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New covalent inorganic perchlorates were prepared from chlorine perchlorate. The compound $I(ClO_4)_3$ was partially characterized and $N(ClO_4)_3$ deduced as a primary reaction product. The one-valent iodine perchlorate could not be prepared and the new complex perchlorate, $CsI(ClO_4)_4$, was synthesized. The action of $ClSO_3F$ and I_2 produces a variety of iodine fluorosulfates. One partially characterized species is OIF_2SO_3F. Fluorosulfates of nitrogen could not be made from the reaction of NCl_3 and $ClSO_3F$. Neither chlorine perbromate nor chlorine bromate could be isolated from reactions of Cl_2O_4 with appropriate salts. Unstable primary reactions products were formed that decomposed to bromine oxide. The reaction of $ClSO_3F$ and metal periodates gives IO_4SO_3F which is apparently a covalent peroxide. Its decomposition to IO_2SO_3F and O_2 was quantitative. Further, the oxygen is quite labile and IO_4SO_3F is an effective oxygenating agent in that perfluoroalkylene oxides could be readily formed from it and fluoroolefins at low temperatures. Iodyl fluorofulfate and F_2 at ambient temperature give SO_3F_2, IF_5O, and IF_7. The covalent nature of IO_2SO_3F was supported by the formation of SO_3F_2. The use of SF_4 as a fluorinating agent toward IO_2SO_3F resulted in the formation of IF_5 and $S_2O_5F_2$. The synthesis of ClO_6 could not be effected through the reaction of Cl_2O_4 and O_2AsF_6. Based on the nature of the products obtained, a reaction sequence was constructed consistent with the intermediacy of ClO_6. The new chlorofluorine of selenium, SeF_5Cl, was prepared from $CsSeF_5$ and $ClSO_3F$. Extensive data on SeF_5Cl are reported. 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, the crystal structure of $BrF_4^+Sb_2F_{11}^-$ has been determined.

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6. Infrared Spectra						
7. Raman Spectra						
8. X-Ray Powder Patterns						
9. Crystal Structure						
10. Epoxidation						
11. Fluorosulfates						
12. Covalent Perchlorates						
13. Chalcogen Fluorides						

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FOREWORD

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.

ABSTRACT

New covalent inorganic perchlorates were prepared from chlorine perchlorate. The compound $I(ClO_4)_3$ was partially characterized and $N(ClO_4)_3$ deduced as a primary reaction product. The one-valent iodine perchlorate could not be prepared and the new complex perchlorate, $CsI(ClO_4)_4$, was synthesized.

The action of $ClSO_3F$ and I_2 produces a variety of iodine fluorosulfates. One partially characterized species is OIF_2SO_3F. Fluorosulfates of nitrogen could not be made from the reaction of NCl_3 and $ClSO_3F$.

Neither chlorine perbromate nor chlorine bromate could be isolated from reactions of Cl_2O_4 with appropriate salts. Unstable primary reactions products were formed that decomposed to bromine oxides.

The reaction of $ClSO_3F$ and metal periodates gives IO_4SO_3F which is apparently a covalent peroxide. Its decomposition to IO_2SO_3F and O_2 was quantitative. Further, the oxygen is quite labile and IO_4SO_3F is an effective oxygenating agent in that perfluoroalkylene oxides could be readily formed from it and fluoroolefins at low temperatures.

Iodyl fluorosulfate and F_2 at ambient temperature give SO_3F_2, IF_5O, and IF_7. The covalent nature of IO_2SO_3F was supported by the formation of SO_3F_2. The use of SF_4 as a fluorinating agent toward IO_2SO_3F resulted in the formation of IF_5 and $S_2O_5F_2$.

The synthesis of ClO_6 could not be effected through the reaction of Cl_2O_4 and O_2AsF_6. Based on the nature of the products obtained, a reaction sequence was constructed consistent with the intermediacy of ClO_6.

The new chlorofluoride of selenium, SeF_5Cl, was prepared from $CsSeF_5$ and $ClSO_3F$. Extensive data on SeF_5Cl 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 $ClO_2F_2^-$, SF_4, BrF_3, N_2F^+, halogen perchlorates, and the group SF_5^-, SeF_5^-, TeF_5^-. In addition, the crystal structure of $BrF_4^+Sb_2F_{11}^-$ 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_2O_4. This intermediate arose through our studies involving the reactions of positive chlorine species such as ClF and $ClSO_3F$.

The availability of a novel chemical such as Cl_2O_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 $I(ClO_4)_X$ was the reactions aimed at chemicals such as $N(ClO_4)_3$ and $N(SO_3F)_3$. 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_4Cl.

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 $ClO_2F_2^-$. Our principal involvement with the chemical $CsClO_2F_2$ 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 $ClOClO_3$ were also described at that time, notably, its usefulness in forming $BrOClO_3$ and several fluorocarbon perchlorates. In the case of the $BrOClO_3$ synthesis, chlorine perchlorate was used to oxidize elemental bromine to the +I oxidation state.

$$Br_2 + 2ClOClO_3 \longrightarrow Cl_2 + 2BrOClO_3$$

Stoichiometric amounts of $ClOClO_3$ were always used and thus no attempt to achieve further oxidation of the Br_2 was made. This has now been done with the goal of preparing $Br(OClO_3)_3$. Since related compounds of bromine with electronegative ligands are more stable in the +III oxidation state than in the +I state (e.g., BrF_3 vs BrF), it was hoped that the tris-perchlorate might have enhanced stability relative to the mono substituted material. However, when excess $ClOClO_3$ was reacted with Br_2 at -45 C, a quantitative yield of $BrOClO_3$ was obtained. When the reaction temperature was raised to about -20 C, there occurred a gradual decomposition of all bromine species to Br_2, O_2, and Cl_2O_7. Hence, definite evidence for a trisperchlorate of bromine was not obtained.

Iodine is, of course, more readily oxidized than bromine and $ClOClO_3$ might be expected to convert I_2 to the +III state despite the failure to do so with bromine. Indeed a facile, quantitative reaction of I_2 and $ClOClO_3$ was noted, according to the following equation:

$$I_2 + 6ClOClO_3 \xrightarrow{-45\ C} 2I(OClO_3)_3 + 3Cl_2$$

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.

Attempts were made to prepare a mono perchlorate of iodine by limiting the quantity of $ClOClO_3$ reacting with I_2. 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 F_2, IF_5 and ClF were formed, indicating the presence of iodine chlorides. The solid, nonvolatile residue exhibited an infrared spectrum similar to that of the $I(OClO_3)_3$ decomposition product.

Since complexing is known to stabilize lower, otherwise unstable, oxidation states, we have attempted the synthesis of $Cs^+I(OClO_3)_2^-$, according to:

$$CsIBr_2 + 2ClOClO_3 \longrightarrow CsI(OClO_3)_2 + 2BrCl$$

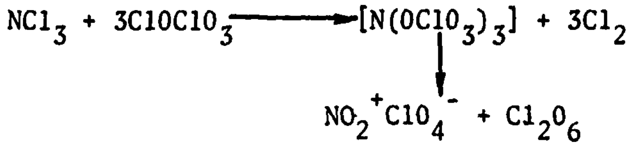
Consequently, a sample of $CsIBr_2$ was prepared and reacted with $ClOClO_3$. The derived reaction occurred at -45 C as indicated by $ClOClO_3$ uptake and BrCl liberation. Visually, though, the solid product appeared to be a mixture. This was confirmed by infrared analysis which a portion of the solid showed the characteristic perchlorate absorptions. Thus, some of the perchlorate must have been incorporated in a more highly oxidized iodine species, such as $I(OClO_3)_4^-$, leaving the bottom layers unreacted.

To verify this assumption, it was decided to react CsI directly to $CsI(OClO_3)_4$ with excess of $ClOClO_3$.

$$CsI + 4ClOClO_3 \xrightarrow{-45\ C} CsI(OClO_3)_4 + 2Cl_2$$

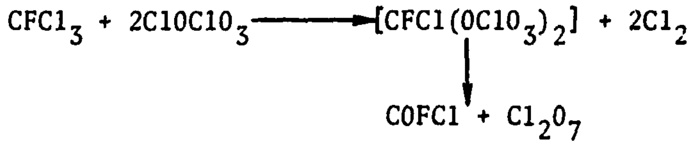
Based on the weight increase of the solid and the consumption of $ClOClO_3$, better than 90 percent of the CsI was converted to the tetrakisperchlorate. More importantly, the white solid compound is stable at ambient temperature. The composition of this new perchlorate derivative was confirmed by its infrared and low-temperature Raman spectrum. The spectra show the absorption characteristic for covalently bound perchlorate groups. In addition, the IO_4 skeletal modes are very similar to those previously reported for the analogous $I(OSO_2F)_4^-$ salts (Ref. 2), suggesting a square planar 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 $ClOClO_3$ suggested the possible synthesis of the novel and highly energetic molecule, nitrogen trisperchlorate. The reaction between NCl_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: Cl_2O_6, Cl_2O_7, $NO_2^+ClO_4^-$, COFCl, Freon 11, and unreacted $ClOClO_3$. The observation of $NO_2^+ClO_4$ and Cl_2O_6 is interesting since it might be interpreted in terms of the formation of an unstable intermediate, $N(OClO_3)_3$:



$$\begin{tikzcd} NCl_3 + 3ClOClO_3 \arrow[r] & {[N(OClO_3)_3]} \arrow[d] + 3Cl_2 \\ & NO_2^+ClO_4^- + Cl_2O_6 \end{tikzcd}$$

The formation of some COFCl and Cl_2O_7 indicates:



$$\begin{tikzcd} CFCl_3 + 2ClOClO_3 \arrow[r] & {[CFCl(OClO_3)_2]} \arrow[d] + 2Cl_2 \\ & COFCl + Cl_2O_7 \end{tikzcd}$$

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 $N(OClO_3)_3$ is not stable enough to allow its isolation and characterization.

REACTIONS OF CHLORINE NITRATE WITH IODINE AND $CsNO_3$

In addition to $ClOClO_3$ and $ClOSO_2F$, the behavior of a related ClOX compound, $ClONO_2$, towards iodine was investigated. The expected product was $I(ONO_2)_3$. Using excess chlorine nitrate, a quantitative synthesis of the trinitrate was obtained at -45 C, based on the amount of produced chlorine and recovered $ClONO_2$.

$$I_2 + 6ClONO_2 \longrightarrow 2I(ONO_2)_3 + 3Cl_2$$

Previous preparation of iodine trinitrate had also used $ClONO_2$ as starting material; however, instead of iodine, ICl_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 $ClONO_2$ - $CsNO_3$ system was studied in an attempt to prepare the most simple member of the novel class of nitrate chlorates according to:

$$ClONO_2 + Cs^+NO_3^- \longrightarrow Cs^+ \ [O_2NOClONO_2]^-$$

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 $ClONO_2$ at ambient temperature for 24 hours did not result in any $ClONO_2$ uptake.

In a third experiment, CH_3CN was added as a solvent to the $ClONO_2$-$CsNO_3$ mixture. Upon warming up of the mixture, a violent explosion occurred, terminating the experiment.

As an alternate approach, $Cl(ONO_2)_2^-$ might be formed according to:

$$Cl_3^- + 2ClONO_2 \xrightarrow{?} Cl(ONO_2)_2^- + 2Cl_2.$$

Since Allied had previously reported (Ref. 4) evidence for the formation of $CsCl_3^-$ and $Cs^+Cl_2F^-$, we have attempted to duplicate their experiments. However, no evidence at all could be found for any adduct formation in the $CsCl-Cl_2$ and the $CsF-Cl_2$ systems.

REACTION OF CHLORINE FLUOROSULFATE WITH IODINE AND NCl_3

In view of the foregoing results for I_2-ClOX oxidation reactions, it would seem likely that the corresponding I_2-ClSO_2F 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 $S_2O_6F_2$. To confirm this expectation and to parallel the preceding studies, the $I_2-ClOSO_2F$ reaction was examined at -45 C. It was found that complete conversion of the I_2 was not accomplished even after several weeks. Increasing the temperature to 0 C resulted in complete consumption of the I_2, but it was noted that 10 moles of the $ClOSO_2F$ had reacted per mole of I_2, liberating 5 moles of Cl_2. This direct evidence for the formation of +V iodine was thought, by analogy to the other ClOX oxidations, to be indicative of the generation of $I(OSO_2F)_5$. However, further examination of the products revealed that appreciable amounts of SO_3 were also liberated in the reaction as well as smaller, variable amounts of $S_2O_5F_2$.

The liquid iodine fluorosulfate material which remained undistilled after the removal of byproducts was subjected to ^{19}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 $CFCl_3$) 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_3F 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:

$$I_2 + 10\ ClOSO_2F \longrightarrow 5Cl_2 + 2\ [I(OSO_2F)_5]$$

$$[I(OSO_2F)_5] \longrightarrow nSO_3 + FI(OSO_2F)_4,\ F_2I(OSO_2F)_3,\ \text{etc.}$$

$$[I(OSO_2F)_5] \longrightarrow S_2O_5F_2 + OI(OSO_2F)_3,\ O_2IOSO_2F$$

$$[I(OSO_2F)_5] \longrightarrow SO_3 + S_2O_5F_2 + OIF_2(OSO_2F)$$

At least one example of each of the types of products shown is known. Thus, $IF_3(OSO_2F)_2$, (Ref. 8) and IO_2SO_3F (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_3F and IF resonances (the range observed was 1.9 to 2.5:1). The unusual and novel molecule $OIF_2(OSO_2F)$ shown in the last equation was obtained during this study by reacting IF_5 with an excess of SO_3. Its nmr spectrum also contains two somewhat broad lines at -21 and -44 ppm with the $IF:SO_3F$ 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_3 and a band of strongly varying intensity at about 930 cm^{-1} which we attribute to an I=O 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:

$$NCl_3 + 3ClOSO_2F \xrightarrow{-45\ F} N(OSO_2F)_3 + 3Cl_2$$

However, instead of the desired and still unknown nitrogen trisfluorosulfate, only a small amount of $HOSO_2F$ 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.

$$KBrO_4 \xrightarrow{400\ C} KBr + 2O_2$$

By volume, the measured O_2 yield was 100.2 percent of theory. By weight loss, the $KBrO_4$ sample had an observed 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:

$$MBrO_4 + ClSO_3F \longrightarrow MSO_3F + ClOBrO_3$$

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 $ClSO_3F$ 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 $ClSO_3F$ reacted, even at -80 C. Subsequent warming allowed the separation of the volatile products, ClO_2 and Cl_2O, 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 $ClSO_3F$ 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:

$$MBrO_4 + ClSO_3F \longrightarrow MSO_3F + [ClOBrO_3]$$

$$+ [ClBrO_4] \longrightarrow ClO\cdot + (BrO_3)_X$$

$$2ClO\cdot \longrightarrow ClO_2 + 1/2Cl_2$$

$$2ClO\cdot \longrightarrow Cl_2O + 1/2O_2$$

$$(BrO_3)_X \longrightarrow 3/2O_2 + 1/2Br_2$$

The only significant variation from run to run was the relative amounts of Cl_2, Cl_2O, and ClO_2. This only depends on the course of the $ClO\cdot$ 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_3F_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_xSO_3F were present and served as the source of the SO_3F_2. Control experiments were run showing that $MBrO_4$ salts do not react with F_2 to give $FBrO_3$ and thus a covalent Br-O compound such as $(BrO_3)_x$ must have been its precursor. Further proof of the formation of $(BrO_3)_x$ in this reaction was the approximate, $Br_2{:}O_2$ 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 $Y\text{-}XO_3$ are not known except where Y is fluorine. In the preceding report on this program (Ref. 1), an unsuccessful effort to form chlorine chlorate, $Cl\text{-}ClO_3$, from $KClO_3$ and $ClSO_3F$ was described. More recently, experiments were carried out aimed at producing $Cl\text{-}BrO_3$.

$$MBrO_3 + ClSO_3F \xrightarrow{?} MSO_3F + Cl\text{-}BrO_3$$

In the case of the bromate, as with the perbromate, reaction of the $ClSO_3F$ occurred readily at -45 C. However, again the product formed was unstable. Free Cl_2 was first found and later large quantities of Br_2 and O_2 were liberated. No evidence for any stable Br-O 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_x^- salts, the well established superior stability of iodine oxide moieties suggested their examination in this respect. Thus, $ClSO_3F$ was reacted with periodate salts, initially with the intention of preparing chlorine periodate, $ClOIO_3$.

$$MIO_4 + ClSO_3F \longrightarrow MSO_3F + ClOIO_3 \qquad M = Na,K$$

Reactions conducted at -45 C revealed that the $ClSO_3F$ was rapidly taken up, but that at the same time elemental Cl_2 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 (MSO_3F and unreacted MIO_4) 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 SO_3F^- in background (Ref. 13). If also exhibited prominent bands in the I=0 region, 820 cm^{-1} (Ref. 14) and covalent-SO_3F 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 IO_4SO_3F. In order to test this hypothesis, preparative reactions were conducted using 2 moles of $ClSO_3F$ for each IO_4^- in anticipation of the reaction stoichiometry:

$$MIO_4 + 2ClSO_3F \longrightarrow MSO_3F + Cl_2 + \text{"}IO_4SO_3F\text{"}$$

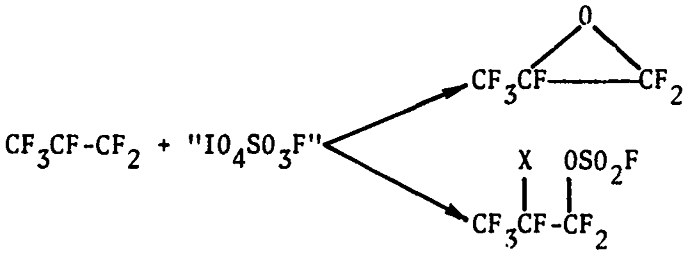
The evolved Cl_2 approximated this stoichiometry, but was usually only 80 to 85 percent of theoretical, even though no $ClSO_3F$ was left unreacted. Again, only traces of O_2 were formed, thus confirming apparently the integrity of the IO_4 group. Vacuum separation of the iodine oxide fluorosulfate was still not wholly successful. Efforts to dissolve the red oil in $CFCl_3$ or FC-78 fluorocarbons were negative while reaction occurred with CH_3CN, CCl_4, and HF.

Additional experiments designed to elucidate the composition of this liquid oxyfluorosulfate involved its pyrolysis. Upon reaction of the $ClSO_3F$ and removal of the evolved Cl_2, the products were pyrolyzed at 90 to 125 C for several days. The remaining Cl_2 was recovered together with 1 mole of O_2 for each mole of the suspected IO_4SO_3F.

$$\text{"}IO_4SO_3F\text{"} \xrightarrow{\Delta} O_2 + IO_2SO_3F$$

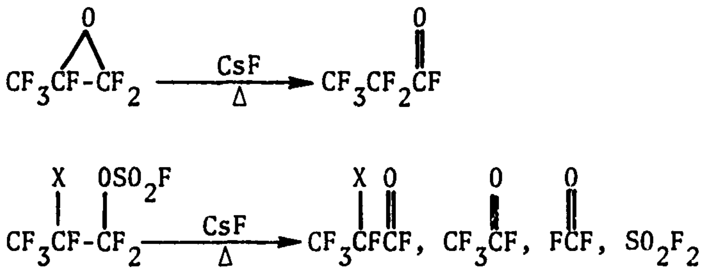
The presence of IO_2SO_3F was established gravimetrically and by infrared spectra of the pyrolysis residue which showed only a mixture of MSO_3F and IO_2SO_3F.

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.



(X=Cl, OSO_2F)

The Cl containing adduct probably arose through reaction of impurity $ClSO_3F$ 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).



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=0 link or it might even be a peroxyfluorosulfate link, $-\overset{|}{\underset{|}{I}}-OSO_2F$. Similar iodine peroxides have been reported to function well as epoxidizing agents (Ref. 17).

Appreciable amounts of unreacted $ClSO_3F$ were not recovered from these periodate reactions, but generally some chlorine species were retained with the "IO_4SO_3F". Therefore, it was decided to investigate whether complete fluorosulfonation had been attained. When increasing ratios of $ClSO_3F$ to IO_4^- were used (up to 8:1) essentially all the $ClSO_3F$ reacted. Surprisingly though, this reaction still produced Cl_2, a little O_2, and almost no volatile $-SO_3F$ 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 fluorosufonated material were subjected to ^{19}F nmr analysis. The undistilled sample showed two types of fluorines with lines at -41 ppm, clearly an SO_3F resonance (Ref. 6), and -17 ppm, outside the SO_3F region but readily assignable to IF (Ref. 7). The area ratio for the two resonances was $5SO_3F:3IF$. The distilled sample, however, contained only one type of fluorine (-39 ppm) due to SO_3F. 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 $ClSO_3F$. Just as found in the I_2-$ClSO_3F$ system, here also the $ClSO_3F$ functions in part as a fluorinating agent. No other examples of this type of behavior have been published.

Investigation of the IO_4^--$ClSO_3F$ 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 $ClSO_3F$ 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:

$$KIO_3 + 2ClSO_3F \longrightarrow KSO_3F + IO_2SO_3F + Cl_2 + 1/2O_2$$

The X-ray powder pattern for the resultant IO_2SO_3F 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_2O_5 was reacted with $ClSO_3F$ since this compound was the source of the SO_3F group in the present iodine oxide studies. The observed reaction was:

$$I_2O_5 + 2ClSO_3F \longrightarrow 2IO_2SO_3F + Cl_2 + 1/2O_2$$

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_2SO_3F 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_3F are lacking and are replaced by bonds of intermediate wavelength. This is illustrated in Table 1.

TABLE 1

COMPARISON OF THE INFRARED BANDS OF VARIOUS FLUOROSULFATES

$M^+SO_3F^-$ cm^{-1} Relative Intensity	IO_2SO_3F cm^{-1} Relative Intensity	$ClSO_3F$ (Ref. 18) cm^{-1} Relative Intensity
1285 vs	1345 vs	1481 vs
1080 s	1185 vs	1248 vs
	1025 s	
	875 s	855 vs
780 s	840 s	830 ms
	650 m	
585 s, complex	575 m, complex	570 ms

The observed bands closely resemble those of $SnCl_2(SO_3F)_2$ (1385, s; 1130, vs; 1087, s; 864 s, 628 m; 586 cm^{-1}, s) which are attributed to a bidentate SO_3F bridges (Ref. 19). A more complete study of the vibrational spectrum of IO_2SO_3F will be made.

REACTIONS OF IODYL FLUOROSULFATE

Attempts were made to fluorinate IO_2SO_3F to form any of several possible iodine oxyfluorides; e.g., FIO_2, F_3IO_2, F_3IO, 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 IO_2SO_3F according to:

$$IO_2SO_3F + xssF_2 \longrightarrow SO_3F_2 + IF_5O/IF_7 + O_2$$

Use of increasing fluorine pressures increased the relative amount of IF_7 to IF_5O, and at the lowest pressures, essentially all the iodine was converted to IF_5O. The formation of SO_3F_2 indicates the non-ionic nature of the SO_3F group in this compound since ionic fluorosulfates do not yield SO_3F_2 in this manner. A sample of chloryl fluorosulfate was also prepared and fluorinated as indicated by the equations:

$$2ClO_2 + S_2O_6F_2 \longrightarrow 2ClO_2SO_3F \text{ (Ref. 20)}$$

$$ClO_2SO_3F + F_2 \longrightarrow FClO_2 + SO_3F_2$$

Virtually, a quantitative yield of each product was realized in the fluorination reaction. Again, the formation of SO_3F_2 points to a non-ionic SO_3F 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:

$$2IO_2SO_3F + 5SF_4 \longrightarrow 2IF_5 + S_2O_5F_2 + 5SOF_2$$

$$2IO_2SO_3F + 5SOF_2 \longrightarrow 2IF_5 + S_2O_5F_2 + 5SO_2$$

Thus no new iodine oxyfluorides were obtained from IO_2SO_3F.

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.

$$O_2^+AsF_6^- + ClOClO_3 \xrightarrow{?} O_2^+ClO_4^- + ClF + AsF_5$$

A 3 week reaction period at -45 C showed incomplete but substantial reaction of the $ClOClO_3$ (75 percent). Surprisingly, nearly 1 mole of $FClO_2$ was formed for each $ClOClO_3$ reacted. Oxygen and Cl_2 were also noted. The yields of these materials suggested the following reaction sequence:

$$O_2^+AsF_6^- + ClOClO_3 \longrightarrow [O_2ClO_4] + [ClAsF_6]$$

$$[O_2ClO_4] \longrightarrow 3/2O_2 + \cdot ClO_3$$

$$\cdot ClO_3 + [ClAsF_6] \longrightarrow FClO_3 + 1/2Cl_2 + AsF_5$$

Not all the AsF_5 was observed as such. Some was consumed in forming the minor product, ClO_2AsF_6, and some remained undetected. The only other product was a small amount of Cl_2O_7. Since all the chlorine and oxygen were accounted for, no O_2ClO_4 could have remained.

GROUP VIA FLUORIDES

Because $ClSO_3F$ was very effective in functioning as a chlorinating agent; e.g., in chlorinating the ClO_4^- ion to $ClOClO_3$, it was investigated further for this activity. This led to the following reaction:

$$CsSeF_5 + ClSO_3F \longrightarrow CsSO_3F + SeF_5Cl$$

Previous to this, both SF_5Cl and TeF_5Cl 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 SeF_5Cl could be also obtained directly from Se or SeF_4 and ClF or ClF_3, but in lower yields. Optimally then it seemed possible that the reaction of equimolar quantities of Se and ClF_5 might furnish SeF_5Cl. When tried, however, the observed reaction was:

$$2Se + 2ClF_5 \longrightarrow SeF_4 + SeF_6 + Cl_2$$

Fluorination occurred to the complete exclusion of chlorination.

ATTEMPTED PREPARATION OF THE NCl_4^+ CATION

The successful preparation of NF_4^+ from

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4^+AsF_6^- \text{ (Ref. 23)}$$

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

$$NCl_3 + Cl_2 + SbCl_b \xrightarrow{CCl_4} NCl_4^+SbCl_6^-$$

Samples of NCl_3 (which is unstable towards light and shock-sensitive) were prepared and reacted with $SbCl_5$ and Cl_2 in CCl_4 solution. A small amount of solid residue, insoluble in CCl_4, was obtained. However, no evidence for attributable to either NCl_4^+ or $SbCl_6^-$ could be obtained by vibrational spectroscopy.

