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A simple method for the purification of fluorine is described. The formation of $NF_3^{(+)}$ radical cation salts in the low-temperature uv-photolytic synthesis of $NF_4^{(+)}$ salts was demonstrated by ESR spectroscopy. The mechanism of the $NF_4^{(+)}$ salt formation is discussed. Metathetical $NF_4^{(+)}$ salt processes based on NF_4BiF_6 were studied. A previous literature claim for the synthesis of $N_2F_5^{(+)}$ salts is refuted. The novel $N_2F_3^{(+)}$ salts $N_2F_3SnF_5$ and $N_2F_3SbF_6$ were prepared and the

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20. ABSTRACT

planar structure of the $N_2F_3^{(+)}$ cation was established. The reaction chemistry of electropositive chlorine compounds with fluorocarbons was reviewed. The vibrational spectra and force fields of BrF_3O, $FBrO_2$, $ClF_4O^{(-)}$, $BrF_4O^{(-)}$, and $IF_4O^{(-)}$ were determined. The novel oxonium salt, $H_3O^{(+)}BiF_6^{(-)}$ was prepared and its properties were investigated. Three patents on the syntheses of ClF_3O_2, nitryl perchlorate, and anhydrous metal perchlorates were issued.

FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 473, with Dr. R. S. Miller as Scientific Officer. This report covers the period 1 January 1977 through 31 December 1977. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, W. W. Wilson, and Mr. R. D. Wilson. The program was administered by Dr. L. Grant, Manager, Exploratory, Propellant and Analytical Chemistry, and Dr. K. O. Christe, Program Engineer.

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INTRODUCTION

This report covers a 12-month period and describes Rocketdyne's research efforts in the area of halogen chemistry. As in the past years, our research was kept diverse and covered areas ranging from the exploration of new synthetic methods and the syntheses of novel compounds to structural studies. Because of the importance of NF_x^+ salts as ingredients for solid propellant NF_3-F_2 gas generators for chemical HF-DF lasers, our main efforts were concentrated in this area. The existence of stable NF_4^+ salts was originally discovered by one of us in 1965 (Ref. 1) under ONR sponsorship, and much of the development in this field has since been achieved at Rocketdyne under the current ONR program. The results obtained under this program have been successfully applied to a number of past and ongoing Navy, Army, and Air Force programs, thus demonstrating the usefulness of goal-oriented basic research.

Starting with this report, only completed pieces of research will be included. As in the past (Ref. 2) completed work was summarized in manuscript form suitable for publication. Thus, time spent for report and manuscript writing is minimized, and widespread dissemination of our data is achieved.

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

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*Papers that were published during 1977, but were previously given in our last years's annual report (Ref. 2) in manuscript form, are not repeated.

PUBLICATIONS AND PATENTS DURING PAST CONTRACT YEAR

PAPERS PUBLISHED

1. "On the Synthesis and Characterization of NF_4BiF_6 and Some Properties of NF_4SbF_6," by K. O. Christe, R. D. Wilson, and C. J. Schack, Inorg. Chem., 16, 937 (1977).
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6. "Vibrational Spectra of Thionyl Tetrafluoride, SF_4O," by K. O. Christe, C. J. Schack, and E. C. Curtis, Spectrochim. Acta, 33A, 323 (1977).
7. "A Simple Method for the Purification of Fluorine," by E. Jacob and K. O. Christe, J. Fluor. Chem., 10, 169 (1977).
8. "Synthesis and Characterization of $(NF_4)_2NiF_6$," by K. O. Christe, Inorg. Chem., 16, 2238 (1977).

PAPERS PRESENTED AT MEETINGS

9. "NF_4^+ Chemistry," by K. O. Christe, 3rd Winter Fluorine Conference, St. Petersburg, Fl (January 1977).
10. "Reactions of Electropositive Chlorine With Fluorocarbons," by C. J. Schack, 3rd Winter Fluorine Conference, St. Petersburg, Fl (January 1977).

11. "Recent Progress in NF_4^+ Chemistry," by K. O. Christe, R. D. Wilson, and I. B. Goldberg, 6th European Symposium on Fluorine Chemistry, Dortmund, W-Germany (April 1977).

12. Invited seminars were given at the University of Stuttgart and the University of Ulm, Germany (April 1977).

13. "Inorganic Oxidizers and the Potential to Improve Materials," by K. O. Christe, DOD Workshop on New Opportunities for Research in Energetic Materials, Wrightsville Beach, NC (November 1977).

PAPERS SUBMITTED FOR PUBLICATION

14. "Vibrational Spectra and Force Fields of the Tetrafluorooxohalate (V) Anions, ClF_4O^-, BrF_4O^-, and IF_4O^-," by K. O. Christe, R. D. Wilson, E. C. Curtis, W. Kuhlmann, and W. Sawodny, Inorg. Chem.

15. "Bromine Trifluoride Oxide. Vibrational Spectrum, Force Constants, and Thermodynamic Properties," by K. O. Christe, E. C. Curtis, and R. Gougon, Inorg. Chem.

16. "ESR Evidence for the Formation of the NF_3^+ Radical Cation as an Intermediate in the Syntheses of NF_4^+ Salts by Low-Temperature UV-Photolysis," by K. O. Christe and I. B. Goldberg, Inorg. Chem.

17. "On the Syntheses and Properties of Some Hexafluorobismuthate (V) Salts and their Use in the Metathetical Synthesis of NF_4^+ Salts," by K. O Christe, W. W. Wilson, and C. J. Schack, J. Fluor. Chem.

18. "On the Synthesis of the $N_2F_5^+$ Cation. A Critical Comment on the Paper by Toy and Stringham," by K. O. Christe, C. J. Schack, and R. D. Wilson, J. Fluor. Chem.

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ISSUED PATENTS

21. "Stable Chlorine Trifluoride Dioxide," by K. O. Christe, U.S. 4,038,374 (July 26, 1977).

22. "Synthesis of Anhydrous Metal Perchlorates," by C. J. Schack and D. Pilipovich, U. S. 4,012,492 (March 15, 1977).

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DISCUSSION

NITROGEN FLUORIDE CHEMISTRY

NF_4^+ salts, first discovered by one of us in 1965 under an ONR contract at Stauffer Chemical (Ref. 1), are the most promising oxidizers for solid propellant NF_3-F_2 gas generators. The concept of such a gas generator was conceived (Ref. 3) and to a large extent (Ref. 4 through 9) developed at Rocketdyne. It offers significant logistics and safety advantages over cryogenic or storable liquid oxidizers for use in chemical HF-DF lasers, for example. As reported in our last annual report (Ref. 2), our work during the past several years has resulted in significantly improved oxidizers containing increased amounts of active fluorine and having the additional advantage of being self-clinkering.

During this contract year, we have continued efforts to synthesize NF_4^+ salts of even higher fluorine content, such as $(NF_4)_3AlF_6$. Efforts in this direction were unsuccessful. Alternate metathetical processes for the production of NF_4^+ salts were studied (see Appendix C). It was found that a $CsSbF_6$ based process appears most attractive. The mechanism of the UV-photolytic NF_4^+ salt formation was investigated by ESR spectroscopy. It was shown that the NF_3^+ radical cation is the key intermediate in these reactions. These results and their implications on the reaction mechanism of the NF_4^+ salt formation are summarized in Appendix B. A detailed analysis of the $^{14}NF_3^+$ and $^{15}NF_3^+$ ESR spectra will be given in next year's report in manuscript form. Samples of $^{15}NF_3$ were prepared and converted to $^{15}NF_4^+$ salts. Their vibrational spectra were recorded and the ^{14}N-^{15}N isotopic shifts were used to compute a general valence force field. These data will be summarized in the next annual report. Halogen exchange studies of NF_4^+ and NOF_2^+ salts with BCl_3 and $SiCl_4$ were studied, but the desired NCl_4^+ and $NOCl_2^+$ salts could not be isolated.

