895 w, sh | 895 w, sh | $\nu_{4} + \nu_{3} = 827$
| 820 | 820 w | 820 w | $\nu_{2} + \nu_{6} = 795$
band coupled with the appearance of a new, intense, sharp band at 558 cm^{-1}. Judging from the overall appearance of the two types of spectra, that of the glassy solid was simpler and more closely resembled that of matrix-isolated BrF₃. In no case did the spectrum of solid BrF₃ [12] show the bands characteristic for BrF₂⁺ [12] and BrF₄⁻ [13] indicating that solid BrF₃ does not exist in the ionic form, BrF₂⁺BrF₄⁻, but prefers association through covalent fluorine bridges. This finding is in good agreement with the results from a crystallographic study on solid BrF₃ [14].

Vibrational Force Constants

Vibrational force constants were computed for BrF₃ assuming the simplest possible modified valence force field. The kinetic and potential energy metrics were computed by a standard machine method [15] using the geometry determined by microwave spectroscopy [10]. The force constants given in Table II were found by trial and error with a time sharing computer. The computed frequencies agreed exactly with the observed values since there were as many force constants as frequencies. The deformation coordinates were weighted by unit distance (1 R). The force constant designations follow those used for the square-pyramidal interhalogens [16] with $f_R$ for both BrF₃ and BrF₅, referring to the unique fluorine and $f_\theta$ to the deformation of the angle between that fluorine and the equivalent fluorines.

For comparison, we also report the force constants computed for BrF₅, ClF₅ [17], and ClF₃ [18] assuming a similar force field. Table II shows similar trends between BrF₃ and BrF₅ and ClF₃ and ClF₅, although it should be noted that the force
The force constant is required to fit the frequencies. It is not certain whether this should be \( f_{\alpha} \), \( f_{\beta} \), or \( f_{\gamma} \). The value for \( f_{\alpha} \) reported for \( \text{BrF}_3 \) was computed to permit comparison with the similar motion in \( \text{BrF}_5 \), the \( E \) block deformation. Definition of \( f_{\alpha} \) requires placing fictitious atoms to give \( \text{BrF}_3 \) the same geometry as \( \text{BrF}_5 \). These fictitious atoms serve no purpose other than to define \( f_{\alpha} \) and contribute nothing to the molecular motion or force constant [19]. The similarity of \( f_{\alpha} \) for the tri- and penta-fluorides is noteworthy.

**Thermodynamic Properties**

The thermodynamic properties were computed for \( \text{BrF}_3 \) using the rigid-rotor harmonic-oscillator approximation [20]. The moments of inertia were taken from the microwave data [10] and the vibrational frequencies from this work. The results are given in Table III.

**Acknowledgment.**

We are indebted to Dr. J. P. McTague of the Science Center of North American Rockwell Corporation for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research Power Branch and by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force under Contract AF49(638)-1734.

Rocketdyne, A Division of North American Rockwell Corporation Canoga Park, California 91304

Karl O. Christie  
E. C. Curtis  
Donald Pilipovich

R-8725  
E-9
Table II. COMPARISON OF THE FORCE CONSTANTS OF BrF₅, BrF₃, ClF₃, and ClF₅

(Units of the stretching constants are millidyne Angstrom⁻¹ and of the bending constants millidyne Angstrom⁻¹ radian⁻¹.)

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
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<tbody>
<tr>
<td>f₁</td>
<td>4.07</td>
<td>4.01</td>
<td>3.88</td>
<td>3.60</td>
</tr>
<tr>
<td>f₂</td>
<td>3.10</td>
<td>3.26</td>
<td>2.74</td>
<td>2.75</td>
</tr>
<tr>
<td>f₃</td>
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<td>2.32</td>
<td>1.97</td>
<td>2.80</td>
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<tr>
<td>f₄</td>
<td>0.78</td>
<td>0.84</td>
<td>1.03</td>
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<tr>
<td>f₅</td>
<td>0.31</td>
<td>0.26</td>
<td>0.38</td>
<td>0.18</td>
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<tr>
<td>f₆</td>
<td>0.09</td>
<td>0.56</td>
<td>0.17</td>
<td>0.29</td>
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</table>

Table III. THERMODYNAMIC PROPERTIES OF BrF₅ ASSUMING AN IDEAL GAS AT 1 ATM. PRESSURE.

UNITS FOR Cº, Sº, and -(Fº-Hº)/T ARE CALORIES PER MOLE - DEGREE AND Hº IS KILOCALORIES PER MOLE.

<table>
<thead>
<tr>
<th>T</th>
<th>Cº</th>
<th>Hº-Hº º</th>
<th>-(Fº-Hº)/T</th>
<th>Sº</th>
<th>T</th>
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<td>0</td>
<td>0</td>
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<td>100</td>
<td>9.948</td>
<td>0.847</td>
<td>48.095</td>
<td>56.561</td>
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<tr>
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<td>54.483</td>
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<tr>
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<td>58.939</td>
<td>70.785</td>
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<td>5.236</td>
<td>62.522</td>
<td>75.611</td>
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</tr>
<tr>
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<td>18.232</td>
<td>7.034</td>
<td>65.551</td>
<td>79.600</td>
<td></td>
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<tr>
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<tr>
<td>1600</td>
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<td>84.255</td>
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<tr>
<td>1700</td>
<td>19.713</td>
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<td>103.124</td>
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<td>34.196</td>
<td>87.321</td>
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<tr>
<td>2000</td>
<td>19.757</td>
<td>36.171</td>
<td>88.246</td>
<td>106.332</td>
<td></td>
</tr>
</tbody>
</table>
REFERENCES

[19] This could be done formally in a fashion similar to that reported earlier for NF$_3$ [E. C. Curtis and J. S. Mairhead, J. Phys. Chem. 70, 3330 (1966)], but is not needed here since the wagging motion is in its own symmetry block.
Diagram Caption

Figure 1. Infrared spectrum of BrF$_3$ in argon matrix at 40 K, trace A (MR = 100), trace B (MR = 1600). Bands marked by an asterisk and b are due to SiF$_4$ and cell window background, respectively.
APPENDIX F

VIBRATIONAL SPECTRUM OF THE $N_2F^+$ CATION

R-8725
F-1/F-2
THE VIBRATIONAL SPECTRUM OF THE $\text{N}_2\text{F}^+$ CATION

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Received . . . . 1970

Abstract

The infrared and Raman spectra are reported for $\text{N}_2\text{F}^+\text{AsF}_6^-$ and $\text{N}_2\text{F}_2^+1.3\text{SbF}_5$. For $\text{N}_2\text{F}^+$ previous assignments for the two stretching modes are confirmed, however, the assignment for the deformational mode needs revision. It occurs at 390 and not at 803 cm$^{-1}$. Force constants were calculated for $\text{N}_2\text{F}^+$ and are compared to those of a series of isoelectronic molecules and ions.

Introduction

The existence of solid adducts between $\text{N}_2\text{F}_2$ and Lewis acids, such as $\text{AsF}_5$ and $\text{SbF}_5$ is well known. In all cases an infrared band at about 1060 cm$^{-1}$ was observed which was attributed to the N-F stretching vibration of the $\text{N}_2\text{F}^+$ cation. Recently, Shamir and Binenboym reported the Raman spectrum of $\text{N}_2\text{F}^+\text{AsF}_6^-$ and assigned bands at 2370 and 803 cm$^{-1}$ to the two remaining fundamentals of $\text{N}_2\text{F}^+$. In this paper we wish to report the infrared and Raman spectra of $\text{N}_2\text{F}^+\text{AsF}_6^-$ and $\text{N}_2\text{F}_2^+1.3\text{SbF}_5$ showing that the deformational mode of $\text{N}_2\text{F}^+$ occurs at 390 and not at 803 cm$^{-1}$.

Experimental

The sample of $\text{N}_2\text{F}^+\text{AsF}_6^-$ was prepared as previously described. Its 1:1 composition was ascertained by quantitative synthesis. The sample of $\text{N}_2\text{F}_2^+\text{SbF}_5^-$ was prepared in a passivated (with ClF$_3$) 80 ml Kel-F ampoule equipped with a stainless steel valve. Distilled SbF$_5$ (12.35 mmole) was...
transferred into the Kel-F ampoule in the dry nitrogen atmosphere of a glove box. The ampoule was connected to a stainless steel-Teflon PEP vacuum system and about 20 ml of electrolytically dried liquid HF was added. The SbF$_5$ was dissolved in the HF at ambient temperature. Then the ampoule was cooled to -196$^0$ and a mixture of cis and trans N$_2$F$_2$ (total = 25.5 mmole) containing a small amount of N$_2$F$_4$ as impurity was added. The mixture was allowed to warm up to -80$^0$ for 3 - 4 hours and then to ambient temperature for two days under autogenous pressure. Unreacted material (HF and trans N$_2$F$_2$) was removed in vacuo at 0$.^0$. The material balance and weight increase of the solid residue indicated that SbF$_5$ had combined with N$_2$F$_2$ in a mole ratio of 1.3:1.

The infrared spectra of the solids were recorded on a Perkin Elmer Model 457 spectrophotometer as dry powders between AgBr or AgCl plates or by placing the powder between two single crystal platelets of AgBr and pressing them in a micro pellet press to a disk. The AgBr windows were eventually attacked by the samples with bromine evolution. However, useful spectra could be obtained by fast scanning before noticeable attack on the windows occurred.

The Raman spectra of the solids were recorded with a Spex Model 1400 spectrophotometer. The green (5145 Å) line of a Coherent Radiation Lab. Model 52 argon ion laser was used as the exciting line. Glass melting point capillaries or Pyrex glass tubes of 7 mm o.d. with a hollow inside glass cone for variable sample thicknesses were used as sample containers. The former were employed in the transverse viewing-transverse excitation and the latter in the axial viewing-transverse excitation mode.

Results and Discussion

(1) Synthesis

The synthesis of the N$_2$F$_2$·xSbF$_5$ adduct deserves some comment. Three different groups had reported the preparation of an adduct of N$_2$F$_2$ with SbF$_5$, however, their data disagree. Ruff obtained$^2$ a 1:2 adduct, N$_2$F$_2$·2 SbF$_5$, by reacting SbF$_5$ with excess of either cis or trans N$_2$F$_2$ at 40 - 50$^0$. Roesky et al. reported$^3$ that only the cis isomer of N$_2$F$_2$ is capable of forming an adduct with SbF$_5$ resulting in a 1:1 adduct, N$_2$F$_2$·SbF$_5$. Pankratov and Savenkova prepared$^4$ a 1:1 adduct, N$_2$F$_2$·SbF$_5$, from mixtures of cis and

R-8725
P-4
trans $N_2F_2$ and SbF$_5$ at -5 to 10°C using excess $N_2F_2$ and pressures of up to 15 atm. Since according to Pankratov and Sokolov$^7$ trans $N_2F_2$ readily equilibrates at ambient temperature to form a 9:1 mixture of cis and trans $N_2F_2$, trans $N_2F_2$ should also be capable of forming a SbF$_5$ adduct by continuous removal of cis $N_2F_2$ from the equilibrium in the form of solid $N_2F_2$·xSbF$_5$.

In the present study we have not attempted to resolve these conflicting reports on either the composition (1:1 versus 2:1) of the adduct or on the capability of trans $N_2F_2$ to produce a SbF$_5$ adduct.

Our main interest was to determine the vibrational spectrum of $N_2F^+$. However, in our study several interesting observations were made. The composition of our adduct, $N_2F_2$·1.3 SbF$_5$, would seem to indicate that both, 1:1 and 1:2 complexes, and mixtures thereof can be formed. The unreacted $N_2F_2$ consisted exclusively of the trans isomer. Owing to the apparent nonreactivity of the trans isomer with Lewis acids and the failure of the trans isomer to equilibrate to the cis isomer under our reaction conditions, the 1:1.3 composition of our adduct may have been due to the limited amount of cis $N_2F_2$ present in the mixture. We had chosen HF as a reaction medium to suppress the formation of polymeric anions. Previously, this approach had been successfully applied$^8,9$ in the synthesis of ClF$_4^+$SbF$_6^-$ and NF$_2O^+$SbF$_6^-$, and in the case of $N_2F_2$ and SbF$_5$ it should also result in a well defined 1:1 adduct provided a large enough excess of cis $N_2F_2$ is present.