Since the ClF bond is already polarized in the direction $\overset{+\!\!\!\longrightarrow}{\mathrm{Cl\text{-}F}}$, its heterolytic fission according to

$$NCl_3 + Cl\text{-}F + AsF_5 \longrightarrow NCl_4^+AsF_6^-$$

might be more facile than that of Cl_2 in the NCl_3-Cl_2-$SbCl_5$ system. The NCl_3-ClF-AsF_5 system was investigated in different solvents (Freon 11 and FC-78), the desired reaction being:

$$NCl_3 + ClF + AsF_5 \longrightarrow NCl_4^+AsF_6^-$$

A solid product was obtained in low yields. Its infrared spectrum shows it to be an AsF_6^- salt. Further characterization by Raman spectroscopy revealed, however, that the solid was $ClO_2^+AsF_6^-$, (Ref. 22). Thus, no evidence for the existence of a stable NCl_4^+ salt could be obtained.

ATTEMPTED SYNTHESIS OF THE BrF_6^+ and ClF_6^+ CATIONS

A number of new approaches were studied which might lead to the novel cations ClF_6^+ and BrF_6^+. These attempts included the use of uv photolysis, of PtF_6 and IrF_6 as fluorinating agents, and of XeF^+ or NF_4^+ salts as starting materials. Since the existence of NF_4^+ salts is well established (Ref. 23), the following model reaction was investigated:

$$NF_3 + F_2 + AsF_5 \xrightarrow{uv} NF_4^+AsF_6^-$$

A small amount of white solid was obtained when a mixture of NF_3, F_2, and AsF_5, contained in a quartz bulb, was exposed to sunlight. It was identified by infrared and Raman spectroscopy as $O_2^+AsF_6^-$. The small amount of O_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 $NF_4^+AsF_6^-$.

In another approach, $NF_4^+AsF_6^-$, prepared by the known pressure-temperature method, was heated in the presence of BrF_5 for several days to 90 C, 165 C, and 185 C, the desired reaction being:

$$NF_4^+AsF_6^- + BrF_5 \xrightarrow{?} BrF_6^+AsF_6^- + NF_3$$

At each temperature, only a small amount of NF_3 was detected in the volatile products, but no BrF_5 was consumed. This indicates that the NF_3 evolution was due to attack of $NF_4^+AsF_6^-$ on the metal cylinder and not due to BrF_6^+ formation.

Since the previous (Ref. 24) Raman studies of NF_4^+ were carried out before a Laser Raman spectrometer was avilable, 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 BrF_6^+ cation using $XeF^+AsF_6^-$ as the oxidizing species:

$$XeF^+AsF_6^- + BrF_5 \longrightarrow BrF_6^+AsF_6^- + Xe$$

Two reactions were carried out at 75 C and 130 C. In both experiments, no $BrF_6AsF_6^-$ 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 $CsBrF_6$

$$2PtF_6 + Cs^+BrF_6^- \xrightarrow{?} Cs^+PtF_6^- + BrF_6^+PtF_6^-$$

However, several experiments showed that the weight increase after the reaction was minimal and that no detectable amounts of $BrF_6^+PtF_6^-$ were formed in this reaction.

ATTEMPTED PREPARATION OF ClO_2F_3 AND $ClOF_5$

Recently, the existence of the salt $Cs^+ClO_2F_2^-$ 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 $ClO_2F_2^-$ might be possible, yielding the novel oxyfluoride, ClO_2F_3. Therefore, a sample of $Cs^+ClO_2F_2^-$ was prepared and characterized since no structural data had previously been given (Ref. 26) for this interesting compound. The structural data on $ClO_2F_2^-$ have been summarized in Appendix C .

Four fluorination reactons of $Cs^+ClO_2F_2^-$ 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 $CsClO_2F_2^-$ (82 percent) had decomposed into CsF and ClO_2F. No evidence for a new chlorine oxyfluoride was obtained. When PtF_6 was tried as a fluorinating agent again no evidence for ClO_2F_3 could be obtained.

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:

ClF (excess) + $HONO_2$:

$$ClF + HONO_2 \longrightarrow HF + ClONO_2$$

ClF_3 (excess) + $HONO_2$:

$$2ClF_3 + 2HONO_2 \longrightarrow 2HF + ClO_2F + ClF + 2NO_2F$$

ClF_3 + $HONO_2$ (excess):

$$3ClF_3 + 9HONO_2 \longrightarrow 9HF + 2ClO_2 + ClONO_2 + 4N_2O_5$$

ClF_5 (excess) + $HONO_2$:

$$ClF_5 + 2HONO_2 \longrightarrow 2HF + ClO_2F + 2NO_2F$$

ClF_5 + $HONO_2$ (excess):

$$ClF_5 + 5HONO_2 \longrightarrow 5HF + 2N_2O_5 + [O_2ClONO_2] \left. \begin{array}{l} \rightarrow ClONO_2 + O_2 \\ \rightarrow ClO_2 + 1/2N_2O_5 + 1/4O_2 \end{array} \right.$$

ClF_5 + HOH (excess):

$$2ClF_5 + 5HOH \longrightarrow 10HF + 2ClO_2 + 1/2O_2$$

ClO_2F + $HONO_2$ (excess):

$$2ClO_2F + 2HONO_2 \longrightarrow 2HF + 2ClO_2 + N_2O_5 + 1/2O_2$$

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·$2IF_5$ SALTS

With the exception of the Cl_2F^+ 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 IF_4Cl as an intermediate in the CsCl-IF_5 reaction. This intermediate, however, supposedly attacked glass rapidly and, hence, could not be isolated or identified. We have studied the CsCl-IF_5 system in a metal -Teflon vacuum system. In the first experiment, CsCl was allowed to react with a large excess of IF_5 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 Cl_2 (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 $CsIF_6 \cdot 2IF_5$. Vacuum pyrolysis of the product at 100 C resulted in the evolution of two moles of IF_5 per mole of $CsIF_6 \cdot 2IF_5$. A second experiment between CsCl and IF_5 was carried out in a Teflon U-trap at 0 C. Under these conditions, almost no conversion of CsCl to Cl_2 occured. This is most likely due to the high melting point (+9 C) of IF_5.

Whereas the desired IF_4Cl could not be isolated, the results of one experiment suggest the solution to the mystery previously encountered in the structural study of the IF_6^- anion. Four independent groups, Argonne National Laboratory, University of Glasgow, University of Berlin, and Rocketdyne had obtained different spectroscopic data on the CsF·IF_5 adduct (Ref. 29 through 31). The infrared and Ramam spectra obtained now for $CsIF_6$ and $CsIF_6 \cdot 2IF_5$ indicate the discrepancies of the spectra were due to the presence of various amounts of $CsIF_6 \cdot 2IF_5$ in the $CsIF_6$ 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 estalished 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); $CsF\cdot 3IF_5$ (97 percent) + CsF (3 percent); and $RbI\cdot 3IF_5$ (50 percent) + $RbIF_6$ (23 percent) + RbF (27 percent). Attempts to prepare an $NaF\cdot IF_5$ 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_2O

The existence of alkali metal fluoride adducts of Cl_2O 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_2O 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_2O^+ cation and hexafluoroacetone could not be confirmed. Carbonyl fluoride also was shown not to interact with NOF_2^+.

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 BrF_3, $ClOClO_3$, and $BrOClO_3$ 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 $Cs^+SF_5^-$, $Cs^+SF_5O^-$, $Cs^+SeF_5^-$, SeF_5Cl, $N_2F^+AsF_6^-$, $N_2F^+SbF_6^-$, SF_4, BrF_3, ClF_5, $BrOClO_3$, $ClOClO_3$, and $Cs^+ClO_2F_2^-$. 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 $BrF_5 \cdot 2SbF_5$ 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., $BrF_4^+Sb_2F_{11}^-$, with weak cis fluorine bridges resulting in long zigzag 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, $ClSO_3F$ (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 $ClSO_3F$, and ~0.5 mmol $S_2O_5F_2$. The -78 C fraction contained SO_3 and approximately half the reamining 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 $ClSO_3F$ 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 $ClSO_3F$. 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_2O, 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_2O (0.87 mmol), and ClO_2 (0.60 mmol) accounted for all the charged $ClSO_3F$, 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 $ClOBrO_3$.

ATTEMPTED SYNTHESIS OF CHLORINE BROMATE

Potassium bromate (5.63 mmol) and $ClSO_3F$ (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 $ClSO_3F$ 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 2

REACTION CONDITIONS AND PRODUCTS OBTAINED FOR THE MIO_4 + $ClSO_3F$ SYSTEM

MIO_4, mmol	$ClSO_3F$, mmol	Temperature, ~C	Time, days	O_2, ~mmol	Cl_2, mmol
5.05	4.01	-45	35	0.1	1.87
2.34	4.74	25	3	0.1	2.19
1.14	9.58	25	10	0.25	4.26

Generally, small amounts of $ClSO_3F$ (~1 percent) were also found, together with variable, but quite small yields of $S_2O_5F_2$ and $ClO_2/FClO_2$. The potassium salt gave rise to more O_2 on reaction at ambient temperature than did the sodium salt.

In the case where IO_4SO_3F was pyrolyzed, the experiment was carred out according to the preceding general procedure. A 2.57 mmol sample of $NaIO_4$ was reacted with 5.32 mmol $ClSO_3F$ 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 additonal O_2 and Cl_2, along with a small amount of $S_2O_5F_2$ 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 $NaSO_3F$ and IO_2SO_3F 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 $ClSO_3F$ (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 KIO_3 and product KSO_3F and IO_2SO_3F 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 $ClSO_3F$ 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 $ClSO_3F$ and $S_2O_5F_2$. 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 IO_2SO_3F prepared via $S_2O_6F_2$. Powder diffraction data for IO_2SO_3F are shown in Table 3.

TABLE 3

X-RAY POWDER DIFFRACTION DATA FOR IO_2SO_3F

(α spacing)

Å	Intensity	Å	Intensity	Å	Intensity
7.75	w	2.68	w	1.66	w
6.55	w	2.66	w	1.57	w
6.36	s	2.26	w	1.53	w
5.15	w	2.15	w	1.48	w
3.91	m	2.12	m	1.45	w
3.52	vs	2.06	w	1.41	w
3.23	w	1.98	w	1.35	w
3.09	w	1.90	w	1.33	w
2.90	m	1.78	m	1.24	w
2.84	w	1.69	w	1.16	w

FLUORINATION OF IODYL FLUOROSULFATE

A 2.15 mmol sample of IO_2SO_3F was reacted with approximately 22 mmol F_2 in a 30 milliliter cylinder at ambient temperature for 10 days. The material not condensable at -196 C (F_2 and 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 IF_5O, 1.07 mmol IF_7, 1.91 mmol SO_3F_2, and 0.13 mmol $S_2O_6F_2$. Thus, all the IO_2SO_3F had reacted.

A 2.05 mmol sample of IO_2SO_3F was reacted with 3.28 mmol 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 IF_5, $S_2O_5F_2$, SO_2, and SOF_2. No unreacted SF_4 was recovered.

REACTION OF IODINE AND CHLORINE PERCHLORATE

Sublimed I_2 (0.545 mmol) was placed in an FEP Teflon tube fitted with a stainless steel valve. Freshly fractionated $ClOClO_3$ (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 Cl_2 (1.72 mmol), which was contaminated with a small amount of $FClO_3$ and CO_2. Based on 1 mole of I_2 reacting with 6 moles of $ClOClO_3$ to give $I(OClO_3)_3$ and Cl_2, the yield of Cl_2 was 102 percent. The product was a pale yellow solid.

Thermal decomposition of the $I(OClO_3)_3$ 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 Cl_2O_7 was the primary volatile decomposition product, but other highly colored chlorine oxides such as ClO_2 and probably Cl_2O_6 were also given off. The decomposed $I(OClO_3)_3$ 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 Cl_2O_7 from each $I(OClO_3)_3$.

REACTION OF IODINE AND CHLORINE NITRATE

In the same manner as the above I_2-$ClOClO_3$ reaction, 1.005 mmol I_2 and 8.20 mmol $ClONO_2$ were reacted at -45 C. After 1 week, the materials volatile at -45 C were removed and separated. These were unreacted $ClONO_2$ (2.23 mmol) and Cl_2 (3.01 mmol). Based on $3Cl_2$ from each I_2 reacting to give $I(ONO_2)_3$, the Cl_2 yield was 99.8-percent. The product $I(ONO_2)_3$ was a fluffy light yellow colored solid at -45 C. Thermal decomposition of the $I(ONO_2)_3$ was accomplished by the same method used for the trisperchlorate compound. An excellent yield of N_2O_5 (2.05 mmol) was obtained based on one N_2O_5 from each $I(ONO_2)_3$. The resulting solid was tan colored. Gradually over the next week, additional decomposition was evident since the typical brown colored fumes of NO_2 became visible in the tube. An infrared spectrum of the solid at that time showed no N=O absorption.

APPENDIX A

SELENIUM CHLORIDE PENTAFLUORIDE

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SELENIUM CHLORIDE PENTAFLUORIDE

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

The existence of SF_5Cl has been known[1] for some time, while TeF_5Cl has been reported[2] more recently. However, no report concerning the preparation of the intermediate member of the S-Se-Te triad, SeF_5Cl, has appeared. Since the best synthetic routes[3] to SF_5Cl involve chlorination of sulfur fluoride substrates, and since this reaction had been found to be enhanced by added alkali metal fluorides[4], this technique was applied to the formation of SeF_5Cl. 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 described[5] 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, $ClSO_3F$, and CsF have been given.[5] Additional materials were purchased and used as received.

SeF_4. - Selenium tetrafluoride was first prepared from Se powder and ClF according to Pitts and Jache.[6] Later it was determined that ClF_3 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 -196° 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 -196° furnished SeF_4 (12.3 mmol) in the highest temperature trap. The purity and identity of the

SeF_4 was verified by its vapor pressure[6] and infrared spectrum.[7] Based on the equation

$$3Se + 4ClF_3 \longrightarrow 3SeF_4 + 2Cl_2$$

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

$\underline{SeF_5Cl}$. - Selenium chloride pentafluoride was prepared by first forming the solid complex, $CsSeF_5$, from CsF and SeF_4.[8] Weighed samples of the complex were placed in prepassivated cylinders and $ClSO_3F$ added at -196°. After warming to room temperature for several hours or more, the volatile products were separated by fractional condensation at -95, -112, and -196°. Unreacted $ClSO_3F$ was retained at -95° while by-products and impurities such as ClF, $FClO_2$, and Cl_2 passed into the trap cooled to -196°. Pure SeF_5Cl was found in the -112° fraction. From 4.50 mmol $CsSeF_5$, 4.13 mmol SeF_5Cl was obtained, corresponding to a yield of 91.7% for the equation.

$$CsSeF_5 + ClSO_3F \longrightarrow CsSO_3F + SeF_5Cl$$

The presence of uncomplexed CsF in the salt does not inhibit the formation of SeF_5Cl directly, but does result in the loss of some $ClSO_3F$ by reaction to form ClF.[5]

Because the system $CsF/SF_4/ClF$ was very effective[4] in producing SF_5Cl, it was expected that $CsF/SeF_4/ClF$ would behave similarly. Such was not the case and unreacted ClF was always fully recoverable after one day or several weeks in contact with $CsSeF_5$. However, in the course of preparing SeF_4 from Se and ClF or ClF_3, it was found that excesses of the chlorine fluorides gave detectable yields of SeF_5Cl. To determine the extent of this reaction, 4.19 mmol SeF_4 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 SeF_4 and ClF (1.45 mmol each), as well as trace amounts of SeF_6 and Cl_2. The main product was SeF_5Cl (2.62 mmol), representing a 95% yield based on the SeF_4 that had reacted. With ClF_3, up to 10% yields of SeF_5Cl were obtained, but always accompanied by much greater amounts of SeF_6. Thus the direct reaction of SeF_4 and ClF affords an alternate, albeit less efficient, route to SeF_5Cl.

Properties of SeF_5Cl. - 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 ClF_3 did not serve for handling SeF_5Cl. It seems likely that this property hindered the earlier discovery of this compound.

Analysis. - A 0.2001 g sample of SeF_5Cl 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.[9] Fluoride was also determined by the usual thorium nitrate titration. The amount of base consumed was calculated, assuming the hydrolysis equation

$$SeF_5Cl + 8OH^- \longrightarrow SeO_4^{2-} + 4H_2O + 5F^- + Cl^-.$$

Anal. Calcd for SeF_5Cl: 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 SeF_5Cl over the temperature range -79 to 3° is $[t^{\circ}C, P(mm)]$: -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 $\log P_{mm} = 7.779 - 1360/T^{\circ}K$. The normal boiling point calculated from the equation is 4.5°; 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°. 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 SeF_5Cl in the range 4000 - 250 cm^{-1} shows several absorptions with the most prominent ones occurring at 745 (vvs), 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_5OF[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.[11] A detailed analysis of the vibrational spectrum of SeF_5Cl is in progress.[12]

Nuclear Magnetic Resonance Spectrum. - The ^{19}F nmr spectrum of SeF_5Cl is shown in Figure 1. It is an AB_4 spectrum and resembles that of SF_5Cl[13] so closely as to be virtually identical. The reported[13] chemical shifts for SF_5Cl when converted to a $CFCl_3$ reference point are -62.3 and -125.8 ppm, respectively, for the axial and equatorial fluorines. For SeF_5Cl, the corresponding values taken from Figure 1 are -71.3 and -132.0 ppm. The only part of the spectrum of SeF_5Cl not identical with the SF_5Cl 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.[14]

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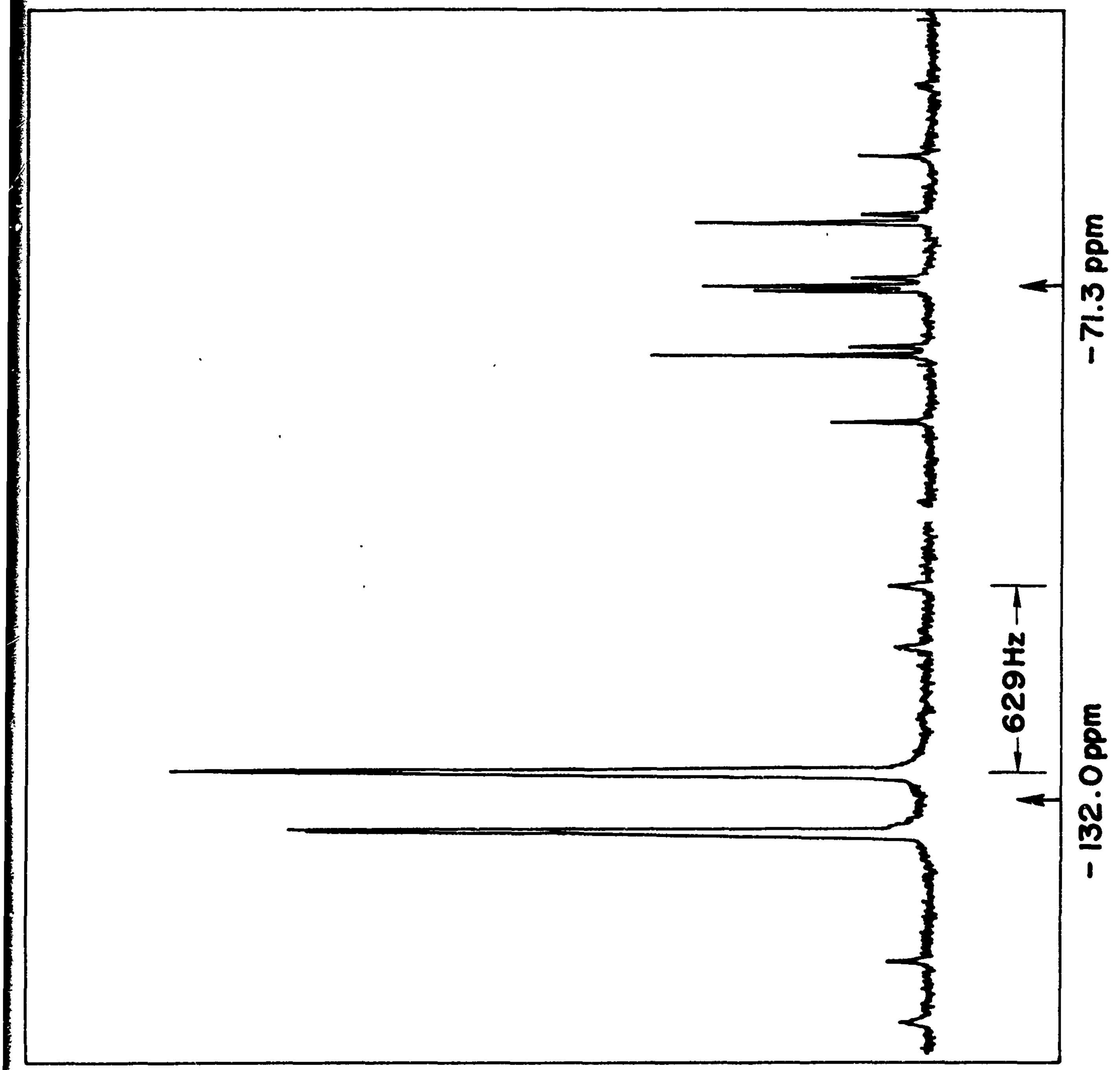

Figure 1. ^{19}F nmr Spectrum of SeF_5Cl

APPENDIX B

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

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

SELENIUM PENTAFLUORIDE CHLORIDE, SeF_5Cl. VIBRATIONAL SPECTRUM, FORCE CONSTANTS, AND THERMODYNAMIC PROPERTIES

By K. O. Christe,* C. J. Schack, and E. C. Curtis

Received ...

Abstract

The infrared spectrum of gaseous and the Raman spectrum of liquid SeF_5Cl is reported. The observed spectrum is consistent with symmetry C_{4v}. The structure of SeF_5Cl 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°K were computed for SeF_5Cl.

Introduction

The existence of the novel selenium fluoride chloride, SeF_5Cl, has recently been discovered.[1] 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_5Cl will be described elsewhere.[1] 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.[2] 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_5Cl was 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° 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_5Cl, respectively. The observed frequencies are listed in Table I.

Since SeF_5Cl 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_5Cl of symmetry C_{4v} can be classified as $4a_1 + 2b_1 + b_2 + 4e$. 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.[3] Similarly, the SeCl stretching mode should be of higher Raman intensity than the SeF_4 umbrella deformation.[3] 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_5OF,[4] 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 I

Vibrational Spectrum of SeF_5Cl

obsd frequencies, cm^{-1}		assignment for point
Infrared, gas	**Raman, liquid**	
1449 vw		$2\nu_1 = 1442\ (A_1)$
1380 w		$\nu_5 + \nu_8 = 1381\ (E)$
865 vw		$\nu_3 + \nu_9 = 861\ (E)$
821 w		$\nu_3 + \nu_4 = 824\ (A_1)$
745 vvs	745 (0.3) dp	$\nu_8\ (e)$
729 ms, sh	721 (1.8) p	$\nu_1\ (a_1)$
654 w	656 (10) p	$\nu_2\ (a_1)$
———	636 (0.6) dp	$\nu_5\ (b_1)$
587 vw		$\nu_7 + \nu_{11} = 593\ (E)$
529 w		$\nu_8 - \nu_{11} = 532\ (A_1 + A_2 + B_1 + B_2)$
468 w, sh		
440 vs	443 (2.2) p	$\nu_3\ (a_1)$
421 s	424 (0.4) dp	$\nu_9\ (e)$
384 mw	385 (8.5) p	$\nu_4\ (a_1)\ Cl^{35}$
———	380 dp	$\nu_7\ (b_2) + \nu_4(a_1)\ Cl^{37}$
334 m	336 (1.2) dp	$\nu_{10}\ (e)$
	213 (1.4) dp	$\nu_{11}\ (e)$

TABLE II

Fundamental Frequencies of SeF_5Cl and SF_5Cl[a]

			SF_5Cl	SeF_5Cl
a_1	ν_1	$\nu\ XF'$	855	729
	ν_2	ν symXF_4	707	654
	ν_3	δ symXF_4 out of plane	602	440
	ν_4	$\nu\ XCl$	402	384
b_1	ν_5	ν symXF_4 out of phase	625	636
	ν_6	δ asXF_4 out of plane	—	—
b_2	ν_7	δ symXF_4 in plane	505	380
e	ν_8	ν asXF_4	909	745
	ν_9	$\delta\ FXF_4$	579	421
	ν_{10}	δ asXF_4 in plane	441	334
	ν_{11}	$\delta\ ClXF_4$	287	213

(a) Frequency values taken from Reference 3

SeF_4 stretching vibration. For $SeF_4(OF)_2$ and SeF_5OF, this mode was observed[4] at 743 and 750 cm^{-1}, respectively. By analogy with the known spectrum[3,5] of the SF_5Cl 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 $F-Se-F_4$ 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, ν_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, ν_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^-,[7] 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 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, ν_3 and ν_4 show the expected band shape. The band shape of ν_1 is not clear-cut; however, its band shape may have been influenced by Coriolis interaction with $\nu_8(e)$, which occurs at almost the same frequency. The band contour of ν_2 does not show a sharp PQR structure. This was also the case for ν_2 of SF_5Cl.[3,5] The band contour of $\nu_9(e)$ agrees with that expected for a perpendicular band, but that of ν_{10} closely resembles that of the parallel bands. It is interesting to note that $\nu_{10}(e)$ of SF_5Cl[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_5Cl agree well with those[3] observed for SF_5Cl, even though differing somewhat from those predicted on the basis of the rigid rotor, harmonic oscillator approximation.

Comparison between the vibrational spectra of SF_5Cl[3,5] and SeF_5Cl shows good agreement. However, the SeF_5Cl data and results from force constant calculations[9] indicate that for SF_5Cl, the original assignment of the S-Cl wagging mode, $\nu_{11}(e)$, to the 287 cm^{-1} band by Cross 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, ν_4, at 402 cm^{-1} the splitting and relative intensity being in good agreement with predictions. Furthermore, the infrared spectrum of SF_5Cl 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 ν_{11} does not violate the selection rules and results in a more reasonable frequency value. The high relative intensity of the 396 cm^{-1} band in the Raman spectrum of SF_5Cl and its infrared activity also argue against its proposed assignment[5] to ν_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_5Cl, ν_6 has either not been observed or is hidden underneath the intense ν_4 band.

In summary, the vibrational spectrum of SeF_5Cl 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: $R_{SeF'} = 1.68Å$, $D_{SeCl} = 2.14Å$, $r_{SeF} = 1.68Å$, $\alpha = \sphericalangle FSeF = 90^\circ$, $\beta = \sphericalangle_{F'SeF} = 90^\circ$, and $\delta = \sphericalangle_{ClSeF} = 90^\circ$, 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 $f_R = 4.42$, $f_D = 2.75$, $f_r = 4.31$, $f_{rr} = 0.07$, and $f_{rr'} = 0.35$ mdyn/Å, $f_\alpha = 1.26$, $f_\beta = 1.92$, $f_\delta = 1.16$, $f_{\beta\beta'} = 0.30$, and $f_{\delta\delta'} = 0.18$ mdyn/Å rad^2, and $f_{D\delta} = 0.28$ mdyn/Å rad. The two interactions, $f_{\beta\beta'}$ and $f_{\delta\delta'}$, were determined from only one symmetry force constant value making the assumption $f_{\beta\beta'}/f_{\delta\delta'} = f_\beta/f_\delta$.