Toy and Stringham had previously reported (Ref. 10) the existence of $N_2F_5^+$ salts. Since these salts can be considered as NF_4^+ derivatives in which a fluorine ligand is substituted by an NF_2 group. We examined the possible existence of this cation. It was concluded that the previous work is most likely incorrect (see Appendix D).

Because $N_2F_3^+$ salts are useful burning aids in solid-propellant NF_3-F_2 gas generator formulations, we have studied the synthesis and characterization of these salts. Although the existence of $N_2F_3^+Sb_2F_{11}^-$ and $N_2F_3^+Sb_3F_{16}^-$ (Ref. 11) was known, the synthesis of $N_2F_3^+SbF_6^-$ had not been reported. This salt was desirable as both, a burning aid by itself and a starting material for the metathetical production of other $N_2F_3^+$ salts. We have found that $N_2F_3SbF_6$ can be prepared in quantitative yield from N_2F_4 and SbF_5 if anhydrous HF is used as a solvent. Furthermore, this salt was successfully converted to the novel $N_2F_3SnF_5$ by metathesis according to:

$$2N_2F_3SbF_6 + Cs_2SnF_6 \xrightarrow[-78C]{HF} \underset{\downarrow}{2CsSbF_6} + N_2F_3SnF_5 + N_2F_4$$

This salt is useful as a burning aid in self-clinkering formulations based on $(NF_4)_2SnF_6$. The vibrational and ^{19}F NMR spectra of $N_2F_3^+$ were reinvestigated and it was shown, that, contrary to a previous report (Ref. 12), $N_2F_3^+$ is planar. These results are summarized in Appendix E. Various NF_2X type compounds were also synthesized for testing as starting materials for NF lasers.

Bromine Oxyfluorides

Since several new bromine oxyfluorides have become known during the past 2 years, systematic studies of their spectroscopic properties and structures were carried out. Appendixes G, H, and I summarize the results obtained for BrF_3O, $FBrO_2$, and the series ClF_4O^-, BrF_4O^-, and IF_4O^-. Reactions of perhalates with halogen fluorides were studied, but these studies have not been completed as yet.

Miscellaneous

Attempts to synthesize $O_2^+ClO_4^-$ were unsuccessful. Neutron diffraction and low-temperature X-ray powder data were obtained for $O_2^+AsF_6^-$, $H_3O^+AsF_6^-$, and $D_3O^+AsF_6^-$. However this study is still under progress. The novel oxonium salt $H_3O^+BiF_6^-$ was prepared and characterized (see Appendix C). It was shown that BiF_5 is an excellent water removing agent for wet HF. Such a process could be of extreme importance for large-scale production of NF_4^+ salts by metathesis in anyhdrous HF. A simple method was developed for the purification of elemental fluorine (see Appendix A). Its main advantage is that only the impurities, but not the bulk of the fluorine, are converted into other compounds. Much work has been recently performed in the area of electropositive chlorine compounds. Since a large percentage of this work was done under this contract, this field was reviewed (see Appendix F). Three patents on ClF_3O_2, NO_2ClO_4, and anhydrous metal perchlorates have issued during 1977 and are given as Appendices J, K, and L.

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APPENDIX A

A SIMPLE METHOD FOR THE PURIFICATION OF FLUORINE

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SHORT COMMUNICATION

A Simple Method for the Purification of Fluorine

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A simple method for the purification of fluorine gas is described. With the exception of nitrogen and argon, all impurities usually present in commercial fluorine can be readily removed by 1) conversion of O_2 to non-volatile O_2^+ salts, and 2) a 70 to 63°K trap-to-trap distillation.

Commercial fluorine gas contains 1-2% of impurities, primarily O_2, N_2 and HF with trace amounts of Ar, CO_2, CF_4, C_2F_6, C_3F_8, COF_2, NF_3, OF_2, SiF_4, SF_6, SO_2F_2, and others [1-5]. For most preparative purposes the O_2 content of fluorine does not interfere with the desired reactions, and the purification of F_2 can be limited to the removal of HF by a NaF scrubber. For example, a nearly quantitative synthesis of IrF_6 is possible by heating Ir metal in an atmosphere of 20% F_2 and 80% O_2 [6]. However, there are applications, where oxygen free fluorine is needed. A typical example is the HF-DF chemical laser. It is known [7,8] that molecular oxygen acts as an inhibitor for the chain branching reaction of H_2 and F_2. In addition, the presence of O_2 causes the formation of water which is a very strong deactivator for vibrationally excited HF or DF [9]. In order to obtain meaningful baseline data, oxygen free fluorine is required. Furthermore, in the syntheses of the very expensive platinum metal hexafluorides RuF_6, RhF_6, and PtF_6 the yield of the products is decreased by the formation of the undesired and volatile [10] $O_2^+MF_6^-$ salts. Similarly, in the syntheses of ReF_7 and OsF_6 the presence of O_2 results in the formation of the corresponding oxide pentafluorides. Other applications requiring high purity fluorine include calorimetry [1], and spectroscopic [11, 12] and analytical [3] studies.

Previously described methods for the purification of fluorine involved either low-temperature distillation [2-4], low-temperature uv-photolysis [13], or the pyrolysis of K_2NiF_6 in the presence of KF [4]. These methods have the following shortcomings. The low-temperature distillations require rather complex and expensive equipment which is beyond the reach of most laboratories. The low-temperature uv-photolysis involves the irradiation of liquid fluorine in a glass apparatus to convert O_2 to the less volatile O_2F_2, followed by a distillation at 90°K. This method is not suitable for scale-up, and the handling of larger amounts of liquid fluorine in a glass apparatus presents a potential hazard. The pyrolysis of K_2NiF_6-KF mixtures is somewhat cumbersome, because the bulk of the material and not the impurity must be converted to a nonvolatile compound. In this paper, we describe an alternate method which we have found to be more convenient than those previously reported.

(1) Removal of Oxygen

We have found that the well known [14-16] reaction

$$O_2 + F_2 + nSbF_5 \xrightarrow{\Delta E} O_2^+SbF_6^- \cdot (n-1)SbF_5$$

is ideally suited for the removal of oxygen impurities from fluorine. Either heating [14] or uv-photolysis [15] can be used for activation of the reaction. Of these two activation energy sources, thermal activation is preferred owing to its scalability and simplicity.

In a typical example, crude F_2 (17 g, 500 mmol) [17] and SbF_5 (2.1 g, 10 mmol) [18] in a 1.2 ℓ Monel reactor were heated for 2 h to 460°K. The vessel was cooled to 90°K and the F_2 was distilled into a container kept at 77°K. The excess of unreacted SbF_5 was removed from the Monel vessel by pumping at room temperature. The vessel was opened in a dry box and contained 1.1 g of a white solid which was identified by its vibrational spectra [16] as $O_2^+Sb_2F_{11}^-$. The above procedure was repeated with pretreated F_2. In this case, no evidence for the formation of any O_2^+ salt was obtained and the reaction vessel showed clean inner surfaces. It can therefore be assumed that the oxygen was quantitatively removed by a single heating cycle.

