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INORGANIC HALOGEN OXIDIZER RESEARCH

Karl O. Christe, et al

Rocketdyne

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Synthesis of novel ClF_3O_2 was scaled up and its physical properties were determined. Force constants and thermodynamic properties were computed. Its complex formation with strong Lewis acids was studied and two new salts, $ClF_2O_2^+BF_4^-$ and $ClF_2O_2^+AsF_6^-$, were synthesized.

The ClF_5–OF_2 photolysis yielded no ClF_5O and the BrF_5–OF_2 system produced no BrF_3O or BrF_5O. Reaction parameters for the synthesis of ClF from Cl_2 and ClF_3 were determined.

Reactions of PtF_6 with OF_2, O_3, BrF_5, ClF_3O, $Cs^+ClF_4O^-$, CF_3NO, were studied. Synthesis of $(CF_3)_2NO^+$ was studied by using $O_2^+AsF_6^-$ as the oxidizing agent on $(CF_3)_2NO$.

A systematic study of low-temperature ozonization reactions was performed involving $ClOClO_3$, $BrOClO_3$, ClO_2, $BrOSO_2F$, $ClONO_2$, and $ClOSO_2F$.

From C_6F_5I or C_6F_5Br and $ClOClO_3$, novel compounds, $C_6F_5I(OClO_3)_2$ and $(O_3ClO)_2C_6F_5Cl$, were obtained.

Efforts were made to synthesize Br_2O_7 and I_2O_7 by reaction of perhalate salts with SO_3. For the BrO_4^- and IO_4^- salts the isolation of Br_2O_7 and I_2O_7 was not possible owing to complexing with the starting materials

Covalent fluorosulfates are useful for chemical syntheses and a number of reaction systems were studied involving iodine, sulfur, and selenium fluorides.

A novel synthesis of NF_4^+ salts was discovered employing uv photolysis. The PtF_6^-, AsF_6^-, and BF_4^- salts were prepared in this way. This study suggests that F_2 in the presence of a strong Lewis acid has an oxidizing power comparable to that of PtF_6.

A number of structural studies were conducted. Among the compounds studied were ClF_4^+, BrF_4^+, IF_4^+, and SF_5O^- salts, trifluoroacetates of iodine, SF_4, SF_4O, and Cl_2O_6.

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PREPARED BY

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R.D. Wilson, E.C. Curtis,
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CONTENTS

Appendix A

Appendix B

Appendix C

Appendix D

Appendix E

Appendix F

Appendix G

Appendix H

Appendix I

Appendix J

Appendix K

Appendix L

FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 429, with Dr. Ralph Roberts as Scientific Officer. This report covers the period 1 April 1972 through 31 March 1973. 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, and Dr. E. C. Curtis. The Program Manager was Dr. B. Tuffly.

ABSTRACT

The synthesis of the novel heptavalent chlorine oxyfluoride, ClF_3O_2, was scaled up and its physical properties were determined. Its structure was established by ^{19}F nmr and vibrational spectroscopy and both force constants and thermodynamic properties were computed. Its complex formation with strong Lewis acids was studied and two new salts, $ClF_2O_2^+BF_4^-$ and $ClF_2O_2^+AsF_6^-$, were synthesized. With Lewis bases, such as CsF, FNO, or FNO_2, ClF_3O_2 does not form adducts. The structure of the $ClF_2O_2^+$ cation was determined by nmr and vibrational spectroscopy and a force field was computed.

A thorough study of the ClF_5-OF_2 photolysis yielded no evidence at all of the existence of ClF_5O. It appears that the claim by Zuechner and Glemser for its formation is invalid. Photolysis of the BrF_5-OF_2 system did not produce any evidence of new compounds such as BrF_3O or BrF_5O. The interaction between ClF_3O and SF_4 in the presence of CsF did not yield FClO, but all the secondary reaction products expected for its disproportionation to $FClO_2$ and ClF. Reaction parameters for the synthesis of ClF from Cl_2 and ClF_3 were determined.

We have continued to study the reaction chemistry of PtF_6. Its reactions with OF_2, O_3, BrF_5, ClF_3O, $Cs^+ClF_4O^-$, CF_3NO, and $(CF_3)_2NO$ were investigated in an attempt to synthesize the novel species, OF_3^+, O_3^+, BrF_6^+, ClF_4O^+, and $(CF_3)_2NO^+$, respectively. The synthesis of $(CF_3)_2NO^+$, a potential precursor for the synthesis of a CF_3- group substituted ONF_3 molecule, was also studied by using $O_2^+AsF_6^-$ as the active oxidizing agent.

A systematic study of low-temperature ozonization reactions was carried out, involving the following starting materials: $ClOClO_3$, $BrOClO_3$, ClO_2, $BrOSO_2F$, $ClONO_2$, and $ClOSO_2F$. In all cases, the starting materials were successfully oxygenated. Interestingly, the high yield product from the $ClONO_2$ ozonization is $NO_2^+ClO_4^-$.

The reaction chemistry of chlorine perchlorate, $ClOClO_3$, was further investigated. Attempts were made to synthesize members of the so-far unknown class of

perfluorarylperchlorates from C_6F_5I or C_6F_5Br and $ClOClO_3$. In both cases, novel compounds, i.e., $C_6F_5I(OClO_3)_2$ and $(O_3ClO)_2C_6F_5Cl$, respectively, were obtained.

Efforts were made to synthesize the as-yet unknown halogen heptoxides, Br_2O_7 and I_2O_7, by reaction of perhalate salts with SO_3. In the case of $Cs^+ClO_4^-$, the known Cl_2O_7 was indeed obtained in high yield, but for the BrO_4^- and IO_4^- salts the isolation of Br_2O_7 and I_2O_7 was not possible owing to complexing with the starting materials.

Covalent fluorosulfates have significant usefulness for chemical synthesis and a number of reaction systems were studied involving iodine, sulfur, and selenium fluorides. In addition, a new and more convenient synthesis of $S_2O_5F_2$ was found by reacting $COCl_2$ with $ClOSO_2F$.

A novel synthesis of NF_4^+ salts was discovered employing uv photolysis. The PtF_6^-, AsF_6^-, and BF_4^- salts were prepared in this way. A plausible mechanism for the formation and decomposition of NF_4^+ salts is presented which does not require the assumption of NF_5 as an intermediate. Moreover, this study suggests that F_2 in the presence of a strong Lewis acid has an oxidizing power comparable to that of PtF_6. This enhancement of oxidizing power by a Lewis acid was also demonstrated for ClF which, in the presence of AsF_5, can oxidize xenon to the +II oxidation state.

As in the past, a number of structural studies were conducted. Among the compounds studied were ClF_4^+, BrF_4^+, IF_4^+ and SF_5O^- salts, trifluoroacetates of iodine, SF_4, SF_4O, and Cl_2O_6. Our collaboration with other scientists (Professors Sawodny, Edwards, and Naumann) in some of these areas continues, and a new connection was established with Dr. F. Lovas from the National Bureau of Standards, who will carry out a structive determination of ClF_3O by microwave spectroscopy.

During the past contract year 17 papers were published and an additional 7 manuscripts were submitted and have already been accepted for publication on the work done under this contract.

INTRODUCTION

This report describes the activities during the past year at Rocketdyne in the area of halogen oxidizer chemistry. As in the past, the research areas were diverse and were both technique and new compound oriented. A large number of compound types were investigated including halogen perchlorate chemistry, halogen oxyfluoride synthesis, PtF_6 chemistry, new fluorination catalysts, novel energetic cation synthesis, halogen oxide chemistry and halogen fluoride reactions. In addition, pertinent structural data for a number of species were generated. As in the past (Ref. 1 - 4), most of the data have been summarized in manuscript form.

A number of papers also were published or presented which arose from work supported on this program. These are listed below.

PUBLICATIONS DURING PAST CONTRACT YEAR

Papers Published

1. "Chlorine Trifluoride Oxide. I. Preparation and Properties." by D. Pilipovich, C. B. Lindahl, C. J. Schack, R. D. Wilson, and K. O. Christe, Inorg. Chem., 11, 2189 (1972).
2. "Chlorine Trifluoride Oxide II. Photochemical Synthesis," by D. Pilipovich, H. H. Rogers, and R. D. Wilson, Inorg. Chem., 11, 2192 (1972).
3. "Chlorine Trifluoride Oxide, III. Vibrational Spectrum, Force Constants, and Thermodynamic Properties," by K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 2196 (1972).
4. "Chlorine Trifluoride Oxide. IV. Reaction Chemistry," by C. J. Schack, C. B. Lindahl, D. Pilipovich, and K. O. Christe, Inorg. Chem., 11, 2201 (1972).
5. "Chlorine Trifluoride Oxide. V. Complex Formation with Lewis Acids and Bases," by K. O. Christe, C. J. Schack, and D. Pilipovich, Inorg. Chem., 11, 2205 (1972).

6. "Chlorine Trifluoride Oxide. VI. The ClF_4O^- Anion. Vibrational Spectra and Force Constants," by K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 2209 (1972).

7. "Chlorine Trifluoride Oxide, VII. The ClF_2O^+ Cation. Vibrational Spectrum and Force Constants," by K. O. Christe, E. C. Curtis, and C. J. Schack, Inorg. Chem., 11, 2212 (1972).

8. "The $ClO_2F_2^+$ Cation," by K. O. Christe, Inorg. Nucl. Chem. Letters, 8, 453 (1972).

9. "Chlorine Trifluoride Dioxide, ClF_3O_2," by K. O. Christe, Inorg. Nucl. Chem. Letters, 8, 457 (1972).

10. "The ClF_6^+ Cation," by K. O. Christe, Inorg. Nucl. Chem. Letters, 8, 741 (1972).

11. "On the Reactions of Chlorine Fluorides with Hydroxyl Compounds," by K. O. Christe, Inorg. Chem., 11, 1220 (1972).

12. "Iodine Trisperchlorate and Cesium Tetraperchlorato Iodate (III)," by K. O. Christe and C. J. Schack, Inorg. Chem., 11, 1682 (1972).

13. "On Alkali Metal Fluoride - IF_5 Adducts," by K. O. Christe, Inorg. Chem., 11, 1215 (1972).

14. "Vibrational Spectra and Force Constants of the Square Pyramidal Anions, SF_5^-, SeF_5^-, and TeF_5^-," by K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, Inorg. Chem., 11, 1679 (1972).

15. "The Tetrafluoroiodate (III) Anion, IF_4^-," by K. O. Christe and D. Naumann, Inorg. Chem., 12, 59 (1973).

16. "A ^{19}Fnmr Study of Chlorine Fluoride Cations," by K. O. Christe, J. F. Hon, and D. Pilipovich, Inorg. Chem., 12, 84 (1973).

17. "Vibrational Spectrum and Force Constants of the SF_5O^- Anion," by K. O. Christe, C. J. Schack, E. C. Curtis, D. Pilipovich, and W. Sawodny, Inorg. Chem., 12, 620 (1973).

Papers in Press (Submitted and Accepted)

18. "Halogen Perchlorates: Additions to Perhaloolefins," by C. J. Schack, D. Pilipovich, and J. F. Hon, Inorg. Chem., 12, 897 (1973).

19. "On the Reaction of $Cl_2F^+AsF_6^-$ with Xenon, by K. O. Christe and R. D. Wilson, Inorg. Nucl. Chem. Letters.

20. "The Difluoroperchloryl Cation, ClO_2^+," by K. O. Christe, R. D. Wilson, and E. C. Curtis, Inorg. Chem.

21. "Chlorine Trifluoride Dioxide, ClF_3O_2," by K. O. Christe and R. D. Wilson, Inorg. Chem.

22. "The Hexafluorochlorine (VII) Cation, ClF_6^+. Synthesis and Vibrational Spectrum," by K. O. Christe, Inorg. Chem.

23. "Vibrational Spectra of Trifluoroacetates," by K. O. Christe and D. Naumann, Spectrochim. Acta.

24. "Chlorine Trifluoride Dioxide Vibrational Spectrum Force Constants, and Thermodynamic Properties," by K. O. Christe and E. C. Curtis, Inorg. Chem.

Papers Presented at Meetings

25. "Chlorine (VII) Fluorides: Preparation, Characterization, and Properties," by K. O. Christe, D. Pilipovich, and R. D. Wilson, 4th European Symposium on Fluorine Chemistry, Ljubljana, Yugoslavia (August 1972).

26. "Inorganic Halogen Oxidizers," by K. O. Christe, invited lectures at the Universities of California, Los Angeles, Riverside, and Berkeley (1972-1973).

DISCUSSION

CHLORINE TRIFLUORIDE DIOXIDE

The syntnesis of ClF_3O_2 from $FClO_2$ and PtF_6 was successfully scaled up and the reaction parameters were studied. In spite of enormous handling and purification problems, sufficient amounts of material were prepared to allow the determination of its physical, chemical, spectroscopic, and thermodynamic properties. The results from these studies were summarized in two manuscripts and are presented as Appendixes A and B.

THE $ClF_2O_2^+$ CATION

Two novel $ClF_2O_2^+$ salts, $ClF_2O_2^+AsF_6^-$ and $ClF_2O_2^+BF_4^-$ were prepared and characterized by vibrational and ^{19}Fnmr spectroscopy. A modified valence force field was computed for $ClF_2O_2^+$. Attempts to synthesize the $ClF_4O_2^-$ cation from ClF_3O_2 and strong Lewis bases such as CsF, FNO, or FNO_2 were unsuccessful. The results from this study are given in manuscript form in Appendix C.

THE ClF_6^+ CATION

The investigation of the ClF_6^+ cation was completed and a detailed manuscript was written (see Appendix D) summarizing Rocketdyne's work. In this manuscript we have also included a vibrational analysis and force constant computations for the PtF_6^- and IF_6^- anions.

ON THE EXISTENCE OF ClF_5O AND RELATED PHOTOLYSIS REACTIONS

Recently, Zuechner and Glemser (Ref. 5) claimed the synthesis of ClF_5O by photolysis of ClF_5-OF_2 mixtures. However, Rocketdyne studies on this system show quite conclusively that no detectable amounts of ClF_5O are formed in this system. Data on this system are summarized in Appendix E. Because ClF_3O is the main product of the ClF_5-OF_2 photolysis, BrF_5-OF_2 photolysis also has been studied in more detail.

Contrary to ClF_5, the BrF_5 starting material did not react and was recovered unchanged. Similarly, the $FClO_2$-OF_2 system, when exposed at -78° to filtered uv-irradiation, did not produce any novel compound.

SYNTHESIS OF FClO

The ClF_3O-SF_4 reaction system was studied in an attempt to synthesize FClO according to:

$$SF_4 + ClF_3O \longrightarrow SF_6 + FClO$$

When no catalyst was used, the starting material did not interact at -50 and 25 C. In the presence of CsF, however, the following products were obtained: SF_6, SF_5Cl, SF_4O, and $FClO_2$. These results indicate that the desired reaction may have initially occurred, but was followed by:

$$2FClO \longrightarrow FClO_2 + ClF$$

$$ClF + SF_4 \longrightarrow SF_5Cl$$

In addition, a competing reaction, i.e., oxygenation of SF_4 to SF_4O, must have occurred to a lesser extent. This finding, i.e., the ready disproportionation of FClO to $FClO_2$ and ClF, was recently confirmed by Cooper et al. (Ref. 6). They studied the hydrolysis of ClF_3 in a flow reactor and obtained infrared spectroscopic evidence for an unstable intermediate which rapidly decomposed to $FClO_2$ and ClF.

SYNTHESIS OF ClF

The reaction parameters were studied for the synthesis of ClF from ClF_3 and Cl_2. It was found that ClF can be prepared in almost quantitative yield at temperatures as low as 150 C. The results are summarized in manuscript form in Appendix F.

PtF_6 REACTION CHEMISTRY

Because PtF_6 has proved to be such a useful fluorinating oxidizer for the synthesis of ClF_3O_2, $ClF_2O_2^+$, and ClF_6^+, its reaction chemistry has been under continuing study. A logical extension of the ClF_6^+ synthesis was the attempt to prepare BrF_6^+ salts. However, in the BrF_5-PtF_6 system at 25 C, no reaction occurs between BrF_5 and PtF_6. Using unfiltered uv irradiation, PtF_6 decomposes to lower platinum fluorides and F_2, but no BrF_6^+ salt is formed. The ternary system, $FClO_2$-BrF_5-PtF_6, was also investigated. Upon melting of the halogen fluorides, a rapid reaction occurs, producing exclusively $ClO_2^+PtF_6^-$ and F_2, but no BrF_6^+. The third system, $Cs^+BrF_6^-$+BrF_5 + PtF_6, was kept at 25C for 93 days. Analysis of the products showed no evidence for the desired BrF_6^+ cation, but indicated the formation of some $Cs^+PtF_6^-$ and PtF_5 as only new products.

Much effort was concentrated on the synthesis of ClF_4O^+ salts, which would allow the synthesis of the new and very desirable compound ClF_5O. Because the reaction of PtF_6 with ClF_3O in the absence of a solvent had to be carried out above -42 C (m.p. of ClF_3O) and yielded only $ClF_2O^+PtF_6^-$ and F_2, this system has been studied in a low melting solvent. An ideal inert solvent was found with $FClO_3$ which melts at about -150 C, has a high solubility for PtF_6, and is completely inert to PtF_6. Two reactions of ClF_3O with PtF_6 were carried out in $FClO_3$ solution, differing in the warm-up conditions. In both cases, again only $ClF_2O^+PtF_6^-$ and F_2, but no ClF_4O^+, were obtained. Because previous attempts to prepare either ClF_4O^+ or ClF_5O directly from ClF_3O and PtF_6 were unsuccessful (see Appendix D), the reaction of $Cs^+ClF_4O^-$ with PtF_6 was studied in the presence and absence of a solvent. Without any solvent and using ultrasonic mixing, solid $Cs^+ClF_4O^-$ interacted with PtF_6 at 25 C within 48 hours quantitatively, according to:

$$2PtF_6 + Cs^+ClF_4O^- \longrightarrow Cs^+PtF_6^- + ClF_2O^+PtF_6^- + F_2$$

Using $FClO_3$ as a solvent, the reaction of PtF_6 was much faster and proceeded at a lower temperature. However, the reaction products were identical to those given above. The possibility of using BrF_5 as a solvent was also examined. It was found to be incompatible with $Cs^+ClF_4O^-$, owing to the following quantitative displacement reaction:

$$Cs^+ClF_4O^- + BrF_5 \longrightarrow Cs^+BrF_6^- + ClF_3O$$

Another desirable, energetic species would be the OF_3^+ cation. It is isoelectronic with NF_3 and, hence, might possess a reasonable stability. In its attempted synthesis, a mixture of OF_2 and PtF_6 was kept for 100 days in a sapphire reactor at 25 C. While all of the PtF_6 was consumed, all of the OF_2 was recovered unreacted. Based on the observed weight changes and the infrared spectrum of the solid residue, the following interaction between the reactor and PtF_6 occurred:

$$\text{Metal} + PtF_6 \longrightarrow \text{Metal fluoride} + PtF_5$$

The reaction of ozone and PtF_6 has also been investigated for the possible formation of $O_3^+PtF_6^-$. The O_3^+ cation might exist, being isoelectronic with NO_2. During several weeks reaction at temperatures of -80 to -45 C, it was found that very little O_3 reacted and nearly all was recoverable. Thus, it appears that the PtF_6 has a stablizing effect on O_3 under these conditions. At ambient temperature, O_3 and PtF_6 gave a nearly quantitative yield of $O_2^+PtF_6^-$. This was based both on the amount of excess O_2 recovered and the weight increase of the PtF_6. Thus, $O_3^+PtF_6^-$ does not appear to be preparable in this manner.

Since PtF_6 can oxidize ClF_5 to ClF_6^+ and since $XeOF_4$ is pseudo-isoelectronic with ClF_5, it might be possible to prepare $XeOF_5^+$ according to:

$$2\ XeOF_4 + 2PtF_6 \longrightarrow XeOF_5^+PtF_6^- + XeOF_3^+PtF_6^-$$

The first attempt to synthesize the $XeOF_4$ starting material according to a literature report by hydrolysis of XeF_6 came to an explosive halt. In the meantime, several grams of $XeOF_4$ were prepared by the alternate procedure based on the slow interaction between XeF_6 and quartz. In addition, a PtF_6 preparation, which in the past has successfully been carried out many times, failed owing to burn out. As soon as new platinum wire is received, this study will be resumed.

Reactions of PtF_6 with free nitroxide radicals such as $(CF_3)_2NO$ were investigated with the intent of achieving the synthesis of a novel CF_3 substituted NF_3O molecule, according to:

$$(CF_3)_2NO + PtF_6 \longrightarrow (CF_3)_2NO^+PtF_6^-$$

$$(CF_3)_2NO^+PtF_6^- + FNO \longrightarrow NO^+PtF_6^- + (CF_3)_2NFO$$

The nitroxide starting materials were synthesized and allowed to interact with PtF_6 at the lowest possible temperature. However, in all cases the reaction was so violent (confined explosions) that the only products obtained were $NO^+PtF_6^-$, CF_4, COF_2, CF_3NO_2, $(CF_3)_2NOCF_3$, and small amounts of NF_3. It is planned to repeat these reactions in the future using the milder oxidizers ReF_6 or MoF_6 in place of PtF_6.

The reaction of $O_2^+AsF_6^-$ with $(CF_3)_2NO$ at low temperature was also studied as an alternate route to $(CF_3)_2NO^+$ salts:

$$O_2^+AsF_6^- + (CF_3)_2NO \longrightarrow (CF_3)_2NO^+AsF_6^- + O_2$$

However, the solid was shown to be $NO^+AsF_6^-$ and COF_2 and CF_4 were obtained as volatile products. This indicates that $(CF_3)_2NO^+$ may have initially formed, but is unstable. This experiment will be repeated at a lower temperature, substituting $O_2^+AsF_6^-$ with the more stable salt $O_2^+SbF_6^-$. The latter starting material was synthesized from $O_2 + F_2 + SbF_5$.

OZONE OXIDATIONS

Compounds containing the terminal haloxy group, XO-, are uniformly reactive and utilitarian reagents. However, nearly all of the known chemistry of these materials centers on their reaction through cleavage of the haloxy bond, e.g., the use of $ClOSO_2F$ to produce $ClOClO_3$ from $Ag^+ClO_4^-$ (Ref. 3) and the use of $ClOClO_3$ to prepare $Cl\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}OClO_3$ compounds (Ref.3). To change the nature of these XO- moieties and thus perhaps to change their types of reactivity and stability, studies were aimed at the oxidative oxygenation of the terminal halogen.

The only report of such an oxidation was given by Schmeisser and Taglinger (Ref.7). They reported the ozonization of $BrONO_2$ at -78 C as shown in the equation:

$$BrONO_2 + 2O_3 \longrightarrow BrO_2NO_3 + 2O_2$$

The good results realized in that system offered promise of equally useful reactions with other XO- species. Of immediate interest were the halogen perchlorates, $ClOClO_3$ and $BrOClO_3$. In the case of $ClOClO_3$ it was found that oxidation via ozonization occurred under a variety of conditions according to the equation:

$$ClOClO_3 + 2O_3 \longrightarrow Cl_2O_6 + 2O_3$$

At -80 C the reaction was slow, providing only a 35-percent yield of Cl_2O_6 after more than a 24-hour reaction. At -45 C the reaction was studied with and without CF_3Cl as a solvent. In the former case, and using excess $ClOClO_3$, an 80-percent yield of Cl_2O_6 based on O_3, was obtained with the unreacted $ClOClO_3$ bein recovered. Thus, an even higher conversion of the reacted $ClOClO_3$ was realized. Without the solvent, but with a slight excess of O_3 over the required 2:1 ratio, a virtually quantitative formation of Cl_2O_6 was achieved.

To prove the identity of the chlorine oxide produced by this reaction and that reported for Cl_2O_6, alternative syntheses were carried out. One of these involved the slow degradation of $ClOClO_3$ in the dark (Ref. 8):

$$2ClOClO_3 \xrightarrow{-15\ C} Cl_2O_6 + O_2 + Cl_2$$

Another employed the usual ozonization of chlorine dioxide (Ref. 9):

$$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$$

When this ozonization was run at -45 C, it was found that Cl_2O_6 was formed at a faster rate than with $ClOClO_3$ as a substrate. In all respects -- appearance, vapor pressure, composition, and mass spectra -- the Cl_2O_6 from each of these sources was the same and no indication of isomeric forms of Cl_2O_6 was noted.

Some disagreement regarding the mass spectrum of Cl_2O_6 exists. Cordes and Smith (Ref. 10) observed a weak ClO_3^+ ion as the highest m/e from Cl_2O_6. However, Fisher (Ref. 11) found no ClO_x^+ ions above ClO_2^+, but his samples showed appreciable $HClO_4$ impurity. In Rocketdyne's work, samples without $HClO_4$ gave a small (5-percent of base) peak for ClO_3^+. Even samples with some $HClO_4$ exhibited a modest but reproducible ClO_3^+ peak when the spectrum was corrected for that impurity.

The novel process for ozonizing the terminal chlorine of $ClOClO_3$ was applied to $BrOClO_3$. Surprisingly, it was found that neat O_3 and $BrOClO_3$ in the temperature range of -80 to -45 C reacted to cause their complete degradation to the elements. An effort was therefore made to moderate the reaction through the use of CF_3Cl as a solvent. This was successful and the reaction observed at -45 C was:

$$BrOClO_3 + 2O_3 \longrightarrow BrO_2ClO_4 + 2O_2$$

Excellent oxygen balance for this stoichiometry was realized and confirmed by analysis of the product. This showed that $3O_2$ was present for each BrCl in the molecule.

The new composition, BrO_2ClO_4, is a bright orange solid that does not melt up to at least -40 C. Decomposition at room temperature occurs slowly in well-passivated metal. Efforts to further characterize and utilize the compound are in progress. An attempt to displace $FBrO_2$ using FNO_2 was unsuccessful since only a small amount of FNO_2 reacted.

In view of the failure to secure a controlled reaction of O_3 and $BrOClO_3$ in the absence of a solvent, it was not unexpected that $BrOSO_2F$ would behave similarly. Thus, it was determined that neat O_3 and $BrOSO_2F$ did not produce an ozonization product. Instead, all the O_3 was decomposed to O_2 and most of the $BrOSO_2F$ degraded to Br_2, SO_2F_2 and $S_2O_5F_2$. Results of solution ozonization of $BrOSO_2F$ are not in hand as yet.

Bromine nitrate was also sought for use in the ozone oxidation studies. Its synthesis from Br_2 and $ClNO_3$ (Ref. 7) at -45 C was extremely sluggish. Also, long reaction times were ineffective because of an apparent degrading reaction which produced Br_2, ClO_2, and N_2O_5. The formation of these products probably occurs through a competitive and previously unsuspected interaction of $BrNO_3$ and $ClNO_3$, as shown by the equations:

$$2ClNO_3 + Br_2 \longrightarrow 2BrNO_3 + Cl_2$$

$$ClNO_3 + BrNO_3 \longrightarrow N_2O_5 + BrOCl\left(\text{or } Br\cdot + ClO\cdot\right)$$

$$2\,Br\cdot \longrightarrow Br_2$$

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

Alternate routes to $BrNO_3$ are being investigated.

An initial attempt to effect the ozonization of $ClONO_2$ at -80 C without a solvent indicated no reaction occurred. With CF_3Cl as a solvent, at either -80 or -45 C, a successful oxidation was achieved as shown:

$$ClONO_2 + 3O_3 \longrightarrow NO_2^+ClO_4^- + 3O_2$$

Yields of $NO_2^+ClO_4^-$ on the order of 80- to 90-percent are routinely obtainable. This reaction represents a new process for preparing nitronium perchlorate and avoids the use of the troublesome ClO_2 which is commonly employed as part of that synthesis (Ref. 9).

Chlorine fluorosulfate was expected to undergo oxidative ozonization since a predicted product, ClO_2SO_3F, is known from other synthetic schemes (Ref. 9 and 12). It was found that no solvent was required to produce the reaction:

$$ClOSO_2F + 2O_3 \longrightarrow ClO_2SO_3F + 2O_2$$

A moderate reaction occurred even at 0 C furnishing 70- to 90-percent yields of chloryl fluorosulfate. Further oxygen up-take beyond this composition was not observed.

CHLORINE PERCHLORATE REACTIONS

Several examples of the synthesis of the previously unknown class of compounds, perhaloalkylperchlorates, were discovered on this program (Ref. 3) through the use of chlorine perchlorate. More examples were obtained recently under another program (Ref. 13). However, no examples of aromatic perchlorates have been reported and it was of interest to ascertain whether Cl_2O_4 would be useful in this regard. Iodopentafluorobenzene was selected as a test vehicle. Reaction at -45 C produced excellent volumetric and gravimetric data in accordance with the equation:

$$C_6F_5I + 2Cl_2O_4 \longrightarrow C_6F_5I(ClO_4)_2 + Cl_2$$

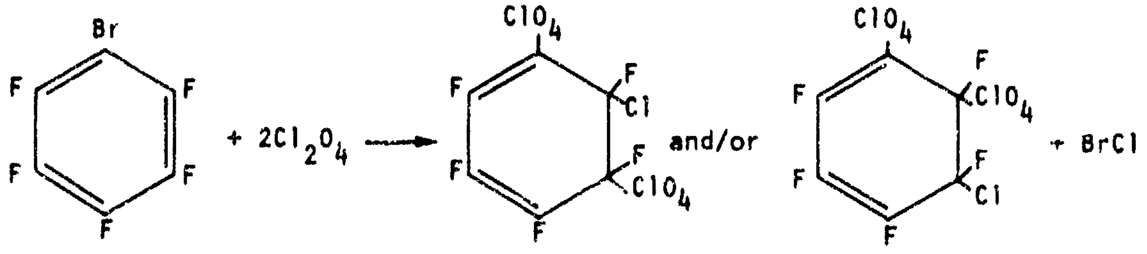
The perchlorate product is a shiny, pale yellow solid completely stable at ambient temperature and nonvolatile. It is probably similar to $I(ClO_4)_3$ (Ref. 2) or $(CF_3)_2CFI(ClO_4)_2$ (Ref. 13), although this stoichiometry does not rule out a composition such as $(C_6F_5)_2I^+I(ClO_4)_4^-$ as was found for the compound $(C_4F_9)_2I^+IF_6^-$ (Ref. 14). Retention of the aromatic character of the ring was shown by the infrared spectrum which also showed the presence of perchlorate groups.

Although thermally stable, the solid is either friction or impact sensitive. Thus, while attempting to break up a lump of this solid with a metal spatula, it exploded. While insoluble in water, the solid is slowly hydrolyzed, producing a pale yellow powder.

$$C_6F_5I(ClO_4)_2 + H_2O \longrightarrow C_6F_5I{=}O + 2HClO_4$$

The identity of the iodoso derivative was confirmed by comparison of its infrared and melting point to that given in the literature (Ref. 15). Investigation and characterization of this new perchlorate is continuing.

When the reaction of C_6F_5Br and Cl_2O_4 was examined at -45 C, a different result was obtained. Again, two moles of Cl_2O_4 reacted for each mole of the aryl compound. However, displacement of the bromine was accomplished as evidenced by the evolution of BrCl. Nevertheless, the product was not a simple R_fClO_4 moiety. After pumping for several hours at 0 C to room temperature, there remained a colorless, slightly viscous liquid. The by-products observed and the weight of the product indicated a composition for this liquid of $(ClO_4)_2C_6F_5Cl$. The infrared spectrum of the neat liquid revealed very strong covalent ClO_4 group bands but no 1500 cm^{-1} aromatic ring band. These results indicate the probable reaction to be:



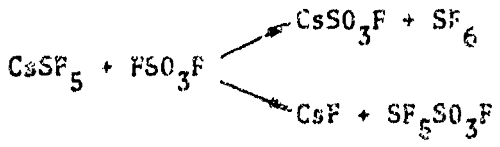
The mass spectrum of the liquid confirms the lack of aromatic character for the liquid. Moreover, ion peaks for fragments such as $C_4F_3Cl_2O^+$, $C_3F_3Cl_2O^+$, $C_3F_2ClO^+$, and $C_2F_2ClO^+$ tend to support the above formulation. However, there appears to be an abnormally high number of peaks tentatively assigned to saturated molecular fragments such as $CFCl_2^+$ and CF_2Cl^+. Also, the infrared spectrum shows a strong band near 1870 cm^{-1}. Typically, such a band is due to the C=O stretching mode of an $R_fC(O)F$ species. If such were the case here, then it would mean the aromatic ring had been opened. Additional spectral investigations including ^{19}F nmr are planned to resolve these points.

HALOGEN HEPTOXIDES

New approaches for the synthesis of Cl_2O_7 from perchlorate salts were studied. These will be applied to the syntheses of the as-yet unknown heptavalent halogen oxides Br_2O_7 and I_2O_7. We found that Cl_2O_7 can be prepared from $Cs^+ClO_4^-$ and SO_3 in high yield. Extension of this reaction to $Cs^+BrO_4^-$ and $K^+IO_4^-$ resulted in interaction of the starting materials; however, the products appeared to form adducts and could not be isolated and characterized without decomposition to the elements. Further experiments are planned in which SO_3 will be substituted by the more volatile FSO_2-O-SO_2F. This should facilitate the product workup. The new Br_2O_7 and I_2O_7 species would be excellent candidates for high detonation pressure explosives.

COVALENT FLUOROSULFATE STUDIES

The covalent inorganic fluorosulfates have significant synthetic usefulness and a number of reaction systems were studied involving iodine, sulfur, and selenium fluorides. Fluorine fluorosulfate and $CsSF_5$ were reacted to determine which of two possible reaction paths would be followed.



$$CsSF_5 + FSO_3F \begin{cases} \nearrow CsSO_3F + SF_6 \\ \searrow CsF + SF_5SO_3F \end{cases}$$

As has often been noted with the other halogen fluorosulfates, the tendency to form the fluorosulfate ion predominates and, accordingly, the upper path was followed exclusively. While all the FSO_3F that reacted liberated SF_6, not all the FSO_3F or $CsSF_5$ reacted. A 55-percent conversion of the available SF_5^- was achieved.

Chlorine fluorosulfate has repeatedly demonstrated an ability to serve as a source of positively polarized chlorine in converting anions to covalent species. An attempt to utilize this property was made with the goal of forming IF_4Cl as indicated by the equation

$$CsIF_4 + ClSO_3F \longrightarrow CsSO_3F + IF_4Cl$$

Despite the use of a maximum reaction temperature of -80 C, it was found that Cl_2 was quantitatively released at that temperature. At higher temperatures the coproducts IF_5 and I_2 were found leaving a residue of $CsSO_3F$. The indicated stoichiometry is:

$$CsIF_4 + ClSO_3F \longrightarrow CsSO_3F + 1/2\ Cl_2 + 4/5\ IF_5 + 1/10\ I_2$$

Perhaps IF_4Cl was formed, but it was certainly unstable even at -80 C.

In a similar manner, NF_2SO_3F was reacted with $CsIF_4$ in an effort to make the substituted IF_5 derivative, IF_4NF_2. With excess $CsIF_4$, a prolonged reaction at -45 C did not consume all the NF_2SO_3F. However, no IF_4NF_2 was detected, but only IF_5/I_2 and SO_2F_2. The apparent reaction sequence is:

$$CsIF_4 + NF_2SO_3F \longrightarrow CsSO_3F + [IF_4NF_2]$$

$$[IF_4NF_2] \longrightarrow [IF_3] + NF_3$$

$$[IF_3] \longrightarrow IF_5/I_2$$

Nitrogen trifluoride was not observed but it would have been pumped away in the course of the work-up procedure used. The SO_2F_2 arose from the fluorination of SO_2 which was an impurity in the NF_2SO_3F. It seems certain that IF_4NF_2 is incapable of synthesis in this manner.

Peroxydisulfuryl difluoride was reacted with the salt, $CsSeF_5$, with the expectation that a simple fluorosulfonation would occur.

$$CsSeF_5 + S_2O_6F_2 \longrightarrow CsSO_3F + SeF_5SO_3F$$

Reaction at ambient temperature did not occur in this manner, however. Instead the exclusive reaction was the fluorination process represented by the equation:

$$CsSeF_5 + S_2O_6F_2 \longrightarrow CsS_2O_6F + SeF_6$$

The fluorodisulfate anion is not especially well known and only one other example of its formation from $S_2O_6F_2$ is known to Rocketdyne (Ref. 16). That synthesis entailed the fluorination of peroxydisulfate salts with $S_2O_6F_2$.

In contrast to this result, the interaction of $S_2O_6F_2$ and SeF_4 did proceed via cleavage of the peroxy bond but again fluorination was encountered. The observed ambient temperature reaction was:

$$3SeF_4 + S_2O_6F_2 \longrightarrow SeF_6 + 2SeF_3{}^+SO_3F^-$$

This constitutes a new synthesis of this salt which was previously prepared (Ref. 17) from SeF_4 and SO_3. Compared to the SF_4 - $S_2O_6F_2$ reaction (Ref. 18) which yields $SF_4(SO_3F)_2$, the tendency of the selenium fluorides to undergo fluorination is remarkable.

Among the useful properties of chlorine fluorosulfate is its ability to serve as a precursor for other covalent inorganic fluorsulfates. This has led to its use (Ref. 19) in preparing $S_2O_6F_2$ and $BrSO_3F$, for example. Another such synthetic application was found in the following reaction:

$$COCl_2 + 2ClSO_3F \longrightarrow CO_2 + 2Cl_2 + S_2O_5F_2$$

Pyrosulfuryl fluoride can be obtained in at least 90 percent yield and quickly by this process. Purification is simple since the by-product CO_2 and Cl_2 are apreciably more volatile.

NF_4^+ CHEMISTRY

A new synthesis of NF_4^+ salts has been discovered at Rocketdyne. When mixtures of NF_3, F_2, AsF_5 or NF_3, F_2, BF_3 at 200-psi pressure in a sapphire reactor were exposed to uv radiation, the solids $NF_4^+ AsF_6^-$ and $NF_4^+ BF_4^-$, respectively, were formed. It was shown that in the absence of light, no reaction occurs, and that based on the observed rates, the $NF_4^+ AsF_6^-$ formation must be a chain reaction. Rationalization of the following reaction systems led to the conclusion that the common reactive intermediate must be the AsF_6 radical having an oxidizing power comparable to that of PtF_6 (>12 ev).

$$O_2 + F_2 + AsF_5 \longrightarrow O_2^+AsF_6^-$$

$$Xe + F_2 + AsF_5 \longrightarrow XeF^+AsF_6^-$$

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4^+AsF_6^-$$

A plausible mechanism was written for both the formation and thermal decomposition of NF_4^+ salts. Contrary to the mechanism suggested by I. Solomon of IITRI, the Rocketdyne mechanism does not require formation of the energetically unfavorable NF_5 molecule as an intermediate. These results are summarized in Appendix G.

In addition, the photolysis of NF_3 - F_2 - SbF_5 has been studied at a 1-atmosphere pressure in a quartz bulb. Within several days, all of the SbF_5 was converted to a white solid, which was shown to be an equimolar mixture of $NF_4^+Sb_3F_{16}^-$ and $O_2^+Sb_3F_{16}^-$ in agreement with the following equations:

$$NF_3 + F_2 + 3SbF_5 \longrightarrow NF_4^+Sb_3F_{16}^-$$

$$2F_2 + SiO_2 \longrightarrow SiF_4 + O_2$$

$$O_2 + 1/2\ F_2 + 3SbF_5 \longrightarrow O_2^+Sb_3F_{16}^-$$

OXIDATION OF XENON BY $Cl_2F^+AsF_6^-$

The Xe, ClF, AsF_5 system was studied as a model reaction for the heterolytic fission of ClF according to:

$$Xe + ClF + AsF_5 \longrightarrow XeCl^+AsF_6^-$$

However, the following competing reactions occurred:

$$2ClF + AsF_5 \longrightarrow Cl_2F^+AsF_6^-$$

$$Cl_2F^+AsF_6^- + Xe \longrightarrow XeF^+AsF_6^- + Cl_2$$

$$2\ XeF^+AsF_6^- \longrightarrow Xe_2F_3^+AsF_6^- + AsF_5$$

$$Cl_2 + ClF + AsF_5 \longrightarrow Cl_3^+AsF_6^-$$

These results demonstrate that Cl_2F^+ is a stronger oxidizer than ClF_3 or ClF, both of which do not oxidize Xe, and establish the following order of oxidizing power:

$$Cl_2F^+ > XeF^+ > BrF_2^+$$

Results from this study were summarized in manuscript form (Appendix H).

STRUCTURAL STUDIES

The vibrational spectra of the following halogen pentafluoride·Lewis acid adducts were recorded: $ClF_4^+SbF_6^-$, $ClF_4^+AsF_6^-$ $BrF_4^+Sb_2F_{11}^-$, and $IF_4^+SbF_6^-$. Complete force constant ellipses were computed for the ClF_4^+ cation. In addition, the ^{19}F nmr spectra of these adducts were studied in HF solution. Results are given in Appendix I.

To be able to assign the ClF_4^+ spectrum, it was necessary to clarify the existing discrepancies for isoelectronic SF_4 by force constant and mean square amplitudes of vibration computations. The results are summarized in Appendix J.

Because the vibrational spectra of chlorine fluorides or oxyfluorides were found to closely resemble those of the isoelectronic sulfur compounds, we studied the spectrum of SF_5O^-. This anion is isoelectronic with ClF_5O, an as-yet unprepared oxidizer in which we have much interest. The results from this study are given in Appendix K. For the same reason, an investigation was begun on the vibrational spectrum of SF_4O which is isoelectronic with the as-yet unknown ClF_4O^+ cation. This study is still in progress and the results will be presented in a future report.

Rocketdyne has conducted studies on the structure of the $CsI(O_2CCF_3)_4$ and $Cs_3I(O_2CCF_3)_6$ adducts by infrared and Raman spectroscopy and by X-ray powder diffraction techniques. It was shown that the trifluoroacetate group forms a highly polarized covalent bond with iodine. The results from this study are summarized in Appendix L.

A strong effort was made to establish the structure of free dichlorine hexoxide by both matrix isolation and mass spectroscopic techniques. Unfortunately, Cl_2O_6 decomposes in the gas phase extremely rapidly to ClO_2 and oxygen. Consequently, no clear-cut evidence for either covalent chloryl perchlorate present in its ionic form in solid Cl_2O_6 (Ref. 20) or for the ClO_3 radical could be obtained. Two novel species were observed, but could not be identified conclusively.

A sample of ClF_3O was prepared, purified, and shipped to Dr. F. Lovas of the National Bureau of Standards where a structure determination will be conducted using microwave spectroscopy.

EXPERIMENTAL

PREPARATION OF OZONE

Ozone was prepared by electric discharge of O_2 in a Pyrex U-tube cooled with liquid nitrogen. A 15-kv power supply through internal copper electrodes provided the discharge. Upon conversion of a charge of O_2 to O_3 (which was easily followed manometrically), the discharge was stopped and the O_3 was transferred to the vacuum line. After expanding and measuring the O_3 in the line, it was immediately loaded into a precooled reactor. Somewhat more than one millimole of pure O_3 was obtained from each batch. Larger quantities could be easily prepared but would, of course, not be as safe to handle.

OZONIZATION OF CHLORINE PERCHLORATE

Freshly prepared (Ref. 8) and purified chlorine perchlorate (1.35 millimole) was condensed into a prepassivated, 30-milliliter stainless-steel cylinder cooled to -196 C. To the *same* cylinder, freshly prepared O_3 (2.86 millimoles) was subsequently added. The reaction was allowed to proceed by warming and maintaining the reactor at approximately -45 C for 2 days or longer. At that time, recooling to -196 C showed O_2 was present as indicated by its vapor pressure. The oxygen was pumped from the reactor and measured (2.96 millimoles). Additional pumping on the reactor, while warming to -45 C, produced less than 1 cc of condensable materials. Thus all the Cl_2O_4 had reacted with sufficient O_3, as indicated by the by-product O_2, producing Cl_2O_6. The identity of the Cl_2O_6 was established by its elemental analysis after decomposition at elevated temperature. Thus from 1.35 millimole of Cl_2O_6 there was obtained 1.33 millimole Cl_2 and 3.95 millimole O_2. Furthermore, transferring this product to a Teflon U-trap on the vacuum line showed it to have the same physical appearance and properties described for Cl_2O_6 synthesized by other processes (Ref. 9). It was a very dark red liquid or solid, melting near 0 C and exhibiting only several mm vapor pressure near ambient temperature. On standing at ambient temperature, slow bubbling within the sample was noted and the gas pressure increased gradually. This was found to be caused by the formation of ClO_2, Cl_2, and O_2, resulting from the decomposition of the Cl_2O_6.

OZONIZATION OF CHLORINE DIOXIDE

Chlorine dioxide was prepared from $NaClO_2$ and Cl_2 (Ref. 21) at -45 C and purified by fractional condensation. The ozonization of ClO_2 is the favored method for synthesizing Cl_2O_6 (Ref. 9). The procedure followed at Rocketdyne was identical to that described previously for the Cl_2O_4-O_3 reaction. After an 18-hour reaction at -45 C, 1.26 millimole of ClO_2 and 3.16 millimoles of O_3 yielded 1.85 millimole of unreacted O_3 and 1.34 millimole of O_2. This indicated 1.30 millimole of atomic oxygen had been taken up in good agreement with the reported stoichiometry for the reaction. Essentially, a quantitative conversion to Cl_2O_6 was confirmed by the failure to recover any ClO_2 or other by-products. The product Cl_2O_6 was as described in the literature.

OZONIZATION OF BROMINE PERCHLORATE

Bromine perchlorate was prepared in reactors in which subsequent ozonization could be performed without transfering the $BrClO_4$. Thus decomposition of $BrClO_4$ through handling was avoided. The reaction of Br_2 and Cl_2O_4 was used to synthesize $BrClO_4$ (Ref. 22). A 1.29-millimole sample of $BrClO_4$ and 3.06 millimoles of O_3 were reacted at -45 C in the presence of 12 millimoles of CF_3Cl solvent. After several days the mixture was recooled to -196 C and the by-product O_2 (3.26 millimoles) was measured indicating one mole of O_2 was taken up per mole of $BrClO_4$ present. The solvent was removed by warming and pumping, and finally the sample was pumped on for an hour at -45 C. Only the solvent, CF_3Cl, was observed among the volatile species. Analysis of the indicated BrO_2ClO_4 product was obtained by decomposition of the sample at 90 C for several hours. From the 1.29 millimole of BrO_2ClO_4 was obtained 1.28 millimole of a mixture of Cl_2, BrCl, and Br_2 which was identified by its mass spectrum. In addition, 3.97 millimoles of O_2 were obtained. Thus, the product contained BrCl and O_2 in the ratio 1.00:3.07. Bromyl perchlorate samples prepared in sapphire reactors were observed to be bright orange solids that did not melt to about -40 C. Decomposition to the elements also occurred at ambient temperature over several days.