(2) Vibrational Spectra

Figures 1 - 3 show the infrared and Raman spectra of $N_2F^+$AsF$_6^-$ and $N_2F_2$·1.3 SbF$_5$. The observed frequencies are listed in Table 1. The Raman spectrum of $N_2F^+$AsF$_6^-$ is in good agreement with that previously reported$^5$ by Shamir and Binenboym except for the absence of the 803 cm$^{-1}$ band in our spectrum. Consequently, we prefer to assign the distinct band of medium intensity at 391 cm$^{-1}$ to the deformational mode, $V_2$, of $N_2F^+$. This band at 391 cm$^{-1}$ was also observed$^5$ by Shamir and Binenboym, however, they offered no explanation or assignment for this band. Since in $N_2F^+$AsF$_6^-$ the 391 cm$^{-1}$
### Table I

**Vibrational Spectra of \( \text{N}_2\text{F}^+\text{AsF}_6^- \) and \( \text{N}_2\text{F}_2\cdot\text{AsF}_6^- \) Compared With That of FCN**

<table>
<thead>
<tr>
<th></th>
<th>( \text{N}_2\text{F}_2\cdot\text{AsF}_6^- )</th>
<th>( \text{N}_2\text{F}^+\text{AsF}_6^- )</th>
<th>FCN(^{(a)})</th>
<th>( \text{FXN (C}_{\text{oov}} )</th>
<th>( \text{AsF}_6^- (O_h) )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ir</strong></td>
<td>RA</td>
<td>RA</td>
<td>ir</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2373 w</td>
<td>2373 (0.3)</td>
<td>2371 (0.5)</td>
<td>2323</td>
<td>( \nu_3 (\Sigma^+) )</td>
<td></td>
</tr>
<tr>
<td>1059 ms</td>
<td>1059 (2.3)</td>
<td>1058 ms</td>
<td>1057 (3.1)</td>
<td>( \nu_1 (\Sigma^+) )</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1069.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>830 vw</td>
<td></td>
<td></td>
<td></td>
<td>( \nu_2 + \nu_6 (F_{1u} + F_{2u}) )</td>
<td></td>
</tr>
<tr>
<td>698 vs, br</td>
<td></td>
<td></td>
<td></td>
<td>( \nu_3 (F_{1u}) )</td>
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**R-8725 F-6**

<table>
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<tr>
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<th>( \text{N}_2\text{F}_2\cdot\text{AsF}_6^- )</th>
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<th>FCN(^{(a)})</th>
<th>( \text{FXN (C}_{\text{oov}} )</th>
<th>( \text{AsF}_6^- (O_h) )</th>
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<tr>
<td>640 - 720 vs, br</td>
<td>689 (2.5)</td>
<td>689 (10)</td>
<td>780 (0+)</td>
<td>( 2\nu_2 (\Sigma^+) )</td>
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<tr>
<td>600 w, sh</td>
<td>604 (0.6)</td>
<td>661 (10)</td>
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<td>682 (0.5)</td>
<td></td>
<td></td>
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<td>( \nu_1 (A_{1g}) )</td>
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</tr>
<tr>
<td>568 (1.0)</td>
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<td>576 (1.8)</td>
<td>( \nu_2 (E_g) )</td>
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<td>520 mw, sh</td>
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<td>478 ms</td>
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<tr>
<td>388 ms</td>
<td>389 (1.6)</td>
<td>391 s</td>
<td>391 (0.7)</td>
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<td>260-300 s</td>
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<td>376 (3.2)</td>
<td>451.3</td>
<td>( \nu_4 (F_{1u}) )</td>
<td></td>
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<tr>
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<td></td>
<td></td>
<td>( \nu_5 (F_{2g}) )</td>
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<tr>
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<td>100</td>
<td>Lattice</td>
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<td>99</td>
<td></td>
<td></td>
<td></td>
<td>Vibrations</td>
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</tbody>
</table>

\(^{(a)}\) Ref. 10, 11
band occurs in the range of the AsF₆⁻ deformational modes and since breakdown of the selection rules for Oh symmetry has been observed for several AsF₆⁻ containing salts,¹²,¹³ the 391 cm⁻¹ band in the AsF₆⁻ salt cannot unambiguously be assigned to V₂(υ₁) of N₂F⁺. However, if the band at 391 cm⁻¹ is indeed due to V₂(υ₁) of N₂F⁺, it should also be observed in the spectra of other N₂F⁺ salts containing anions not absorbing in this region. Since for Sbf₆⁻ and SbF₁₁⁻ no vibrations occur²,¹⁴ in the range 300 - 450 cm⁻¹, we have prepared a sample of N₂F₂·xSbf₅ and recorded its vibrational spectrum. As can be seen from Fig. 1 and 3, both the infrared and Raman spectrum of N₂F₂·1.3 Sbf₅, show a prominent absorption at about 390 cm⁻¹ but none at 803 cm⁻¹. Consequently, the band at 390 cm⁻¹ may with confidence be assigned to V₂(υ₁) of N₂F⁺.

The spectrum of N₂F⁺ was previously compared⁵ to that of isoelectronic N₂O. However, based on bond order and electronegativity considerations, we prefer to compare the spectrum of N₂F⁺ with that of isoelectronic FCN. As can be seen from Table I, the two stretching modes of N₂F⁺ are close to those⁴ of FCN and, hence, one might expect this analogy to also hold for the deformational mode which in FCN occurs at about 450 cm⁻¹. Based on this comparison a frequency value of 390 cm⁻¹ appears more plausible for V₂(υ₁) of N₂F⁺ than that of 803 cm⁻¹ previously suggested.⁵

The assignments for the remaining bands of N₂F⁺AsF₆⁻ present no difficulties and are listed in Table I. The observed frequencies and intensities agree well with those predicted for a linear, asymmetric [N₂N-F]⁺ cation of symmetry Cᵥ and for an octahedral AsF₆⁻ anion.⁵,⁹ For N₂F₂·1.3 Sbf₅ three additional bands of low relative intensity were observed at 1300, 1124, and 926 cm⁻¹ which can be assigned²,¹⁴ to small amounts of N₂F₃⁺ present in our sample as an impurity. Infrared spectra, recorded after N₂F₂·1.3 Sbf₅ had attacked the AgBr window material, showed the complete absence of the bands assigned to N₂F⁺, whereas the bands due to N₂F₃⁺ had not decreased in intensity. This confirms the previously made observation² that the N₂F⁺ salts are more reactive than the corresponding N₂F₃⁺ salts. It is interesting to note that for N₂F₂·1.3 Sbf₅ the NN stretching mode of N₂F⁺ was also observed in the infrared spectrum. However, this band is
quite weak and is not easily observed. Since the combining ratio of our 
$N_2F_2\cdot xSbF_5$ adduct is intermediate between 1:1 and 1:2, no attempt is made 
to assign the Sb-F vibrations to individual modes. However, their 
frequencies and relative intensities are similar to those previously 
reported\textsuperscript{2,11} for $SbF_6^-$ and $Sb_2F_{11}^-$. Whereas the Raman spectra of 
$N_2F^+AsF_6^-$ and $N_2F^+1.3SbF_5$ did not show any evidence for a band at 
803 cm\textsuperscript{-1} (the frequency previously assigned\textsuperscript{5} to $v_2$ of $N_2F^+$), both show a 
weak band at 780 cm\textsuperscript{-1}. This band appears to belong to the $N_2F^+$ cation, 
but its relative intensity is quite low. Further, it does not have a 
counterpart in the infrared spectrum and its frequency is exactly twice 
that of the 390 cm\textsuperscript{-1} band. Consequently, it is assigned to the first 
overtone of $v_2$ of $N_2F^+$.

(3) Force Constants

For a linear, asymmetric ion of symmetry $C_{\text{ovv}}$, such as $N_2F^+$, a general 
valence force field contains four force constants. Since only three 
frequency values are available, the problem is underdetermined and 
simplification must be made. Shamir and Binenboym\textsuperscript{5} used a modified valence 
force field for their computation assuming the off-diagonal constant, $f_{\text{RR'}}$ 
to equal zero. However, this assumption is not valid for most of the 
known force fields of linear $XYZ$ molecules. Furthermore, the influence of 
the value of $f_{\text{RR'}}$ upon the diagonal force constants can usually not be 
neglected. Therefore, $f_{\text{RR'}}$ was assumed to have a fixed value, and the $NN$ 
and $NF$ stretching force constants, $f_{\text{N}}$ and $f_{\text{R}}$, respectively, were computed 
as a function of $f_{\text{RR'}}$ (see Table II). The value of $f_{\text{RR'}}$ was varied over the 
most probable range (-0.5 to 2.0 mdyne/R) and computations were made at 
0.5 mdyne/R intervals. A closer estimate of the stretching force constants 
might be obtained provided one could further narrow the range of possible 
$f_{\text{RR'}}$ values.

A theoretical interpretation of the stretch-stretch interaction force constant 
as a measure for resonance effects between the two bonds has previously been 
given by Coulson, Duchesne and Manneback\textsuperscript{19} and is in good agreement with the 
experimental observations. Thus, linear $XYZ$ molecules might be classified
into three different groups: (i) molecules with one single and one multiple bond, but without the possibility of resonance, e.g. HCN$^6$ and HCP$^5$ for which $f_{RN}$ is negative; (ii) molecules with one single and one multiple bond, where some resonance is possible, e.g. Hal-C-N. For these molecules $f_{RN}$ was found$^{17}$ to be 0.4 ±0.1 mdyne/R but it is not unreasonable to extend the possible range to 0.5 ±0.5 mdyne/R; and (iii) molecules with two multiple bonds and stronger resonance, e.g. N$_2$O and NCO$^{-}$, with $f_{RN}>1$ mdyne/R.

The symmetric molecules and ions, CO$_2$, NO$_2^+$, N$_3^-$, might be included into this group.

For N$_2$F$^+$ the NN stretching force constant has a value similar to or slightly lower than that found for N$_2$ (22.39 mdyne/R)$^{18}$ throughout the range of probable $f_{RN}$ values. On the other hand, the N-F stretching force constant is the highest one obtained so far for any N-F bond.$^{5,20}$ The lowest value possible for N$_2$F$^+$ based upon the observed frequencies is 7.45 mdyne/R. Comparison of this value with those obtained for NF$_4^+$ (5.91)$^{21}$ and NF$_2O^+$ (6.46 mdyne/R)$^{20}$ indicates that the marked increase cannot be due exclusively to a change in hybridization (i.e. increasing s-character of N-F bond), but strongly suggests partial double bond character. Consequently, N$_2$F$^+$ should belong to group (ii) for which $f_{RN}$ might be restricted to the range 0-1 mdyne/R. Assuming $f_{RN} = 0.5 ±0.5$ the stretching force constants become $f_{NN} = 21.23 ±0.75$ and $f_{NF} = 8.16 ±0.29$ mdyne/R. Further support for the assumption, $f_{RN}<1$ mdyne/R, was obtained by computing a set of force constants for N$_2$F$^+$ by the eigenvector method.$^{22,23}$ This computation yielded a value of 1.33 mdyne/R for $f_{RN}$ of N$_2$F$^+$. However, for 17 different linear XYZ molecules the eigenvector method always resulted$^{24}$ in $f_{RN}$ values considerably larger than those of the GVFF. Therefore, one might expect $f_{RN}$ of N$_2$F$^+$ to be considerably smaller than 1.33 mdyne/R.

The deformation constant, $f_\alpha$, of N$_2$F$^+$ can be uniquely determined provided the two bond lengths are known. For N$_2$F$^+$ this is not the case, however, reasonable estimates can be made. Assuming $r_{NN}$ to be the same as that in N$_2$ (1.10 R)$^{18}$ and $r_{NF}$ to be 1.37 R ($r_{N-F}$ in trans N$_2$F$_2$ = 1.398 and in NF$_3$ = 1.371 R)$^{25}$ one obtains for $f_\alpha$ of N$_2$F$^+$ a value of 0.202 mdyne/R or
0.304 mdyne·Å·rad⁻¹. Using the frequency value of 803 cm⁻¹, previously suggested for ν₂ of N₂F⁺, fₐ would become 0.856 mdyne/Å. Comparison of the frequencies and force constants of N₂F⁺ with those of a series of isoelectronic molecules and ions (see Table III) shows that a value of 0.86 mdyne/Å for fₐ of N₂F⁺ would be out of line. Table III also demonstrates that fₐ appears to be quite useful for distinguishing single bonds from multiple bonds, especially in cases where no additional experimental data are available to uniquely determine f₊. Thomas et al.²⁶ have recently published a relation having the form fₓ = 37.3/r₀.⁷³ between the valence force constant and bond length of NN bonds. This relation might be used to crosscheck our estimate of r NN used for the computation of fₐ. Assuming fₓ = 21.23 mdyne/Å, r NN becomes 1.10 Å, which is identical with our estimated value.

The conclusions,²⁵ reached by Shamir and Binenboym, that N₂F⁺ is linear and asymmetric and that the NN bond has triple bond character, are certainly correct. Based on the force constant values, contributions of the mesomeric structure (II) to the bonding in N₂F⁺ are noticeable, but must be relatively small contrary to the

\[
\begin{align*}
\text{[I]} & \quad \leftrightarrow & \quad \text{[II]} \\
\text{N=N=\text{F}} & \quad \leftrightarrow & \quad \text{N=N=\text{F}}
\end{align*}
\]

situation in N₂O where II strongly contributes.