The values of the stretching force constants, f_R and f_r, of SeF_5Cl 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] SeO_2F_2 (4.44 mdyn/Å),[12] or SeO_3F^- (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[11] towards SeF_5Cl parallels that found for the analogous pair, SF_6[15] and SF_5Cl[12] (see Table III). It can be explained by the substitution of one fluorine atom in XF_6 by a less electronegative ligand, such as Cl. This causes an increased polarity ($\overset{\delta+}{S} - \overset{\delta-}{F}$) of the remaining SF bonds. Since stretching force constants reflect only the contributions from covalent bonding,[12,14] their value should correspondingly decrease.

Table III. Stretching Force Constants (in mdyn/Å) of SeF_6 and SeF_5Cl Compared to Those of SF_6 and SF_5Cl

	SF_6 [a]	SF_5Cl [b]	SeF_6 [c]	SeF_5Cl
f_R	5.26	4.83	5.01	4.42
f_r		4.52		4.31

(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 $f_{D\delta}$ was determined from $\sqrt{2}(f_{D\delta}-f_{D\beta}) \approx 0.4$, which was required to fit ν_3 and ν_4. This is not too surprising considering the mixing of the two modes (see Table IV). No evidence was found for the similar terms, $f_{R\beta}$, $f_{r\beta}$, and $f_{r\delta}$ 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_5Cl hoping that the e-block band contours could support the assignment. The computed values using the above given force constants were $\zeta_8 = 0.5$, $\zeta_9 = 0.5$, $\zeta_{10} = -0.4$ and $\zeta_{11} = 0.7$. However, the values of the moments of inertia are such that these values for ζ 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 ζ'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 ν_3 and ν_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 ν_6. The moments of inertia used were $I_x = I_y = 312$ and $I_z = 214$ amu $Å^2$ 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 SeF_5Cl.

Contributions of less than 0.10 are not listed.

a_1	ν_1	729	$0.88\ f_R$
	ν_2	654	$0.90\ f_r$
	ν_3	440	$0.41\ f_D + 0.36 f_\beta + 0.21\ f_\delta + 0.11\ f_R$
	ν_4	384	$0.58\ f_D + 0.15 f_\beta + 0.15 f_\delta$
b_1	ν_5	636	$0.95\ f_r$
	ν_6	(336)	$0.54\ f_\beta + 0.33\ f_\delta$
b_2	ν_7	380	$1.10\ f_\alpha - 0.10\ f_{\alpha\alpha'}$
e	ν_8	745	$1.00\ f_r$
	ν_9	421	$1.04\ f_\beta - 0.16\ f_{\beta\beta'}$
	ν_{10}	334	$0.79\ f_\alpha$
	ν_{11}	213	$1.02\ f_\zeta - 0.16\ f_{\delta\delta'}$

TABLE V

Computed Thermodynamic Properties of SeF_5Cl[a]

T, °K	C_p^o	$H^o - H_0^o$	$-(F^o - H_0^o)/T$	S^o
0	0.	0.	0.	0.
100	12.035	0.895	51.149	60.103
200	21.720	2.604	58.534	71.554
298.15	27.800	5.062	64.494	81.472
300	27.885	5.113	64.600	81.644
400	31.338	8.091	69.959	90.186
500	33.331	11.333	74.746	97.412
600	34.548	14.732	79.053	103.605
700	35.336	18.228	82.954	108.994
800	35.870	21.790	86.512	113.750
900	36.248	25.397	89.778	117.998
1000	36.524	29.037	92.795	121.832
1100	36.731	32.700	95.596	125.323
1200	36.891	36.381	98.208	128.526
1300	37.016	40.077	100.656	131.484
1400	37.116	43.784	102.957	134.231
1500	37.197	47.499	105.128	136.795
1600	37.264	51.223	107.183	139.198
1700	37.320	54.952	109.134	141.458
1800	37.367	58.686	110.989	143.593
1900	37.406	62.425	112.759	145.614
2000	37.440	66.167	114.450	147.534

(a) Units for C_p^o, S^o, and F^o are g calories, g moles, and degrees Kelvin and for H^o, kilocalories, and moles.

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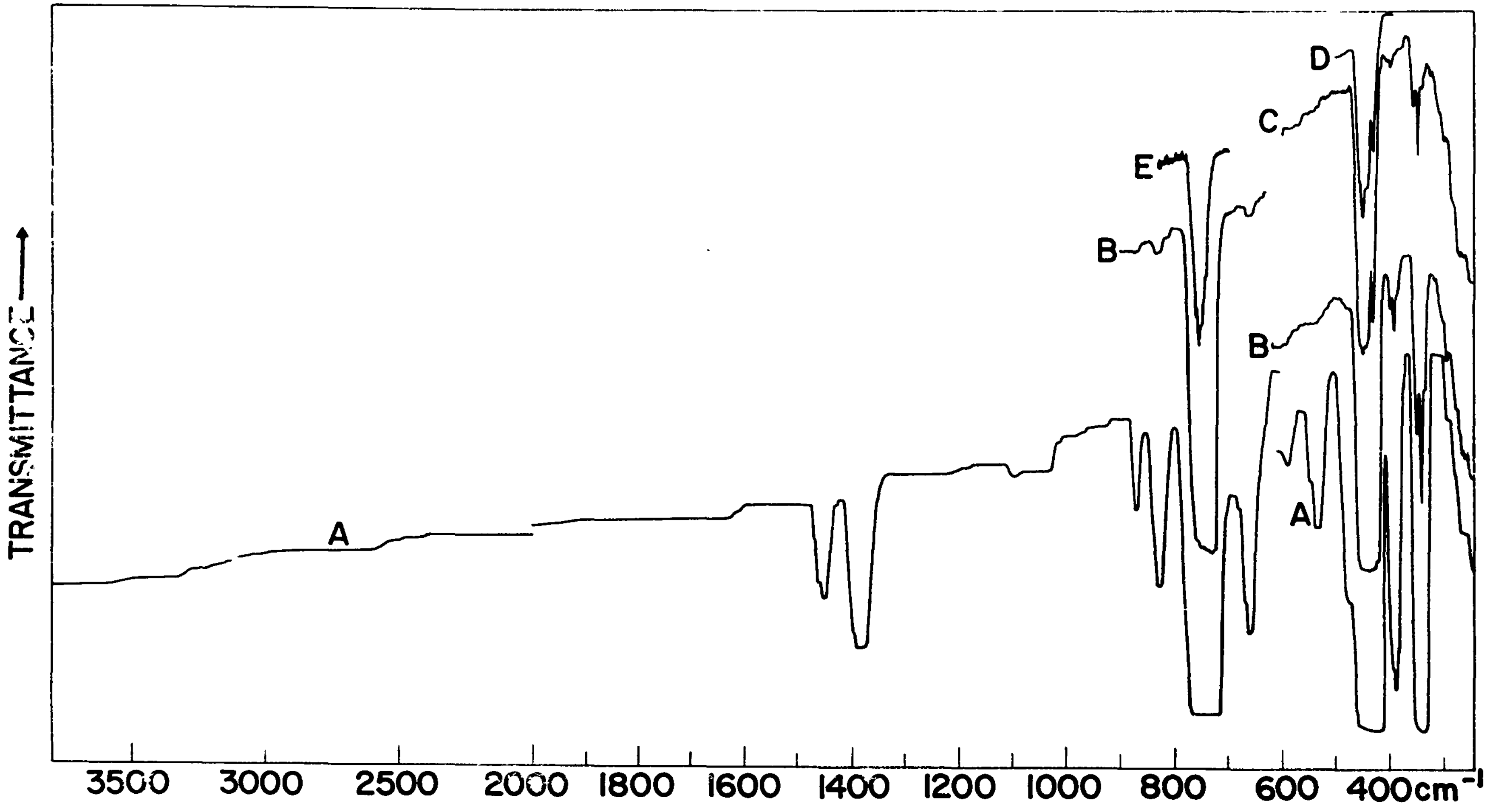
Diagram Captions

Figure 1. - Infrared spectrum of gaseous SeF_5Cl 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_5Cl. 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.


TRANSMITTANCE
A
B
B
A
C
D
E
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3000
2500
2000
1800
1600
1400
1200
1000
800
600
400cm^{-1}

Figure 1.

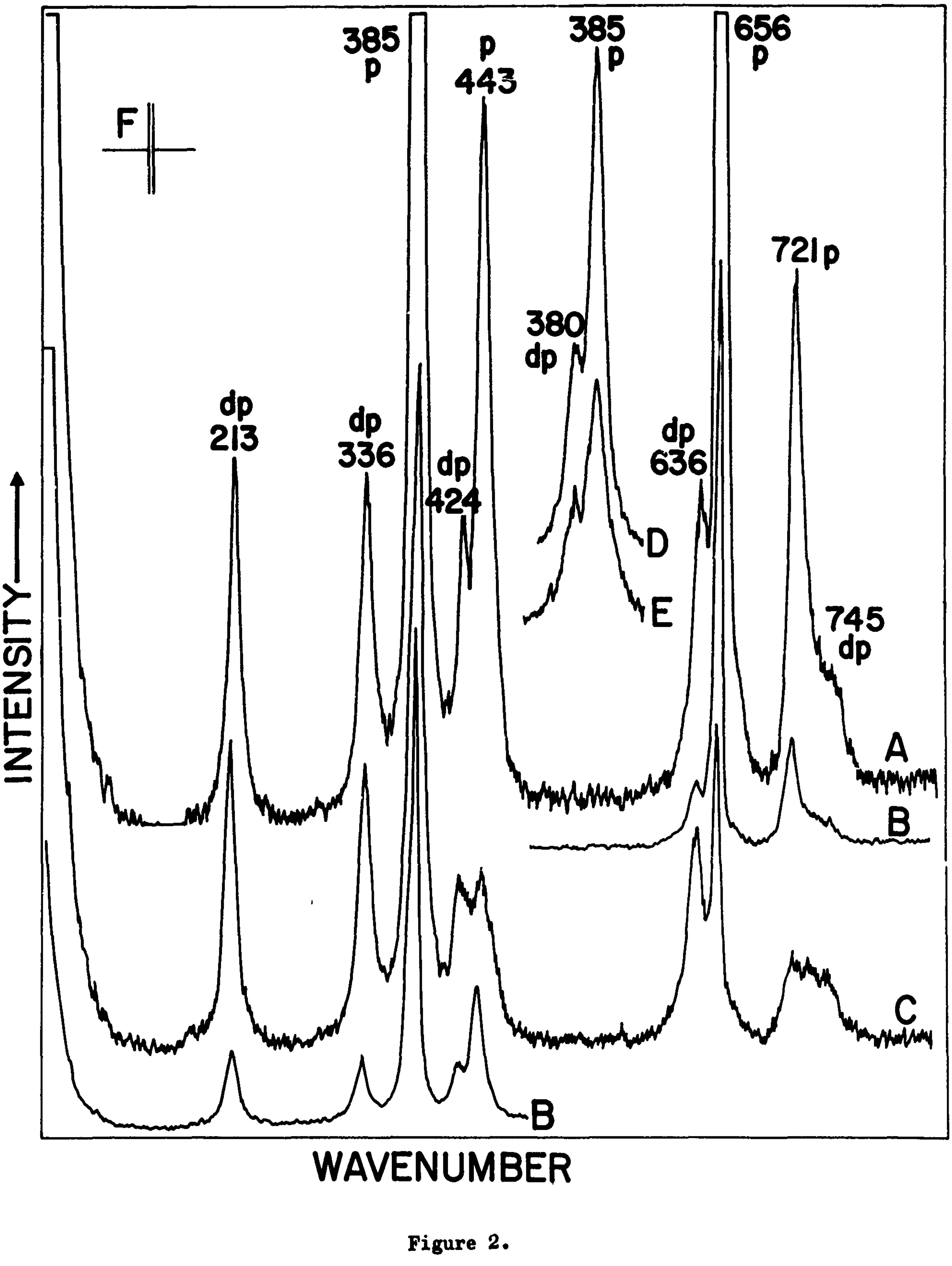

Figure 2.

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B-17/B-18

APPENDIX C

DIFLUOROCHLORATE (V) ANION, $ClO_2F_2^-$ VIBRATIONAL SPECTRUM AND FORCE CONSTANTS

Contribution from Rocketdyne, a Division of North American Rockwell

Canoga Park, California 91304

The Difluorochlorate (V) Anion, $ClO_2F_2^-$.

Vibrational Spectrum and Force Constants

By Karl O. Christe* and E. C. Curtis

Received ... 1971

Abstract

The infrared and the Raman spectrum of solid $CsF \cdot ClO_2F$ have been recorded. They are consistent with a $ClO_2F_2^-$ anion of symmetry C_{2v}. 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 $ClO_2F_2^-$, indicating double bond character for the ClO bonds and rather weak ClF bonds with high ionic contributions.

Introduction

Huggins and Fox have recently reported[1] the existence of $CsClO_2F_2$. 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 $CsClO_2F_2$.

Experimental Section

Materials and Apparatus. - The materials used in this work were manipulated in a well-passivated (with ClF_3) 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 $KClO_3$ and F_2)[2]

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 $\sim-25^{0}$, 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 $CsClO_2F_2$. - Dry CsF (7.64 mmol) was placed into a 10 ml prepassivated (with ClF_3) 316 stainless steel cylinder and ClO_2F (22.50 mmol) was added at -196^{0}. The cylinder was kept at -25^{0} for 24 hours and subsequently placed on a mechanical shaker for 24 hours at 25^{0}. Unreacted ClO_2F (16.89 mmol) was removed in vacuo at 25^{0}, indicating that 73.4% of the CsF had been converted to $CsClO_2F_2$.

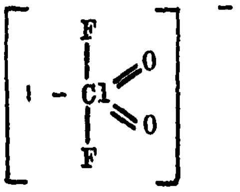
Results and Discussion

Synthesis and Properties. - The synthesis and properties of $CsClO_2F_2$ were in good agreement with those previously reported.[1] The hydrolysis of $CsClO_2F_2$ was studied by exposing a sample of $CsClO_2F_2$ 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 $ClO_2F_2^-$ (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:

$$ClO_2F_2^- + H_2O \longrightarrow ClO_3^- + 2HF$$

Vibrational Spectra. - Figures 1 and 2 show the infrared and Raman spectra, respectively, of solid $CsClO_2F_2$. 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 $CsClO_2F_2$ 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 $ClO_2F_2^-$. 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 $ClO_2F_2^-$. 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], XeO_2F_2[11], or $IO_2F_2^-$[12] shows that the two axial positions are always occupied by the two most electronegative ligands.[13] Theoretical explanations for this behavior have previously been given.[13-16] Therefore, the most plausible structure for $ClO_2F_2^-$ is



This type of structure has also been suggested[11] for XeO_2F_2 which is isoelectronic with $ClO_2F_2^-$.

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.[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.[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.[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^+ [17] and ClO_2F.[22] The bands assignable to the three corresponding ClF_2 motions show frequencies somewhat lower than those[20] observed for ClF_2^-.

All nine fundamentals expected for XO_2F_2 of symmetry C_{2v} (these are classified as $4A_1 + A_2 + 2B_1 + 2B_2$) were observed if a coincidence of $\nu_7(B_1)$ and $\nu_9(B_2)$ 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[11] for isoelectronic XeO_2F_2. The assignment of the observed bands to the individual modes is straight forward 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[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[23], SF_5^-, SeF_5^-, TeF_5^-[24], ClF_2^+, BrF_2^+[25], or ClF_4^-, BrF_4^-[26]. The assignment of the weak and broad Raman band at 480 cm^{-1} to $\nu_5(A_2)$ should be considered tentative. This band may contain some contribution from $\nu_6(B_1)$; however, its band center at 480 cm^{-1} differs by 30 cm^{-1} from the band center observed for ν_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 $ClO_2F_2^-$. This band cannot be due to a fundamental vibration and, hence, is assigned to the combination band, $\nu_3 + \nu_6(B_1)$. The splitting of $\nu_1(A_1)$ into three components in the Raman spectrum and of $\nu_8(B_2)$ 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 $ClO_2F_2^-$ to be similar to those found for ClO_2^+[17] and ClO_2F.[22] Since the $ClO_2F_2^-$ 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 $ClO_2F_2^-$ 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: $r_{ClF} = 1.79A$, $R_{ClO} = 1.43A$, $\alpha = \measuredangle_{OClO} = 120^\circ$, $\beta = \measuredangle_{OClF} = 90^\circ$, and $\measuredangle_{FClF} = 180^\circ$. 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 $ClO_2F_2^-$. 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.

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 $f_R = 8.3$, $f_{RR} = 0.1$, $f_r = 1.6$, and $f_{rr} = -0.1$ mdyn/A; $f_\alpha = 1.95$, $f_\beta = 1.2$, $f_{\beta\beta}' = 0.57$, and $f_{\beta\beta} = 0.1$ ndyn/A rad^2; and $f_{r\beta} - f_{r\beta}' = 0.3$. The deformation coordinates were weighted by unit (1A) 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 $ClO_2F_2^-$ 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^+ [17] and ClO_2F[22]. 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 versa gas). Hence, no attempt will be made to evaluate the relative contributions from each effect.

Whereas the ClO bonds in $ClO_2F_2^-$ exhibit double bond character, the value of the ClF stretching force constant, f_r, of 1.6 mdyn/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 $ClO_2F_2^-$ has a pseudo trigonal bipyramidal structure. As pointed out previously[31], this type of structure appears to be energetically unfavorable as also indicated by the low thermal stability of the $CsF \cdot ClO_2F$ adduct.

The small negative value of the ClF stretch-stretch interaction constant, f_{rr}, is comparable to that found[32] for KrF_2 for which an explanation was given by Coulson[33]. The values found for the OClF and OClO deformation constants are as expected. The large values found for the interaction constant $f_{\beta\beta}'$, and the stretch-bend interaction term, $f_{r\beta}$, are in accord with those obtained for the halogen pentafluoride molecules[23].

From the above discussion of the stretching force constants, it became obvious that the Cl = O bonds are predominantly covalent, whereas the Cl-F bonds contain strong contributions from ionic bonds. This finding confirms the previous predictions[34] 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 sp^2 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 $p-\sigma$ bond pair[20,35-38]. For an ideal semi-ionic 3c4e bond, one should therefore expect f_r to have a value about half that of a covalent Cl-F bond. The low value of 1.6 mdyn/Å obtained for $ClO_2F_2^-$ obviously fulfills these requirements (covalent Cl-F bonds show stretching force constants ranging from about 3.5 to 4.7 mdyn/Å) 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. Silvera 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.

TABLE I

Vibrational Spectrum of $Cs^+ClO_2F_2^-$ and its Assignment Compared to Those of Similar Molecules and Tons

$Cs^+ClO_2F_2^-$		XeO_2F_2 [a]		ClO_2^- [b]	ClO_2 [b]	ClO_2^+ [c]	ClO_2F [d]	ClF_3 [e]	ClF_2^- [f]	Assignment for XO_2F_2 in Point Group C_{2v}	Approximate Description of Vibration
IR	Raman	IR	Raman								
1225 1191 vs	1221(0.8)	905s	902W	844	1111	1296	1271			$\nu_8(B_2)$	$\nu_{as} XO_2$
1070s	1076(10) 1064 1055	848ms	845vs	786	945	1044	1106			$\nu_1(A_1)$	$\nu_s XO_2$
855vw										$\nu_3+\nu_6(B_1)$?	
559m	559(1.2)	328ms,sh	333ms	402	445	521	547			$\nu_2(A_1)$	$\delta s XO_2$
510vs,br		585vs	578W					702	635	$\nu_6(B_1)$	$\nu_{as} XF_2$
	480(1),br									$\nu_5(A_2)$?	τ
330–370m	363(10)		490s					529	475	$\nu_3(A_1)$	$\nu_s XF_2$
	337(8)	324s 317ms	313ms							$\nu_7(B_1), \nu_9(B_2)$	δrock, δwag
	198(0.7)		198W					328		$\nu_4(A_1)$	$\delta s XF_2$

(a) Reference 11.

(b) H. Siebert, Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer-Verlag, Berlin, 1966.

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(f) Reference 20.

TABLE II

Stretching Force Constants (mdyn/Å) of $ClO_2F_2^-$ Compared to Those of Related Molecules and Ions

	$ClO_2F_2^-$	ClO_2^+[a]	ClO_2[b]	ClO_2^-[c]	ClO_2F[d]	ClF_2^-[e]	ClF_4^-[f]	ClF[g]	ClF_2^+[h]
f_R	8.3	8.96	7.02	4.26	9.07				
f_{RR}	0.1	−0.45	−0.17	0.11	−0.12				
f_r	1.6				2.53	2.35	2.11	4.36	4.74
f_{rr}	−0.1					0.17	0.23		0.14

(a) Reference 17.

(b) M. G. Krishna Pillai and R. F. Curl, Jr., J. Chem. Phys., 37, 2921(1962).

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Diagram Captions

Figure 1. - Infrared spectrum of solid $Cs^+ClO_2F_2^-$ as dry powder in an AgBr disk.

Figure 2. - Raman spectrum of solid $Cs^+ClO_2F_2^-$. Sample container, glass capillary. C indicates spectral slit width.

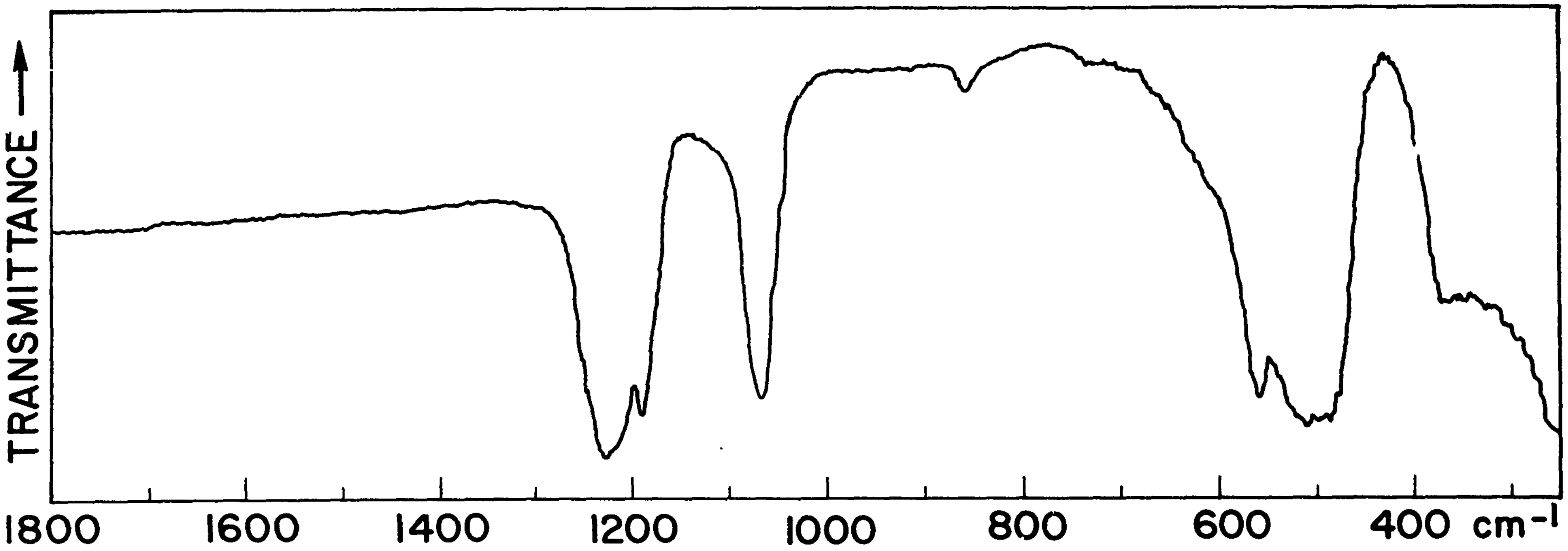

Figure 1.

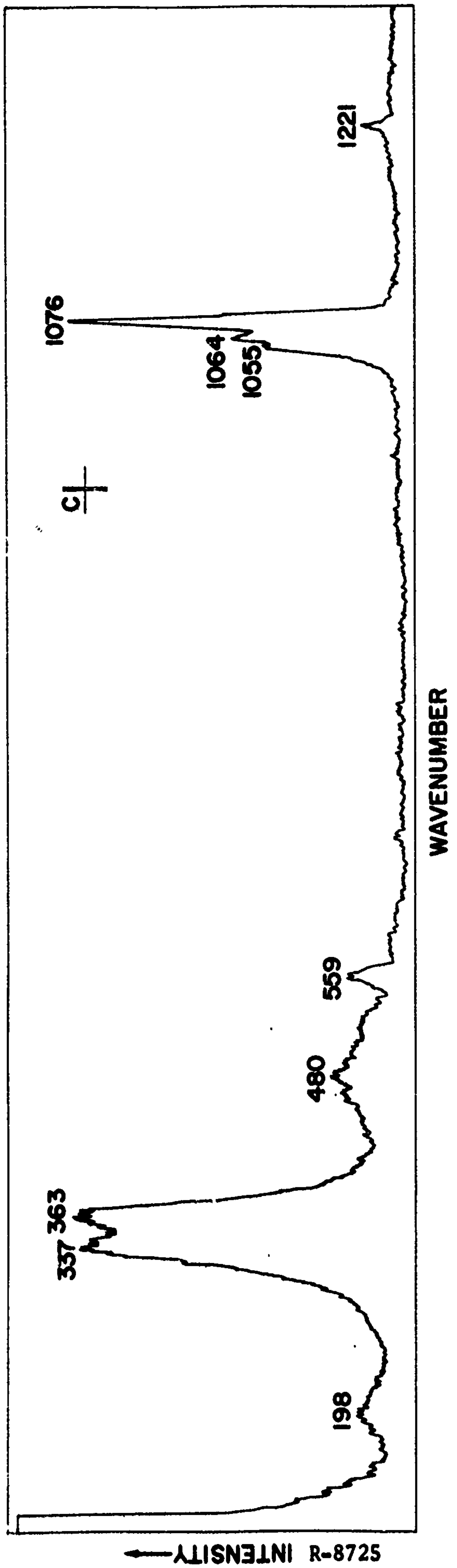
1221
1076
1064
1055
Cl
559
480
363
337
198
WAVENUMBER
INTENSITY
R-8725

Figure 2.

Vibrational Assignment of SF_4

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In a previous paper[1] we reported the Raman spectrum of gaseous SF_4. The Raman data suggested the need of revising all assignments for the deformational modes except for ν_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, $\nu_6(B_1)$ and $\nu_8(B_2)$, based on a comparison with the spectra of the structurally related molecules, BrF_3 and 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 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 SF_4. Valence Force Constants in mdynes/Å, Deformation Constants in mdynes·Å, and Stretching-Deformation Coupling Terms in mdynes. Set I: $\nu_6 \geq \nu_8$; Set II: $\nu_8 \geq \nu_6$.