OZONIZATION OF BROMINE FLUOROSULFATE

Bromine fluorosulfate was prepared from Br_2 and $ClSO_3F$ in a 30-milliliter cylinder. After purification by removal of by-product Cl_2 and excess $ClSO_3F$, ozone (3.37 millimoles) was added to the $BrSO_3F$ (1.25 millimole) at -196 C. The reactor was allowed to warm very slowly to -45 C by placing it into a liquid N_2-CO_2 slush bath that was permitted to evaporate in a -45 C chamber. After 6 days, recooling to -196 C revealed all the O_3 had decomposed and part of the $BrSO_3F$ to give 5.14 millimoles of O_2. Further evidence for partial decomposition of the $BrSO_3F$ was the discovery of SO_2F_2, $S_2O_5F_2$, and some Br_2 by fractional condensation of the -45 C volatile products. Additional fractionation led to the recovery of $BrSO_3F$ only and no other product.

OZONIZATION OF CHLORINE NITRATE

Chlorine nitrate (1.03 millimole) prepared from ClF and HNO_3 (Ref. 23) was loaded into a 30-milliliter cylinder at -196 C followed by CF_3Cl solvent (21 millimoles) and O_3 (4.04 millimoles). The reaction was then allowed to proceed at -45 C for several days. At that time the O_2 present was measured (4.73 millimoles) and removed together with the solvent. The latter had a faint yellow color but no infrared absorbances other than those of CF_3Cl itself, thus indicating some Cl_2 as an impurity. Finally, the cylinder was pumped on at room temperature for 30 minutes before weighing.

The nonvolatile residue, a white fluffy powder, weighed 135 milligrams and was identified as $NO_2^+ClO_4^-$ by its infrared spectrum (Ref. 24). This yield of 0.92 millimole was 89 percent of theory.

OZONIZATION OF CHLORINE FLUOROSULFATE

Chlorine fluorosulfate (1.06 millimole) prepared from ClF and SO_3 (Ref. 19) was condensed into a 10-milliliter cylinder cooled with liquid N_2, followed by O_3 (2.30 millimoles). After reaction at -45 C for several days, the -196 C noncondensable gas, O_2, which had formed was measured (2.44 millimoles) and removed.

Warming to -45 C while pumping liberated about 1 cc of -196 C condensable material. Thus, nearly all the $ClSO_3F$ had reacted producing ClO_2SO_3F in 97 yield (1.03 millimole). The product is a low-volatility dark red liquid (Ref. 12).

REACTION OF Cl_2O_4 AND IODOPENTAFLUOROBENZENE

A passivated 30 milliliter cylinder was charged with C_6F_5I (1.39 millimole) in the dry box. Upon evacuation, freshly purified Cl_2O_4 (3.04 millimoles) was condensed into the liquid N_2-cooled cylinder. Reaction was obtained by warming the reactor very slowly (through evaporation of a liquid N_2-CO_2 slush) to room temperature. After a couple of days at ambient temperature, it was noted that a few milliliters of -196 C noncondensables were present along with 1.72 millimole Cl_2 (contaminated with a little $FClO_3$). No other volatile materials were observed and the nonvolatile shiny, slightly yellow solid product (0.681 grams) corresponded to a 99.6-percent yield of $C_6F_5I\ (ClO_4)_2$.

REACTION OF Cl_2O_4 AND BROMOPENTAFLUOROBENZENE

Bromopentafluorobenzene (1.31 millimole) was loaded into a 30-milliliter cylinder in the dry box. Subsequently, Cl_2O_4 (3.17 millimoles) was added at -196 C from the vacuum line and the reactor was then kept at -45 C for several days. Removal at ambient temperature of all volatile species showed them to be mainly a mixture of BrCl and Cl_2, which were identified mass spectrometrically together with some unreacted Cl_2O_4 and lesser amounts of $S_2O_5F_2$ (impurity in the Cl_2O_4 originally used) and Cl_2O_7. Unreacted C_6F_5Br or other volatile C-F moieties were not detected. After pumping on the cylinder at ambient temperature for several hours, the remaining product (0.507 grams) was examined in the dry box. An oily, colorless liquid, its infrared spectrum showed C-F bands and very strong covalent $-ClO_4$ group bands. Based on the recovered BrCl, Cl_2, and Cl_2O_4, the composition of this liquid approaches $(ClO_4)_2\ C_6F_5Cl$. The theoretical weight for 1.31 millimole of this product was 0.525 grams.

REACTION OF Cl_2O_4 AND SULFURYL CHLORIDE

Chlorine perchlorate (3.87 millimoles) and sulfuryl chloride (1.95 millimole) were reacted at -23 C in a stainless-steel cylinder for several months. At that time it was found that much O_2 was present which was pumped away without measuring. The -196 C condensable products were Cl_2 (3.79 millimoles), a trace of ClO_2, and unreacted SO_2Cl_2, which was identified by its infrared spectrum. No Cl_2O_4 was recovered.

FLUORINE FLUOROSULFATE-$CsSF_5$ REACTION

A sample of $CsSF_5/CsF$ (60:40 millimole percent, 0.40 gram) was reacted with FSO_3F (1.77 millimole) in a 30-milliliter cylinder at ambient temperature for several days. Only a trace of -196 C noncondensable material was observed and the other products were subjected to fractional condensation in a series of cold U-traps. These consisted of unreacted FSO_3F (1.23 millimole) and SF_6 (0.53 millimole), both identified by their infrared spectra (Ref. 25). Pyrolysis of the solid left in the reactor liberated SF_4 (0.43 millimole). Thus, of the available SF_5^- (0.96 millimole), 55 percent had been converted to SF_6. An infrared spectrum of the solid showed only $CsSO_3F$ (Ref. 26).

CHLORINE FLUOROSULFATE-$CsIF_4$ REACTION

Solid $CsIF_4$ (1.13 millimole) was placed into a 30-milliliter cylinder in the dry box and freshly purified $ClSO_3F$ (1.02 millimole) was added from the vacuum line by condensing at -196 C. The reactants were maintained at -80 C for 48 hours. Recooling to -196 C showed no noncondensables had formed. Gradual warming first to -45 C then room temperature while pumping any volatile materials through successive U-traps cooled to -80, -112, and -196 C led to the separation of 0.52 millimole of Cl_2 and trace amounts of $S_2O_5F_2$. These were accompanied by a mixture of I_2/IF_5 as shown by appearance and an infrared spectrum. The solid by-product weighed 0.236 gram, which compares well with that calculated (0.277 gram) for 1.02 millimole of $CsSO_3F$ and 0.11 millimole of unreacted $CsIF_4$.

DIFLUORAMINO FLUOROSULFATE-$CsIF_4$ REACTION

Cesium tetrafluoroiodine (0.69 millimole) was loaded into a 30-milliliter cylinder in the dry box. After evacuation and cooling the cylinder to -196 C, a sample of NF_2SO_3F containing ~20 percent SO_2 (0.69 millimole) was condensed in. Several weeks of reaction at -45 C was followed by workup via fractional condensation of the volatile products at -80, -112, and -196 C. These were unreacted NF_2SO_3F (0.23 millimole), SO_2F_2 (0.46 millimole), and a mixture of I_2/IF_5.

PEROXYDISULFURYL DIFLUORIDE-$CsSeF_5$ REACTION

After loading $CsSeF_5$ (3.62 millimoles) into a 30-milliliter cylinder, purified $S_2O_6F_2$ (3.22 millimoles) was condensed in at -196 C and the reaction was allowed to proceed at ambient temperature for a couple of weeks. No -196 C noncondensables were formed and fractional condensation of the gases present was carried out at -45, -95, and -196 C. Unreacted $S_2O_6F_2$ (0.94 millimole) was recovered and SeF_6 (2.30 millimoles). No other volatile material was found. The weight of solid product (1.10 grams) agreed well with that expected (1.12 grams) for a mixture of 2.30 millimoles of CsS_2O_6F and 1.32 millimoles of $CsSeF_5$.

PEROXYDISULFURYL DIFLUORIDE-SeF_4 REACTION

A 10-milliliter cylinder was cooled to -196 C and charged with SeF_4 (1.64 millimole) followed by $S_2O_6F_2$ (1.92 millimole). The reactor was warmed slowly to room temperature and left for 1 week.

Vacuum fractionation of the volatile species led to the recovery of unreacted $S_2O_6F_2$ (1.34 millimole) and product SeF_6 (0.55 millimole) as the only gaseous materials. The cylinder contained a white solid (0.260 gram) which was identified as $SeF_3^+SO_3F^-$ by its infrared spectrum (Ref. 17). The yield (1.10 millimole) was 95 percent based on the reacted $S_2O_6F_2$.

CHLORINE FLUOROSULFATE-PHOSGENE REACTION

Chlorine fluorosulfate (3.55 millimole) and phosgene (1.84 millimole) were separately condensed into a 30-milliliter cylinder which was held at -196 C. The reactor was warmed to ambient temperature and then heated at 50 C for several hours. The products were separated by fractional condensation at -65, -112, and -196 C. These consisted of CO_2 and Cl_2 together with traces of COFCl and SO_2F_2, all of which were retained at -196 C. The -112 C fraction was $S_2O_5F_2$ (1.60 millimole) and the -65 C fraction was $ClC(O)SO_3F$ (0.20 millimole), both of which were identified by their infrared spectra and vapor pressure (Ref. 27 and 28). The yield of $S_2O_5F_2$ was 90 percent.

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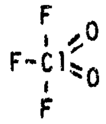
Chlorine Trifluoride Dioxide, ClF_3O_2. Synthesis and Properties

by Karl O. Christe* and Richard D. Wilson

Received: Oct. 24, 1972

Abstract

Chlorine trifluoride dioxide was prepared from FNO_2 and $ClF_2O_2^+PtF_6^-$, the latter being synthesized from $FClO_2$ and PtF_6. Physical properties and the ^{19}F nmr spectrum are reported. The nmr spectrum suggests the following trigonal bipyramidal structure of symmetry C_{2v}



$$\mathrm{F{-}\overset{F}{\underset{F}{Cl}}{\lesssim}^{O}_{O}}$$

Chlorine trifluoride dioxide forms stable adducts with BF_3 and AsF_5 but not with FNO, FNO_2 or CsF.

Introduction

A brief note on the existence of ClF_3O_2 has recently been published by Christe[1]. In this paper we report details on its synthesis, purification, and properties. The infrared spectrum of the gas, the solid, and of the matrix isolated species, and the Raman spectrum of the gas and the liquid together with a normal coordinate analysis and computation of thermodynamic properties will be published elsewhere[2].

Experimental

Materials and Apparatus. The stainless steel-Teflon FEP vacuum system[3], the glove box, the ^{19}F nmr spectrometer and sampling technique[4], and the syntheses and purification of PtF_6, $FClO_2$, FNO,[3] FNO_2, BF_3, and $ClF_2O_2^+BF_4^-$[5] have previously been described. Cesium fluoride was fused in a platinum crucible and powdered in a drybox prior to use. All equipment was passivated with ClF_3 and BrF_5 prior to its use.

Purification of ClF_3O_2. A sample of $ClF_2O_2^+ BF_4^-$ (2.41 mmole), prepared and purified as previously reported[5], was placed in a passivated Teflon FEP ampoule. Nitryl fluoride (6.83 mmole) was added at -196° and the mixture was kept at -78° for 12 hours with periodic agitation. Volatile products were removed at -78° and separated by fractional condensation through a series of traps kept at -95, -126, and -196°. The -95° trap contained only a very small amount of material which was discarded. The -126° trap contained 2.22 mmole of ClF_3O_2 which according to its infrared spectrum[2] at 700 mm pressure showed as the only detectable impurity less than 0.1 mole % of $FClO_2$. This sample was used for the subsequent characterization studies. The -196° trap contained the unreacted FNO_2 (4.4 mmole) and a small amount of ClF_3O_2 (0.2 mmole). The solid residue was shown by its weight and infrared spectrum to be $NO_2^+BF_4^-$.

The ClF_3O_2-CsF System. Two reactions between ClF_3O_2 (1.5 mmole) and CsF (1.0 mmole) were carried out in 10 ml stainless steel cylinders at 25° and 105°, respectively. At the lower temperature the cylinder was placed on a mechanical shaker for five days. The volatile material consisted of F_2, $FClO_2$, and some ClF_3O_2. The solid residue had gained 33 mg in weight and was identified by its infrared spectrum[6] as a mixture of $Cs^+ClO_2F_2^-$ and CsF. When the starting materials were heated to 105° for 68 hours, the ClF_3O_2 had quantitatively decomposed to $FClO_2$ and F_2.

Results and Discussion

Synthesis. The synthesis of ClF_3O_2 is best described by the following reaction sequence:

$$2FClO_2 + 2PtF_6 \rightarrow ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- \qquad (1)$$

Several side reactions compete with (1) and the yield of $ClF_2O_2^+$ varies greatly with slight changes in the reaction conditions[3]. The ClF_3O_2 is then displaced from its $ClF_2O_2^+$ salt according to:

$$ClF_2O_2^+PtF_6^- + ClO_2^+PtF_6^- + 2FNO_2 \rightarrow 2NO_2^+PtF_6^- + ClF_3O_2 + FClO_2 \qquad (2)$$

Chloryl fluoride is slightly less volatile than ClF_3O_2. Therefore, most of it can be removed from ClF_3O_2 by fractional condensation in a -112° trap. The remaining $FClO_2$, however, has to be removed by complexing with BF_3:

$$ClF_3O_2 + FClO_2 + 2BF_3 \rightarrow ClF_2O_2^+BF_4^- + ClO_2^+BF_4^- \qquad (3)$$

Since $ClF_2O_2^+BF_4^-$ is stable[5] at 20° whereas $ClO_2^+BF_4^-$ is not[7], the latter can be pumped away at 20°. The resulting pure $ClF_2O_2^+BF_4^-$ is then treated with an excess of FNO_2 and the evolved ClF_3O_2 and unreacted FNO_2 are readily separated by fractional condensation through a series of -126 and -196° traps:

$$ClF_2O_2^+BF_4^- + FNO_2 \rightarrow NO_2^+BF_4^- + ClF_3O_2 \qquad (4)$$

Whereas the overall yield of pure ClF_3O_2 based on the PtF_6 used in step 1 was found to be rather low (about 10 mole %), the method was satisfactory to provide enough material to characterize ClF_3O_2. Therefore, no effort was undertaken to search for alternate synthetic routes which might give higher yields of ClF_3O_2.

Properties. Pure ClF_3O_2 is colorless as a gas or liquid and white in the solid state. It melts at -81.2°. Vapor pressures were measured over the range -96 to -32° and the data for the range -64 to -32° were fitted by the method of least squares to the equation

$$\log P_{mm} = 7.719 - \frac{1217.2}{T(°K)}$$ with an index of correlation of .99998.

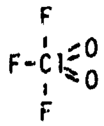
The extrapolated boiling point is -21.58°. Measured vapor pressures at the noted temperatures are [T(°C), P(mm)]: -95.64, 7.3; -78.73, 25.5; -64.34, 77.5; -57.69, 117.5; -46.32, 226.5; -31.93, 470. The two lowest temperature points were not used for the computation of the vapor pressure equation because the lowest point was measured for solid ClF_3O_2 and the second lowest was too close to the melting point of ClF_3O_2. While at -78.73° the ClF_3O_2 sample was all liquid, the observed vapor pressure was reproducibly lower than expected from the above vapor pressure curve. This indicates that close to the melting point some ordering effect occurs in the liquid causing a decrease of the vapor pressure. The latent heat of vaporization of ClF_3O_2 is 5.57 kcal/mole and the derived Trouton constant is 22.13, indicating little association in the liquid phase. This is in agreement with the low boiling point and the good agreement between the Raman spectra of the gas and of the liquid[2]. The molecular weight was determined from the vapor density and found to be 122.1 (calcd. for ClF_3O_2 124.5). The good agreement indicates little or no association in the gas phase at the pressures used (P ~ 1 atm).

Chlorine trifluoride dioxide resembles chlorine fluorides and oxyfluorides in its corrosive and oxidizing properties. It appears to be marginally stable in a well passivated system at ambient temperature. It is a strong oxidative fluorinator as evidenced by its tendency to fluorinate metal surfaces to metal fluorides with $FClO_2$ formation. It reacts explosively with organic materials and care must be taken to avoid such combinations. The hydrolysis of ClF_3O_2 was not quantitatively studied; however, on one occasion a slight leak in an infrared gas cell containing ClF_3O_2 resulted in the formation of $FClO_3$ and HF indicating the following reaction:

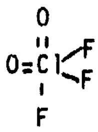
$$ClF_3O_2 + H_2O \rightarrow FClO_3 + 2HF \qquad (5)$$

^{19}F nmr Spectrum. The ^{19}F nmr spectrum of liquid ClF_3O_2 was measured in the temperature range -20 to -80°. It showed at all temperatures one partially resolved signal centered at -413 ppm below the external standard $CFCl_3$. Figure 1 shows the details of the spectrum recorded at -77°. The observed signal is in excellent agreement with an AB_2 pattern[8] with $\frac{J}{\nu_0\delta} = 1.0$ (for the computed pattern see Figure 1). From these data a value of $J_{FF} = 443$ Hz was calculated. The low chemical shift of -413 ppm for ClF_3O_2 is in excellent agreement with a heptavalent chlorine fluoride and compares favorably with those observed[4] for $FClO_2$ (-315 ppm), ClF_6^+ (-388 ppm) and $ClF_2O_2^+$ (-310 ppm). The fact that the resonance of the $ClF_2O_2^+$ cation was observed upfield from that of ClF_3O_2 is difficult to rationalize, but seems to be quite general for chlorine fluorides[4]. The fluorine-fluorine coupling constant of 443 Hz observed for ClF_3O_2 is similar to that of 421 Hz observed for the structurally related ClF_3[4].

Since the chlorine atom in ClF_3O_2 does not possess a free valence electron pair, it is pentacoordinated and the ligands should form a trigonal bipyramide. To account for an AB_2 pattern one has to assume two fluorine atoms in either the axial or the equatorial positions:



I



II

Of these two models, I has to be preferred for the following four reasons. (i) The B_2 part of the AB_2 pattern occurs downfield from the A part and in trigonal bipyramidal species the resonance for the axial fluorines occurs at a lower field than that of the equatorial ones[9,10]. (ii) In trigonal bipyramidal molecules the most electronegative ligands generally occupy the axial positions[11]. (iii) The vibrational spectrum[2] is consistent only with model 1. (iv) In the structually related ClF_3O[12] and ClF_3[13] molecules (in which the oxygen ligands are replaced by one and two sterically active free electron pairs, respectively) both axial positions are occupied by fluorine atoms.

Adduct Formation. Chlorine trifluoride dioxide forms stable adducts with strong Lewis acids, such as BF_3, AsF_5, or PtF_5[5]. These adducts have ionic structures containing the $ClF_2O_2^+$ cation. A detailed discussion of the vibrational and nmr spectra of this cation will be given elsewhere[5]. The high stability of these adducts can be explained by the change from the energetically unfavorable trigonal bipyramidal structure of ClF_3O_2 to the more favorable tetrahedral $ClF_2O_2^+$ configuration[14]. Contrary to ClF_3[15] but by analogy with ClF_3O[14], it does not form stable adducts with FNO or FNO_2 at temperatures as low as -78°. This was demonstrated by the various displacement reactions where ClF_3O_2 and unreacted FNO or FNO_2 could be readily removed from the reactor at -78°. With the stronger base, CsF, it does not form a stable adduct but decomposes to $FClO_2$ and F_2 with CsF possibly catalyzing the decomposition.

Acknowledgement. We thank Drs. D. Pilipovich and C. J. Schack for helpful discussions. We are pleased to acknowledge support of this work by the Office of Naval Research, Power Branch.

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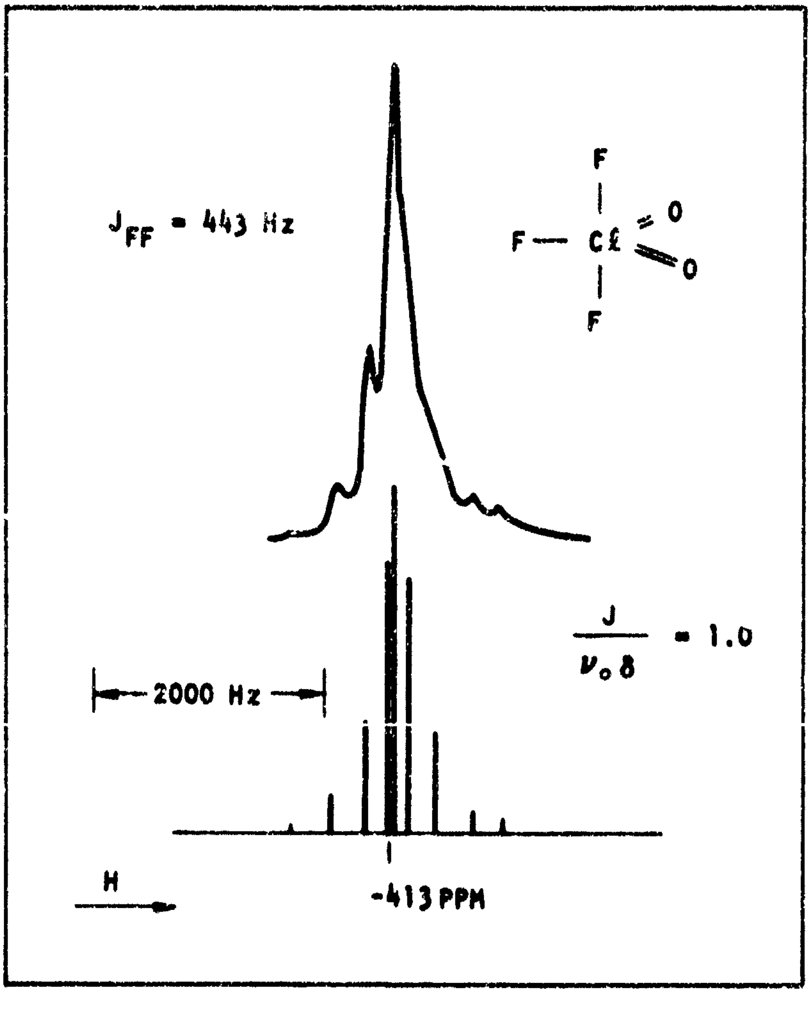
Diagram Caption

Figure 1. ^{19}F nmr Spectrum of Liquid ClF_3O_2 at -77° Recorded at 56.4 MHZ. The Chemical Shift was Measured Relative to the External Standard $CFCl_3$.


J_{FF} = 443 Hz
F
F — Cℓ = O
O
F
$\frac{J}{\nu_o \delta}$ = 1.0
2000 Hz
H
-413 PPM

Contribution from Rocketdyne, A Division of Rockwell International,
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Chlorine Trifluoride Dioxide. Vibrational Spectrum, Force Constants, and Thermodynamic Properties

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

Received: March 16, 1973

Abstract

The infrared spectra of gaseous, solid, and matrix isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 are reported. Twelve fundamental vibrations were observed, consistent with a structure of symmetry C_{2v}. A modified valence force field and thermodynamic properties were computed for ClF_3O_2.

Introduction

A brief note on the existence of ClF_3O_2 was recently published by Christe[1]. In a subsequent paper[2], more details on its synthesis and physical properties were given. Proof for a pseudo-trigonal bipyramidal structure of symmetry C_{2v} was obtained[2] from its ^{19}F nmr spectrum, which showed an AB_2 pattern with strong evidence for the two equivalent fluorine atoms occupying the apical positions. In this paper, we report the complete vibrational spectrum, force constants, and thermodynamic properties of ClF_3O_2.

Experimental

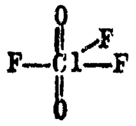
The synthesis and purification of ClF_3O_2 has previously been described[1,2]. The sample used in this investigation showed no detectable impurities except for small amounts of $FClO_2$ which easily forms during handling and cannot be separated from ClF_3O_2 by fractional condensation[2]. The amount of $FClO_2$ formed, however, could be minimized by thorough passivation of the stainless steel-Teflon FEP vacuum system with BrF_5 and ClF_3. For example, the infrared spectrum of gaseous ClF_3O_2 at 700 mm pressure showed the presence of less than 0.1 mole percent of $FClO_2$.

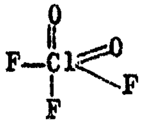
The infrared spectra were recorded on a Perkin Elmer Model 457 spectrophotometer in the range of 4000 to 250 cm^{-1}. The instrument was calibrated by comparison with standard gas calibration points[3]. The gas cell was made of Teflon and had a path length of 5 cm and AgCl windows. The apparatus, materials, and technique used for the matrix isolation study have previously been described[4,5]. Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å line of an Ar-ion laser as the exciting line. A stainless steel cell with Teflon O-rings and sapphire windows was used for obtaining the spectrum of the gas. The design of this cell was similar to that of a cell described previously[6]. The spectrum of the liquid was obtained using a Teflon FEP capillary as the sample container in the transverse excitation transverse viewing mode.

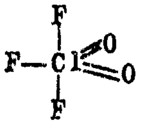
Results and Discussion

Vibrational Spectra. Figure 1 shows the infrared spectra of gaseous, solid, and N_2-matrix isolated ClF_3O_2 and the Raman spectra of gaseous and liquid ClF_3O_2 at various concentrations. The spectra of solid ClF_3O_2 were corrected for small amounts of $FClO_2$. The $FClO_2$ bands were verified by depositing pure $FClO_2$ on top of the ClF_3O_2 sample and observing the relative growth rates of the bands. Figure 2 shows the most intense infrared bands of gaseous and matrix isolated ClF_3O_2 at higher resolution allowing some conclusions about the band contours and the determination of the ^{35}Cl-^{37}Cl isotopic shifts. Table I lists the observed frequencies. Table II lists the fundamental vibrations of ClF_3O_2 and their assignment compared to those of the related species, ClF_3,[7] ClF_3O,[8] $ClF_2O_2^-$,[9] ClF_4^+,[10] and ClO_2^+.[11]

The structure of ClF_3O_2 can be derived from a trigonal bipyramid, in which the two oxygen ligands could occupy either both apical (I), or one apical and one equatorial (II), or two equatorial (III) positions. These three models belong to different point groups and should differ markedly in their







	I	II	III
Point Group	D_{3h}	C_s	C_{2v}
Total Number of Fundamentals	8	12	12
Infrared Active	5	12	11
Raman Active	6	12	12
Polarized Raman Bands	2	8	5

vibrational spectra. The observation of a total of 12 fundamentals for ClF_3O_2 (see Figures 1 and 2 and Table I) with a minimum of ten bands being active in the infrared and the Raman spectrum, together with the occurrence of four or five

TABLE I

Vibrational Spectra of ClF_3O_2 and their Assignment in Point Group C_{2v}

Observed Frequencies (cm^{-1}), Intensities[a]					Assignment	
Infrared			Raman			
Gas	Solid: Matrix Isolated	Solid: Neat	Gas	Liquid		
2655 vw					2 x 1327 = 2654	2 ν_{10} (A_1)
2415 vw	2420 2405 2385 vw	2405 vw			1093 + 1327 = 2420	$\nu_1 + \nu_{10}$ (B_2)
2184 vw		2180 vw			2 x 1093 = 2186	2 ν_1 (A_1)
2012 vw	2012 vw	2010 vw			683 + 1327 = 2010	$\nu_2 + \nu_{10}$ (B_2)
1860 vw		1850 vw			520 + 1327 = 1847	$\nu_3 + \nu_{10}$ (B_2)
1776 vw					1093 + 695 = 1788 1093 + 683 = 1776	$\nu_1 + \nu_7$ (B_1) $\nu_1 + \nu_2$ (A_1)
1625 vw					1093 + 531 = 1624	$\nu_1 + \nu_{11}$ (B_2)
1615 vw		1610 vw			1093 + 520 = 1613 286 + 1327 = 1613	$\nu_1 + \nu_3$ (A_1) $\nu_5 + \nu_{10}$ (B_2)
1579 vw					1093 + 487 = 1580	$\nu_1 + \nu_4$ (A_1)
1499 vw		1495 vw			2 x 487 + 520 = 1494 683 + 286 + 531 = 1500	2 $\nu_4 + \nu_3$ (A_1) $\nu_2 + \nu_5 + \nu_{11}$ (B_2)
1375 vw		1375 vw			683 + 695 = 1378	$\nu_2 + \nu_7$ (B_1)
1368 vw	1365 vw				2 x 683 = 1366	2 ν_2 (A_1)
1341 1331	1331.4 s	1327 s				ν_{10} ^{35}Cl (B_2)
1317 vs	1318.8 ms	1315 m, sh		1320 (0.1),br	1093 + 222 = 1315	$\nu_1 + \nu_{12}$ (B_2)
1306	1307.8 ms	1305 m, sh				ν_{10} ^{37}Cl (B_2)
1230 vw	1230 vw				520 + 695 = 1215	$\nu_3 + \nu_7$ (B_1)
1218 vw	1218 vw				683 + 531 = 1214	$\nu_2 + \nu_{11}$ (B_2)
	1207 vw	1200 vw			683 + 520 = 1203	$\nu_2 + \nu_3$ (A_1)

TABLE I (continued)

Vibrational Spectra of ClF_3O_2 and their Assignment in Point Group C_{2v}

Observed Frequencies (cm^{-1}), Intensities[a]					Assignment	
Infrared			Raman			
Gas	Solid		Gas	Liquid		
	Matrix Isolated	Neat				
1195 vw	1203 vw				2 x 592 = 1184	2 ν_8 (A_1)
1186 vw		1150 vw			487 + 695 = 1182	$\nu_4 + \nu_7$ (B_1)
1174 vw	1173 1169 vw				683 + 487 = 1170	$\nu_2 + \nu_4$ (A_1)
	1116 vw				417 + 695 = 1112	$\nu_6 + \nu_7$ (B_2)
					520 + 592 = 1112	$\nu_3 + \nu_8$ (B_1)
1093 s	1093 ms		1093(3.5)	1090(4.1) pol[b]		ν_1 ^{35}Cl (A_1)
	1086 m					ν_1 ^{37}Cl (A_1)
	1080 vw					
	1073 vw	1070 vw,sh			695 + 372 = 1067	$\nu_7 + \nu_9$ (A_1)
	1065 vw				2 x 531 = 1062	2 ν_{11} (A_1)
985 vw					286 + 695 = 981	$\nu_5 + \nu_7$ (B_1)
978 vw	974 vw	968 vw			2 x 487 = 974	2 ν_4 (A_1)
881 vw					286 + 592 = 878	$\nu_5 + \nu_8$ (B_1)
856 vw					487 + 372 = 859	$\nu_4 + \nu_9$ (B_1)
805 797 vw	810 vw	806 vw			520 + 286 = 806	$\nu_3 + \nu_5$ (A_1)
786 vw					417 + 372 = 789	$\nu_6 + \nu_9$ (B_2)
772 vw		760 sh, vw			487 + 286 = 773	$\nu_4 + \nu_5$ (A_1)
758 vw					531 + 222 = 753	$\nu_{11} + \nu_{12}$ $(A_1$

TABLE I (continued)

Vibrational Spectra of ClF_3O_2 and their Assignment in Point Group C_{2v}

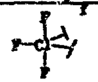
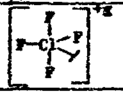
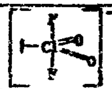
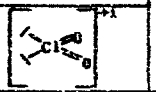
Observed Frequencies (cm^{-1}), Intensities[a]					Assignment
Infrared			Raman		
Gas	Solid		Gas	Liquid	
	Matrix Isolated	Neat			
702					
695	686.3 vs	655 vs, br			ν_7 ^{35}Cl (B_1)
687 sh vs	682.6 m	700 sh,s	683(10)	675(6.5) pol	
683	674.7 s				ν_7 ^{35}Cl (B_1)
679 sh					ν_2 ^{35}Cl (A_1)
593 s	591 ms	570 s		586(0.1)	ν_8 (B_1)
543 m	531 m	527 m	540 sh	530 sh	ν_{11} ^{35}Cl (B_2)
531	528 mw				ν_{11} ^{37}Cl (B_2)
520 sh,mw	519 w	520 sh,w	520(7.5)	518(10) pol	ν_3 (A_1)
	487 vw	473 mw	487(6.1)	481(9.0) pol	ν_4 (A_1)
	417 vw	417 vw		402 (0+)	ν_6 (A_2)
	372 w	368 w			ν_9 (B_1)
	287 w	290 w	285(0.9)	285(1.6)	ν_5 (A_1)
			222(0.7)	222(1.2)	ν_{12} (B_2)

(a) Uncorrected Raman intensities representing the relative peak height; the relative peak widths, and hence, the relative peak heights change from gaseous to liquid ClF_3O_2.

(b) Only qualitative polarization measurements could be obtained, owing to the optical activity of the sapphire windows of the gas cell and owing to the tendency of ClF_3O_2 to act as a plasticizer for the Teflon FEP capillaries.

TABLE II

Vibrational Spectrum of ClF_3O_2 Compared to Those of Similar Molecules and Ions

Observed Frequencies (cm^{-1}), Intensities												Assignment for ClF_3O_2 in Point Group C_{2v}	Approximate Description of Mode[k]
		 [d]		 [f]		 +[g]		 −[h]		 +[i]			
IR	RA	IR	RA	IR	RA	IR	RA	IR	RA	IR	RA		
1093 s	1093(4)p	(1222)		—		—		1070 s	1075(10)	1044 s	1044(10)	A_1 ν_1	sym. ClO_2 stretch
683 m	683(10)p	806 s	694(2.4)p	752 s	752 s,p	830 – 810		—				ν_2	ClF_{eq} stretch
518 w	520(8)p	—		—		—		559 m	559(1.2)	521 s	521(3)	ν_3	ClO_2 scissor
487 vw	487(6)p	478 mw	482(10)p	530 m	529 vs,p	586 w	567(7)	330–370 m	363(10)	—		ν_4	sym. $F_{ax}ClF_{ax}$ stretch
287 w	285(1)	c,e	224(0.4)p	328 s	329 w,p	c	237(1)	c	198(0.7)	—		ν_5	$F_{ax}ClF_{ax}$ scissor in ClF_3 plane
(417)[a]	402(0+)	412 w	414(0.2)dp	—			474(1)		460(1)	—		A_2 ν_6	torsion
686 vs		682 vs		702 vs		770 vs		510 vs		—		B_1 ν_7	antisym. $F_{ax}ClF_{ax}$ stretch
382 s	386(0+)	480 m	500(1)	—		536 mw	536(2)	330–370 m	337(	—		ν_8	ClO_2 wagging
372 w				442 w	431 w,dp			—		—		ν_9	Antisym. $F_{eq}ClF_{2ax}$ deform. in ClF_3 plane
1327[b] vs	1320(0+)	(1222)		—		—		1225 vs	1221(0.8)	1296 vs	1296(3)	B_2 ν_{10}	Antisym. ClO_2 stretch
531 m	530(1)	323 mw[e]	319(0.1)	—		—		330–370 m	378(8)	—		ν_{11}	ClO_2 rocking
c	222(1)			328 s	329 w	386 m	388(0+)			—		ν_{12}	$F_{ax}ClF_{ax}$ scissor out of $ClClF_3$ plane

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(a) Observed only for solid ClF_3O_2

(b) Frequency corrected for disturbance by Fermi resonance

(c) Below frequency range of spectrometer used

(d) K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 2196 (1972).

(e) According to the potential energy distribution, the 224 and 320 cm^{-1} modes are an almost equal mixture of the corresponding symmetry coordinates and, hence, not very characteristic

(f) H. Selig, H. H. Claassen, and J. H. Holloway, J. Chem. Phys., 52, 3517 (1970).

(g) K. O. Christe and W. Sawodny, to be published.

(h) K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 35 (1972).

(i) K. O. Christe, C. J. Schack, D. Pilipovich, and W. Sawodny, Inorg. Chem., 8, 2489 (1969).

(k) The modes in the B_1 block are highly mixed (see PED, Table VI) and, therefore, difficult to associate with the frequencies.

polarized Raman bands rule out point group D_{3h} and favor C_{2v} over C_s. Additional strong evidence for symmetry C_{2v} consists of the relative infrared and Raman intensities and of the frequency separation of the ClF_2 stretching modes, indicating a highly symmetric, i.e., approximately linear, FClF arrangement. Comparison with the vibrational spectra of a number of related species having geometries similar to that of model III (see Table II) also supports model III. This conclusion in favor of model III, reached exclusively on the basis of the observed vibrational spectrum, is in excellent agreement with the observed ^{19}F nmr spectrum[2] and the general observation[12] that in trigonal bipyramidal molecules, the most electronegative ligands always occupy the apical positions.

The 12 fundamentals expected for an XY_3Z_2 molecule of symmetry C_{2v} are classified as $5A_1 + A_2 + 3B_1 + 3B_2$. All of these should be active in both the infrared and Raman spectrum except for the A_2 mode which should be only Raman active. The strong bands at about 1327 and 1093 cm^{-1} have frequencies too high for any Cl-F stretching modes and, hence, must be assigned to the antisymmetric and symmetric ClO_2 stretching modes, respectively. The antisymmetric axial F-Cl-F stretching mode should occur in the 600-800 cm^{-1} frequency range, be of very high infrared and very low Raman intensity, and by comparison with ClF_3O [8] and ClF_3 [7] show a $^{35}Cl-^{37}Cl$ isotopic shift of about 11 cm^{-1}. Consequently, this mode must be assigned to the bands observed at 686.3 and 674.7 cm^{-1} in the N_2 matrix. The symmetric axial F-Cl-F stretching mode should occur in the 450 - 570 cm^{-1} frequency range and be of high intensity in the Raman and of very low intensity in the infrared spectrum. There are two intense polarized Raman bands at 520 and 487 cm^{-1}, respectively, which might be assigned to this mode. Since the 487 cm^{-1} band is of much lower infrared intensity (for an ideal linear, symmetric F-Cl-F group, this mode should be infrared inactive and indeed was not observed for gaseous ClF_3O_2), it is assigned to the symmetric axial FClF stretching mode. The fifth stretching mode involving the equatorial fluorine is expected to occur between 650 and 800 cm^{-1}, to be of medium to strong infrared intensity, and to give rise to an intense polarized Raman line. Clearly this mode must be assigned to the 682.8 cm^{-1} band in the matrix and the 683 cm^{-1} Raman band. Comparison with ClF_3O and ClF_3 [7] indicates a ^{35}Cl-^{37}Cl isotopic shift of about 7 cm^{-1} for this mode. Its ^{37}Cl part could not directly be observed for the matrix isolated sample owing to its accidental coincidence with the much more intense ^{37}Cl antisymmetric FClF stretching mode.

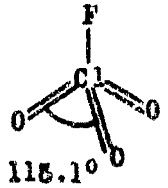
The remaining seven bands must be assigned to the deformation modes. Of these, only the A_2 torsion mode ideally should be infrared inactive. Since the Raman band at about 410 cm^{-1} shows no counterpart in the infrared spectrum of the gas, it is assigned to this torsion mode. The 520 cm^{-1} Raman band is clearly polarized and, hence, must belong to species A_1. Based on its relatively high frequency, it must represent the ClO_2 scissoring mode and not the axial F-Cl-F deformation. Based on the observed Fermi resonance (see below) between the 1327 cm^{-1} band and the 1093 + 222 combination band, the 222 and 1327 cm^{-1} bands must belong to the same symmetry species. Consequently, the 222 cm^{-1} band must represent the B_2 axial F-Cl-F deformation. There are four bands occurring at about 590, 530, 370, and 290 cm^{-1}, respectively, left for assignment. Two of these represent a rocking and wagging motion, respectively, of the ClO_2 group and, therefore, should have higher frequencies than the two remaining FClF deformations. Assignment of the 591 cm^{-1} band to the ClO_2 wag and of the 531 cm^{-1} band to the ClO_2 rock can be made based on the observed gas phase band contours and the observed ^{35}Cl-^{37}Cl isotopic splittings (see Figure 2, traces G to K). The 591 cm^{-1} band shows a Q-R branch splitting for $^{35}ClF_3O_2$ of about 8 cm^{-1} comparable to that observed for the antisymmetric FClF stretch, ν_7 (B_1). The 531 cm^{-1} band exhibits a missing Q branch and a P-R branch separation of about 11 cm^{-1} comparable to that observed for the antisymmetric ClO_2 stretch, ν_{10} (B_2). Furthermore, the 531 cm^{-1} band shows a larger ^{35}Cl-^{37}Cl isotopic splitting than the one at 591 cm^{-1} in agreement with the values (see Table IV) computed for the ClO_2 rocking and wagging motions, respectively. The remaining two bands at 286 and 272 cm^{-1} are assigned to the axial F-Cl-F scissoring mode ν_5 (A_1) and the antisymmetric in plane ClF_3 deformation mode, ν_9 (B_1), respectively. This assignment is based on the observed frequencies and the relative infrared and Raman intensities. The assignment of the 286 cm^{-1} Raman band to an A_1 mode is further supported by the fact that it appears to be weakly polarized. The excellent fit between all the observed and computed combination bands and overtones (see Table I) without violation of the selection rules ($B_1 + B_2 = A_2$ and $A_1 + A_2 = A_2$ combinations are infrared forbidden) also suggests the correctness of the above assignments.

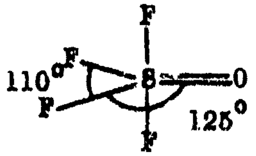
The observation of three relatively intense bands in the N_2 matrix for the antisymmetric ClO_2 stretching mode, ν_{10} (B_2), requires further explanation. For this mode, a ^{35}Cl-^{37}Cl isotopic splitting of about 15 cm^{-1} might be predicted by comparison with that observed for related ClO_2^+[11]. The combination band, 1093 + 222 = 1315 cm^{-1}, should show a considerably smaller ^{35}Cl-^{37}Cl isotopic splitting of about 8 cm^{-1} (see Table IV) and based on its frequency fall between the ^{35}Cl and ^{37}Cl isotopic bands of ν_{10}. As shown schematically in Figure 2, Fermi resonance between ν_{10} and $\nu_1 + \nu_{12}$ will increase the frequency separation between the ^{35}Cl and ^{37}Cl components of ν_{10} and decrease that between the two isotopic combination bands. This assignment is supported by the observed bandwidths at half height which are similar (~ 2.0 cm^{-1}) for the 1331.4 and 1307.8 cm^{-1} bands, but larger ($\sim$3.0 cm^{-1}) for the 1318.8 cm^{-1} band. The disturbance by Fermi resonance can also account for the strongly increased intensity of the combination band. The fact that the frequency of the 1318.3 cm^{-1} band is closer to 1307.8 than to 1331.4 cm^{-1}, agrees with the observed relative intensities. The 1307.8 cm^{-1} band has lost relatively more of its original intensity as demonstrated by the observed intensity ratio of 1:4.4 for the 1307.8 and 1331.4 cm^{-1} bands. For undisturbed ^{35}Cl-^{37}Cl isotopic species, this ratio should be 1:3.07.

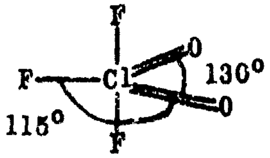
The observed gas phase infrared band contours are complicated by the ^{35}Cl-^{37}Cl isotopic splittings, Fermi resonance, and two double coincidences of ν_7 with ν_2 and of ν_{11} with ν_3, respectively. However, for most of the bands, the R branches of the ^{35}Cl isotope are well separated (see Figure 2). Since the geometry of ClF_3O_2 of symmetry C_{2v} can be estimated (see below), the three principal moments of inertia were computed resulting in A = 0.150, B = 0.106, and C = 0.095 cm^{-1}. Based on these values, the infrared band contours were estimated for ClF_3O_2, according to the method of Ueda and Shimanouchi[13]. Using No. 33 of Ueda's Figure 3,[13] one should expect for the B_1 modes an A-type band contour with a sharp Q branch and a P-R branch separation of about 16 cm^{-1}. As can be seen from Figure 2, the 686 and 591 cm^{-1} bands show the predicted band shape and branch separation and, therefore, may be assigned with confidence to ν_7 and ν_8, respectively. The 1331 and 531 bands do not show a Q branch as expected for B-type bands of species B_2. Consequently, the observed band contours are consistent with the proposed structure of symmetry C_{2v} and the assignments listed in Table I.

Comparison between the vibrational spectrum of ClF_3O_2 and those of related species (Table II) shows good agreement and strongly supports the above assignments for ClF_3O_2. Two features in the ClF_3O_2 spectrum, however, require further comment. The ClO_2 scissoring mode, ν_3 (A_1), is unexpectedly intense in the Raman spectrum. Since the frequency of ν_3 is close to that of the intense ν_2 (A_1) mode and since these motions could easily couple (as indicated by the normal coordinate transformation L^{-1} and to some extent by the PED), this represents a plausible explanation for its high intensity. Alternate explanations, such as Fermi resonance between the symmetric axial FClF stretching mode ν_4 and 222 + 286 = 508 can be ruled out because they belong to different symmetry species. Resonance between ν_3 and ν_4 can also be eliminated because the observed combination bands involving either ν_3 or ν_4 show a good frequency fit, indicating that the fundamentals are undisturbed. Secondly, the frequencies of the two axial FClF scissoring modes (in and out of the ClF_3 plane, respectively) are strongly influenced by the point group of the corresponding molecules and by the presence or absence of other modes in the same symmetry species and, hence, are difficult to correlate. Furthermore, in ClF_3O, these two frequencies are not characteristic and are an almost equal mixture of the corresponding symmetry coordinates[8].

Force Constants. The potential and kinetic energy metrics for ClF_3O_2 were computed by a machine method[14]. The geometry assumed for this computation was $D(ClO) = 1.40$ Å, $R(ClF_{eq}) = 1.62$ Å, $r(ClF_{ax}) = 1.72$ Å, $\alpha(\sphericalangle OClO) = 130^\circ$, $\beta(\sphericalangle F_{eq}ClF_{ax}) = \delta(\sphericalangle OClF_{ax}) = 90^\circ$, and $\gamma(\sphericalangle OClF_{eq}) = 115^\circ$, based on the observed geometries of ClF_3 [15] and $FClO_3$ [16] and a correlation[17] between ClO bond length and stretching frequency. The deviation of the OClO band angle from the ideal 120° was estimated by comparison with the known geometries of SF_4O [18] and $FClO_3$ [16].







The symmetry coordinates used for ClF_3O_2 are given in Table III. The bending coordinates were weighted by unit (1 Å) distance so the stretching force constants have units of mdyn/Å, the deformation force constants units of mdynÅ/radian^2, and the stretch-bend interaction constants mdyn/radian. The G matrix and Z transformation were found numerically by the computer and, hence, are not given here.