Acknowledgment

We are indebted to Mr. M. Warner for making a sample of N₂F⁺AsF₆⁻ available to us and to Dr. I. Silvera for the use of the Raman spectrometer. Helpful discussions with Drs. E. C. Curtis, D. Pilipovich, and C. J. Schack were greatly appreciated. This work was supported by the Office of Naval Research, Power Branch.
### TABLE II

Stretching Force Constants of $N_2F^+$ as a Function of the Assumed Value of the Interaction Constant

(All values in mdyne/Å)

<table>
<thead>
<tr>
<th>$f_{RR}$</th>
<th>$f_R$</th>
<th>$f_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.5</td>
<td>19.66</td>
<td>8.82</td>
</tr>
<tr>
<td>0</td>
<td>20.48</td>
<td>8.46</td>
</tr>
<tr>
<td>0.5</td>
<td>21.23</td>
<td>8.17</td>
</tr>
<tr>
<td>1.0</td>
<td>21.92</td>
<td>7.95</td>
</tr>
<tr>
<td>1.5</td>
<td>22.57</td>
<td>7.78</td>
</tr>
<tr>
<td>2.0</td>
<td>23.19</td>
<td>7.65</td>
</tr>
</tbody>
</table>

### TABLE III

Frequencies and Force Constants of $N_2F^+$ Compared to Those Of Isoelectronic Molecules and Ions

<table>
<thead>
<tr>
<th>Species</th>
<th>$v_3$</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$f_R$</th>
<th>$f_R$</th>
<th>$f_{RR}$</th>
<th>$f_{RR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-C≡P</td>
<td>3216.9</td>
<td>1278.4</td>
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<td>8.95</td>
<td>5.59</td>
<td>-0.20</td>
<td>0.15</td>
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<tr>
<td>H-C≡N</td>
<td>3438.3</td>
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<td>726.6</td>
<td>18.77</td>
<td>6.23</td>
<td>-0.21</td>
<td>0.21</td>
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<tr>
<td>$\Sigma N≡N-F$</td>
<td>2372</td>
<td>1058</td>
<td>390</td>
<td>21.23</td>
<td>8.17</td>
<td>0.5</td>
<td>0.20</td>
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<td>N≡C-F</td>
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<td>451.3</td>
<td>17.81</td>
<td>8.54</td>
<td>0.39</td>
<td>0.26</td>
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<tr>
<td>N≡C-Cl</td>
<td>2215.6</td>
<td>744.2</td>
<td>378.4</td>
<td>17.50</td>
<td>5.21</td>
<td>0.44</td>
<td>0.18</td>
</tr>
<tr>
<td>N≡C-Br</td>
<td>2198.3</td>
<td>586.6</td>
<td>341.7</td>
<td>17.51</td>
<td>4.17</td>
<td>0.41</td>
<td>0.15</td>
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<tr>
<td>N≡C-I</td>
<td>2189.5</td>
<td>485.8</td>
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<tr>
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<td>1.75</td>
<td>0.58</td>
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</table>

(a) Ref. 15 (b) Ref. 16 (c) Ref. 17 (d) Ref. 18
(e) The broken lines indicate partial bonds due to appreciable contribution from other mesomeric structures.

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F-11


References

14. A. M. Qureshi and F. Aubke, Canad. J. Chem., ...

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Figure 1.
Figure 2.
Halogen Perchlorates: Vibrational Spectra
By Karl O. Christe, Carl J. Schack, and E. C. Curtis
Received November 17, 1970

Abstract. The infrared spectra of gaseous, solid, and matrix isolated and the Raman spectrum of liquid ClOClO\textsubscript{3} have been measured. All twelve fundamentals expected for symmetry C\textsubscript{3v} were observed and assigned. The infrared spectra of gaseous and matrix isolated BrOClO\textsubscript{3} have also been recorded. Some vibrational force constants and the thermodynamic properties have been computed.

Introduction

Recently, the existence of the two novel halogen oxides, ClOClO\textsubscript{3} and BrOClO\textsubscript{3}, has been discovered\textsuperscript{1,2}. Their chemical and physical properties\textsuperscript{1,2} were in accordance with covalent halogen perchlorate structures. In this paper we wish to present spectroscopic data supporting these suggested structures.

Experimental

The preparation, purification and handling of ClOClO\textsubscript{3} and BrOClO\textsubscript{3} has been reported elsewhere\textsuperscript{1,2}. The apparatus used for the low-temperature matrix isolation and infrared spectroscopic studies has previously been described\textsuperscript{2,3}. The low-temperature infrared spectrum of solid ClOClO\textsubscript{3} was recorded by condensing the sample on the cold (-196\degree) internal AgCl window of a conventional low-temperature cell. The Raman spectra of liquid ClOClO\textsubscript{3} were obtained using Kel-F or Teflon FEP capillaries in the transverse viewing-transverse excitation mode. The capillaries were cooled (-20 to -80\degree) by a stream of cold gaseous N\textsubscript{2}. The intense light from the exciting laser beam (1.3 w at 5145 \textlambda) tended to
partially decompose the sample causing gas evolution, thus rendering the
recording of spectra difficult. However, reproducible spectra could be
obtained by rapidly scanning the spectrum by band. Under these conditions
no lines could be detected due to Cl₂O₄\(^4\),\(^5\) which is the major decomposition
product in the photolysis of Cl₂O₅\(^1\). The Raman instrument used in this
study has previously been described.

Results and Discussion

Caution. Halogen perchlorates are shock sensitive\(^1\) and should be handled with
proper safety precautions.

Figure 1 shows the infrared spectrum of gaseous Cl₂O₅. The infrared spectra
of solid and matrix-isolated Cl₂O₅ are given in Figure 2. Since chlorine has
two natural isotopes (Cl\(^{35}\) and Cl\(^{37}\) in a 3:1 mole ratio), the spectra of matrix-
isolated species were recorded at 10 fold scale expansion under high resolution
conditions (see Figure 3) to determine the isotopic shifts. Figure 4 shows the
Raman spectrum of liquid Cl₂O₅. Figure 5 shows the infrared spectrum of gaseous
and matrix-isolated Br₂O₅. The observed frequencies are listed in Table 1.

The recording of the vibrational spectra of Cl₂O₅ and Br₂O₅ presented several
experimental challenges since these two halogen perchlorates are shock and light
sensitive, thermally unstable (they decompose at or below ambient temperature),
and highly reactive\(^1,\(^2\) (they attack infrared windows such as AgCl causing for-
mation of AgClO₄ and Cl₂). Consequently, numerous spectra had to be recorded
under varying experimental conditions to be able to eliminate bands due to de-
composition products.

For a chlorine oxide, having the empirical formula Cl₂O₄, many possible structures
can be written. However, the number of observed fundamentals (8 polarized and
4 depolarized ones), the resemblance between the spectrum of Cl₂O₄ and those of
TABLE I
Vibrational Spectra of ClOClO$_3$ and BrOClO$_3$

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<thead>
<tr>
<th>Frequency, cm$^{-1}$</th>
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G-S
TABLE I (Cont'd.)

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<th>512 m</th>
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G-6
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<th>C10SO₃⁺</th>
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<th>ClO₃⁻</th>
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<th>HOClO₃⁻</th>
<th>O₃ClOClO₃⁻</th>
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<td>0, 0.9</td>
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\(^a\) for ClOClO\(_3\); \(^b\) for BrOClO\(_3\)
BrClO$_4$, HOClO$_3$,$^7$, O$_2$ClOCIO$_3$$^{4,7}$, FC1O$_5$,$^8$, FUC1O$_9$, and ClOSO$_2$F$_{10}$, (see Table III), and its chemical and physical properties can only be explained in terms of the following covalent perchlorate structure of symmetry C$_6$:

For a six atomic molecule of symmetry C$_6$, a total of 12 fundamentals is expected. Of these, 8 belong to species A' and should be polarized, and 4 belong to species A'' and should be depolarized. Indeed, three lines (at 561, 382, and 92 cm$^{-1}$) appear to be depolarized and a fourth one (at 1280 cm$^{-1}$) may contain a depolarized component. Hence, these four fundamentals are assigned to the four A'' modes. Of these four, the highest and lowest frequency band can be readily assigned to the anti-symmetric ClO$_3$ stretch and the -O-Cl torsion, respectively. Since the antisymmetric ClO$_3$ deformation mode should be of higher frequency and infrared intensity than the ClO$_2$ torsional mode, it is assigned to the 561 cm$^{-1}$ band.

Of the 8 A' modes, the antisymmetric and symmetric ClO$_3$ stretch should have the highest frequencies since they involve double bonds. Consequently they are assigned to the bands at 1287 and 1040 cm$^{-1}$, respectively. The coincidence of the A' and A'' antisymmetric ClO$_3$ stretching modes at about 1280 cm$^{-1}$ is supported by the splitting of this band into two intense components in the spectrum of matrix isolated ClOCIO$_3$. Furthermore, the computation of the frequencies of the fundamentals from estimated force constants results in almost identical frequency values for $\nu_1$ and $\nu_9$. The observed Cl$^{35}$ and Cl$^{37}$ isotope splittings (see below) confirm these assignments. The complexity of the bands in the 1280 and 1040 cm$^{-1}$ region renders the assignment to individual bands somewhat uncertain. However, in the matrix spectra of both ClOCIO$_3$ and BrOCIO$_3$ a similar pattern of band pairs was observed. The splitting of each pair is about 15 cm$^{-1}$ and the components have a relative intensity of approximately 3:1. The two most intense pairs were chosen to be due to $\nu_1$ and $\nu_9$, respectively. The remaining band pairs (marked by B to D in Table I) might
be caused by possible Fermi resonance of $v_1$ and $v_2$ with $2v_4$, respectively, and/or matrix site splittings. The bands at 749 and 646 cm$^{-1}$ should represent the two remaining stretching modes of species $A'$. Comparison between the spectra of ClOClO$_3$ and BrOClO$_3$ shows that the 749 cm$^{-1}$ band is shifted to 683 cm$^{-1}$ in BrOClO$_3$ whereas the 646 cm$^{-1}$ band exhibits practically no frequency shift. Consequently, the 749 cm$^{-1}$ must be due to the -O-Hal. stretching mode and 646 cm$^{-1}$ represents the O$_2$Cl-O stretch.

There are four frequencies (580, 511, 355, and 198 cm$^{-1}$) left for assignment to the four deformational modes in species $A'$. Of these, the Cl-O-Cl deformation should have the lowest and the rocking mode the second lowest frequency. Consequently, they are assigned to 198 and 355 cm$^{-1}$, respectively. The two remaining frequencies belong to the ClO$_2$ scissoring and the ClO$_3$ umbrella deformational mode. Of these two, the umbrella mode should have the higher relative intensity in the Raman spectrum. Furthermore, force constant arguments (see below) favor a higher frequency value for the scissoring mode. This is due to the fact that the scissoring mode involves mainly an angle change between two double bonds, whereas the umbrella mode involves also a change of the angle between the single and double bands. Consequently, the 580 cm$^{-1}$ band is assigned to the scissoring and the 511 cm$^{-1}$ band to the umbrella mode. This assignment agrees well with that made for FC1O$_3$.

Additional support for the above given assignments can be obtained from the observed band contours of gaseous ClOClO$_3$ (see Figure 1). Thus, the bands at 1040, 749, and 511 cm$^{-1}$, assigned to the $A'$ modes, $v_2$, $v_3$, and $v_6$, respectively, exhibit a PQR structure close to that expected for parallel bands of an almost symmetric top molecule.

The vibrational spectrum of BrOClO$_3$ is not as complete as that of ClOClO$_3$ owing to the lack of Raman data. However, nine out of the expected 12 fundamentals were observed. Eight out of the nine observed fundamentals of BrOClO$_3$ show frequencies almost identical to those of ClOClO$_3$ and, hence, were assigned.
by analogy. The ninth mode exhibits a shift to a lower frequency and is
assigned to the 0-Br stretching vibration. The magnitude of the shift agrees
well with that predicted assuming the 0-Br bond strength to be comparable to
that of the 0-Cl bond and taking the different mass into consideration.

Comparison of the vibrational spectra of ClOClO\textsubscript{3} and BrOClO\textsubscript{3} with those of
HOC1O\textsubscript{3}\textsuperscript{7}, \ O\textsubscript{3}ClOC1O\textsubscript{3}\textsuperscript{4,5}, FCIO\textsubscript{3}\textsuperscript{8}, FOC1O\textsubscript{3}\textsuperscript{9} and ClOSO\textsubscript{2}\textsuperscript{10} (see Table II)
shows excellent agreement.

Normal Coordinate Analysis. The potential and kinetic energy metrics for
chlorine and bromine perchlorates were evaluated by a machine method\textsuperscript{12}. An
assumed geometry was used, with the perchlorate group taken the same as in
perchloric acid\textsuperscript{15, 14}. The remaining parameters, the 0-Cl and 0-Br bond
lengths and the Cl-0-Hal bond angle were taken to be 1.63 and 1.85 Å, and
110°, respectively, based on a comparison with related molecules\textsuperscript{15}.

The force constants were adjusted by trial and error with the aid of a time-
sharing computer to give a reasonably close fit between the computed frequencies
and those reported in Table II. The results obtained for the force constants
are $f_{\text{Cl-0}} = 8.8$, $f_{\text{Cl-0}}$, $f_{\text{Cl-0}}$, $f_{\text{Cl-Br}} = 2.65$, $f_{\text{Cl-Br}} = 1.9$, $f_{\text{Cl-0-Cl}} = 1.4$, and
$f_{\text{0-Cl-0}} = 1.1$, with the units for the stretching constants being millidyne/Å
and for the bending constants millidyne/Å radian\textsuperscript{2}. The bending
coordinates were weighted by unit (Å) distance. The only significant interaction
found were $f_{\text{Cl-0/0-Cl-0}}$ which has a value about 0.2 millidyne/Å radian and
$f_{\text{Cl-0/0-Cl}} = f_{\text{Cl-0/0-Br}} = 0.35$ millidyne/Å. The isotope shifts were
computed using these force constants and are reported in Table III. A some-
what better frequency fit was obtained with slightly different force constants
and additional interaction constants with small numerical values, but they were
not used here because they are underdetermined and not particularly transferable
between the two perchlorates. The computed potential energy distribution for
chlorine perchlorate is given in Table IV. The results for bromine perchlorate
were very similar.
### TABLE IV

**Potential Energy Distribution for Chlorine Perchlorate**

The results do not add up to unity since the less important terms are not shown.