(2) Removal of Trace Impurities

It is known that impurities which have no measurable vapor pressure at 90°K can be removed from F_2 by a 90 to 77°K trap-to-trap distillation. For the removal of the more volatile impurities CF_4, NF_3, and OF_2, however, lower temperatures are required. In our experience, a 70 to 63°K trap-to-trap distillation can be carried out with relative ease and removes all remaining impurities, except for N_2 and Ar which usually do not interfere with most applications. Since the amount of N_2 present in commercial F_2 can vary strongly depending on the batch and supplier, no meaningful number can be quoted for the overall purity of the F_2 obtained by our method. The temperature of 63°K (nitrogen slush bath) is easily obtained by either pumping on liquid N_2 or by passing a stream of helium, precooled to 77°K, through liquid N_2. The temperature of 70°K is obtained either by passing He through liquid N_2 or by allowing a 63°K trap to gradually warm towards 70°K. The purity of F_2 after two 70 to 63°K trap-to-trap distillations was tested by recording its infrared spectrum as a solid [12] at 12°K. No detectable impurities were observed. The absence of impurities volatile at 70°K but nonvolatile at 63°K in the purified fluorine was established by mass spectroscopy.

Thus, a 70 to 63°K trap-to-trap distillation combined with the O_2 scavenging method using SbF_5 provides a convenient purification method for fluorine.

One of us (KOC) is indebted to Drs. L. R. Grant and C. J. Schack for helpful discussions and to the Office of Naval Research,Power Branch, for financial support.

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Contribution from Rocketdyne, A Division of
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ESR Evidence for the Formation of the NF_3^+ Radical Cation as an Intermediate in the Syntheses of NF_4^+ Salts by Low-Temperature UV-Photolysis

Karl O. Christe* and Ira B. Goldberg

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The mechanism of the formation of NF_4^+ salts is of significant practical and theoretical interest. From a practical point of view, a better understanding of this mechanism would permit optimization of the reaction conditions for the direct syntheses of NF_4^+ salts, such as NF_4BF_4, NF_4PF_6, or NF_4GeF_5.[1] From a theoretical point of view, the formation of the NF_4^+ cation is intriguing[2] because its parent molecule, NF_5, does not exist as a stable species. Since under the conditions used for most of the syntheses of NF_4^+ salts an F^+ cation should be extremely difficult, if not impossible, to prepare by chemical means, the following mechanism has previously been proposed[2] for the formation of NF_4AsF_6:

$$F_2 \xrightarrow{\Delta E} 2F^{\cdot} \qquad (1)$$

$$F^{\bullet} + AsF_5 \longrightarrow AsF_6^{\bullet} \qquad (2)$$

$$AsF_6^{\bullet} + NF_3 \longrightarrow \dot{N}F_3^{+}AsF_6^{-} \qquad (3)$$

$$\dot{N}F_3^{+}AsF_6^{-} + F_2 \longrightarrow NF_4^{+}AsF_6^{-} + F^{\bullet} \qquad (4)$$

In good agreement with the known experimental facts,[2] this mechanism requires only a moderate activation energy ($D^{\circ}(F_2) = 36.8$ kcal mol^{-1})[3]. The two critical intermediates are the $AsF_6^{\bullet}$ radical and the $\dot{N}F_3^{+}$ radical cation. Whereas the $AsF_6^{\bullet}$ radical is unknown, the $\dot{N}F_3^{+}$ radical cation was shown[4] to form during γ-irradiation of NF_4^{+} salts at -196°. Although this observation of the $\dot{N}F_3^{+}$ cation demonstrated its possible existence at low temperature, it remained to be shown that the $\dot{N}F_3^{+}$ radical cation is indeed formed as an intermediate in the syntheses of NF_4^{+} salts. We have now succeeded in observing experimentally the $\dot{N}F_3^{+}$ radical cation by esr spectroscopy as an intermediate in the low-temperature uv-photolyses of both the NF_3-F_2-AsF_5 and the NF_3-F_2-BF_3 system. The results and implications derived from the observations are given in this paper.

Experimental Section

Binary and ternary mixtures of the starting materials were prepared for both the NF_3-F_2-BF_3 and the NF_3-F_2-AsF_5 systems in a stainless steel Teflon FEP vacuum system. The sample tubes consisted of flamed out quartz tubes of 4 mm o.d., 30 cm long, with a ballast volume of about 150 ml attached at the top. The starting materials were condensed into these tubes at -210° and the tubes were flame sealed. The NF_3 (Rocketdyne) was used without further purification, F_2 (Rocketdyne) was passed through a NaF scrubber for HF removal, and BF_3 (Matheson) and AsF_5 (Ozark Mahoning) were purified by fractional condensation prior to use. About 300 cc of gas mixture was used for each sample tube in the following mol ratios, $NF_3:F_2$ = 1:10; $BF_3:F_2$ = 1:10; $AsF_5:F_2$ = 1:10; $NF_3:BF_3$ = 1:1; $NF_3:AsF_5$ = 1:1; $NF_3:F_2:BF_3$ = 1:4:1 and 1:2:1; $NF_3:F_2:AsF_5$ = 1:4:1.

The ESR spectra were recorded as previously described.[5,6] Variable temperature control over the temperature range 4-300°K was achieved with an Air Products liquid helium transfer refrigerator Model LTD110. For the photolyses, an Oriel Model 6240 Arc Lamp with a 200 watt Hg lamp was used. In some of the experiments, the starting materials were condensed at -196°C into the tip of the ESR tube and were irradiated for 10 to 30 minutes while inserted in a liquid nitrogen filled unsilvered dewar. The ESR tube was then quickly transferred to the precooled esr spectrometer. In other experiments, the sample tubes were irradiated at various temperatures inside the ESR cavity.

Results and Discussion

Uv-photolysis of both the NF_3-F_2-AsF_5 and the NF_3-F_2-BF_3 system produced an intensely violet colored species which exhibited the ESR signal shown in Figure 1, traces A and B. Comparison with the previously published[4] anisotropic spectrum of the $\dot{N}F_3^+$ cation (trace C, Figure 1) establishes beyond doubt the presence of $\dot{N}F_3^+$ in our samples. The spectra are assigned on the basis of anisotropic hyperfine coupling to three fluorine atoms (I=1/2) and approximately isotropic hyperfine coupling to one nitrogen atom (I=1). The g-matrix is isotropic to within the linewidth. The spectra thus appear as a quartet of triplets as shown in Figure 1. The broader linewidths observed in the spectra of UV irradiated NF_3-F_2-AsF_5 and NF_3-F_2-BF_3 mixtures than in γ-irradiated

NF_4SbF_6 may be the result of exchange or of dipolar interactions of materials on the surfaces of the solid components of the mixtures.

The observation of identical signals for both the BF_3 and the AsF_5 containing system proves that the signal must be due to a species not containing boron or arsenic. By carrying out irradiation experiments of the sample within the ESR cavity at -196°C, it was shown that the signal strength increased during irradiation, but did not decrease when the lamp was turned off. The thermal stability of the signal in the absence of uv radiation depended on the strength of the Lewis acid used. For the stronger Lewis acid AsF_5, the signal did not change significantly up to about -105°C, whereas for BF_3 decomposition started at about -155°C. When the sample tubes were warmed to ambient temperature, they contained white stable solids which were identified by Raman spectroscopy as NF_4AsF_6 and NF_4BF_4, respectively. [1,7,8] Irradiation of all possible binary mixtures, i.e. NF_3-F_2, Lewis acid -F_2, and NF_3 - Lewis acid, under comparable conditions did not product any ESR signal attributable to $\dot{N}F_3^+$.

A positive identification of the proposed $AsF_6^\bullet$ or $BF_4^\bullet$ radical intermediates was not possible in the above experiments. The observation of hyperfine splittings for the free $AsF_6^\bullet$ or $BF_4^\bullet$ radical at temperatures above several °K is not likely because they would be in orbitally degenerate states which could cause rapid spin relaxation resulting in a strongly temperature dependent line width. Furthermore, if we assume the existence of an $AsF_6^\bullet$ or $BF_4^\bullet$ radical in an ionic lattice, rapid electron exchange between the radicals and the corresponding anions is possible which would destroy hyperfine structure. The line width of the resulting signal would depend on the rate of exchange. Finally, in our experiments we were dealing with polymeric solid AsF_5 or BF_3 phases which on combination with a fluorine radical are not likely to result in an isolated $AsF_6^{\cdot}$ r $BF_4^{\bullet}$ radical. In our experiments, several ESR signals were observed in addition to $\dot{N}F_3^+$. However, in the absence of observable hyperfine structure we prefer not to make any assignments.