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. Owing to the underdetermined nature (28 symmetry force constants and 12 frequencies) of the problem a diagonal force field was computed assuming all off-diagonal symmetry force constants equal to zero. In the A_1 and B_1 block, however, non-zero values were required for several off-diagonal constants to be able to reproduce the observed frequencies. The quality of the resulting force field was examined by comparing the computed ^{35}Cl-^{37}Cl isotopic shifts with those observed. The observed Cl isotopic shifts were then used to improve the force field by introducing off-diagonal constants until the calculated isotopic shifts agreed with the observed ones. Those interaction constants not significantly influencing the isotopic shift were not changed while those introduced were required to achieve a fit between observed and computed isotopic shifts. The force field is still not unique and other solutions are certainly possible. Species A_1 contains 15 symmetry force constants. Of these, three off diagonal terms, i.e. F_{14}, F_{24}, and F_{34}, may be neglected[19] since their corresponding G matrix elements are zero. Therefore, eight frequencies (5 ^{35}Cl + 3 ^{37}Cl) are available for obtaining 12 symmetry force constants. In species B_1 and B_2 5 frequency values are available for obtaining six symmetry force constants. Numerical experiments indicated that plausible force fields and PED values

TABLE III

Symmetry Coordinates[a] for ClF_3O_2

A_1	S_1	$1/\sqrt{2}\ (\Delta D_1 + \Delta D_2)$
	S_2	ΔR
	S_3	$1/\sqrt{6}\ (2\Delta\alpha - \Delta\gamma_1 - \Delta\gamma_2)$
	S_4	$1/\sqrt{2}\ (\Delta r_1 + \Delta r_2)$
	S_5	$1/\sqrt{12}\ (2\Delta\beta_1 + 2\Delta\beta_2 - \Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$
	S_{r1}	$1/\sqrt{3}\ (\Delta\alpha + \Delta\gamma_1 + \Delta\gamma_2) \equiv 0$
	S_{r2}	$1/\sqrt{6}\ (\Delta\beta_1 + \Delta\beta_2 + \Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4) \equiv 0$
A_2	S_6	$1/\sqrt{4}\ (\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 + \Delta\delta_4)$
B_1	S_7	$1/\sqrt{2}\ (\Delta r_1 - \Delta r_2)$
	S_8	$1/\sqrt{4}\ (\Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 - \Delta\delta_4)$
	S_9	$1/\sqrt{2}\ (\Delta\beta_1 - \Delta\beta_2)$
B_2	S_{10}	$1/\sqrt{2}\ (\Delta D_1 - \Delta D_2)$
	S_{11}	$1/\sqrt{2}\ (\Delta\gamma_1 - \Delta\gamma_2)$
	S_{12}	$1/\sqrt{4}\ (\Delta\delta_1 + \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$

(a) S_{r1} and S_{r2} are the redundant coordinates and $\delta_1 = \angle O_1ClF_2$, $\delta_2 = \angle O_1ClF_3$, $\delta_3 = \angle O_2ClF_2$, and $\delta_4 = \angle O_2ClF_3$.

TABLE IV

Observed Frequencies (cm^{-1}), Symmetry Force Constants[a], and Computed and Observed ^{35}Cl and ^{37}Cl Isotopic Shifts (cm^{-1})

					Δν Comp.	Δν Obsd.
A_1	ν_1	1093	$F_{11} = f_D + f_{DD}$	= 9.14	7.1	7.2
			$F_{13} = 1/\sqrt{3}\ (2f_{D\alpha} - f_{D\gamma} - f_{D\gamma'})$	= 0.70		
	ν_2	683	$F_{22} = f_R$	= 3.35	6.8	~7
			$F_{23} = \sqrt{2/3}\ (f_{R\alpha} - f_{R\gamma})$	= −0.30		
	ν_3	520	$F_{33} = 1/3\ (2f_\alpha + f_\gamma + f_{\gamma\gamma} - 4f_{\alpha\gamma})$	= 1.27	0.8	~1
	ν_4	487	$F_{44} = f_r + f_{rr}$	= 2.65	0	
	ν_5	286	$F_{55} = 1/3\ (2f_\beta + f_\delta + 2f_{\beta\beta} + f_{\delta\delta} + f_{\delta\delta'} + f_{\delta\delta''} - 4f_{\beta\delta} - 4f_{\beta\delta'})$	= 1.37	0.5	
A_2	ν_6	417	$F_{66} = f_\delta - f_{\delta\delta} - f_{\delta\delta'} + f_{\delta\delta''}$	= 1.13	0	
B_1	ν_7	695	$F_{77} = f_r - f_{rr}$	= 2.75	11.7	11.6
			$F_{78} = \sqrt{2}\ (f_{r\delta} - f_{r\delta'})$	= 0.70		
			$F_{79} = f_{r\beta} - f_{r\beta'}$	= 0.20		
	ν_8	592	$F_{88} = f_\delta - f_{\delta\delta} + f_{\delta\delta'} - f_{\delta\delta''}$	= 2.15	0	~0
			$F_{89} = \sqrt{2}\ (f_{\beta\delta} - f_{\beta\delta'})$	= −0.44		
	ν_9	372	$F_{99} = f_\beta = f_{\beta\beta}$	= 1.31	1.0	
B_2	ν_{10}	1327	$F_{10,10} = f_D - f_{DD}$	= 9.33	16.8	16 − 17[b]
	ν_{11}	531	$F_{11,11} = f_\gamma - f_{\gamma\gamma}$	= 1.63	2.2	2.6
	ν_{12}	222	$F_{12,12} = f_\delta + f_{\delta\delta} - f_{\delta\delta'} - f_{\delta\delta''}$	= 0.78	0.6	

(a) Stretching constants in mdyn/Å, deformation constants in mdynÅ/radian², and stretch-bend interaction constants in could be achieved only with values reasonably close to those shown in Table IV. The requirement of a large off-diagonal constant for B_1 has previously also been found for the structurally related pseudo-trigonal bipyramidal SF_4O molecule[20].

The internal coordinate stretching force constants can be computed; however, the bending valence force constants cannot be completely separated from the interaction constants without making additional simplifying assumptions (see Table V). The constants of greatest interest are the stretching force constants since they are a measure of the strength of the various bonds. Uncertainty estimates are difficult to make owing to the underdetermined nature of the force field. The value of the Cl=O stretching force constant should have the smallest uncertainty (0.1 mdyn/Å or less) owing to the highly characteristic nature of the ClO_2 stretching modes and the use of isotopic shifts for its computation. Its value of 9.23 mdyn/Å is in excellent agreement with that of 9.37 mdyn/Å found for ClF_3O [8] and the General Valence Force Field values of 9.07 and 8.96 mdyn/Å reported for $FClO_2$ [21] and ClO_2^+ [11], respectively. The values of the ClF stretching force constants are comparable to those previously reported for the related pseudo-trigonal bipyramidal molecules, ClF_3 [22] and ClF_3O [8] (see Table VI). In all three molecules, the stretching force constant of the equatorial ClF bond is significantly higher than that of the two axial bonds, although their relative difference decreases with increasing oxidation state of the central atom. The difference in bond strength between equatorial and axial bonds implies significant contributions from semi-ionic three-center four-electron bonds to the axial ClF bonds. This bonding scheme has previously been discussed in detail [23] for the related pseudo-trigonal bipyramidal ClF_2^- anion and, hence, will not be repeated.

TABLE V

Internal Force Constants of ClF_3O_2[a,b]

$f_D = 9.23$

$f_R = 3.35$

$f_r = 2.70$

$f_\alpha = 1.41$

$f_\beta = 1.40$

$f_\gamma = 1.33$

$f_\delta = 1.30$

$f_{DD} = -0.09$

$f_{rr} = -0.04$

$f_{\beta\beta} = 0.09$

$f_{r\beta} = -f_{r\beta'} = 0.10$

$f_{r\delta} = -f_{r\delta'} = 0.25$

$f_{D\alpha} = 0.61$

$f_{\beta\delta} = -f_{\beta\delta'} = -0.16$

$f_{\delta\delta} = -f_{\delta\delta'} = -0.34$

$f_{\delta\delta''} = -0.17$

$f_{\gamma\gamma} = -0.30$

$f_{R\alpha} = -0.37$

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

(b) Only the values of the stretching force constants can be uniquely determined from the symmetry force constants; for the computation of the remaining constants, the following assumptions were made: $f_{r\beta} = -f_{r\beta'}$, $f_{r\delta} = -f_{r\delta'}$, $f_{\beta\delta} = -f_{\beta\delta'}$, $f_{\delta\delta} = -f_{\delta\delta'}$, and $f_{R\gamma} = f_{D\gamma} = f_{\alpha\gamma} = 0$; $f_{\delta\delta}$, $f_{\delta\delta'}$, and $f_{\delta\delta''}$ are the interactions between angles having a common oxygen, fluorine, and no common atom, respecitvely.

TABLE VI

ClF Stretching Force Constants (mdyn/Å) of ClF_3O_2 Compared to Those of Pseudo-Trigonal Bipyramidal ClF_3O[8], ClF_3[22], ClF_2^-[23], and $ClF_2O_2^-$[9]

	f_R	f_r	f_{rr}	$\frac{f_R - f_r}{f_R}$
ClF_3	4.2	2.7	0.36	0.36
ClF_3O	3.2	2.3	0.26	0.26
ClF_3O_2	3.4	2.7	-0.04	0.19
ClF_2^-	—	2.4	0.17	—
$ClF_2O_2^-$	—	1.6	-0.1	—

Inspection of Table VI also reveals that the value of f_r does not depend exclusively on the oxidation state of the central atom. Obviously, formal negative charges (as in the anions) and increasing oxygen substitution facilitate[9] the formation of semi-ionic bonds and, hence, counteract the influence of the oxidation state of the central atom. It is interesting to note that the relative contribution from semi-ionic bonding to the axial ClF bonds ($= \frac{f_R - f_r}{f_R}$) decreases from ClF_3 to ClF_3O and ClF_3O_2 (see Table VI). This can be attributed to the decreasing electron density around the central atom with increasing oxidation state, thus making it more difficult to release electron density to the axial fluorine ligands as required for the formation of semi-ionic bonds.

In summary, the bonding in ClF_3O_2 might be described by the following approximation:[24] The bonding of the three equatorial ligands, ignoring the second bond of the Cl=O double bond, is mainly due to a sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic three-center four-electron pσ bond.

The potential energy distribution[25] for ClF_3O_2 was obtained from the internal force constants of Table V using a least square force field computation code without using least square refinement. With this code, we also verified that no computational errors had been made in the trial and error force field computation. The computed PED is given in Table VII. The results were normalized, but the sums do not in all cases add up to 1.0 since the less important terms are not listed. As can be seen from Table VII, most vibrations are reasonably characteristic, except for ν_7 and ν_8, which are mixtures of the symmetry coordinates S_7 and S_8.

TABLE VII

Potential Energy Distribution for ClF_3O_2

	Assignment	Frequency, cm^{-1}	Potential Energy Distribution
A_1	ν_1	1093	$0.99\ f_D + 0.06\ f_R - 0.06\ f_{D\alpha}$
	ν_2	683	$0.71\ f_R + 0.20\ f_\alpha - 0.13\ f_{R\alpha} + 0.10\ f_\gamma + 0.05\ f_\beta$
	ν_3	520	$0.50\ f_\alpha + 0.23\ f_\gamma + 0.22\ f_R + 0.12\ f_{R\alpha} - 0.05\ f_{\gamma\gamma} - 0.05\ f_{D\alpha}$
	ν_4	487	$1.02\ f_r$
	ν_5	286	$0.61\ f_\beta + 0.28\ f_\delta + 0.14\ (f_{\beta\delta} - f_{\beta\delta'}) + 0.07\ (f_{\delta\delta'} - f_{\delta\delta}) + 0.06\ f_\alpha$
A_2	ν_6	417	$1.15\ f_\delta + 0.30\ (f_{\delta\delta} - f_{\delta\delta'}) - 0.15\ f_{\delta\delta''}$
B_1	ν_7	695	$0.86\ f_r + 0.39\ f_\delta - 0.22\ (f_{r\delta} + f_{r\delta'}) + 0.10\ (f_{\delta\delta} + f_{\delta\delta'}) + 0.05\ f_{\delta\delta''}$
	ν_8	592	$0.26\ f_\delta + 0.25\ f_r + 0.10\ (f_{r\delta} + f_{r\delta'}) + 0.07\ (f_{\delta\delta} + f_{\delta\delta'}) + 0.06\ f_\beta$
	ν_9	372	$1.10\ f_\beta - 0.10\ (f_{\beta\delta} + f_{\beta\delta'}) + 0.08\ f_\delta - 0.07\ f_{\beta\beta}$
B_2	ν_{10}	1327	$0.93\ f_D$
	ν_{11}	531	$0.75\ f_\gamma + 0.16\ f_{\gamma\gamma}$
	ν_{12}	222	$1.58\ f_\delta - 0.41\ (f_{\delta\delta} + f_{\delta\delta'}) + 0.21\ f_{\delta\delta''}$

Association in the Liquid and Pure Solid. The relatively low boiling point (-21.58°)[2] and Trouton constant (22.13)[2] of ClF_3O_2 imply little association in the liquid phase. This prediction is confirmed by the vibrational spectra of the liquid and the neat solid which exhibit only minor frequency shifts when compared to the spectra of the gas and the matrix isolated solid. This finding is somewhat surprising since both ClF_3[24] and ClF_3O[8] show a pronounced tendency to associate in the liquid and solid state through bridges involving the axial fluorine atoms. For the pure solid, the infrared spectrum indicates the lowering of symmetry C_{2v} due to slight distortion or a lower site symmetry in the crystal because the A_2 torsion mode, ideally forbidden in the infrared spectrum and not observed for the gas, becomes infrared active. Similarly, the symmetric axial FClF stretching mode, $\nu_4(A_1)$, which was not observed in the infrared spectrum of gaseous ClF_3O_2, gained for solid ClF_3O_2 in relative intensity and was observed as a medium weak band.

Thermodynamic Properties. The thermodynamic properties were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation[26]. These properties are given for the range 0 - 2000°K in Table VIII.

Acknowledgment. The authors wish to express their gratitude to Mr. R. D. Wilson for his help in the experimental efforts, to Drs. D. Pilipovich and C. J. Schack for helpful discussions, and to Dr. D. Lawson of the Jet Propulsion Laboratory for the use of the Raman spectrophotometer. This work was supported by the Office of Naval Research, Power Branch.

TABLE VIII

Thermodynamic Properties for ClF_3O_2

T, °K	C_p^o, cal/mol	$H^o - H_o^o$, kcal/mol	$-(F^o - H_o^o)/T$, cal/(mol deg)	S^o, cal/(mol deg)
0	0	0	0	0
100	10.127	0.847	48.967	57.437
200	16.511	2.179	55.516	66.411
298.15	21.256	4.049	60.375	73.956
300	21.327	4.089	60.459	74.088
400	24.384	6.386	64.711	80.675
500	26.362	8.930	68.484	86.344
600	27.685	11.636	71.881	91.275
700	28.599	14.453	74.968	95.615
800	29.251	17.347	77.795	99.479
900	29.727	20.298	80.400	102.953
1000	30.085	23.289	82.816	106.105
1100	30.360	26.312	85.066	108.985
1200	30.574	29.359	87.171	111.637
1	30.745	32.425	89.148	114.091
1400	30.883	35.507	91.012	116.375
1500	30.995	38.601	92.775	118.509
1600	31.089	41.705	94.447	120.513
1700	31.167	44.818	96.036	122.400
1800	31.233	47.938	97.551	124.183
1900	31.289	51.064	98.997	125.873
2000	31.337	54.196	100.382	127.480

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DIAGRAM CAPTIONS

Figure 1. Infrared and Raman Spectra of ClF_3O_2.

Traces A and B represent the infrared spectrum of 22.3 and 230 μ mole, respectively, of neat solid ClF_3O_2 at 4°K; traces C and D, the infrared spectrum of 0.89 and 20.6 μ mole, respectively, of ClF_3O_2 in a N_2 matrix (mole ratio 1:760) at 4°K; traces E to H, the infrared spectrum of gaseous ClF_3O_2 at the denoted pressures in a 5 cm path-length cell; traces I and K, the Raman spectrum of gaseous ClF_3O_2 at 4 atm pressure in a stainless steel cell with sapphire windows; traces L and M, the Raman spectrum at two different recorder voltages, respectively, of liquid ClF_3O_2 in a Teflon FEP capillary at 25°; S indicates spectral slit-widths and P indicates polarized bands.

Figure 2. Principal infrared bands of gaseous and N_2 matrix isolated ClF_3O_2 recorded at ten-fold scale expansion under higher resolution conditions. The frequency denotations refer to the matrix isolation spectra. The frequency scale of the gas bands has been slightly shifted to line up the matrix band centers with the corresponding Q branches of the gas band contours.

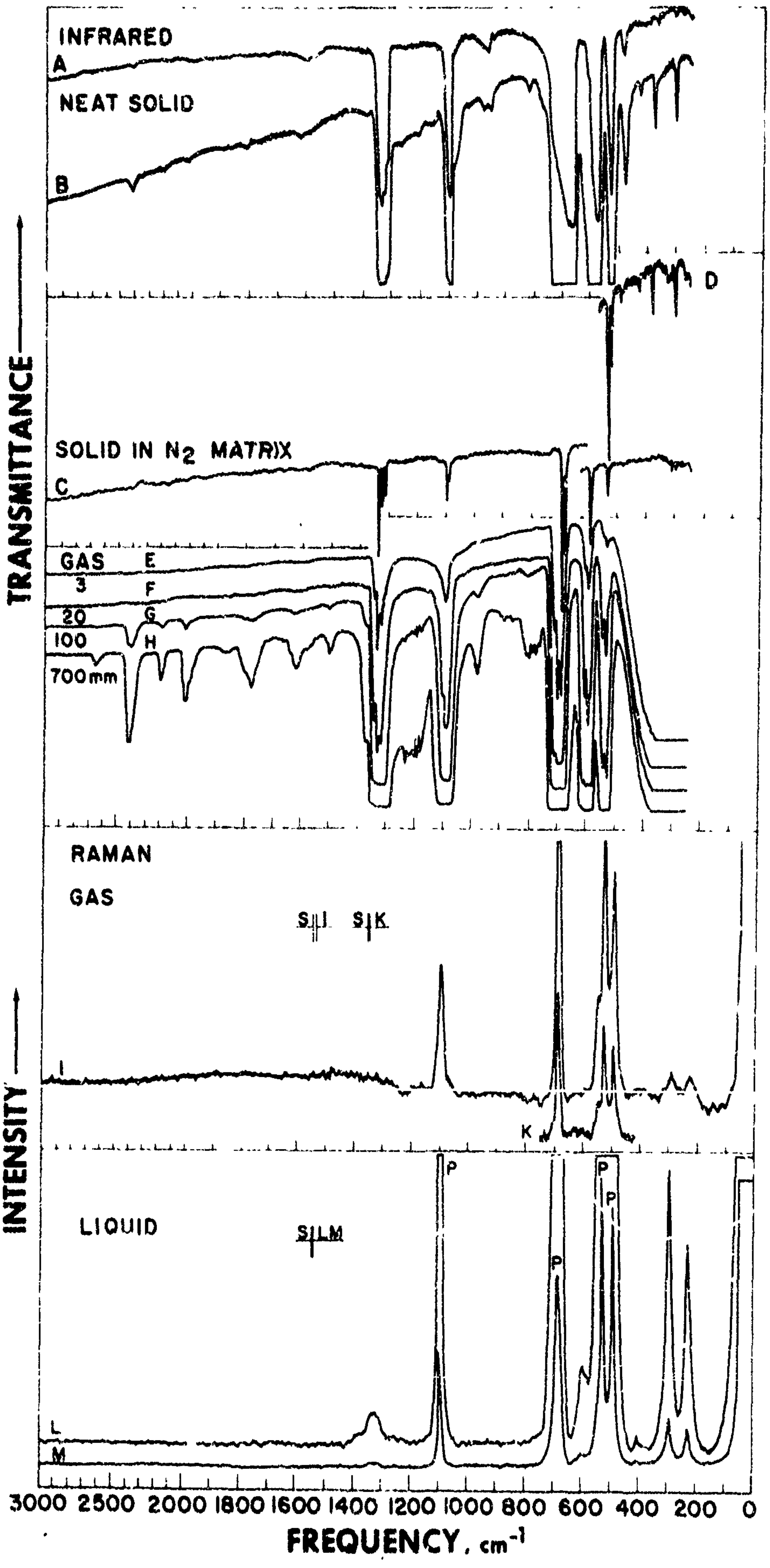
INFRARED
A
NEAT SOLID
B
D
SOLID IN N$_2$ MATRIX
C
GAS E
3 F
20 G
100 H
700mm
TRANSMITTANCE
RAMAN
GAS
S J
S K
I
K
LIQUID
S L M
P
P
P
P
L
M
INTENSITY
3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 200 0
FREQUENCY, cm^{-1}

Figure 1.

DIAGRAM CAPTIONS

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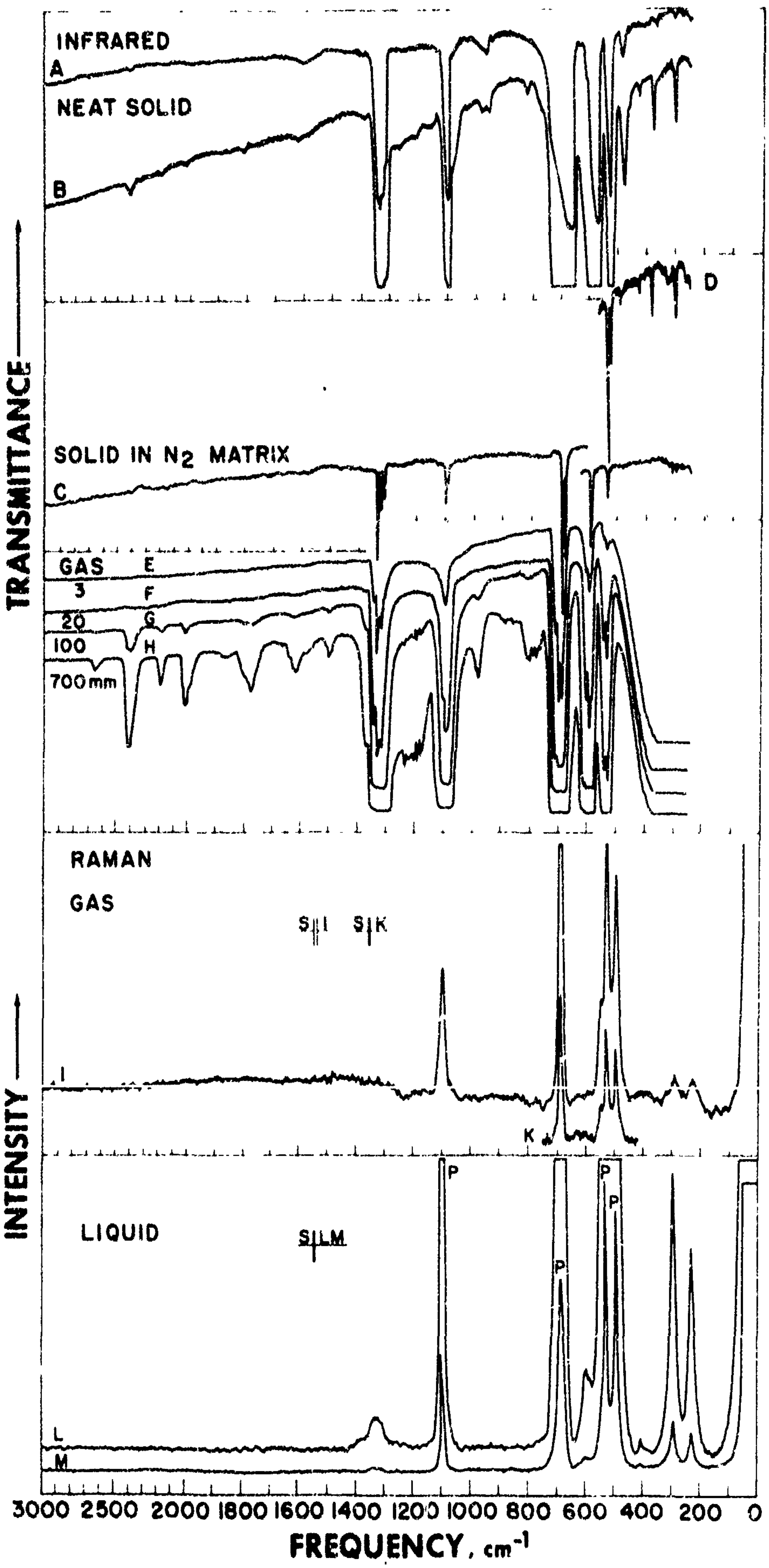
INFRARED
A
NEAT SOLID
B
D
SOLID IN N2 MATRIX
C
GAS
E
3
F
20
G
100
H
700mm
TRANSMITTANCE
RAMAN
GAS
S‖I
S|K
I
K
INTENSITY
LIQUID
S|LM
P
P
P
P
L
M
3000
2500
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1800
1600
1400
1200
1000
800
600
400
200
0
FREQUENCY, cm-1

Figure 1.

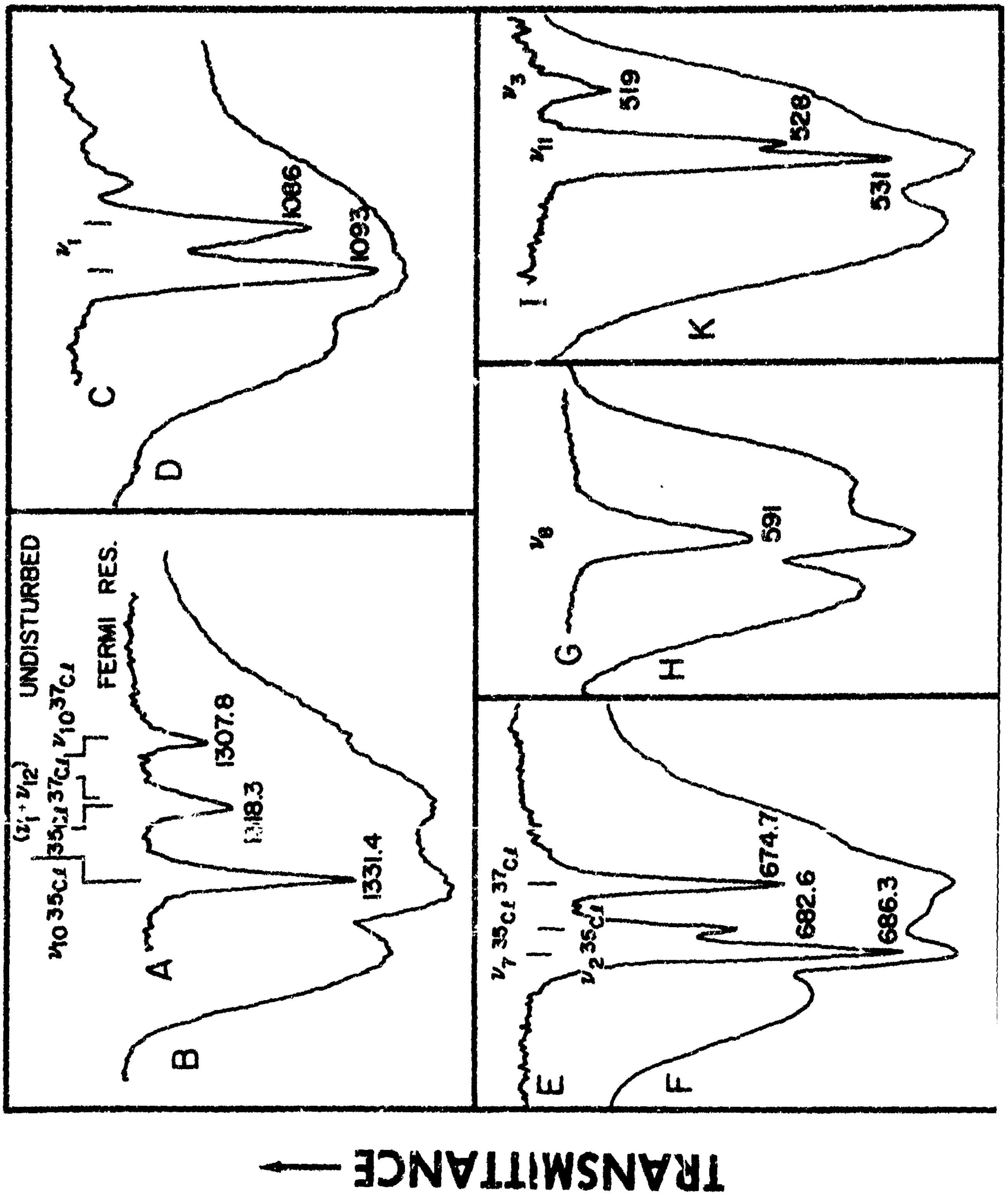
A
B
ν10 35Cl
(ν1 + ν12) 35Cl 37Cl
ν10 37Cl
UNDISTURBED
FERMI RES.
1331.4
1318.3
1307.8
C
D
ν1
1086
1093
E
F
ν7 35Cl 37Cl
ν2 35Cl
674.7
682.6
686.3
G
H
ν8
591
K
ν3
ν11
519
528
531
TRANSMITTANCE

Figure 2.

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

The Difluoroperchloryl Cation, $ClO_2F_2^+$

By Karl O. Christe*, Richard D. Wilson, and E. C. Curtis

Received 1972

Abstract

The reaction of $FClO_2$ with PtF_6 yields a product containing $ClO_2F_2^+PtF_6^-$. A synthetic method is described that convents this salt into $ClO_2F_2^+BF_4^-$ or $ClO_2F_2^+AsF_6^-$. All three salts are stable at 25° C and according to their infrared, Raman, and ^{19}F nmr spectra are ionic in both the solid state and HF solution. The vibrational spectrum of $ClO_2F_2^+$ closely resembles that of isoelectronic SO_2F_2, suggesting a pseudo-tetrahedral structure of symmetry C_{2v}. A modified valence force field is reported for $ClO_2F_2^+$.

Introduction

A preliminary note on the existence of $ClO_2F_2^+PtF_6^-$ has recently been published[1] by Christe. This salt was prepared from $FClO_2$ and PtF_6.[1] A detailed report on this interesting system, yielding under different reaction conditions $ClF_6^+PtF_6^-$ has been given elsewhere.[2] A ^{19}F nmr chemical shift of -310 ppm relative to external $CFCl_3$ has been tentatively assigned to $ClO_2F_2^+$.[3] A more complete characterization of the $ClO_2F_2^+$ cation in the original PtF_6^- salt, however, was pre-empted by interference from the PtF_6^- anion and from substantial amounts of by-products such as $ClO_2^+PtF_6^-$. Consequently, efforts were made to prepare $ClO_2F_2^+$ salts containing different anions and to eliminate the undesirable by-products. We have now succeeded in preparing $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ and in more fully characterizing the $ClO_2F_2^+$ cation. These results are described below.

Experimental

Apparatus and Materials. The stainless steel - Teflon-FEP vacuum system, the glove box, the infrared, Raman, and ^{19}F nmr spectrometers and sampling techniques, and the syntheses and purification of PtF_6, AsF_5, and $FClO_2$ have been described elsewhere.[2,3] Nitryl fluoride, prepared from N_2O_4 and F_2, and BF_3 (from The Matheson Co.) were purified by fractional condensation. Debye-Scherrer x-ray diffraction powder patterns were taken as previously described.[4]

Syntheses of $ClO_2F_2^+$ Salts. The synthesis of $ClO_2F_2^+PtF_6^-$ has been described elsewhere.[2] For the synthesis of $ClO_2F_2^+BF_4^-$, a mixture of $ClO_2F_2^+PtF_6^-$ (4.8 mmole) and $ClO_2^+PtF_6^-$ (12.2 mmole) was treated in a passivated (with ClF_3 and BrF_5) 75 ml stainless steel cylinder with FNO_2 (25.3 mmole) at -78° for 48 hours. The reaction products volatile at 25° consisted of $FClO_2$, ClF_3O_2, and unreacted FNO_2 and were separated by fractional condensation through a series of traps kept at -112°, -126°, -142°, and -196°. The -126° fraction contained most of the ClF_3O_2 and some $FClO_2$. Attempts to further separate the ClF_3O_2 and $FClO_2$ mixture by fractional condensation were unsuccessful. Consequently, 2.76 mmole of this mixture was combined with BF_3 (3.00 mmole) at -196° in a passivated Teflon-FEP ampoule and the temperature was cycled several times between -196° and 25°. The product was kept at -78° for several hours and unreacted BF_3 (0.22 mmole) was removed at this temperature in vacuo. Removal of volatile material in vacuo was continued at 20°. The volatile material (2.60 mmole) consisted according to its infrared spectrum of a 1:1 mixture of $FClO_2$ and BF_3. The white, solid, nonvolatile residue (280 mg = 1.46 mmole) was identified by infrared, Raman, and ^{19}F nmr spectroscopy as $ClO_2F_2{}^+BF_4{}^-$.

For the preparation of the $AsF_6{}^-$ salt, $ClO_2F_2{}^+BF_4{}^-$ (0.62 mmole) and AsF_5 (1.43 mmole) were combined at -196° in a passivated Teflon-FEP ampoule. The contents of the ampoule were kept at -78° for 30 minutes and at 25° for 1 hour. Volatile products were removed at 25° and consisted of unreacted AsF_5 (0.79 mmole) and BF_3 (0.59 mmole). The white, stable solid weighed 185 mg (weight calcd for 0.62 mmole of $ClO_2F_2{}^+AsF_6{}^-$ = 183 mg) and was identified as $ClO_2F_2{}^+AsF_6{}^-$ by infrared, Raman, and ^{19}F nmr spectroscopy.

Results and Discussion

Syntheses and Properties of $ClO_2F_2{}^+$ Salts. The synthesis of $ClO_2F_2{}^+PtF_6{}^-$ from $FClO_2$ and PtF_6 and its temperature dependence has been discussed elsewhere.[1,2] Since the $PtF_6{}^-$ anion interfered with the vibrational spectroscopic studies of $ClO_2F_2{}^+$, the $BF_4{}^-$ and $AsF_6{}^-$ salts were prepared according to the following scheme:

$$ClO_2{}^+PtF_6{}^- + ClO_2F_2{}^+PtF_6{}^- + FNO_2 \rightarrow FClO_2 + ClF_3O_2 + 2NO_2{}^+PtF_6{}^-$$

Unreacted FNO_2 and some of the $FClO_2$ could be separated from ClF_3O_2 by fractional condensation. The remaining $FClO_2$ was separated from ClF_3O_2 by complexing with

BF_3. Since the resulting $ClO_2^+BF_4^-$ has a dissociation pressure[5] of 182 mm at 22.1° while $ClO_2F_2^+BF_4^-$ is stable, the former salt could be readily removed by pumping at 20°. Conversion of $ClO_2F_2^+BF_4^-$ to the corresponding AsF_6^- salt was accomplished through displacement of BF_4^- by the stronger Lewis acid AsF_5.

All three salts, $ClO_2F_2^+PtF_6^-$, $ClO_2F_2^+AsF_6^-$, and $ClO_2F_2^+BF_4^-$, are solids, stable at 25°, and react violently with water or organic materials. The PtF_6^- compound is canary yellow, while those of AsF_6^- and BF_4^- are white. The salts dissolve in anhydrous HF without decomposing. They are crystallinic in the solid state and the x-ray powder diffraction patterns of $ClF_2O_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$ are listed in Table I. The powder pattern of $ClO_2F_2^+BF_4^-$ is much simpler than that of $ClO_2F_2^+AsF_6^-$. This is not surprising since the anion and cation in the former salt are both approximately tetrahedral and of similar size. The powder pattern of $ClO_2F_2^+BF_4^-$ can be indexed on the basis of an orthorhombic unit cell with $a = 5.45$, $b = 7.23$, and $c = 13.00Å$. Assuming four molecules per unit cell and neglecting contributions from the highly charged central atoms to the volume,[6,7] a plausible average volume of 16$Å^3$ per F or O atom is obtained. However, the agreement between the observed and calculated reflections is somewhat poor for several lines and, hence, the above unit cell dimensions are tentative.

The thermal stability of $ClO_2F_2^+BF_4^-$ is higher than those of $ClO_2^+BF_4^-$,[5] $ClF_2^+BF_4^-$,[8] or other similar salts. This is in good agreement with the previously made correlations[9] between the stability of an adduct and the structure of the parent molecule and its ions. Thus, tetrahedral $ClO_2F_2^+$ (see below) should be energetically much more favorable than trigonal bipyramidal ClF_3O_2.[10]

<u>^{19}F nmr Spectra</u>. A broad singlet at -310 ppm relative to external $CFCl_3$ has previously been observed for $ClO_2F_2^+PtF_6^-$ at low concentration in anhydrous HF

Table I. X-Ray Powder Patterns for $ClO_2F_2^+BF_4^-$ and $ClO_2F_2^+AsF_6^-$

$ClO_2F_2^+BF_4^-$		$ClO_2F_2^+AsF_6^-$			
d,Å	Intens	d,Å	Intens	d,Å	Intens
5.47	s	7.49	w	2.12	w
5.06	m	5.50	ms	2.01	w
4.37	ms	4.98	w	1.94	mw
4.15	w	4.35	ms	1.90	mw
3.70	vs	4.02	w	1.86	w
3.56	s	3.86	s	1.80	w
3.00	m	3.70	w	1.76	mw
2.77	m	3.57	m	1.72	w
2.57	vw	3.40	mw	1.70	mw
2.41	m	3.02	mw	1.65	w
2.18	s	2.77	m	1.62	w
2.08	s	2.69	m	1.59	w
1.86	ms	2.60	w	1.54	w
1.80	w	2.41	w	1.50	w
		2.30	w	1.41	w
		2.20	w	1.37	w
				1.34	w

and was tentatively assigned to $ClO_2F_2^+$.[3] This tentative assignment is confirmed by the present study. The spectrum of $ClF_2O_2^+BF_4^-$ in HF shows a strong temperature dependence. At 30° it consists of a single peak at 185 ppm relative to external $CFCl_3$. With decreasing temperature the peak at first becomes broader, then separates at about 0° into three signals at -301 ($ClO_2F_2^+$), 146 (BF_4^-),[12] and 194 ppm (HF) which become narrower with further decrease in temperature. The observed peak area ratio of approximately 2:1 for the 146 and -301 ppm signals confirms their assignment to BF_4^- and $ClO_2F_2^+$, respectively, and proves the ionic nature of the $ClF_3O_2 \cdot BF_3$ adduct in HF solution.

The spectrum of $ClF_2O_2^+AsF_6^-$ in HF (which was acidified with AsF_5)[3] consists of two resonances at -307 ($ClO_2F_2^+$) and 105 ppm (HF, AsF_5, AsF_6^-)[3], respectively. Rapid exchange between HF, AsF_5, and AsF_6^- preempted the measurement of the $ClO_2F_2^+$ to AsF_6^- peak area ratio.

<u>Vibrational Spectra</u>. Fig. 1 shows the infrared and Raman spectrum of solid $ClO_2F_2^+BF_4^-$ and the Raman spectrum of an HF solution of $ClO_2F_2^+BF_4^-$. Fig. 2 depicts the infrared and Raman spectrum of solid $ClO_2F_2^+AsF_6^-$. Fig. 3 shows the infrared spectrum of a mixture of solid $ClO_2F_2^+PtF_6^-$ and $ClO_2^+PtF_6^-$. The observed frequencies are listed in Table II and are compared with those reported for isoelectronic SO_2F_2.[12]

Inspection of Figures 1 to 3 and of Table II reveals that the spectra of $ClF_3O_2 \cdot BF_3$, $ClF_3O_2 \cdot AsF_5$, and $ClF_3O_2 \cdot PtF_5$ contain the bands characteristic for BF_4^-,[13-16] AsF_6^-[16-19] and PtF_6^-,[2,20] respectively. Furthermore, the Raman spectra of $ClF_3O_2 \cdot BF_3$ are practically identical for both the solid and its HF solution. These observations together with the ^{19}F nmr spectrum of the BF_3 adduct in HF solution, establish that these adducts are ionic and contain the $ClO_2F_2^+$ cation.

Table II. Vibrational Spectra of $ClO_2F_2^+$ Salts Compared to that of SO_2F_2

Observed Frequencies (cm^{-1}) and relative intensities[a]										Assignment (Point Group)			
SO_2F_2			$ClO_2F_2^+BF_4^-$			$ClO_2F_2^+AsF_6^-$		$ClO_2F_2^+PtF_6^-$ + $ClO_2^+PtF_6^-$		XO_2F_2 (C_{2v})	YF_6^- (O_h)[d]	BF_4^- (T_d)	ClO_2^+ (C_{2v})
Ra[b]		IR[c]	Ra		IR	Ra	IR	Ra	IR				
Gas	Liquid	Gas	HF Sol.	Solid									
									2340 2320 w				$\nu_1+\nu_3(B_1)$
									2115vw				$2\nu_1(A_1)$
1562	1497(1)dp	1562vs	1495(0.3)dp	1485(0.6) 1469(0.2)	1485 1469 s	1452(0.25)	1489 1473 s		1486 1470 s	$\nu_6(B_1)$			
					1295m							$\nu_1+\nu_4(F_2)$	
								1299(0.5) 1285(0.17)	1297vs 1283s				$\nu_3(B_1)$
270vs	1263(7)p	1269vs	1252(4.4) 1244(1.5) p	1245(3.9) 1237(1.3)	1245 1237 s	1252 1244 (1.9)	1250 1242 s	1246(0+)	1245 1237 s	$\nu_1(A_1)$			
								1051(2.7)	1052s 1047m				$\nu_1(A_1)$
												$\nu_3(F_2)$	
			1050(0+),br	1050(0+),br	990- 1150vs,br								
883	887(1)	885vs	834(0.7),dp	823(?.6)	824s	834(0.6)	832s		827s	$\nu_8(B_2)$			
			771sh,P	772(6.3)	772w							$\nu_1(A_1)$	
847vs	846(10),p	848vs	761(10),p	753(10)	754s	761(4.5)	759s	754(0.1)	756s	$\nu_2(A_1)$			
							700vs,br	617(2.5)	640vs,br		$\nu_3(F_{1u})$		
						683(10)		642(10)			$\nu_1(A_{1g})$		
						573(1.9)	564w	564(1.3) 552(1.8)	580w 552s		$\nu_2(E_g)$		
543vbr	547(6),dp	552.8 544.3 539.4 s	538(3.8) 533sh 517(1.6) p	534(4.7) 530sh 515(1.5)	534sh 529s 516w	534(2.9) 528sh 514(1)	534sh 527s 514m	514(0.4)	532w 514s	$\nu_7(B_1)$ $\nu_3(A_1)$ $\nu_9(B_2)$		$\nu_4(F_2)$	$\nu_2(A_1)$
388vbr	389(4),dp	384.5w	388(4.0)dp	394sh 387(?.9)	395w	390(3.8)	395sh			$\nu_4(A_1)$ $\nu_5(A_2)$			
							385vs		284m 265s		$\nu_4(F_{1u})$		
						373(3)			239(2.9)		$\nu_5(F_{2g})$		
			355sh	355(0.3)								$\nu_2(E)$	
									180(0+)		$\nu_6(F_{2u})$		

(a) Uncorrected Raman intensities; (b) P. Bender and J. M. Wood, Jr., J. Chem. Phys., 23, 1316 (1955); (c) D. R. Lide, Jr., D. E. Mann, and J. J. Comeford, Spectrochim. Acta, 21, 497 (1965), and G. R. Hunt and M. K. Wilson, Ibid., 16, 570 (1960); (d) Assignments for PtF_6^- are made for simplicity on the basis of point group O_h, though the site symmetry of PtF_6^- is lower than O_h (K. O. Christe, Inorg. Chem., in press).

The assignments for the anions are well established and are summarized in Table II. Consequently, only the assignments for $ClO_2F_2^+$ will be discussed in more detail. The $ClO_2F_2^+$ cation is isoelectronic with SO_2F_2 which was shown by microwave spectroscopy to possess symmetry C_{2v}.[21] The SO_2F_2 structure can be derived from a tetrahedron with two oxygen and two fluorine ligands occupying the corners and with the O=S=O angle increased to 123°58' and the F-S-F angle compressed to 96°7'. Comparison of the bands due to $ClO_2F_2^+$ with those previously reported[12,22,23] for SO_2F_2 (see Table II) reveals a pronounced similarity indicating closely related structures and bonding. Therefore, assignments for $ClO_2F_2^+$ were made by analogy with those of SO_2F_2 which were reliably established by infrared,[23] Raman,[22] matrix isolation,[12] and microwave[12] studies. The analogy appears to include the triple and double coincidences between $\nu_7(B_1)$, $\nu_3(A_1)$, and $\nu_9(B_2)$ at about 530 cm^{-1} and between $\nu_4(A_1)$ and $\nu_5(A_2)$ at about 390 cm^{-1}, respectively. As for SO_2F_2,[12] only tentative assignments to the individual modes can be made for the bands observed in the 520 cm^{-1} region.

The close analogy between the vibrational spectra of isoelectronic $ClO_2F_2^+$ and SO_2F_2 parallels those found for the isoelectronic pairs ClF_2O^+-SF_2O,[16] ClF_6^+-SF_6,[2] ClF_5-SF_5^-,[24] and ClF_4^+-SF_4.[25] It demonstrates the usefulness of knowing the vibrational spectra of the corresponding sulfur compounds for predicting and assigning those of the isoelectronic chlorine fluorides.

Additional evidence for the pseudo-tetrahedral structure of symmetry C_{2v} of $ClO_2F_2^+$ consists of the ^{35}Cl - ^{37}Cl isotopic splittings observed for the stretching modes (see Table III and Force Constant section).

Table III. Observed Frequencies (cm^{-1}), Approximate Description of Modes, and Computed Symmetry and Most Important Internal Force Constants[a] (Stretching Constants in mdyne /Å, Deformation Constants[b] in mdyne Å/radian^2, and Stretch-Bend Interaction Constants in mdyne / radian) of $ClO_2F_2^+$. Values [illegible] in Brackets are the Computed ^{35}Cl-^{37}Cl Isotopic Shifts (cm^{-1})

										Observed Isotopic Shifts
	∠OClO				124	114	109	124	114	
	∠FClF				96	105	109	96	105	
A_1	ν_1	1241	$\nu_{sym}ClO_2$	$F_{11} = f_D + f_{DD}$	11.33[9.2]	10.66[10.7]	10.12[12.4]	11.74[8.0]	11.38[8.5]	[7.5-8.5]
				$F_{12} = 2f_{DR}$				0.50	1.00	
	ν_2	756	$\nu_{sym}ClF_2$	$F_{22} = f_R + f_{RR}$	4.28[5.4]	4.85[3.4]	4.83[3.5]	4.08[6.4]	4.56[4.9]	[-5]
	ν_3	514	$\delta_{sym}ClO_2$	$F_{33} = 0.56f_\alpha + 0.06f_\beta + 0.38f_\gamma - 0.72f_{\alpha\beta} + 0.06(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') + 0.59f_{\beta\gamma} - 0.93f_{\alpha\gamma}$[d]	1.62[0.6]	1.85[0.2]	1.79[1.6]	1.64[0.4]	1.86[0.1]	
				$F_{34} = 0.32_\alpha + 0.13_\beta - 0.45f_\gamma - 1.01f_{\alpha\beta} + 0.13(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') + 0.31f_{\beta\gamma} + 0.28f_{\alpha\gamma}$	(0)[c]	(0)[c]	(0)[c]	(0)[c]	(0)[c]	
	ν_4	390	$\delta_{sym}ClF_2$	$F_{44} = 0.18f_\alpha + 0.29f_\beta + 0.52f_\gamma - 0.91f_{\alpha\beta} + 0.29(f_{\beta\beta} + f_{\beta\beta}' + f_{\beta\beta}'') - 1.56f_{\beta\gamma} + 0.63f_{\alpha\gamma}$	1.29[1.0]	1.06[1.9]	1.16[0.1]	1.29[1.0]	1.07[1.8]	
A_2	ν_5	390	τ	$F_{55} = f_\beta - f_{\beta\beta} - f_{\beta\beta}' + f_{\beta\beta}''$	1.16	1.16	1.16	1.16	1.16	
B_1	ν_6	1479	$\nu_{asym}ClO_2$	$F_{66} = f_D - f_{DD}$	11.48[18.7]	11.98[17.9]	12.25[17.5]	12.66[16.2]	12.70[16.4]	[15.9-16.
				$F_{67} = \sqrt{2}\,(f_{D\beta} - f_{D\beta}')$	(0)[c]	(0)[c]	(0)[c]	1.00	0.60	
	ν_7	530	$\delta_{rock}ClO_2$	$F_{77} = f_\beta + f_{\beta\beta} - f_{\beta\beta}' - f_{\beta\beta}''$	1.61[2.7]	1.78[3.3]	1.89[4.5]	1.54[3.6]	1.71[3.8]	
B_2	ν_8	830	$\nu_{asym}ClF_2$	$F_{88} = f_R - f_{RR}$	4.71[10.9]	4.50[11.5]	4.43[11.7]	4.71[10.9]	4.50[11.5]	[-11]
				$F_{89} = \sqrt{2}\,(f_{R\beta} - f_{R\beta}')$	(0.5)[c]	(0.5)[c]	(0.5)[c]	(0.5)[c]	(0.5)[c]	
	ν_9	514	$\delta_{rock}ClF_2$	$F_{99} = f_\beta - f_{\beta\beta} + f_{\beta\beta}' - f_{\beta\beta}''$	2.01[2.5]	1.72[2.2]	1.61[2.1]	2.01[2.5]	1.72[2.2]	
f_D					11.41	11.32	11.19	12.20	12.04	
f_{DD}					- 0.08	- 0.66	- 1.07	- 0.46	- 0.66	
f_R					4.50	4.68	4.63	4.40	4.53	
f_{RR}					- 0.21	0.17	0.20	- 0.32	0.03	

(a) Symmetry force constants not shown were assumed to be zero; (b) $f_{\beta\beta}$, $f_{\beta\beta}'$, and $f_{\beta\beta}''$ refer to the interactions between the deformations of two angles having a common oxygen atom, a common fluorine atom, and no common oxygen or fluorine atom, respectively; (c) assumed values; (d) the numerical coefficients in the F matrix are based on the 124 and 96° bond angle geometry.