<table>
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<tr>
<th>( \nu )</th>
<th>E (cm(^{-1}))</th>
<th>( f_{\text{Cl}=0} )</th>
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<tbody>
<tr>
<td>( \nu_1 )</td>
<td>1287</td>
<td>0.91</td>
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<td>( \nu_2 )</td>
<td>1040</td>
<td>0.94</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>749</td>
<td>0.58 ( f_{0-\text{Cl}'} + 0.20 f_{\text{Cl}-0-\text{Cl}'} + 0.15 f_{0-\text{Cl}-0} )</td>
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<tr>
<td>( \nu_4 )</td>
<td>616</td>
<td>0.78 ( f_{\text{Cl}-0} + 0.16 f_{0-\text{Cl}'} - 0.10 f_{\text{Cl}-0/0-\text{Cl}-0} + 0.10 f_{0=\text{Cl}=0} )</td>
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<tr>
<td>( \nu_5 )</td>
<td>580</td>
<td>0.92 ( f_{0=\text{Cl}=0} )</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>511</td>
<td>0.44 ( f_{0=\text{Cl}=0} + 0.33 f_{0-\text{Cl}-0} + 0.10 f_{\text{Cl}-0-\text{Cl}'} )</td>
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<td>( \nu_7 )</td>
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<td>0.60 ( f_{0=\text{Cl}=0} + 0.21 f_{0-\text{Cl}'} )</td>
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<td>0.60 ( f_{\text{Cl}-0-\text{Cl}'} + 0.25 f_{0=\text{Cl}=0} )</td>
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<td>( \nu_9 )</td>
<td>1271</td>
<td>0.94 ( f_{\text{Cl}=0} )</td>
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<td>( \nu_{10} )</td>
<td>561</td>
<td>0.99 ( f_{0=\text{Cl}=0} )</td>
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<td>( \nu_{11} )</td>
<td>382</td>
<td>1.05 ( f_{0=\text{Cl}=0} )</td>
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Further attempts to refine the force constants using both the usual least squares methods and the reparameterization method were unsuccessful. This appears to be due to mixing of $\nu_3$ and $\nu_7$. The problem was investigated at some length by varying the interaction constants with the time sharing computer until we became convinced that any reasonable set of harmonic force constants that fit the other frequencies in the A' block could not fit $\nu_7$. The same problem occurred with two other molecules with similar geometry, CF$_3$OF$^7$ and ClO$\text{SO}_2$F$^{10}$. The failure of the force constants to duplicate the observed Cl$^{35}$-Cl$^{37}$ isotope splittings for all modes, suggests that the chosen valence force field might be too simple. In particular, the frequency shift of 8.5 cm$^{-1}$ observed for $\nu_4$ is about twice that calculated. Since $\nu_1$ is the only mode in the A' block having an isotope splitting larger than 5 cm$^{-1}$, mixing between $\nu_1$ and $\nu_4$ is indicated, though difficult to rationalize due to the great dissimilarity of the force constants involved.

**Thermodynamic Properties**

The thermodynamic properties for chlorine and bromine perchlorate were computed for the ideal gas using the rigid-rotor harmonic oscillator approximation$^{18, 19}$. The vibrational frequencies used were those of Table III. The rotational constants computed from the geometry assumed above were $A = 5636$, $B = 1821$, and $C = 1808$ Mc for chlorine perchlorate and $A = 5626$, $B = 1155$, and $C = 1150$ Mc for bromine perchlorate. The reduced moment of inertia was 24 Gc for chlorine perchlorate and 18 Gc for bromine perchlorate. The thermodynamic properties are given in Tables V and VI.

**Acknowledgement**

We are indebted to Dr. D. Pilipovich for continuous encouragement, to Dr. J. Silvera for the use of the Raman spectrometer, to Dr. J. D. Witt for the computation of the thermodynamic properties, and to Drs. J. D. Witt and R. M. Hammaker for making their results on Cl$_2$O$_7$ available to us prior to publication. This work was supported by the Office of Naval Research, Power Branch.

R-8725

G-13
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**TABLE V**

Computed Thermodynamic Properties for ClOClO\(^a\)

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\(^a\)Units for C^0_P, S^0, and F^0 are g calories, g moles, and degrees Kelvin and for H^0, kilocalories, and moles.
TABLE VI

Computed Thermodynamic Properties for BrOC103 α

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<th>T, °K</th>
<th>C^0_P</th>
<th>H^0 - H^0_0</th>
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<td>106.948</td>
<td>133.948</td>
</tr>
</tbody>
</table>

α Units are identical to those of Table V.
References

(2) C. J. Schack, K. O. Christe, D. Pilipovich, and R. D. Wilson, ibid., in press.
(15) L. E. Sutton, "Interatomic Distances" (Chemical Society Special Publication No. 18, 1965).
(19) J. D. Witt (private communication) computed that the barrier to internal rotation is 3.6 kcal based on the assignment given for $\gamma_{12}$. This implies that at temperatures below 2000 K internal rotation contributes little to the internal partition function.
Diagram Captions

Figure 1. Infrared spectrum of ClOClO₃ at 180 and 8 mm pressure (5 cm path length).

Figure 2. Infrared spectrum of solid ClOClO₃. Trace A, 8.2 μ mole of sample in Ar matrix (MR = 800) at 4°K; trace B, crystalline solid.

Figure 3. Infrared spectra of matrix isolated ClOClO₃ and BrOC1O₃ at 4°K under high resolution conditions and ten fold scale expansion (1 scale unit = 5 cm⁻¹). Trace A, ClOClO₃ sample of Figure 2A; trace B, 4.6 μ mole of ClOClO₃ in Ar matrix (MR = 400); trace C, 2.5 μ mole of BrOClO₃ in Ar matrix (MR = 400).

Figure 4. Raman spectrum of liquid ClOClO₃ at -40°. Traces A and B scanned manually, trace C automatically. Traces B and C, incident polarization perpendicular; trace A, incident polarization parallel. D indicates spectral slit width.

Figure 5. Infrared spectrum of BrOC1O₃. Trace A, 2.5 μ mole of sample in Ar matrix (MR = 400) at 4°K; trace B, gas at 20 mm pressure (5 cm path length).

R-8725
G-17
Figure 4.

R-8725
G-21
Vibrational Spectra and Force Constants of the Square-Pyramidal Anions, $\text{SF}_5^-$, $\text{SeF}_5^-$, and $\text{TeF}_5^-$

By Karl O. Christie, E. C. Curtis, Carl J. Schack, and D. Pilipovich

Received ....

Abstract

The adducts of CsF with $\text{SeF}_4$ and $\text{SF}_4$ have been prepared and characterized by vibrational spectroscopy. The observed spectra closely resemble those of $\text{BrF}_5$ and $\text{ClF}_5$, respectively, indicating ionic structures with square-pyramidal anions of symmetry $C_{4v}$. Force constants have been computed for the series, $\text{SF}_5^-$, $\text{SeF}_5^-$, and $\text{TeF}_5^-$, and are compared to those of the isoelectronic $\text{ClF}_5$, $\text{BrF}_5$, and $\text{IF}_5$ molecules, respectively.

Introduction

The chalcogen tetrafluorides, $\text{SF}_4$, $\text{SeF}_4$, and $\text{TeF}_4$, are known to be amphoteric and to form adducts with Lewis acids and bases. Whereas numerous papers dealing with the vibrational spectra and structure of their Lewis acid adducts have been published (Ref. 1-6), of their Lewis base adducts only the complexes of $\text{TeF}_4$ were studied (Ref. 7-9) in detail. These $\text{TeF}_4$-Lewis base adducts were shown (Ref. 7-9) to contain a $\text{TeF}_5^-$ anion of symmetry $C_{4v}$. The existence of 1:1 adducts between $\text{SeF}_4$ and alkali metal fluorides was reported (Ref. 10) in 1952 by Aynsley, Peacock, and Robinson. However, their adducts were only characterized by elemental analyses. Whereas Bartlett and Robinson (Ref. 4) and Tunder and Siegel (Ref. 11) reported that alkali metal fluorides, such as CsF, do not form adducts with $\text{SF}_4$, Tullock, Coffman, and Muetterties (Ref. 12) successfully prepared a stable $\text{CaF}_2\cdot \text{SF}_4$ adduct. Furthermore, Tunder and Siegel obtained (Ref. 11) evidence for a $(\text{CH}_3)_4\text{NF}\cdot \text{SF}_4$ adduct of marginal stability at ambient temperature.
No further information has been published on either the $\text{SF}_4$ or $\text{SeF}_4$ adducts. In this paper, we wish to report the vibrational spectra of the $\text{SeF}_5^-$ and $\text{SF}_5^-$ anions and their force constants. Since the vibrational spectra of the series of square-pyramidal molecules, $\text{ClF}_5$, $\text{BrF}_5$, and $\text{IF}_5$, are known (Ref. 13-15), it appeared particularly interesting to compare them with those of the isoelectronic series, $\text{SF}_5^-$, $\text{SeF}_5^-$, and $\text{TeF}_5^-$. 

**Experimental**

**Materials and Apparatus.** Volatile materials used in this work were manipulated in a well passivated (with $\text{ClF}_3$) stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise, Bourdon tube-type gage (0-1500 mm$\pm$ 0.1%). Selenium tetrafluoride was prepared by the method (Ref. 16) of Pitts and Jache from selenium powder and $\text{ClF}$ and was purified by fractional condensation. Cesium fluoride was fused in a platinum crucible and powdered in a dry box prior to use. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin Elmer Model 457 spectrophotometer in the range 4000 - 250 cm$^{-1}$. The spectra of gases were obtained using 304 stainless steel cells of 5 cm path length fitted with AgCl windows. Screw-cap metal cells with AgCl or AgBr windows and Teflon FEP gaskets were used for obtaining the spectra of solids as dry powders at ambient temperature. The quality of the infrared spectra could be somewhat improved by pressing two small single crystal platelets of either AgCl or AgBr to a disk in a pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 w of exciting light at 5145 $\AA$. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim$ -25$^\circ$ and a d.c. ammeter. Pyrex-glass tubes (7-mm o.d.) with a R-8725

H-4
hollow inside glass cone for variable sample thicknesses or melting point.
Capillaries were used as sample containers. For the conical tubes, the axial viewing - transverse excitation technique and for the capillaries the transverse viewing - transverse excitation technique was used.

Preparation of the Adducts

Cs⁺SF₅⁻: A 30 ml prepassivated stainless steel cylinder was loaded with powdered CsF (36.2 mmol) and SF₄ (46.9 mmol). The adduct was formed by shaking the cylinder at room temperature for several days, followed by heating to 125°C for several more days. On cooling to room temperature, the unreacted SF₄ was removed by pumping. The white solid product that remained in the cylinder was a single fused mass which was chipped from the cylinder. The weight of the solid (7.41 g) indicated that approximately half the CsF charged (5.50 g) had been converted to the adduct. This was confirmed by pyrolyzing in vacuo a portion of the adduct at 150°C and trapping the evolved gas at -196°C. From 0.82 g of the adduct, 1.88 mmol of pure SF₄ was obtained, indicating a mixture of 48 mole % Cs⁺SF₅⁻ and 52 mole % CsF.

Cs⁺SeF₅⁻: Powdered CsF (13.1 mmol) was loaded into a prepassivated 30 ml stainless steel cylinder followed by SeF₄ (8.04 mmol). The cylinder was allowed to stand at room temperature overnight. Pumping on the cylinder revealed that all the SeF₄ had reacted since no volatile product was recovered. The weight of the white solid adduct (3.25 g) obtained was in agreement with this observation. Therefore, the product was a mixture of 61 mole % Cs⁺SeF₅⁻ and 39 mole % CsF.

Results and Discussion

Synthesis and Properties. The reaction conditions used for the synthesis of Cs⁺SeF₅⁻ were similar to those (Ref. 10) used by Aynsley, Peacock, and Robinson. Since the presence of some unreacted CsF was not expected to interfere with the spectroscopic investigation, no attempt was made to achieve complete conversion of CsF to CsSeF₅⁻. Our product appeared to be completely stable in vacuo at ambient temperature contrary to the claim of Aynsley et al who reported (Ref. 10) slight decomposition under similar conditions.
The CsF·SF₄ adduct was prepared by the method (Ref. 12) of Tullock et al, confirming the existence of a stable complex. Again, no attempt was made to achieve complete conversion of CsF to Cs⁺SF₅⁻.

Vibrational Spectra. Figures 1 and 2 show the Raman and infrared spectrum, respectively, of the solid CsF·SeF₄ adduct. Figures 3 and 4 show the corresponding spectra of solid CsF·SF₄. The observed frequencies are listed in Table 1. The Raman spectra are of better quality than the infrared spectra as is generally the case for this type of compound. Consequently, assignments will be based mainly on the Raman spectra. The absorption between 300 and 240 cm⁻¹ in the infrared spectra is due to the AgBr window material.