Based on the above results, the following conclusions can be reached concerning the formation mechanism of NF_4^+ salts: (i) the $\dot{N}F_3^+$ radical cation is indeed an important intermediate. (ii) The requirement of uv activation and of both F_2 and a Lewis acid for the synthesis of $\dot{N}F_3^+$ is in agreement with steps (1) and (2) of the above given mechanism. (iii) The strength of the Lewis acid determines the thermal stability and lifetime of the intermediate $\dot{N}F_3^+$ salt formed. This can account for the low temperature conditions required for the synthesis of the NF_4^+ salts of weaker Lewis acids. (iv) In the absence of uv irradiation, the $\dot{N}F_3^+$ salts do not spontaneously react with the large excess of liquid F_2 present. This indicates that in the absence of an activation energy source the thermodynamically feasible[2] chain propagation step $\dot{N}F_3^+AsF_6^- + F_2 \longrightarrow NF_4^+AsF_6^- + F^{\cdot}$ does not play an important role. Possibly, the conversion of $\dot{N}F_3^+AsF_6^-$ to $NF_4^+AsF_6^-$ may require $F^{\bullet}$ atoms according to:

$$\dot{N}F_3^+AsF_6^- + F^{\bullet} \longrightarrow NF_4^+AsF_6^- \qquad (5)$$

Since the intermediate $\dot{N}F_3^+$ salt is an ionic solid, its reaction with a fluorine atom might well be a heterogeneous diffusion controlled reaction and step (5) might be the rate determining step in the above mechanism. It was shown that at temperatures above -196°C, where a given $\dot{N}F_3^+$ salt is still stable in the absence of light, uv irradiation causes a rapid decay

decay of the $\dot{N}F_3^+$ ESR signal. However, it was not possible to distinguish whether this decay was caused by photodecomposition of the intermediate $\dot{N}F_3^+$ salt or by the reaction of the latter with the generated F atoms according to step (5).

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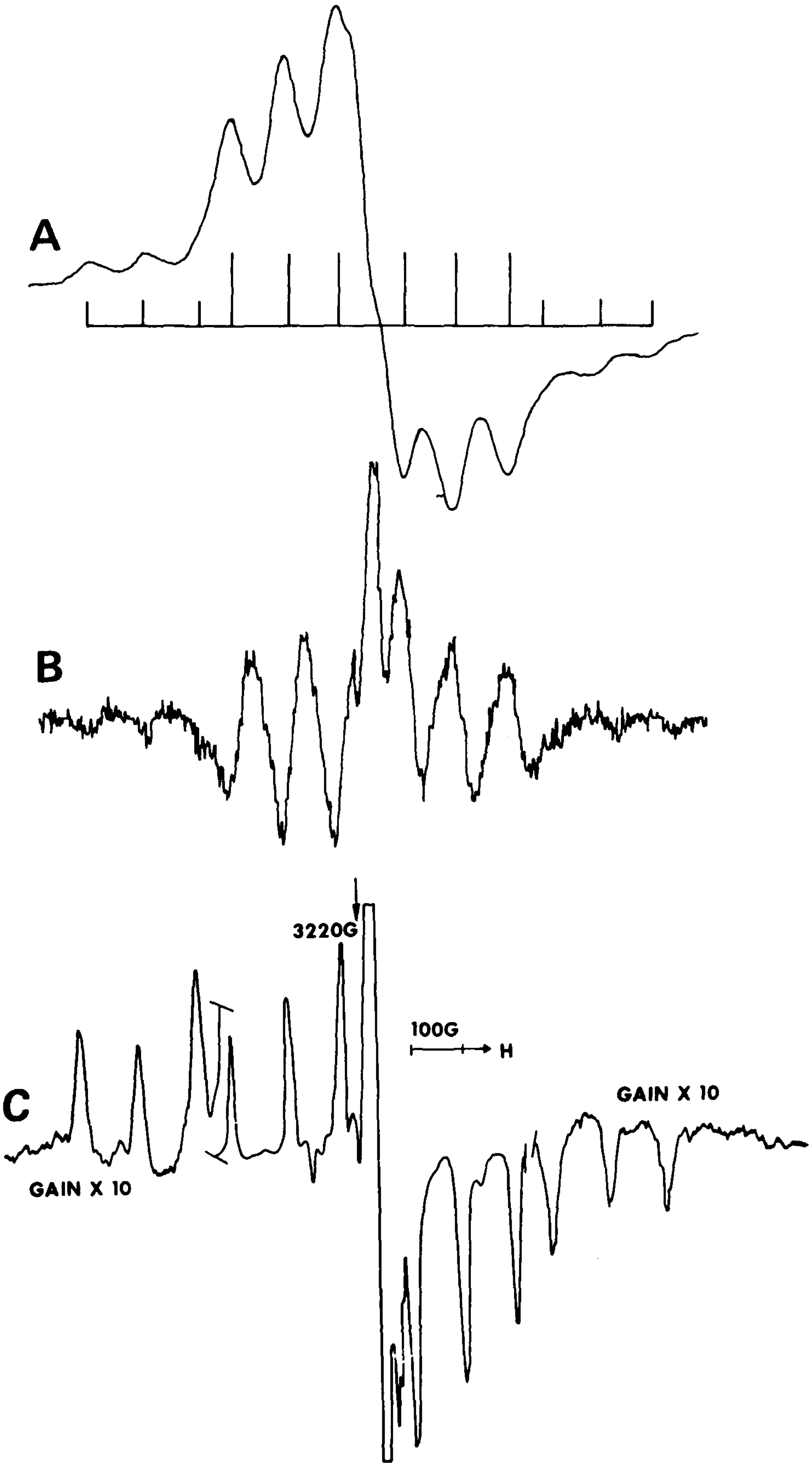
Figure Caption

Figure 1. ESR spectra of the $\dot{N}F_3^+$ radical cation obtained by uv photolysis of $NF_3 - F_2 - BF_3$ at -196°C; trace A, first derivative; trace B, second derivative. For comparison, the known[4] first derivative spectrum of $\dot{N}F_3^+$ obtained by γ-irradiation of polycrystalline NF_4SbF_6 at -196°C is given as trace C.



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APPENDIX C

ON THE SYNTHESES AND PROPERTIES OF SOME HEXAFLUOROBISMUTHATE (V) SALTS AND THEIR USE IN THE METATHETICAL SYNTHESIS OF NF_4^+ SALTS

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SUMMARY

The salts $LiBiF_6$, $NaBiF_6$, $KBiF_6$, $CsBiF_6$ and NF_4BiF_6 were prepared and characterized. Differences in the observed numbers and relative intensities of some of the Raman bands of these salts are explained by crystal effects. Solubilities of these salts in anhydrous HF at -78° were determined and compared to those of the corresponding SbF_6^- salts. It was shown that, contrary to a previous report, $CsBiF_6$ does not exhibit any unusual properties such as forming a mushy volatile HF adduct. The potential of NF_4BiF_6 based metathetical processes for the production of other NF_4^+ salts was evaluated. The novel $H_3O^+BiF_6^-$ salt was prepared and characterized. The usefulness of BiF_5 for water removal from HF is briefly discussed.