		Set I	Set II	SF_6[a]	SF_5^-[b]	ClF_3[c]	BrF_3[c]
B_1	F_{66}	3.66	2.65				
	F_{67}	0.45	0.60				
	F_{77}	2.20	2.24				
B_2	F_{88}	3.33	4.77				
	F_{89}	0.20	0.17				
	F_{99}	2.01	1.98				
f_R		3.57	3.07		2.16	2.70	3.01
f_R'		-0.09	0.42		0.38	0.36	0.34
f_r		4.54	5.25	5.26	4.40	4.19	4.08
f_r'		1.21	0.49		—	—	—
r		1.545 ± 0.003[d]		1.56 ± 0.02[e]	—		

(a) Ref. 7

(b) Ref. 8

(c) Ref. 5

(d) Ref. 9

(e) Ref. 10

Table II. Mean-Square Amplitudes of SF$_4$ (in Å).

	$<q^2>_{calc}^{1/2}$			$<q^2>_{obs}^{1/2}$
	Set I	Set II	Set III	
S-F$_1$	0.050	0.049	0.049	0.047 ± 0.005
S-F$_3$	0.044	0.041	0.041	0.041 ± 0.005
F$_1$···F$_2$	0.061	0.061	0.061	0.059 ± 0.01
F$_3$···F$_4$	0.063	0.063	0.094	0.068 ± 0.01
F$_1$···F$_3$ (ν_5 = 200)	0.091	0.091	0.086	0.067 ± 0.005
=(400)	0.074	0.073	0.068	
=(600)	0.070	0.069	0.064	
=(800)	0.068	0.068	0.063	

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[6] is slightly better for set II. It should be noted that the values reported in our previous paper[1] for $< q^2 >^{1/2}$ $F_1 \ldots F_3$ are incorrect due to a computational error. The revised values are in agreement with the experimental data[6] if $\nu_5(A_2)$ is assumed to be larger than 500 cm^{-1}. In the Raman spectra of the gas[1] and the liquid[2], there was evidence indicating a frequency of about 400 cm^{-1} for this mode. For this frequency value $< q^2 >^{1/2}$ $F_1 \ldots F_3$ would be just outside the uncertainty limit given for the experimental data[6]. This discrepancy might be eliminated by reversing the assignment of $\delta_{SF_2(eq.)}$ and $\delta_{SF_2(ax.)}$ in species A_1. This reduces all $< q^2 >^{1/2}$ $F_1 \ldots F_3$ values by 0.005 Å, but increases the value of $< q^2 >^{1/2}$ $F_3 \ldots F_4$ to 0.094 Å (set III, Table II). However, the latter value is clearly outside of the experimentally found range of 0.068 $\pm$ 0.01 Å. Consequently, it appears that for SF_4, $\delta_{SF_2(eq.)}$ is higher than $\delta_{SF_2(ax.)}$, contrary to the findings for PF_5[11,12] and the assignments[13] made by Bartell for related trigonal-bipyramidal molecules. The remaining slight discrepancy (0.005 Å) for $< q^2 >^{1/2}$ $F_3 \ldots F_4$ and $< q^2 >^{1/2}$ $F_1 \ldots F_3$ between set II and the observed[6] 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[14] indicates considerable mixing of the different modes. Set III of Table II indicates that some mixing between ν_3 and ν_4, i.e. the introduction of a larger value for the interaction force constant F_{34}, might increase the value of $< q^2 >^{1/2}$ $F_3 \ldots F_4$ and decrease that of $< q^2 >^{1/2}$ $F_1 \ldots F_3$. 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_α and f_β.

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 ($\measuredangle$F-S-F = 103.8°)[6] 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^-[8], ClF_3[5], and BrF_3[5]; (3) The bond length of the equatorial S-F bonds in SF_4 (1.545 ± 0.003 Å)[9] is similar to that in SF_6 (1.56 ± 0.02 Å)[10]. 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)[6] 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[5] reassignment of $\nu_6(B_1)$ and $\nu_8(B_2)$ results in a more satisfactory set of force constants for SF_4, although it remains difficult to rationalize the observed infrared band contours.[2,4] Table III lists the preferred assignment and set of force constants which can be derived from the presently available experimental data.

Acknowledgments

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Table III. Preferred Assignment and Symmetry Force Constants of SF_4

obs frequency (cm^{-1})			assignment
A_1	ν_1	891	ν sym SF_2 eq.
	ν_2	558	ν sym SF_2 ax.
	ν_3	475	δ sciss SF_2 eq.
	ν_4	226	δ sciss SF_2 ax.
A_2	ν_5	414	SF_2 twist
B_1	ν_6	730	ν asym SF_2 ax.
	ν_7	532	δ rock
B_2	ν_8	867	ν asym SF_2 eq.
	ν_9	353	δ wag

Symmetry Force Constants					
A_1	F_{11}	3.48	A_2	F_{55}	1.52
	F_{12}	0	B_1	F_{66}	2.65
	F_{13}	0.02		F_{67}	0.60
	F_{14}	0.01		F_{77}	2.24
	F_{22}	5.74	B_2	F_{88}	4.77
	F_{23}	0.13		F_{89}	0.17
	F_{24}	0.05		F_{99}	1.98
	F_{33}	1.97			
	F_{34}	-0.04			
	F_{44}	0.37			

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APPENDIX E

VIBRATIONAL SPECTRUM OF BROMINE TRIFLUORIDE

VIBRATIONAL SPECTRUM OF BROMINE TRIFLUORIDE

(Received 21 July 1970)

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° being used. It was handled in a passivated (with ClF_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 4° 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 BrF_3 was recorded using a Coherent Radiation Laboratories Model 52 Ar ion laser as a source of 1.3 W of exciting light at 5145Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to approximately -25° 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 BrF_3 in argon matrix at 4° K. Since BrF_3 even in the gas phase shows a tendency to associate [5], the spectrum was recorded at the following argon to BrF_3 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 SiF_4, i.e. ν_3 and ν_4 at about 1030 and 390 cm^{-1}, respectively [6], were observed. The formation of SiF_4 was due to interaction of BrF_3 with sections of the metal vacuum line, and extensive passivation of the line with ClF_3 and BrF_3 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 ν_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 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 ν_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 demformational modes. The fact that the symmetric F-Br-F stretching mode, ν_2 (A_1), is the most intense band in the Raman spectrum of 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 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 BrF_3, thus lending additional support to the given assignment.

The infrared spectrum of non-matrix-isolated, solid 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 BrF_3 showed a decrease in the relative intensity of the 600 cm^{-1}

Table 1

VIBRATIONAL SPECTRUM OF BrF_3

Gas		Matrix Isolated Solid	Assignment in Pointgroup C_{2v}
RA [1]	IR [1, 9]	IR	
675 s, p	675 s	672 s	ν_1 (A_1) $\nu_{Br-F'}$
612 vvw	614 vs	592 vs	ν_4 (B_1) νas F-Br-F
552 vs, p	552 w	545 mw	ν_2 (A_1) ν s F-Br-F
	350 vw	346 mw	ν_5 (B_1) δas in plane
	242 s	250 m	ν_6 (B_2) δ out of plane
	242 s	235 mw	ν_3 (A_1) δs in plane
	1340 vw	1345 vw	$2\nu_1 = 1344$
	1287 vw	1265 mw	$\nu_1 + \nu_4 = 1264$
		1217 w	$\nu_1 + \nu_2 = 1217$
	1162 w	1170 mw	$2\nu_4 = 1184$
		1138 mw	$\nu_2 + \nu_4 = 1137$
		1062 mw	?
		977 mw	?
		920 } w, br	$\nu_1 + \nu_6 = 922$, $\nu_1 + \nu_3 = 905$
		895 } w, br	$\nu_2 + \nu_5 = 891$
		820 w	$\nu_4 + \nu_3 = 827$
		795 vw, sh	$\nu_2 + \nu_6 = 795$

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 BrF_3. In no case did the spectrum of solid BrF_3 [12] show the bands characteristic for BrF_2^+ [12] and BrF_4^- [13] indicating that solid BrF_3 does not exist in the ionic form, $BrF_2^+BrF_4^-$, but prefers association through covalent fluorine bridges. This finding is in good agreement with the results from a crystallographic study on solid BrF_3 [14].

Vibrational Force Constants

Vibrational force constants were computed for BrF_3 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 Å). The force constant designations follow those used for the square-pyramidal interhalogens [16] with f_R for both BrF_3 and BrF_5, referring to the unique fluorine and f_β to the deformation of the angle between that fluorine and the equivalent fluorines.

For comparison, we also report the force constants computed for BrF_5, ClF_5 [17], and ClF_3 [18] assuming a similar force field. Table II shows similar trends between BrF_3 and BrF_5 and ClF_3 and ClF_5, although it should be noted that the force constants of ClF_5 are not very certain, since a relatively large interaction force constant is required to fit the frequencies. It is not certain whether this should be $f_{r\beta}$, $f_{R\beta}$, or f_{Rr}. The value for f_α reported for BrF_3 was computed to permit comparison with the similar motion in BrF_5, the E block α deformation. Definition of f_α requires placing fictitious atoms to give BrF_3 the same geometry as BrF_5. These fictitious atoms serve no purpose other than to define f_α and contribute nothing to the molecular motion or force constant [19]. The similarity of f_α for the tri- and penta-fluorides is noteworthy.

Thermodynamic Properties

The thermodynamic properties were computed for 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.

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Table II. COMPARISON OF THE FORCE CONSTANTS OF BrF_3, BrF_5, ClF_3, and ClF_5

(Units of the stretching constants are millidyne Ångstrom^{-1} and of the bending constants millidyne Ångstrom^{-1} radian^{-2}.)

	BrF_3	BrF_5[17]	ClF_3[18]	ClF_5[17]
f_R	4.07	4.01	3.88	3.66
f_r	3.10	3.26	2.74	2.75
f_β	1.39	2.32	1.97	2.80
f_α	0.78	0.84	1.03	1.09
f_{rr}'	0.31	0.26	0.38	0.18
$f_{\beta\beta}'$	0.09	0.56	0.17	0.29

Table III. THERMODYNAMIC PROPERTIES OF BrF_3 ASSUMING AN IDEAL GAS AT 1 ATM. PRESSURE. UNITS FOR $C_p°$, S°, and $-(F°-H_o°)/T$ ARE CALORIES PER MOLE • DEGREE AND H° IS KILOCALORIES PER MOLE.

T	$C_p°$	$H°-H_o°$	$-(F°-H_o°)/T$	$S_T°$
0	0.	0.	0.	0.
100	9.948	0.847	48.095	56.561
200	13.751	2.041	54.483	64.690
298.15	16.117	3.518	58.866	70.665
300	16.150	3.548	58.939	70.765
400	17.477	5.236	62.522	75.611
500	18.232	7.024	65.551	79.600
600	18.688	8.872	68.180	82.967
700	18.981	10.757	70.505	85.872
800	19.179	12.665	72.588	88.420
900	19.319	14.591	74.476	90.688
1000	19.420	16.528	76.201	92.729
1100	19.497	18.474	77.789	94.583
1200	19.555	20.427	79.260	96.282
1300	19.601	22.385	80.631	97.850
1400	19.638	24.347	81.913	99.304
1500	19.668	26.312	83.118	100.659
1600	19.692	28.280	84.255	101.930
1700	19.713	30.250	85.330	103.124
1800	19.730	32.222	86.350	104.251
1900	19.744	34.196	87.321	105.318
2000	19.757	36.171	88.246	106.332

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Diagram Caption

Figure 1. Infrared spectrum of BrF_3 in argon matrix at $4^{o}K$, 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.

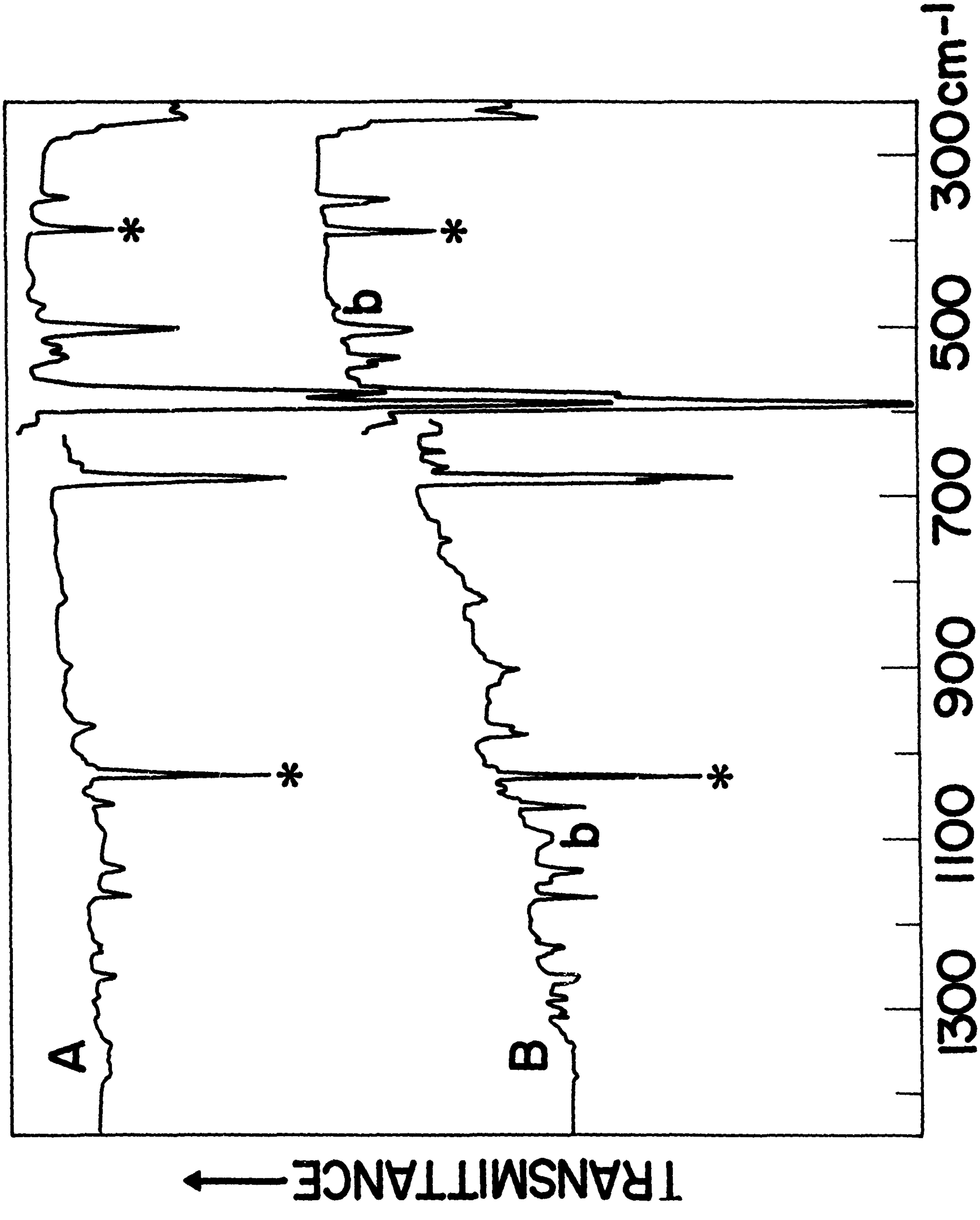

Figure 1.

APPENDIX F

VIBRATIONAL SPECTRUM OF THE N_2F^+ CATION

THE VIBRATIONAL SPECTRUM OF THE N_2F^+ CATION

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Abstract

The infrared and Raman spectra are reported for $N_2F^+AsF_6^-$ and $N_2F_2 \cdot 1.3\ SbF_5$. For N_2F^+ 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 N_2F^+ and are compared to those of a series of isoelectronic molecules and ions.

Introduction

The existence of solid adducts between N_2F_2 and Lewis acids, such as AsF_5 and SbF_5 is well known.[1-4] In all cases an infrared band at about 1060 cm^{-1} was observed which was attributed to the N-F stretching vibration of the N_2F^+ cation. Recently, Shamir and Binenboym reported[5] the Raman spectrum of $N_2F^+AsF_6^-$ and assigned bands at 2370 and 803 cm^{-1} to the two remaining fundamentals of N_2F^+. In this paper we wish to report the infrared and Raman spectra of $N_2F^+AsF_6^-$ and $N_2F_2 \cdot 1.3\ SbF_5$ showing that the deformational mode of N_2F^+ occurs at 390 and not at 803 cm^{-1}.

Experimental

The sample of $N_2F^+AsF_6^-$ was prepared as previously described.[1] Its 1:1 composition was ascertained by quantitative synthesis. The sample of $N_2F_2 \cdot x\ SbF_5$ 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 FEP vacuum system and about 20 ml of electrolytically dried,[6] liquid HF was added. The SbF_5 was dissolved in the HF at ambient temperature. Then the ampoule was cooled to -196^o and a mixture of cis and trans N_2F_2 (total = 25.5 mmole) containing a small amount of N_2F_4 as impurity was added. The mixture was allowed to warm up to -80^o for 3 - 4 hours and then to ambient temperature for two days under autogenous pressure. Unreacted material (HF and trans N_2F_2) was removed in vacuo at 0^o. The material balance and weight increase of the solid residue indicated that SbF_5 had combined with N_2F_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 $N_2F_2 \cdot xSbF_5$ adduct deserves some comment. Three different groups had reported the preparation of an adduct of N_2F_2 with SbF_5, however, their data disagree. Ruff obtained[2] a 1:2 adduct, $N_2F_2 \cdot 2\ SbF_5$, by reacting SbF_5 with excess of either cis or trans N_2F_2 at 40 - 50^o. Roesky et al. reported[3] that only the cis isomer of N_2F_2 is capable of forming an adduct with SbF_5 resulting in a 1:1 adduct, $N_2F_2 \cdot SbF_5$. Pankratov and Savenkova prepared[4] a 1:1 adduct, $N_2F_2 \cdot SbF_5$, from mixtures of cis and trans N_2F_2 and SbF_5 at -5 to 10° 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 $N_2F_2 \cdot xSbF_5$.

In the present study we have not attempted to resolve these conflicting reports on either the composition (1:1 versa 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, $N_2F_2 \cdot 1.3\ SbF_5$, 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 $N_2F_2 \cdot 1.3\ SbF_5$. 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, ν_2 (π), 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 $N_2F^+AsF_6^-$ and $N_2F_2\cdot 1.3\ SbF_5$ Compared With That of FCN

Observed Frequency					Assignment (Pointgroup)	
$N_2F_2\cdot 1.3\ SbF_5$		$N_2F^+AsF_6^-$		FCN[a]	FXN ($C_{\infty v}$)	AsF_6^- (O_h)
ir	RA	ir	RA	ir		
2373 w	2373 (0.3)		2371 (0.5)	2323	ν_3 (Σ^+)	
1059 ms	1059 (2.3)	1058 ms	1057 (3.1)	1069.4	ν_1 (Σ^+)	
		830 vw				$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
		698 vs,br				ν_3 (F_{1u})
	781 (0+)		780 (0+)		$2\nu_2$ (Σ^+)	
640 - 720 vs,br	689 (2.5)					
	661 (10)		689 (10)			ν_1 (A_{1g})
600 w,sh	604 (0.6)					
	582 (0.5)					
	568 (1.0)		576 (1.8)			ν_2 (E_g)
520 mw,sh						
478 ms						
388 ms	389 (1.6)	391 s	391 (0.7)	451.3	ν_2 (Π)	ν_4 (F_{1u})
260-300 s	285 (2.7)		376 (3.2)			ν_5 (F_{2g})
	231 (0.7)					
	127		100			Lattice Vibrations
	99					

(a) Ref. 10,11

band occurs in the range of the AsF_6^- deformational modes and since breakdown of the selection rules for O_h symmetry has been observed for several AsF_6^- containing salts,[12,13] the 391 cm^{-1} band in the AsF_6^- salt cannot unambiguously be assigned to ν_2 (π) of N_2F^+. However, if the band at 391 cm^{-1} is indeed due to ν_2 (π) of N_2F^+, it should also be observed in the spectra of other N_2F^+ salts containing anions not absorbing in this region. Since for SbF_6^- and $Sb_2F_{11}^-$ no vibrations occur[2,14] in the range 300 - 450 cm^{-1}, we have prepared a sample of $N_2F_2 \cdot xSbF_5$ and recorded its vibrational spectrum. As can be seen from Fig. 1 and 3, both the infrared and Raman spectrum of $N_2F_2 \cdot 1.3\ SbF_5$, 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 ν_2 (π) of N_2F^+.

The spectrum of N_2F^+ was previously compared[5] to that of isoelectronic N_2O. However, based on bond order and electronegativity considerations, we prefer to compare the spectrum of N_2F^+ with that of isoelectronic FCN. As can be seen from Table I, the two stretching modes of N_2F^+ are close to those[10,11] 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 ν_2 (π) of N_2F^+ than that of 803 cm^{-1} previously suggested.[5]

The assignments for the remaining bands of $N_2F^+AsF_6^-$ present no difficulties and are listed in Table I. The observed frequencies and intensities agree well with those predicted for a linear, asymmetric $[N\equiv N\text{-}F]^+$ cation of symmetry $C_{\infty v}$ and for an octahedral AsF_6^- anion.[5,9] For $N_2F_2 \cdot 1.3\ SbF_5$ three additional bands of low relative intensity were observed at 1300, 1124, and 926 cm^{-1} which can be assigned[2,14] to small amounts of $N_2F_3^+$ present in our sample as an impurity. Infrared spectra, recorded after $N_2F_2 \cdot 1.3\ SbF_5$ had attacked the AgBr window material, showed the complete absence of the bands assigned to N_2F^+, whereas the bands due to $N_2F_3^+$ had not decreased in intensity. This confirms the previously made observation[2] that the N_2F^+ salts are more reactive than the corresponding $N_2F_3^+$ salts. It is interesting to note that for $N_2F_2 \cdot 1.3\ SbF_5$ the $N\equiv N$ stretching mode of N_2F^+ 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[2,14] for SbF_6^- and $Sb_2F_{11}^-$. Whereas the Raman spectra of $N_2F^+AsF_6^-$ and $N_2F_2 \cdot 1.3\ SbF_5$ did not show any evidence for a band at 803 cm^{-1} (the frequency previously assigned[5] to ν_2 of N_2F^+), both show a weak band at 780 cm^{-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^{-1} band. Consequently, it is assigned to the first overtone of ν_2 of N_2F^+.

(3) Force Constants

For a linear, asymmetric ion of symmetry $C_{\infty v}$, 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[5] used a modified valence force field for their computation assuming the off-diagonal constant, f_{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_{rR} upon the diagonal force constants can usually not be neglected. Therefore, f_{rR} was assumed to have a fixed value, and the NN and NF stretching force constants, f_r and f_R, respectively, were computed as a function of f_{rR} (see Table II). The value of f_{rR} was varied over the most probable range (-0.5 to 2.0 mdyne/Å) and computations were made at 0.5 mdyne/Å intervals. A closer estimate of the stretching force constants might be obtained provided one could further narrow the range of possible f_{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[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[16] and HCP[15] for which f_{rR} 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_{rR} was found[17] to be 0.4 ±0.1 mdyne/Å but it is not unreasonable to extend the possible range to 0.5 ±0.5 mdyne/Å;and (iii) molecules with two multiple bonds and stronger resonance, e.g. N_2O and NCO^-,[18] with $f_{rR} > 1$ mdyne/Å. The symmetric molecules and ions, CO_2, NO_2^+, N_3^-,[18] might be included into this group.)

For N_2F^+ the NN stretching force constant has a value similar to or slightly lower than that found for N_2 (22.39 mdyne/Å)[18] throughout the range of probable f_{rR} 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_2F^+ based upon the observed frequencies is 7.45 mdyne/Å. Comparison of this value with those obtained for NF_4^+ (5.91)[21] and NF_2O^+ (6.46 mdyne/Å)[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_2F^+ should belong to group (ii) for which f_{rR} might be restricted to the range 0-1 mdyne/Å. Assuming $f_{rR} = 0.5 \pm 0.5$ the stretching force constants become $f_{NN} = 21.23 \pm 0.75$ and $f_{NF} = 8.16 \pm 0.29$ mdyne/Å. Further support for the assumption, $f_{rR} < 1$ mdyne/Å, was obtained by computing a set of force constants for N_2F^+ by the eigenvector method.[22,23] This computation yielded a value of 1.33 mdyne/Å for f_{rR} of N_2F^+. However, for 17 different linear XYZ molecules the eigenvector method always resulted[24] in f_{rR} values considerably larger than those of the GVFF. Therefore, one might expect f_{rR} of N_2F^+ to be considerably smaller than 1.33 mdyne/Å.

The deformation constant, f_α, of N_2F^+ can be uniquely determined provided the two bond lengths are known. For N_2F^+ 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 Å)[18] and r_{N-F} to be 1.37 Å (r_{N-F} in trans N_2F_2 = 1.398 and in NF_3 = 1.371 Å)[25] one obtains for f_α of N_2F^+ a value of 0.202 mdyne/Å or

0.304 mdyne·Å·rad^{-1}. Using the frequency value of 803 cm^{-1}, previously suggested[5] for ν_2 of N_2F^+, f_α would become 0.856 mdyne/Å. Comparison of the frequencies and force constants of N_2F^+ with those of a series of isoelectronic molecules and ions (see Table III) shows that a value of 0.86 mdyne/Å for f_α of N_2F^+ would be out of line. Table III also demonstrates that f_α 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_{rR}. Thomas et al.[26] have recently published a relation having the form $f_r = 37.3/r^{5.71}$ 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 f_α. Assuming $f_r = 21.23$ mdyne/Å, r_{NN} becomes 1.10 Å which is identical with our estimated value.

The conclusions,[5] reached by Shamir and Binenboym, that N_2F^+ 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 N_2F^+ are noticeable, but must be relatively small contrary to the situation in N_2O where II strongly contributes.