Since the chalcogen tetrafluoride-Lewis acid adducts (Refs. 1-6) and CsF·TeF₄ (Refs. 7-9) were shown to be ionic, the same might be expected for the CsF adducts of SF₄ and SeF₄. In the pentafluoro chalcogenate (IV) anions, the central atoms possess a free electron pair which should be sterically active. Hence, these anions should have a square-pyramidal structure of symmetry C₄ᵥ similar to that of the isoelectronic halogen pentfluoride series (Ref. 13).

For a pentafluoro chalcogenate (IV) anion, XF₅⁻, of symmetry C₄ᵥ nine fundamental vibrations should be observed. These are classified as 3A₁ + 2B₁ + B₂ + 3E. All nine modes should be Raman active whereas only the A₁ and E modes should be infrared active. Table 1 lists the vibrational frequencies of the two isoelectronic series SF₅⁻, SeF₅⁻, TeF₅⁻ and ClF₅, BrF₅, I₅⁻. As can be seen from Table 1, the vibrational frequencies of the two series are very similar. In particular, the Raman spectra of SF₅⁻ and SeF₅⁻ are almost exact copies of the Raman spectra of ClF₅ and BrF₅, respectively (Ref. 13) disregarding the expected frequency decreases when going from the neutral molecules to the anions. Since the assignments for the halogen pentfluorides are well established (Refs. 13-15), the spectra of SF₅⁻ and SeF₅⁻ can be assigned (see Table 1) by complete analogy. For TeF₅⁻, the previously reported (Ref. 7) assignments had to be slightly revised to fit the overall intensity and frequency pattern. Greenwood et al. had assigned (Ref. 7) the symmetric out of phase stretching vibration, ν₄⁻, to a weak Raman band at 572 cm⁻¹, and the antisymmetric stretching vibration ν₇⁻, to a strong Raman band at 472 cm⁻¹. Furthermore, this assignment results in ν₄⁻ having a higher frequency than ν₂ which was not observed for any other member in this series. It appears more satisfactory to assign the strong Raman line at 472 cm⁻¹ to ν₄⁻ and to assume that the low intensity Raman counterpart of the intense infrared band at 466 cm⁻¹ is hidden under the 472 cm⁻¹ band.
<table>
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<th>Infrared</th>
<th>Raman</th>
<th>Infrared</th>
<th>Raman</th>
<th>Infrared</th>
<th>Raman</th>
<th>Infrared</th>
<th>Raman</th>
<th>Infrared</th>
<th>Raman</th>
<th>Assignment in Point Group</th>
<th>Description of Vibration</th>
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<td>799(3.7)</td>
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<td>666(10)</td>
<td>613w</td>
<td>611wa</td>
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<td>663w</td>
<td>662(7)</td>
<td>710s</td>
<td>A1</td>
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<td>520sh</td>
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<td>[466vs, br]</td>
<td>504s</td>
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<td>570(10)</td>
<td>(595)</td>
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<td>450m</td>
<td>[480(10)]</td>
<td>369m</td>
<td>365(2)</td>
<td>312s</td>
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<td>-</td>
<td>460(7.0)</td>
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<td>-</td>
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<td>414(1)</td>
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<td>296(0.4)</td>
<td>237(0w)</td>
<td>189(0w)</td>
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<td>-</td>
<td>-</td>
<td>ν 3X4 in plane</td>
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</table>

(a) Data from Ref. 7
(b) Data from Ref. 13
(c) Data from Ref. 14
(d) Frequencies in brackets indicate coincidences with other modes, thus resulting in increased relative intensities
(e) Frequency estimated from combination bands
Comparison of the vibrational spectra of the \(\text{XF}_5^-\) series with those of the isoelectronic \(\text{XF}_5\) molecules (Refs. 13-15) reveals several interesting features. The Raman spectra of the corresponding members of each series are completely analogous, even showing several rather unusual coincidences of some of the bands (Refs. 13-15). In the infrared spectra, the antisymmetric \(\text{XF}_4\) stretching mode, \(\nu_4'(E)\), appears for all three anions as a very broad band which makes it difficult to accurately locate its band center. Since \(\nu_7\) is of low relative intensity in the Raman spectrum, it can easily be masked by more intense Raman bands occurring in the same frequency range. Fortunately, the observation of a weak band and a shoulder in the Raman spectra of \(\text{SF}_5^-\) and \(\text{SeF}_5^-\), respectively, confirms the location of the band centers estimated from the infrared data. The frequency trends within each series are consistent. Thus, the stretching modes, \(\nu_2\) and \(\nu_4'\), involving no motion of the central atom, show frequency values reflecting the trends in the stretching force constants. Whereas the stretching modes \(\nu_1\) and \(\nu_7\), involving a motion of the central atom, exhibit an additional mass effect, the deformational modes show, as expected, a pronounced frequency increase with decreasing size of the central atom.

An unexpected, but explicable, feature in the spectra of \(\text{SeF}_5^-\) and \(\text{TeF}_5^-\) is the unusual occurrence of the antisymmetric \(\text{XF}_4\) stretching mode, \(\nu_7(E)\), at a frequency lower than that of the totally symmetric \(\text{XF}_5\) stretching mode, \(\nu_2(A_1)\). In \(\text{SF}_5^-\) the frequency value of \(\nu_7\) is only \(45\ \text{cm}^{-1}\) higher than that of \(\nu_2\). Since the mass of the central atom increases from \(\text{SF}_5^-\) towards \(\text{TeF}_5^-\) and since only the frequency of \(\nu_7\) is mass dependent, for \(\text{SeF}_5^-\) and \(\text{TeF}_5^-\) this frequency becomes lower than that of \(\nu_2\). A similar unusual occurrence of the symmetric out of phase stretching mode, \(\nu_2(E_2)\), at a frequency higher than that of the totally symmetric \(\nu_1(A_{1g})\) mode was recently established for the octahedral \(\text{IF}_6^+\) ion (Ref. 17). These two cases demonstrate the possibilities for incorrect assignments (Refs. 7, 18) when ignoring relative intensities of bands and frequency trends in related molecules.

In summary, the vibrational spectra of \(\text{SF}_5^-\), \(\text{SeF}_5^-\), and \(\text{TeF}_5^-\) show that these anions are isostructural with \(\text{ClF}_5^-, \text{BrF}_5^-, \) and \(\text{IF}_5\). Consequently, the following square-pyramidal structure of symmetry \(C_{4v}\) can be assigned to these anions:
Force Constants. Force constants were computed for the three isoelectronic pairs of molecules, SF$_5^-$-ClF$_5^-$, SeF$_5^-$-BrF$_5^-$, and TeF$_5^-$-IF$_5^-$, assuming a general harmonic valence force field. The required potential and kinetic energy metrics were computed with a machine method (Ref. 19) adopting the geometries given in Table II. The force constant definitions used are those of Begun, Smith, and Fletcher (Ref 13), except for the deformation coordinates being weighted by unit (1Å) distance. A rough fit of the force constants with the observed frequencies was obtained by trial and error. This set of constants served as a support for the assignments and as a starting point for subsequent refinements.

Force constant refinements were made using the reparameterization method (Ref. 20) with the valence force constants of all molecules assumed independent, but with the interaction constants of the isoelectronic pairs considered to be precisely equal. The starting force constants, computed by trial and error, are given in Table III. The refined force constants are listed in Table IV. The uncertainty estimates, given in Table III, are considered to be somewhat conservative. The uncertainty estimates in Table IV were obtained by adding the information matrices (Ref. 20). As can be seen, the uncertainties were substantially reduced from the initial guesses for some of the force constants; for others, however, not at all as expected for so highly an underdetermined problem.

The eigenvalues of the information matrices for the three pairs of molecules indicated that 14 parameters were determinable for the pair IF$_5^-$-TeF$_5^-$, 15 for BrF$_5^-$-SeF$_5^-$, and 16 for ClF$_5^-$-SF$_5^-$; Attempts at refinement indicated that only the 13 which corresponded to the larger eigenvalues could be adjusted. This suggests that three of the frequencies from each pair added inconsistent data, as might also be expected from the product rule.

The fit between the computed and observed frequencies was quite good for the pairs, IF$_5^-$-TeF$_5^-$ and BrF$_5^-$-SeF$_5^-$, and poor for ClF$_5^-$-SF$_5^-$; For the last pair, the average difference between observed and computed frequencies was 12 cm$^{-1}$ and four frequencies differed by as much as 20 to 30 cm$^{-1}$. This indicates that the interaction constants do not transfer as well between ClF$_5^-$ and SF$_5^-$ as might be expected for two isoelectronic species. The simplest sets of force constants (assuming as many interaction terms as possible to be zero), that precisely fit ClF$_5^-$ and the SF$_5^-$ anion are given in Table V and required more non-zero force constants for SF$_5^-$ than there are frequencies available. Based on the observed
Table II. Assumed Molecular Parameters for Square-Pyramidal Penta-Fluoride Ions and Molecules

<table>
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<tr>
<th></th>
<th>SF$_5^{a}$</th>
<th>ClF$_5^{b}$</th>
<th>SeF$_5^{a}$</th>
<th>BrF$_5^{c}$</th>
<th>TeF$_5^{d}$</th>
<th>IF$_5^{b,e}$</th>
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<td>R(Å)</td>
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<td>1.62</td>
<td>1.68</td>
<td>1.68</td>
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<td>γ(°)</td>
<td>90</td>
<td>90</td>
<td>84.5</td>
<td>84.5</td>
<td>79.0</td>
<td>90</td>
</tr>
</tbody>
</table>

(a) Assumed values
(b) Values assumed in Ref. 13
(d) Ref. 9
(e) S. J. Cyvin, J. Brunvoll, and A. G. Robiette, J. Mol. Structure, 2, 259, (1969), refer to unpublished, preliminary electron diffraction measurements for IF$_5$ by T. G. Hewitt, A. G. Robiette, and G. M. Sheldrick, indicating the following geometry: R = 1.83, r = 1.87 Å, and γ = 82°. The resulting deviation from the geometry assumed above is not expected to strongly influence the force constants.
### Table III. Unrefined Force Constants* and Uncertainties (Given in Parenthesis) for Some $XF_5$ Moieties

Force constants not shown were assumed zero and uncertainties not shown were assumed $0.2$. The variance of sum of squares of the differences between observed and computed frequencies is given for each pair.

<table>
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<tr>
<th></th>
<th>ClF$_5$</th>
<th>SF$_5^-$</th>
<th>BrF$_5$</th>
<th>SeF$_5^-$</th>
<th>IF$_5$</th>
<th>TeF$_5^-$</th>
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<tbody>
<tr>
<td>$f_R$</td>
<td>4.4 (0.5)</td>
<td>3.9 (0.5)</td>
<td>4.0 (0.5)</td>
<td>4.85 (0.5)</td>
<td>3.5 (0.5)</td>
<td>4.85 (0.5)</td>
</tr>
<tr>
<td>$f_r$</td>
<td>2.9 (0.5)</td>
<td>3.3 (0.5)</td>
<td>3.3 (0.5)</td>
<td>3.65 (0.5)</td>
<td>2.3 (0.4)</td>
<td>3.65 (0.5)</td>
</tr>
<tr>
<td>$f_R$</td>
<td>2.5 (0.5)</td>
<td>2.3 (0.5)</td>
<td>2.1 (0.5)</td>
<td>1.9 (0.3)</td>
<td>1.7 (0.3)</td>
<td>1.9 (0.3)</td>
</tr>
<tr>
<td>$f_w$</td>
<td>1.2 (0.1)</td>
<td>0.9 (0.3)</td>
<td>0.84 (0.3)</td>
<td>0.64 (0.3)</td>
<td>0.6 (0.2)</td>
<td>0.55 (0.2)</td>
</tr>
</tbody>
</table>

* (Stretching constants in mdyne/Å and deformation constants in mdyne/Å radian$^2$, and stretch-bend interaction constants in mdyne/Å radian)
Table IV. Refined Force Constants (Units are Identical to Those of Table III) and Uncertainties for Some $XF_5$ Species. Those force constants not shown are approximately zero and their uncertainty estimates little reduced from the prior estimate.