INTRODUCTION

In the course of our work on oxonium salts [1] and metathetical NF_4^+ salt processes [2-6], we became interested in pentavalent bismuth compounds as possible replacements for the corresponding antimony compounds. For example, the use of the less volatile BiF_5 has been proposed [1], but has never been tested, as an alternative to SbF_5

for removal of small amounts of water from HF. Because NF_4BiF_6 has become readily accessible by direct thermal synthesis from NF_3, F_2, and BiF_5 [7], it holds potential as a starting material in metathetical processes for the production of other less accessible NF_4^+ salts. However, its usefulness in such a process depends on the relative solubilities of its salts in a suitable solvent, such as anhydrous HF. Although BiF_6^- salts have been known [8] since 1950, only a small number of papers [7, 9-18] dealing with BiF_6^- salts have been reported since then, and some of the reported data are very much open to question. For example, Surles and coworkers reported [13] that HF formed a stable adduct with $CsBiF_6$ and that this adduct readily sublimed on heating. Consequently, a more systematic study of BiF_6^- salts was necessary in order to be able to properly evaluate the potential of BiF_6^- salts in the above applications.

EXPERIMENTAL

Materials and Apparatus

The apparatus, handling procedures, and the method used for the HF drying have previously been described [1,6]. Bismuth pentafluoride (Ozark Mahoning Co.) did not contain any detectable impurities and was used as received. Antimony pentafluoride (Ozark Mahoning Co.) was distilled prior to use. Lithium fluoride (Baker, A. R.) and NaF (MCB, Reagent grade) were used as received. Potassium fluoride (Allied, Reagent grade) and CsF (KBI) were dried by fusion in a platinum crucible and powdered in the drybox. The syntheses of NF_4BiF_6 [7] and NF_4SbF_6 [4] have previously been described. Except for $NaBF_4$ which was obtained from H_3BO_3 and Na_2CO_3 in concentrated aqueous HF solution, all the alkali metal tetrafluoroborates were prepared by introducing a slight excess of gaseous BF_3 into stirred solutions of the corresponding alkali metal fluorides in anhydrous HF at 20°, followed by removal of the volatile products.

Syntheses of BiF_6^- and SbF_6^- Salts

For the syntheses of the alkali metal hexafluorobismuthates, equimolar amounts of finely powdered alkali metal fluoride and BiF_5 were heated in a Monel cylinder for several days to 280° under 2 atm of F_2. The vibrational spectra of the resulting products showed no evidence for the presence of either unreacted BiF_5 [19] or polybismuthate salts [7]. When these reactions were carried out at 150°, however, the products contained some polybismuthate salts. The alkali metal hexafluoroantimonates were prepared in a similar manner by heating equimolar mixtures of SbF_5 and the corresponding alkali metal fluoride in a F_2 atmosphere to 280°. Again, vibrational spectra of the solid products showed no evidence for the presence of polyantimonates.

Spectra

Infrared spectra of solids were recorded as dry powders between pressed AgCl or AgBr disks on a Perkin Elmer Model 283 spectrometer. Raman spectra were recorded in glass melting point, quartz or Kel-F capillaries on a Cary Model 83 spectrophotometer using the 4880Å exciting line of an Argon ion laser. Debye-Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel filtered copper Kα radiation and quartz capillaries as sample containers. The thermal decomposition of salts was examined with a Perkin Elmer differential scanning calorimeter (Model DSC-1B) using crimp-sealed aluminum pans as sample containers and a heating rate of 2.5°/min at atmospheric pressure.

Solubility Measurements

Solubilities of the salts in anhydrous HF at -78° were measured in an apparatus similar to that previously described [6] for metathetical reactions, except for eliminating trap I. Saturated solutions were prepared at -78° and separated from excess undissolved salt by filtration at -78°. The HF solvent was pumped off at ambient temperature, and the amount of HF used and of the solid residues obtained after HF removal were determined by weighing.

Metathetical Reactions

Metathetical reactions between NF_4BiF_6 or NF_4SbF_6 and different alkali metal tetrafluoroborates in anhydrous HF solution were carried out as previously described [4,6].

Synthesis of H_3OBiF_6

Bismuth pentafluoride (10.08 mmol) was transferred in the glove box into a passivated (with ClF_3) Teflon FEP ampule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10.12 g) which had been stored over BiF_5 was condensed into the ampule at -196°. The mixture was warmed to room temperature, and the Raman spectrum of the resulting clear solution was recorded. It showed bands similar, but not identical, to those expected for either BiF_6^- (see below) or solid BiF_5 [16, 19]. The ampule was cooled to -196°, and distilled H_2O (10 mmol) was syringed into the ampule. On warm up to ambient temperature, a copius white precipitate was formed. The mixture was stirred for ten hours at 25°. The Raman spectrum of the clear solution above the white solid precipitate showed the bands characteristic for BiF_6^- (see below). Removal of the HF solvent in a dynamic vacuum at -45° resulted in the formation of a white solid (3.469g, weight calcd for 10.08 mmol of H_3OBiF_6 = 3.447g) which was identified by Raman and infrared spectroscopy as $H_3O^+BiF_6^-$. This solid was stable at ambient temperature only under an HF pressure of about 20mm. On evacuation of the ampule, the white solid would immediately turn dark brown. When the valve of the ampule was closed to allow the pressure to build up again, the white color of the sample was restored. Complete decomposition of H_3OBiF_6 in a dynamic vacuum at 35°for 3 days resulted in a light cream colored solid. Based on its weight, physical properties (nonhygroscopic, insoluble in H_2O and aqueous HCl, sublimination at the softening point of glass), and elemental analysis (found: Bi, 77.2; F, 23.3; O, 0.2; calcd for BiF_3: Bi, 78.57, F, 21.43; O, 0) this solid appeared to be mainly BiF_3. The vibrational spectra of the solid decomposition product did not show any evidence for the presence of either H_3O^+ or BiF_6^-.

RESULTS AND DISCUSSION

Syntheses and Properties of Hexafluorobismuthates

The alkali metal hexafluorobismuthates were prepared from equimolar amounts of BiF_5 and the corresponding alkali metal fluoride by heating to 280° in a Monel cylinder. Fluorine was added to the cylinder to suppress possible decomposition of BiF_5 to BiF_3 and F_2. This synthesis is similar to that [9] previously reported, except for using a significantly higher temperature. Using the previously reported [9] temperature conditions (85-150°), the product always contained some polybismuthate salt. For the syntheses of the alkali metal hexafluoroantimonates, similar reaction conditions were required to suppress the formation of polyantimonates.

The rather unusual properties previously reported [13] for $CsBiF_6$ could not be confirmed. Thus, $CsBiF_6$ was quantitatively recovered from HF solutions by pumping at ambient temperature, without any evidence for the formation of a stable $CsBiF_6 \cdot xHF$ adduct. Furthermore, no evidence was found for sublimation without decomposition for either HF treated or untreated $CsBiF_6$. DSC data obtained for $CsBiF_6$ showed a small reversible endotherm at 190°, attributed to a phase change, and the onset of a large endotherm at 308°, attributed to decomposition. Thermal decomposition of $CsBiF_6$ around 300° was confirmed by visual observation of samples sealed in melting point capillaries. At this temperature, sublimation of BiF_5 to the colder parts of the capillary occurred. For comparison, DSC data were also recorded for $CsSbF_6$. They showed a small reversible endotherm (phase change) at 187° and the onset of endothermic decomposition at 296°. These data show that the thermal stabilities of $CsSbF_6$ and $CsBiF_6$ are similar, with the bismuth salt being slightly more stable.