Force Constants. Three sets of force constants were computed for $ClO_2F_2^+$ assuming different geometries. Two additional sets were computed requiring agreement between observed and computed ^{35}Cl - ^{37}Cl isotopic shifts (see Table III). The potential and kinetic energy matrices were computed using a machine method.[26] The three different geometries adopted for $ClO_2F_2^+$ differ only in the bond angles but not in the bond lengths. The bond lengths were estimated to be D(ClO) = 1.41 and R(ClF) = 1.53Å by comparison with related molecules and based on the correlation of Robinson[27] between frequencies and bond lengths. The bond angles of set I, $\alpha(\sphericalangle$ OClO$)$ = 124°, $\beta(\sphericalangle$ OClF$)$ = 108° 15', and $\gamma(\sphericalangle$ FClF$)$ = 96°, were chosen to be identical with those of isoelectronic SO_2F_2.[21] For set III, tetrahedral bond angles were used and for set II a geometry was selected intermediate between those of sets I and III. The redundant coordinate was found numerically, and the deformation symmetry coordinates S_3 and S_4 were made orthogonal to it. To demonstrate that the redundancy condition was correct, it was verified that the frequencies of each block taken separately and the corresponding frequencies of the direct sum of all symmetry coordinates were the same.

The force constants were computed by trial and error with the aid of a computer, requiring exact fit between the observed and computed frequencies. The results are given in Table III where the force constants not shown were assumed to be zero. The values shown for sets I to III were the simplest set that would give an exact fit and, with the exception of F_{89}, represent a diagonal symmetry force field. By analogy with isoelectronic SO_2F_2,[28] a nonzero value was required for F_{89} to fit the observed frequencies. Its value was assumed to be 0.5 to obtain a plausible value for F_{99}. Table III demonstrates the dependence of the force constants on the chosen bond angles and the impossibility to achieve a fit between the observed and the computed ^{35}Cl - ^{37}Cl isotopic shifts by simple variation of the bond angles. Numerical experiments confirmed that nonzero off-diagonal symmetry force constants are required to fit the observed isotopic shifts. The results for the more likely geometries I and II are listed as sets IV and V, respectively, in Table III. In the A_1 symmetry block, the only interaction constant capable of sufficiently decreasing the ν_1 isotopic shift is F_{12}. The experimental data do not permit to distinguish between sets IV and V. However, the variation in the two force constants of greatest interest, f_D and f_R, is relatively small. Consequently, their values might be expected to approach those of a General Valence Force Field. A statistically meaningful uncertainty estimate cannot be made for the force constant values owing to their underdetermined nature and to the lack of exact structural data. However, the numerical data of Table III allow some conclusions concerning the ranges of possible solutions. It should also be mentioned that the observed ^{35}Cl - ^{37}Cl isotopic shifts varied slightly depending on the nature of the anion. In $ClO_2F_2^+BF_4^-$ for both the solid state and the HF solution, isotopic shifts of 7.5 and 15.9 cm^{-1} were observed for $\nu_1(A_1)$ and $\nu_6(B_1)$, respectively. For solid $ClO_2F_2^+PtF_6^-$ the corresponding values were 8.5 and 16.6 cm^{-1}.

Of the internal force constants, the stretching force constants are of greatest interest since they can be used as a measure for the relative covalent bond strength. The stretching force constants of $ClO_2F_2^+$ are listed in Table IV and compared to those of related molecules and ions. Comparison of the ClO stretching force constant of $ClO_2F_2^+$ (12.1 mdyne /Å) with those listed in Table IV shows that it is the highest value known for a ClO bond. This is not surprising, since the central atom in $ClO_2F_2^+$ has a high oxidation state (+ VII), highly electronegative ligands, and a formal positive charge (cation). The influence of these

Table IV. Stretching Force Constants (mdyne /Å) of $\mathrm{ClO_2F_2^+}$ Compared to Those of Related Compounds

	f_{ClO}		f_{ClF}	$f_{\mathrm{ClF'}}$[a]
$\mathrm{ClO_2F_2^+}$	12.1	$\mathrm{ClF_6^+}$[i]	4.7	
$\mathrm{ClF_2O^+}$[b]	11.2	$\mathrm{ClF_2^+}$[k]	4.7	
$\mathrm{FClO_3}$[c]	9.4	$\mathrm{ClF_4^+}$[l]	4.5	3.2
$\mathrm{ClF_3O}$[d]	9.4	$\mathrm{ClO_2F_2^+}$	4.46	
$\mathrm{FClO_2}$[e]	9.1	$\mathrm{ClF_3}$[m]	4.2	2.7
		$\mathrm{FClO_3}$[c]	3.9	
$\mathrm{ClO_2^+}$[f]	9.0	$\mathrm{ClF_5}$[n]	3.5	2.7
$\mathrm{ClF_4O^-}$[g]	8.9	$\mathrm{ClF_2O^+}$[b]	3.4	
$\mathrm{ClF_2O_2^-}$[h]	8.3	$\mathrm{ClF_3O}$[d]	3.2	2.3
		$\mathrm{FClO_2}$[e]	2.5	
		$\mathrm{ClF_2^-}$[o]		2.4
		$\mathrm{ClF_4^-}$[p]		2.1
		$\mathrm{ClF_4O^-}$[g]		1.9
		$\mathrm{ClF_2O_2^-}$[h]		1.6

(a) ClF bonds for which strong contributions from semi-ionic 3 center-4 electron bonds can be invoked.

(b) Ref. 16.

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(f) Ref. 19.

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(h) K. O. Christe and E. C. Curtis, Inorg. Chem., 11, 35 (1972).

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(k) K. O. Christe and C. J. Schack, Inorg. Chem., 9, 2296 (1970).

(l) Ref. 25.

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(n) Ref. 24.

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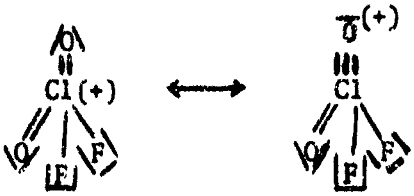
factors on f_{ClO} has previously been discussed[16] for ClF_2O^+ and, hence, will not be reiterated. By analogy with ClF_2O^+, the only other known species exhibiting a f_{ClO} value of similar magnitude, contributions from the following resonance structure



might be invoked[16] to explain the high f_{ClO} value. The value of the ClF stretching force constant (4.46 mdyne /Å) falls within the range expected for a predominantly covalent ClF bond. The interpretation of relatively small differences (~0.3 mdyne /Å) in the ClF stretching force constant values listed in Table IV should be done only with caution since most values were computed from underdetermined systems and might be significantly influenced by the chosen stretch-bend interaction constants.

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Diagram Captions

Figure 1. Vibrational spectrum of $ClO_2F_2^+BF_4^-$. Trace A, infrared spectrum of the solid as a AgCl disk; trace B Raman spectrum of the solid; traces D and E Raman spectrum of the HF solution, incident polarization perpendicular and parallel, respectively; exciting line 4880 Å, C indicates spectral slit width.

Figure 2. Vibrational spectrum of solid $ClO_2F_2^+AsF_6^-$. Trace A, infrared spectrum as AgCl disk; trace B, Raman spectrum; exciting line 4880 Å.

Figure 3. Infrared spectrum of a mixture of solid $ClO_2F_2^+PtF_6^-$ and $ClO_2^+PtF_6^-$ as a AgCl disk.

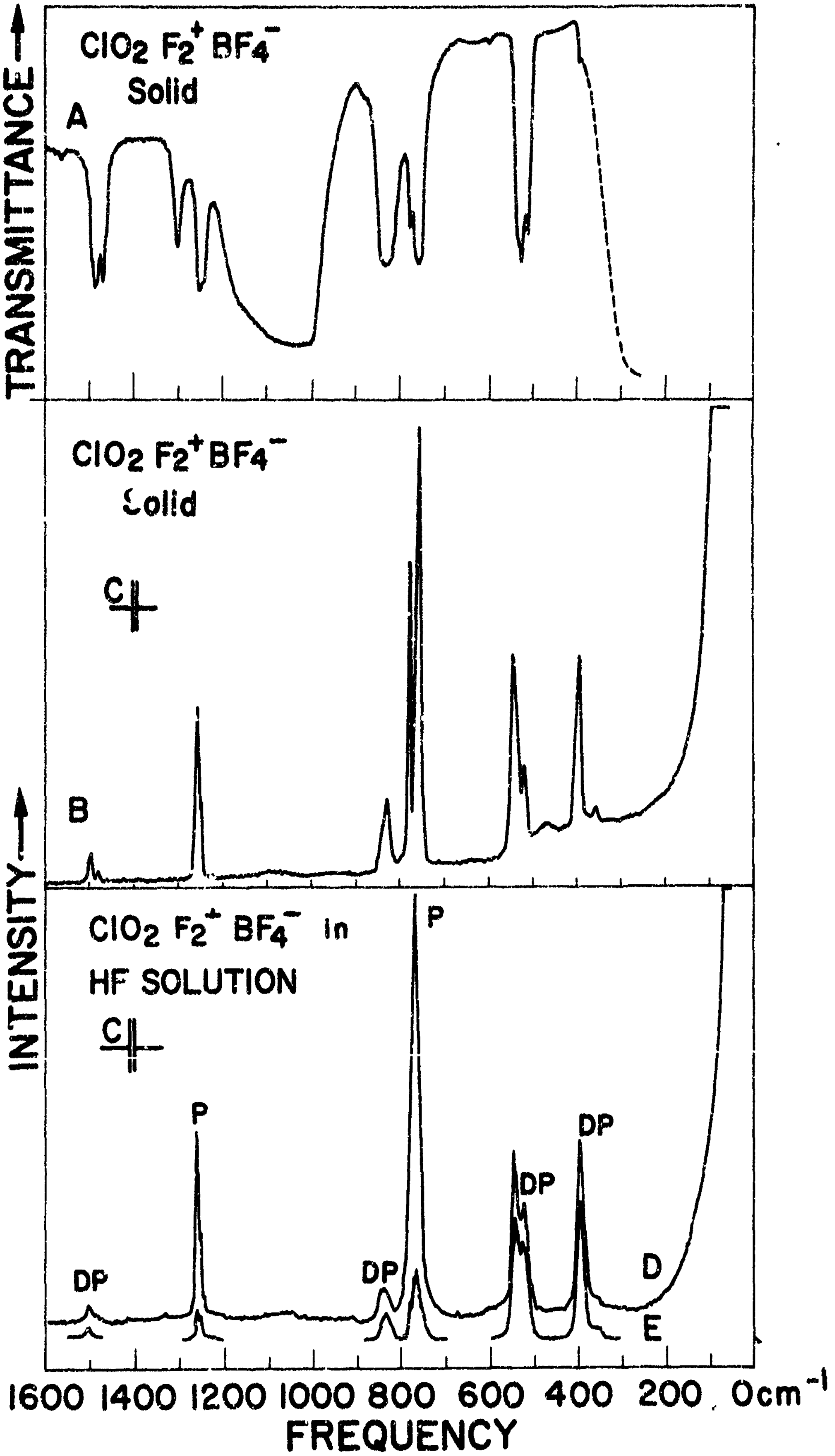

TRANSMITTANCE
ClO₂ F₂⁺ BF₄⁻
Solid
A
ClO₂ F₂⁺ BF₄⁻
Solid
C ∥
B
INTENSITY
ClO₂ F₂⁺ BF₄⁻ in
HF SOLUTION
C ∥
P
P
DP
DP
DP
DP
D
E
1600
1400
1200
1000
800
600
400
200
0cm⁻¹
FREQUENCY

Figure 1.

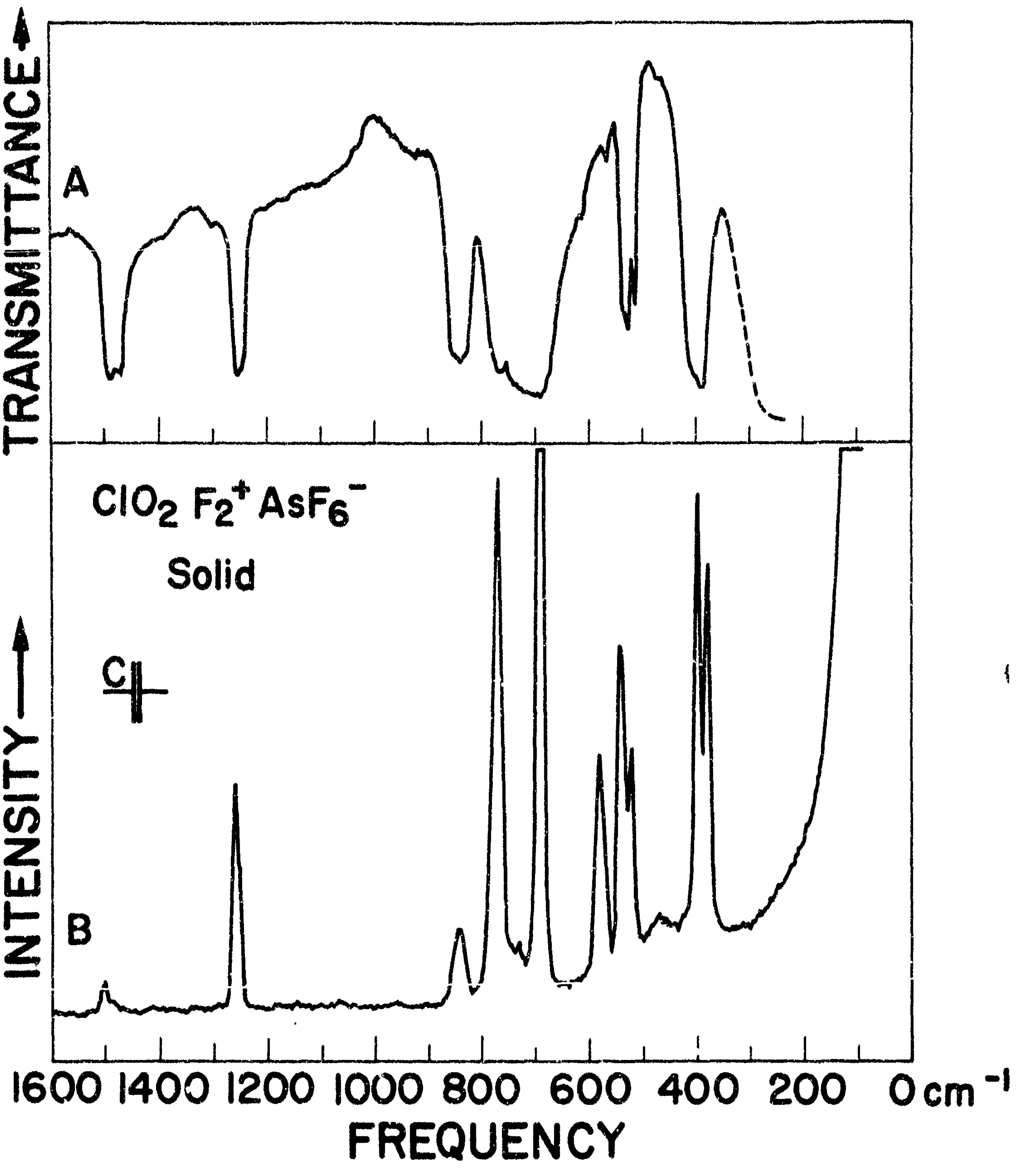
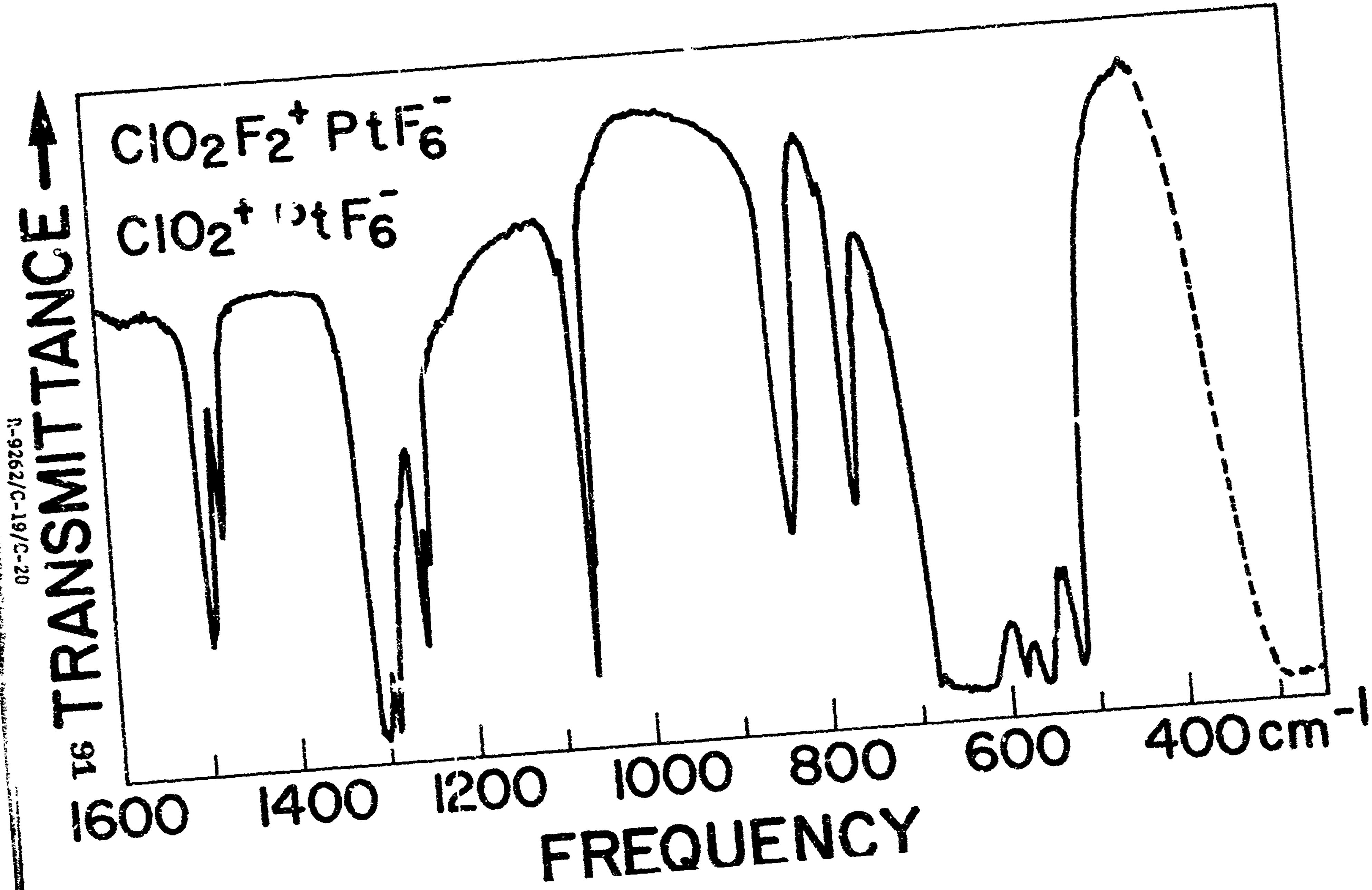


Figure 2.

R-9262/C-18


$ClO_2F_2^+PtF_6^-$
$ClO_2^+PtF_6^-$
TRANSMITTANCE
1600
1400
1200
1000
800
600
400 cm-1
FREQUENCY
91
R-9262/C-19/C-20

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

The Hexafluorochlorine (VII) Cation, ClF_6^+. Synthesis and Vibrational Spectrum

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Abstract

The ClF_6^+ cation was prepared in the form of its PtF_6^- salt from the reactions of PtF_6 with either $FClO_2$ or ClF_5. A displacement reaction between $ClF_6^+PtF_6^-$ and FNO at -78° yielded only ClF_5 and F_2, indicating that ClF_7 cannot exist under the given reaction conditions. Attempts were unsuccessful to prepare either $ClF_6^+BF_4^-$ by low temperature glow discharge of a ClF_5-F_2-BF_3 mixture, or ClF_6^+ salts from ClF_5, F_2, and the Lewis acids SbF_5, AsF_5, or BF_3 at elevated temperatures and pressures, or ClF_4O^+ salts either from ClF_3O and PtF_6 or from ClF_3O, F_2, and SbF_5. Iridium hexafluoride was found to be too weak an oxidizer to produce any heptavalent, chlorine containing cations from $FClO_2$. Vibrational spectra were recorded for PtF_6^- salts of ClF_6^+, ClF_4^+, ClF_2^+, $ClF_2O_2^+$, ClF_2O^+, and ClO_2^+ and for $ClO_2^+IrF_6^-$. Modified valence force fields were computed for the ClF_6^+, PtF_6^-, and IrF_6^- ions.

Introduction

Two preliminary notes on the synthesis of $ClF_6^+PtF_6^-$ from PtF_6 and chlorine fluorides or oxyfluorides have recently been published[1,2], and the identity of

ClF_6^+ was established beyond doubt by ^{19}F nmr spectroscopy[2,3]. The ClF_6^+ cation is of particular interest for two reasons: (1) except for the recently discovered $ClO_2F_2^+$ cation[4], it is the only known heptavalent chlorine cation and (2) in addition to the NF_4^+ salts[5-9], it is the only known example of the synthesis of a fluoro cation derived from hitherto unknown compounds (i.e., NF_5 and ClF_7, respectively). In this paper, we give a full account of the synthesis, vibrational spectrum, and force constants of the ClF_6^+ cation.

Experimental

Apparatus and Materials. - 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 bellow-seal valves (Hoke, Inc., 425 1F4Y). Pressures were measured with a Heise, Bourdon Tube-type gauge (0-1500 mm ± 0.1%). Because of the rapid hydrolytic interaction with moisture, all 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. The spectra of solids were obtained by pressing two small single-crystal platelets of either AgCl or AgBr to a disk in a Wilks mini pellet press. The powdered sample was placed between the platelets before starting the pressing operation.

The Raman spectra were recorded on either Cary Models 82 or 83 spectrophotometers using the 4880 and 6471 Å exciting lines, respectively. Glass melting point capillaries or clear thin-walled Kel-F tubes were used as sample containers in the transverse viewing-transverse excitation technique.

Mass spectra were recorded on a Quad 300 (Electronic Associates Inc.) quadrupole mass spectrometer using a passivated all stainless steel inlet system.

Platinum hexafluoride was either purchased (from Ozark Mahoning Company) or freshly prepared by burning Pt wire in an F_2 atmosphere at -196°, according to the method of Weinstock and his coworkers[10]. Iridium hexafluoride was obtained from Ozark Mahoning Company. Prior to use, both IrF_6 and PtF_6 were purified by fractional condensation at -78° in a dynamic vacuum. Arsenic pentafluoride (Ozark Mahoning Company) was purified by fractional condensation and SbF_5 (Ozark Mahoning Company) by distillation. Chlorine pentafluoride (Rocketdyne) was stored over dry CsF to remove any ClF_3 and purified by fractional condensation through traps kept at -112 and -126° with the material retained at -126° being used. Fluorine (Rocketdyne) was passed over NaF to remove HF. Chloryl fluoride was prepared from $KClO_3$ and ClF_3[11], ClF_3O by fluorination of $ClONO_2$[12], and FNO from NO and F_2 at -196°. The purity of the volatile starting materials was determined by measurements of their vapor pressures and infrared spectra.

The $FClO_2$-PtF_6 System. Platinum hexafluoride (17.0 mmole) and $FClO_2$ (46.1 mmole) were combined at -196° in a passivated (with ClF_3) 75-ml stainless steel cylinder. The mixture was allowed to warm up slowly to 25° and was kept at this temperature for three days. The cylinder was cooled to -196° and 3.75 mmole of material volatile at this temperature was removed and identified as F_2 by its vapor pressure and mass spectrum. The products volatile at 25° were separated by fractional condensation through traps kept at -78, -126, and -196°. The -126° fraction consisted of $FClO_2$ (28.7 mmole) and the -196° one of $FClO_2$ (0.3 mmole), ClF_5 (0.1 mmole), and a small amount of $FClO_3$. The cylinder contained a stable canary yellow solid (6.618 g), which was identified by infrared spectroscopy as a mixture of $ClO_2^+PtF_3^-$ and $ClO_2F_2^+PtF_6^-$. Hence, PtF_6 (17.0 mmole) had reacted with $FClO_2$ (17.1 mmole) in a 1:1 mole ratio yielding F_2 (3.75 mmole), $ClO_2^+PtF_6^-$ (12.2 mmole = 4.594 g), and $ClO_2F_2^+PtF_6^-$ (4.8 mmole = 2.000 g) as the main products.

Platinum hexafluoride (2.04 mmole) and $FClO_2$ (3.08 mmole) were combined at -196^0 in a passivated sapphire reaction tube (Varian, Model CS-4250-3). The reactor was rapidly warmed from -196^0 to -78^0 and kept at -78^0 for 48 hours. At the end of this time period, the brown PtF_6 color had completely disappeared and a canary yellow solid had formed. The reactor was cooled to -196^0 and noncondensible material (0.33 mmole of O_2) was removed. The product volatile at 25^0 consisted of $FClO_2$ (1.03 mmole). The yellow, solid residue weighed 800 mg and was shown by infrared, Raman, and ^{19}F nmr spectroscopy to be a mixture of $ClF_6^+PtF_6^-$ and $ClO_2^+PtF_6^-$ (weight calculated for a mixture of 1.70 mmole of $ClO_2^+PtF_6^-$ and 0.34 mmole of $ClF_6^+PtF_6^-$ = 796 mg). Hence, PtF_6 (2.04 mmole) had reacted with $FClO_2$ (2.05 mmole) in a 1:1 mole ratio producing O_2 (0.33 mmole) and a 1:5 mole ratio mixture of $ClF_6^+PtF_6^-$ and $ClO_2^+PtF_6^-$.

The ClF_5-PtF_6 System. Platinum hexafluoride (2.70 mmole) and ClF_5 (3.90 mmole) were combined at -196^0 in a passivated sapphire reactor. The mixture was kept at 25^0 for 24 hours. Since the brown PtF_6 color was still very intense, the tube was exposed to unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury-vapor arc. After 24 hours of uv irradiation, the dark brown PtF_6 color had disappeared and a yellow to brown solid had formed. The product was kept for 12 hours at -20^0 without irradiation and its color changed to yellow-orange. The reactor was cooled to -196^0 and noncondensibles (2.58 mmole of F_2) were removed. The reactor was warmed up to 25^0 and the volatile products were separated by fractional condensation. They consisted of ClF_5 (1.08 mmole) and ClF_3 (0.12 mmole). The yellow solid residue weighed 1.096 g (weight calculated for a mixture of 0.84 mmole $ClF_6^+PtF_6^-$ and 1.86 mmole $ClF_2^+PtF_6^-$ = 1.097 g). The identity of this solid as $ClF_2^+PtF_6^-$ and $ClF_6^+PtF_6^-$ was verified by ^{19}F nmr, infrared, and Raman spectroscopy. Hence, PtF_6 (2.70 mmole) had reacted with ClF_5 (2.70 mmole) producing $ClF_6^+PtF_6^-$ (0.84 mmole), $ClF_2^+PtF_6^-$ (1.86 mmole), and F_2 (2.46 mmole). In addition, some of the ClF_5 (0.12 mmole), which had been used in excess, had decomposed to ClF_3 and F_2.

In a second experiment, PtF_6 (5.26 mmole) and ClF_5 (8.02 mmole) were combined at -196° in a sapphire reactor. The mixture was exposed at ambient temperature to uv radiation from a Hanovia Model 616A high pressure Hg arc using a Pyrex-water filter. After 14 days of irradiation, the PtF_6 color had disappeared and a yellow to orange solid had formed. The volatile products consisted of F_2 (0.23 mmole), ClF_5 (3.23 mmole), and a trace of ClF_3. The solid residue weighed 2.245 g and was, according to its infrared spectrum, a mixture of $ClF_6^+PtF_6^-$ and $ClF_4^+PtF_6^-$. It appears that owing to the long reaction time and uv irradiation, some PtF_6 (0.46 mmole as indicated by the F_2 evolution and by the weight of the solid reaction product) had reacted with the container walls. Hence, PtF_6 (4.80 mmole) had reacted with ClF_5 (4.79 mmole) producing $ClF_4^+PtF_6^-$ (2.40 mmole) and $ClF_6^+PtF_6^-$ (2.40 mmole). The observed weight of the solid product (2.245 g) agreed well with that calculated (2.252 g) for the above reactions.

Displacement Reaction Between FNO and $ClF_6^+PtF_6^-$. To a mixture (0.390 g) of $ClF_6^+PtF_6^-$ (0.30 mmole) and $ClF_2^+PtF_6^-$ (0.66 mmole) in a passivated Teflon-FEP ampoule, FNO (6.75 mmole) was added at -196°. The contents of the ampoule were kept at -78° for 12 hours. The ampoule was cooled to -196° and F_2 (0.28 mmole) was removed. The products volatile at ambient temperature were separated by fractional condensation and consisted of FNO (5.76 mmole), ClF_3 (0.64 mmole), and ClF_5 (0.27 mmole). The yellow, solid residue weighed 0.329 g (calculated weight for 0.96 mmole of $NO^+PtF_6^-$ = 0.326 g) and was identified by its infrared spectrum as $NO^+PtF_6^-$.

Reaction Between ClF_3O and PtF_6. Platinum hexafluoride (1.87 mmole) and ClF_3O (4.71 mmole) were combined at -196° in a sapphire reaction tube. When the mixture was allowed to warm to 25°, a rapid reaction with gas evolution occurred and the characteristic PtF_6 color disappeared within a few minutes. The mixture was kept at 25° for several hours and was then cooled to -196°. Fluorine (0.78 mmole) was removed at -196° and ClF_3O (2.05 mmole), ClF_5 (0.14 mmole), and $FClO_2$ (0.48 mmole) at 25°. The canary yellow residue weighed 0.749 g (weight calculated for 1.87 mmole of $ClF_2O^+PtF_6^-$ = 0.746 g) and was identified as $ClF_2O^+PtF_6^-$ by its infrared, Raman, and ^{19}F nmr spectrum.

In another experiment, PtF_6 (2.12 mmole) and ClF_3O (5.51 mmole) were allowed to interact at -45° for 12 hours. The volatile products consisted of F_2 (1.60 mmole), ClF_3O (3.35 mmole), $FClO_2$ (0.07 mmole), and a small amount of ClF_5 and PtF_6. The yellow solid residue weighed 0.837 g (weight calculated for 2.12 mmole of $ClF_2O^+PtF_6^-$ = 0.845 g). The infrared spectrum of the solid showed it to be mainly $ClF_2O^+PtF_6^-$, but also revealed the presence of smaller amounts of $ClO_2F_2^+$ and ClF_6^+ salts.

Reaction Between $FClO_2$ and IrF_6. Chloryl fluoride (2.57 mmole) and IrF_6 (1.96 mmole) were combined at -196° in a sapphire reactor. The mixture was kept at -78° for 48 hours, then cooled to -196°. All products were condensed at this temperature. At 25°, almost all of the starting materials were recovered unchanged except for 0.011 g of a yellowish solid which was identified by its infrared spectrum as $ClO_2^+IrF_6^-$. The unreacted starting materials were condensed back into the reactor and kept at 25° for 11 days. After this period, the product still showed the original brown color but had partially solidified. The mixture was cooled to -196° at which temperature 0.03 mmole of noncondensible material was removed. The material volatile at 25° consisted of IrF_6 (1.12 mmole), $FClO_2$ (1.88 mmole), and ClF_5 (0.21 mmole). The yellow crystalline solid weighed 0.147 g (0.39 mmole) and was identified by infrared and Raman spectroscopy as $ClO_2^+IrF_6^-$.

Attempted Syntheses of $ClF_6^+SbF_6^-$, $ClF_6^+AsF_6^-$, $ClF_6^+BF_4^-$, and $ClF_4O^+SbF_6^-$.

When mixtures of ClF_5, F_2, and AsF_5 in different mole ratios were heated in Monel cylinders for five to ten days at 125 to 145° under autogenous pressures of 500 to 1000 psi, only unreacted starting materials were recovered in addition to very small amounts of metal AsF_6^- salts. Heating the mixture to 160° resulted in partial breakdown of ClF_5 to ClF_3 and F_2.

Heating a BF_3, F_2, and ClF_5 mixture (mole ratio 1:2.7:2) for eight days to 95° under an autogenous pressure of 450 psi did not result in the formation of a solid product.

Mixtures of ClF_5, F_2, and SbF_5 (mole ratio 1:5:3) were heated for three to 40 days in Monel cylinders at 140 to 225° under autogenous pressures of ~ 1000 psi. At 140° and three days reaction time, no F_2 consumption was observed. At 160° and 25 days reaction time, 6.5% of the F_2 used was consumed due to attack on the cylinder. The solid product was a mixture of ClF_2^+, ClF_4^+, Ni^{++}, and Cu^{++} salts of $SbF_6^- \cdot xSbF_5$. Controlled vacuum pyrolysis of this solid resulted in the evolution of ClF_5 at lower and of ClF_3 at higher temperatures. The composition of the solid residues of this stepwise pyrolysis was monitored by infrared and Raman spectroscopy. It was shown that the more stable component having strong absorptions in the infrared and Raman spectrum at 825 and 830 cm^{-1} generated only ClF_3 when heated in the presence of CsF. When the reaction between ClF_5, F_2, and SbF_5 was carried out at 225°, $ClF_2^+SbF_6^-$ was formed with F_2 evolution.

Glow discharge of a BF_3, F_2, and ClF_5 mixture (mole ratio 1:1.42:1) at -78° in a Pyrex apparatus at pressures ranging from 20 to 50 mm produced only $ClF_2^+BF_4^-$ and no ClF_6^+ salt.

Heating a mixture of ClF_3O, F_2, and SbF_5 (mole ratio 1:10:5) in a Monel cylinder to 135° for six days under an autogenous pressure of 600 psi produced exclusively $ClF_2O^+SbF_6^-\cdot xSbF_5$.

Results and Discussion

Synthesis of ClF_6^+ Salts. Complex fluoro cations of the type XF_{y-1}^+ are generally prepared through fluorine abstraction from the parent compound XF_y by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus[13] for BrF_3:

$$BrF_3 + SbF_5 \longrightarrow BrF_2^+SbF_6^- \qquad (1)$$

The synthesis of a fluoro cation from a lower fluoride, according to:

$$XF + F^+ \longrightarrow XF_2^+ \qquad (2)$$

is pre-empted by the fact that fluorine is the most electronegative element. Hence, F^+ should be extremely difficult if not impossible to prepare by chemical means. The first and only known synthesis of a fluoro cation derived from a nonexisting parent compound was achieved[5,9] in 1966, according to:

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4{}^+AsF_6{}^- \qquad (3)$$

This synthesis involved either glow-discharge[5] or elevated temperature and pressure[9]. Since tetrahedral and octahedral species exhibit outstanding stability, as demonstrated by CF_4 and SF_6, the successful synthesis of $NF_4{}^+$ suggested the feasibility of synthesizing $ClF_6{}^+$ salts.

The application of glow-discharge to the synthesis of $ClF_6{}^+$ salts is limited to the ClF_5-F_2-BF_3 system. Stronger Lewis acids, such as AsF_5, form adducts with ClF_5[14], thus preventing the use of the low-temperature glow-discharge technique. In the case of BF_3, we did not successfully prepare $ClF_6{}^+BF_4{}^-$, owing to rapid breakdown of ClF_5 to ClF_3 and F_2, followed by removal of the ClF_3 from the gas phase by complex formation with BF_3[15]. The possible utility of the second technique, involving elevated temperature and pressure, for the synthesis of $ClF_6{}^+$ salts was also examined with BF_3, AsF_5, or SbF_5 as Lewis Acids. At lower temperatures, no fluorination of ClF_5 occurred, whereas at higher temperatures, breakdown of ClF_5 to ClF_3 and F_2 was observed. Since $ClF_2{}^+$ salts are thermally more stable than the corresponding $ClF_4{}^+$ salts, ClF_3 was continuously removed from the $ClF_5 \rightleftarrows ClF_3 + F_2$ equilibrium by complexing until essentially all the ClF_5 was converted to $ClF_2{}^+$ and F_2.

Since the techniques which had successfully been used for the synthesis of $NF_4{}^+$ salts did not result in $ClF_6{}^+$, other fluorinating agents were investigated. Of particular interest were the third transition series hexafluorides which exhibit an astonishing oxidizing power[16]. It was found[17] that PtF_6 and $FClO_2$, when combined at -196° and allowed to slowly warm up to 25°, interacted according to:

$$2FClO_2 + 2PtF_6 \longrightarrow ClO_2F_2{}^+PtF_6{}^- + ClO_2{}^+PtF_6{}^- \qquad (4)$$

The yield of $ClO_2F_2{}^+$ was not 50% as expected from the above equation, but generally about 25% owing to the following competing reaction:

$$2FClO_2 + 2PtF_6 \longrightarrow 2ClO_2{}^+PtF_6{}^- + F_2 \qquad (5)$$

In some of the experiments, small amounts of $ClF_6{}^+PtF_6{}^-$ (see below) or ClF_5 and $FClO_3$ were observed, depending on the exact reaction conditions. The formation of some $FClO_3$ is not surprising since it is known that $FClO_2$ readily interacts with nascent oxygen to yield $FClO_3$.[18,19]

Attempts to suppress the competing reaction (5) by changing the reaction conditions (rapid warm up from -196 to -78° and completion of the reaction at -78°) resulted in an entirely different course for the reaction:

$$6FClO_2 + 6PtF_6 \longrightarrow 5ClO_2{}^+PtF_6{}^- + ClF_6{}^+PtF_6{}^- + O_2 \qquad (6)$$

The observed material balance was in excellent agreement with equation (6) and the identity of $ClF_6{}^+$ was unequivocally established by ^{19}F nmr spectroscopy[20]. Further modification of the reaction conditions (rapid warm up of the $FClO_2$-PtF_6 mixture from -196 to either -78 or 25° and completion of the reaction at 25°) did not produce detectable amounts of either $ClO_2F_2{}^+$ or $ClF_6{}^+PtF_6{}^-$, but only $ClO_2{}^+PtF_6{}^-$ and ClF_5, F_2, and O_2. This indicates that the nature of the reaction products are more influenced by the warm up rate of the starting materials from -196 to about -78° than by the final reaction temperature. Slow warm up favors the formation of $ClO_2F_2{}^+$, whereas rapid warm up yields $ClF_6{}^+$ or ClF_5 and F_2.

The above results for the $FClO_2$-PtF_6 system indicated that ClF_5 might be an important intermediate in the formation of ClF_6^+. In order to prove the correctness of this assumption and in order to possibly increase the yield of ClF_6^+, which according to equation (6) can be at best 1/6 based on PtF_6, we have studied also the ClF_5-PtF_6 system. For the latter system, Roberto reported[1] the formation of a ClF_6^+ salt. Owing to the slow reaction rates in the ClF_5-PtF_6 system, we have used uv radiation. Two reactions were carried out at 25°. When unfiltered uv radiation was used, the reaction was complete in several hours, according to:

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{unfiltered} ClF_2^+PtF_6^- + ClF_6^+PtF_6^- + F_2 \qquad (7)$$

and

$$2ClF_5 + 2PtF_6 \longrightarrow 2ClF_2^+PtF_6^- + 3F_2 \qquad (8)$$

The relative contribution from (7) and (8) were 62 and 38%, respectively. In addition, some of the ClF_5, which had been used in excess, was recovered in the form of ClF_3 and F_2.

Using a Pyrex-water filter, a reaction time of two weeks was required with the products being:

$$2ClF_5 + 2PtF_6 \xrightarrow[uv]{Pyrex\ filter} ClF_4^+PtF_6^- + ClF_6^+PtF_6^- \qquad (9)$$

Since unfiltered uv light can decompose ClF_5 into ClF_3 + F_2[21] and since ClF_2^+ salts are more stable than ClF_4^+ salts[14], the displacement of ClF_4^+ by ClF_3, observed for (7), is not surprising. The identity of the ClF_6^+ salt obtained from the $FClO_2$-PtF_6 system with that from the ClF_5-PtF_6 system was established by infrared, Raman, and ^{19}F nmr spectroscopy.

The unusual nature of these reactions and products ask for a possible rationalization. In spite of the complexity of the $FClO_2$-PtF_6 system, the following assumptions appear plausible:

(a) An initial electron transfer from $FClO_2$ to PtF_6, according to:

$$FClO_2 + PtF_6 \longrightarrow FClO_2^{+\cdot}\ PtF_6^- \qquad (10)$$

(b) The resulting $FClO_2^{+\cdot}$ radical cation could either stabilize by generating an active fluorine radical, according to:

$$FClO_2^{+\cdot}\ PtF_6^- \longrightarrow ClO_2^+PtF_6^- + F\cdot \qquad (11)$$

or act itself as the active fluorinating agent, depending upon the relative life times of these two radicals.

(c) In both cases ($F\cdot$ or $ClO_2F\cdot^+$), the radical might react either with PtF_6 with F_2 evolution:

$$F\cdot + PtF_6 \longrightarrow F_2 + PtF_5 \qquad (12)$$

followed by:

$$PtF_5 + FClO_2 \longrightarrow ClO_2^+PtF_6 \qquad (13)$$

or with $FClO_2$:

$$FClO_2 + F\cdot \longrightarrow F_2ClO_2\cdot \qquad (14)$$

(d) The resulting $F_2ClO_2\cdot$ radical could readily stabilize by transfer of an electron to PtF_6:

$$F_2ClO_2\cdot + PtF_6 \longrightarrow ClO_2F_2^+PtF_6^- \qquad (15)$$

This sequence would account for the formation of $ClO_2F_2^+$ and for the competitive F_2 evolution reaction. Similarly, the formation of ClF_6^+ from ClF_5 and PtF_6 might involve an intermediate $ClF_5^{+\cdot}$ radical cation and suggests a search for radical cations in these systems. The formation of ClF_6^+ from $FClO_2$ might involve either an intermediate ClF_5 molecule or the direct fluorination of $ClO_2F_2^+$ to ClF_6^+. A definitive answer to these interesting questions concerning the most important intermediates is beyond the scope of the present study.

Properties of ClF_6^+ Salts. The $ClF_6^+PtF_6^-$ salts are canary yellow solids. They were stored at 25° in Teflon-FEP containers for several months without noticeable decomposition and formed stable HF solutions. They are very powerful oxidizers and react explosively with organic materials or water. Contrary to a previous statement[1], no evidence was found during our investigation that the ClF_6^+ salts themselves can be explosive.

On the Existence of ClF_7. A displacement reaction between $ClF_6^+PtF_6^-$ and FNO was carried out under conditions similar to those which had successfully been used for the synthesis of ClF_3O_2 from $ClO_2F_2^+PtF_6^-$ and FNO[4]. Since $ClF_6^+PtF_6^-$ can be considered as a Lewis acid adduct between ClF_7 and PtF_5, the products from the FNO displacement reaction allow some conclusions concerning the stability of the hypothetical compound ClF_7. The following results were obtained for the displacement reaction:

$$ClF_6^+PtF_6^- + FNO \xrightarrow{-78^{\circ}} NO^+PtF_6^- + ClF_5 + F_2 \qquad (17)$$

This indicates that ClF_7 under the given reaction conditions (-78°) cannot exist.

Iridium Hexafluoride Reactions. Replacement of PtF_6 by IrF_6 in the $FClO_2$ reaction did not result in an oxidative fluorination of Cl(+V) to Cl(+VII). At 25° and long reaction times, only $ClO_2^+IrF_6^-$ and ClF_5 were formed in moderate yields. This demonstrates that IrF_6 is a weaker fluorinating oxidizer than PtF_6 as has previously been demonstrated by Bartlett[16].

Attempted Synthesis of ClF_4O^+ Salts. The successful syntheses[1,2,4] of the $ClO_2F_2^+$ and the ClF_6^+ cation suggested the possible synthesis of the intermediate ClF_4O^+ cation from ClF_3O and PtF_6. At 25°, the main reaction was:

$$2ClF_3O + 2PtF_6 \xrightarrow{25^\circ} 2ClF_2O^+PtF_6^- + F_2 \qquad (18)$$

In addition, small amounts of $FClO_2$ and ClF_5 were observed among the volatile reaction products. When the reaction temperature was lowered to -45°, the main products were again $ClF_2O^+PtF_6^-$ and F_2. However, small amounts of $ClO_2F_2^+$ and $ClF_6^+PtF_6^-$ had also formed. No evidence for the presence of any ClF_4O^+ could be obtained. This suggests that tetrahedral $ClF_2O_2^+$ and octahedral ClF_6^+ are more favorable products than the pseudo trigonal bipyramidal ClF_4O^+. The formation of small amounts of $ClO_2F_2^+$ and ClF_6^+ (or $FClO_2$ and ClF_5) might be due either to the decomposition of an unstable intermediate, such as ClF_4O^+, into $ClO_2F_2^+$ and ClF_6^+, or at least partially to the formation of some $FClO_2$ from the difficult to handle ClF_3O[12]. Attempts to synthesize $ClF_4O^+SbF_6^-$ from ClF_3O-F_2-SbF_5 at elevated temperature and pressure produced exclusively $ClF_2O^+SbF_6^- \cdot xSbF_5$.