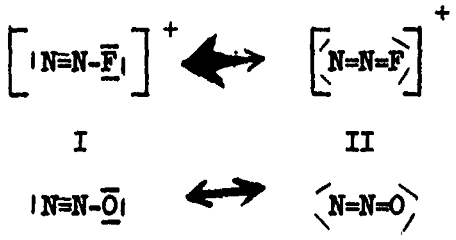

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TABLE II

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

(all values in mdyne/Å)

f_{rR}	f_r	f_R
-0.5	19.66	8.82
0	20.48	8.46
0.5	21.23	8.17
1.0	21.92	7.95
1.5	22.57	7.78
2.0	23.19	7.65

TABLE III

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

	Species	Frequency (cm^{-1})			Force Constants (mdyne/Å)			
		ν_3	ν_1	ν_2	f_r	f_R	f_{rR}	f_α
(i)	$\mathrm{H{-}C{\equiv}P}$[a]	3216.9	1278.4	674.7	8.95	5.59	-0.20	0.15
	$\mathrm{H{-}C{\equiv}N}$[b]	3438.3	2131.8	726.6	18.77	6.23	-0.21	0.21
(ii)	$[\mathrm{N{\equiv}N{-}F}]^{+}$	2372	1058	390	21.23	8.17	0.5	0.20
	$\mathrm{N{\equiv}C{-}F}$[c]	2323	1069.4	451.3	17.81	8.54	0.39	0.26
	$\mathrm{N{\equiv}C{-}Cl}$[c]	2215.6	744.2	378.4	17.50	5.21	0.44	0.18
	$\mathrm{N{\equiv}C{-}Br}$[c]	2198.3	586.6	341.7	17.51	4.17	0.41	0.15
	$\mathrm{N{\equiv}C{-}I}$[c]	2189.5	485.8	304.5	17.87	3.08	0.50	0.11
(iii)	$\mathrm{N{\equiv}N{=}O}$[d,e]	2224	1285	589	17.7	11.4	1.2	0.50
	$[\mathrm{N{\equiv}C{=}O}]^{-}$[d,e]	2165	1302 1207	632	15.9	11.0	1.4	0.51
	$[\mathrm{O{=}N{=}O}]^{+}$[d]	2360	1396	570	17.17		1.19	0.47
	$\mathrm{O{=}C{=}O}$[d]	2349	1286 1388	667	15.61		1.43	0.57
	$[\mathrm{N{=}N{=}N}]^{-}$[d]	2036	1344	647	13.15		1.75	0.58

(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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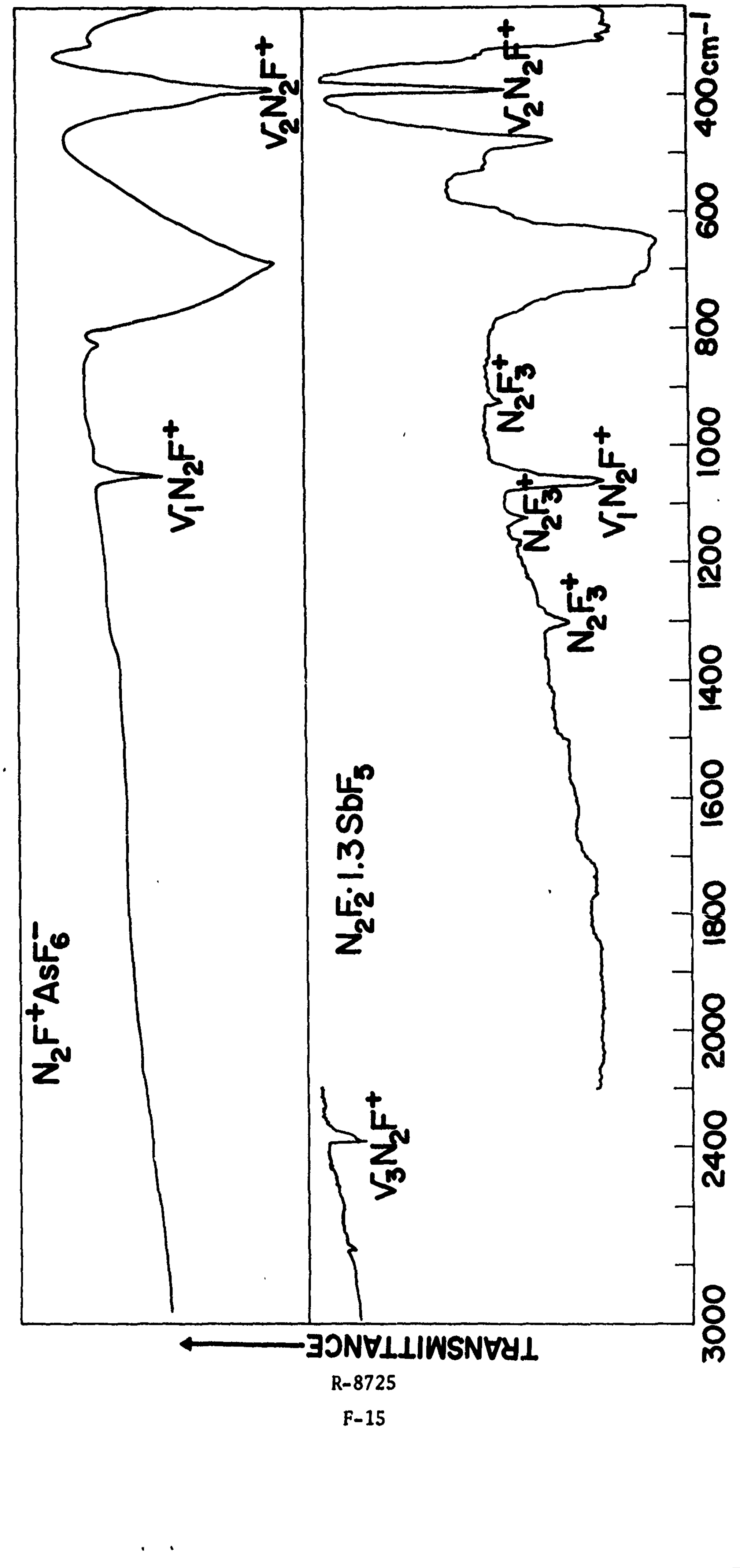
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$\nu_2 N_2F^+$
$\nu_1 N_2F^+$
$N_2F_2 \cdot 1.3\,SbF_5$
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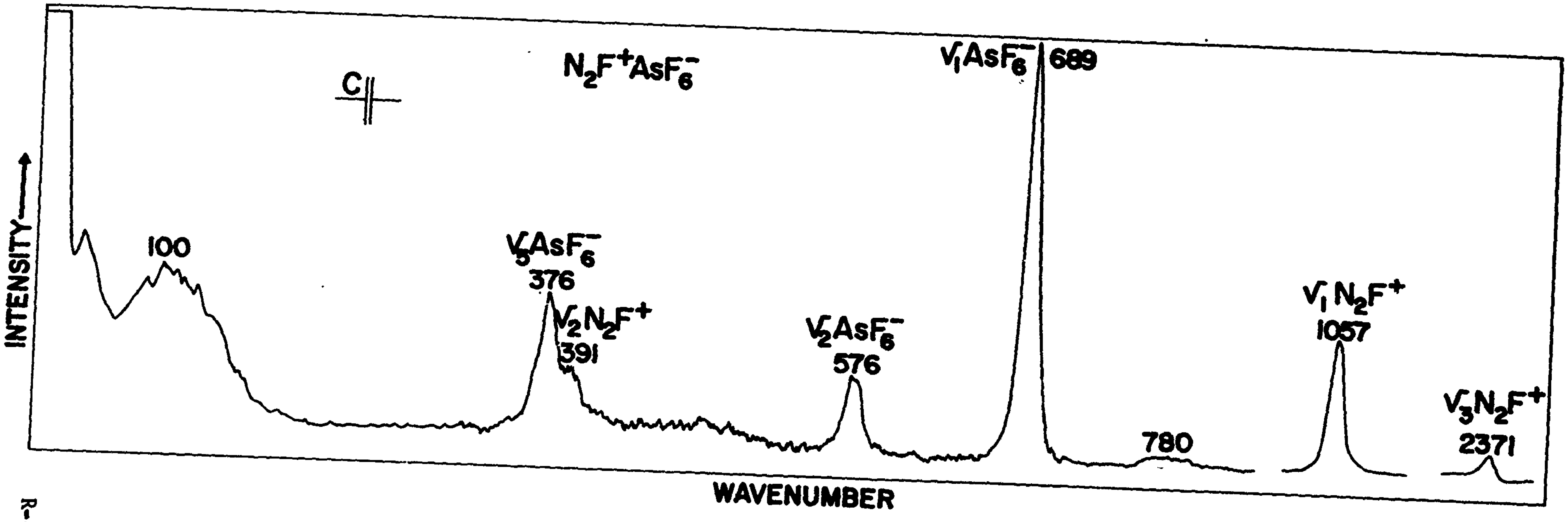
$N_2F_3^+$
$N_2F_3^+$
$\nu_1 N_2F^+$
$N_2F_3^+$
$\nu_3 N_2F^+$
400cm-1
600
800
1000
1200
1400
1600
1800
2000
2400
3000
TRANSMITTANCE

Figure 1.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C||
INTENSITY
100
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$\nu_2 N_2F^+$ 391
$\nu_2 AsF_6^-$ 576
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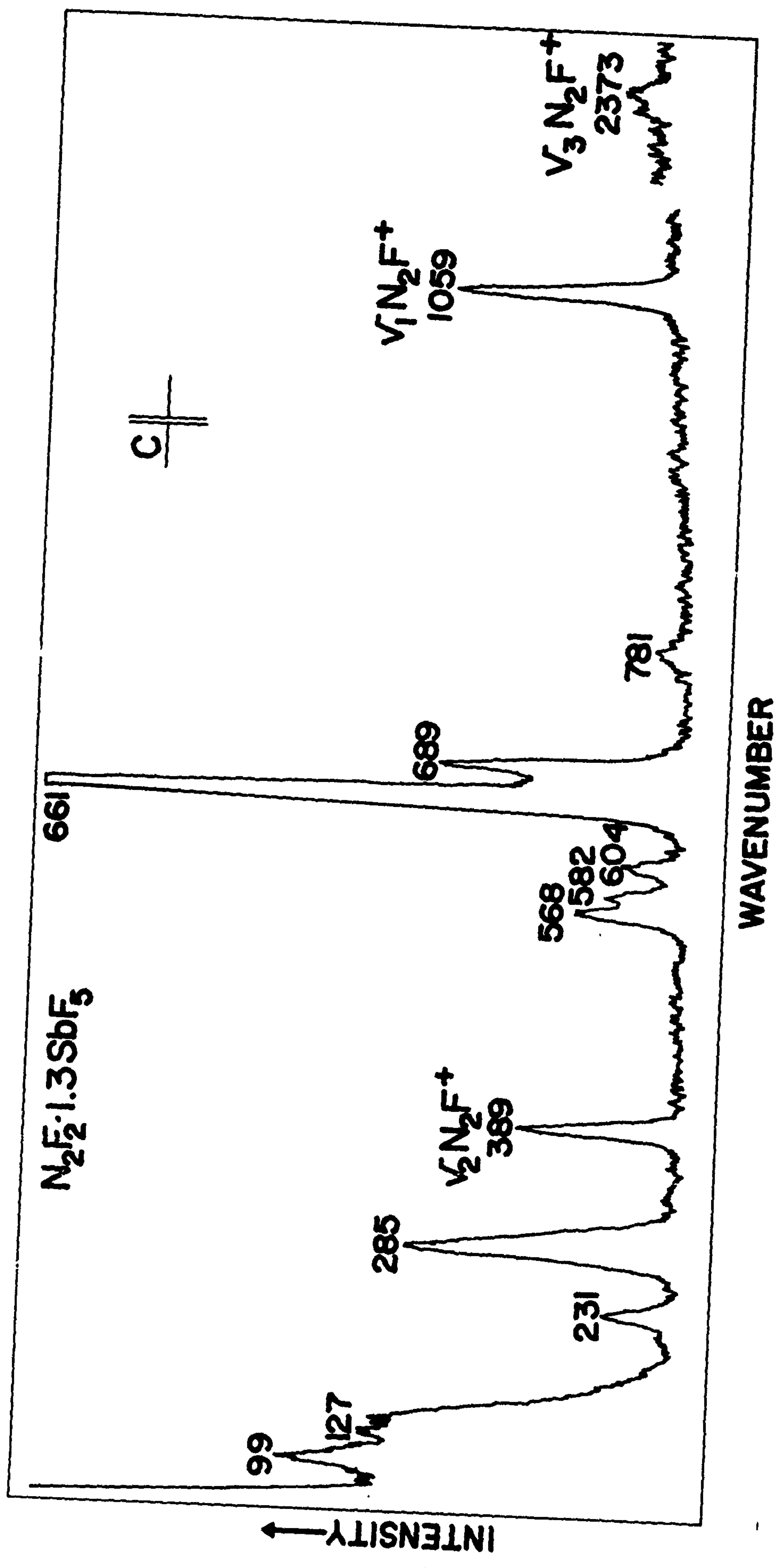
780
$\nu_1 N_2F^+$ 1057
$\nu_3 N_2F^+$ 2371
WAVENUMBER

Figure 2.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C
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389
568
582
604
661
689
781
$\nu_1 N_2F^+$
1059
$\nu_3 N_2F^+$
2373
WAVENUMBER
INTENSITY →

Figure 3.

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

Halogen Perchlorates: Vibrational Spectra

By Karl O. Christe*, Carl J. Schack, and E. C. Curtis

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Abstract. The infrared spectra of gaseous, solid, and matrix isolated and the Raman spectrum of liquid $ClOClO_3$ have been measured. All twelve fundamentals expected for symmetry C_s were observed and assigned. The infrared spectra of gaseous and matrix isolated $BrOClO_3$ 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, $ClOClO_3$ and $BrOClO_3$, has been discovered[1,2]. Their chemical and physical properties[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 $ClOClO_3$ and $BrOClO_3$ has been reported elsewhere[1,2]. The apparatus used for the low-temperature matrix isolation and infrared spectroscopic studies has previously been described[2,3]. The low-temperature infrared spectrum of solid $ClOClO_3$ was recorded by condensing the sample on the cold (-196°) internal AgCl window of a conventional low-temperature cell. The Raman spectra of liquid $ClOClO_3$ were obtained using Kel-F or Teflon FEP capillaries in the transverse viewing-transverse excitation mode. The capillaries were cooled (-20 to -80°) by a stream of cold gaseous N_2. The intense light from the exciting laser beam (1.3 w at 5145 Å) 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 hand. Under these conditions no lines could be detected due to Cl_2O_7[4,5] which is the major decomposition product in the photolysis of $ClOClO_3$[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 $ClOClO_3$. The infrared spectra of solid and matrix-isolated $ClOClO_3$ 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 $ClOClO_3$. Figure 5 shows the infrared spectrum of gaseous and matrix-isolated $BrOClO_3$. The observed frequencies are listed in Table 1.

The recording of the vibrational spectra of $ClOClO_3$ and $BrOClO_3$ 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 formation of $AgClO_4$ and Cl_2). Consequently, numerous spectra had to be recorded under varying experimental conditions to be able to eliminate bands due to decomposition products.

For a chlorine oxide, having the empirical formula Cl_2O_4, many possible structures can be written. However, the number of observed fundamentals (8 polarized and 4 depolarized ones), the resemblance between the spectrum of Cl_2O_4 and those of

TABLE I

Vibrational Spectra of $ClOClO_3$ and $BrOClO_3$

Observed frequency, cm^{-1}						assignment
$ClOClO_3$				$BrOClO_3$		in point group
infrared			Raman	infrared		C_s
gas	matrix	solid	liquid	gas	matrix	
2570 vw						$2\nu_1$
2322 w		2290 w		2300 w		$\nu_1+\nu_2$, $\nu_9+\nu_2$
2090 vw		2070 vw				$2\nu_2$
1934 vw						$\nu_1+\nu_4$
1500 vw						$2\nu_3$
	1289 sh				1280 sh	B^{35}
	1287 vs				1278.5 vs	ν_1 Cl^{35}(A′)
	1278 m				1270.5 m	C^{35}
	1274 sh				1265 sh	B^{37}
	1272 sh				1263 sh	ν_1 Cl^{37} (A′)
1283 vs	1271 vs	1278 sh	1280 mw	1275 vs	1262 vs	ν_9 Cl^{35} (A″)
	1264 mw	1259 vs			1256 sh	C^{37}
	1258 sh	1239 sh			1252 m	D
	1256 m				1246 mw	ν_9 Cl^{37} (A″)
					1240 w	
	1044 m				1041 m	
1040, s PQR	1039 s	1031 vs	1036 vs, p	1039 s	1037 s	ν_2 (A′)
	1036.5 m				1033 m	and $2\nu_6$
	1029 m					
749 mw, PQR	746 m					
	742 mw	743 m	744 ms, p	683 m	686 m	ν_3 (A′)
646 vs	647 vs	635 vs	643 ms, p	648 s	651 vs	
	638.5 vs				643 s	ν_4 (A′)
580 sh	582 m	580 m	582 m, p		572 mw	ν_5 (A′)
	579.5 mw			570 ms		
561 m	561 ms	558 ms	561 w, dp		566 m	ν_{10} (A″)
	558.5 m					

TABLE I (Cont'd.)

511, mw, PQR	513 m 512 sh	512 m	516 s, p	509 m	516 m	ν_6 (A′)
	382 w	384 vw	382 w, dp		387 vw	ν_{11} (A″)
	355 vw	360 vw	353 vs, p			ν_7 (A′)
			198 ms, p			ν_8 (A′)
			92 w, dp			ν_{12} (A″)

TABLE II

Fundamental Vibrations of Halogen Perchlorates Compared to Those of Similar Molecules

Observed requencies, cm^{-1}							Assignment in point group C_s	Approximate description of vibration for $YOXO_2Z$
$ClOSO_2F$[a]	$FOClO_3$[b]	$ClOClO_3$	$BrOClO_3$	$HOClO_3$[c]	$O_3ClOClO_3$[d]	$FClO_3$[e]		
1248	1298	1287	1279	1263	1313,1300	1314	A′ ν_1	$\nu_{as}XO_2Z$
855	1049	1040	1039	1050	1060,1024	1062	ν_2	$\nu_s XO_2Z$
703	885	749	683	3560	698,704		ν_3	ν O-Y
831	666	646	648	725		716	ν_4	ν X-O
572		580	572	563	598,571	573	ν_5	δ sciss XO_2
486		511	509	519	521,512	549	ν_6	δ umbrella XO_2Z
364		355	[278][f]	402	283,272	414	ν_7	δ rocking
<250		198	[159][f]	1200	154		ν_8	δ XOY
1481	1298	1271	1262	1326	1300	1314	A″ ν_9	$\nu_{as}XO_2Z$
532		561	566	579	567	573	ν_{10}	δas XO_2Z
390		382	387	430	495,283	414	ν_{11}	torsion XO_2
<250		92		310			ν_{12}	torsion O-Y

[a]Reference 10. [b]Reference 9. [c]Reference 7. [d]Reference 5. [e]Reference 8. [f]Computed values

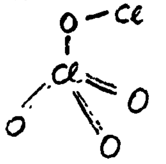
TABLE III

Comparison Between Observed and Calculated Cl^{35}-Cl^{37} Isotopic Shifts of $HalOClO_3$

normal mode	isotopic shift (cm^{-1}) and relative abundance		
	calculated		observed
A′ ν_1	0, 16.2	3:1	0, 15[a, b]
ν_2	0, 4.8	3:1	0, 4.6[b]
ν_3	0, 0.5, 3.1, 3.6	9:3:3:1	0, 3.8[a]
ν_4	0, 0.5, 4.5, 4.9	9:3:3:1	0, 8.5
ν_5	0, 1.8	3:1	0, 2.1[a]
ν_6	0, .3, 3.0, 3.3	9:3:3:1	< 1.5[a]
ν_7	0, 1.0, 2.8, 3.9	9:3:3:1	not observed
ν_8	0, 0.3, 2.5, 2.8	9:3:3:1	not observed
A″ ν_9	0, 15.8	3:1	0, 15[a, b]
ν_{10}	0, 1.7	3:1	0, 2.5[a, b]
ν_{11}	0, 0.9	3:1	< 1

[a] for $ClOClO_3$; [b] for $BrOClO_3$

$BrClO_4$, $HOClO_3$[7], $O_3ClOClO_3$[4,5] $FClO_3$[8], $FOClO_3$[9], and $ClOSO_2F$[10], (see Table III), and its chemical and physical properties[1] can only be explained in terms of the following covalent perchlorate structure of symmetry C_s:



For a six atomic molecule of symmetry C_s, 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 $ClOClO_3$. Furthermore, the computation of the frequencies of the fundamentals from estimated force constants results in almost identical frequency values for ν_1 and ν_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 $ClOClO_3$ and $BrOClO_3$ 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 ν_1 and ν_9, respectively. The remaining band pairs (marked by B to D in Table I) might be caused by possible Fermi resonance of ν_1 and ν_2 with 2 ν_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_3Cl-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 arguements (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 $FClO_3$[8,11].

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, ν_2, ν_3, and ν_8, 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 $ClOClO_3$ and $BrOClO_3$ with those of $HOClO_3$[7], $O_3ClOClO_3$[4,5], $FClO_3$[8], $FOClO_3$[9] and $ClOSO_2F$[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[12]. An assumed geometry was used, with the perchlorate group taken the same as in perchloric acid[13, 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[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 $f_{Cl=O} = 8.8$, $f_{Cl-O} = f_{O-Cl}, = f_{O-Br} = 2.65$, $f_{O=Cl=O} = 1.9$, $f_{Cl-O-Cl} = 1.4$, and $f_{O=Cl-O} = 1.1$, with the units for the stretching constants being millidynes/Ångstrom and for the bending constants millidynes/Ångstrom radian^2. The bending coordinates were weighted by unit (1Å) distance. The only significant interaction found were $f_{Cl-O/O=Cl-O}$ which has a value about 0.2 millidyne/Ångstrom radian and $f_{Cl-O/O-Cl} = f_{Cl-O/O-Br} = 0.35$ millidynes/Angstrom. The isotope shifts were computed using these force constants and are reported in Table III. A somewhat better frequency fit was obtained with slightly different force constants and additional interaction constants with small numercial 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.

A′	ν_1	1287	$0.91\ f_{\mathrm{Cl=O}}$
	ν_2	1040	$0.94\ f_{\mathrm{Cl=O}}$
	ν_3	749	$0.58\ f_{\mathrm{O-Cl'}} + 0.20\ f_{\mathrm{Cl-O-Cl'}} + 0.15\ f_{\mathrm{O=Cl-O}}$
	ν_4	646	$0.78\ f_{\mathrm{Cl-O}} + 0.16\ f_{\mathrm{O-Cl'}} - 0.10\ f_{\mathrm{Cl-O/O=Cl-O}} + 0.10\ f_{\mathrm{O=Cl=O}}$ $- 0.10\ f_{\mathrm{Cl-O/O-Cl'}}$
	ν_5	580	$0.92\ f_{\mathrm{O=Cl=O}}$
	ν_6	511	$0.44\ f_{\mathrm{O=Cl=O}} + 0.33\ f_{\mathrm{O=Cl-O}} + 0.10\ f_{\mathrm{Cl-O-Cl'}}$
	ν_7	355	$0.60\ f_{\mathrm{O=Cl-O}} + 0.21\ f_{\mathrm{O-Cl'}}$
	ν_8	198	$0.60\ f_{\mathrm{Cl-O-Cl'}} + 0.25\ f_{\mathrm{O=Cl-O}}$
A″	ν_9	1271	$0.94\ f_{\mathrm{Cl=O}}$
	ν_{10}	561	$0.99\ f_{\mathrm{O=Cl=O}}$
	ν_{11}	382	$1.05\ f_{\mathrm{O=Cl-O}}$

Further attempts to refine the force constants using both the usual least squares methods and the reparameterization method[16] were unsuccessful. This appears to be due to mixing of ν_7 and ν_8. 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 ν_7. The same problem occured with two other molecules with similar geometry, CF_3OF[17] and $ClOSO_2F$[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 ν_4 is about twice that calculated. Since ν_1 is the only mode in the A′ block having an isotope splitting larger than 5 cm^{-1}, mixing between ν_1 and ν_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[19] 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_2O_7 available to us prior to publication. This work was supported by the Office of Naval Research, Power Branch.

TABLE V

Computed Thermodynamic Properties for $ClOClO_3$[a]

T, °K	C^o_p	$H^o - H^o_o$	$(F^o - H^o_o)/T$	S_o
0	0	0	0	0
100	11.451	0.938	51.985	61.362
200	16.471	2.333	59.166	70.829
298.15	20.563	4.161	64.256	78.211
300	20.628	4.199	64.343	78.339
400	23.572	6.418	68.658	84.701
500	25.623	8.883	72.428	90.195
600	27.058	11.522	75.799	95.001
700	28.077	14.281	78.852	99.253
800	28.816	17.128	81.643	103.053
900	29.363	20.038	84.216	106.481
1000	29.778	22.996	86.601	109.597
1100	30.097	25.991	88.823	112.450
1200	30.348	29.013	90.903	115.080
1300	30.549	32.059	92.857	117.518
1400	30.711	35.122	94.701	119.788
1500	30.844	38.200	96.445	121.911
1600	30.954	41.290	98.099	123.905
1700	31.046	44.390	99.673	125.785
1800	31.124	47.498	101.174	127.502
1900	31.191	50.614	102.607	129.246
2000	31.248	53.736	103.980	130.848

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[a] Units for C^o_p, S^o, and F^o are g calories, g moles, and degrees Kelvin and for H^o, kilocalories, and moles.

TABLE VI

Computed Thermodynamic Properties for $BrOClO_3$[a]

T, °K	C^o_p	$H^o - H^o_o$	$(F^o - H^o_o)/T$	S_o
0	0	0	0	0
100	12.042	0.972	53.975	63.692
200	16.926	2.420	61.434	73.533
298.15	20.898	4.286	66.697	81.073
300	20.961	4.325	66.786	81.202
400	23.819	6.572	71.217	87.649
500	25.809	9.060	75.071	93.191
600	27.202	11.715	78.503	98.027
700	28.190	14.487	81.603	102.299
800	28.907	17.344	84.433	106.112
900	29.438	20.262	87.036	109.549
1000	29.840	23.227	89.446	112.672
1100	30.149	26.227	91.689	115.532
1200	30.393	29.254	93.787	118.166
1300	30.587	32.304	95.757	120.606
1400	30.744	35.371	97.614	122.879
1500	30.873	38.452	99.370	125.005
1600	30.980	41.545	101.035	127.001
1700	31.069	44.647	102.619	128.882
1800	31.145	47.758	104.128	130.660
1900	31.209	50.876	105.569	132.345
2000	31.265	54.000	106.948	133.948

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[a] Units are identical to those of Table V.