<table>
<thead>
<tr>
<th></th>
<th>ClF$_5$</th>
<th>SF$_5^-$</th>
<th>BrF$_5$</th>
<th>SeF$_5^-$</th>
<th>IF$_5$</th>
<th>TeF$_5^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_R$</td>
<td>3.53 (0.4)</td>
<td>4.39 (0.4)</td>
<td>4.03 (0.2)</td>
<td>3.82 (0.2)</td>
<td>4.85 (0.2)</td>
<td>3.53 (0.2)</td>
</tr>
<tr>
<td>$f_r$</td>
<td>2.99 (0.2)</td>
<td>1.95 (0.3)</td>
<td>3.24 (0.14)</td>
<td>2.41 (0.15)</td>
<td>3.65 (0.12)</td>
<td>2.30 (0.11)</td>
</tr>
<tr>
<td>$f_\theta$</td>
<td>2.69 (0.3)</td>
<td>2.34 (0.3)</td>
<td>2.23 (0.12)</td>
<td>1.95 (0.11)</td>
<td>1.89 (0.15)</td>
<td>1.78 (0.17)</td>
</tr>
<tr>
<td>$f_\alpha$</td>
<td>1.25 (0.2)</td>
<td>0.89 (0.2)</td>
<td>0.82 (0.13)</td>
<td>0.63 (0.13)</td>
<td>0.62 (0.11)</td>
<td>0.55 (0.12)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>f$^{rr'}$</th>
<th>f$^{BB'}$</th>
<th>f$^{\alpha\alpha'}$</th>
<th>f$^{rr}$</th>
<th>f$^{BB}$</th>
<th>f$^{R\theta}$</th>
<th>f$^{rB}$</th>
<th>f$^{R\theta''}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.17 (0.2)</td>
<td>0.98 (0.3)</td>
<td>-0.03 (0.2)</td>
<td>0.14 (0.09)</td>
<td>0.10 (0.2)</td>
<td>0.42 (0.15)</td>
<td>0.46 (0.3)</td>
<td>0.35 (0.4)</td>
</tr>
<tr>
<td></td>
<td>0.27 (0.14)</td>
<td>0.32 (0.10)</td>
<td>0.04 (0.12)</td>
<td>0.15 (0.03)</td>
<td>0.11 (0.05)</td>
<td>0 (0.16)</td>
<td>0.04 (0.2)</td>
<td>0.20 (0.15)</td>
</tr>
<tr>
<td></td>
<td>0.28 (0.10)</td>
<td>0.38 (0.10)</td>
<td>0.04 (0.11)</td>
<td>0.07 (0.14)</td>
<td>0.15 (0.13)</td>
<td>0 (0.2)</td>
<td>0.02 (0.2)</td>
<td>-0.03 (0.2)</td>
</tr>
</tbody>
</table>

q

3495 147 501

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Table V. Comparison of the Force Constants (Units are Identical to Those of Table III) Found for the Pair of Molecules CIF₅ and SF₅. Either Forcing Transferability (Set I) or Requiring a Perfect Fit (Set II).

<table>
<thead>
<tr>
<th></th>
<th>Set I</th>
<th></th>
<th>Set II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CIF₅</td>
<td>SF₅</td>
<td>CIF₅</td>
<td>SF₅</td>
</tr>
<tr>
<td>$f_\beta$</td>
<td>3.53</td>
<td>4.39</td>
<td>3.47</td>
<td>4.40</td>
</tr>
<tr>
<td>$f_r$</td>
<td>2.99</td>
<td>1.95</td>
<td>2.92</td>
<td>2.16</td>
</tr>
<tr>
<td>$f_\beta$</td>
<td>2.69</td>
<td>2.34</td>
<td>2.47</td>
<td>2.40</td>
</tr>
<tr>
<td>$f_\alpha$</td>
<td>1.25</td>
<td>0.89</td>
<td>1.20</td>
<td>0.87</td>
</tr>
<tr>
<td>$f_{rr'}$</td>
<td>0.17</td>
<td>0</td>
<td>0</td>
<td>0.38</td>
</tr>
<tr>
<td>$f_{R'B'}$</td>
<td>0.98</td>
<td>1.25</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>$f_{rr}$</td>
<td>0.14</td>
<td>0.16</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>$f_{RR}$</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$f_{R'R}$</td>
<td>0.42</td>
<td>0.35</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>$f_{R'R'}$</td>
<td>0.46</td>
<td>0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>$f_{RR'}$</td>
<td>-0.35</td>
<td>0</td>
<td>-0.4</td>
<td></td>
</tr>
</tbody>
</table>

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frequency trends (see Table I), the nontransferability of the interaction constants between ClF\(_5\) and SF\(_5\)\(^-\) is not surprising, although the differences are larger than expected. Apparently, the difference in the effective size and electronegativity of the central atom influences the smallest pair, ClF\(_5\)-SF\(_5\)\(^-\) most strongly, thus causing pronounced differences in the interaction constants. Consequently, for ClF\(_5\) and SF\(_5\)\(^-\), the force constants listed as Set II in Table V are preferred over those shown in Table IV.

The valence force constants and to a somewhat lesser degree the interaction terms of these pentafluorides (see Tables IV and V) show plausible values and trends. The relatively large values of \(f_{rr}^{p}\) and \(f_{rr}^{e}\) are in accord with the expectations for three center bonds. The relatively small values of \(f_{rr}^{p}\), \(f_{R}^{p}\), and \(f_{rr}^{e}\) found for the pairs, IF\(_5\) - TeF\(_5\)\(^-\), and BrF\(_5\) - SeF\(_5\)\(^-\), indicate that Urey-Bradley forces are small and that orbital following forces are also small except, as required, for \(f_{rr}^{p}\), and \(f_{rr}^{e}\). For the pair, ClF\(_5\) - SF\(_5\)\(^-\), \(f_{R}^{p}\) could be accounted for by a Urey-Bradley force, but we found that a Urey-Bradley force field fits the frequencies of these molecules only little better than a simple valence force field. It may be noted that the large values found for \(f_{R}^{p}\), \(f_{R}^{e}\), and \(-f_{R}^{e}\) are not easily accounted for by an orbital following field. A lone pair model computed (Ref. 21) for IF\(_5\) (the present study argues that such a model is not required to fit the data of IF\(_5\)) can account for the large values of \(f_{R}^{p}\) and \(f_{R}^{e}\) but not for a similarly large value of \(f_{R}^{e}\). Comparison of the general trends within the \(XF\(_5\)\) and \(XF\(_5\)\(^-\) series shows a remarkable difference. Whereas the deformation force constants in each series have comparable values and follow the same trends, the valence force constants, \(f_{R}\) and \(f_{rr}\), show reverse trends. Thus, for the \(XF\(_5\)\) group, the lightest member, ClF\(_5\), shows the lowest stretching force constant values, but for \(XF\(_5\)\(^-\)\) the heaviest member, TeF\(_5\)\(^-\) exhibits the lowest \(f_{R}\) value. However, a closer inspection of the trends of the valence force constants of fluorides throughout the periodic system (Ref. 22) reveals a general reversal of the direction of that trend either within or close to the sixth main group. Furthermore, increasing stretching force constant values from chlorine to the corresponding bromine fluorides were also found for the ClF\(_3\) and BrF\(_3\) molecules (Ref. 23) and the ClF\(_4\)\(^-\) and BrF\(_4\)\(^-\) anions (Refs. 24, 25).

The usefulness of stretching force constants for the distinction between mainly covalent and semi-ionic three center-four electron bonds has previously been demonstrated for numerous halogen fluorides (Refs. 25, 26). The square
pyramidal pentafluorides of the present study contain two types (i.e., axial and equatorial) of fluorine ligands and a comparison of their stretching force constants should permit some conclusions concerning the nature of their bonds. Since ionic bonds do not contribute to the stretching force constants, semi-ionic bonds ideally should exhibit values half as large as those of covalent bonds. As can be seen from Table VI, the \( f_r/f_R \) ratios of the pentafluorochalcogenate anions range from 0.49 for \( \text{SF}_5^- \) to 0.65 for \( \text{TeF}_5^- \). This indicates strong contributions from semi-ionic 3c-4e bonds to the bonding of the four equatorial fluorine ligands and mainly covalent character for the single axial fluorine bond. This finding agrees with a model involving a \( sp^3 \) hybrid of the central atom for the sterically active, free electron pair and the single, axial fluorine atom while two \( p \) electrons of the central atom form two semi-ionic 3c-4e bond pairs with the remaining four equatorial fluorine atoms. For the halogen pentafluoride molecules, there is also a substantial contribution to the bonding of the four equatorial fluorine ligands from semi-ionic 3c-4e bonds. However, this contribution is somewhat less than in the corresponding pentafluoro chalcogenate anions.

**Table VI.**

**Stretching Force Constants (mdyne/Å) and Their Ratio for Square Pyramidal X\( F_5 \) Anions and Molecules**

<table>
<thead>
<tr>
<th></th>
<th>( \text{SF}_5^- )</th>
<th>( \text{SeF}_5^- )</th>
<th>( \text{TeF}_5^- )</th>
<th>ClF(_5)(^a)</th>
<th>BrF(_5)</th>
<th>IF(_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_r )</td>
<td>2.16</td>
<td>2.41</td>
<td>2.30</td>
<td>2.6 - 2.9</td>
<td>3.24</td>
<td>3.65</td>
</tr>
<tr>
<td>( f_R )</td>
<td>4.40</td>
<td>3.82</td>
<td>3.53</td>
<td>3.5 - 3.7</td>
<td>4.03</td>
<td>4.25</td>
</tr>
<tr>
<td>( f_r/f_R )</td>
<td>.49</td>
<td>.63</td>
<td>.65</td>
<td>.75 - .84</td>
<td>.80</td>
<td>.75</td>
</tr>
</tbody>
</table>

(a) These ranges cover the values reported in Ref. 13, 20, 27, and in this paper. For BrF\(_5\) and IF\(_5\) no ranges are given due to the similar values obtained by the different workers. The larger discrepancies for ClF\(_5\) are due to the various choices of the more significant interaction constants.
Acknowledgement. We are indebted to Dr. I. Silvera of the Science Center of NAR for the use of the Raman spectrometer. This work was supported by the Office of Naval Research, Power Branch, and by the Air Force Office of Scientific Research under Contract AF49(638)-1734.
References


14. After completion of this work, H. Selig and H. Holzman (Israel J. Chem., 7, 417 (1969) have published the Raman spectrum of gaseous IF_5. Their observed frequencies agree reasonably well with those observed for the liquid (Ref. 13) which were also used for the evaluation of the force constants. Since the exact geometry of IF_5 is still unknown, a recomputation of its force constants using the Raman frequencies of the gas is deferred until its exact geometry is available (see also footnote (e) of Table II).


Diagram Captions

Figure 1 - Raman spectrum of solid Ca$^{+}$SeF$_5$\textsuperscript{\textsuperscript{-}}. Sample container, glass capillary. C indicates spectral slit width.

Figure 2 - Infrared spectrum of solid Ca$^{+}$SeF$_5$\textsuperscript{\textsuperscript{-}} as AgBr disk.

Figure 3 - Raman spectrum of solid Ca$^{+}$SF$_5$\textsuperscript{\textsuperscript{-}}. Sample container, glass capillary.

Figure 4 - Infrared spectrum of solid Ca$^{+}$SF$_5$\textsuperscript{\textsuperscript{-}} as AgBr disk.
Figure 1.
APPENDIX I

THE CRYSTAL STRUCTURE OF $[\text{BrF}_4^+] [\text{Sb}_2\text{F}_{11}^-]$
The Crystal Structure of $[\text{BrF}_4]^+[\text{Sb}_2\text{F}_{11}]^-$

by M. D. Lind

North American Rockwell Science Center

and

K. O. Christe

Rocketdyne Division, North American Rockwell Corporation

Abstract

The crystal structure of the 1:2 adduct formed by $\text{BrF}_5$ and $\text{SbF}_5$ has been determined. The crystals consist of infinite chains of discrete $\text{BrF}_4^+$ and $\text{Sb}_2\text{F}_{11}^-$ ions coupled by relatively weak fluorine bridges and, accordingly, should be formulated as $[\text{BrF}_4^+][\text{Sb}_2\text{F}_{11}]^-$. This is the first direct evidence for the existence of the $\text{BrF}_4^+$ ion. The crystals are monoclinic with most probable space group $P2_1/a$, lattice constants $a = 14.19 \pm 0.03$, $b = 14.50 \pm 0.03$, $c = 5.27 \pm 0.01$, $\beta = 90.6 \pm 0.1^\circ$, and four formula units per unit cell; the calculated density is 3.72 g cm$^{-3}$. The structural parameters were refined by the method of least-squares with visually estimated Weissenberg photographic intensity data. The final value of the conventional agreement index $R$ was 0.14 for 773 reflections having $|F_0|$ greater than $\sigma(|F_0|)$. 

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Introduction

Previous investigations of solid halogen fluoride adducts have provided evidence that some are predominantly ionic\textsuperscript{1-4} and others are predominantly covalent.\textsuperscript{5-7} Infrared and Raman spectroscopic studies\textsuperscript{4} of the 1:2 adduct\textsuperscript{8} formed by BrF\textsubscript{5} and SbF\textsubscript{5} yielded equivocal results concerning the nature of this compound because of the large number of possible fundamental vibrations and the low symmetry of the bromine and antimony environments. For the same reasons, the arguments recently presented by Meinert and Gross\textsuperscript{9} in favor of the ionic structure are not convincing. To resolve the ambiguity, we have determined the structure from single crystal X-ray diffraction data. Our investigation was complicated by the marginal stability of the adduct and its tendency to decompose on contact with atmospheric moisture and with glass.
Experimental

Preparation of Crystals. The metal-Teflon FEP vacuum system used and the preparation of BrF$_5$·2SbF$_5$ have been described elsewhere.$^4$ The single crystals were grown by slow sublimation at 30° in dry N$_2$. In a dry N$_2$ glovebox, they were transferred to Teflon FEP capillaries, which were subsequently sealed with high melting point Halocarbon wax. A powder X-ray diffraction photograph of crushed single crystals was identical to that of the polycrystalline material from which the single crystals were grown and the composition of which was established by quantitative synthesis.$^4$

Crystallographic Data. Oscillation, Weissenberg, and Buerger precession photographs were obtained with Zr filtered MoKα (λ = 0.7107 Å) radiation. These data showed that the crystals have monoclinic symmetry. From the systematic extinctions, h0l with h odd and Ok0 with k odd, the most probable space group was determined to be P2$_1$/a. The lattice constants, measured from Buerger precession photographs taken at 23°C, are $a = 14.19 \pm 0.03$, $b = 14.50 \pm 0.03$, $c = 5.27 \pm 0.01$ Å, $β = 90.6 \pm 0.1°$, and $V = 1085$ Å$^3$. Assuming that the unit cell contains four empirical formula units BrSb$_2$F$_{15}$ of formula weight 608.4, the calculated density is 3.72 g cm$^{-3}$. The density of the crystals has not been measured, but the calculated volume per fluorine atom, 18.1 Å$^3$, is very nearly the value expected for approximately close-packed fluorine atoms.$^1,10$ For MoKα radiation the linear absorption coefficient of the crystals is 9.15 mm$^{-1}$.