Vibrational Spectra. The infrared and Raman spectra of the solid reaction products are shown by Figures 1 and 2, respectively. The spectrum of $ClF_2O^+PtF_6^-$ was identical to that previously reported[22] and hence, is not depicted. Attempts to record the Raman spectrum of the $ClF_4^+PtF_6^-$ - $ClF_6^+PtF_6^-$ mixture were unsuccessful owing to rapid sample decomposition by the laser beam. From a large number of experiments, those spectra and products were selected which showed the least amounts of by-products. Depending upon the exact reaction conditions, however, the products sometimes were more complex mixtures of ClO_2^+, $ClO_2F_2^+$, and ClF_6^+, or of ClF_2^+, ClF_4^+, and ClF_6^+. The observed frequencies are listed in Table I.

Since most products contain the PtF_6^- anion, its spectrum will be discussed first. The simplest spectrum is that of $NO^+PtF_6^-$. Our observed spectrum is in good agreement with that previously reported[16,23,24] for this compound. In addition to the reported bands, we have observed an infrared band at 268 cm^{-1}. The crystal structure of $O_2^+PtF_6^-$ (which is isomorphous with $NO^+PtF_6^-$)[16] has been determined[25]. It was shown that PtF_6^- is approximately octahedral[25]; however, its site symmetry[26] is lower than O_h. This site symmetry lowering can cause splitting of most of the bands and violations of the selection rules expected for symmetry O_h. Since the crystal structures and, hence, the actual site symmetries of PtF_6^- in the other chlorine fluoride salts are unknown and since the observed splittings are relatively small, the assignments for PtF_6^- in Table I were made based on the group symmetry O_h. In addition to the previously assigned bands[16,23,24], the antisymmetric deformation, ν_4 (F_{1u}), and the normally inactive ν_6 (F_{2u}) mode were observed at about 265 and 180 cm^{-1}, respectively. The spectrum observed for IrF_6^- is in good agreement with that of PtF_6^-. In addition to the previously reported[23] bands, the ν_4 and ν_6 modes were also observed for IrF_6^-.

The vibrational spectra of ClO_2^+ [27], $ClF_2O_2^+$ [4,28], ClF_2^+ [29,30], ClF_2O^+ [22,31,32], and ClF_4^+ [33] have been reported elsewhere. The assignments given in Table I are in excellent agreement with those previously given for these ions and, hence, require no further discussion. Assignments for ClF_6^+, whose identity and

TABLE 1. VIBRATIONAL SPE

$NO^+PtF_6^-$		
Obsd Frequency, cm^{-1}		
IR	RA	Assignment for PtF_6^- in O_h
2385 mw		
2329 ms	2326 (0+)	νNO
1280 w, br		$\nu_1 + \nu_3(F_{1u})PtF_6^-$
1212 w, br		$\nu_2 + \nu_3(F_{1u} + F_{2u})PtF_6^-$
880 vw, br		$\nu_3 + \nu_5(A_{2u} + E_u + F_{1u} + F_{2u})PtF_6^-$
830 vw, br		$\nu_2 + \nu_4(F_{1u} + F_{2u})PtF_6^-$
640 vs, br		$\nu_3(F_{1u})PtF_6^-$
	644(10)	$\nu_1(A_{1g})PtF_6^-$
	589(0+)	
570 s	579(2)	$\nu_2(E_g)PtF_6^-$
295 mw		
		$\nu_4(F_{1u})PtF_6^-$
269 ms		
	249(4)	
	236 sh	$\nu_5(F_{2g})PtF_6^-$

$ClO_2^+, ClF_2O_2^+PtF_6^-$		
Obsd Frequency, cm^{-1}		
IR	RA	Assignment for ClO_2^+ and $ClF_2O_2^+$ in C_{2v}, for PtF_6^- in O_h
2340		
2320 w		$\nu_1 + \nu_3(B_1)ClO_2^+$
2115 vw		$2\nu_1(A_1)ClO_2^+$
1486		
1470 s		$\nu_6(B_1)\ ClF_2O_2^+$
1297 vs	1299 (0.5)	$\nu_3(B_1)\ ClO_2^+$
1283 s	1285 (0.17)	
1245	1246 (0+)	
1237 s		$\nu_1(A_1)ClF_2O_2^+$
1210 w		$\nu_2 + \nu_3(F_{1u} + F_{2u})PtF_6^-$
1052 s	1051 (2.7)	$\nu_1(A_1)ClO_2^+$
1047 m		
827 s		$\nu_8(B_2)ClF_2O_2^+$
756 s	754 (0.1)	$\nu_2(A_1)ClF_2O_2^+$
640 vs	617 (215)	$\nu_3(F_{1u})PtF_6^-$
	642 (10)	$\nu_1(A_{1g})PtF_6^-$
580 w	564 (1.3)	
552 s	552 (1.8)	$\nu_2(E_g)PtF_6^-$
530 sh		$\nu_3(A_1),\ \nu_7(B_1),\ \nu_9(B_2)ClF_2O_2^+$
514 s	514 (0.4)	$\nu_2(A_1)ClO_2^+$
284 m		
266 s		$\nu_4(F_{1u})PtF_6^-$
	230 (2.9)	$\nu_5(F_{2g})PtF_6^-$
	180 (0+)	$\nu_6(F_{2u})PtF_6^-$

ClO_2	
Obsd Frequency, cm^{-1}	
IR	RA
2340	
2320 w	
1297 vs	1299 (0 3)
1263 s	1285 (0.1)
1210 w	
1055 s	1054 (2.0)
1049 m	
890 s	
	679 (0.5)
640	
620 vs	618 (3.1)
	644 (10)
580 ms	569 (1.8)
552 s	554 (2.5)
516 s	518 (0.6)
	240 (4.5)
	185 (0.2)
	130 (0.1)
	98 (1.0)

1. VIBRATIONAL SPECTRA OF SEVERAL PtF_6^- SALTS AND OF $C\ell O_2^+IrF_6^-$ AND THEIR ASSIGNMENT - RAMAN INTE

$C\ell O_2^+$, $C\ell F_6^+$ PtF_6^-		
Obsd Frequency, cm^{-1}		Assignment for $C\ell O_2^+$ in C_{2v}, for $C\ell F_6^+$ and PtF_6^- in O_h
IR	RA	
2340 2320 w		$\nu_1 + \nu_3(B_1)C\ell O_2^+$
1297 vs 1283 s	1299 (0.3) 1285 (0.1)	$\nu_3(B_1)C\ell O_2^+$
1210 w		$\nu_2 + \nu_3(F_{1u} + F_{2u})PtF_6^-$
1053 s 1049 m	1054 (2.0)	$\nu_1(A_1)C\ell O_2^+$
890 s		$\nu_3(F_{1u})C\ell F_6^+$
	679 (0.5)	$\nu_1(A_{1g})C\ell F_6^+$
640 620 vs	618 (3.1)	$\nu_3(F_{1u})PtF_6^-$
	644 (10)	$\nu_1(A_{1g})PtF_6^-$
580 ms 552 s	569 (1.8) 554 (2.5)	$\nu_2(E_g)PtF_6^-$
516 s	518 (0.6)	$\nu_2(A_1)C\ell O_2^+$, $\nu_5(F_{2g})C\ell F_6^+$
	249 (4.5)	$\nu_5(F_{2g})PtF_6^-$
	185 (0.2)	$\nu_6(F_{2u})PtF_6^-$
	130 (0.1) 98 (1.6)	Lattice Vibrations

$C\ell F_2^+$, $C\ell F_6^+$ PtF_6^-		
Obsd Frequency, cm^{-1}		Assignment for $C\ell F_2^+$ in C_{2v}, for $C\ell F_6^+$ and PtF_6^{2-} in O_h
IR	RA	
1576 w		$\nu_1 + \nu_3(B_1)C\ell F_2^+$
1554 w		$\nu_1 + \nu_3(F_{1u})C\ell F_6^+$
1510 w		$\nu_2 + \nu_3(F_{1u} + F_{2u})C\ell F_6^+$
1298 1284 w		$\nu_3(B_1)C\ell O_2^+$ $\nu_1 + \nu_3(F_{1u})PtF_6^-$
1240 1216 w		$\nu_2 + \nu_3(F_{1u} + F_{2u})PtF_6^-$ $\nu_2 + \nu_4(F_{1u} + F_{2u})C\ell F_6^+$
1160 vw		$\nu_1 + \nu_2(A_1)C\ell F_2^+$
890 vs		$\nu_3(F_{1u})C\ell F_6^+$
799 vs	799 (1.3)	$\nu_3(B_1)C\ell F_2^+$
789 vs	788 (5.0) 784 (1)	$\nu_1(A_1)C\ell F_2^+$
733 vw		$\nu_2 + \nu_6(F_{1u} + F_{2u})PtF_6^-$
	704 (0+)	
	679 (1.0)	$\nu_1(A_{1g})C\ell F_6^+$
655 vs, br	661 (0+) 651 (2.5)	$\nu_3(F_{1u})PtF_6^-$
	639 (10)	$\nu_1(A_{1g})PtF_6^-$
	630 sh	$\nu_2(E_g)C\ell F_6^+$
585 s, br	582 576 (0.8) 561 (3.1)	$\nu_2(E_g)PtF_6^-$
510 w, sh	513 (0.3)	$\nu_5(F_{2g})C\ell F_6^+$
478 w, sh		
383 s 376 sh	381 (0.2)	$\nu_2(A_1)C\ell F_2^+$
304 m 265 s	300 (0.5) 282 (0.2)	$\nu_4(F_{1u})PtF_6^-$
	249 (3.2) 236 sh 229 (2.5)	$\nu_5(F_{2g})PtF_6^-$
	170 (0.3)	$\nu_6(F_{2u})PtF_6^-$
	101 (0.9) 72 (0.3) 54 (1.5) 42 (5.0) 26 (0.4)	Lattice Vibrations

$C\ell F_2O^+$ PtF_6^-		
Obsd Frequency, cm^{-1}		Assignment for $C\ell F$ in C_s, for PtF_6^- i
IR	RA	
1326 ms 1313 mw	1324 (0.6) 1311 (0.2)	$\nu_1(A')C\ell F_2O^+$
737 s	737 (2.7)	$\nu_2(A')C\ell F_2O^+$
705 s	705 (0.8)	$\nu_5(A'')C\ell F_2O^+$
643 vs	658 (4.2)	$\nu_3(F_{1u})PtF_6^-$
630 sh	630 (10)	$\nu_1(A_{1g})PtF_6^-$
564 s	575 sh 564 (2.9)	$\nu_2(E_g)PtF_6^-$
508 s	506 (0.5)	$\nu_3(A')C\ell F_2O^+$
401 ms	401 (0.7)	$\nu_6(A'')C\ell F_2O^+$
386 ms	386 (0.2)	$\nu_4(A')C\ell F_2O^+$
	280 (0.3)	$\nu_4(F_{1u})PtF_6^-$
	230 (7.9)	$\nu_5(F_{2g})PtF_6^-$
	140 (0.3) 115 (0.2) 58 (1.0)	Lattice Vibrations

SSIGNMENT - RAMAN INTENSITIES ARE UNCORRECTED

$C\ell F_2O^+ PtF_6^-$		
Frequency, cm^{-1}		Assignment for $C\ell F_2O^+$ in C_s, for PtF_6^- in O_h
	RA	
ms	1324 (0.6)	$\nu_1(A')C\ell F_2O^+$
mw	1311 (0.2)	
s	737 (2.7)	$\nu_2(A')C\ell F_2O^+$
s	705 (0.8)	$\nu_5(A'')C\ell F_2O^+$
vs	656 (4.2)	$\nu_3(F_{1u})PtF_6^-$
sh	630 (10)	$\nu_1(A_{1g})PtF_6^-$
s	575 sh	$\nu_2(E_g)PtF_6^-$
	564 (2.9)	
s	506 (0.5)	$\nu_3(A')C\ell F_2O^+$
ms	401 (0.7)	$\nu_6(A'')C\ell F_2O^+$
ms	386 (0.2)	$\nu_4(A')C\ell F_2O^+$
	280 (0.3)	$\nu_4(F_{1u})PtF_6^-$
	230 (7.9)	$\nu_5(F_{2g})PtF_6^-$
	140 (0.3)	Lattice Vibrations
	115 (0.2)	
	58 (1.0)	

$C\ell F_4^+$, $C\ell F_6^+ PtF_6^-$	
Obsd Frequency, cm^{-1} IR	Assignment for $C\ell F_4^+$ in C_{2v}, for $C\ell F_6^+$ and PtF_6^- in O_h
1560 w	$\nu_1 + \nu_3(F_{1u})C\ell F_6^+$
1515 w	$\nu_2 + \nu_3(F_{1u} + F_{2u})C\ell F_6^+$
1200 w, br	$\nu_2 + \nu_3(F_{1u} + F_{2u})PtF_6^-$
890 vs	$\nu_3(F_{1u})C\ell F_6^+$
878 sh	
785 vs	$\nu_8(B_2), \nu_1(A_1), \nu_6(B_1)C\ell F_4^+$
720 vw	$\nu_2 + \nu_6(F_{1u} + F_{2u})PtF_6^-$
670 vs	$\nu_3(F_{1u})PtF_6^-$
620	
580 ms	$\nu_2(E_g)PtF_6^-$ $\nu_2(A_1)C\ell F_4^+$ $\nu_7(B_1)C\ell F_4^+$
572 mw	
551 sh	
545 s	
500 s	$\nu_3(A_1)C\ell F_4^+$
383 s	$\nu_9(B_2)C\ell F_4^+$
281 sh	$\nu_4(F_{1u})PtF_6^-$
271 s	

$C\ell O_2^+ IrF_6^-$		
Obsd Frequency, cm^{-1}		Assignment for $C\ell O_2^+$ in C_{2v}, for IrF_6^- in O_h
IR	RA	
1300 vs	1301 (0.6)	$\nu_3(B_1)C\ell O_2^+$
1206 s	1287 (0.2)	
1057 s	1057 (6.1)	$\nu_1(A_1)C\ell O_2^+$
	670 (10)	$\nu_1(A_{1g})IrF_6^-$
640 vs, br	613 (0.9)	$\nu_3(F_{1u})IrF_6^-$
580 w	561 (2.5)	$\nu_2(E_g)IrF_6$
548 s	549 (4.8)	
518 s	519 (1.1)	$\nu_2(A_1)C\ell O_2^+$
279 m		$\nu_4(F_{1u})IrF_6^-$
258 s		
	248 (8.5)	$\nu_5(F_{2g})IrF_6^-$
	185 (0.5)	$\nu_6(F_{2u})IrF_6^-$

octahedral structure has been established beyond doubt by ^{19}F nmr spectroscopy[3], were made on the basis of the following arguments. For octahedral ClF_6^+, we would expect ideally six normal modes of vibration which are classified as $A_{1g} + E_g + 2F_{1u} + F_{2g} + F_{2u}$. Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g}, E_g, and F_{2g} modes will be Raman active, assuming no other solid state effects such as site symmetry lowering or slight distortion of the octahedron. Three different salts containing $ClF_6^+PtF_6^-$ have been studied. In addition to ClF_6^+, they contain either the ClO_2^+, or the ClF_2^+, or the ClF_4^+ cation. All three salts show a strong infrared absorption at 890 cm^{-1}. The frequency of this band is higher than that of any known ClF fundamental vibration and is assigned to the antisymmetric stretching vibration, ν_3 (F_{1u}) of ClF_6^+. This assignment is supported by the following observation. In all three salts, the 890 cm^{-1} band shows a pronounced shoulder at 877 cm^{-1}. The observed frequency difference of about 13 cm^{-1} is in good agreement with the ^{35}Cl - ^{37}Cl isotopic shift value of 12.5 cm^{-1} computed for octahedral ClF_6^+, assuming 100-percent characteristic modes. Of the remaining unassigned bands, the second highest frequency belongs to a relatively intense Raman line at 679 cm^{-1}. Clearly, this line must be due to the totally symmetric stretching mode, ν_1 (A_{1g}). The Raman spectrum of ClF_2^+, $ClF_6^+PtF_6^-$ (trace d, Figure 2) shows a band at 513 cm^{-1}. It has the same frequency as the ClO_2^+ deformation mode but cannot be due to ClO_2^+ since there is no evidence for its more intense ν_1 (A_1) mode at about 1050 cm^{-1}. The 513 cm^{-1} band might be assigned to either ν_2 (E_g) or ν_5 (F_{2g}) of ClF_6^+.

It has previously been shown that the vibrational spectra of ClO_2^+ [27], ClF_2O^+ [31], $ClF_2O_2^+$ [4,28], ClF_5 [34], and ClF_4^+ [33] closely resemble those of isoelectronic SO_2, SF_2O, SF_2O_2, SF_5^-, and SF_4, respectively. A similar relationship might be expected for the isoelectronic pair ClF_6^+-SF_6 (see Table II). Comparison with the vibrationa spectrum of SF_6[35,36] suggests that the 513 cm^{-1} band is due to ν_5 (F_{2g}). This is further supported by the absence of another band below 513 cm^{-1}, which might be assigned to this mode and by the observed combination bands in the infrared spectrum. Generally, octahedral species exhibit two relatively intense combination bands in the infrared spectrum due to $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$. For ClF_6^+, two bands were observed at about 1560 and 1515 cm^{-1}, respectively. The 1560 cm^{-1} band represents $\nu_1 + \nu_3$ (computed frequency: 1569 cm^{-1}). Assuming the 1515 cm^{-1} band to be due to $\nu_2 + \nu_3$, a value of 625 cm^{-1} can be assigned to ν_2. Inspection of trace d of Figure 2 reveals a shoulder at 630 cm^{-1}, which is assigned to ν_2 (E_g) of ClF_6^+. Since there is no indication in the infrared spectrum for a combination band at about 1400 cm^{-1} (890 + 513 = 1403), the 513 cm^{-1} Raman band is assigned to ν_5 (F_{2g}).

An alternate, although less probable, assignment is possible for ν_2 (E_g) of ClF_6^+. Trace d of Figure 2 exhibits two bands at 582 and 576 cm^{-1}, respectively. We prefer, however, to attribute both of them to ν_2 (E_g) of PtF_6^- since the ν_5 (F_{2g}) PtF_6^- bands also show additional splitting and since again no evidence for the corresponding $\nu_2 + \nu_3$ combination band can be found in the infrared spectrum at about 1470 cm^{-1}. Thus all the expected active modes have been assigned for ClF_6^+ except for the antisymmetric deformation, ν_4 (F_{1u}). This mode should be infrared active and by comparison with SF_6, occur in the range 550 - 610 cm^{-1}. A frequency of 582 cm^{-1} is tentatively assigned to ν_4 based on traces c, d, and e of Figure 1 and by comparison with the infrared spectrum of $ClF_2O^+PtF_6^-$[22].

TABLE II

Fundamental Vibrations of ClF_6^+ Compared to Those of Isoelectronic SF_6

ClF_6^+	$SF_6^{(a)}$	Assignment in Point Group O_h
679	769.4	ν_1 (A_{1g})
630	639.5	ν_2 (E_g)
890	947.9	ν_3 (F_{1u})
582	614.5	ν_4 (F_{1u})
513	522	ν_5 (F_{2g})

(a) Data from Reference 35 and 36.

Force Constants. A modified valence force field was computed for ClF_6^+ in order to obtain a more quantitative understanding of its relative bond strength. Except for the F_{1u} block, all the symmetry force constants are unique. The F_{1u} block is underdetermined since only two frequency values are available for the determination of three force constants. A third frequency value for the F_{1u} block might be obtained from the ^{35}Cl-^{37}Cl isotopic shifts which would allow the computation of a general valence force field. Unfortunately, the isotopic shift for ν_3 could not be determined with sufficient accuracy. Consequently, the usefulness of mathematica constraints, such as minimizing or maximizing the value of one of the symmetry force constants was tested for isoelectronic SF_6, for which a general valence force field has been reported[37]. It was found that the condition, F_{44} = minimum[38], is the best approximation to the general valence force field, though it yields too high a value for F_{34}, due to appreciable coupling of the bonds[39]. It also results in a rather large negative value (-0.269 mdyn/Å) for the stretch-stretch interactio constant, f_{rr}', which is difficult to rationalize. Using the same condition for computing the force field of ClF_6^+, a comparable negative value (- 0.297 mdyn/Å) was obtained for f_{rr}' of ClF_6^+. Since for SF_6 the GVFF value of f_{rr}' is essentially zero, we prefer for ClF_6^+ the condition $f_{rr}' = 0$. The resulting force field is listed in Table III and compared to the GVFF values of SF_6[37].

TABLE III

Symmetry and Internal Force Constants (mdyn/Å) of ClF_6^+ Computed for a Modified Valence Force Field Assuming $f_{rr}' = 0$ and Using the Frequency Values of Table II. For Comparison the GVFF Values of SF_6 are also Listed.

	ClF_6^+	SF_6
F_{11}	5.161	6.626
F_{22}	4.443	4.578
F_{33}	4.682	5.256
F_{34}	0.726	0.885
F_{44}	0.955	1.035
F_{55}	0.736	0.763
f_r	4.682	5.258
f_{rr}	0.120	0.341
f_{rr}'	0	0.002
$f_{r\alpha}-f_{r\alpha}''$	0.363	0.443

The force constant of greatest interest is the stretching force constant, f_r. Its value is 4.7 mdyn/Å with a conservative uncertainty estimate of ± 0.2 mdyn/Å considering the uncertainties in the frequency of ν_4 (F_{1u}) and in the approximating method used for the force constant computation. This value is comparable to those of ClF_2^+ (4.74 mdyn/Å)[40] and of the equatorial Cl-F bonds in ClF_4^+ (4.59 mdyn/Å)[33], but significantly higher than those of the remaining known chlorine fluorides. The high value of f_r in ClF_6^+ can be explained to some extent by the formal positive charge which generally increases the stretching force constant values. It also suggests strong covalent contributions to the bonding. The high f_r value is entirely consistent with the high stability observed for the ClF_6^+ salts and parallels the findings for the NF_4^+ salts[6-9]. In both cases, comparison with the isoelectronic molecules SF_6 and CF_4, respectively, suggested unusual stability, although it proved difficult to actually synthesize these salts. In particular, it appears that the synthesis of ClF_6^+ requires an unusually powerful oxidative fluorinating agent such as PtF_6.

Since ν_4 (F_{1u}) and ν_6 (F_{2u}) have been observed for both PtF_6^- and IrF_6^-, a modified valence force field was also computed for these two anions assuming octahedral symmetry and F_{44} = minimum. For PtF_6^- and IrF_6^-, this extremal condition is expected to give a force field close to that of a GVFF owing to the large mass of the central atoms and the resulting weak coupling. The frequencies used for the computation are listed in Table IV, together with the resulting force constants. The value of f_r of PtF_6^- (3.89) is intermediate between those of PtF_6 (4.46)[41] and PtF_6^{--} (3.42 mdyn/Å)[41] as expected on the basis of the increasing formal negative charge.

Summary. The successful synthesis of ClF_6^+ and the evidence for the nonexistence of a stable ClF_7 molecule and ClF_6^- anion[14] completes the series of possible binary chlorine fluoride molecules and ions. Table V summarizes the presently known species. The existence of ClF_6^+ suggests the possibility of preparing ClF_5O and efforts to synthesize this new oxyfluoride will be continued.

TABLE IV

Symmetry and Internal Force Constants (mdyn/Å) of PtF_6^- and IrF_6^- Computed for a Modified Valence Force Field Assuming F_{44} = Minimum

	PtF_6^{-} (a)	IrF_6^{-} (b)
F_{11}	4.613	5.025
F_{22}	3.573	3.510
F_{33}	3.870	3.861
F_{34}	0.100	0.101
F_{44}	0.308	0.307
F_{55}	0.161	0.172
F_{66}	0.181	0.192
f_r	3.894	3.940
f_{rr}	0.173	0.255
f_{rr}'	0.024	0.079
$f_{r\alpha}-f_{r\alpha}''$	0.050	0.051
$f_{\alpha}-f_{\alpha\alpha}-f_{\alpha\alpha}'+f_{\alpha\alpha}''$	0.171	0.182
$f_{\alpha\alpha}-f_{\alpha\alpha}'-f_{\alpha\alpha}''+f_{\alpha\alpha}'''$	−0.010	−0.010

Frequencies Used:

(a) $\nu_1 = 642$, $\nu_2 = 565$, $\nu_3 = 640$, $\nu_4 = 270$, $\nu_5 = 240$, $\nu_6 = 180$ cm^{-1}.

(b) $\nu_1 = 670$, $\nu_2 = 560$, $\nu_3 = 640$, $\nu_4 = 270$, $\nu_5 = 248$, $\nu_6 = 185$ cm^{-1}.

TABLE V

Summary of Existing Binary Chlorine Fluorides. Nonexisting Species Are Given in Parentheses.

Cl_2F^+ (a)	ClF (b)	ClF_2^- (c)
ClF_2^+ (d)	ClF_3 (e)	ClF_4^- (f)
ClF_4^+ (g)	ClF_5 (h)	(ClF_6^-) (g)
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Diagram Captions

Figure 1. Infrared spectra of the solid products obtained from the following reactions: trace a, displacement reaction between FNO and a mixture of $ClF_2^+PtF_6^-$ and $ClF_6^+PtF_6^-$; traces b and c, $FClO_2$ + PtF_6 at 25 and -78°, respectively; traces d and e, ClF_5 and PtF_6 using unfiltered and filtered uv radiation, respectively; trace f, $FClO_2$ + IrF_6 at 25°. All spectra were recorded as pressed AgBr disks, except for trace c for which a AgCl disk was used.

Figure 2. Raman spectra of some of the solid products shown in Figure 1 using the same notations. All spectra were recorded for dry powders in glass melting point capillaries, using the 6471 Å exciting line on a Cary Model 82.

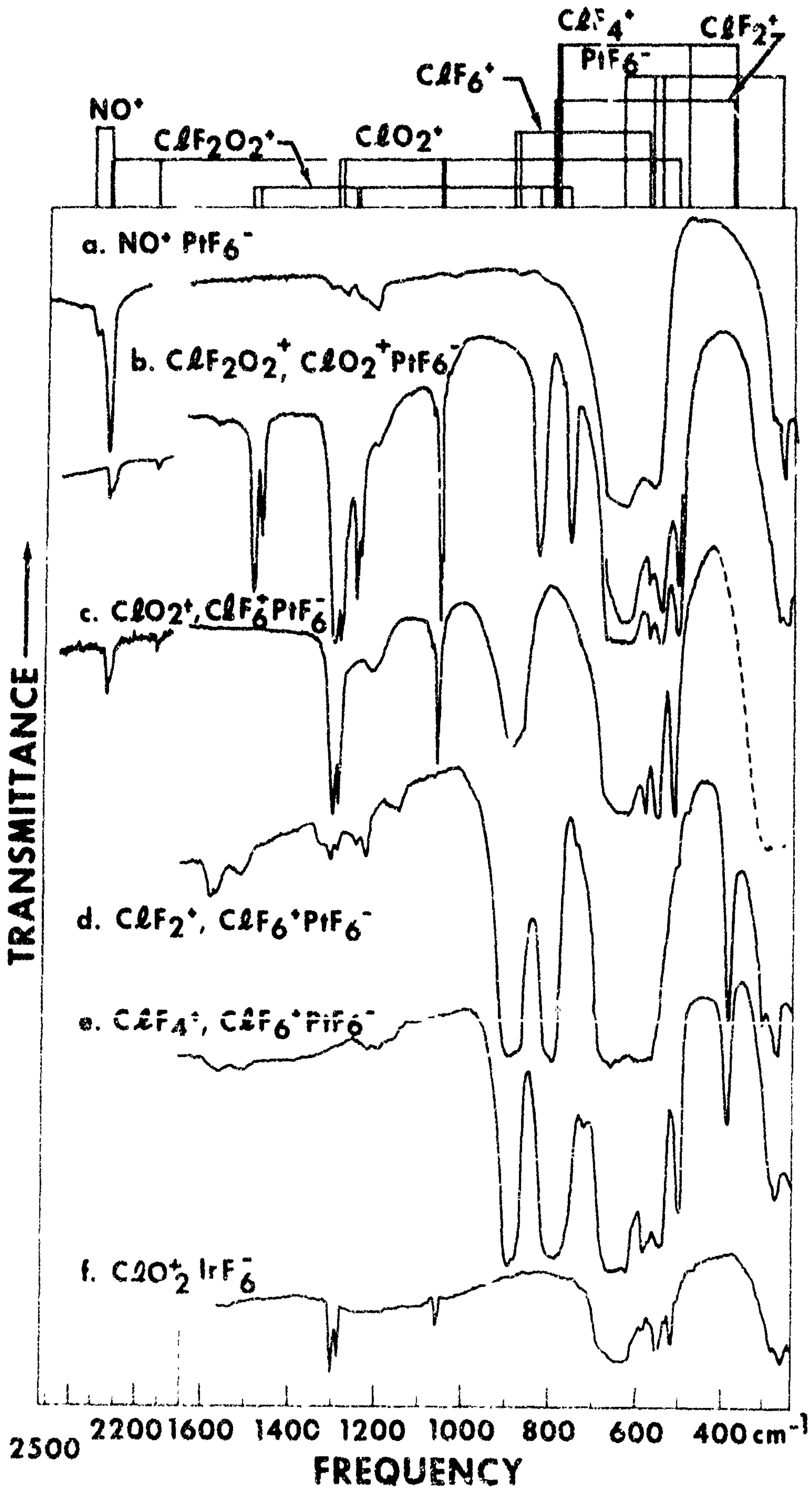
NO⁺
CℓF₂O₂⁺
CℓO₂⁺
CℓF₆⁺
CℓF₄⁺
PtF₆⁻
CℓF₂⁺
a. NO⁺ PtF₆⁻
b. CℓF₂O₂⁺, CℓO₂⁺PtF₆⁻
c. CℓO₂⁺, CℓF₆⁺PtF₆⁻
d. CℓF₂⁺, CℓF₆⁺PtF₆⁻
e. CℓF₄⁺, CℓF₆⁺PtF₆⁻
f. CℓO₂⁺ IrF₆⁻
TRANSMITTANCE
2500
2200
1600
1400
1200
1000
800
600
400 cm⁻¹
FREQUENCY

Figure 1.

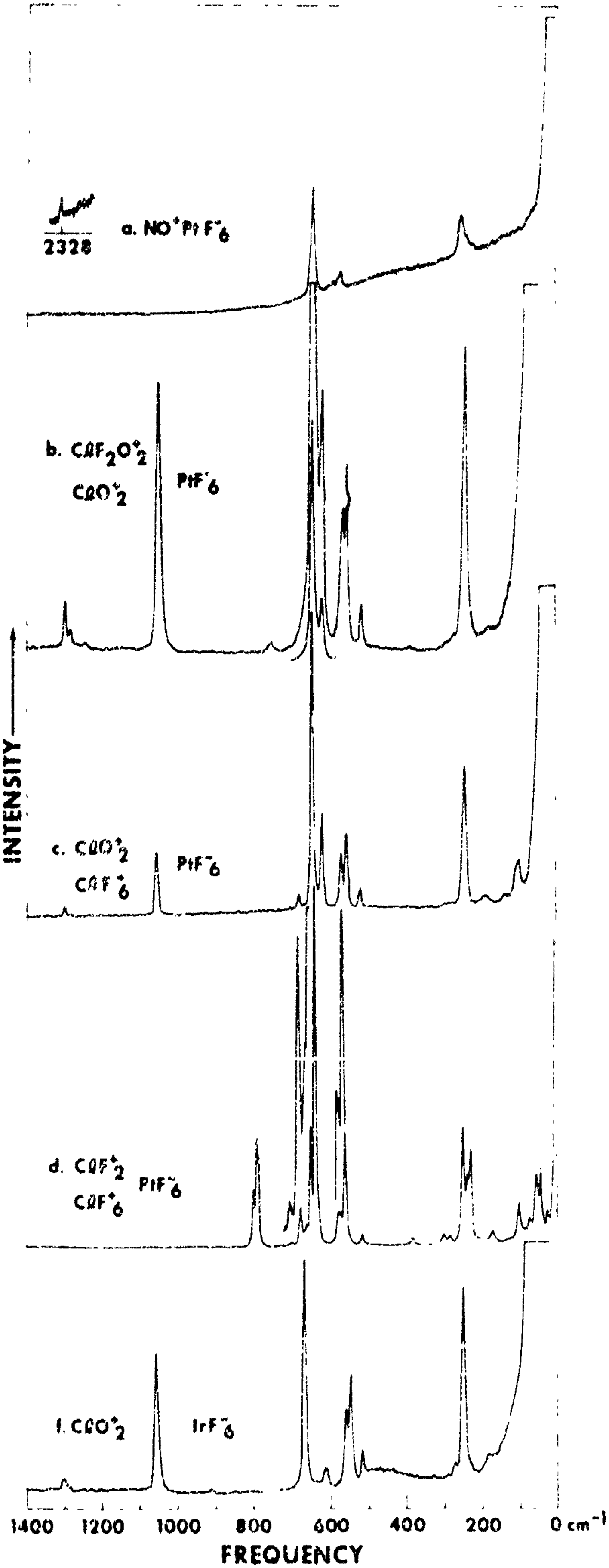
2328
a. NO⁺PtF⁻₆
b. ClF₂O⁺₂
ClO⁺₂
PtF⁻₆
c. ClO⁺₂
ClF⁺₆
PtF⁻₆
d. ClF⁺₂
ClF⁺₆
PtF⁻₆
f. ClO⁺₂
IrF⁻₆
INTENSITY
1400
1200
1000
800
600
400
200
0 cm⁻¹
FREQUENCY

Figure 2.

On The Existence of Chlorine Oxide Pentafluoride[**]

By Karl O. Christe, Richard D. Wilson, and Donald Pilipovich[*]

The recent report by Zuechner and Glemser[1] on the synthesis of ClF_5O from the photolysis of ClF_5-OF_2 mixtures prompted us to thoroughly study this system. Contrary to the previous report[1], no evidence for the existence of ClF_5O could be obtained in the temperature range -78° to 30°C, using both unfiltered and Pyrex filtered uv radiation. All reactions were carried out in a stainless steel reactor equipped with a sapphire window. The progress of the reactions was periodically monitored by gas chromatography. At the end of an experiment, the products were also separated by fractional condensation, in a Teflon-stainless steel vacuum system and were characterized by vibrational spectroscopy. It was shown that in the ClF_5-OF_2 system, when exposed to unfiltered uv radiation, ClF_5 rapidly decomposes to ClF_3 and F_2 and, therefore, yields only the same products obtainable from the photolysis of ClF_3-OF_2 mixtures.

The following properties reported by Zuechner and Glemser[1] for ClF_5O do not agree with the general trends observed for the remaining chlorine fluorides and oxyfluorides: i) nonvolatility at -78°C, (ii) a ^{19}F nmr resonance between -146 and -103 ppm relative to $CFCl_3$, and (iii) exchange broadening in the nmr spectrum even at -76°C. For ClF_5O, we would expect (i) a volatility comparable to those of ClF_5[2] or SF_6[3], (ii) an averaged ^{19}F nmr chemical shift of about -390 ppm[4], and (iii) the absence of intramolecular exchange owing to chlorine having its maximum coordination number and no free valence electron pair and owing to the lack of a plausible exchange mechanism.

The only remaining piece of evidence presented[1] for ClF_5O is the presence of a low intensity fragment due to ClF_4O^- in the negative ion mass spectrum of the crude reaction product. We prefer to attribute this fragment to a recombination process in the mass spectrometer since a 52% peak was also reported for F_2^- which can form only by recombination. Furthermore, negative ion spectra frequently show species of higher mass than that of the parent molecule due to attachment of other atoms or groups[5].

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THE PREPARATION OF CHLORINE MONOFLUORIDE

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Chlorine monofluoride is a very vigorous and useful reagent which exhibits a diversity of reaction paths. Thus fluorinating, chlorinating, and chlorofluorinating reactions are well known (1) as well as amphoteric behavior in forming Lewis acid and base complexes (1, 2). Despite this broad utility, specific details regarding the synthesis of ClF are lacking. The experiments reported herein describe a simple, laboratory scale, procedure for the preparation of ClF.

Although ClF can be prepared from the elements (3), it is generally preferable to employ $\mathrm{ClF_3}$ and $\mathrm{Cl_2}$ according to the equation:

$$\mathrm{ClF_3} + \mathrm{Cl_2} \xrightarrow{\Delta} 3\mathrm{ClF}$$

This reaction was first reported (4) by Schmitz and Schumacher. In their work and in later applications (5, 6) the reactions were carried out at temperatures in the range of 250 - 350°C and at unspecified pressures and/or times. Therefore, it appeared desirable to better define the most significant parameters, i.e., temperature, pressure, and time. The following table summarizes some of our typical results.

TABLE 1

Reaction Data For 1.06 ClF_3 - 1.00 Cl_2

Run No.	T°C	Max. Pressure psi	Time, hr.	ClF3 Recovered	% Yield Purified ClF
1	120	160	65	Yes	65
2	150	200	18	Yes	79
3	150	620	18	No	95
4	180	375	5	No	92
5	180	670	6	Trace	92

From these experiments it is evident that a temperature of 120°C is too low for obtaining a high yield in a reasonable time. However, a temperature of 180°C, still much lower than those most often used, is quite satisfactory for producing complete reaction in a short time, over a broad pressure range. At 150°C a slightly higher yield was achieved, perhaps due to reduced wall reactions. The longer time required, 18 hr., is still a convenient overnight period. In all cases a 5-7 mole percent excess of ClF_3 was used to ensure sufficient material for the desired reaction since inevitably some fluorine is "lost" through formation of metal fluorides. These conditions have been successfully tested on a reaction scale of a few mmoles to about one mole of ClF.

Experimental

Commercial (The Matheson Co.) ClF_3(98%) and Cl_2 (99.5%) were used without further purification. Stainless steel (304), single ended, high pressure (1800 psi) cylinders (Hoke, Inc.) were used together with stainless steel (316) valves (Hoke, Inc.) and bourdon tube gauges (The Matheson Co.). Clean, assembled reactors were passivated with ClF_3 at ambient temperature before use. Measured amounts of ClF_3 and Cl_2 were condensed into the cylinder held at -196°C. After warming to ambient temperature, the loaded reactors were heated to the final reaction temperature in an oven or with heating tape. Because the temperature-pressure maximums employed were well below ratings for the equipment, small reactors could be placed completely (valve, gauge and all) and safely in an inexpensive drying oven set at the desired temperature. The heating cycle was conducted in an outdoor, pressure safe facility. On completion of the reaction, the contents of the cooled cylinders were separated by fractional condensation in a metal-Teflon vacuum line. A trap cooled to -142°C (methylcyclopentane slush) was used to retain impurities such as Cl_2, ClF_3, and $FClO_2$, while the ClF was condensed in a trap held at -196°C. The purity of the ClF was determined by gas chromatography (7) and its infra-red spectrum.

Acknowledgement

The authors are grateful to the Office of Naval Research, Power Branch, for support of this work and to Dr. K. O. Christe for helpful discussion.

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On A New Synthesis of NF_4^+ Salts and its Mechanistic Interpretation Involving A New and Exceptionally Powerful Oxidizing Species

by Karl O. Christe*, Richard D. Wilson, and Arthur E. Axworthy

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Complex fluoro cations are generally prepared through fluorine abstraction from the parent molecule by means of a strong Lewis acid. This was first demonstrated in 1949 by Woolf and Emeleus[1] for BrF_3:

$$BrF_3 + SbF_5 \longrightarrow BrF_2^+SbF_6^- \tag{1}$$

In the case of NF_4^+ salts, this approach was impossible since the parent molecule NF_5 is unknown and unlikely to exist owing to the validity of the octet rule for first row elements such as nitrogen and fluorine. The synthesis of NF_4^+ from NF_3 and F^+ is preempted by the fact that fluorine is the most electronegative element and, hence, F^+ should be extremely difficult, if not impossible, to prepare by chemical means. In 1965, Christe and co-workers discovered[2] that NF_4^+ salts can be prepared from NF_3, F_2, and a strong Lewis acid in the presence of an activation energy source. Presently, three methods are known which are capable of producing NF_4^+ salts. These are (1) glow discharge at low temperature[3,4], (2) heating under high pressure[5,6], and (3) bremsstrahlung at -196° [7]. In this note, we describe a fourth method, i.e., uv photolysis, which is capable of producing NF_4^+ salts.

In addition to the great challenge which the preparation of NF_4^+ salts presented to the synthetic chemist, the NF_4^+ formation is of unusual interest from a mechanistic point of view. In view of the second and fourth methods of formation (see above), the originally suggested[2] mechanism cannot be considered satisfactory and a more plausible mechanism is offered. Based on the revised mechanism, we postulate a new intermediate of unusual oxidizing power comparable to that[8] of PtF_6.

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), BF_3 (The Matheson Company), 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 windows in the form of pressed disks. The pressing operation was carried out using a Wilks mini pellet press. All reactions were carried out in a sapphire reaction tube brazed to a 304 stainless steel tube (Varian, Model CS-4250-3). This reactor had a volume of 23 ml. For the photolyses, unfiltered uv radiation from a Hanovia Model 616A high-pressure quartz mercury-vapor arc was used. In all reactions, NF_3, F_2, and the corresponding Lewis acid were used in 1:1:1 mole ratios (2 mmol of each) resulting in an autogenous pressure of about 6.5 atmospheres.

Preparation of $NF_4^+AsF_6^-$. A mixture of NF_3, F_2, and AsF_5, when kept for three days at 25° in a sapphire reactor in the dark, showed no detectable trace of solid formation. Upon exposing the sapphire section of the reactor to unfiltered uv radiation, clouds of suspended solid appeared within seconds inside the reactor resulting in an instant coating on the reactor walls. Continued exposure (for several days) of the reactor to uv radiation did not significantly increase the solid formation. After removal of the volatile reaction products, the weight gain of the reactor varied from 2 to 8 mg in several experiments. The solid residue was identified by vibrational spectroscopy[9,10] as $NF_4^+AsF_6^-$ and in all cases did not show any detectable impurities.

Preparation of $NF_4^+BF_4^-$. The NF_3-F_2-BF_3 reaction was carried out in the same way as described for NF_3-F_2-AsF_5. The reactants behaved similarly and the reaction rate decreased sharply with increasing solid deposition on the inside walls of the reactor. The yield of $NF_4^+BF_4^-$ was between 1 and 2 mg. The infrared spectrum of the solid was in excellent agreement with that previously reported[7] for $NF_4^+BF_4^-$.

Results and Discussion

When gaseous mixtures of NF_3, F_2, and the strong Lewis acids AsF_5 or BF_3 are exposed to unfiltered uv irradiation, the following rapid and reproducible reactions occur:

$$NF_3 + F_2 + AsF_5 \longrightarrow NF_4^+AsF_6^- \qquad (2)$$

$$NF_3 + F_2 + BF_3 \longrightarrow NF_4^+BF_4^- \qquad (3)$$

In all experiments, the yield of the NF_4^+ salt was less than one percent. This low yield, however, appears not to be caused by a low reaction rate, but by deposition of the solid product on the reactor walls, thus preventing further irradiation of the reactants. Significant improvement of the yields should be possible by continuous removal of the deposits from the wall or the use of a more sophisticated flow system. However, efforts in this direction were beyond the scope of the present study. In view of the relatively low intensity of the uv lamp used in our experiments and the small diameter of the sapphire reactor, the observed high initial reaction rate strongly suggests a quantum yield larger than one, i.e., a chain reaction.

Taking all the presently available experimental data on the synthesis of NF_4^+ compounds into consideration, additional conclusions concerning a plausible reaction mechanism can be reached. Based on the glow-discharge synthesis, we had originally invoked the intermediate formation of a F^+ or NF_3^+ cation[2]. Whereas these cations might indeed be produced under glow-discharge conditions, the high ionization potentials of NF_3 (13.00 eV)[11], F_2 (15.69 eV)[12], or F·(17.44 eV)[13] preclude their formation in the uv photolysis, since the maximum energy available from the uv source does not exceed 7 eV. Even stronger evidence for an alternate mechanism stems from the thermal synthesis (method 2). Heating to about 120° cannot provide the activation energies required for the formation of NF_3^+, F_2^+, or F^+. However, it has been found for the Cl_2-F_2 dark reaction[14,15] that a temperature of about 120° is sufficient to dissociate some of the F_2 into F· radicals [$D^0(F_2)$ is only 37.5 kcal mol^{-1} = 1.62 eV][16]. Inspite of the very low F· atom concentrations expected at 120°, a chain reaction may result in relatively fast reaction rates. Based on these considerations and the observed fast initial reaction rate in the NF_3-F_2-AsF_5 photolysis, it seems safe to postulate F_2 dissociation as the first reaction step in the $NF_4^+AsF_6^-$ synthesis:

$$F_2 \longrightarrow 2\,F\cdot \qquad (4)$$

The next step could involve the reaction of F· with either NF_3 or AsF_5. Since the hypothetical $NF_4\cdot$ containing only first row elements would violate the octet rule, its formation is very unlikely. Therefore, the second step should be:

$$F\cdot + AsF_5 \longrightarrow AsF_6\cdot \qquad (5)$$

This step appears plausible since AsF_5 generally acts as an excellent acceptor molecule and changes from a trigonal bipyramidal to an energetically more favorable octahedral AsF_6 configuration. The $AsF_6\cdot$ radical is pseudo-isoelectronic with SF_6^+ and, hence, a rough estimate for the exothermicity of the reaction

$$AsF_6\cdot + e \longrightarrow AsF_6^-$$

can be obtained from the known[17] photoionization threshold of SF_6 (15.29 eV). This high value strongly suggests that the $AsF_6\cdot$ radical is the only likely intermediate capable of oxidizing NF_3, which has a first ionization potential of 13.00 eV.[11] Consequently, the third reaction step in the $NF_4^+AsF_6^-$ formation should be:

$$AsF_6\cdot + NF_3 \longrightarrow NF_3^+AsF_6^- \qquad (6)$$

In order to maintain a chain reaction, the $NF_3^+AsF_6^-$ could react with F_2, according to:

$$NF_3^+AsF_6^- + F_2 \longrightarrow NF_4^+AsF_6^- + F\cdot \qquad (7)$$

A crude estimate of the bond energy changes involved in this step can again be obtained by comparison between the isoelectronic species:

$$NF_3^+ + F\cdot \longrightarrow NF_4^+$$

and

$$CF_3\cdot + F\cdot \longrightarrow CF_4$$

Since the CF_3-F bond energy $(139.4\ \mathrm{kcal\ mol^{-1}})^{18}$ is considerably higher than that of the F-F bond $(37.5\ \mathrm{kcal\ mol^{-1}})^{16}$, reaction (7) should also be exothermic. Chain termination steps could occur by combination of any two of the radicals involved in this mechanism. The overall sequence, equations (4), (5), (6), and (7) appear to be a very plausible mechanism requiring only a low activation energy for (4) in excellent agreement with the experimental observations.