The vibrational spectra of the alkali metal hexafluorobismuthates were also recorded and showed some remarkable differences (see Figure 1). Particularly, the Raman active deformation mode exhibited different numbers of bands and intensity ratios. In order to determine whether the observed splittings were caused by the simultaneous presence of more than one crystal modification, the Debye-Scherrer powder patterns of these compounds were recorded. In excellent agreement with a previous report [10], it was found that $LiBiF_6$ and $NaBiF_6$ were rhombohedral ($LiSbF_6$ type), $KBiF_6$ was cubic (low-temperature α-modification), and $CsBiF_6$ was rhombohedral ($KOsF_6$ type). No evidence was found for the presence of other modifications in either the thermally prepared (280°) or the HF recrystallized (-78°) samples. The observed splittings can be readily explained, however, by solid state effects. In the rhombohedral compounds (space group $R\bar{3}-C_{3i}^2$, Nr. 148, 1 molecule per Bravais cell [10]), the site symmetry of BiF_6^- is C_{3i}.

TABLE I. Correlation Table for Isolated BiF_6^- of Point Group O_h and for Site Symmetry C_{3i}

O_h	C_{3i}
A_{1g}	A_g
E_g	E_g
F_{2g}	$A_g + E_g$
F_{1u}	$A_u + E_u$
F_{2u}	$A_u + E_u$

Therefore, from Table I only the F_{2g} mode in the Raman and the F_{1u} modes in the infrared are expected to be split into two components. For cubic $KBiF_6$ (space group Ia3, Nr. 206) the site symmetry of BiF_6^- is again C_{3i}, but since the Bravais cell contains four molecules, factor group splitting can further cause the doubly degenerate E_g modes to split into two components. These predictions are in good agreement with our observations (see Figure 1), except for $NaBiF_6$ which exhibits only one Raman band in the BiF_6^- deformation region. This lack of splitting for $NaBiF_6$ is attributed to a coincidence of the frequencies of the A_g and the E_g components of ν_5. This is plausible since the weaker (probably the E_g) component has a higher frequency in $LiBiF_6$ and a lower frequency in $CsBiF_6$ than the more intense (probably the A_g) component. The frequency separation of the two components in $NaBiF_6$ must be rather small since, even at a spectral slit width of 1 cm^{-1}, we could not resolve the band into two components.

The infrared spectrum of $CsBiF_6$ (see Figure 1) shows a very intense and broad band for the antisymmetric BiF_6^- stretching mode ν_3 (F_{1u}) at 570 cm^{-1}. It exhibits a pronounced shoulder at 590 cm^{-1} which probably represents the second component of ν_3 predicted for C_{3i} symmetry (see Table 1). In addition, several infrared allowed combination bands were observed (see Figure 1). From these, the frequencies of the two remaining deformation modes can be derived as: $\nu_4(F_{1u}) = 277$ and $\nu_6(F_{2u}) = 147$ cm^{-1}. It should be noted that the combination bands involving ν_3 show splittings of about 20 cm^{-1}, analogous to that exhibited by ν_3 itself. This lends further support to the above assignments.

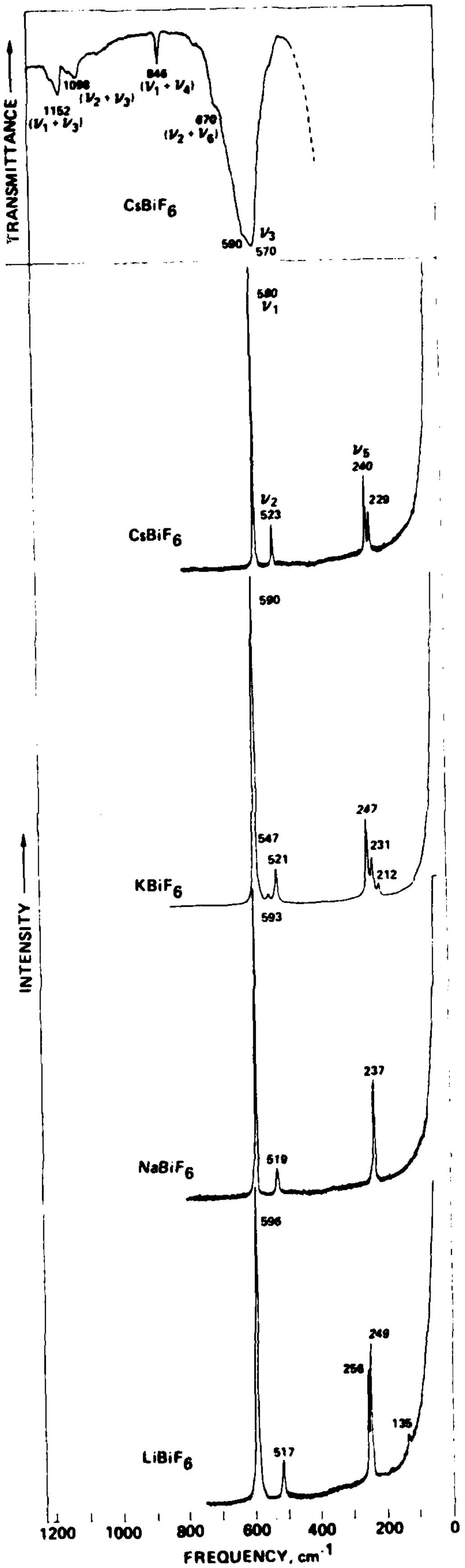
The previously reported [16] Raman spectrum of $NOBiF_6$ exhibits the same splittings and intensity pattern as α-$KBiF_6$, indicating that the two compounds are probably isotypic. Of the six frequency values reported by Bougon and coworkers [14] for BiF_6^-, ν_4 and ν_5 appear too low and should be revised. In agreement with a previous report [7], it was found that infrared spectroscopy is well suited for the detection of polybismuthate impurities in BiF_6^- salts. The polyanions result in an intense infrared band at around 440 cm^{-1}.

Solubility Measurements

The metathetical production of NF_4^+ salts is based on the following principle. A readily available and highly soluble NF_4^+ salt, such as NF_4SbF_6, is reacted in a suitable solvent, such as anhydrous HF, with

<u>Figure 1</u>.

Infrared spectrum of $CsBiF_6$ and Raman spectra of $CsBiF_6$, $KBiF_6$, $NaBiF_6$, and $LiBiF_6$. The infrared spectrum was recorded as a dry powder between pressed AgCl disks. The broken line is due to absorption by the window material.



an alkali metal salt containing the desired anion. If the alkali metal is chosen in such a manner that the starting materials and the desired NF_4^+ salt product are highly soluble and the resulting alkali metal SbF_6^- salt, for example, is of very low solubility, the following general equilibrium, where X=Sb, can be shifted far to the right hand side:

$$MY + NF_4XF_6 \xrightarrow{HF} MXF_6\downarrow + NF_4Y$$

The principle has been demonstrated for salts where Y = BF_4^- [2-4], SnF_6^{2-}[6], TiF_6^{2-}[5], and NiF_6^{2-}[20]. Prior to now, X had always been Sb; but the case where X could be Bi had not been tested. Since NF_4BiF_6 has recently become readily available by direct synthesis [7], and since an extrapolation of crude solubility data, previously measured [2] for alkali metal XF_6^- salts (X=As, Sb) in HF at room temperature, indicated that $LiBiF_6$ might possess the lowest solubility of any MXF_6 salt, quantitative solubility data for MXF_6 salts in anhydrous HF were desired. These data should allow to determine whether a BiF_6^- based process would offer any significant advantages over one based on SbF_6^-.

The solubilities of NF_4^+ and of several alkali metal BiF_6^- and SbF_6^- salts were measured in anhydrous HF at -78°. The low temperature was chosen based on our past experience [4]. The results of our measurements are summarized in Table II. As can be seen, the measured solubilities clearly favor a process based on a cesium rather than a lithium salt. Furthermore, the solubility of $CsBiF_6$ is only slightly lower than that of $CsSbF_6$, thus not compensating for the significantly lower solubility of the NF_4BiF_6 starting material in HF and its less favorable formation rate [7], compared to those of NF_4SbF_6 [4]. Consequently, based on all the presently available experimental data, a $CsSbF_6$ based process appears to be the most attractive method for the metathetical preparation of other NF_4^+ salts.