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Diagram Captions

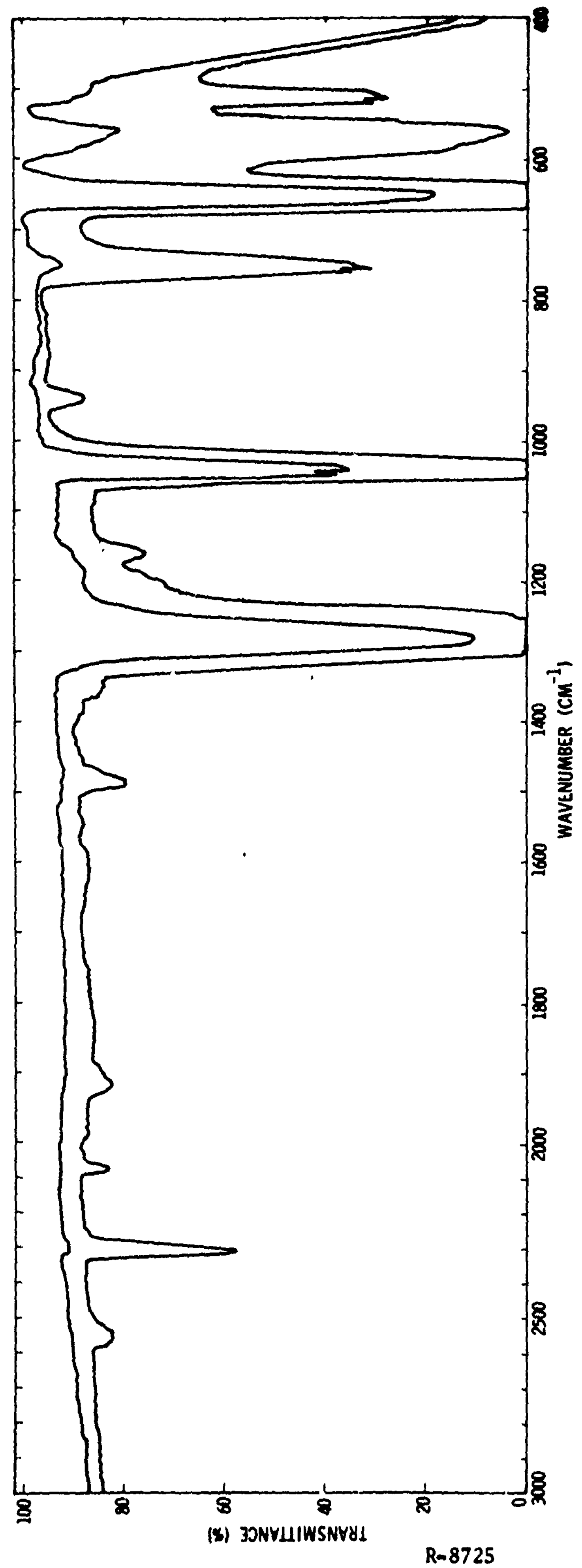
Figure 1. Infrared spectrum of $ClOClO_3$ at 180 and 8 mm pressure (5 cm path length).

Figure 2. Infrared spectrum of solid $ClOClO_3$. Trace A, 8.2 μmole of sample in Ar matrix (MR = 800) at 4^0K; trace B, crystalline solid.

Figure 3. Infrared spectra of matrix isolated $ClOClO_3$ and $BrOClO_3$ at 4^0 K under high resolution conditions and ten fold scale expansion (1 scale unit = 5 cm^{-1}). Trace A, $ClOClO_3$ sample of Figure 2A; trace B, 4.6 μmole of $ClOClO_3$ in Ar matrix (MR = 400); trace C, 2.5 μmole of $BrOClO_3$ in Ar matrix (MR = 400).

Figure 4. Raman spectrum of liquid $ClOClO_3$ at -40^0. 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 $BrOClO_3$. Trace A, 2.5 μmole of sample in Ar matrix (MR = 400) at 4^0K; trace B, gas at 20 mm pressure (5 cm path length).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80
60
40
20
0
WAVENUMBER (CM^{-1})
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2500
2000
1800
1600
1400
1200
1000
800
600
400

Figure 1.

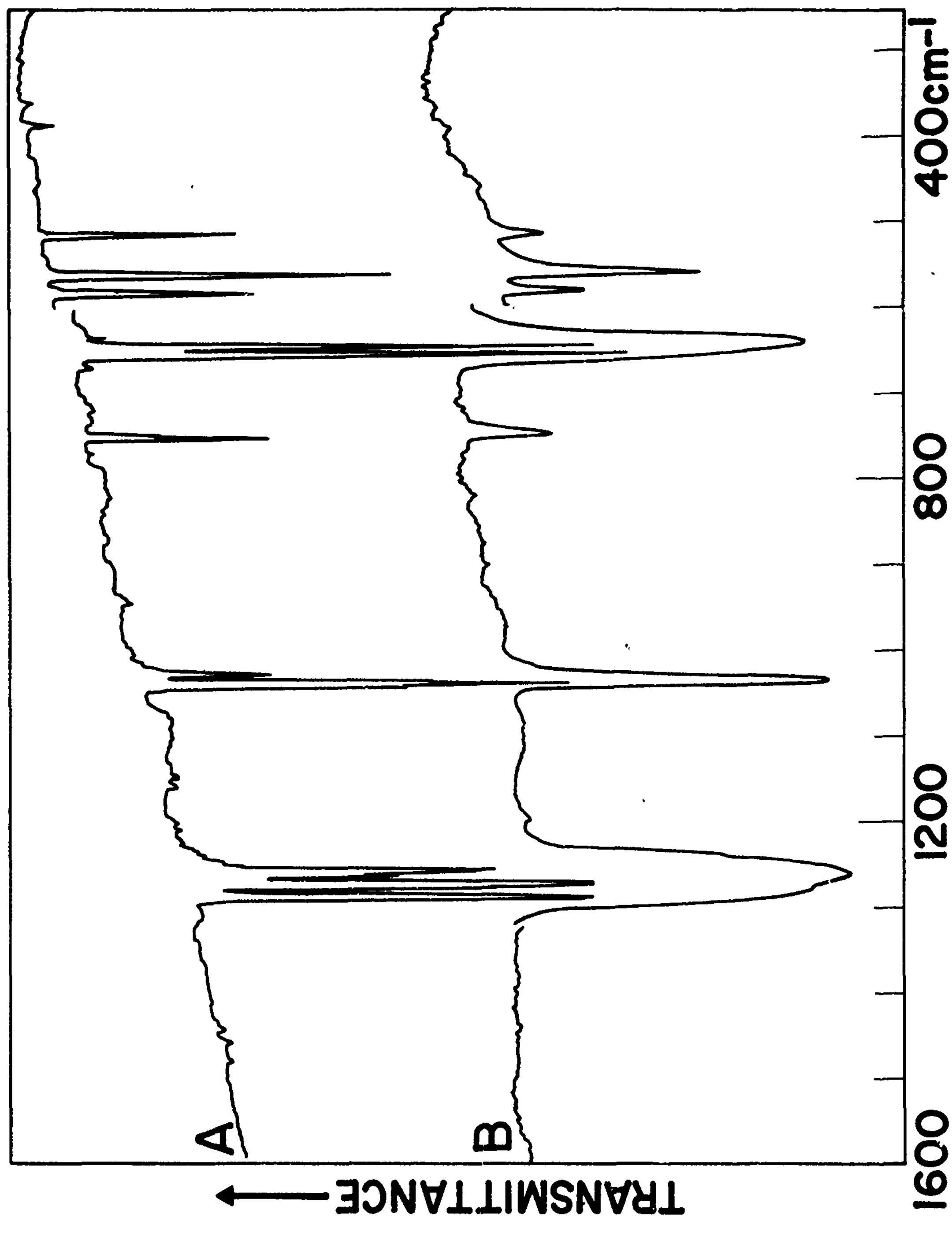
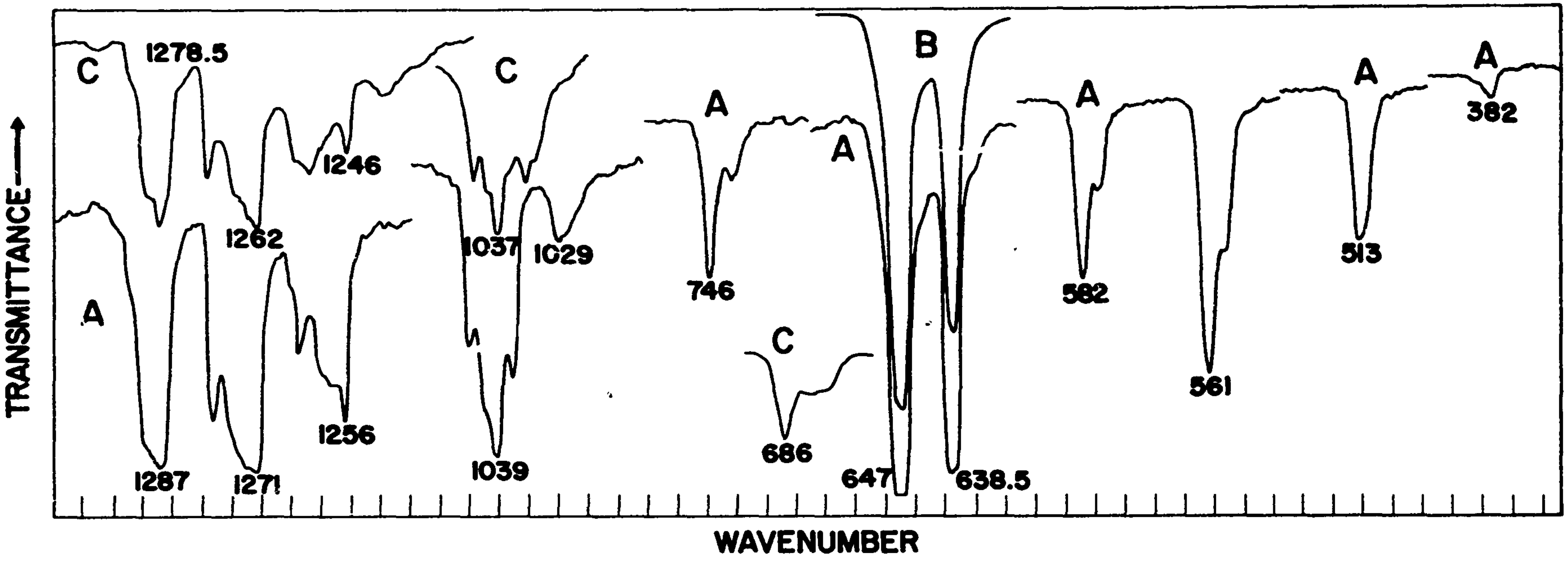


Figure 2.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WAVENUMBER
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1246
A
1287
1271
1256
C
1037
1029
1039
A
746
C
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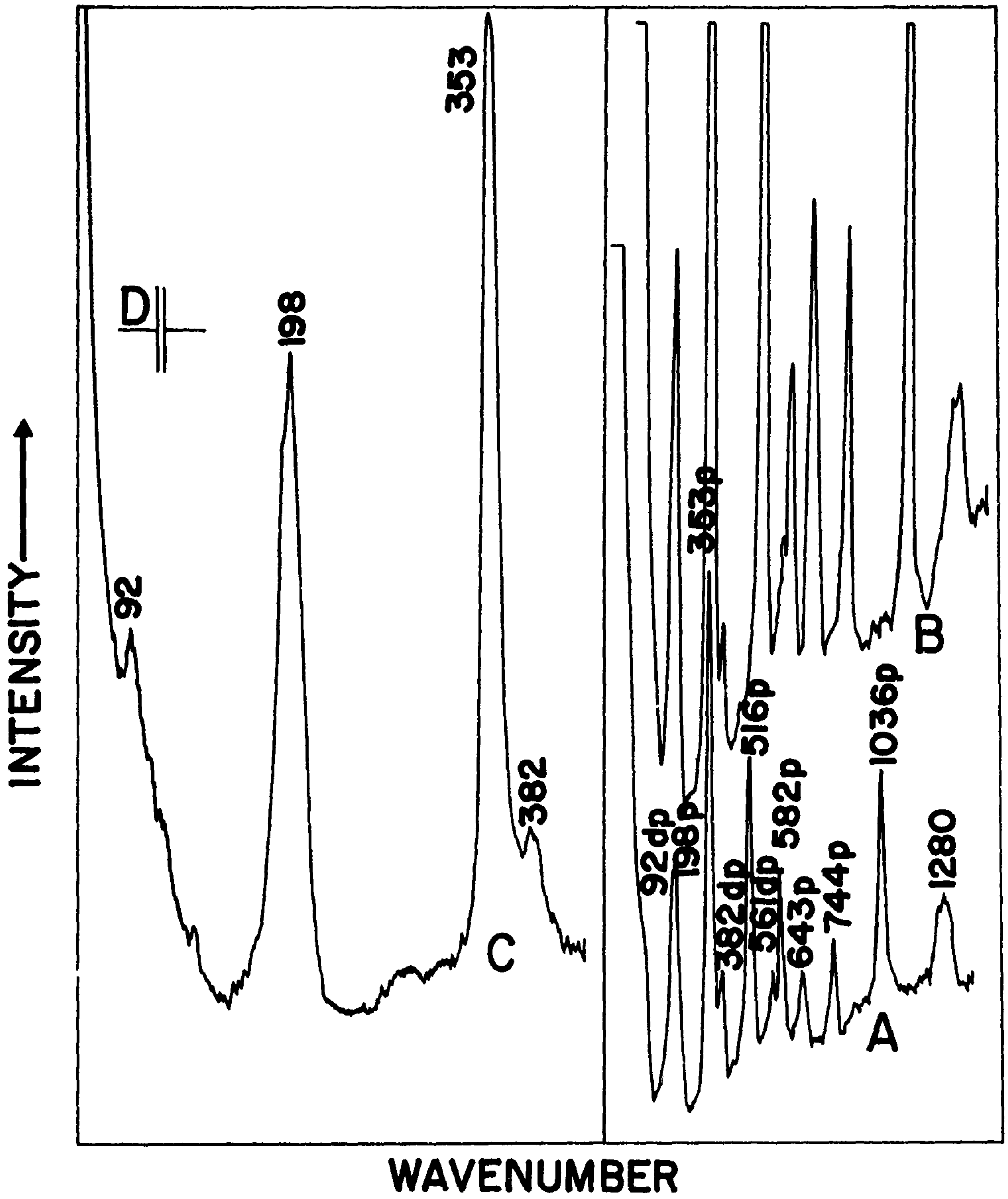
B
A
647
638.5
A
582
561
A
513
A
382

Figure 3.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WAVENUMBER
D
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198
353
382
C
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198p
353p
382dp
516p
561dp
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643p
744p
1036p
1280
A
B

Figure 4.

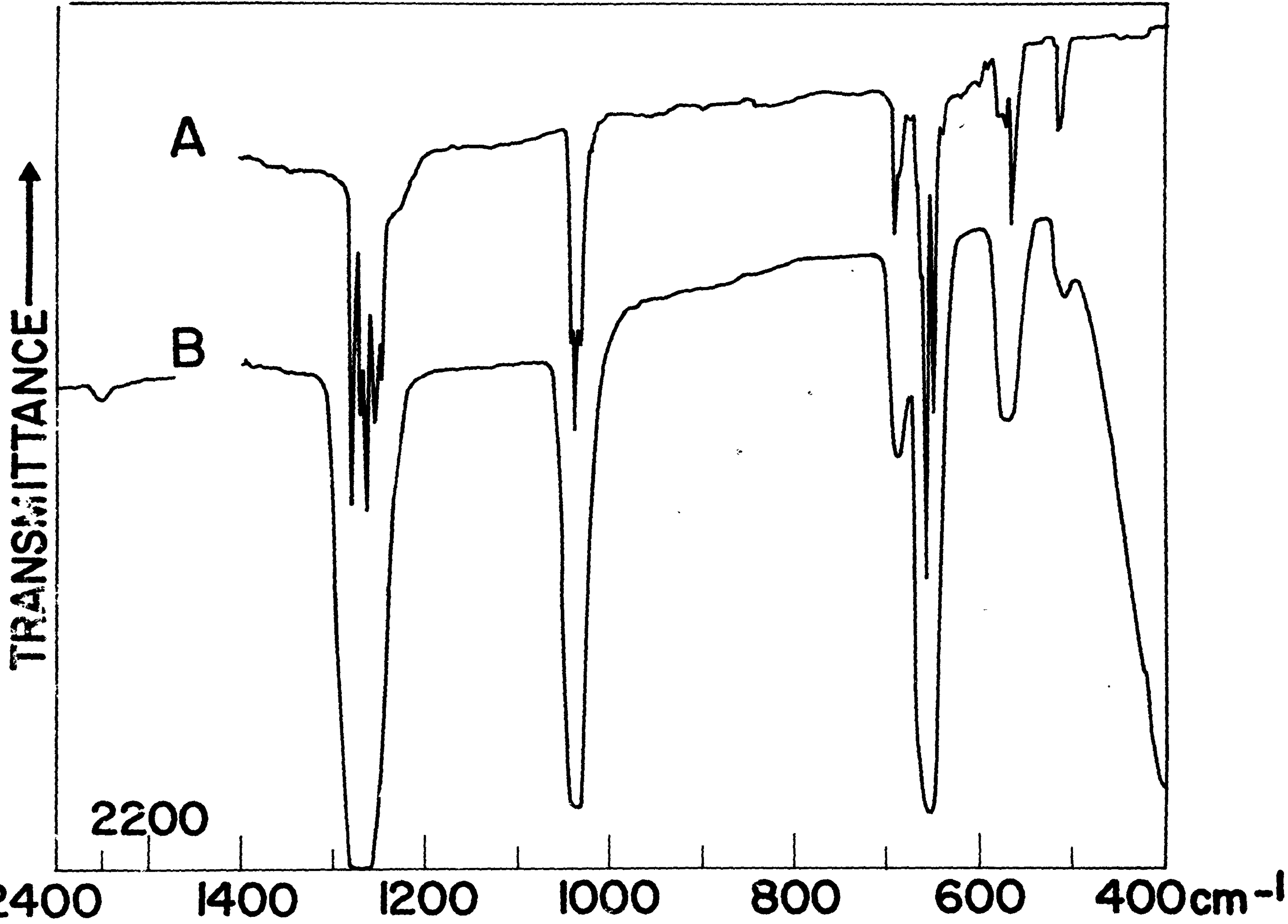


Figure 5.

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

Vibrational Spectra and Force Constants of the Square-Pyramidal Anions, SF_5^-, SeF_5^-, and TeF_5^-

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

Received ....

Abstract

The adducts of CsF with SeF_4 and SF_4 have been prepared and characterized by vibrational spectroscopy. The observed spectra closely resemble those of BrF_5 and ClF_5, respectively, indicating ionic structures with square-pyramidal anions of symmetry C_{4v}. Force constants have been computed for the series, SF_5^-, SeF_5^-, and TeF_5^-, and are compared to those of the isoelectronic ClF_5, BrF_5, and IF_5 molecules, respectively.

Introduction

The chalcogen tetrafluorides, SF_4, SeF_4, and 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 TeF_4 were studied (Ref. 7-9) in detail. These TeF_4·Lewis base adducts were shown (Ref. 7-9) to contain a TeF_5^- anion of symmetry C_{4v}. The existence of 1:1 adducts between 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 SF_4, Tullock, Coffman, and Muetterties (Ref. 12) successfully prepared a stable CsF·SF_4 adduct. Furthermore, Tunder and Siegel obtained (Ref. 11) evidence for a $(CH_3)_4NF\cdot SF_4$ adduct of marginal stability at ambient temperature.

No further information has been published on either the SF_4 or SeF_4 adducts. In this paper, we wish to report the vibrational spectra of the SeF_5^- and SF_5^- anions and their force constants. Since the vibrational spectra of the series of square-pyramidal molecules, ClF_5, BrF_5, and IF_5, are known (Ref. 13-15), it appeared particularly interesting to compare them with those of the isoelectronic series, SF_5^-, SeF_5^-, and TeF_5^-.

Experimental

Materials and Apparatus. Volatile materials used in this work were manipulated in a well passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows - seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise, Bourdon tube-type gage (0-1500 mm ± 0.1%). Selenium tetrafluoride was prepared by the method (Ref. 16) of Pitts and Jache from selenium powder and 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 Å. The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to $\sim -25^0$ and a d.c. 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. 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

$Cs^+SF_5^-$: A 30 ml prepassivated stainless steel cylinder was loaded with powdered CsF (36.2 mmol) and SF_4 (46.9 mmol). The adduct was formed by shaking the cylinder at room temperature for several days, followed by heating to 125° for several more days. On cooling to room temperature, the unreacted SF_4 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° and trapping the evolved gas at -196°. From 0.82 g of the adduct, 1.88 mmol of pure SF_4 was obtained, indicating a mixture of 48 mole % $Cs^+SF_5^-$ and 52 mole % CsF.

$Cs^+SeF_5^-$: Powdered CsF (13.1 mmol) was loaded into a prepassivated 30 ml stainless steel cylinder followed by SeF_4 (8.04 mmol). The cylinder was allowed to stand at room temperature overnight. Pumping on the cylinder revealed that all the SeF_4 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 % $Cs^+SeF_5^-$ and 39 mole % CsF.

Results and Discussion

Synthesis and Properties. The reaction conditions used for the synthesis of $Cs^+SeF_5^-$ were similar to those (Ref. 10) used by Aynsley, Peacock, and Robinson. Since the presence of some unreacted CsF was not expected to interfer with the spectroscopic investigation, no attempt was made to achieve complete conversion of CsF to $CsSeF_5$. 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 $CsF \cdot SF_4$ 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 $Cs^+SF_5^-$.

Vibrational Spectra. Figures 1 and 2 show the Raman and infrared spectrum, respectively, of the solid $CsF \cdot SeF_4$ adduct. Figures 3 and 4 show the corresponding spectra of solid $CsF \cdot SF_4$. 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 $CsF \cdot TeF_4$ (Refs. 7-9) were shown to be ionic, the same might be expected for the CsF adducts of SF_4 amd SeF_4. 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 C_{4v} similar to that of the isoelectronic halogen pentafluoride series (Ref. 13).

For a pentafluoro chalcogenate (IV) anion, XF_5^-, of symmetry C_{4v} nine fundamental vibrations should be observed. These are classified as $3A_1 + 2B_1 + B_2 + 3E$. All nine modes should be Raman active whereas only the A_1 and E modes should be infrared active. Table 1 lists the vibrational frequencies of the two isoelectronic series SF_5^-, SeF_5^-, TeF_5^- and ClF_5, BrF_5, IF_5. As can be seen from Table 1, the vibrational frequencies of the two series are very similar. In particular, the Raman spectra of SF_5^- and SeF_5^- are almost exact copies of the Raman spectra of ClF_5 and BrF_5, respectively (Ref. 13) disregarding the expected frequency decreases when going from the neutral molecules to the anions. Since the assignments for the halogen pentafluorides are well established (Refs. 13-15), the spectra of SF_5^- and SeF_5^- can be assigned (see Table 1) by complete analogy. For TeF_5^-, 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, ν_4, to a weak Raman band at 572 cm^{-1} , and the antisymmetric stretching vibration ν_7, to a strong Raman band at 472 cm^{-1}. Furthermore, this assignment results in ν_4 having a higher frequency than ν_2 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 ν_4 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 1

Vibrational Spectra of $Cs^+SF_5^-$, $Cs^+SeF_5^-$, and $Cs^+TeF_5^-$ and Their Assignment Compared to Those of Isoelectronic ClF_5, BrF_5, and IF_5

— Observed frequencies, cm^{-1}

$Cs^+SF_5^-$		$Cs^+SeF_5^-$		$Cs^+TeF_5^-$ [a]		ClF_5 [bc]		BrF_5 [b]		IF_5 [b]		Assignment in Point Group C_{4v}		Approximate Description of Vibration
Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman			
793s	790(3.7)	665vs	666(10)	618ms	611vs	708m	709(3)	683s	682(7)	710s	698(6)	A_1	ν_1	$\nu XF'$
520w,sh	519(2.7)	520sh	515(7.5)	[466vs,br]	504s	539w	538(1)	587m	570(10)	(595)[e]	593(10)		ν_2	$\nu_s XF_4$ in phase
463s	469sh	335s	332(3.2)	283m	282mw	495mw	[480(10)]	369s	365(2)	318m	315(1)		ν_3	$\delta_s XF_4$ umbrella
—	[432(10)][d]	—	460(7.0)	—	[472s]	—	[480(10)]	—	535(10)	—	575(8)	B_1	ν_4	$\nu_s XF_4$ out of phase
—	—	—	236(0.6)	—	—	—	—	—	—	—	—		ν_5	$\delta_{as} XF_4$ out of plane
—	338(1.6)	—	282(2.6)	—	231mw	—	375(1)	—	312(1)	—	273(2)	B_2	ν_6	$\delta_s XF_4$ in plane
565vs,br	564(0.6)	475vs,br	480sh	[466vs,br]	[472s]	~25vs	—	644vs	—	640vs		E	ν_7	$\nu_{as} XF_4$
430sh	[432(10)	396mw	399(1.9)	336m	338mw	484m	[480(10)]	415m	414(1)	372m	374(2)		ν_8	δ $F'XF_4$
(240)	241(1.2)		202(0.7)	164mw		299mw	296(0.4)		237(0+)		189(0+)		ν_9	$\delta_{as} XF_4$ in plane

(a) Data from Ref. 7

(b) Data from Ref. 13

(c) Data from Ref. 14

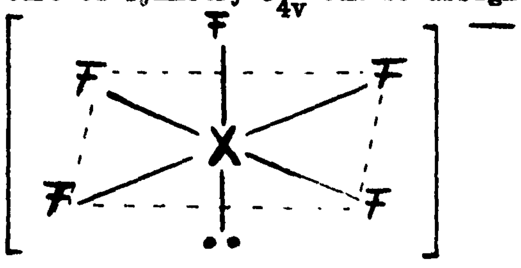
(d) Frequencies in brackets indicate coincidences with other modes, thus resulting in increased relative intensities

(e) Frequency estimated from combination bands

Comparison of the vibrational spectra of the XF_5^- series with those of the isoelectronic 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 XF_4 stretching mode, ν_4 (E), appears for all three anions as a very broad band which makes it difficult to accurately locate its band center. Since ν_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 SF_5^- and 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, ν_2 and ν_4, involving no motion of the central atom, show frequency values reflecting the trends in the stretching force constants. Whereas the stretching modes ν_1 and ν_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 SeF_5^- and TeF_5^- is the unusual occurrence of the antisymmetric XF_4 stretching mode, $\nu_7(E)$, at a frequency lower than that of the totally symmetric XF_4 stretching mode, $\nu_2(A_1)$. In SF_5^- the frequency value of ν_7 is only 45 cm^{-1} higher than that of ν_2. Since the mass of the central atom increases from SF_5^- towards TeF_5^- and since only the frequency of ν_7 is mass dependent, for SeF_5^- and TeF_5^- this frequency becomes lower than that of ν_2. A similar unusual occurrence of the symmetric out of phase stretching mode, $\nu_2(E_g)$, at a frequency higher than that of the totally symmetric $\nu_1(A_{1g})$ mode was recently established for the octahedral 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 SF_5^-, SeF_5^-, and TeF_5^- show that these anions are isostructural with ClF_5, BrF_5, and 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

	SF_5^{-a}	ClF_5^{b}	SeF_5^{-a}	BrF_5^{c}	TeF_5^{-d}	$IF_5^{b,e}$
R(Å)	1.62	1.62	1.68	1.68	1.86	1.75
r(Å)	1.72	1.72	1.78	1.78	1.95	1.86
β(°)	90	90	84.5	84.5	79.0	90

(a) Assumed values

(b) Values assumed in Ref. 13

(c) R. D. Burbank and F. N. Bensey, Jr., J. Chem. Phys., 27, 982 (1957).