Solomon and co-workers have studied[19] the kinetics of the thermal decomposition of $NF_4^+AsF_6^-$ to NF_3, F_2, and AsF_5 in the temperature range 175 to 222° at low pressure. Since Tolberg et al. have shown[5] that $NF_4^+AsF_6^-$ can be formed in this temperature range from NF_3, F_2, and AsF_5 under high pressure, reversibility of these reactions is indicated. Consequently, the $NF_4^+ AsF_6^-$ formation mechanism should allow us also to better understand the thermal decomposition. Solomon et al. observed[19] that both NF_3 and AsF_5 inhibit the decomposition reaction and suggest that the decomposition mechanism involves the reversible dissociation of the solid to NF_5 and AsF_5, followed by the irreversible decomposition of NF_5 as the rate determining step. However, the observed fractional-order kinetics could not be explained by an elementary reaction mechanism. The mechanism, suggested[19] by Solomon and co-workers has several shortcomings. In our opinion, the most serious ones are (1) NF_5 violates the octet rule which is strictly valid for first row elements. Promotion of nitrogen electrons to the 3s level would result in a prohibitively large activation energy for the NF_5 formation; (2) the $NF_4^+AsF_6^-$ formation and decomposition appear to be reversible; and (3) the inhibition of the $NF_4^+AsF_6^-$ decomposition by NF_3 addition suggests that the steps involving NF_3 cannot be irreversible. For these reasons and by analogy with the mechanism discussed above for the $NF_4^+AsF_6^-$ formation, a more plausible decomposition mechanism would be:

$$NF_4^+AsF_6^- \rightleftarrows NF_3^+AsF_6^- + F\cdot \tag{10}$$

$$NF_3^+AsF_6^- \rightleftarrows NF_3 + AsF_6\cdot \tag{11}$$

$$AsF_6\cdot \rightleftarrows F\cdot + AsF_5 \tag{12}$$

$$2\ F\cdot \longrightarrow F_2 \tag{13}$$

Because the steady-state F atom concentration would be determined by a number of reactions, including the reverse of reaction (7), a very complex rate expression might be expected. The recombination of F atoms could occur either homogenously via a three-body collision or heterogenously. The inhibiting effects of NF_3 and AsF_5 could result from the reduction of the steady-state F atom concentration caused by the shifting of the equilibria (10), (11), and (12) to the left.

The postulate of an $AsF_6\cdot$ radical intermediate which can act as a powerful oxidizer, could also explain the following two previously reported[20-22] and highly unusual reactions.

$$2\ O_2 + F_2 + 2\ AsF_5 \xrightarrow[\text{or uv}]{130^0} 2\ O_2^+AsF_6^- \tag{14}$$

and

$$Xe + F_2 + AsF_5 \xrightarrow{\text{uv}} XeF^+AsF_6^- \tag{15}$$

Both reactions proceed again under very mild conditions, resulting in the oxidation of two species, O_2 and Xe, with very high first ionization potentials of 12.06 and 12.13 eV, respectively. Reactions (14) and (15) are directly comparable to the following known[8,23,24] PtF_6 reactions:

$$O_2 + PtF_6 \longrightarrow O_2^+PtF_6^- \qquad (16)$$

and

$$Xe + 2\,PtF_6 \longrightarrow XeF^+Pt_2F_{11}^- \qquad (17)$$

This analogy suggests that the oxidizing power of a Lewis acid-F· radical, such as AsF_6·, is comparable to that of PtF_6, which is one of the strongest oxidizing fluorinators[8] known. The applicability of the Lewis acid-activated F_2 system, however, seems to be limited to starting materials which themselves do not form stable adducts with the Lewis acid. The given examples demonstrate that the oxidizing power of fluorine can be promoted significantly by the simultaneous use of a strong Lewis acid and an energy source promoting dissociation of F_2 into F· atoms. Consequently, many reactions previously requiring the use of the prohibitively expensive PtF_6 may now be carried out at a reasonable expense by the use of Lewis acid-promoted activated fluorine.

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ON THE REACTION OF $Cl_2F^+AsF_6^-$ WITH XENON

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In the presence of strong Lewis acids, XeF_2 can act as a powerful fluorinating oxidizer (1,2). For example, it can fluorinate Br_2 or I_2 (3) resulting in the formation of BrF_3 and IF_5, respectively, as shown by the following idealized equation:

$$3\ XeF^+BF_4^- + Br_2 \longrightarrow 2\ BrF_2^+BF_4^- + BF_3 + 3\ Xe$$

followed by dissociation of the thermally unstable $BrF_2^+BF_4^-$ complex to BrF_3 and BF_3 (4). However, to our knowledge, no example has been reported for the reverse reaction of this type, i.e., the oxidative fluorination of Xe by a halogen fluoride under mild conditions. Furthermore, previous studies have shown that both ClF (5) and ClF_3 (6) do not interact with Xe.

We have now found that the addition of a Lewis acid to ClF, which causes Cl_2F^+ formation (7), also increases the oxidizing power of ClF significantly so that it can fluorinate Xe according to:

$$Cl_2F^+AsF_6^- + Xe \longrightarrow XeF^+AsF_6^- + Cl_2$$

followed by the known (8) reaction:

$$2\ XeF^+AsF_6^- \longrightarrow Xe_2F_3^+AsF_6^- + AsF_5$$

These results suggest that the oxidizing power of cations decreases in the following order, $Cl_2F^+ > XeF^+$ or $Xe_2F_3^+ > BrF_2^+$, and that the enhancement of the oxidizing power of an amphoteric molecule by the addition of a strong Lewis acid is not limited to XeF_2 but is probably quite general. Furthermore, the fact that ClF is pseudo-isoelectronic with XeF^+ but acts as a rather mild fluorinating oxidizer, indicates that a specific valence electron configuration is not the main cause for unusual oxidizing power. Rather, it appears that cation formation, i.e., a formal positive charge, is more important.

Experimental Section

Xenon, ClF, and AsF_5 (2.09 mmol each) were combined at -196^0 in a passivated (with ClF_3) 25 ml sapphire-stainless steel reaction tube. The mixture was allowed to warm up to 25^0 and was kept at this temperature for one hour. The mixture was recooled to -196^0 and did not show the presence of any noncondensible material. After removal of the products volatile at 25^0 by pumping, a white solid residue (83 mg) was obtained. The volatile material was condensed back into the reactor at -196^0. The contents were kept at -80^0 for 1.5 hours. The reactor was allowed to warm to 25^0 and the volatile products were separated by fractional condensation. They consisted of Xe (1.68 mmol) and a mixture of ClF, Cl_2, and AsF_5 (total of 3 mmol) which could not be separated completely by fractional condensation owing to partial formation of the known $Cl_2F^+AsF_6^-$ (7) and $Cl_3^+AsF_6^-$ (9) adducts. The white solid residue (157 mg) showed the vibrational spectrum and x-ray powder diffraction pattern characteristic (10) for monoclinic $Xe_2F_3^+AsF_6^-$. The latter probably formed from the original $XeF^+AsF_6^-$ (as indicated by the material balance) by loss of AsF_5 during sample preparation in the glove box (8). Previous reports (8,11) on the infrared spectrum and x-ray powder pattern diverge. Our data are in excellent agreement with the data of Bartlett et al. (8), but disagree with those reported by Binenboym et al.(11).

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On Halogen Pentafluoride·Lewis Acid Adducts[1]

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Abstract

Vibrational spectra have been recorded for the known adducts, $ClF_5 \cdot AsF_5$, $ClF_5 \cdot xSbF_5$ ($x=1.08$ and 1.36), $BrF_5 \cdot 2SbF_5$, and $IF_5 \cdot SbF_5$. Furthermore, the new adduct, $BrF_5 \cdot AsF_5$, has been prepared. It is marginally stable at -95°. The spectra of the ClF_5 adducts are consistent with predominantly ionic structures containing the ClF_4^+ cation. The spectrum of ClF_4^+ is very similar to that of isoelectronic SF_4 thus indicating a pseudo-trigonal bipyramidal structure of symmetry C_{2v}. All fundamentals have been assigned and a valence force field has been computed for ClF_4^+. The vibrational spectra of $IF_5 \cdot SbF_5$ and $BrF_5 \cdot 2SbF_5$ are compatible with the predominantly ionic structures, $IF_4^+SbF_6^-$ and $BrF_4^+Sb_2F_{11}^-$, respectively, established by x-ray diffraction data. Tentative assignments are given for BrF_4^+ and IF_4^+. The ^{19}Fnmr spectra of $BrF_5 \cdot 2SbF_5$ and $IF_5 \cdot SbF_5$ in HF solution are also reported.

Introduction

Halogen fluorides exhibit amphoteric character. By combining with strong Lewis acids, they can form cations containing one F^- ion less than the parent molecule. In recent years these salts have received much attention, and numerous papers dealing with their syntheses and structures have been published[2]. Whereas the structures of the halogen mono-, tri-, and hepta-fluoride adducts are reasonably well established, much less is known about the complexes of the halogen pentafluorides.

Chlorine pentafluoride combines with Lewis acids such as AsF_5,[3] SbF_5,[3,4] and PtF_5[5,6]. Ionic structures containing the ClF_4^+ cation were suggested,[3,5] however, no supporting data were presented. Recently, the ^{19}F nmr spectrum of $ClF_5 \cdot 1.36\ SbF_5$ in HF-AsF_5 solution was studied[7]. The observation of two resonances of equal intensity at low field is strong evidence for the presence of a ClF_4^+ cation having a pseudo-trigonal bipyramidal structure of symmetry C_{2v}, analogous to that found[8,9] for isoelectronic SF_4.

Bromine pentafluoride forms with SbF_5 the adduct, $BrF_5 \cdot 2SbF_5$[10]. A brief report on the ^{19}F nmr spectrum of the solid and melt has been published[11] indicating the presence of two different kinds of fluorine ligands, however, the observed area ratio was in poor agreement with that expected for the postulated[11] structure $BrF_4^+Sb_2F_{11}^-$. Recently, the crystal structure of $BrF_5 \cdot 2SbF_5$ has been determined establishing[12] its predominantly ionic nature. After completion of our study[1], Surles and coworkers have reported[13] the Raman spectra of $BrF_4^+Sb_2F_{11}^-$ and of BrF_5 in SbF_5 solution and proposed a tentative assignment for BrF_4^+. Solutions of BrF_5 in SbF_5 were shown[13] to be highly conductive suggesting an ionic formulation for the $BrF_5 \cdot SbF_5$ adduct.

Iodine pentafluoride forms 1:1 adducts with SbF_5[14] and PtF_5[15]. Recently, the crystal structure of $IF_5 \cdot SbF_5$ has independently been studied by x-ray diffraction by two groups[16,17]. Unfortunately, $IF_5 \cdot SbF_5$ tends to form twin crystals[17] thus rendering the structural determination somewhat difficult. Both groups suggest for $IF_5 \cdot SbF_5$ a mainly ionic structure containing a distorted trigonal bipyramidal IF_4^+ cation of symmetry C_{2v} and an SbF_6^- anion distorted from symmetry O_h. However, several interesting questions such as the difference in bond length between the axial and equatorial IF bonds remain unresolved. Shamir and Yaroslavsky have reported[18] in a preliminary communication the Raman spectra of a number of adducts including that of $IF_5 \cdot SbF_5$. However, their experimental data are incomplete and, therefore, their conclusions are little convincing.

Experimental

Apparatus - The materials used in this work were manipulated either in a well passivated (with ClF_3) 304 stainless steel vacuum system equipped with Teflon FEP U-traps or in the dry nitrogen atmosphere of a glove box. Pressures were measured with a Heise Bourdon tube-type gage (0-1500 mm ± 0.1%).

The Raman spectra of the solids were recorded with a Spex Model 1400 spectrophotometer. The green (5145 Å) or the blue (4880 Å) line of a Coherent Radiation Lab. Model 52 Ar ion laser and the red (6328 Å) line of a Spectra-Physics Model 125 He-Ne laser were used as exciting lines. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses or clear Teflon FEP or Kel-F capillaries (1 to 4 mm i.d.) were used as sample containers. For the capillaries the transverse viewing-transverse excitation technique was applied. The Raman spectra of the HF solutions were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line. The samples were contained in Teflon FEP capillaries which were also used for the ^{19}F nmr spectra.

The infrared spectra of the solids were recorded on a Beckman Model IR-7 with CsI interchange and Perkin-Elmer Models 337 and 457 spectrophotometers in the range 4000-250 cm^{-1} as dry powders between AgCl or AgBr plates or thin (2 mil) Teflon FEP sheet. Compensation for bands due to the Teflon FEP window material was achieved by placing an empty cell in the reference beam. Screw-cap metal cells with Teflon FEP gaskets were used as window holders. The low-temperature infrared spectrum of $ClF_5 \cdot AsF_5$ was taken by preparing the complex on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex-glass, all windows being AgCl. Temperature cycling of the internal window in vacuo was essential to obtain spectra free of unreacted starting materials.

The ^{19}F nmr spectra were recorded at 56.4 MHZ on a Varian high-resolution nmr spectrometer equipped with a variable-temperature probe. Chemical shifts were determined by the sideband technique with an accuracy of ± 1 ppm relative to the external standard $CFCl_3$.

Preparation of the ClF_5 Adducts - The purification of ClF_5, SbF_5, AsF_5, and HF and the preparation of the $ClF_5 \cdot$Lewis acid adducts has previously been described[3]. Since the melting point and the composition of the $ClF_5 \cdot SbF_5$ samples varied somewhat with the method of preparation, three different samples were investigated. Sample I had the composition $ClF_5 \cdot 1.08\ SbF_5$ and showed first signs of melting at 88°. It was prepared by adding an SbF_5-HF solution to excess ClF_5. Sample II had the composition $ClF_5 \cdot 1.36\ SbF_5$ and was prepared by combining SbF_5 dissolved in HF with an excess of ClF_5 at -196° followed by warm up to 25° and removal of volatile material in vacuo. It showed first indications of partial melting at ~ 35°. With increasing temperature, however, the sample solidified again showing the onset of a second melting at 88°. Sample III had the same composition as sample II and was prepared by treating a part of sample II with excess ClF_5 in a Monel cylinder at 50° for 48 hours with agitation. It melted at about 33° to form a milky, highly viscous liquid. The synthesis of the $ClF_4^+PtF_6^-$ and $ClF_6^+PtF_6^-$ mixture has previously been described[6].

Preparation of $BrF_5 \cdot 2\ SbF_5$ - Bromine pentafluoride (from The Matheson Company) was treated with F_2 at ambient temperature until the material was colorless. It was purified by fractional condensation through two traps kept at -64 and -95°. The material retained in the -95° trap showed no detectable impurities in the infrared spectrum.

Bromine pentafluoride (112.3 mmole) was condensed at -196° into a passivated 100 ml Monel cylinder containing 68.8 mmole of SbF_5. The cylinder was heated for three days to 120°. Subsequently, unreacted BrF_5 (78.3 mmole) was removed in vacuo at ambient temperature leaving behind a white, crystallinic solid. Consequently, BrF_5 (34.0 mmole) had reacted with SbF_5 (68.8 mmole) in a mole ratio of 1:2.02 producing the complex $BrF_5 \cdot 2\ SbF_5$.

Preparation of $BrF_5 \cdot AsF_5$ - Bromine pentafluoride (4.42 mmole) was combined with AsF_5 (13.15 mmole) at -196° in a Teflon FEP U-trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 1200 mm, the mixture was cooled again to -196°. This procedure was repeated several times until the reaction was complete. Unreacted AsF_5 (8.77 mmole) was removed in vacuo at -95° leaving behind a white solid which melted at higher temperature to form an almost colorless liquid Prolonged pumping on the adduct at -95° resulted in the removal of additional small amounts of AsF_5 indicating that the adduct has a slight dissociation pressure even at -95°. The infrared spectrum of the gas obtained by exhaustive dissociation of the solid showed BrF_5 and AsF_5 in a 1:1 mole ratio. Based on the above given material balance, BrF_5 (4.42 mmole) had combined with AsF_5 (4.38 mmole) in a mole ratio of 1:0.99 producing the complex $BrF_5 \cdot AsF_5$.

Preparation of $IF_5 \cdot SbF_5$ - This product was prepared as previously described[14]. The material was a white, crystallinic solid. The material balance was as expected for a 1:1 adduct. Anal. Calcd. for $ISbF_{10}$: I, 28.9; Sb, 27.8; F, 43.3. Found: I, 29.4; Sb, 27.4; F, 43.0.

Liquid IF_5 and gaseous AsF_5 when combined at 20° with stirring did not form a stable adduct.

Results and Discussion

Syntheses and Properties - The preparation of the ClF_5 adducts has previously been discussed[3]. In the BrF_5-SbF_5 system we could not isolate a 1:1 adduct even when employing a large excess of BrF_5 and temperatures above 100° in the synthesis. The $BrF_5 \cdot 2\ SbF_5$ complex is a white crystallinic solid. It can be stored in Teflon FEP containers without appreciable decomposition. Exposure to small amounts of moisture or reactive surfaces produces a pink to deep red color due to the formation of Br_2^+ salts[2]. Single crystals of

$BrF_5 \cdot 2\ SbF_5$ can be readily grown by slow sublimation at temperatures slightly higher than ambient. The results of a single crystal x-ray diffraction study on $BrF_5 \cdot 2\ SbF_5$ have been reported[12] elsewhere. With AsF_5, however, BrF_5 does form a 1:1 adduct, but its thermal instability preempted its use for structural studies. Upon melting, the complex forms a colorless liquid. If impure BrF_5 is used in the synthesis, the color of the liquid is an intense burgundy red indicating the presence of Br_2^+ ions[2]. The fact that AsF_5 and SbF_5 combine with BrF_5 in different mole ratios, might be explained by the pronounced tendency of SbF_5 to form polymeric anions such as $Sb_2F_{11}^-$.

Our data obtained for $IF_5 \cdot SbF_5$ confirm Woolf's reports[14]. Single crystals of $IF_5 \cdot SbF_5$ were grown by slow sublimation at 40°. A single crystal x-ray diffraction study in our laboratory was discontinued when we learned about the work[15] of Baird and Giles. The fact that AsF_5, a weaker Lewis acid than SbF_5, does not form a stable adduct with IF_5 is not surprising. As previously pointed out[19], halogen pentafluorides possess an energetically favorable pseudo-octahedral structure and show little tendency to form the energetically less favorable pseudo-trigonal bipyramidal XF_4^+ cations.

<u>^{19}F nmr Spectra</u> - The ^{19}F nmr spectrum of $ClF_5 \cdot 1.36\ SbF_5$ in acidified HF has previously been discussed[7]. The observation of two signals of equal intensity at -256 and -274 ppm, respectively, relative to $CFCl_3$ below -60° is strong evidence for a ClF_4^+ cation having two nonequivalent sets of two fluorine ligands[7].

The ^{19}F nmr spectrum of $BrF_5 \cdot 2\ SbF_5$ in HF or HF-AsF_5 solution showed between 20 and -80° for the BrF part of the spectrum, a single resonance at -197 ppm relative to external $CFCl_3$. In the HF-SbF region at 20° a very broad unresolved common peak centered at about 130 ppm was observed indicating fast exchange between the solvent and the anion. In more dilute solutions the HF-$Sb_2F_{11}^-$ signal shifted to about 150 ppm and gained in relative intensity whereas the chemical shift of the BrF_4^+ resonance remained constant. At lower temperatures (-60 to -80°) the peak in the SbF region started to separate into several peaks at about 76, 93, 120, and 127 ppm. Whereas the identity of these peaks could not definitely be established, the chemical shifts of some of them are similar to those (93, 120, and 142 ppm) previously found for $Sb_2F_{11}^-$ in HF solution[20]. The chemical shift of -197 ppm found for BrF_4^+ in HF differs significantly from that (-167 ppm) reported by Meinert and Gross for the melt[11]. This discrepancy might be caused by the different environment.

A solution of $IF_5 \cdot SbF_5$ in HF exhibited between 20 and -80° only one signal at 133 ppm indicating rapid exchange between all species present. Acidification of the solvent with AsF_5 did not influence the exchange rates sufficiently to cause a separation into individual signals.

The fact that the inter- and intra-molecular exchange rates decrease in the order $IF_5 \cdot SbF_5 > BrF_5 \cdot 2\ SbF_5 > ClF_5 \cdot SbF_5$ might be explained by the decreasing size and polarizability of the corresponding halogen pentafluorides.

Vibrational Spectra - The vibrational spectra of the halogen pentafluoride-Lewis acid adducts are shown in Figures 1 to 10. The infrared spectrum of the $ClF_4^+PtF_6^-$ and $ClF_6^+PtF_6^-$ mixture has previously been given[6] and, hence, is not shown here. The deserved frequencies are listed in Tables I and II.

Since the ionic nature and structure of the Lewis acid adducts of ClF_5, BrF_5 and IF_5 has been established by x-ray diffraction,[12,16,17] nmr,[7] and conductivity studies,[13] the discussion of their vibrational spectra can be kept relatively short. The main objective of this study is to demonstrate that the vibrational spectra are consistent with the known ionic structures, to define the principal bands of the $HalF_4^+$ cations, and to examine the plausibility of the given assignments by comparison with the known spectra of isoelectronic chalcogen tetrafluorides and by force field computations.

Chlorine Pentafluoride Adducts - The infrared spectra of the $ClF_5 \cdot xSbF_5$ adducts are relatively insensitive to changes in the ClF_5:SbF_5 combining ratio owing to the relative broadness of the bands due to the Sb-F vibrations (see Figure 3). In the corresponding Raman spectra (Figures 1 and 2), however, slight changes in the composition of the adducts or in the procedures used for their preparation may cause significant changes. As expected, sample I, having the composition $ClF_5 \cdot 1.08\ SbF_5$, shows the simplest spectrum. With increasing SbF_5 content and tempering features attributable to polymeric anions such as $Sb_2F_{11}^-$ become more pronounced. Similarly, the low-temperature infrared spectrum of the $ClF_5 \cdot AsF_5$ adduct (Figure 5) indicates the presence of the $As_2F_{11}^-$ anion[21,22]. However, the $As_2F_{11}^-$ anion is much less stable

TABLE I

Vibrational Spectra of ClF_5·Lewis Acid Adducts and Their Assignments Compared to That[a] of SF_4

Obsd. Frequencies (cm^{-1}) and Relative Intensities[b]								Assignment (point group)[c]	
SF_4 (gas)		ClF_5·AsF_5[f]		ClF_5·SbF_5[g]			$ClF_4^+PtF_6^-$ $ClF_6^+PtF_6^-$ [h]		
IR[d]	Ra[e]	IR	Ra	IR	Ra (solid)	Ra (HF sol.)	IR	XF_4 (C_{2v})	YF_6 (O_h)
1744vw		1600vw,br							
1617vw								$\nu_1+\nu_8(B_2)$	
		1390vw							720 + 671
1281w		1340vw		1335w			1330w,br	$\nu_2+\nu_6(B_1)$	$\nu_1+\nu_3$ (F_{1u})
867s	865(0+)	827s	830(2.5)	825s,sh	822(2.5)	825sh		ν_8 (B_2)	
891s	888(9.0)	796vs	799(10)	803vs	802(10)	802(10)	790vs	$\nu_1(A_1)$	
730vs	730(0+)							$\nu_6(B_1)$	
		720vs	711(0.3)						
		699s	695(0.3)	669vs	670(0.5-2.5)		670-620vs		$\nu_3(F_{1u})$
		673ms	671(8.0)	648vs	653(8.6)	656(8)			$\nu_1(A_{1g})$
		584m	579(4)	579w	583(0.6-4)				$\nu_2(Eg)$
		576mw							
558m	553(10)	568w	567(6.5)		566(5.5)	574(5.5)		$\nu_2(A_1)$	
		553w							$\nu_2(Eg)$
532ms	532(4.0)	536mw	538(2.5)	535ms*	534(5)*	537(1)*	545s,br*	$\nu_7(B_2)$ and	$\nu_2(Eg)$*
464vw	475(1.2)	511ms**	519(1)	510sh	515(0.2)	515(0+)	500s	$\nu_3(A_1)$ and	νASFAs**
	414(0+)		473(1)		475(0.4)	475(0.4)		$\nu_5(A_2)$	
353ms	350(0+)	395s		386m			383s	$\nu_9(B_2)$	
			399(0.6)	280s			271s		$\nu_4(F_{1u})$
			372(2.7)		279(1.4)	277(1)			$\nu_5(F_{2g})$
226w	223(1.0)		237(1.1)		235(0.5)	245sh		$\nu_4(A_1)$	

(a) Ref. 25; (b) Uncorrected Raman intensities; (c) Assignments for the anion bands are made assuming for simplicity octahedral symmetry, although in most cases the actual symmetry is expected to be lower than O_h; (d) Ref. 23; (e) Ref. 24; (f) The low-temperature infrared spectrum indicates the presence of substantial amounts of $As_2F_{11}^-$; (g) The listed frequencies are those obtained for ClF_5·1.08 SbF_5; The relative intensities of the 670, 583, and to a lesser extent of the 534 cm^{-1} Raman bands varied, indicating different degrees of deviation of SbF_6^- from symmetry O_h or slight inhomogeneity of the sample; (h) Ref. 6.

TABLE II

Vibrational Spectra of $BrF_5 \cdot 2SbF_5$ and $IF_5 \cdot SbF_6$ Compared to Those of SeF_4 and TeF_4

Obsd. Frequency (cm^{-1}), Rel. Intensity[a]					Tentative Assignment, for XF_4 in C_{2v}	Obsd. Frequency, Rel. Intensity[a]				Tentative Assignment, for XF_4 in C_{2v}
SeF_4[b]		$BrF_5 \cdot 2\ SbF_5$				TeF_4[c]	$IF_5 \cdot SbF$			
		solid		in HF			solid		in HF	
IR	RA	IR	RA	RA		IR	IR	RA	RA	
723s	724w,sh	730sh	736sh		$\nu_8(B_2)$	695m	728sh	729(9)	704(10)	$\nu_1(A_1)$
744ms	749vs,p		723(10)	680sh	$\nu_1(A_1)$	682m	719m	720(1,6)		$\nu_8(B_2)$
622vs		690vs	704(2.4)		$\nu_6(B_1)+Sb_2F_{11}^-$ (?)		691sh	693(2.2)		
		655vs	650sh	660(10)	$Sb_2F_{11}^-$	587s	668sh	662(10)	663(8)	SbF_6^-
		645sh	651(6.9)				655vs			
				600sh						$+\nu_6(B_1)$
	574s,p	606mw	606(4.8)	575(5)	$\nu_2(A_1)$		625m,sh	625(3)		
		568m	555(3.3)		$Sb_2F_{11}^-$	572vw		614(4)	609(9)	$\nu_2(A_1)$
		540mw	545sh	540(1)			567w,sh	569(1.5)	570sh	SbF_6^-
		488ms		490(1)	Sb-F-Sb		520vw,sh	521(1.3)		
405m,	400w	419m		426(2)	$\nu_7(B_1)$	333w	388mw	335(0.8)		$\nu_7(B_1)$
	366m,p		335(0.5)		$\nu_3(A_1)$	293mw	345w	341(0.4)	325sh	$\nu_3(A_1)$
250vw		369mw	359(0.5)	363(5)	$\nu_9(B_2)$		311w	316(0.2)		$\nu_9(B_2)$
			295(1)							
				280sh				299(0.9)		
			254(0.7)		$Sb_2F_{11}^-$		288m	285(0+)	280sh	SbF_6^-
			230(0.5)	235(0+)			263mw	259(0.5)	250sh	
160vw	162w,p		219(0.2)		$\nu_4(A_1)$			151(0.4)		$\nu_4(A_1)$
			45(1.5)		lattice mode			72(1)		lattice modes
								42(6)		

(a) Uncorrected Raman intensities; (b) Best values and assignments taken from Ref. 46–48

(c) Ref. 48

than $Sb_2F_{11}^-$ resulting in the facile removal of the second AsF_5 molecule under the conditions[3] used for the synthesis of the Raman sample (1:1 adduct).

The vibrational assignments for ClF_4^+ in point group C_{2v} (see Table I) were made by analogy with isoelectronic SF_4[23-26] and by comparison with the known spectra of compounds containing AsF_6^-,[21,27-29] $As_2F_{11}^-$,[21,22] SbF_6^- and $Sb_2F_{11}^-$ [20,28,30-33] anions. In solids, the deviation of the spectra of these anions from those expected for the isolated octahedral ions is very common. It can be caused by effects such as site symmetry lowering, slight distortion of the octahedrons owing to crystal packing and anion-cation interaction, and the tendency to form polymeric anions. Unfortunately, the splittings, frequencies, and relative intensities of these bands strongly vary from compound to compound. Therefore, reliable assignments for the cations require the recording of spectra of adducts containing different anions or of solution spectra which usually show the bands characteristic of the unperturbed ions. Contrary to the highly symmetric octahedral XF_6^- anions, the ClF_4^+ cation of symmetry C_{2v} should be very little influenced by solid state effects because it possesses already its maximum number ($3n-6=9$) of modes.

For the ClF_5 adducts sufficient experimental data (see Table I) are available to distinguish the anion from the cation bands. As can be seen, the spectrum of ClF_4^+ is very similar to that of isoelectronic SF_4[23,24]. This close resemblance is comparable to that found for the isoelectronic pairs, SF_2O-ClF_2O^+,[34] SF_2O_2-$ClF_2O_2^+$,[35] SF_6-ClF_6^+,[36] and SF_5^--ClF_5,[37] and, therefore, is not surprising. For ClF_4^+, the assignment to the individual modes was made by analogy with SF_4. For SF_4, the assignment of Frey et al.[25] was used which was recently confirmed[26] by mean square amplitudes of vibration and force field computations.

In the spectra of the ClF_5 adducts, nine bands are found which might be attributed to ClF_4^+. Of these, the intense infrared and Raman band at about 800 cm^{-1} obviously represents the symmetric equatorial ClF_2 stretching mode ν_1. The moderately intense Raman and strong infrared band at about 825 cm^{-1} then must be the antisymmetric equatorial stretch ν_8. The symmetric axial stretch, ν_2, falls within the range of the ν_2 anion bands, but is clearly identified by the strong Raman band at 574 cm^{-1} in the HF solution. The antisymmetric axial stretching mode, ν_6, should be of very high intensity in the infrared and of very low intensity in the Raman spectrum. By comparison with other pseudo-trigonal bipyramidal molecules such as ClF_3[38] or ClF_3O_2,[39] it should occur above 700 cm^{-1}. Since there is no additional yet unassigned strong infrared band above this frequency in all of the observed spectra, a coincidence with ν_1 must be assumed. The assignment of ν_4 and ν_9 to the bands at 237 and 385 cm^{-1}, respectively, is clearcut and needs no further comment. This leaves us with three frequencies, 537, 515, and 475 cm^{-1}, for the assignment to ν_7, ν_3, and ν_5. Since the 475 cm^{-1} band appears to be inactive in the infrared spectrum, we ascribe it to ν_5 which ideally should be forbidden in the infrared spectrum. Based on their relative Raman intensities, when compared to those of SF_4, we prefer to assign ν_3 and ν_7 to 515 and 537 cm^{-1}, respectively. The assignments for ν_3, ν_7, and ν_5 are somewhat tentative. However, a reassignment of these three deformational modes should owing to their similar frequencies, be of minor influence on the principal force constants.

Force Constants - The method used for the computation of the ClF_4^+ force field has previously been described[39]. The following geometry was assumed for ClF_4^+, $r(Cl\text{-}F_{eq}) = 1.57$, $R(Cl\text{-}F_{ax}) = 1.66$Å, $\alpha(\sphericalangle F_{ax}ClF_{eq}) = 90$, $\beta(\sphericalangle F_{eq}ClF_{eq}) = 97$, and $\gamma(\sphericalangle F_{ax}ClF_{ax}) = 180^{\circ}$. The symmetry coordinates were identical to those previously given[23,24] for isoelectronic SF_4, except for $S_3 = \Delta\beta$ and $S_4 = 0.2765\Sigma\alpha_i - 0.8332\gamma$ which *are* different owing to $\gamma = 180^{\circ}$ in ClF_4^+ and were found numerically by a previously described[40] machine method.

A general valence force field for ClF_4^+ contains 17 symmetry force constants. Since only nine frequency values are available for their computation, a unique force field cannot be determined. Inspection of the G matrices of ClF_4^+ shows that in the A_1 block G_{12}, G_{23}, *and* G_{24} are zero and, therefore, F_{12}, F_{23}, and F_{24} can be neglected[41].

The influence of the remaining off-diagonal F terms on the diagonal F values was determined by computing their values as a function of the off-diagonal F terms. The resulting halves of the force constant ellipses are shown in Figures 11 and 12 and represent the possible mathematical solutions of the force field. It has previously been shown[41] that the most probable range for F_{xy} is limited by the extremal values F_{yy} and F_{xy} = minimum. Inspection of Figures 11 and 12 reveals that even with this constraint small variation of certain off-diagonal force constants can strongly influence the values of the diagonal force constants. Consequently, an uncertainty of about ± 0.5 mdyn/Å should be assumed for the stretching force constants F_{11}, F_{66}, and F_{88}. However, in spite of these relatively larger uncertainties, Figures 11 and 12 clearly show that the symmetry force constants involving the equatorial bonds (i.e. F_{11} and F_{88}) are significantly larger than those involving the axial bonds (i.e. F_{22} and F_{66}). The frequencies used for the force constant computations of ClF_4^+ are listed in Table III, together with our preferred force field, obtained by assuming plausible interaction terms. The fact that ClF_4^+ and isoelectronic SF_4 show similar force fields is not surprising in view of their similar frequencies and G matrices.

The significant difference in covalent bond strength between equatorial (5.1) and axial (3.3 mdyn/Å) bonds in ClF_4^+ is in excellent agreement with a generalized bonding scheme previously discussed[42] for a large number of halogen fluorides. It suggests that the bonding in ClF_4^+ might be explained, as previously described for the related pseudo-trigonal bipyramidal species ClF_3, ClF_3O,[40] and ClF_3O_2,[39] by the following approximation. The bonding of the three equatorial ligands (including the free electron pair on Cl as a ligand) is mainly due to a sp^2 hybrid, whereas the bonding of the two axial ClF bonds involves mainly one delocalized p-electron pair of the chlorine atom for the formation of a semi-ionic three-center four-electron $pp\sigma$ bond[43-45].

Bromine Pentafluoride·2 SbF_5 Adduct - The predominantly ionic nature of $BrF_5 \cdot 2\ SbF_5$ has previously been established[12] by a single crystal x-ray diffraction study. Owing to the large number of fundamentals expected for $BrF_4^+Sb_2F_{11}^-$ and to the inavailability of other salts containing the BrF_4^+ cation only tentative assignments can be made for BrF_4^+. These are listed in Table II and are based on comparisons with those reported for isoelectronic SeF_4[46-48] and those of other salts containing the $Sb_2F_{11}^-$ anion[20,28,31,33,49]. Our Raman spectrum[1] of solid $BrF_4^+Sb_2F_{11}^-$ has in the

TABLE III

Observed Frequencies (cm^{-1}), Approximate Description of Modes, And Computed Symmetry and Most Important Internal Force Constants[a] of ClF_4^+

				ClF_4^+	ClF_4^+	ClF_3[b]
A_1	ν_1	800	ν sym eq	$F_{11} = fr + frr$	5.25	
				$F_{13} = \sqrt{2}\, fr\beta$	0.8	
				F_{14}	0.2	
	ν_2	571	ν sym ax	$F_{22} = fR + fRR$	3.65	
	ν_3	510	δ sciss eq	$F_{33} = f_\beta$	2.64	
				F_{34}	-0.2	
	ν_4	237	δ sciss ax	$F_{44} = 0.31\, f\alpha + 0.69\, f\gamma$[c]	0.40	
A_2	ν_5	475	τ	$F_{55} = f\alpha + f\alpha''' - f\alpha' - f\alpha''$	2.08	
B_1	ν_6	795	ν as ax	$F_{66} = fR - fRR$	2.99	
				$F_{67} = \sqrt{2}\,(fR\alpha - fR\alpha')$	0.40	
	ν_7	537	rocking	$F_{77} = f\alpha - f\alpha'' + f\alpha' - f\alpha'''$	2.41	
B_2	ν_8	829	ν as eq	$F_{88} = fr - frr$	4.91	
				$F_{89} = \sqrt{2}\,(fr\alpha - fr\alpha')$	0.6	
	ν_9	385	δ sciss ax out of plane	$F_{99} = f\alpha - f\alpha''' - f\alpha' + f\alpha''$	2.45	
				fr	5.08	4.19
				fR	3.32	2.70
				frr	0.17	
				fRR	0.33	0.36

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

(b) Ref. 25

(c) In addition to interaction constants which are not listed.

meantime been confirmed by Surles et al.[13] and the proposed assignments[1,13] agree for most of the fundamentals. Since the crystal structure of $BrF_4^+Sb_2F_{11}^-$ is known[12] and the assignments for BrF_4^+ are tentative, no force constant computations were carried out for BrF_4^+.

Iodine Pentafluoride•SbF_5 Adduct - Two independent single crystal x-ray diffraction studies[16,17] have shown that the IF•SbF_5 has the predominantly ionic structure $IF_4^+SbF_6^-$, although the bond lengths and angles found by the two groups for IF_4^+ differ somewhat. The observed vibrational spectrum of IF_5•SbF_5 (see Table II) is consistent with such a predominantly ionic structure. The bands were tentatively assigned by comparison with those of TeF_4[48], which is isoelectronic with IF_4^+, and those reported for similar SbF_6^- salts[20,30] containing an SbF_6^- anion distorted from symmetry O_h[50]. Our Raman spectrum of IF_5•SbF_5 is in good agreement with that reported[18] by Shamir and Yaroslavski. However, their interpretation suffers from the incorrect assumption of an ideal octahedral SbF_6^- anion. As for $BrF_4^+Sb_2F_{11}^-$, the tentative nature of the IF_4^+ assignments does not warrant a force constant treatment.

In summary, all the experimental data, i.e., x-ray diffraction data, vibrational and ^{19}F nmr spectra, and conductivity measurements, available for the halogen pentafluoride•Lewis acid adducts are consistent with predominantly ionic structures containing Hal F_4^+ cations. The structure of these cations can be derived from a pseudo-trigonal bipyramide with a free valence electron pair occupying one of the equatorial positions. Deviation from this structure increases, as expected, with increasing size and polarizability of the halogen central atom. This results in a decrease of the axial F-Hal-F angle and increasing F bridging from the ClF_5 to the IF_5 adducts. A comparison of the fundamentals assigned to the Hal F_4^+ cations with those of the isoelectronic chalcogen tetrafluoride series (see Table IV) shows consistent trends and satisfactory agreement.

Acknowledgment. We are indebted to Dr. E. C. Curtis for assistance in the force constant computations, to Drs. D. Pilipovich, C. J. Schack, and R. D. Wilson for their help, and to Dr. D. Lawson for the use of the Raman spectrometer. This work was supported by the Office of Naval Research.

TABLE IV

Comparison of the Fundamental Vibrations of ClF_4^+, BrF_4^+, and IF_4^+ With Those of Isoelectronic SF_4, SeF_4, and TeF_4, Respectively

		ClF_4^+	BrF_4^+	IF_4^+	SF_4	SeF_4	TeF_4
A_1	ν_1	800	723	704	891	749	695
	ν_2	571	606	609	553	574	572
	ν_3	510	385	341	475	366	293
	ν_4	237	216	151	226	162	[151][a]
A_2	ν_5	475	--	--	414	--	--
B_1	ν_6	795	704	655	730	622	587
	ν_7	537	419	385	532	400	333
B_2	ν_8	829	736	720	867	723	682
	ν_9	385	369	316	353	250	[184.8][a]

(a) Computed values

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Diagram Captions

Figure 1 - Raman spectrum of solid $ClF_5 \cdot 1.08\ SbF_5$ (Sample I) contained in Teflon FEP capillary. Exciting line was 5145 Å. C indicates spectral slit width.

Figure 2 - Raman spectrum of solid $ClF_5 \cdot 1.36\ SbF_5$. Traces A and B show Samples II and III, respectively. Kel-F capillaries were used as containers with 5145 Å excitation.

Figure 3 - Infrared spectra of solid $ClF_5 \cdot xSbF_5$ as dry powder between AgBr plates. Trace A, Sample II; trace B, Sample I; trace C, *AgBr* window background.

Figure 4 - Raman spectrum of solid $ClF_5 \cdot AsF_5$ contained in Teflon FEP capillary. Exciting was line 5145 Å. Bands marked by an asterisk are due to the Teflon tube.

Figure 5 - Low-temperature infrared spectrum of solid $ClF_5 \cdot AsF_5$. Window material AgCl.

Figure 6 - Raman spectrum of solid $BrF_5 \cdot 2\ SbF_5$ contained in glass tube with hollow inside glass cone. Exciting was line 5145 Å using the axial viewing-transverse excitation technique.

Figure 7 - Infrared spectrum of solid $BrF_5 \cdot 2\ SbF_5$ as dry powder between AgCl plates.

Figure 8 - Raman spectrum of solid $IF_5 \cdot SbF_5$ contained in glass tube with hollow inside glass cone using 5145 Å excitation.

Figure 9 - Infrared spectrum of solid $IF_5 \cdot SbF_5$ as dry powder between AgBr plates.

Figure 10 - Raman spectra of HF solutions of $IF_5 \cdot SbF_5$ (trace A), $BrF_5 \cdot 2\ SbF_5$ (trace B), $ClF_5 \cdot 1.08\ SbF_5$ (trace C), $ClF_2{}^+SbF_6{}^-$ (trace D, the numbers indicate ν_1, ν_2, and ν_5 of octahedral $SbF_6{}^-$) in Teflon-FEP capillaries using 4880 Å excitation. Trace E shows the spectrum of an empty capillary; Teflon bands are marked by and asterisk. F indicates spectral slit width .

Figure 11 - Force Constant Ellipses for $ClF_4{}^+$. The solid and broken curves represent the solutions for F_{11}, F_{33}, and F_{44} as a function of F_{34} and for F_{11} and F_{33} as a function of F_{13}, respectively. Dimensions are in mdyn/Å.

Figure 12 - Force Constant Ellipses for $ClF_4{}^+$. The solid, broken, and dotted curves represent the solutions for F_{11}, F_{33}, and F_{44} as a function of F_{14}, for F_{66} and F_{77} as a function of F_{67}, and for F_{88} and F_{99} as a function of F_{89}, respectively.