TABLE II. Solubilities of Various BiF_6^- and SbF_6^- Salts in Anhydrous HF at -78°

Anion / Cation	SbF_6^-		BiF_6^-	
	a	b	a	b
NF_4^+	259.0	0.7951	173.1	0.4191
Li^+	9.21	0.0379	11.9	0.0361
Na^+	7.48	0.0289	25.6	0.0740
K^+	c	c	20.2	0.0558
Cs^+	1.80	0.00488	1.71	0.00373

---

a) in mg of solute per g of HF

b) in mole of solute per 1000g of HF

c) not measured

Metathetical NF_4BF_4 Production

Since in the metathetical production of NF_4BF_4 highly concentrated HF solutions are used, the activity coefficients of the ions are expected to differ significantly from those of the more dilute solutions of the solubility measurements. Consequently, the knowledge of solubility data is insufficient to predict accurately the product composition obtainable from metathetical experiments.

Metathetical NF_4BF_4 production runs using different MBF_4 and NF_4XF_6 salts in HF were carried out. Typical results from such experiments are shown in Table III. As can be seen, the data of Tables II and III are only in qualitative, but not quantitative, agreement. As

TABLE III. Comparison of the Composition of the Crude Products Obtained by the Metatheses of NF_4^+ Salts with Different Alkali Metal Tetrafluoroborates in HF at -78°

System[a]	Composition of Product (weight %)		
	NF_4BF_4	NF_4XF_6	MXF_6
$LiBF_4$ - NF_4SbF_6	81.7	8.4	9.9
$LiBF_4$ - NF_4BiF_6	86.7	5.9	7.4
$NaBF_4$ - NF_4SbF_6	68.3	12.6	19.1
KBF_4 - NF_4SbF_6	15.3	79.6	5.1
$CsBF_4$ - NF_4SbF_6	85.4	13.3	1.3

(a) A 5 mole % excess of the NF_4^+ salt was used in all runs, except for the $LiBF_4$ - NF_4BiF_6 system, where approximately stoichiometric amounts of starting materials were used.

expected, the solubilities of the alkali metal hexafluoro-antimonates and bismuthates are much higher in the concentrated solutions of the metathetical runs. Furthermore, Table III shows that a cesium salt-based process results in the best product purity. The extremely low yield of NF_4BF_4 for the KBF_4 - NF_4SbF_6 system is caused by KBF_4 being less soluble in HF than $KSbF_6$. Keeping the difference in the stoichiometry of the used starting materials in mind, (see footnote of Table III) the results obtained for the $LiBF_4$ - NF_4SbF_6 and the $LiBF_4$ - NF_4BiF_6 system are roughly comparable.

Oxonium Hexafluorobismuthate

Our interest in the possible existence of $H_3O^+BiF_6^-$ was twofold. The salt has previously been proposed [1] as a potential candidate for the removal of traces of water from HF. Furthermore, its possible formation in wet HF solutions of BiF_5 might interfere with metathetical experiments, or result in undesired by-products, particularly when BiF_6^- salts are prepared from BiF_5 and alkali metal fluorides in HF solution [13].

It was found that, contrary to a previous literature report [13], BiF_5 is quite soluble in anhydrous HF and has a solubility in excess of 300 mg of BiF_5 per g of HF at 22°. The Raman spectrum of this solution (Figure 2, trace A) significantly differs in the deformation region from those of the BiF_6^- anion in HF solution (Figure 2, trace B) and of solid BiF_5 [16, 19], but is not unreasonable for an associated hexacoordinated bismuth fluoride.

On addition of water to this solution a copious white precipitate formed. The formation of this less soluble solid in the presence of small amounts of water could explain the previous report [13] on the low solubility of BiF_5 in supposedly anhydrous HF. The Raman spectrum (Figure 2, trace B) of the HF solution above the white solid showed one polarized (591 cm^{-1}) and two depolarized bands (520 and 220 cm^{-1}), in agreement with our expectations for octahedral BiF_6^-. These frequency values are similar to those observed for the alkali metal BiF_6^- salts in the solid state (see above). The Raman spectrum of the precipitate was also recorded and was similar to that of the liquid phase. These observations show that water addition converts HF dissolved BiF_5 into a BiF_6^- salt.

Further identification of the formed precipitate was achieved by pumping off the HF solvent at -45°. Based on the observed material

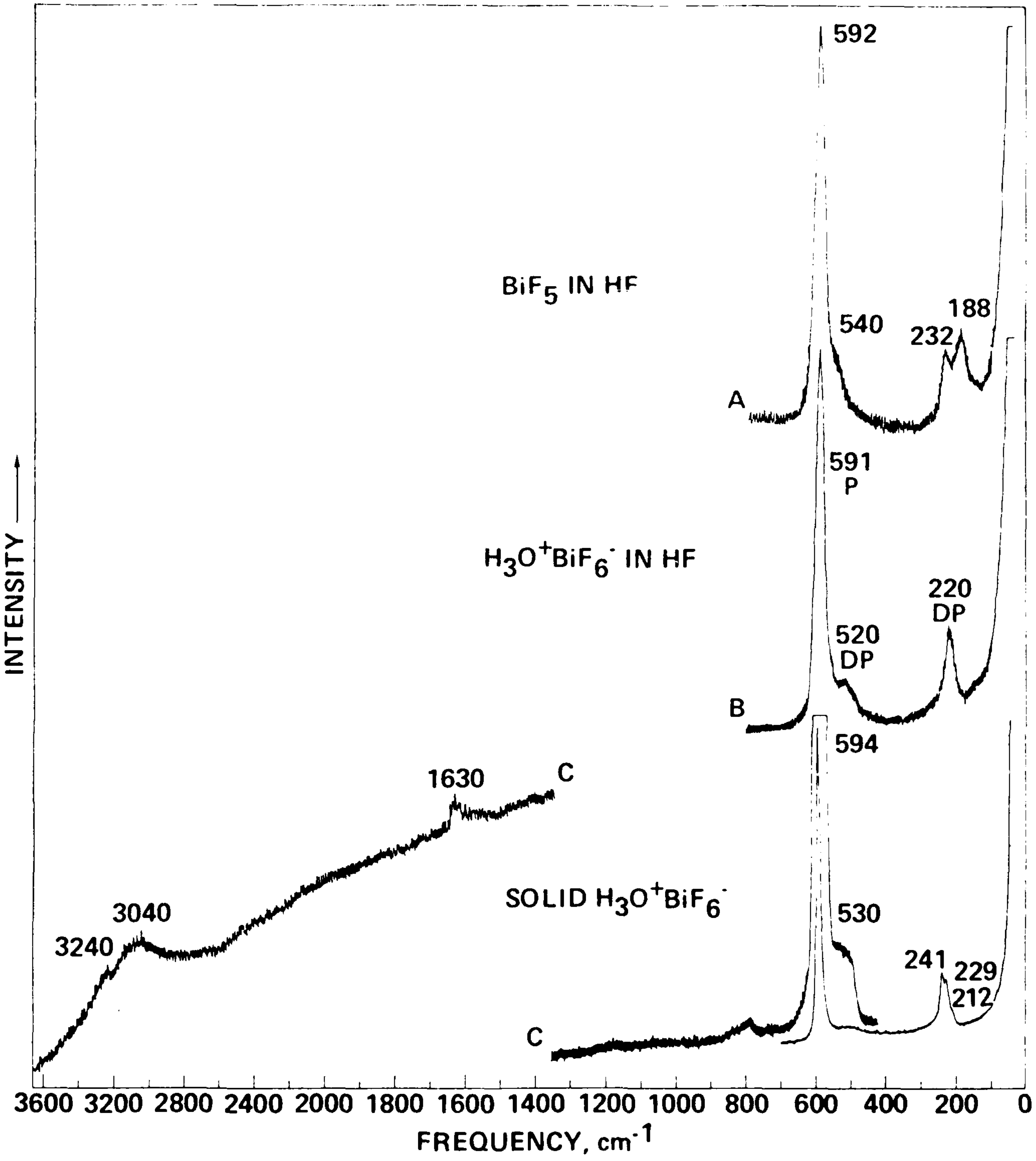


Figure 2. Raman spectra of a 1 molar solution of BiF_5 in HF (trace A), a saturated solution of H_3OBiF_6 in HF (trace B), and of solid H_3OBiF_6 (traces C). All spectra were recorded at room temperature. P and DP indicates polarized and depolarized lines, respectively.