Intensity Data. The X-ray diffraction intensities were determined from Zr filtered MoKα multiple-film equi-inclination Weissenberg photographs by visual comparison with an intensity scale. The specimen was approximately 0.15 x 0.2 x 0.4 mm in dimension with the longest direction nearly parallel to the capillary axis. The axis of rotation was the crystallographic a axis,
because it was the axis most nearly aligned with the capillary axis. Rotation around the $b$ axis is usually preferable for monoclinic crystals, but in this case the angle $\beta$ is near enough to $90^\circ$ to cause no difficulty with the reciprocal lattice levels $h = 0-13$, the levels for which intensities were measured. In each of these levels, intensities were measured in the range $\sin \theta/\lambda \leq 0.65$. A total of 892 independent reflections having intensities above background was measured. Omitted from the intensity measurements were several reflections cut off by the Weissenberg camera beam stop and six reflections too intense to be measured with the intensity scale employed. Within the range of the measurements, there was a large number of reflections too weak to be observed.

After the set of Weissenberg photographs was complete, the $h = 0$ level Weissenberg was repeated to verify that there had been no appreciable decomposition of the crystal. Later, however, the crystal did decompose, and, unfortunately, this happened before its precise shape and dimensions had been recorded; therefore, accurate absorption corrections were impossible, and none were made.

The intensities were reduced to a set of relative structure amplitudes $|F_0(h\kappa\ell)|$ by application of the appropriate Lorentz-polarization factors and extraction of the square roots.
Determination of the Structure

The four bromine, eight antimony, and sixty fluorine atoms per unit cell are all in the fourfold general positions of space group $P2_1/a$, the equivalent positions of which are $x, y, z; -x, -y, -z; 1/2 + x, 1/2 - y, z; 1/2 - x, 1/2 + y, -z$. The asymmetric unit of the structure consists of one $\text{BrSb}_2\text{F}_{15}$ formula unit, or eighteen atoms.

The arrangement of the atoms was deduced from the three-dimensional Patterson function and from the three-dimensional Fourier electron density function calculated with phases determined by the bromine and antimony contributions to the structure factors.

The positional parameters were refined by the method of least-squares\textsuperscript{11}. The function minimized was $\sum w(|F_0| - k|F_c|)^2$. A modification of the Hughes\textsuperscript{12} weighting procedure was used; for $|F_0| > 100$, $w = 100/|F_0|^2$; for $100 \geq |F_0| > 25$, $w = 1/100$; for $|F_0| \leq 25$, $w = 1/625$. Scattering factors were those for the neutral atoms given by Cromer and Waber\textsuperscript{13}. The real parts of the anomalous dispersion corrections for bromine and antimony given by Cromer\textsuperscript{14} were applied, but the imaginary parts were neglected.

The thermal parameters were kept isotropic until the agreement index $R = \Sigma ||F_0| - |F_c||/\Sigma |F_0|$ had decreased to about 0.20, after which the thermal parameters of the bromine and antimony atoms were allowed to become anisotropic. We did not attempt to determine anisotropic thermal parameters for the fluorine atoms because of the large number of variable parameters this would entail.

The final values of the parameters are given in Table 1. In the final refinement cycle, the largest parameter change was 18% of the estimated standard error in that parameter value and most were much smaller. After convergence, the agreement index $R$, defined above, was 0.14 for the 773 reflections having $|F_0|$ greater than $\sigma = \sqrt{w^{-1/2}}$. Including the 119 reflections $R$-8725

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having $|F_0|$ observable but less than $\sigma$, the index $R$ is 0.15. For the full set of 892 data, the weighted agreement index $WR$ was 0.17, and the standard deviation of an observation of unit weight SIG1 was 1.2. Table 2 compares the $|F_0|$ with the $F_C$ calculated from the final parameter values. $F_C$'s were calculated for the reflections too weak to be observed and were found to be satisfactorily small.
Discussion of the Structure

Our results show that the crystals consist of infinite chains of discrete $\text{BrF}_4^+$ and $\text{Sb}_2\text{F}_{11}^-$ ions coupled by relatively weak fluorine bridges. Accordingly the compound should be formulated as $[\text{BrF}_4]^+[\text{Sb}_2\text{F}_{11}]^-$. This conclusion is based on the interatomic distances in the structure, which are given in Figure 1 and Table 3. The two fluorine atoms F(4) and F(5) involved in the Sb-F-Br bridges are bonded strongly to the antimony atoms and only weakly to the bromine atoms. The Sb(1)-F(4) and Sb(2)-F(5) distances are both equal to the average Sb-F bond distance in this structure, 1.86 Å. The Br---F(4) and Br---F(5) distances, 2.49 and 2.24 Å, are very long and indicative of relatively weak bonding compared with the other four Br-F bond distances, which average 1.81 Å; this difference is substantially greater than the limits of error in the distances, which are given in Table 3. The results rule out the alternative possibility of an essentially covalent structure with strong fluorine bridges.

The bromine atom has four strongly bonded fluorine ligands, F(1), F(8), F(11), and F(13). Including the free electron pair on the bromine atom, the $\text{BrF}_4^+$ structure might be described as a distorted trigonal bipyramid with F(1), F(8), and the free pair occupying the three equatorial positions. Part of the cause for the distortion from an ideal trigonal bipyramid appears to be the presence of the two additional, more remote fluorine ligands, F(4) and F(5), which belong to two neighboring $\text{Sb}_2\text{F}_{11}^-$. This results in a coordination number of seven for the bromine atom. For this coordination number, the most likely structures are either a puckered pentagonal bipyramid or an octahedron distorted by having the seventh ligand (the free electron pair) above one of the triangular octahedral faces. As can be seen from Figures 1 and 2 and Table 3, the face is that obviously formed by F(4), F(5), and F(11). This results in F(11) being bent toward F(1) and F(8). The free electron pair of / is probably not directed
at the center of the octahedral face, but much closer to the F(4)-F(5) edge because of their greater distance from the bromine atom; thus, the coordination polyhedron approaches a puckered pentagonal bipyramid. This pseudo-hepta coordinate structure of BrF$_4^+$ closely resembles that found by Edwards and Jones$^{16}$ for SeF$_3^+$ in [SeF$_3^+$][Nb$_2$F$_{11}$]$^-$.

Comparison of the geometry found for BrF$_4^+$ with that of isoelectronic SeF$_4^{17}$ shows good agreement. Gaseous SeF$_4$ has bond angles of 169 and 100º for the axial and equatorial bonds, respectively, compared to 173 and 96º for BrF$_4^+$. The deviation of the bond angles from those predicted for an ideal trigonal bipyramid is due to the nonbonded electron pair being more diffuse than the bonded one, causing an increased repulsion. The equatorial and axial bonds of BrF$_4^+$ and SeF$_4$ show a similar difference in average length (0.085 versus 0.089 Å, respectively), although the experimental BrF$_4^+$ values are statistically rather insignificant because of the relatively large error limits. As expected, the bond distances in BrF$_4^+$ are somewhat smaller than those found$^3$ for the BrF$_4^-$ anion, 1.89 Å.

The Sb$_2$F$_{11}^-$ ion has the expected fluorine bridged structure in which each antimony atom is surrounded by an irregular octahedral array of fluorine atoms with one fluorine atom shared by the two antimony atoms. However, the structure of the Sb$_2$F$_{11}^-$ ion reported here differs somewhat from that reported previously for this ion.$^2$ The essential difference is the pronounced asymmetry of the Sb---F-Sb bridge in the present case. The Sb(1)---F(12) distance of 2.15 Å indicates a relatively weak bond compared with the other Sb-F bonds in the structure; the difference is well outside the limits of error in the distances. Consistent with the long Sb(1)---F(12) distance, the other Sb(1)-F distances, on the average, are considerably shorter than the Sb(2)-F distances; the former average 1.75 Å, while the latter average 1.90 Å. For comparison, in [XeF]$^+[Sb$_2$F$_{11}$]$^-$ the two Sb-F bridge bonds were found to differ by less than

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twice the estimated standard error, and the average Sb-F bond distances of the two antimony atoms were found to be very nearly the same. In the present case, because of the relative weakness of the Sb(1)--F(12) bond, the Sb$_2$F$_{11}^-$ ion should perhaps be considered instead to be an SbF$_6^-$ ion and an SbF$_5$ molecule coupled by a moderately strong fluorine bridge. This view is also supported by the finding that SbF$_6^-$ forms with excess of SbF$_5$ not only Sb$_2$F$_{11}^-$, but also tri- and polymeric anions and that, in most cases, the additional SbF$_5$ molecules can be removed stepwise by controlled pyrolysis.

The fluorine bridges which couple the BrF$_4^+$ and Sb$_2$F$_{11}^-$ ions together are formed by cis-fluorine atoms F(4), F(5), and F(12). Neglecting the differences in bond distances described above, the cis-fluorine bridged chain structure of [BrF$_4^+$][Sb$_2$F$_{11}^-$] crystals resembles that proposed for liquid SbF$_5$ and for [Sb$_n$F$_{5n+1}$]$^-$ ions in solutions. The nature of the fluorine bridges in the [BrF$_4^+$][Sb$_2$F$_{11}^-$] crystals appears to be very similar to that described for [BrF$_2^+$][SbF$_6^-$] crystals, which were found to consist of infinite chains of discrete BrF$_2^+$ and SbF$_6^-$ ions coupled by weak cis-fluorine bridges. In [BrF$_4^+$][Sb$_2$F$_{11}^-$] the Br---F-Sb and Sb---F-Sb bond angles are considerably nearer to 180° than are the analogous bridge bond angles in [BrF$_2^+$][SbF$_6^-$] and [XeF]$^+$[Sb$_2$F$_{11}^-$]. In [BrF$_4^+$][Sb$_2$F$_{11}^-$] the atoms Br, Sb(1), Sb(2), F(1), F(2), F(4), F(5), F(7), F(6), F(9), F(12), and F(15) are all within 0.3 Å of being coplanar; their common plane is very nearly parallel to the 201 planes. This near-coplanarity extends the whole length of any given chain. The planes of adjacent chains (see Figure 2) are parallel but are spaced c/2 or c apart along the c direction. The closest approaches of fluorine atoms bonded to different bromine and antimony atoms within the chains are 3.03, 3.24, and 3.47 Å, all of which are substantially greater than twice the van der Waals radius of fluorine.
The chains are approximately close packed. There is no bridging between chains. The minimum inter-chain F---F separation is 2.72 Å, which is approximately twice the van der Waals radius of fluorine. The minimum inter-chain Br---F and Sb---F distance is 3.56 Å, which is approximately the value expected for the sums of the van der Waals radii of the atom pairs.

In summary, this is the first direct evidence for the existence of the BrF₄⁺ cation. Although the present experimental data do not allow very precise determinations of bond lengths and angles, valuable information about the structure of this interesting adduct was obtained.

Acknowledgments

We thank S. Geller for helpful discussions of this work. The contributions of one of us (K. O. C.) were in part supported by the Office of Naval Research, Power Branch.
References


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<td>Sb(2)</td>
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<td>3945(9)</td>
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<td>674(30)</td>
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<td>F(3)</td>
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<td>2641(68)</td>
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<td>F(10)</td>
<td>806(53)</td>
<td>6322(52)</td>
<td>3657(99)</td>
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<td>F(11)</td>
<td>4049(34)</td>
<td>6454(38)</td>
<td>4(75)</td>
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<td>F(12)</td>
<td>2355(33)</td>
<td>7615(27)</td>
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<td>9409(24)</td>
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^aCalculated from the following anisotropic thermal parameters (estimated standard errors are given in parenthesis):

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<th>$10^4 \beta_{22}$</th>
<th>$10^4 \beta_{33}$</th>
<th>$10^4 \beta_{12}$</th>
<th>$10^4 \beta_{13}$</th>
<th>$10^4 \beta_{23}$</th>
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<td>535(23)</td>
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<td>-42(6)</td>
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<td>Sb(1)</td>
<td>78(9)</td>
<td>38(2)</td>
<td>366(13)</td>
<td>-2(3)</td>
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<td>-3(7)</td>
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<td>Sb(2)</td>
<td>32(8)</td>
<td>25(2)</td>
<td>655(16)</td>
<td>4(4)</td>
<td>39(4)</td>
<td>-3(9)</td>
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The $\beta_{ij}$ are for the expression $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}h^2\lambda+2\beta_{23}kl)]$.