(d) Ref. 9

(e) S. J. Cyvin, J. Brunvoll, and A. G. Robiette, J. Mol. Structure, 3, 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 β = 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.

	ClF_5	SF_5^-	BrF_5	SeF_5^-	IF_5	TeF_5^-
f_R	3.5 (0.5)	4.4 (0.5)	4.0 (0.5)	3.9 (0.5)	4.85 (0.5)	3.5 (0.5)
f_r	2.9 (0.5)	2.15 (0.5)	3.3 (0.5)	2.3 (0.5)	3.65 (0.5)	2.3 (0.4)
f_β	2.5 (0.5)	2.4 (0.5)	2.3 (0.5)	2.1 (0.5)	1.9 (0.3)	1.7 (0.3)
f_α	1.2 (0.1)	0.9 (0.3)	0.84 (0.3)	0.64 (0.3)	0.6 (0.2)	0.55 (0.2)
$f_{rr'}$	0.2 (0.3)		0.2 (0.3)		0.2 (0.2)	
$f_{\beta\beta'}$	1.0 (0.4)		0.4 (0.3)		0.3 (0.2)	
$f_{\alpha\alpha'}$	0 (0.2)		0 (0.2)		0.05 (0.2)	
f_{rr}	0.2 (0.2)		0.1 (0.2)		0.07 (0.2)	
$f_{\beta\beta}$	0 (0.2)		0.1 (0.2)		0 (0.2)	
$f_{R\beta}$	0.37 (0.4)		0 (0.2)		0 (0.2)	
$f_{r\beta}$	0.5 (0.4)		0 (0.2)		0 (0.2)	
$f_{r\beta''}$	- 0.4 (0.4)		0 (0.2)		0 (0.2)	
q^2	9647		2192		2013	

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* (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 Moieties. Those force constants not shown are approximately zero and their uncertainty estimates little reduced from the prior estimate.

	ClF_5	SF_5^-	BrF_5	SeF_5^-	IF_5	TeF_5^-
f_R	3.53 (0.4)	4.39 (0.4)	4.03 (0.2)	3.82 (0.2)	4.85 (0.2)	3.53 (0.2)
f_r	2.99 (0.2)	1.95 (0.3)	3.24 (0.14)	2.41 (0.15)	3.65 (0.12)	2.30 (0.11)
f_β	2.69 (0.3)	2.34 (0.3)	2.23 (0.12)	1.95 (0.11)	1.89 (0.15)	1.78 (0.17)
f_α	1.25 (0.2)	0.89 (0.2)	0.82 (0.13)	0.63 (0.13)	0.62 (0.11)	0.55 (0.12)
$f_{rr'}$	0.17 (0.2)		0.27 (0.14)		0.28 (0.10)	
$f_{\beta\beta'}$	0.98 (0.3)		0.32 (0.10)		0.38 (0.10)	
$f_{\alpha\alpha'}$	- 0.03 (0.2)		0.04 (0.12)		0.04 (0.11)	
f_{rr}	0.14 (0.09)		0.15 (0.03)		0.07 (0.14)	
$f_{\beta\beta}$	0.10 (0.2)		0.11 (0.05)		0.15 (0.13)	
$f_{R\beta}$	0.42 (0.15)		0 (0.16)		0 (0.2)	
$f_{r\beta}$	0.46 (0.3)		0.04 (0.2)		0.02 (0.2)	
$f_{r\beta''}$	0.35 (0.4)		0.20 (0.15)		- 0.03 (0.2)	
q^2	3495		147		501	

Table V. Comparison of the Force Constants (Units are Identical to Those of Table III) Found for the Pair of Molecules ClF_5 and SF_5^- Either Forcing Transferability (Set I) or Requiring a Perfect Fit (Set II).

	Set I		Set II	
	ClF_5	SF_5^-	ClF_5	SF_5^-
f_R	3.53	4.39	3.47	4.40
f_r	2.99	1.95	2.92	2.16
f_β	2.69	2.34	2.47	2.40
f_α	1.25	0.89	1.20	0.87
$f_{rr'}$	0.17		0	0.38
$f_{\beta\beta'}$	0.98		1.25	0.80
f_{rr}	0.14		0.16	0.23
$f_{\beta\beta}$	0.10		0	0
$f_{R\beta}$	0.42		0.35	0.37
$f_{r\beta}$	0.46		0	0.5
$f_{r\beta''}$	- 0.35		0	- 0.4

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 $f_{rr'}$ and $f_{\beta\beta'}$ are in accord with the expectations for three center bonds. The relatively small values of f_{rr}, $f_{\beta\beta}$, $f_{R\beta}$, and $f_{r\beta}$ 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 $f_{rr'}$ and $f_{\beta\beta}'$. For the pair, ClF_5 - SF_5^-, $f_{R\beta}$ 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 $f_{R\beta}$, $f_{r\beta}$, and $-f_{r\beta''}$ 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 $f_{R\beta}$ and $f_{r\beta}$ but not for a similarly large value of $f_{r\beta''}$. 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_r, 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 SF_5^- to 0.65 for TeF_5^-. This indicates strong contributions from semi-ionic 3c-4e p-σ 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 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 XF_5 Anions and Molecules

	SF_5^-	SeF_5^-	TeF_5^-	ClF_5[a]	BrF_5	IF_5
f_r	2.16	2.41	2.30	2.6 - 2.9	3.24	3.65
f_R	4.40	3.82	3.53	3.5 - 3.7	4.03	4.85
f_r/f_R	.49	.63	.65	.75 - .84	.80	.75

(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.

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Diagram Captions

Figure 1 - **Raman** spectrum of solid $Cs^{+}SeF_5^{-}$. Sample container, glass capillary. C indicates spectral slit width.

Figure 2 - Infrared spectrum of solid $Cs^{+}SeF_5^{-}$ as AgBr disk.

Figure 3 - **Raman** spectrum of solid $Cs^{+}SF_5^{-}$. Sample container, glass capillary.

Figure 4 - Infrared spectrum of solid $Cs^{+}SF_5^{-}$ as AgBr disk.

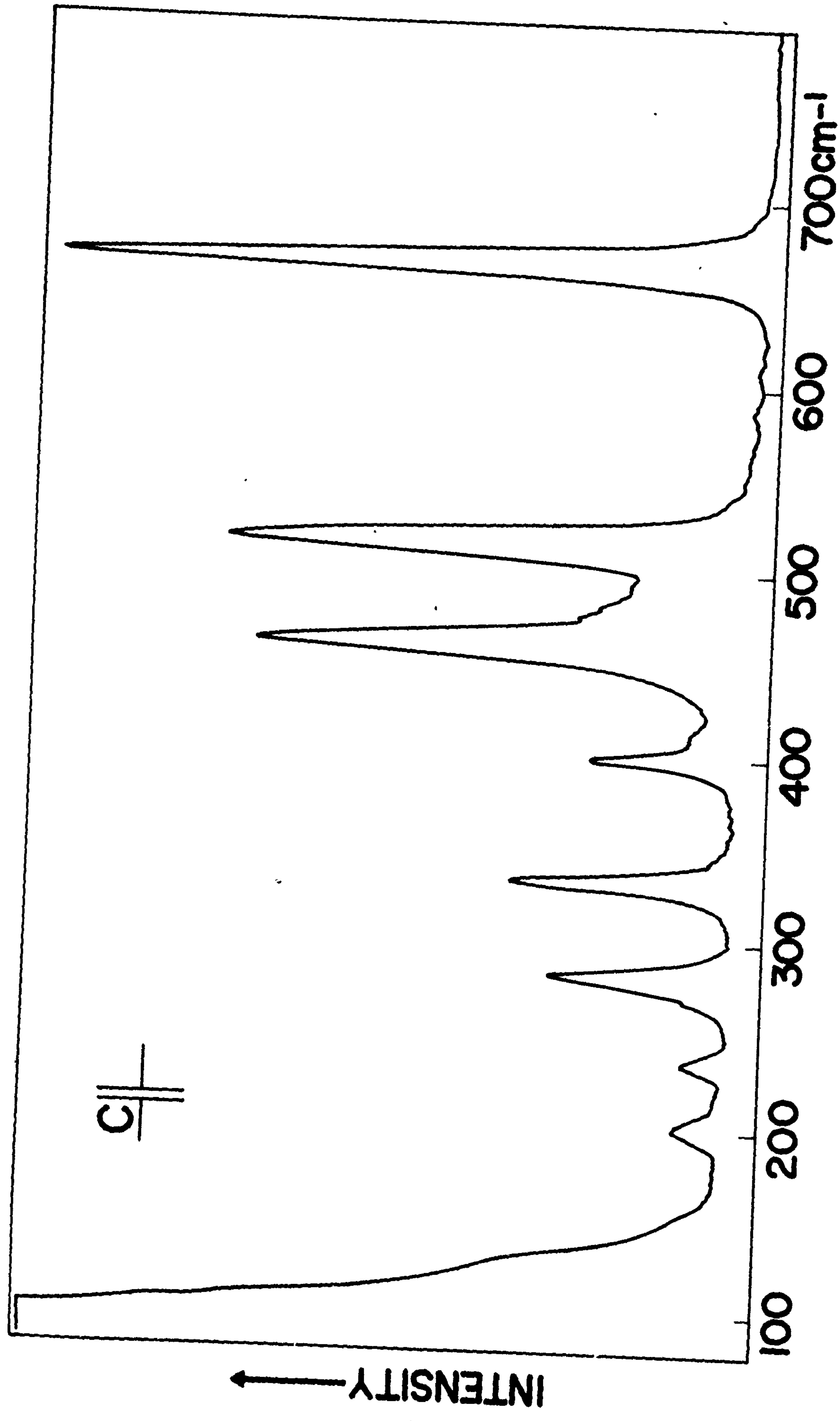

Figure 1.

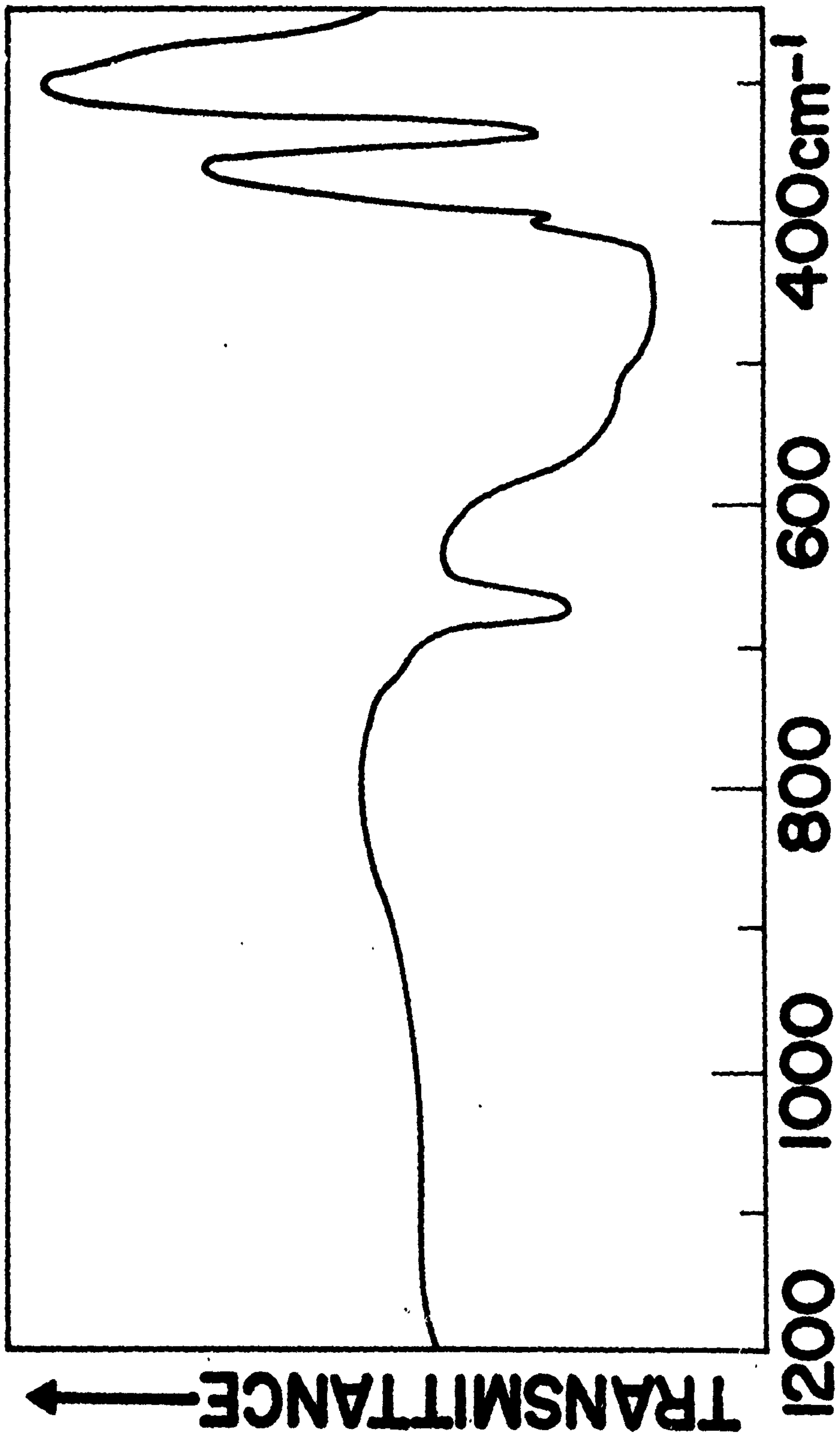

Figure 2.

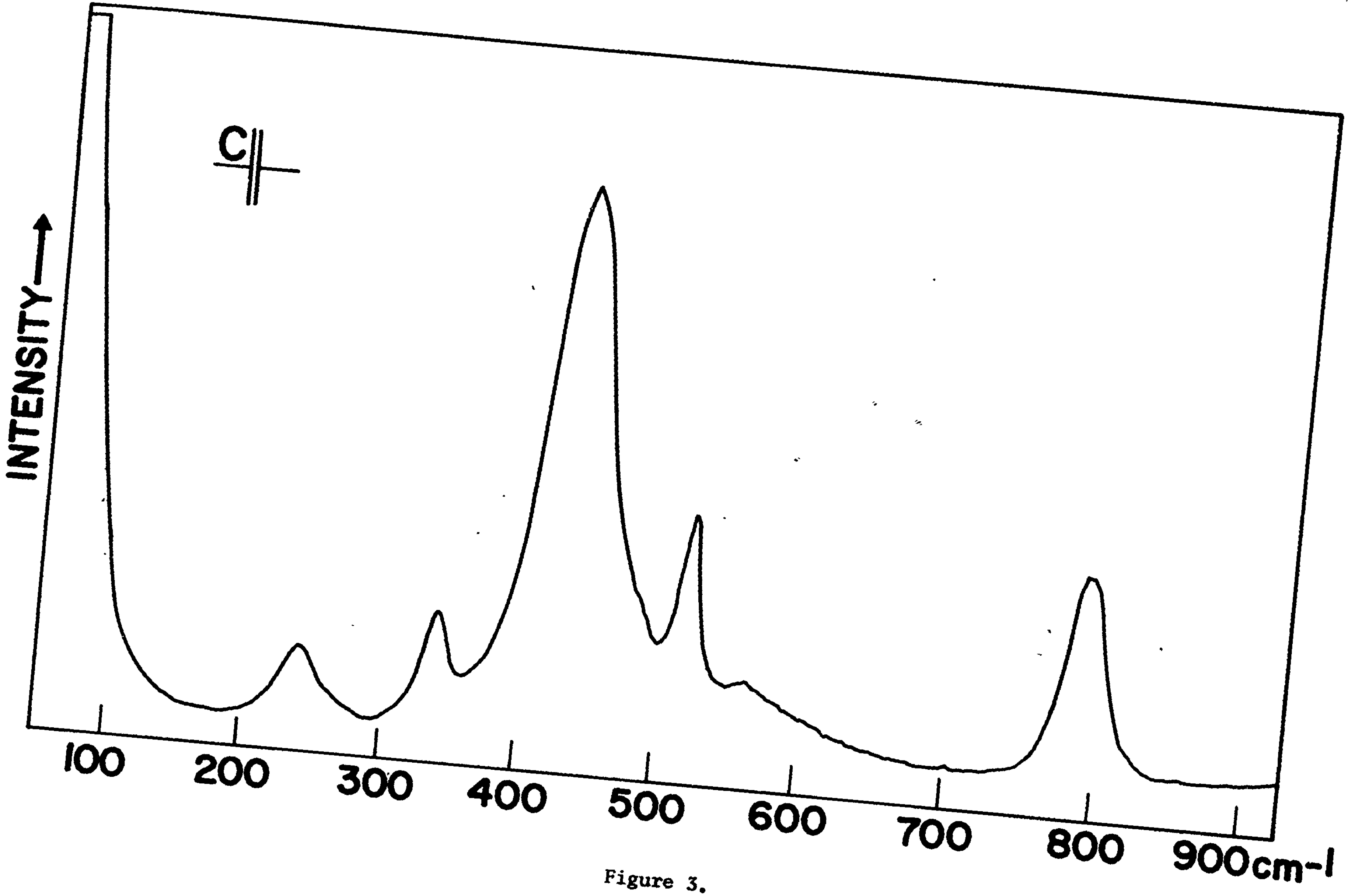

Figure 3.

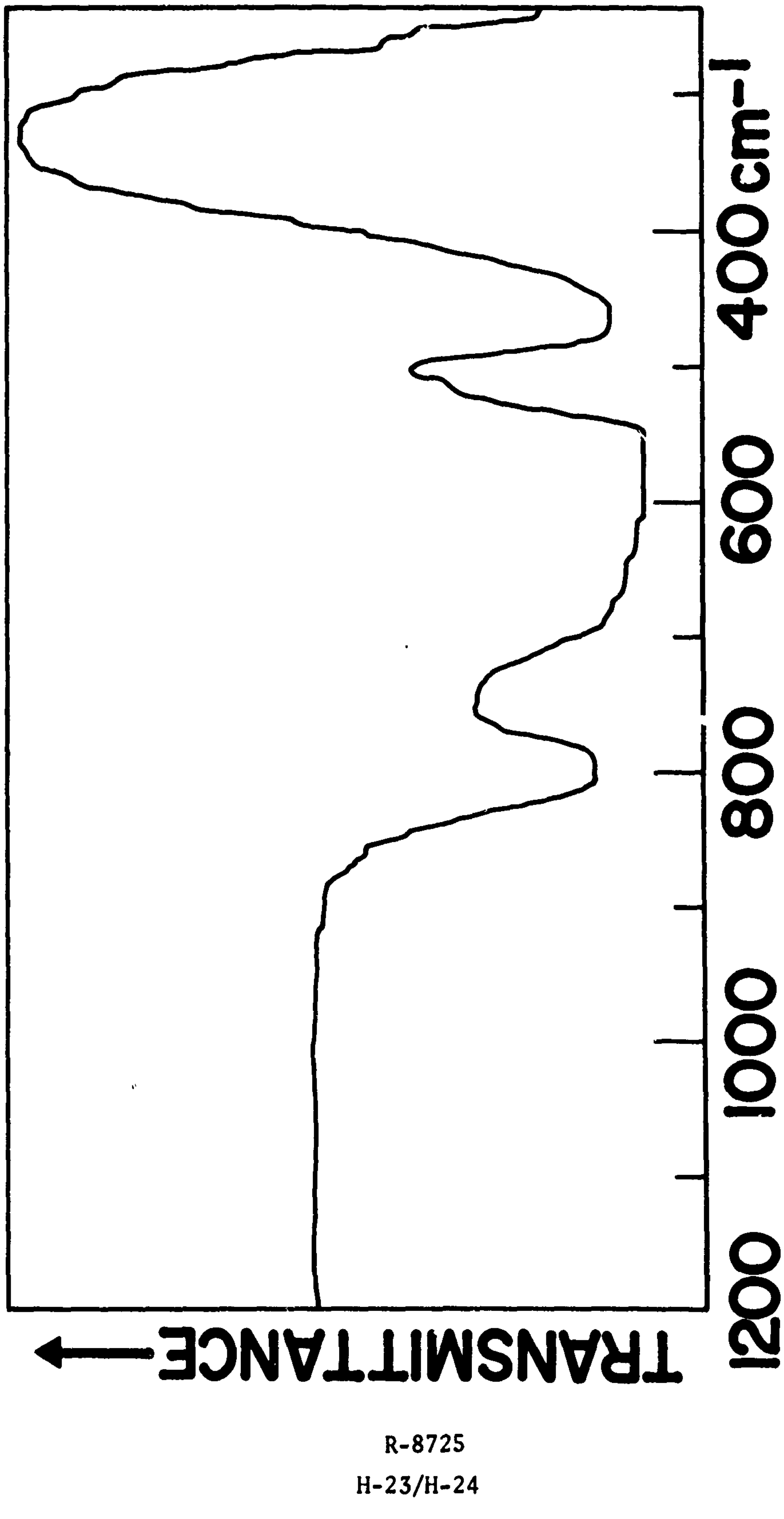

Figure 4.

APPENDIX I

THE CRYSTAL STRUCTURE OF $[BrF_4^+] [Sb_2F_{11}^-]$

The Crystal Structure of $[BrF_4]^+[Sb_2F_{11}]^-$

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Abstract

The crystal structure of the 1:2 adduct formed by BrF_5 and SbF_5 has been determined. The crystals consist of infinite chains of discrete BrF_4^+ and $Sb_2F_{11}^-$ ions coupled by relatively weak fluorine bridges and, accordingly, should be formulated as $[BrF_4]^+[Sb_2F_{11}]^-$. This is the first direct evidence for the existence of the BrF_4^+ ion. The crystals are monoclinic with most probable space group $P2_1/a$, lattice constants $\underline{a} = 14.19 \pm 0.03$, $\underline{b} = 14.50 \pm 0.03$, $\underline{c} = 5.27 \pm 0.01$, $\beta = 90.6 \pm 0.1°$, 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 $|F_o|$ greater than $\sigma(|F_o|)$.

Introduction

Previous investigations of solid halogen fluoride adducts have provided evidence that some are predominantly ionic[1-4] and others are predominantly covalent.[5-7] Infrared and Raman spectroscopic studies[4] of the 1:2 adduct[8] formed by BrF_5 and SbF_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[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 $BrF_5 \cdot 2SbF_5$ 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 ($\lambda = 0.7107$ Å) radiation. These data showed that the crystals have monoclinic symmetry. From the systematic extinctions, $h0\ell$ with h odd and $0k0$ 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 $\underline{a} = 14.19 \pm 0.03$, $\underline{b} = 14.50 \pm 0.03$, $\underline{c} = 5.27 \pm 0.01$ Å, $\beta = 90.6 \pm 0.1°$, and $V = 1085$ Å^3. Assuming that the unit cell contains four empirical formula units $BrSb_2F_{15}$ 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 $\underline{a}$ 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 β is near enough to 90° to cause no difficulty with the reciprocal lattice levels $h = 0\text{-}13$, the levels for which intensities were measured. In each of these levels, intensities were measured in the range $\sin \theta/\lambda \leqq 0.65$. 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 $|F_0(hk\ell)|$ 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 $BrSb_2F_{15}$ 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[11]. The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$. A modification of the Hughes[12] weighting procedure was used; for $|F_o| > 100$, $w = 100/|F_o|^2$; for $100 \geq |F_o| > 25$, $w = 1/100$; for $|F_o| \leq 25$, $w = 1/625$. Scattering factors were those for the neutral atoms given by Cromer and Waber[13]. The real parts of the anomalous dispersion corrections for bromine and antimony given by Cromer[14] were applied, but the imaginary parts were neglected.

The thermal parameters were kept isotropic until the agreement index $R = \Sigma||F_o| - |F_o||/\Sigma|F_o|$ 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 $|F_o|$ greater than $\sigma(=w^{-1/2})$. Including the 119 reflections having $|F_o|$ observable but less than σ, 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 $|F_o|$ 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 BrF_4^+ and $Sb_2F_{11}^-$ ions coupled by relatively weak fluorine bridges. Accordingly the compound should be formulated as $[BrF_4]^+[Sb_2F_{11}]^-$. This conclusion is based on the interatomic distances[15] 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 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 $Sb_2F_{11}^-$. 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 obviously that 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 the bromine atom 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 $[SeF_3]^+[Nb_2F_{11}]^-$.

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 100° for the axial and equatorial bonds, respectively, compared to 173 and 96° for BrF_4^+. The deviation of the bond angles of SeF_4 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 $Sb_2F_{11}^-$ 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 $Sb_2F_{11}^-$ 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 $[XeF]^+[Sb_2F_{11}]^-$ the two Sb-F bridge bonds were found to differ by less than 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.[2] In the present case, because of the relative weakness of the Sb(1)---F(12) bond, the $Sb_2F_{11}^-$ 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[18] that SbF_6^- forms with excess of SbF_5 not only $Sb_2F_{11}^-$, but also tri- and polymeric anions and that, in most cases, the additional SbF_5 molecules can be removed stepwise by controlled pyrolysis.[19]

The fluorine bridges which couple the BrF_4^+ and $Sb_2F_{11}^-$ 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 $[BrF_4]^+[Sb_2F_{11}]^-$ crystals resembles that proposed[18,20] for liquid SbF_5 and for $[Sb_nF_{5n+1}]^-$ ions in solutions. The nature of the fluorine bridges in the $[BrF_4]^+[Sb_2F_{11}]^-$ 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.[1] In $[BrF_4]^+[Sb_2F_{11}]^-$ 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 $[XeF]^+[Sb_2F_{11}]^-$. In $[BrF_4]^+[Sb_2F_{11}]^-$ the atoms Br, Sb(1), Sb(2), F(1), F(2), F(4), F(5), F(7), F(8), 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 $\vec{c}$ 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 BrF_4^+ 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

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TABLE 1

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD ERRORS

	$10^4x(10^4\sigma_x)$	$10^4y(10^4\sigma_y)$	$10^4z(10^4\sigma_z)$	$B(\sigma_B)$
Br	219(4)	1478(5)	3015(10)	2.85Å[a]
Sb(1)	1510(4)	6492(5)	932(7)	4.29[a]
Sb(2)	3149(4)	8532(3)	3945(9)	3.30[a]
F(1)	997(30)	613(28)	4069(63)	5.06(1.05)
F(2)	4293(33)	674(30)	47(65)	5.50(1.14)
F(3)	2837(34)	1482(37)	1562(66)	6.55(1.22)
F(4)	4191(31)	2414(26)	654(54)	4.70(1.01)
F(5)	1171(23)	2525(19)	4841(49)	3.21(0.74)
F(6)	2706(27)	3450(26)	3530(51)	4.15(0.88)
F(7)	997(44)	4405(41)	4796(92)	7.89(1.69)
F(8)	4435(22)	4285(18)	1386(43)	2.81(0.70)
F(9)	2245(33)	5733(28)	2641(68)	5.73(1.19)
F(10)	806(53)	6322(52)	3657(99)	9.42(2.17)
F(11)	4049(34)	6454(38)	4(75)	6.55(1.24)
F(12)	2355(33)	7615(27)	2330(62)	5.07(1.18)
F(13)	541(33)	8389(29)	4292(62)	5.47(1.17)
F(14)	3988(36)	8298(29)	959(67)	6.13(1.36)
F(15)	2480(26)	9409(24)	1989(54)	3.99(0.85)

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[a] Calculated from the following anisotropic thermal parameters (estimated standard errors are given in parenthesis):

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Br	33(8)	20(2)	535(23)	-1(3)	-42(6)	-2(10)
Sb(1)	78(9)	38(2)	366(13)	-2(3)	-24(5)	-3(7)
Sb(2)	32(8)	25(2)	655(16)	4(4)	39(4)	-3(9)

The β_{ij} are for the expression $\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}\ell^2+2\beta_{12}hk+2\beta_{13}h\ell+2\beta_{23}k\ell)]$.