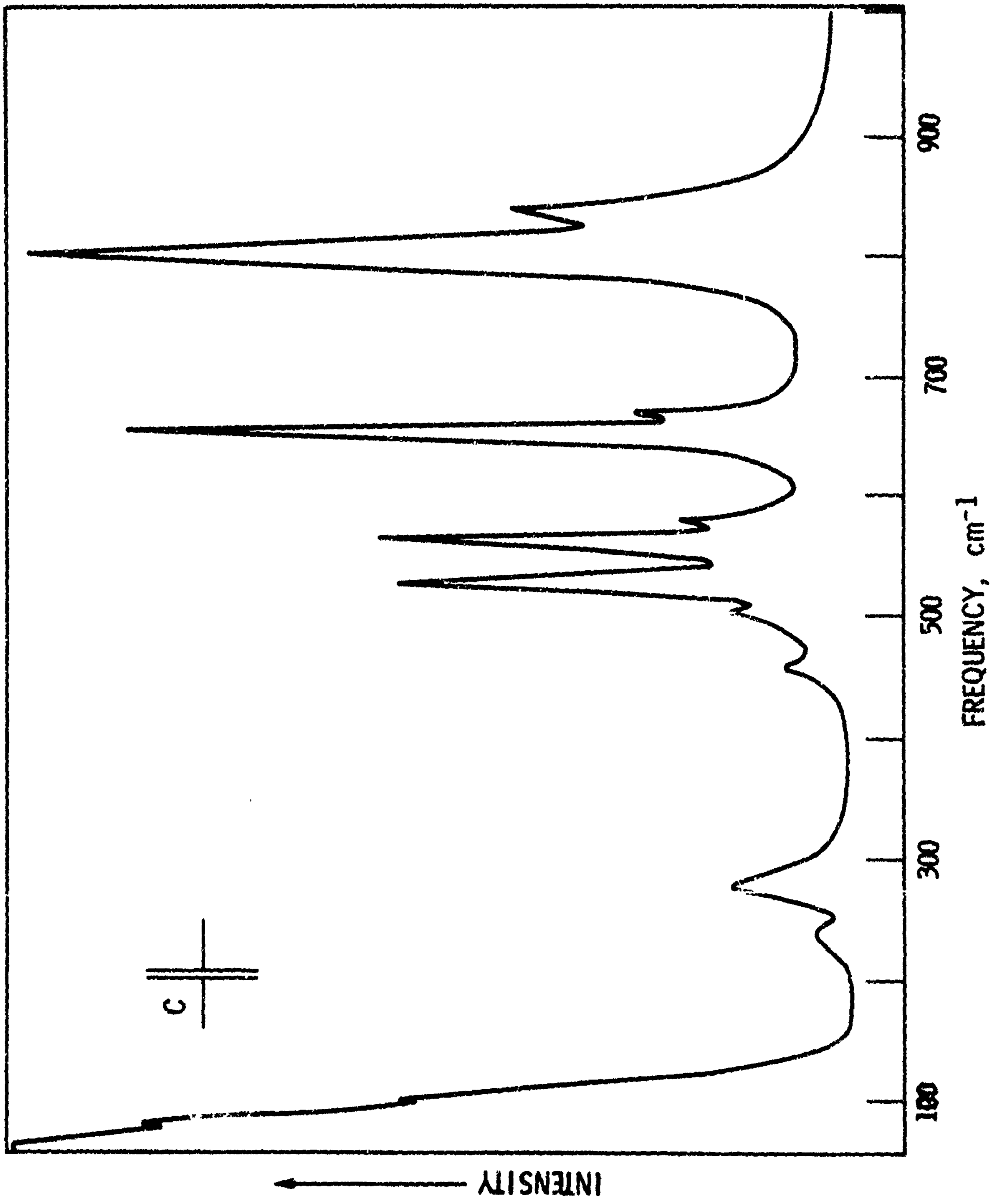
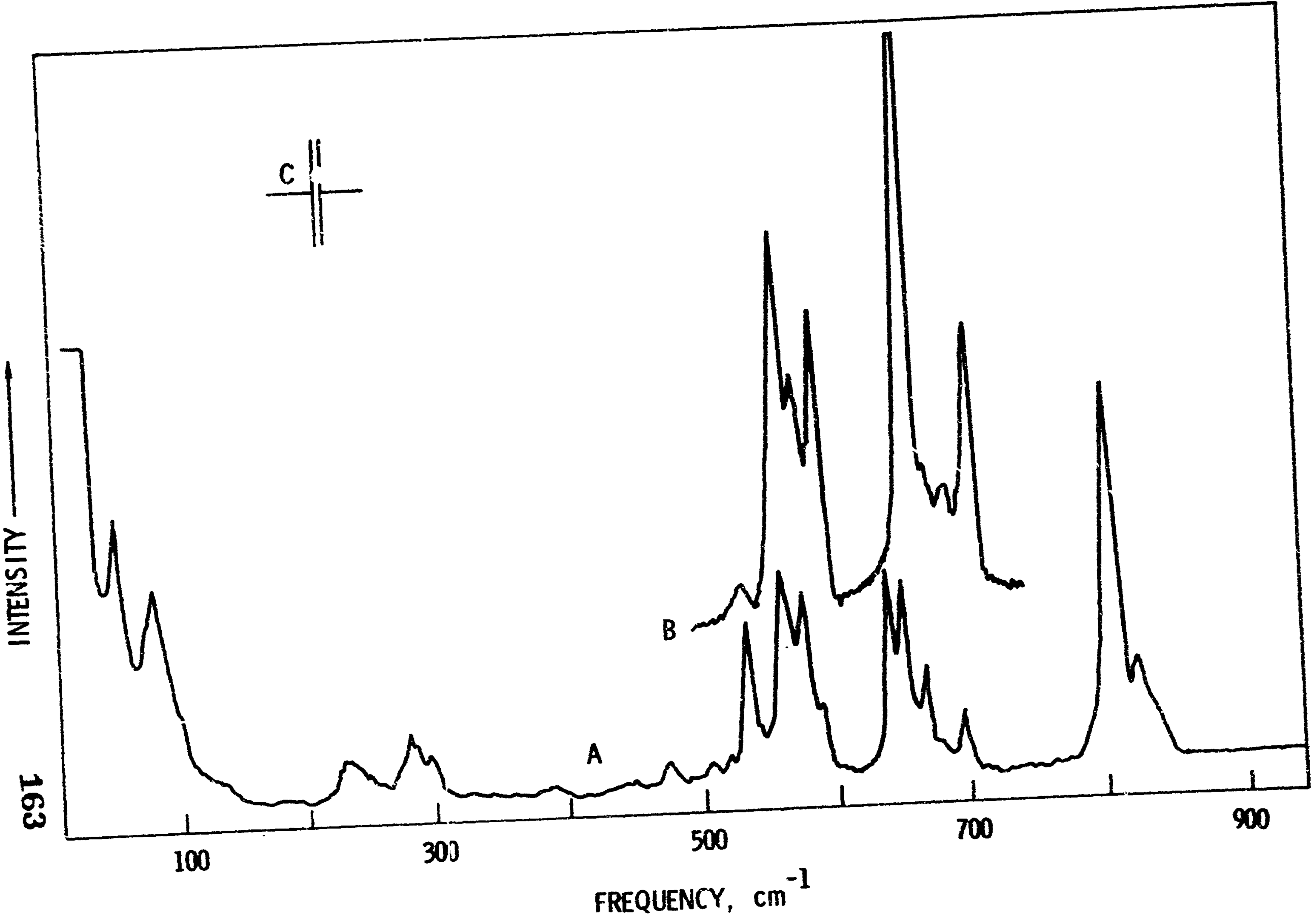


Figure 1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B
A
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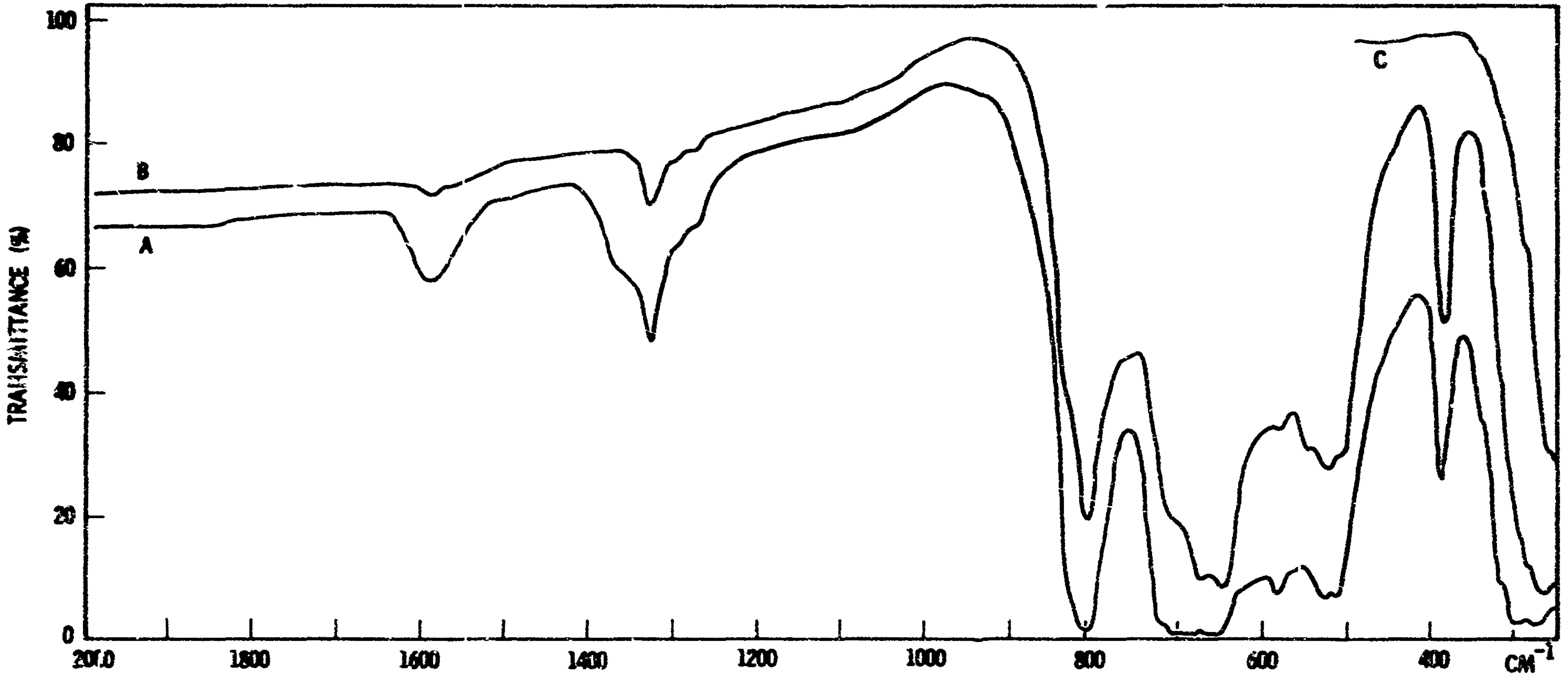
300
500
700
900
FREQUENCY, cm^{-1}



R-9262/[illegible]-26

Figure 3

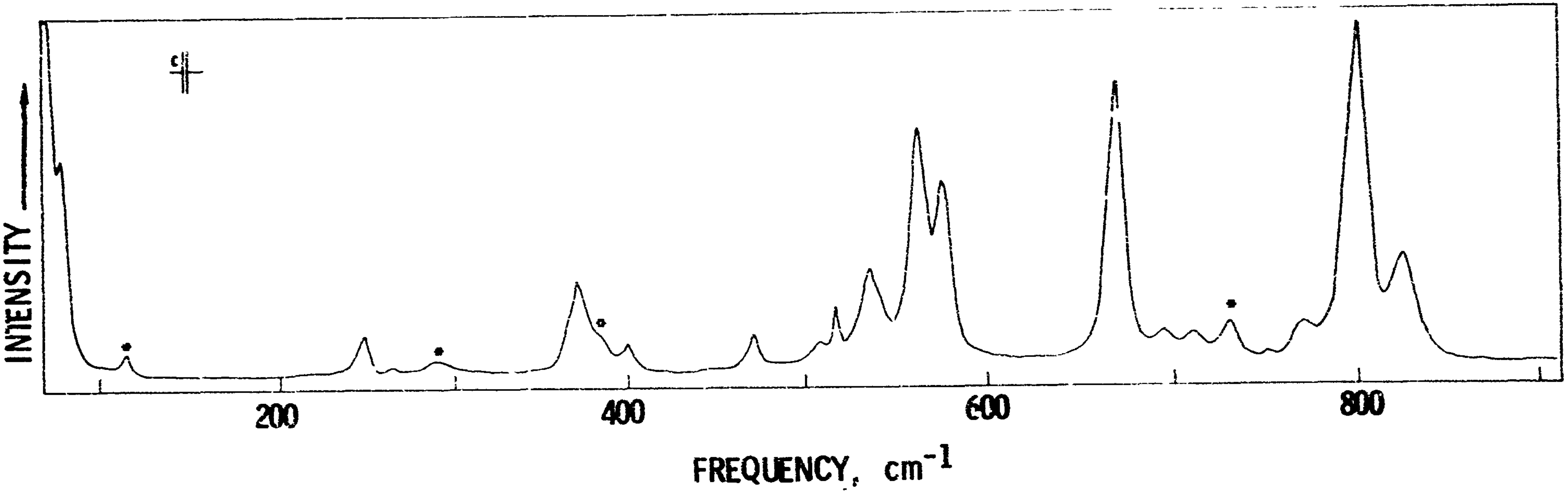


Figure 4

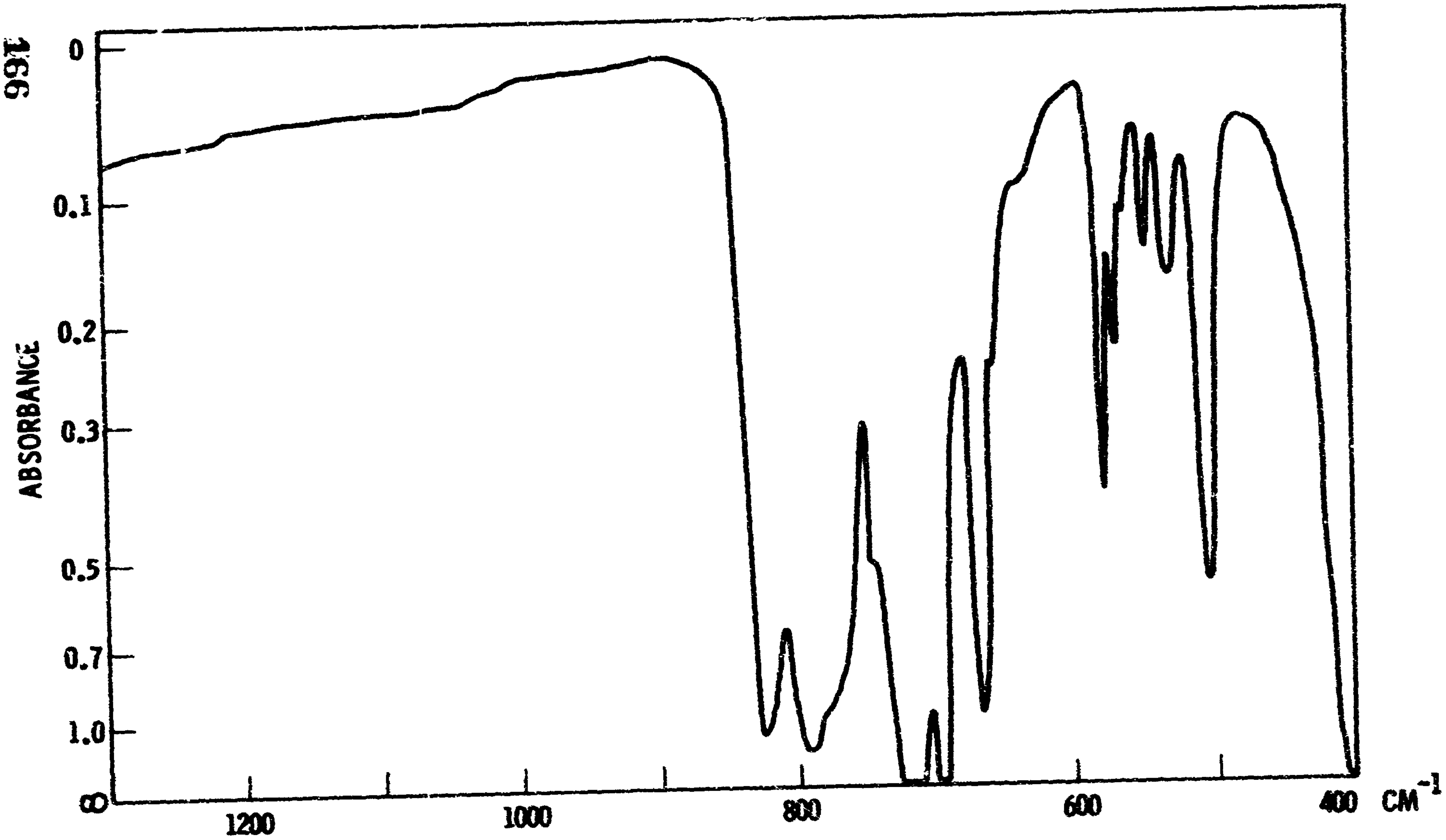
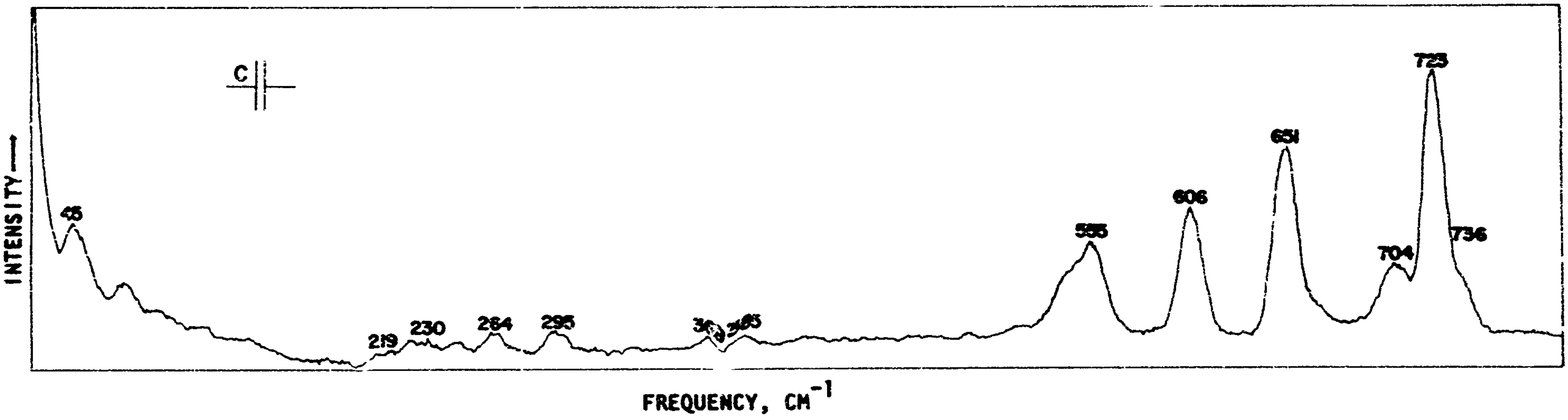


Figure 5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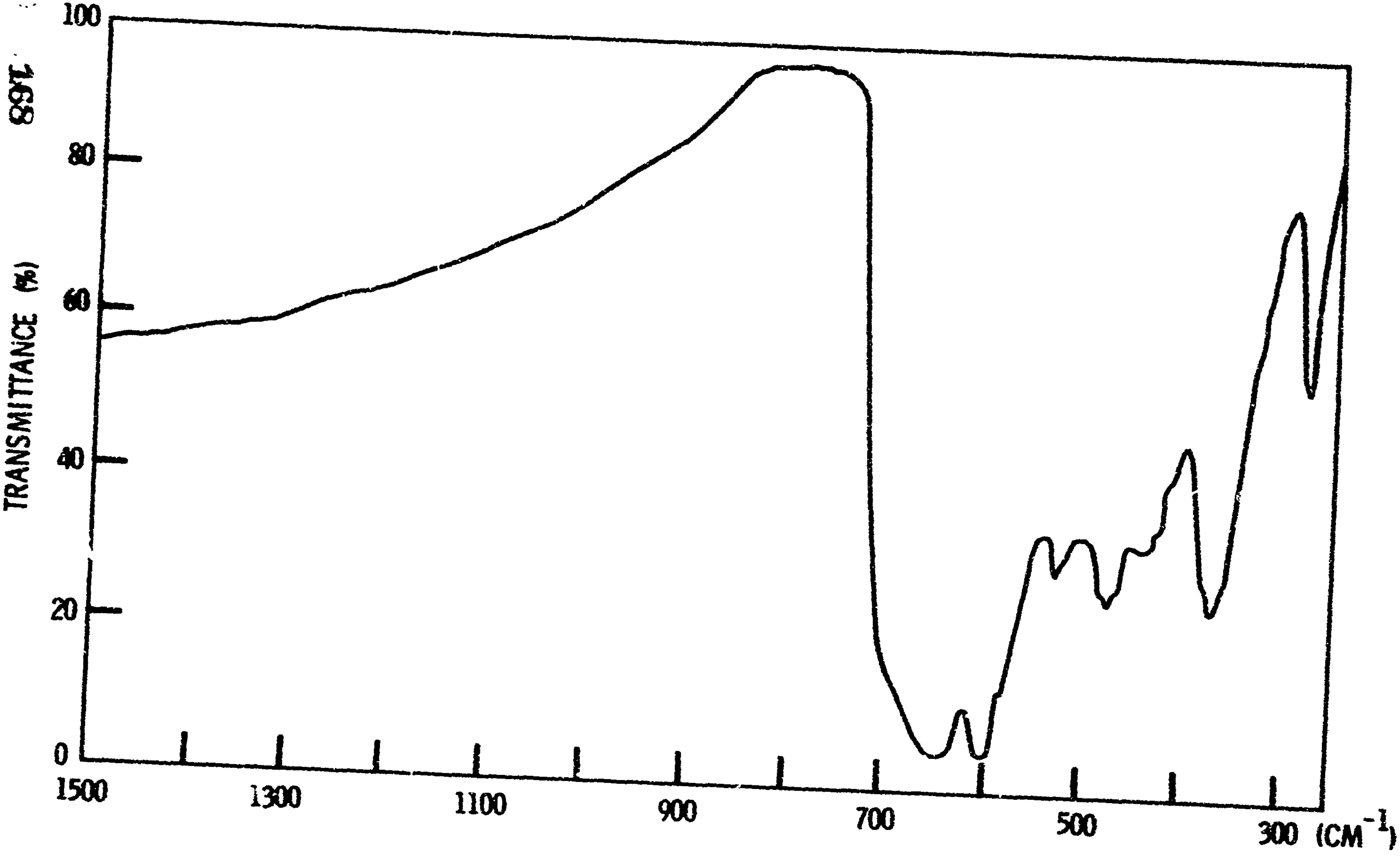
FREQUENCY, CM⁻¹

Figure 6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20
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TRANSMITTANCE (%)
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1300
1100
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300 (CM^{-1})

Figure 7

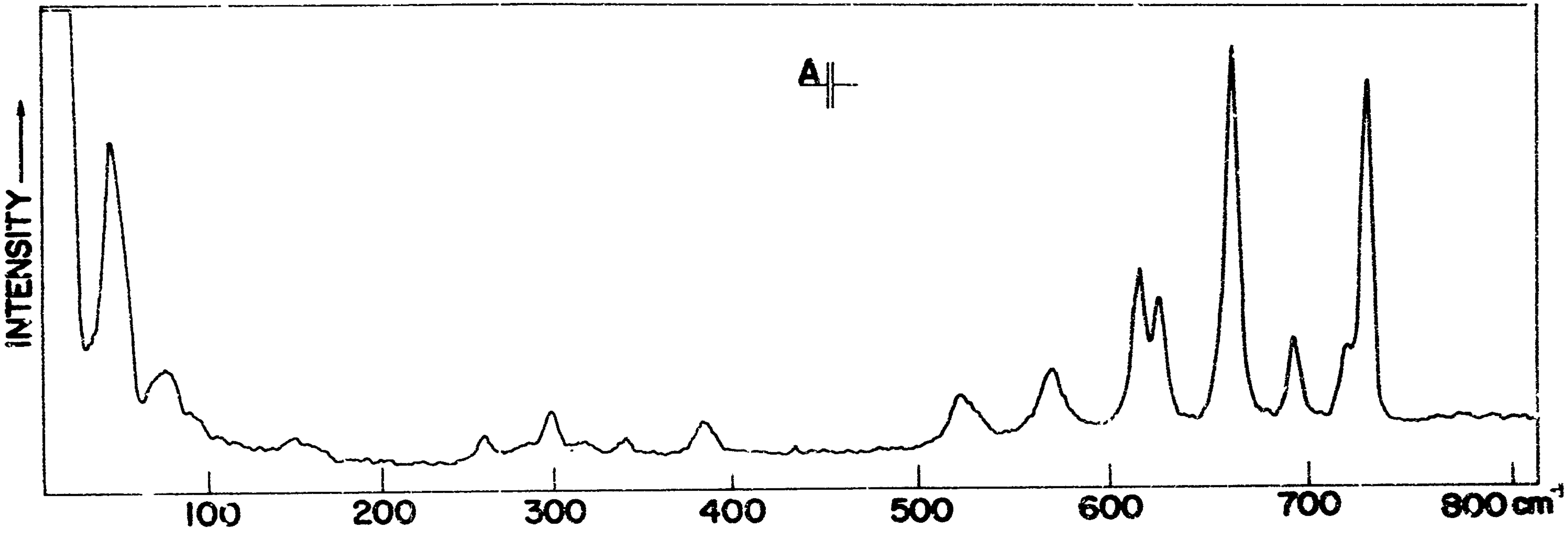
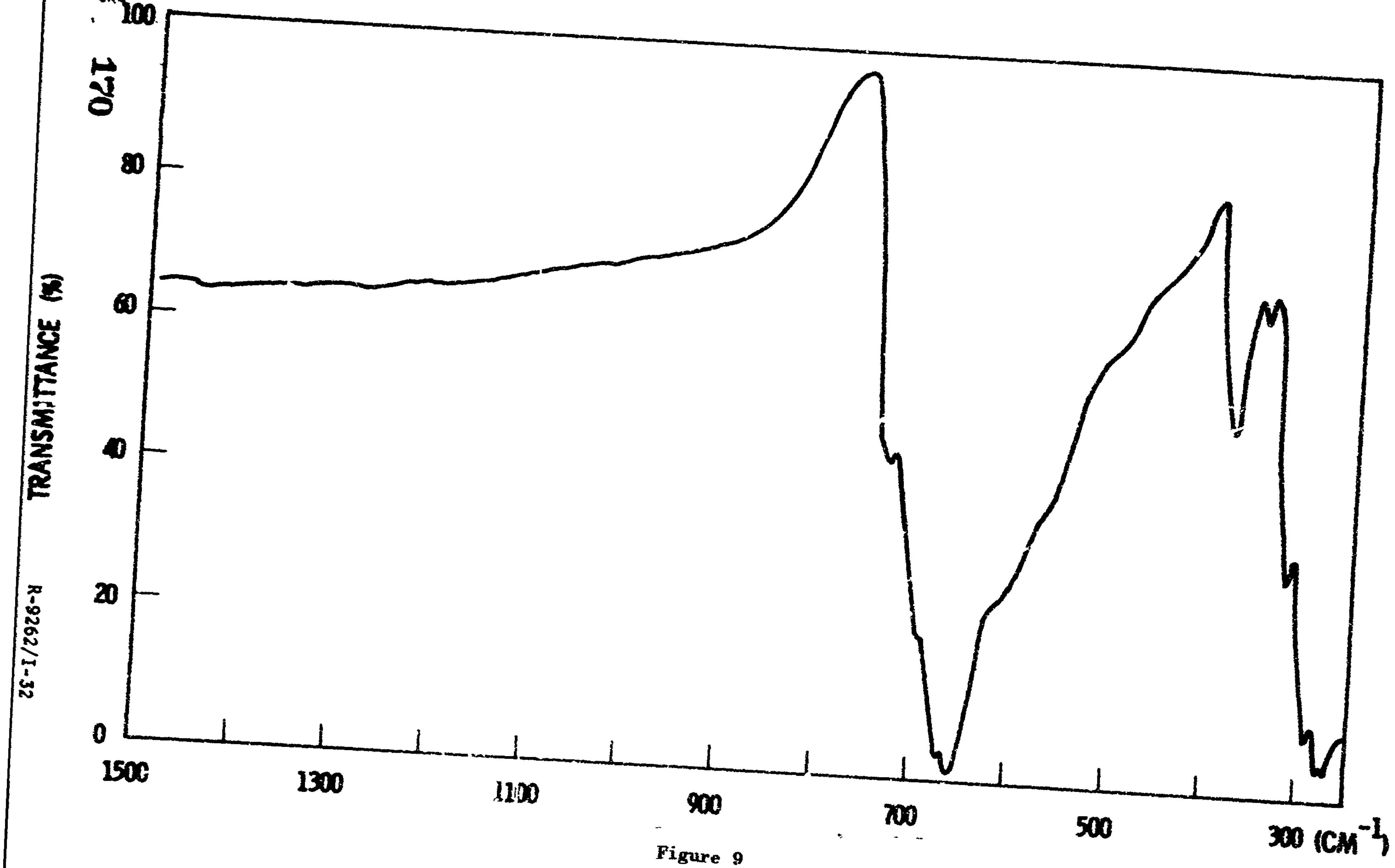


Figure 8


TRANSMITTANCE (%)
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80
60
40
20
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1300
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900
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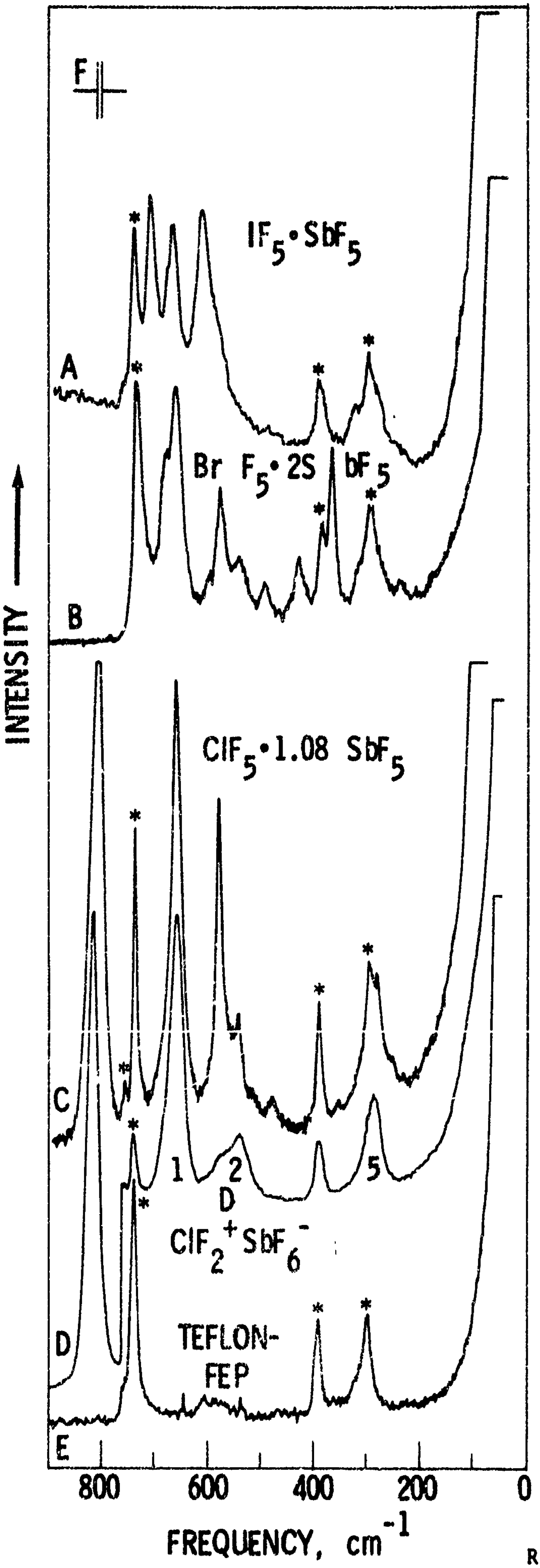
300 (CM^{-1})

Figure 9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IF5•SbF5
A
Br F5• 2S bF5
B
INTENSITY
ClF5•1.08 SbF5
C
1
2
5
D
ClF2+SbF6-
D
TEFLON-FEP
E
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600
400
200
0
FREQUENCY, cm-1

Figure 10

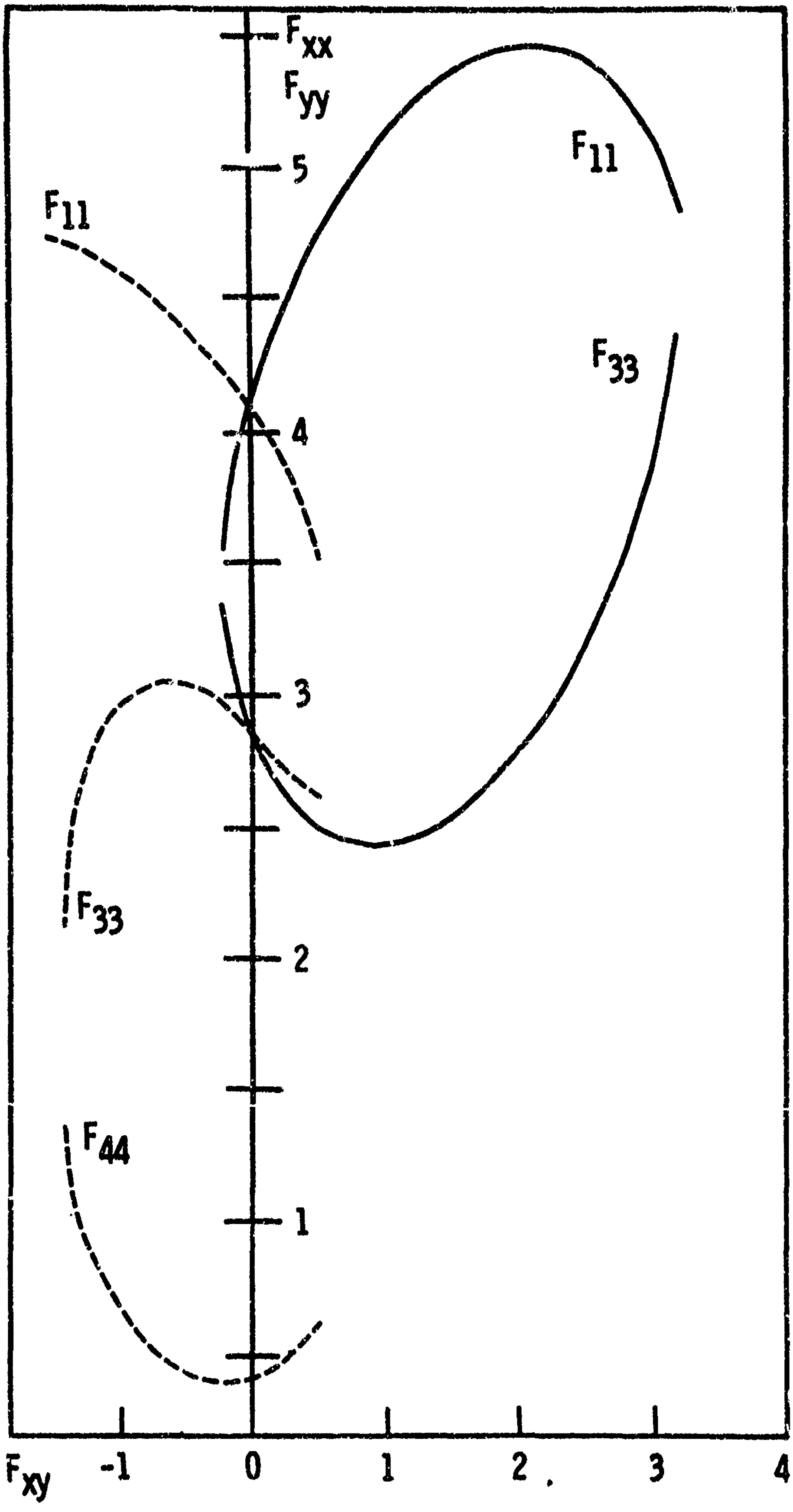

Figure 11

R-9262/I-34

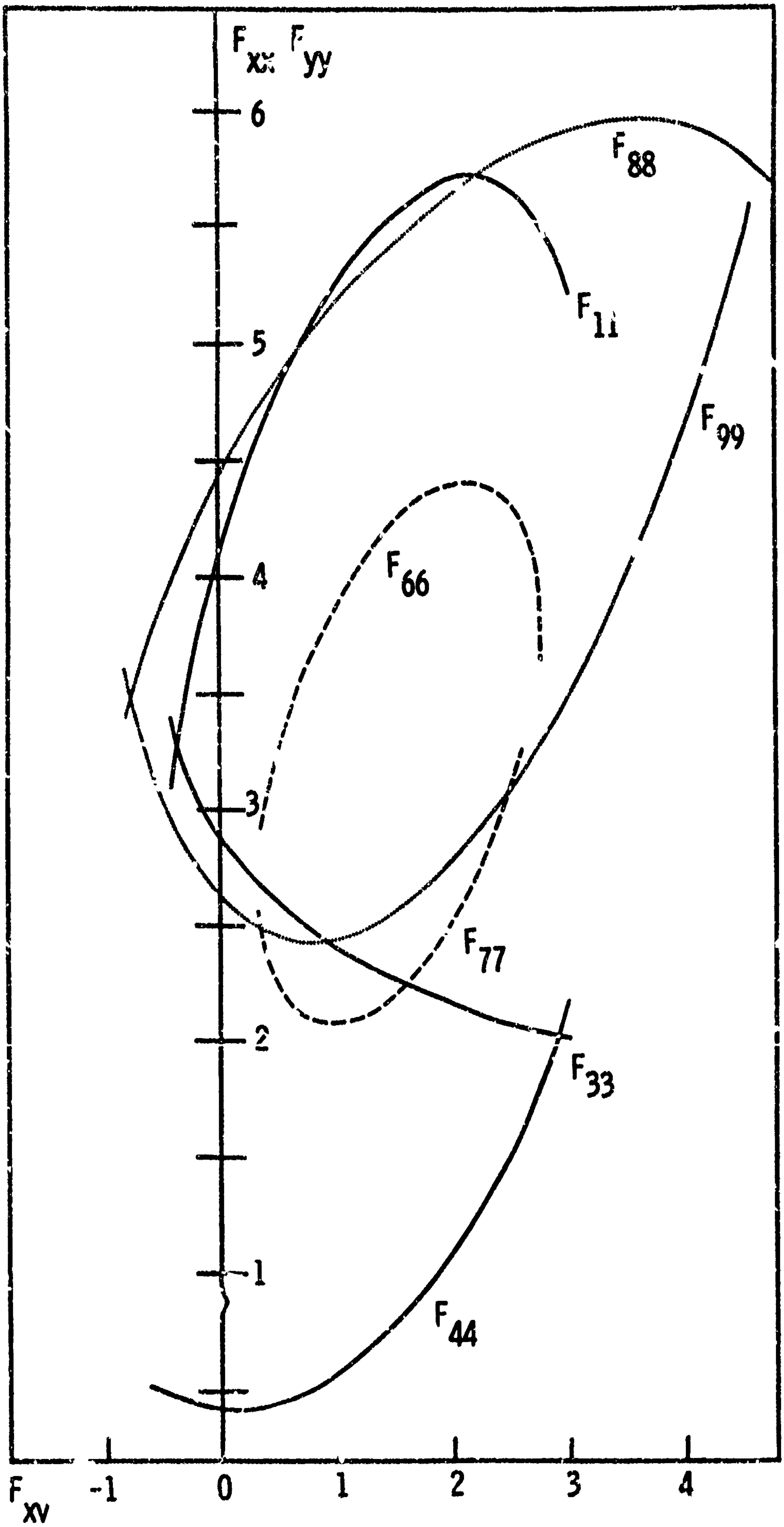

Figure 12

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 and a reinterpretation of the infrared band contours 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] 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. More recently, Levin[6] proposed a reassignment of the deformational modes on the basis of Raman and infrared spectra of solid SF_4 and supported his assignment with a CNDO/2 calculation of the infrared intensities. One of Levin's main arguments for revising the assignment of the deformational modes was the observation of two bands at 245 and 205 cm^{-1}, respectively, in the Raman spectrum of solid SF_4. In a subsequent paper[7], however, Berney showed that the 205 cm^{-1} Raman band is due to residual α-SF_4.

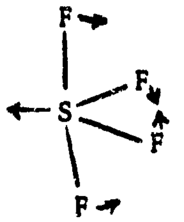
Another unsettled question involves the frequencies of the axial and equatorial SF_2 scissoring modes in species A_1. It was shown[8-12] for related trigonal bipyramidal molecules such as PF_5 that these two deformational modes are highly mixed,[11] and that a better agreement with the observed mean square amplitudes of vibration can be achieved[10] by assigning the lower frequency to the equatorial deformation. This frequency sequence was also proposed by Levin[6] for SF_4, contrary to our assignment[1] and that of Frey et al.[5] which are more consistent with the fact that in SF_4 the equatorial bonds are considerably shorter and hence stronger than the equatorial ones.[13,14] In view of these conflicting assignments, we have recomputed the force field and mean square amplitudes of vibration for SF_4 hoping that these data might allow us to distinguish between the different assignments [1,5,6] (see Table 1).

Since only nine frequency values are available for the computation of seventeen symmetry force constants, a General Valence Force Field cannot be computed. However, it is known that mean square amplitudes of vibration are only slightly influenced by moderate changes in the force field. This was confirmed for SF_4 by calculating mean amplitudes of vibration based on two force fields obtained by two different approximating methods. The first method used was the eigenvector method,[15,16] and the second one was a diagonal MVFF for species A_1 and B_2 combined with the $F_{67} \equiv$ minimum solution for species B_1 since no real values can be obtained for $F_{67} \equiv 0$. The results of these computations are given in Tables 2,3, and 4, and in Figure 1. The mean square amplitudes of vibration computed from the two force fields differed by less than 0.001Å, except for $<q^2>^{1/2}$ $F_3 \ldots F_4$ using the assignment of Levin[6] which showed a difference of 0.004Å. Therefore, only the data obtained by the eigenvector method are listed in Tables 2,3, and 4, except for the preferred (see below) set II, for which the MVFF values are also given for comparison.

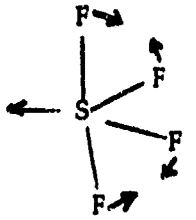
Table [illegible] Figure 1 show that the mean square amplitudes of vibration are useful for discriminating between the different assignments of the deformational modes, but are of little help in finding the correct assignment for the two stretching modes $\nu_6(B_1)$ and $\nu_8(B_2)$. However, the following force field arguments favor set II over set I: (1) Generally, the stretch-stretch interaction constant is relatively small whenever two bonds form an angle close to 90°. For set I, the equatorial interaction constant f_r' exhibits a value of 1.21 mdyn/Å which is unreasonably high for a F-S-F bond angle of 101°. The value of 0.49 mdyn/Å obtained for set II is much more plausible; (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^-[17], ClF_3[5], and BrF_3[5]; (3) The bond length of the equatorial S-F bonds in SF_4 (1.545± 0.003Å)[14] is similar to that in SF_6(1.56± 0.02Å)[18]. Since bond lengths are related to the stretching force constants, one might expect f_r of SF_4 to approach the SF_6 value[19] 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(0.10Å)[14] favors set II which shows the larger difference beteen f_r and f_R; (5) Set II is in better agreement with the values found[17] for SF_5^- if the general decrease in the force constant values owing to the formal negative charge is taken into account. Thus, 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]

The question as to which A_1 deformation mode should be assigned to the higher frequency value, can readily be decided based on the computed mean square amplitudes of vibration (see Table 4 and Figure 1). It should be noted that the $F_1 \ldots F_3$ values reported in our previous paper[1] are incorrect due to a computational error. The revised values are listed as set Ia. It can be seen from Figure 1 that all b sets (i.e. δ sciss ax> δ sciss eq) result in unacceptably high values for $\langle q^2\rangle^{1/2}$ $F_3 \ldots F_4$. Hence, δ sciss eq > δ sciss ax appears to be a better description of the two A_1 deformational modes of SF_4. It should be kept in mind, however, that both ν_3 and ν_1 are not highly characteristic. The potential energy distribution obtained for the diagonal force field shows that ν_3 is made up of 65% equatoial and 35% axial bending motion, and that ν_1 contains significant contributions from both the axial and equatorial bending motions. This high degree of mixing is not surprising[20] since the G matrix elements G_{13}, G_{14}, and G_{34} of SF_4 show large numerical values. The two remaining modes in species A_1 are more characteristic: ν_2 is made up entirely of axial stretching and ν_4 represents 88% axial bending. As can be seen from Figure 1, the fit between observed[13] and computed $\langle q^2\rangle^{1/2} F_3 \ldots F_4$ and $F_1 \ldots F_3$ can be improved by increasing somewhat the mixing between ν_3 and ν_4. However, this increase is too small to justify reversing the assignment of ν_3 and ν_4. Additional support for $\nu_3 > \nu_4$ in the chalcogen tetrafluorides was recently obtained[21] by Adams and Downs in a matrix isolation study of SeF_4. The observed selenium isotopic shifts show that the higher frequency value belongs to ν_3.

The high degree of mixing between the equatorial and axial bending motions for ν_3 can be rationalized. Inspection of the normal coordinates of ν_3 shows that this mode is essentially an umbrella type deformation, i.e. a symmetric combination of the equatorial and axial bending motions. The ν_4 deformation might be considered as the corresponding antisymmetric combination of these motions. It should be the mode mainly involved in an intramolecular exchange process as suggested by Berry,[22] although higher vibrational levels must be invoked since the normal coordinates show only little motion of the equatorial fluorines in the fundamental. The fact that the PED shows ν_4 to be composed mainly of axial bending is due to the fact that the sulfur moves in the same direction as the equatorial fluorines thus suppressing the equatorial scissoring motion.



ν_3, symmetric combination
of axial and equatorial bending



ν_4, antisymmetric combination
of axial and equatorial bending

Inspection of Figure 1 also reveals that the assignment proposed[6] by Levin (set IIIb) results in unsatisfactory values for $\langle q^2\rangle^{1/2}$ $F_3 \ldots F_4$ and $F_1 \ldots F_3$ and, therefore, should be rejected. Furthermore, it can be seen that retaining Levin's frequencies[6] for A_1 but reversing the assignment of ν_3 and ν_4 (set IIIa) results in too high a value for $\langle q^2\rangle^{1/2}$ $F_1 \ldots F_3$. This discrepancy cannot be eliminated by increasing the mixing between ν_3 and ν_4, since a small decrease in $\langle q^2\rangle^{1/2}$ $F_1 \ldots F_3$ results in a large increase in $\langle q^2\rangle^{1/2}$ $F_3 \ldots F_4$. A second strong argument against set IIIa was recently put forward[7] by Berney. He showed that the splitting of the 223 cm^{-1} Raman line in the spectrum of the solid is due to the α, β, and γ forms of SF_4 and not due to two different fundamentals, thus eliminating the basis of Levin's reassignment. Furthermore, the observed infrared band contours[4] and Raman polarization measurements on gaseous SF_4[1] and SeF_4[23] favor set II over III.

Since the MVFF obtained by the eigenvector method[15,16] is not too different from the diagonal force field, numerical experiments were carried out by varying the off diagonal constants within meaningful limits. Whereas for set IIa, the fit between observed and computed $<q^2>^{1/2}F_1...F_3$ could be improved, for set IIb the large discrepancy in $<q^2>^{1/2}F_3...F_4$ could not be eliminated.

In summary, set IIa is the only assignment which can satisfy both the observed[13] mean square amplitudes of vibration and basic force field arguments. Furthermore, the mean square amplitudes of vibration suggest that for SF_4 the higher frequency A_1 deformational mode ν_3 should be assigned to the equatorial scissoring motion. However, a normal coordinate description of ν_3 and ν_4 as symmetric and antisymmetric combinations, respectively, of the equatorial and axial scissoring motions seems more appropriate.

ACKNOWLEDGMENT

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

Table 1

Assignment of Normal Modes of SF_4

Species		Approximate Description		Assignment	
			I Christe and Sawodny[a]	II Frey et al.[b]	III Levin[c]
A_1	ν_1	ν sym SF_2 eq	892	892	892
	ν_2	ν sym SF_2 ax	558	558	558
	ν_3	δ sciss SF_2 eq	475	475	245 (233)
	ν_4	δ sciss SF_2 ax in plane	226	228	353
A_2	ν_5	SF_2 twist	414	414	475
B_1	ν_6	ν asym SF_2 ax	867	730	728
	ν_7	SF_2 rocking	532	532	533
B_2	ν_8	ν asym SF_2 eq	730	867	867
	ν_9	δ sciss SF_2 ax out of plane	353	353	206 (228)

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a ref. 1

b ref. 5

c ref. 6

Table 2

Symmetry Force Constants [a,b] of SF_4 Computed from the Assignments Listed in Table 1 Assuming for Sets a $\delta SF_2eq > \delta SF_2ax(A_1)$ and for Sets b $\delta SF_2eq < \delta SF_2ax\ (A_1)$

		Ia	Ib	IIa	IIa(MVFF)	IIb	IIIa	IIIb
A_1	F_{11}	5.74	5.71	5.74	5.49	5.71	5.83	5.81
	F_{22}	3.48	3.48	3.48	3.48	3.48	3.48	3.48
	F_{33}	1.97	0.57	1.97	2.10	0.57	1.10	0.63
	F_{44}	0.37	1.30	0.37	0.38	1.30	0.41	0.71
	F_{12}	0	0.01	0	0	0.01	0	0
	F_{13}	0.13	0.05	0.13	0	0.05	0.02	0.04
	F_{14}	0.05	0.16	0.05	0	0.16	0.04	0.05
	F_{23}	0.02	0.01	0.02	0	0.01	0	0
	F_{24}	0.01	0.02	0.01	0	0.02	0.01	0.01
	F_{34}	-0.04	-0.03	-0.04	0	-0.03	-0.07	-0.06
A_2	F_{55} $(\nu_5=200cm^{-1})$			0.35				
	$(\nu_5=400cm^{-1})$			1.40				
	$(\nu_5=600cm^{-1})$			3.15				
B_1	F_{66}	3.66	3.66	2.65	2.35	2.65	2.65	2.65
	F_{77}	2.20	2.20	2.24	2.50	2.24	2.24	2.24
	F_{67}	0.45	0.45	0.60	0.54[c]	0.60	0.60	0.60
B_2	F_{88}	3.33	3.33	4.77	4.62	4.77	4.77	4.77
	F_{99}	2.01	2.01	1.98	2.04	1.98	1.98	1.98
	F_{89}	0.20	0.20	0.17	0	0.17	0.17	0.17

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a) Stretching force constants in mdyn/Å, deformation constants in mdyn Å, and stretch-bend interaction constants in mdyn.

b) Unless otherwise indicated the listed force fields were computed by the eigenvector method.

c) Minimum value of F_{67} required for obtaining a real solution.