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### Table 3
INTERATOMIC DISTANCES AND BOND ANGLES

a) Br environment

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<td>Br-F(1)</td>
<td>1.76±0.12Å</td>
<td>2.62±0.15Å</td>
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<tr>
<td>Br-F(8)</td>
<td>1.76±0.09</td>
<td>2.76±0.18</td>
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<tr>
<td>Br-F(13)</td>
<td>1.80±0.12</td>
<td>2.47±0.17</td>
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<tr>
<td>Br-F(11)</td>
<td>1.91±0.13</td>
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<tr>
<td></td>
<td>average 1.81</td>
<td>average 2.60</td>
</tr>
<tr>
<td>Br-F(5)</td>
<td>2.24±0.10</td>
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</tr>
<tr>
<td>Br-F(4)</td>
<td>2.49±0.11</td>
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<tr>
<td></td>
<td>LF(1)-Br-F(4)</td>
<td>168.5±4.2º</td>
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<td>LF(8)-Br-F(5)</td>
<td>175.4±3.5</td>
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<td>LF(11)-Br-F(13)</td>
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b) Sb(1) environment

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<td>Sb(1)-F(3)</td>
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<td>2.51±0.20Å</td>
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<td>1.72±0.14</td>
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<td>1.76±0.13</td>
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<td>Sb(1)-F(10)</td>
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<td>Sb(1)-F(4)</td>
<td>1.86±0.11</td>
<td>2.59±0.20</td>
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<td>average 1.81</td>
<td>average 2.57</td>
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<td>172.4±6.1</td>
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<td>LF(9)-Sb(1)-F(4)</td>
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<td>Distance (Å)</td>
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<tr>
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<td>1.81 ± 0.10Å</td>
<td>F (6)-F (5) 2.65 ± 0.14Å</td>
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<td>1.86 ± 0.09</td>
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<td>Sb(2)-F (7)</td>
<td>1.87 ± 0.18</td>
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<td>Sb(2)-F(15)</td>
<td>1.89 ± 0.10</td>
<td>F (6)-F (12) 2.50 ± 0.13</td>
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<td>Sb(2)-F(12)</td>
<td>1.94 ± 0.12</td>
<td>F (5)-F (7) 2.74 ± 0.18</td>
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<td>F (5)-F (12) 2.56 ± 0.17</td>
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<td>LF(6)-Sb(2)-F(14) 165.6 ± 5.2</td>
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<td>LF(7)-Sb(2)-F(12) 173.8 ± 6.3</td>
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<td>LF(7)-Sb(2)-F(12) 173.8 ± 6.3</td>
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<td></td>
<td>average 1.90</td>
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<tr>
<td>d) Bridge bond angles</td>
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<td>LBr-F(4)-Sb(1)</td>
<td>174.1 ± 6.4°</td>
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<td>LBr-F(5)-Sb(2)</td>
<td>170.8 ± 5.0</td>
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<td>LsB(1)-F(12)-Sb(2)</td>
<td>173.0 ± 6.4</td>
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<td>e) Non-bonded intra-chain distances</td>
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<tr>
<td>F(1)-F (9)</td>
<td>3.03 ± 0.16Å</td>
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<td>F(2)-F (7)</td>
<td>3.47 ± 0.20</td>
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<tr>
<td>F(8)-F(15)</td>
<td>3.24 ± 0.14</td>
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Table 2. Comparison of observed structure amplitudes with those calculated from final parameter values. Reflections omitted from the table are too weak to be observed. Reflections cut off by the Weissenberg camera beam stop are indicated by "c" in the columns for |F₀|. Six reflections too intense to be measured with the intensity scale employed are indicated by "s".

Figure 1. View in perspective of a segment of the chain structure of [BrF₄][Sb₂F₁₁]⁻ crystals.²¹

Figure 2. Stereoscopic view to show the packing arrangement in [BrF₄][Sb₂F₁₁]⁻ crystals.²¹ The viewing direction is normal to the 001 planes.
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**Table 2**
APPENDIX J

LASER RAMAN SPECTRUM OF $\text{NF}_4^+\text{AsF}_6^-$
The preparation \( \text{NF}_4^+ \) and the vibrational spectrum \( \text{NF}_4^+ \text{AsF}_6^- \) have previously been reported. It was shown that the \( \text{NF}_4^+ \) cation is tetrahedral.\(^1\)-\(^5\) Out of the four fundamental vibrations of \( \text{NF}_4^+ \), the \( A_1 \) and the \( E \) mode can be observed only in the Raman spectrum. At the time of the previous spectroscopic study,\(^5\) only a very small amount of material and no laser Raman spectrometer were available to us. The observed infrared spectrum was of very good quality; however, owing to a low signal to noise ratio in the Raman spectrum, only tentative assignments could be made at that time for the \( A_1 \) and the \( E \) mode.

In this communication, we wish to report the laser Raman spectrum of \( \text{NF}_4^+ \text{AsF}_6^- \) (see Figure 1, trace A). It is shown that \( \nu_1 (A_1) \) and \( \nu_2 (E) \) of \( \text{NF}_4^+ \text{AsF}_6^- \) occur at 847 and 445 \( \text{cm}^{-1} \), respectively. The value of 847 \( \text{cm}^{-1} \) for \( \nu_1 (A_1) \) is close to those of 844 and 838 \( \text{cm}^{-1} \) deduced from the infrared active combination bands \( \nu_1 + \nu_4 \) and \( \nu_1 + \nu_3 \), respectively. The symmetry force constants computed with these revised Raman frequencies are: \( F_{11} = 8.03 \) and \( F_{22} = 0.74 \text{ mdyne/\AA} \). Adopting for the \( F_2 \) block the previously reported values,\(^5\) the internal force constants of \( \text{NF}_4^+ \) can be calculated (see Table I). These force constants are not unique since in the \( F_2 \) block, three force constants had to be computed from two vibrational frequencies using the approximating method of Fadini.\(^6\) For the isoelectronic species, \( \text{CF}_4^- \) and \( \text{BF}_4^- \), this method has yielded values close to those of the general valence force field and, hence, may also be a good approximation for \( \text{NF}_4^+ \). A detailed discussion of the trends observed within this isoelectronic series has previously been given.\(^5\)

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The sample used for the present investigation was prepared by the high pressure-temperature method. However, contrary to previous reports, the reaction product was not homogeneous. At the bottom of the Monel reactor, a white, loose solid had accumulated which, according to its elemental analysis, had the approximate composition (in mole %) 93.2 \( \text{NF}_4^+ \text{AsF}_6^-\), 5.8 \( \text{Ni} (\text{AsF}_6)_2 \), and 1.0 \( \text{Cu} (\text{AsF}_6)_2 \). Its vibrational spectrum is depicted by traces A in Figures 1 and 2 and shows the bands expected for the tetrahedral \( \text{NF}_4^+ \) and the approximately octahedral \( \text{AsF}_6^- \) ion. About an equal amount of solid product was uniformly distributed over the walls of the reactor. It was pale yellow and according to its elemental analysis, showed a substantially increased Ni and Cu content. Furthermore, its infrared and Raman spectrum (traces B in Figures 1 and 2) shows that the bands which in traces A could not be accounted for in terms of octahedral \( \text{AsF}_6^- \) and tetrahedral \( \text{NF}_4^+ \), have strongly increased in relative intensity. Therefore, these additional bands must be attributed to the presence of the metal salts. Furthermore, the previous reports on the hydrolysis of \( \text{NF}_4^+ \) were confirmed in that \( \text{NF}_3 \) and \( \text{O}_2 \) were quantitatively evolved in a 2:1 mole ratio, and no evidence for the formation of nitrogen oxides or oxyfluorides was found.

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**TABLE I.**

Force Constants of the Isoelectronic Series, \( \text{NF}_4^+, \text{CF}_4, \text{BF}_4^- \) (mdynes/\( \AA \))

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<tr>
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<th>( \text{NF}_4^+ )</th>
<th>( \text{CF}_4 ) ( (a) )</th>
<th>( \text{BF}_4^- ) ( (a) )</th>
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<tbody>
<tr>
<td>( f_r )</td>
<td>6.22</td>
<td>6.93</td>
<td>4.87</td>
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<tr>
<td>( f_{rr} )</td>
<td>0.60</td>
<td>0.77</td>
<td>0.23</td>
</tr>
<tr>
<td>( f_{\alpha}^{-}f_{\alpha}^{+} )</td>
<td>0.98</td>
<td>1.02</td>
<td>0.72</td>
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<tr>
<td>( f_{\alpha}^{+}f_{\alpha}^{-} )</td>
<td>0.12</td>
<td>0.16</td>
<td>0.13</td>
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<tr>
<td>( f_{\alpha}^{+}f_{\alpha}^{-} )</td>
<td>0.77</td>
<td>0.57</td>
<td>0.43</td>
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</table>

Experimental Section

Materials and Apparatus. - The materials used in this work were manipulated in a well-passivated (with ClF₃) 304 stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves (Hoke Inc., 425 IF4Y). Pressures were measured with a Heise-Bourdon tube-type gauge (0-1500 mm Hg. 0.1%). Nitrogen trifluoride (Air Products) and AsF₅ (Ozark Mahoning Company) were purified by fractional condensation. Prior to its use, fluorine (Rocketdyne) was passed through a NaF trap to remove HF impurities. Because of their hygroscopic nature, materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box. The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer as dry powders between AgCl or AgBr windows or in the form of pressed AgBr disks. The Raman spectra were recorded using a Coherent Radiation Laboratories Model 52 Ar laser as a source of 1.3 W of exciting light at 5145 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to -25°C, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or melting point capillaries were used as sample containers.

Preparation of NF₄⁺AsF₆⁻. Nitrogen trifluoride (180 mmole), AsF₅ (180 mmole), and F₂ (360 mmole) were heated in a passivated 150 ml Monel cylinder under autogenous pressure to 125°C for 20 days. After removal of unreacted starting materials, the cylinder was opened in the glove box and contained about 2.88 g of a solid. About half of the solid had accumulated as a loose white powder (I) at the bottom of the reactor, the rest being distributed in the form of a yellowish layer (II) over the walls of the reactor. Anal. I, Calcd for 93.2 (mole %) NF₄⁺AsF₆⁻, 5.8 Ni(AsF₆)₂, 1.0 Cu(AsF₆)₂; N, 4.50; Ni, 1.21; Cu, 0.22; As, 27.50; total F, 65.59; hydrolyzable F, 6.11; NF₃:O₂ mole ratio upon 2.0:1. Found: N, 4.64; Ni, 1.21; Cu, 0.23; As, 28.9; total F, 65; hydrolyzable F, 6.2; NF₃:O₂, 2.01:1. II, Found: N, 2.14; Ni, 2.95; Cu, 2.37; As, 28.0; NF₃:O₂, 2.02:1.

Elemental Analysis. - For N, Ni, Cu, As, and hydrolyzable F analyses, a weighted sample was hydrolyzed in a Teflon FEP U-trap. The total amount of gas (NF₃ + O₂) was measured volumetrically, then NF₃ was separated from O₂ by fractional condensation at -210°C, measured, and identified by infrared
spectroscopy. The aqueous solution was analyzed for Ni, Cu, and As by atomic absorption and for As by x-ray fluorescence spectroscopy and for hydrolyzable F by both Th(NO₃)₄ titration and by means of a fluoride electrode. For the total fluoride determination, the sample was fused prior to the F⁻ analysis using the Parr bomb technique (Na₂O₂ + starch).

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References

7. Since the elemental analysis of the Ni and Cu rich sample showed an As content somewhat higher than that expected on the basis of the found N, Ni, and Cu values, we have explored the possible presence of a stable As$_{22}F_{11}^-$ ion in more detail. Solutions of the salt in HF showed only the F nmr lines characteristic for NF$_4^+$, AsF$_6^-$, and HF, but no evidence for those previously reported (P.A.W. Dean, R. J. Gillespie, and R. Hulme, Chem. Comm., 990 (1969)) for As$_{22}F_{11}^-$. When CH$_2$CN was used as a solvent, interaction with NF$_4^+$ occurred, resulting in a disappearance of the NF$_4^+$ signals, but in a preservation of the AsF$_6^-$ lines. Again no evidence for the As$_{22}F_{11}^- $ lines was obtained. Attempts to prepare Cs'As$_{22}F_{11}^-$ under conditions similar to those used in the NF$_4^+$-AsF$_6^-$ synthesis, i.e., elevated temperature and pressure, produced exclusively Cs'AsF$_6^-$.

Based on these findings and on the previously reported instability of As$_{22}F_{11}^-$ salts (Dean et al., Chem. Comm. 990 (1969)), the presence of a stable As$_{22}F_{11}^-$ salt in our sample appears unlikely.
Diagram Captions

Figure 1. Replotted Raman spectra of solid $\text{NF}_4^+\text{AsF}_6^-$ containing smaller (sample I, trace A) and larger (sample II, trace B) amounts of metal salts. C indicates spectral slit width.

Figure 2. Infrared spectra of solid $\text{NF}_4^+\text{AsF}_6^-$. Samples of traces A (AgBr pellet) and B (dry powder between AgCl plates) are identical to those of Figure 1.