TABLE 3

INTERATOMIC DISTANCES AND BOND ANGLES

a) Br environment					
Br-F(1)	1.76±0.12Å	F(1)-F(8)	2.62±0.15Å	∠F(1)-Br-F(8)	95.5±5.0°
Br-F(8)	1.78±0.09	F(1)-F(13)	2.76±0.18	∠F(1)-Br-F(13)	101.9±5.5
Br-F(13)	1.80±0.12	F(1)-F(11)	2.47±0.17	∠F(1)-Br-F(11)	84.6±5.9
Br-F(11)	1.91±0.13	F(8)-F(13)	2.62±0.12	∠F(8)-Br-F(13)	94.0±4.9
average 1.81		F(8)-F(11)	2.52±0.17	∠F(8)-Br-F(11)	85.9±5.3
		F(1)-F(5)	2.81±0.14	∠F(1)-Br-F(5)	88.5±4.5
Br-F(5)	2.24±0.10	average 2.60		average 92.4°	
Br-F(4)	2.49±0.11				
		F(8)-F(4)	2.76±0.14	∠F(8)-Br-F(4)	78.5±3.9
		F(13)-F(5)	2.81±0.17	∠F(13)-Br-F(5)	87.3±4.7
		F(13)-F(4)	3.04±0.14	∠F(13)-Br-F(4)	88.4±4.8
∠F(1)-Br-F(4)	168.5±4.2°	F(11)-F(5)	3.00±0.16	∠F(11)-Br-F(5)	92.2±5.1
∠F(8)-Br-F(5)	175.4±3.5	F(11)-F(4)	3.01±0.20	∠F(11)-Br-F(4)	85.2±5.3
∠F(11)-Br-F(13)	173.5±6.1	F(5)-F(4)	3.56±0.14	∠F(5)-Br-F(4)	97.2±3.7
b) Sb(1) environment				average 88.2°	
Sb(1)-F(3)	1.62±0.12Å	F(3)-F(2)	2.51±0.20Å	∠F(3)-Sb(1)-F(2)	97.7±6.6°
Sb(1)-F(2)	1.72±0.14	F(3)-F(9)	2.47±0.16	∠F(3)-Sb(1)-F(9)	93.9±6.5
Sb(1)-F(9)	1.76±0.13	F(3)-F(4)	2.40±0.19	∠F(3)-Sb(1)-F(4)	87.1±6.2
Sb(1)-F(10)	1.77±0.18	F(3)-F(12)	2.64±0.16	∠F(3)-Sb(1)-F(12)	87.9±6.2
Sb(1)-F(4)	1.86±0.11	F(2)-F(9)	2.59±0.20	∠F(2)-Sb(1)-F(9)	96.3±6.5
Sb(1)-F(12)	2.15±0.12	F(2)-F(10)	2.17±0.22	∠F(2)-Sb(1)-F(10)	76.8±8.1
average 1.81		F(2)-F(4)	2.55±0.16	∠F(2)-Sb(1)-F(4)	90.7±5.5
		F(9)-F(10)	2.28±0.25	∠F(9)-Sb(1)-F(10)	80.5±8.0
		F(9)-F(12)	2.74±0.18	∠F(9)-Sb(1)-F(12)	88.4±5.4
∠F(2)-Sb(1)-F(12)	172.4±6.1	F(10)-F(4)	2.77±0.20	∠F(10)-Sb(1)-F(4)	99.2±7.8
∠F(3)-Sb(1)-F(10)	171.5±10.2	F(10)-F(12)	2.98±0.25	∠F(10)-Sb(1)-F(12)	98.3±7.7
∠F(9)-Sb(1)-F(4)	172.7±5.8	F(4)-F(12)	2.70±0.20	∠F(4)-Sb(1)-F(12)	84.5±6.3
		average 2.57		average 90.1°	

TABLE 3, CONTINUED

c) Sb(2) environment

Sb(2)-F (6)	1.81 ± 0.10Å
Sb(2)-F (5)	1.86 ± 0.09
Sb(2)-F (7)	1.87 ± 0.18
Sb(2)-F(15)	1.89 ± 0.10
Sb(2)-F(12)	1.94 ± 0.12
Sb(2)-F(14)	2.01 ± 0.13
average 1.90	

∠F(5)-Sb(2)-F(15)	166.7 ± 4.0°
∠F(6)-Sb(2)-F(14)	165.6 ± 5.2
∠F(7)-Sb(2)-F(12)	173.8 ± 6.3

F (6)-F (5)	2.65 ± 0.14Å
F (6)-F (7)	2.88 ± 0.22
F (6)-F(15)	2.76 ± 0.13
F (6)-F(12)	2.50 ± 0.13
F (5)-F (7)	2.74 ± 0.18
F (5)-F(12)	2.56 ± 0.17
F (5)-F(14)	2.49 ± 0.13
F (7)-F(15)	2.73 ± 0.18
F (7)-F(14)	2.75 ± 0.20
F(15)-F(12)	2.61 ± 0.14
F(15)-F(14)	2.74 ± 0.18
F(12)-F(14)	2.63 ± 0.19
average 2.67	

∠F (6)-Sb(2)-F (5)	92.5 ± 4.3°
∠F (6)-Sb(2)-F (7)	102.7 ± 6.0
∠F (6)-Sb(2)-F(15)	96.3 ± 4.8
∠F (6)-Sb(2)-F(12)	83.5 ± 4.7
∠F (5)-Sb(2)-F (7)	94.4 ± 5.9
∠F (5)-Sb(2)-F(12)	84.8 ± 5.1
∠F (5)-Sb(2)-F(14)	80.1 ± 4.5
∠F (7)-Sb(2)-F(15)	93.3 ± 5.8
∠F (7)-Sb(2)-F(14)	90.3 ± 6.4
∠F(15)-Sb(2)-F(12)	86.3 ± 4.4
∠F(15)-Sb(2)-F(14)	89.1 ± 4.9
∠F(12)-Sb(2)-F(14)	83.5 ± 5.2
average 89.7°	

d) Bridge bond angles

∠Br-F(4)-Sb(1)	174.1 ± 6.4°
∠Br-F(5)-Sb(2)	170.8 ± 5.0
∠Sb(1)-F(12)-Sb(2)	173.0 ± 6.4

e) Non-bonded intra-chain distances

F(1)-F (9)	3.03 ± 0.16Å
F(2)-F (7)	3.47 ± 0.20
F(8)-F(15)	3.24 ± 0.14

Figure Captions

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 $|F_o|$. 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 $[BrF_4]^+[Sb_2F_{11}]^-$ crystals.[21]

Figure 2. Stereoscopic view to show the packing arrangement in $[BrF_4]^+[Sb_2F_{11}]^-$ crystals.[21] The viewing direction is normal to the 001 planes.

TABLE 2

h = 0

k	l	|F₀|	F_c
2	0	C	-176
4	0	5	-634
6	0	228	230
8	0	118	101
10	0	5	-964
12	0	80	72
14	0	249	165
16	0	87	-73
18	0	53	-53
[illegible]	[illegible]	[illegible]	[illegible]

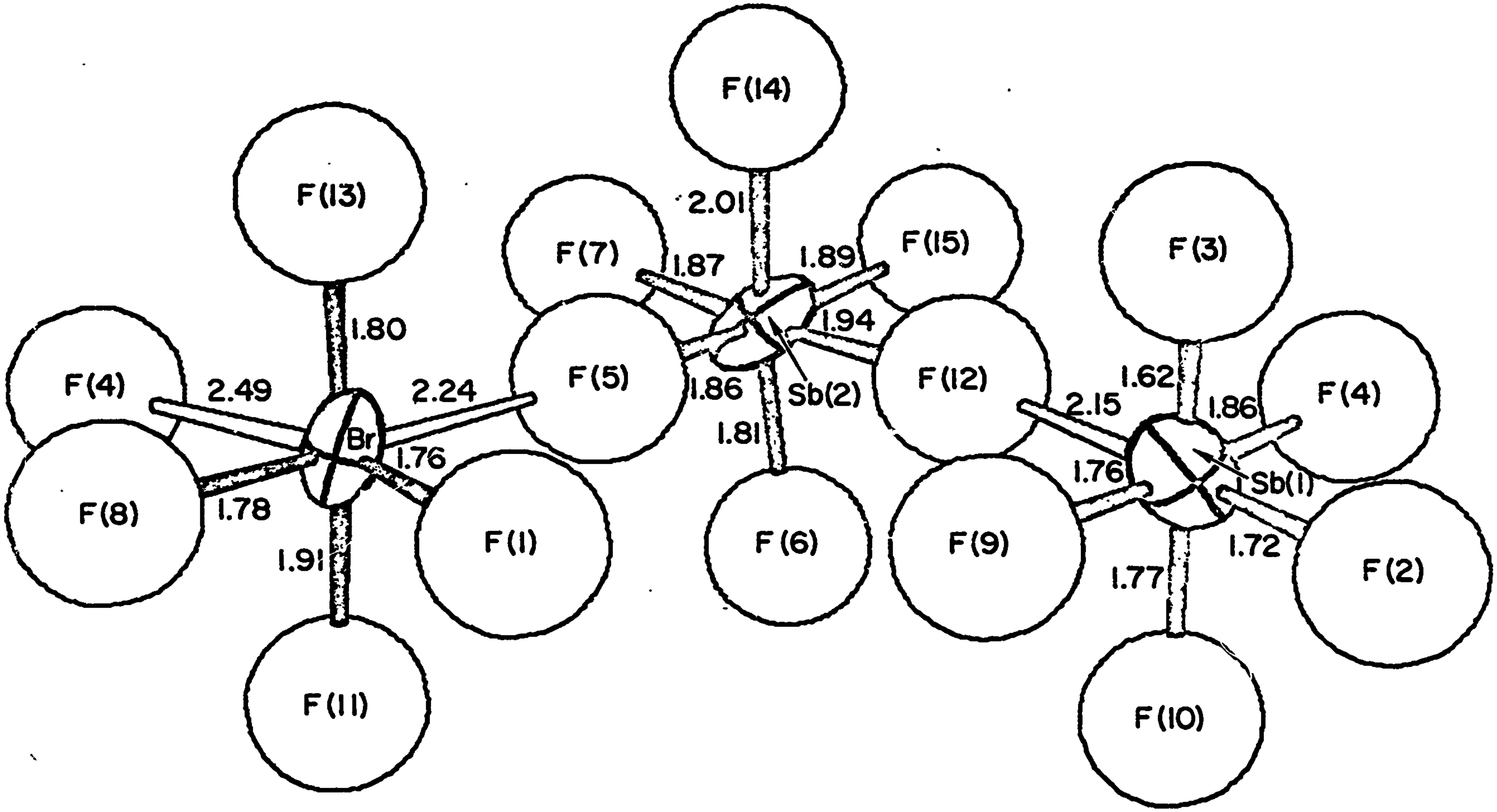
F(13)
F(4)
F(8)
Br
F(1)
F(11)
2.49
1.80
2.24
1.76
1.78
1.91
F(14)
F(7)
F(5)
F(15)
F(12)
F(6)
Sb(2)
2.01
1.87
1.89
1.94
1.86
1.81
F(3)
F(4)
F(9)
F(2)
F(10)
Sb(1)
1.62
1.86
2.15
1.76
1.72
1.77

Figure 1.

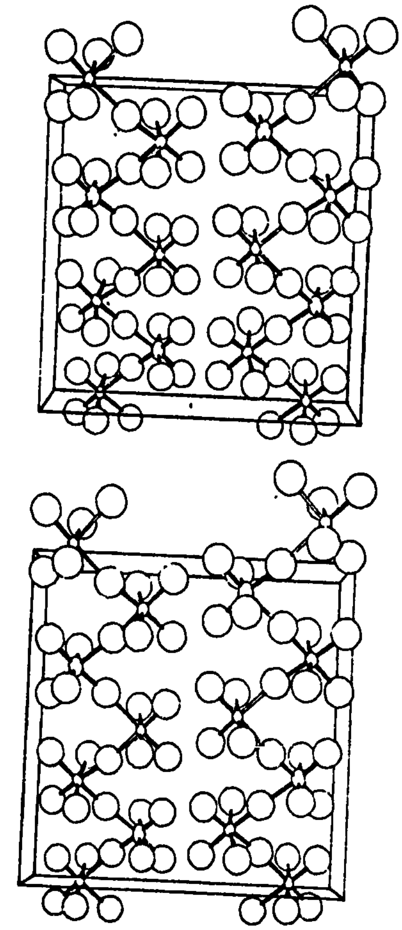

Figure 2.

APPENDIX J

LASER RAMAN SPECTRUM OF $NF_4^+AsF_6^-$

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

LASER RAMAN SPECTRUM OF $NF_4^+AsF_6^-$

By K. O. Christe* and D. Pilipovich

Received February 1, 1971

The preparation[1-4] and the vibrational spectrum[5] of $NF_4^+AsF_6^-$ have previously been reported. It was shown that the NF_4^+ cation is tetrahedral.[1-5] Out of the four fundamental vibrations of 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 $NF_4^+AsF_6^-$ (see Figure 1, trace A). It is shown that ν_1 (A_1) and ν_2 (E) of NF_4^+ occur at 847 and 445 cm^{-1}, respectively. The value of 847 cm^{-1} for ν_1 (A_1) is close to those of 844 and 836 cm^{-1} deduced from the infrared active[5] 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 mdyne/Å. Adopting for the F_2 block the previously reported values,[5] the internal force constants of 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, CF_4 and 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 NF_4^+. A detailed discussion of the trends observed within this isoelectronic series has previously been given.[5]

TABLE I.

Force Constants of the Isoelectronic Series, NF_4^+, CF_4, BF_4^- (mdynes/Å)

	NF_4^+	CF_4 (a)	BF_4^- (a)
f_r	6.22	6.93	4.87
f_{rr}	0.60	0.77	0.62
$f_\alpha - f_{\alpha\alpha'}$	0.98	1.02	0.72
$f_{\alpha\alpha} - f_{\alpha\alpha'}$	0.12	0.16	0.13
$f_{r\alpha} - f_{r\alpha'}$	0.77	0.57	0.43

(a) H. Siebert, " Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie", Springer Verlag, Berlin, 1966, pg. 69.

The sample used for the present investigation was prepared by the high pressure-temperature method.[4] However, contrary to previous reports[4], 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 $NF_4^+AsF_6^-$, 5.8 Ni $(AsF_6)_2$, and 1.0 $Cu(AsF_6)_2$. Its vibrational spectrum is depicted by traces A in Figures 1 and 2 and shows the bands expected for the tetrahedral NF_4^+ and the approximately octahedral 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 AsF_6^- and tetrahedral NF_4^+, have strongly increased in relative intensity. Therefore, these additional bands must be attributed to the presence of the metal salts.[7] Furthermore, the previous reports[4] on the hydrolysis of NF_4^+ were confirmed in that NF_3 and O_2 were quantitatively evolved in a 2:1 mole ratio, and no evidence for the formation of nitrogen oxides or oxyfluorides[3] was found.

Experimental Section

Materials and Apparatus. - The materials used in this work were manipulated in a well-passivated (with ClF_3) 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 ± 0.1%). Nitrogen trifluoride (Air Products) and AsF_5 (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°, 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 $NF_4^+AsF_6^-$. Nitrogen trifluoride (180 mmole), AsF_5 (180 mmole), and F_2 (360 mmole) were heated in a passivated 150 ml Monel cylinder under autogenous pressure to 125° 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 %) NF_4AsF_6, 5.8 $Ni(AsF_6)_2$, 1.0 $Cu(AsF_6)_2$: N, 4.50; Ni, 1.21; Cu, 0.22; As, 27.50; total F, 66.59; hydrolyzable F, 6.11; NF_3:O_2 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; NF_3:O_2, 2.01:1. II, Found: N, 2.14; Ni, 2.95; Cu, 2.37; As, 28.0; NF_3:O_2, 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 (NF_3 + O_2) was measured volumetrically, then NF_3 was separated from O_2 by fractional condensation at -210°, 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 $Th(NO_3)_4$ 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 (Na_2O_2 + starch).

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3. J. P. Guertin, K. O. Christe, and A. E. Pavlath, Inorg. Chem., 5, 1921 (1966).

4. W. E. Tolberg, R. T. Rewick, R. S. Stringham, and M. E. Hill, ibid., 6, 1156 (1967).

5. K. O. Christe, J. P. Guertin, A. E. Pavlath, and W. Sawodny, ibid., 6, 533 (1967).

6. W. Sawodny, A. Fadini, and K. Ballein, Spectrochim. Acta, 21, 995 (1965).

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 $As_2F_{11}^-$ anion in more detail. Solutions of the salt in HF showed only the ^{19}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 $As_2F_{11}^-$. When CH_3CN 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 $As_2F_{11}^-$ lines was obtained. Attempts to prepare $Cs^+As_2F_{11}^-$ 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 $As_2F_{11}^-$ salts (Dean et al., Chem. Comm. 990 (1969)), the presence of a stable $As_2F_{11}^-$ salt in our sample appears unlikely.

Diagram Captions

Figure 1. Replotted Raman spectra of solid $NF_4^+AsF_6^-$ 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 $NF_4^+AsF_6^-$. Samples of traces A (AgBr pellet) and B (dry powder between AgCl plates) are identical to those of Figure 1.

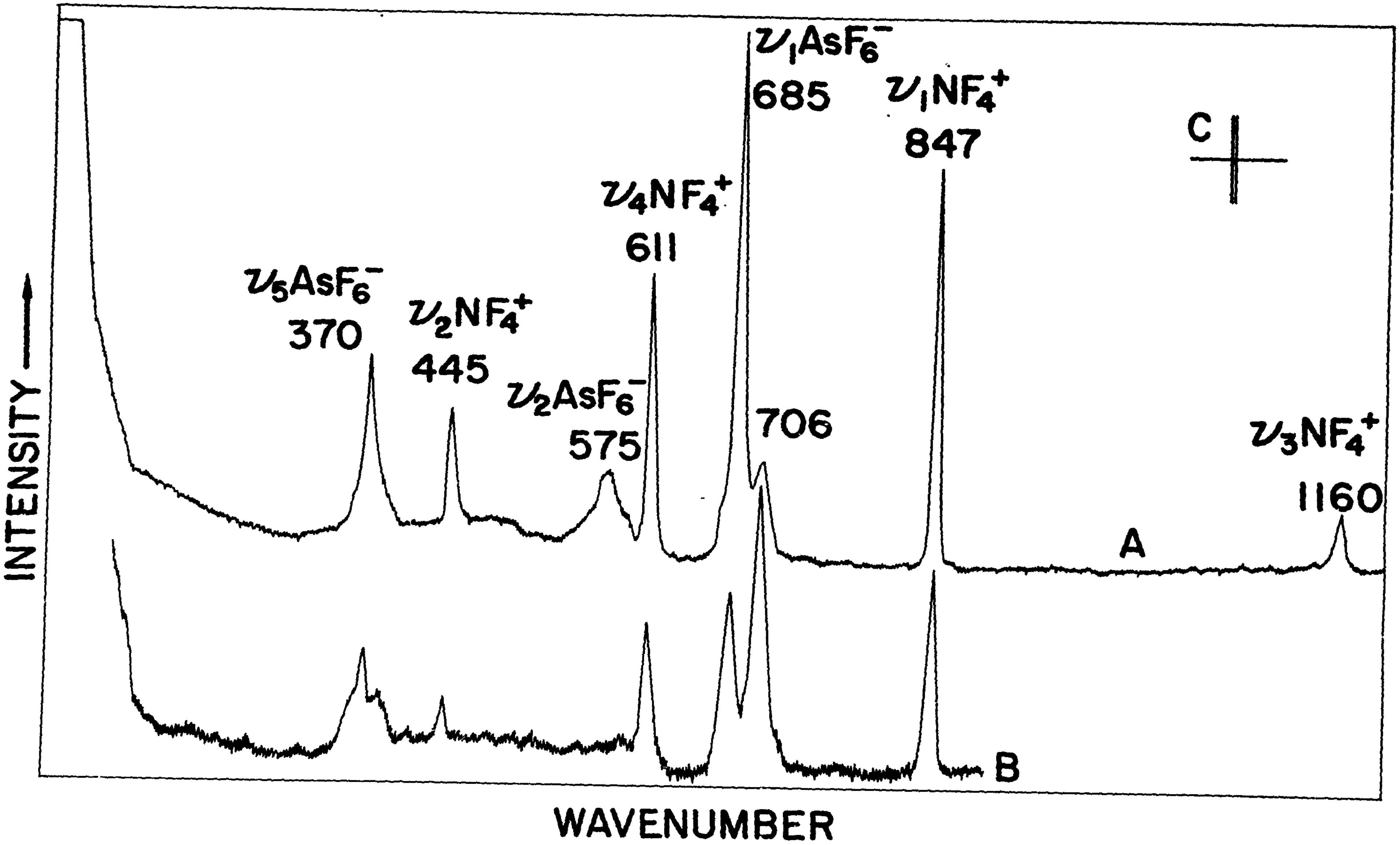
$\nu_1 AsF_6^-$
685
$\nu_1 NF_4^+$
847
C
$\nu_4 NF_4^+$
611
$\nu_5 AsF_6^-$
370
$\nu_2 NF_4^+$
445
$\nu_2 AsF_6^-$
575
706
$\nu_3 NF_4^+$
1160
A
B
INTENSITY
WAVENUMBER

Figure 1.

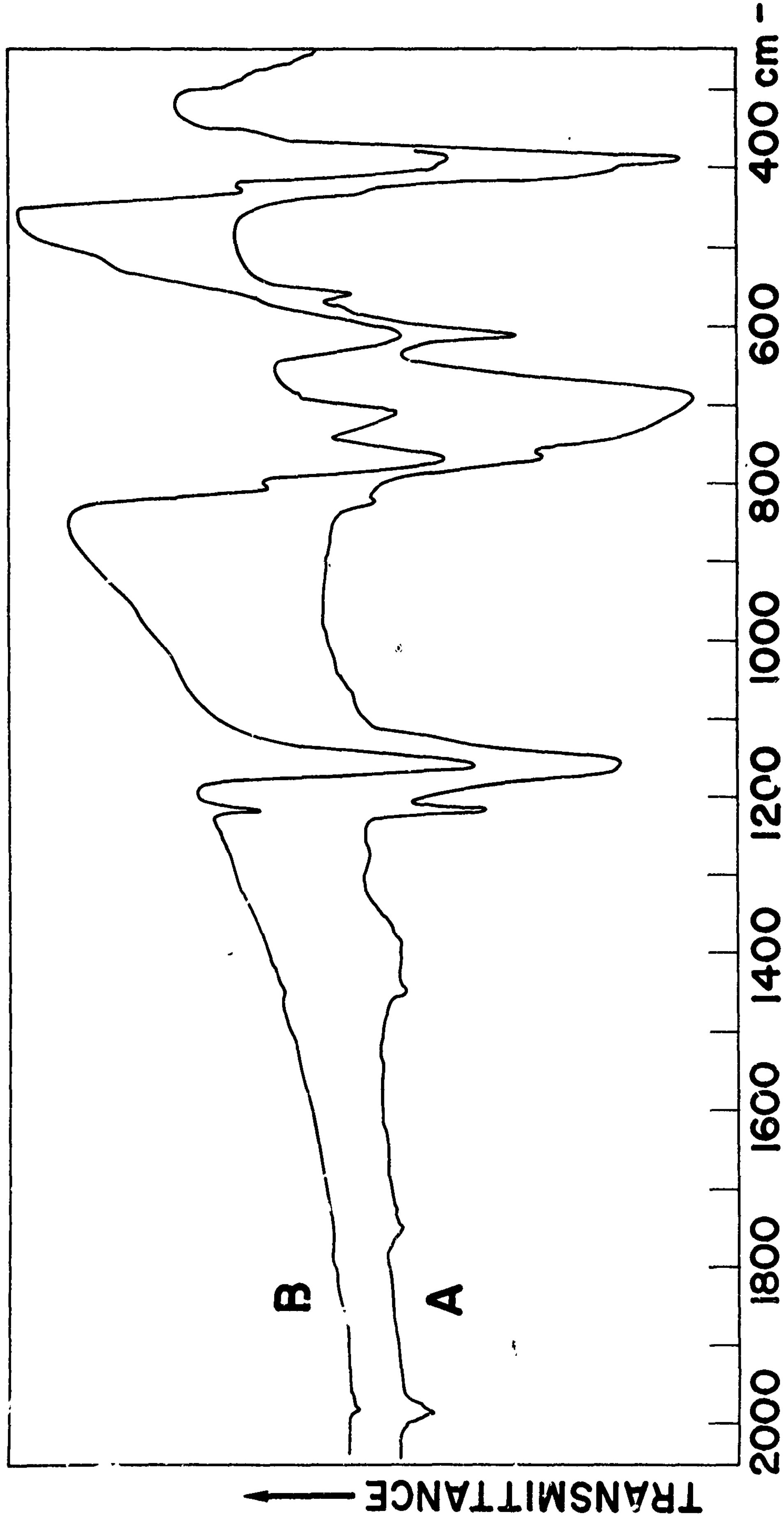
400 cm⁻¹
600
800
1000
1200
1400
1600
1800
2000
B
A
TRANSMITTANCE

Figure 2.