Table 3

Stretching Force Constants (in mdyn/Å) and Bond Lengths (in Å) of SF_4 Compared to Those of Related Molecules and Ions

	SF_4				SF_6[a]	SF_5[b]	ClF_3[c]
	Ia	IIa	IIa(MVFF)	IIIb			
f_R (ax)	3.57	3.07	2.92	3.07		2.06	2.70
f_R'	-0.09	0.42	0.57	0.42		0.52	0.36
f_r (eq)	4.54	5.25	5.05	5.33	5.26	4.12	4.19
f_r'	1.21	0.49	0.43	0.48			
R		1.646±0.003[d]					
r		1.545±0.003[d]		1.56±0.02[e]			

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[a] ref. 19

[b] ref. 17

[c] ref. 5

[d] ref. 14

[e] ref. 18

Table 4

Computed and Observed[13] Mean Square Amplitudes (in Å) of Vibration of SF_4

	$<q^2>_{calc}^{1/2}$						$<q^2>_{obs}^{1/2}$
	Ia	IIa	IIa(MVFF)	IIb	IIIa	IIIb	
$S-F_1$ (ax)	0.050	0.049	0.050	0.049	0.049	0.049	0.047±0.005
$S-F_3$ (eq)	0.044	0.041	0.041	0.041	0.041	0.041	0.041±0.005
$F_1 \ldots F_2$	0.061	0.061	0.061	0.061	0.061	0.061	0.059±0.01
$F_3 \ldots F_4$	0.063	0.063	0.064	0.094	0.076	0.091	0.068±0.01
$F_1 \ldots F_3$ (ν_5=200cm^{-1})	0.091	0.091	0.091	0.086	0.096	0.094	0.067±0.005
(=400)	0.074	0.073	0.074	0.068	0.080	0.077	
(=600)	0.070	0.069	0.070	0.064	0.076	0.073	
(=800)	0.068	0.068	0.068	0.063	0.075	0.072	

Diagram Caption

Figure 1. Mean amplitudes of vibration (Å) of SF_4 for bonded and nonbonded distances. Rectangles represent experimental electron diffraction values ±esd according to ref. 8. Crosses, squares, diamonds, and circles represent amplitudes computed for the different assignments.

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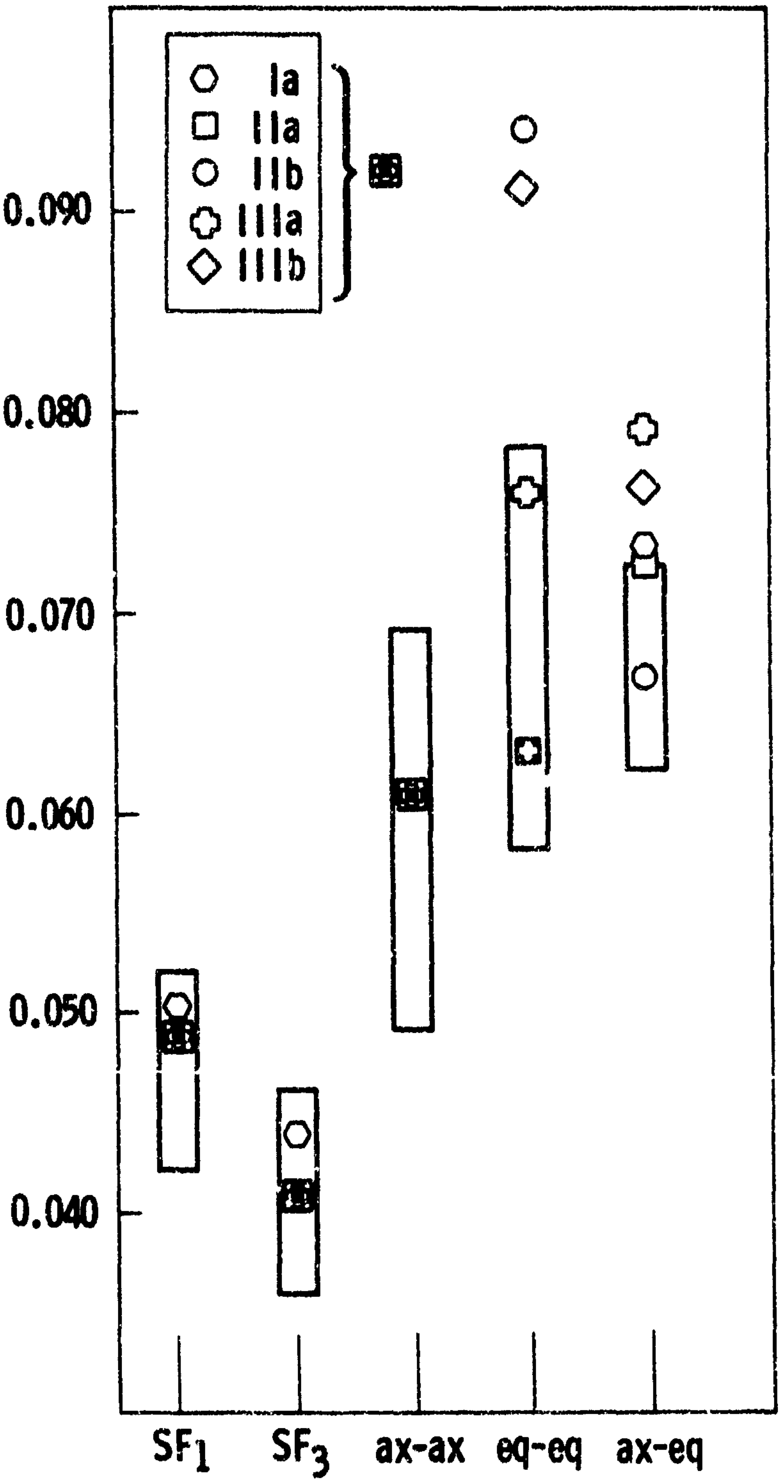
Ia
IIa
IIb
IIIa
IIIb
0.090
0.080
0.070
0.060
0.050
0.040
SF$_1$
SF$_3$
ax-ax
eq-eq
ax-eq

[Reprinted from Inorganic Chemistry, 12, 620 (1973).]

Contribution from Rocketdyne, a Division of North American Rockwell Corporation, Canoga Park, California 91304,
and the Abteilung für Anorganische Chemie, Universität, Ulm, Germany

Vibrational Spectrum and Force Constants of the SF_5O^- Anion

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The $CsF \cdot SF_4O$ adduct has been prepared and characterized by infrared and Raman spectroscopy. All eleven fundamental vibrations expected for a pseudooctahedral anion of symmetry C_{4v} have been observed and are assigned. A modified valence force field has been computed for SF_5O^- and suggests an SO bond order of approximately 1.5.

Introduction

The existence of a $CsF \cdot SF_4O$ adduct has been reported[1] in 1960 by Smith and Englehardt and in 1964 by Ruff and Lustig.[2] However, no details were given regarding its preparation or properties. In a subsequent paper Lustig and Ruff described[3] the synthesis of $Cs^+SF_5O^-$ from CsF and SF_4O in CH_3CN solution. The ionic formulation of this adduct was substantiated[3] by its ^{19}F nmr spectrum which showed a characteristic AB_4 pattern. The vibrational spectrum of this interesting compound is essentially unknown, since only four infrared absorptions were published.[3] In this paper we wish to report the complete vibrational spectrum of the SF_5O^- anion and the results from a force constant computation.

Experimental Section

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 gauge (0-1500 mm ± 0.1%). Sulfur oxide tetrafluoride was prepared by the method[2] of Ruff and Lustig from SF_2O and F_2 and was purified by fractional condensation. Cesium fluoride was fused in a platinum crucible and powdered in a drybox 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} with an accuracy of ±2 cm^{-1} for sharp bands. 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 with an accuracy of ±2 cm^{-1} 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. For the conical tubes the axial viewing-transverse excitation technique and for the capillaries the transverse viewing-transverse excitation techniques were used.

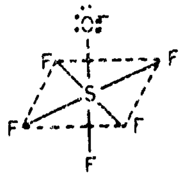
Preparation of $CsSF_5O$. A prepassivated (with ClF_3) 30-ml 316 stainless steel cylinder was loaded with dry, powdered CsF (9.93 mmol). Purified SF_4O (16.1 mmol) was added to the cylinder at -196°. After warming to ambient temperature overnight, the cylinder was heated at 90° for 5 days. Upon recooling to room temperature, all volatiles were removed *in vacuo* and trapped at -196°. The recovered SF_4O (7.32 mmol) indicated that 88.5% of the CsF had been converted to $CsSF_5O$. Confirmation of this was obtained by pyrolyzing a sample of the complex at approximately 250° for 10 min while pumping the evolved gas through a trap cooled to -196°. The evolved gas was identified as SF_4O and the amount found corresponded to an 82% conversion of CsF to $CsSF_5O$. A similar experiment exposing KF to SF_4O at temperatures up to 125° for several days did not result in any complexing

Results and Discussion

Synthesis and Properties. In the absence of a solvent, heating was required to achieve a significant conversion of CsF to $CsSF_5O$. The conversion obtained in the present study is comparable to that of 76% previously achieved[3] by the use of CH_3CN as a solvent. The reversibility of the formation reaction was demonstrated by the pyrolysis experiment which resulted in SF_4O as the only volatile product. $CsSF_5O$ is a white, crystalline solid and does not show any detectable dissociation pressure at ambient temperature; attempts to synthesize the analogous potassium salt failed under similar reaction conditions. This is not surprising since the stability of salts of this type generally decreases with decreasing cation size.

Vibrational Spectra. Figures 1 and 2 show the Raman and the infrared spectra, respectively, of $CsSF_5O$. The absorption between 300 and 250 cm^{-1} in the infrared spectrum is due to the AgBr window material. The observed frequencies are listed in Table I.

Analogy with isoelectronic SF_5Cl[4,5] and the typical AB_4 ^{19}F nmr pattern previously reported[3] for SF_5O^- suggests the following square-bipyramidal structure of symmetry C_{4v} for SF_5O^-



For this ion of symmetry C_{4v} 11 fundamentals are expected. These are classified as $4 A_1 + 2 B_1 + B_2 + 4 E$. All 11 modes should be Raman active, whereas only the A_1 and E modes should be infrared active. The assignment of the observed bands to the individual modes is given in Table I and is supported by the following arguments. The very intense infrared band at 1154 cm^{-1} must be due to the SO stretching mode. As expected for an A_1 mode it was also observed in the Raman spectrum. Its high frequency rules out any alternate assignment. Comparison with the cor-

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Table I. Vibrational Spectrum of $CsSF_5O$ Compared to Those of SF_5Cl and IF_5O

Obsd freq, cm^{-1}, and intens						Assignment in point group C_{4v}		Approximate description of vibration
$CsSF_5O$		SF_5Cl[a]		IF_5O[b]				
Ir	R	Ir	R	Ir	R			
1154 vs	1153 (1)	402 s	403 (10) p	927 s	928 (4) p	A_1	ν_1	$\nu(XY)$
735 vs	722 (0.2)	855 vs	833 (0.2) p	680 s	680 (10) p		ν_2	$\nu(XF)$
697 m	697 (10)	707 s	704 (3.0) p	640 w	640 (9+) p		ν_3	$\nu_{sym}(XF_4)$
506 s	506 (1)	602 s	603 (0.2) p	360 s	c		ν_4	δ_{sym}(out-of-plane XF_4)
	541 (3.3)		625 (0.7) dp		640 (9+) p	B_1	ν_5	ν_{sym}(out-of-phase XF_4)
	472 (0.2)			(275)[d]			ν_6	δ_{asym}(out-of-plane XF_4)
	452 (0.9)		505 (0.2) dp		305 (1) dp	B_2	ν_7	δ_{sym}(in-plane XF_4)
785 vs, br	780 (0.1) br	909 vs	927 (0.2) dp	710 vs	700 (0+) sh	E	ν_8	$\nu_{asym}(XF_4)$
606 s	607 (2.2)	287 vw	271 (0.6) dp	369 s	374 (1) dp		ν_9	$\delta(YXF_4)$
530 sh	530 (2)	579 mw	584 (0.1) dp	342 s	340 (4) dp		ν_{10}	$\delta(FXF_4$
325 mw		441 m	442 (0.8) dp	e	205 (0+)		ν_{11}	δ_{as}(in-plane XF_4)

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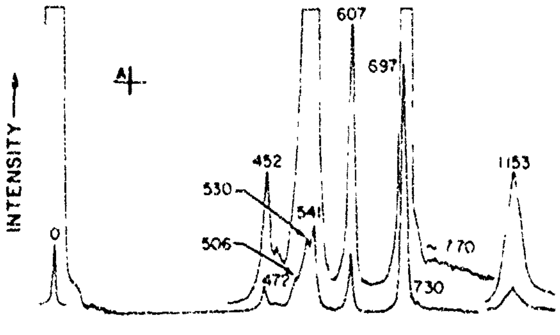

Figure 1. Raman spectrum of solid $Cs^+SF_5O^-$. A indicates spectral slit width.

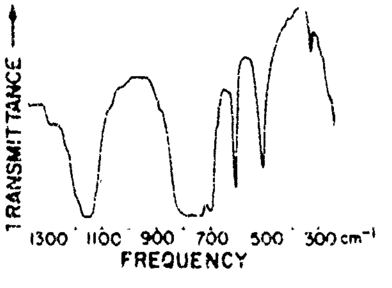

Figure 2. Infrared spectrum of solid $Cs^+SF_5O^-$ as an AgBr disk.

responding mode in SF_3O^+ ($1538\ cm^{-1}$)[6] and SF_4O ($1380\ cm^{-1}$)[7] shows the expected frequency decrease with an increasing formal negative charge. The SF_5O^- anion should have four additional stretching modes. Three of these belong to the approximately square-planar SF_4 part and one involves the unique fluorine ligand. Of these, the totally symmetric SF_4 stretching mode of species A_1 should result in the most intense Raman line and is consequently assigned to the Raman band at $697\ cm^{-1}$. As expected for species A_1, this Raman band has an infrared counterpart. The antisymmetric SF_4 and the SF stretching modes in SF_5Cl are both of very high intensity in the infrared and of very low intensity in the Raman spectrum[4,5] and occur at frequencies higher than that of $\nu_{sym}(SF_4)$ (A_1). Consequently, for SF_5O^- these two modes are assigned to the two weak Raman lines at 780 and $722\ cm^{-1}$, respectively. Of these two, the $780\text{-}cm^{-1}$ line is attributed to $\nu_{as}(SF_4)$ owing to its width, lower Raman intensity, and larger frequency separation from $\nu_{sym}(SF_4)$ (A_1). Both Raman bands show as expected a very intense infrared counterpart. Owing to the broadness of $\nu_{as}(SF_4)$, these two bands are poorly resolved in the infrared spectrum. The broadness of ν_{as} was also observed for several other approximately square-planar XF_4 groups, such as BrF_4^-,[3] ClF_4^-,[9] or those in SF_5^- and SeF_5^-,[10] and hence appears to be quite general. The remaining, yet unassigned, stretching mode, ν_{sym}(out-of-phase SF_4) (B_1), should be of medium Raman intensity, should ideally have no infrared counterpart, and should occur in the range $500\text{–}600\ cm^{-1}$. Since both the 506- and $607\text{-}cm^{-1}$ Raman lines show very intense infrared counterparts, only the 530- or the $541\text{-}cm^{-1}$ line might belong to $\nu_{sym}(SF_4)$ (B_1). Based upon its higher Raman intensity and frequency, we prefer to assign $541\ cm^{-1}$ to $\nu_{sym}(SF_4)$ (B_1).

There are six frequencies left for assignment to the six deformational modes. Of these, the O–SF_4 wagging mode (E) should have the highest frequency since it involves a motion of the oxygen atom which has partial double-bond character (see below). Furthermore, this mode should result in a relatively intense band in both the infrared and Raman spectra. Consequently, this mode is ascribed to $607\ cm^{-1}$. By comparison with SF_5Cl,[4,5] SF_5^-,[10] and SeF_5Cl[11] one would expect δ_{asym}(in-plane SF_4) (E) to have the lowest frequency of the SF_5 group deformational modes and to be infrared active. Consequently, this mode is assigned to the $325\text{-}cm^{-1}$ infrared band. Of the remaining two yet unassigned infrared-active deformational modes, the δ_{sym}(out-of-plane SF_4) or umbrella mode (A_1) should result in a very intense infrared band of relatively high frequency.[4,5,10,11] Consequently, this mode is assigned to $506\ cm^{-1}$, leaving $530\ cm^{-1}$ for assignment to the F–SF_4 wagging mode (E). The two remaining, yet unassigned in-

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Table II. Symmetry Force Constants of SF_5O^- [a]

A_1	ν_1	1154	$F_{11} = f_D$	6.46
	ν_2	733	$F_{22} = f_R$	3.75
	ν_3	697	$F_{33} = f_r + 2f_{rr} + f_{rr}'$	5 43
	ν_4	506	$F_{44} = {}^1/_2(f_\beta + 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma + 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} - 4_{\beta\gamma}' - 2f_{\beta\gamma}'')$	2.52
			$F_{12} = f_{RD}$	0 66
B_1	ν_5	541	$F_{55} = f_r - 2f_{rr} + f_{rr}'$	3 28
	ν_6	472	$F_{66} = {}^1/_2(f_\beta - 2f_{\beta\beta} + f_{\beta\beta}' + f_\gamma - 2f_{\gamma\gamma} + f_{\gamma\gamma}' - 2f_{\beta\gamma} + 4f_{\beta\gamma}' - 2f_{\beta\gamma}'')$	3 19
B_2	ν_7	452	$F_{77} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}$	1 46
E	ν_8	785	$F_{88} = f_r - f_{rr}$	2 84
	ν_9	607	$F_{99} = f_\gamma - f_{\gamma\gamma}'$	2 22
	ν_{10}	530	$F_{1010} = f_\alpha - f_{\alpha\alpha}'$	2 62
	ν_{11}	325	$F_{1111} = f_\beta - f_{\beta\beta}$	1 21
			$F_{89} = f_{r\gamma} - f_{r\gamma}''$	0 40
			$F_{810} = \sqrt{2}(f_{r\alpha} - f_{r\alpha}')$	0 50
			$F_{811} = f_{r\beta} - f_{r\beta}''$	0 28

[a] Stretching constants in mdyn/A, deformation constants in mdyn/A radian^2, and stretch-bend interaction constants in mdyn/A radian

frared inactive modes of species B_1 and B_2, respectively, belong to the Raman lines at 472 and 452 cm^{-1} Since, for numerous structurally related species, δ_{asym}(out-of-plane SF_4) (B_1) either has not been observed or was of very low intensity,[8,9,12] this mode is assigned to the very weak Raman line at 472 cm^{-1}. Hence, the last yet unassigned Raman line at 452 cm^{-1} should represent δ_{sym}(in-plane SF_4) (B_2).

Comparison of the SF_5O^- assignment with that made for SF_5Cl[4,5] (it should be noted that the assignment given in ref 7 for ν_{11} (E) is likely to be incorrect[11]) shows satisfactory agreement (see Table I). The slight discrepancy in the relative Raman intensities observed for ν_{10} (E) between the two species might be ascribed to increased coupling between ν_9 and ν_{10} in SF_5O^- due to O being more similar in mass to F than Cl This might result in a symmetric and antisymmetric rather than in a characteristic $F\text{-}SF_4$ and OSF_4 wagging motion. This assumption appears to be supported by the spectrum[13] of isoelectronic IF_5O (see Table I) for which the Raman intensity of ν_{10} is higher than that of ν_9.

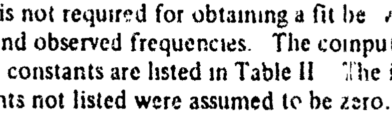
Of the four infrared bands previously reported[3] for $CsSF_5O$ only the two weaker ones agree with our observations Furthermore, the previously suggested[3] assignment of the SO stretching mode to a broad band centered at 718 cm^{-1} is obviously incorrect.

In summary, all 11 fundamentals of SF_5O^- have been observed and an assignment is offered The observed vibrational spectrum definitely supports the proposed structural model of symmetry 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,[14] assuming the following geometry and coordinate definitions. $R_{SF'} = r_{SF} = 1.60$ Å, $D_{SO} = 1.47$ Å, α (FSF) = β (F'SF) = γ (OSF) = 90°, where F' refers to the axial (unique) fluorine ligand. The symmetry coordinates used were identical with those reported[13] for IF_5O. The bond lengths were estimated by comparison with similar molecules using the correlation[15] noted by Gillespie and Robinson between stretching frequencies and bond lengths. The deformation coordinates were weighted by unit (1 Å) distance.

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 valence field has 36 constants and there are only 11 observed frequencies. It was found, that for the A_1 block the values of F_{11} and F_{22} were strongly influenced by the value of the interaction constant F_{12} Since in isoelectronic SF_5Cl[16] and in IF_5O[13] the equatorial and axial fluorine atoms do not significantly differ in their stretching force constants and since in SF_5O^- the equatorial SF stretching force constant f_r is about 3.6 mdyn/Å, we prefer for SF_5O^- a force field with $F_{22} = F_R \approx f_r$. Surprisingly, the interaction constant $F_{13} = 2f_{rD}$ had little influence on the frequencies of ν_1 and ν_3 Hence, its value might be comparable to that of F_{12} although it is not required for obtaining a fit between the computed and observed frequencies. The computed symmetry force constants are listed in Table II The interaction constants not listed were assumed to be zero.

The following values were obtained for the more important internal force constants: $f_D = 6.46$, $f_R = 3.75$, $f_r = 3\ 60$, $f_{RD} = 0.66$, $f_{rr} = 0.54$, and $f_{rr}' = 0.75$ mdyn/Å. Significantly larger values of about 4.6 and 7.7 mdyn/Å are possible for f_R and f_D, respectively, by assuming a much smaller value for f_{RD}. However, the resulting large difference between f_R and f_r renders such a force field less likely. In spite of these uncertainties in the force constants, certain conclusions can be reached. The value of the SO stretching force constant f_D (6.5 mdyn/Å) is much lower than those of 10-12 mdyn/Å generally found for S=O double bonds.[15,16] Its value is comparable to that found for the SO_4^{2-} anion (7.44 mdyn/Å[16]) indicating for SF_5O^- a SO bond order of about 1.5. Furthermore, the values of the SF stretching force constants, f_R and f_r, are somewhat lower than those generally found for covalent SF bonds (4.5-6 mdyn/Å[16]) indicating significant ionic contributions to the SF bonds in SF_5O^-. These results are best interpreted in terms of the resonance structures



These structures together with orbital-following effects could also account for the unusually strong coupling between the SO and SF stretching modes suggested by the force constant computation.

Registry No. $CsF \cdot SF_4O$, 37862-11-6.

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VIBRATIONAL SPECTRA OF TRIFLUOROACETATES

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Abstract

Infrared and Raman spectra of $CsI(O_2CCF_3)_4$ and $Cs_3I(C_2CCF_3)_6$ are reported and compared to those of the free trifluoroacetate anion and covalent trifluoroacetyl compounds. The bonding of the trifluoroacetate group in $\left[I(O_2CCF_3)_4\right]^-$ is best interpreted as being covalent with strong ionic contributions. The vibrational spectrum of the free trifluoroacetate ion is reassigned.

Introduction

The trifluoroacetate group is frequently used as a ligand in coordination chemistry. In most cases, vibrational spectroscopy is used to postulate either ionic, covalent, monodentate, or bidentate structures. However, these postulates are frequently based exclusively on minor frequency changes or splittings and consequently are not convincing. The recent synthesis [1] of $Cs^+\left[I(O_2CCF_3)_4\right]^-$ presented an opportunity to study the vibrational spectrum of a trifluoroacetato ligand expected to be considerably more covalent than metal trifluoroacetates, but more polar than organic trifluoroacetyl compounds. The covalent character of the trifluoroacetato ligand in its iodine (III) compound is suggested by the nature of its analogous perchlorato [2] and nitrato [3] salts, $Cs^+[I(OClO_3)_4]^-$ and $[N(CH_3)_4]^+[I(NO_3)_4]^-$, respectively. In addition, the skeleton of $I(O_2CCF_3)_4^-$ might be expected to have relatively high symmetry since the IF_4^- anion was recently shown [4] to be square planar. When comparing the assignments reported [5 - 8] for the free trifluoroacetate anion with those more recently reported [9 - 12] for a number of simple covalent trifluoroacetyl compounds, the need of revising the assignments for the free ion became obvious.

Experimental

The preparation of $CsI(O_2CCF_3)_4$ and $Cs_3I(O_2CCF_3)_6$ has previously been described [1]. Silver trifluoroacetate was prepared from Ag_2O and CF_3COOH and vacuum dried at 100°C [7]. Sodium and cesium trifluoroacetate were purchased from Peninsular Chemical Research. The infrared spectra of the solids were recorded as dry powders in pressed AgBr disks on a Perkin Elmer Model 457 spectrophotometer in the range 4000 - 250 cm^{-1}. The instrument was calibrated by comparison with standard calibration points [13]. The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å line of an Ar ion laser and melting point glass capillaries as sample containers in the transverse excitation-transverse viewing mode.

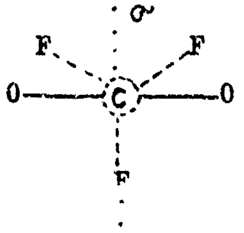
Results and Discussion

Observed Spectra

The vibrational spectra of solid $CsI(O_2CCF_3)_4$, $Cs_3I(O_2CCF_3)_6$, NaO_2CCF_3, and AgO_2CCF_3, and of an aqueous solution of NaO_2CCF_3 are shown in Figures 1 and 2. The observed frequencies are listed in Tables I and II. The Raman spectrum of an aqueous AgO_2CCF_3 solution was also recorded. It closely resembled that of the sodium salt solution and, hence, is not listed. The spectra observed for the metal trifluoroacetates are in good agreement with those previously reported [5 - 8].

Assignments for the Trifluoroacetate Ion

A comparison between the assignments reported [5 - 8] for $CF_3CO_2^-$ and those made for a series of trifluoroacetyl compounds [9] revealed major discrepancies. Consequently, the vibrational spectrum of the free trifluoroacetate ion was reassigned based on the results of the thorough studies of Berney [9] on trifluoroacetyl compounds. For the $CF_3CO_2^-$ anion, a structure of symmetry C_s was assumed based on the known [14] structure of isoelectronic CF_3NO_2. This structure



has only one symmetry element, i.e., a symmetry plane perpendicular to the CO_2 plane. Our revised assignments are summarized in Table I and were made by analogy with the well established assignments of CF_3COF [9]. The observed intensities and Raman polarization measurements are in good agreement with the predictions for symmetry C_s. For species a', one of the Raman bands (598 cm^{-1}) appears to be depolarized. However, the a' bands can be either polarized or depolarized, and the corresponding Raman band in CF_3COF also showed a high depolarization ratio of 0.78 [9].

Nature of the Iodine-Trifluoroacetate Bond in $CsI(O_2CCF_3)_4$ Covalent or Ionic?

The next and most difficult question deals with the nature of the trifluoroacetate ligand in $CsI(O_2CCF_3)_4$. A review of the literature on trifluoroacetate as a ligand reveals numerous studies. However, the conclusions reached are often conflicting. This is due to the fact that most studies deal with trifluoroacetato complexes of metals. In this type of adduct, the trifluoroacetate ligand is essentially a free trifluoroacetate ion [15], which is only weakly bonded to the metal atom. As a consequence, the vibrational frequencies of the trifluoroacetato group are very similar to those of the free trifluoroacetate ion and exhibit only small relative changes. Without detailed structural data, such as x-ray diffraction studies, it is difficult to correlate these small frequency shifts with structural parameters. For example, small changes in the O-C-O bond angle due to the size of the metal atom or crystal packing are difficult to separate from effects caused by mono or bidentate coordination.

In $CsI(O_2CCF_3)_4$, the bands due to the $C-CF_3$ part of the trifluoroacetate group are very characteristic and can readily be assigned (see Table II). Consequently, we will discuss mainly the vibrations associated with the CO_2 group and the IO_4 skeleton. To better understand the nature of the trifluoroacetate group, let us first consider the two extreme cases, i.e., the free trifluoroacetate anion and the highly covalent $CF_3C(O)OCH_3$ molecule [11]. Whereas the average of the two CO stretching frequencies (1500 cm^{-1} for $CF_3C(O)OCH_3$ and 1559 cm^{-1} for $CF_3(CO_2^-)$) and, hence, the average CO bond order changes little, their frequency separation (586 cm^{-1} for $CF_3C(O)OCH_3$ and 242 cm^{-1} for $CF_3CO_2^-$) is very different. Furthermore, in the covalent trifluoroacetates of the type XO_2CCF_3 bands due to the XO vibrations will appear and show increasing frequencies with increasing covalent character of the X-O bond. Inspection of the $CsI(O_2CCF_3)_4$ spectrum reveals a CO stretching frequency separation of about 356 cm^{-1} and the presence of skeletal IO stretching modes as high as 600 cm^{-1}. Since the frequencies of the latter almost approach the frequency range expected for covalent I-O single bonds, the bonding of the trifluoroacetate group in $CsI(O_2CCF_3)_4$ is best described as being covalent with strong ionic contributions. The ionic nature of an $X-O_2CCF_3$ bond might be expected to increase with decreasing electronegativity of the X atom. Experimental evidence for this trend has been found [16] for the trifluoroacetates of C, Si, Ge, and Sn. Within this series, the C=O stretching frequency decreases from 1852 cm^{-1} in $CF_3OC(O)CF_3$ [10] to 1750 cm^{-1} in $Sn(O_2CCF_3)_4$ [16], a frequency approaching those observed for $CsI(O_2CCF_3)_4$ (see Table II). Further proof for the highly covalent nature of the trifluoroacetates of the group IV elements consists of their high volatilities [16]. Unfortunately, only the carbonyl stretching frequencies have been reported for these trifluoroacetates [16], except for $(CH_3)_3SnO_2CCF_3$ which in CCl_4 solution shows CO_2 stretching modes at 1720, 1660, and 1400 cm^{-1} [17]. The fact that a decrease of the carbonyl frequency is generally accompanied by an increase of the C-O frequency has also been recognized by Varetti and Aymonino [18].

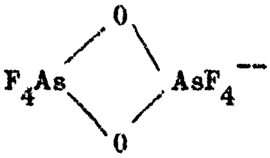
Monodentate or Bidentate? The trifluoroacetate group could function as a monodentate or as a bidentate ligand. In connection with $CsI(O_2CCF_3)_4$, we will discuss mainly covalent ligands. Again, let us consider the two ideal cases, i.e., a monodentate and a symmetric bidentate trifluoroacetate group. A covalent monodentate group should exhibit a spectrum similar to that observed for $CH_3OC(O)CF_3$ [11], i.e., a high C=O double bond and a low C-O stretching frequency. In addition, the trifluoroacetate group no longer possesses a symmetry plane. This removes the degeneracy between the FCF_2 and the antisymmetric CF_3 stretching mode and allows the observation of a total of three CF_3 stretching modes in the 1100 - 1300 cm^{-1} frequency range. For a covalent symmetric bidentate, trifluoroacetate group, the two CO bonds should be equivalent, causing a strong mixing of their stretching motions. Instead of a C=O and a C-O stretch, one obtains a symmetric and an antisymmetric CO_2 stretch with a CO bond order about 1.5. The two CO_2 stretching frequencies and their difference should be comparable to those of the free trifluoroacetate anion [19]. A minor decrease in the frequency difference might be expected for the bidentate ligand when compared to the free ion, if one assumes that the XO_2 bonding in  will decrease the CO_2 bond angle from the 120° value in the free ion towards 90°. This decrease in the bond angle would decrease the coupling between the two CO motions and make their frequencies more similar. In addition, one might expect the bidentate ligand to have the same symmetry (C_s) as the free ion and, therefore, to show only two CF_3 stretching modes owing to the degeneracy between ν_3 and ν_{11} (see Table I). Consequently, distinction between a covalent symmetric bidentate ligand and the free ion may be difficult based upon the CO_2 stretching frequencies alone. However, the appearance of the XO_2 modes in the lower frequency range of the spectrum should clearly distinguish between the two possibilities.

Application of this reasoning to $CsI(O_2CCF_3)_4$ clearly rules out the possibility of a symmetric bidentate structure. To what extent back donation of electrons of the carbonyl group (which is generally a good donor) to iodine in a monodentate structure, such as $I(O_2CCF_3)_4^-$ takes place is difficult to judge from the presently available data and might be a matter of semantics.

Skeletal Modes

It was previously shown that the IF_4^- anion is square planar having symmetry D_{4h} [4]. For the IO_4 skeleton in $I(O_2CCF_3)_4^-$ such a planar configuration is unlikely.

Comparison with other oxygen bridged species such as $F_5AsOAsF_5^{--}$ and



suggests X-O-X bond angles of about 140 and 95° [20] for mono - and bidentate bonding, respectively, of a trifluoroacetate group. The actual I-O-C bond angle should be influenced by the degree of back donation of electrons of the carbonyl oxygen to iodine and mutual repulsion between the atoms involved. In any case distortion of the IO_4 part from symmetry D_{4h} is expected and a puckered arrangement of the oxygens around iodine is likely.

Comparison of the skeletal modes of $I(O_2CCF_3)_4^-$ with those reported for the related $I(OClO_3)_4^-$ [2] and $I(OSO_2F)_4^-$ [21] anions shows relatively poor agreement. This indicates that the assumed structural models may be too simple and calls for structural studies such as x-ray diffraction, which will yield more accurate information. Similar data are required for $Cs_3\ I(O_2CCF_3)_6$.

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DIAGRAM CAPTIONS

Figure 1. - Raman spectrum of solid $Na^+CF_3CO_2^-$ (trace A), of an aqueous solution of $Na^+CF_3CO_2^-$ (traces B and C, incident polarization perpendicular and parallel, respectively, of solid $CsI(O_2CCF_3)_4$ at three different recorder voltages (traces D, E, and F), and of solid $Cs_3I(O_2CCF_3)_6$ at three different recorder voltages (traces G, H, and I). K indicates spectral slit width; exciting line 4880 Å.

Figure 2. - Infrared spectrum of solid $Na^+CF_3CO_2^-$ (trace A), of solid $Ag^+CF_3CO_2^-$ (trace B), of solid $CsI(O_2CCF_3)_4$ (trace C), and of solid $Cs_3I(O_2CCF_3)_6$ (trace D) recorded as AgBr pellets.

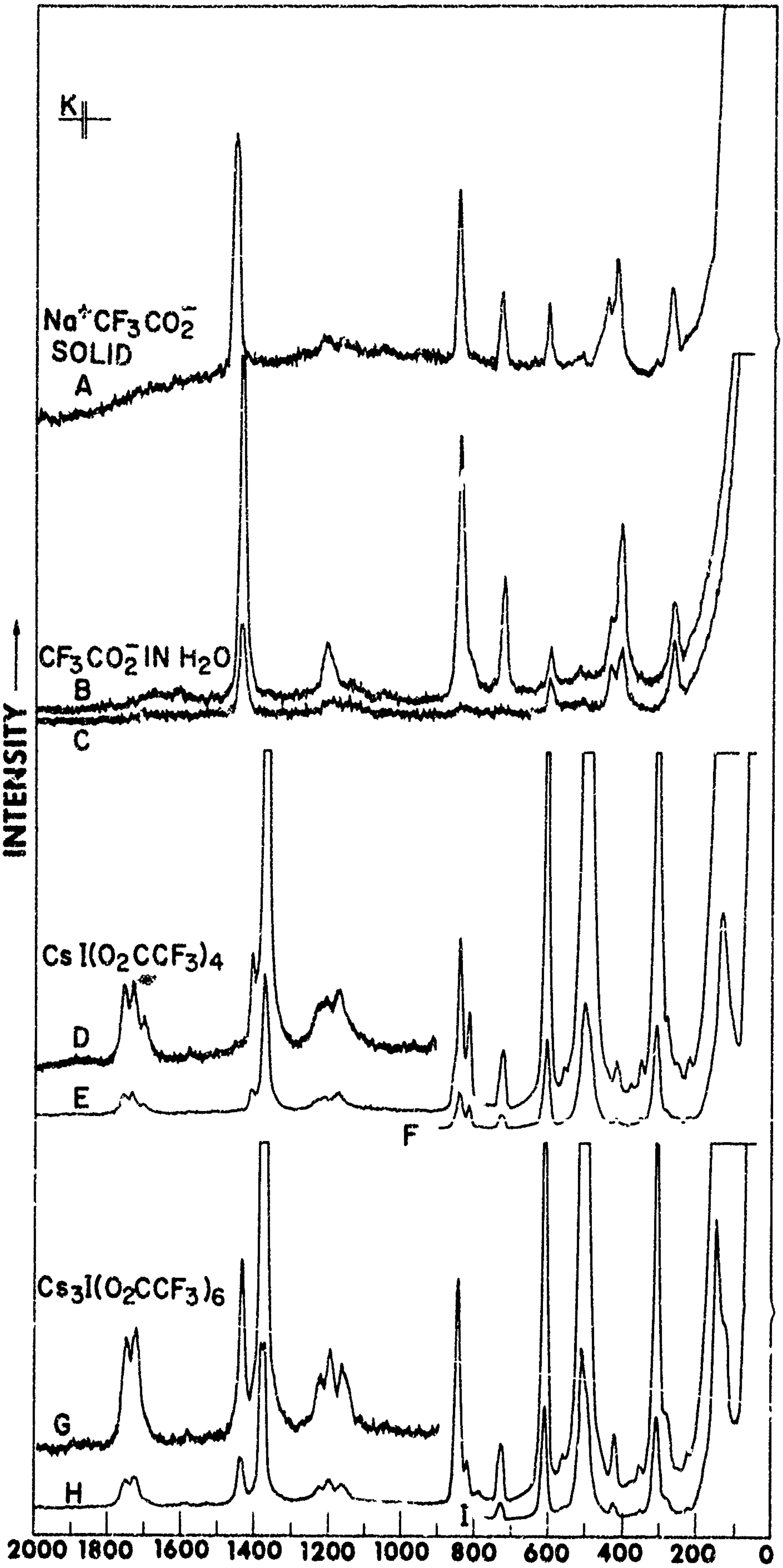K
Na$^+$CF$_3$CO$_2^-$
SOLID
A
CF$_3$CO$_2^-$ IN H$_2$O
B
C
Cs I(O$_2$CCF$_3$)$_4$
D
E
F
Cs$_3$I(O$_2$CCF$_3$)$_6$
G
H
I
INTENSITY
2000
1800
1600
1400
1200
1000
800
600
400
200
0
FREQUENCY, cm^{-1}

Figure 1

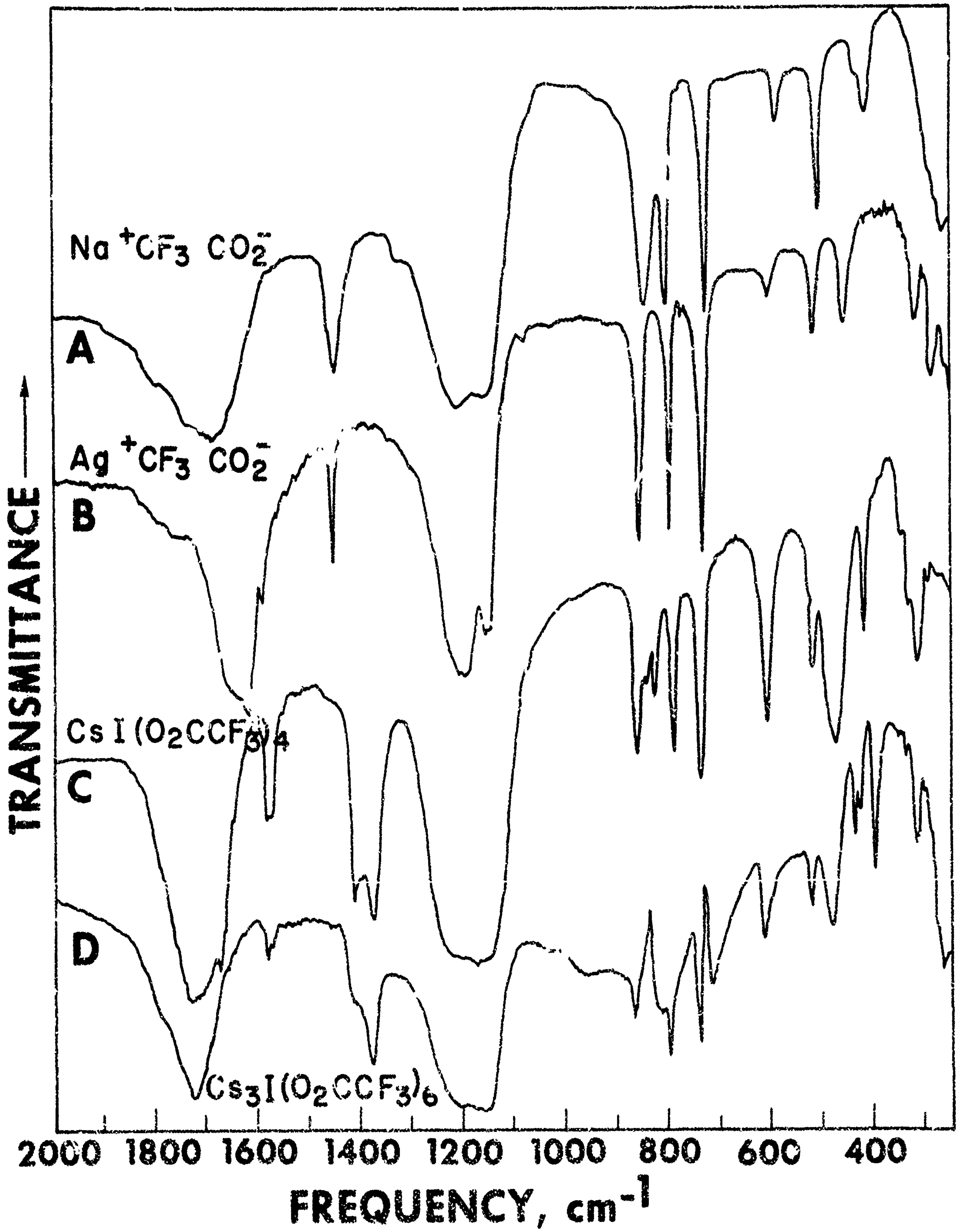
Na $^+CF_3CO_2^-$
A
Ag $^+CF_3CO_2^-$
B
CsI(O$_2$CCF$_3$)$_4$
C
D
Cs$_3$I(O$_2$CCF$_3$)$_6$
TRANSMITTANCE
2000
1800
1600
1400
1200
1000
800
600
400
FREQUENCY, cm^{-1}

Figure 2

TABLE I

Vibrational Spectrum (cm^{-1}) of the Trifluoroacetate Anion and its Assignment in Point Group C_s Compared to that of CF_3COF

$CF_3\overset{O}{C}\text{-}F$ [illegible]^a		$Na^+CF_3CO_2^-$							$Ag^+CF_3CO_2^-$			Assignment and approximate Description of Mode.	
Infrared Gas	Raman Liquid	Infrared Solid			Raman^b Solid	Raman^b Aqueous Solution			Infrared Solid		Raman^{b,c} Solid		
		[illegible]	[illegible]	This Work	This Work	[6]	[ ]	This Work	[7]	This Work			
		1466 m	1445	1446 m	1434 (10)	1441 (10)	143? vs, p	1438 (10) p	1450	1451 m	1449 (7)	a'	ν_1 $\nu_{sym}CO_2$
1340 m	1338	1213 vs	1212	1212 vs	1210 (0+) br	1211 (1.6)	120? m, p	1206 (1.0) p	1200	1206 vs	1201 (1)		ν_2 $\nu_{sym}CF_3$
1364 vs		1189 s				1188 (1.2)							ν_3 ν FCF_2
806 m	808 p	850 ms	845,841	847 ms	847 (7.2)	846 (3.2)	841 s, p	844 (6.0) p	845	852 ms	848 (10)		ν_4 ν_{C-C}
761 m	770, 758 p	807 ms		804 ms				810 sh, p	803,790	794 ms			ν_5 δ_{sciss} CO_2
682 s	694 p	729 ms	724	726 ms	726 (3)	728 (0.4)	72? m, p	727 (2.2) p	722	726 ms			ν_6 δ umbrella CF_3
596 w	596 dp		603	603 mw	602 (2.7)	596 (1.2)	601 m, p	598 (1.2) dp	600	606 mw			ν_7 δ FCF_2
390 w	385 p			422 mw	421 (4.8)	410 (1.6)	41? ms, p	409 (3.8) p	445	457 m	450 (2.5)		ν_8 antigear rock^d
238 mw	~236			—		224 (0.6)							ν_9 gear rock^d
		1689 vs	1685	1688 vs, br		1676 (0+)	168? mw, dp	1680 (0.3) br	1650, 1620	1640,1615		a"	ν_{10} $\nu_{as}CO_2$
1214 vs	~1900	1140 s	1143	1158 vs			1141 w	1145 (0.3)	1130	1150 m			ν_{11} $\nu_{as}CF_3$
519 m	520 dp		516	516 m	516 (0+)	505 (0.8)	521 w, dp	520 (0+)	513	517 m			ν_{12} $\delta_{as}CF_3$
426 W	427 dp			441 W	441 (2)	429 (1.2)	437 mw, dp	434 (1) dp	320	319 m			ν_{13} antigear wag^d
242 m	246 dp			271 W	270 (2.8)	262 (1.2)	267 m, dp	266 (1.9) dp	284	283 m	280 (1)		ν_{14} gear wag^d
50													ν_{15} τ_{C-C}

(a) For both CF_3COF and $CF_3CO_2^-$, symmetry C_s was assumed, but for CF_3COF (assuming free rotation of the CF_3 group), the symmetry plane coincides with the COF plane, whereas for $CF_3CO_2^-$ it is perpendicular to the CO_2 plane.

(b) Uncorrected Raman intensities.

(c) The Raman spectrum of an aqueous solution of $A_g^+CF_3COO^-$ was also recorded; since it was almost identical with that of the aqueous $Na^+CF_3COO^-$ solution, it is not listed.

(d) For description of this motion, see Ref. 9.

TABLE II

Vibrational Spectrum (cm^{-1}) of Solid Cs^+ $I(O_2CCF_3)_4^-$

Infrared	Raman	Assignment
	1750 (0.3)	
1710 vs, br	1725 (0.3)	$\nu_{as}CO_2$ or $\nu_{C=O}$
	1695 (0.1)	
1662 w		816 + 839 = 1655
1571 mw		
1561	1570 (0+)	
1404 m	1405 (0.2)	$\nu_{sym}CO_2$ or ν_{C-O}
1366 s	1369 (1.6)	
	1225 sh	$\nu_{sym}CF_3$
1140-1230 vs	1203 (0.2)	$\nu_{sym}FCF_2$
	1166 (0.2)	$\nu_{as}FCF_2$
854 mw	852 sh	
845 vw		
835 vw	839 (2.3)	ν_{C-C}
820 w	816 (1.3)	
782 mw	781 (0+)	$\delta_{sciss}CO_2$
727 m	725 (0.7)	$\delta_{umbrella}CF_3$
602 m	604 (5.2)	$\delta FCF_2 + \nu_{sym}$ out of phase IO_4
	555 (0.1)	
517 mw	520 sh	$\delta_{as}CF_3$
	501 (7.2)	ν_{sym} in phase IO_4
490 sh	490 sh	
470 ms		$\nu_{as}IO_4$
416 mw	418 (0.3)	antigear rock
380 sh	378 (0.1)	
346 vw	346 (0.3)	
329 vw		
310 m		antigear wag ?
305 sh	306 (5.8)	δ IO_4
293 vw		
275 sh	278 (0.1)	gear wag ?
	249 (0.2)	
	218 (0.3)	gear rock ?
	130 (10)	τ IO_4