balance and vibrational spectra, the following reaction occurred

$$H_2O + HF + BiF_5 \longrightarrow H_3O^+BiF_6^-$$

The Raman spectra of the solid product (Figure 2, traces C) showed the presence of the bands characteristic for BiF_6^- (see above) and H_3O^+ [1]. The presence of these ions was further confirmed by infrared spectroscopy at -196° which showed a strong band at 3240 cm^{-1} with a shoulder at 3000 cm^{-1} due to H_3O^+ stretching and a very intense broad band with maxima at 598, 566 and 538 cm^{-1} due to BiF_6^- stretching. The splittings for the BiF_6^- stretching mode is not surprising since at the low temperature rotational motions of the ions in the crystal lattice are frozen out [1] causing symmetry lowering due to strong anion-cation interactions. The same temperature effect was observed for the Raman spectra. At -100°, the 594 cm^{-1} band was observed to split into the following bands: 595 vs, 586 s, 574 mw, 562 w, 555 sh.

An interesting behavior was observed for solid H_3OBiF_6. At ambient temperature, H_3OBiF_6 appears to be stable only under an HF pressure of about 20 torr.When the HF is pumped off, the compound turns instantly dark brown indicating hydrolysis of BiF_5 [9]. When the HF pressure is restored, the solid turns white again. The nature of the decomposition product was established by allowing a sample of H_3OBiF_6 to completely decompose in a dynamic vacuum for 3 days at 35°. The solid residue was found to be mainly BiF_3, as expected from the known [9] hydrolysis of BiF_5. Based on these observations, it appears that H_3OBiF_6 first undergoes a reversible dissociation according to

$$H_3OBiF_6 \rightleftharpoons H_2O + HF + BiF_5$$

followed by the irreversible hydrolysis

$$BiF_5 + H_2O \longrightarrow BiF_3 + 2HF + 1/2O_2$$

with the first step being strongly suppressed by HF.

Although the thermal stability of H_3OBiF_6 appears to be lower than that [1] of H_3OSbF_6, the following reaction cycle might offer a convenient method for drying HF:

$$BiF_5 + H_2O + HF \longrightarrow H_3OBiF_6$$

$$H_3OBiF_6 \longrightarrow BiF_3 + 3HF + 1/2O_2$$

$$\underline{BiF_3 + F_2 \longrightarrow BiF_5}$$

$$H_2O + F_2 \longrightarrow 2HF + 1/2O_2$$

The advantage of this cycle over one using SbF_5 would be that BiF_5 is a nonvolatile solid which is easier to handle. As shown by the above equations, the proposed cycle amounts to a fluorination of water to yield HF and oxygen. Although this objective can also be achieved by a direct treatment of wet HF with high pressure fluorine with agitation [1], the proposed cycle could offer practical advantages. For example, in the proposed cycle the fluorination step could be limited to a relatively small amount of BiF_3 instead of treating the bulk of the HF with a large excess of high pressure fluorine which has to be recovered.

Acknowledgement

The authors are indebted to Dr. L. R. Grant and Mr. R. D. Wilson for help. To Messrs.R. Kessler and R. Rushworth for analytical support, and to the Office of Naval Research, Power Branch, and the U. S. Army Research and Missile Development Command for financial support.

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APPENDIX D

SHORT COMMUNICATION

On the Synthesis of the $N_2F_5^+$ Cation. A Critical Comment on the Paper by Toy and Stringham.

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

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Toy and Stringham recently reported [1] the synthesis of $N_2F_5^+(CF_3)_3CO^-$, a salt containing the novel pentafluorohydrazinium cation. This cation would be of significant academic and practical interest [2] since it would constitute the first known example of a substituted NF_4^+ cation, i.e. an NF_4^+ cation in which a fluorine ligand is replaced by an NF_2 group. According to the authors of [1], $N_2F_5^+(CF_3)_3CO^-$ was formed in a very unusual reaction involving the transfer of a fluorine cation from $(CF_3)_3COF$ to N_2F_4 according to:

$$(CF_3)_3COF \longrightarrow (CF_3)_3CO^- + F^+ \xrightarrow{+N_2F_4} N_2F_5^+(CF_3)_3CO^-$$

Since such a heterolytic fission [3] of $(CF_3)_3COF$ with F^+ formation is unlikely, the reported [1] synthetic and spectroscopic evidence for $N_2F_5^+(CF_3)_3CO^-$ was critically reviewed. The following points indicate that the reported white solid is not $N_2F_5^+(CF_3)_3CO^-$, but most likely the known [4] compound $(NO^+)_2SiF_6^{2-}$.

(1) The reference, cited by the authors of [1] for the known existence of $N_2F_5^+$, is Sheppard and Sharts' book on Organic Fluorine Chemistry (Benjamin, New York 1969, page 328).

Although this book lists the reaction of N_2F_4 with AsF_5 to yield $N_2F_5^+AsF_6^-$, this is clearly a typographical error. Examination of the original reference [5] shows that the product from this reaction is $N_2F_3^+AsF_6^-$, in agreement with other previous reports [6,7], and unpublished results from this laboratory.

(2) It was also reported [1] that the white solid was formed only in a Pyrex vessel, but not in a copper vessel. The slow reaction proceeded with the formation of a brown gas. This is charcteristic of the well known [8] attack of glass by nitrogen fluorides to form $(NO)_2SiF_6$ as the principal product. The observed [1] weight of the solid product (50% yield based presumably on the molecular weight of $N_2F_5^+(CF_3)_3CO^-$) is in fair agreement with that expected for a high yield formation of $(NO)_2SiF_6$ according to:

$$N_2F_4 + 2(CF_3)_3COF \longrightarrow 2NF_3 + (CF_3)_3COOC(CF_3)_3$$

$$2NF_3 + SiO_2 \longrightarrow (NO)_2SiF_6$$

Unfortunately, no elemental analysis was reported for the white solid, and its identification was based only on infrared, mass, and ^{19}F nmr spectroscopy.

(3) For the infrared spectrum of the solid, pressed as a NaCl disk, the following absorptions were reported [1]: 1450 (s), 1233 (s), 809 (vs), 730 (vs), and 480 (s) cm^{-1}. These bands do not agree with expectations for either a tertiary perfluorobutoxy group [9,10] or a nitrogen fluoride cation [2, 7, 11]. However, the bands at 730 and 480 cm^{-1} are in excellent agreement with those of the SiF_6^{2-} anion [12]. The bands at 1450 and 1233 cm^{-1} are characteristic [12] for the HF_2^- anion, which could readily form from $(NO)_2SiF_6$ and NaCl

in the presence of moisture. No infrared data were reported for the higher frequency range which would allow a positive identification of the NO^+ cation.

(4) For the mass spectrum only 4 mass peaks were reported [1] at 104, 85, 71 and 52 m/e. The peaks at 104 and 85 were assigned to $N_2F_4^+$ and $N_2F_3^+$, respectively, but since N_2 has the same mass as Si, they can equally well be assigned to SiF_4^+ and SiF_3^+. Based on their observed relative abundances of 2 and 100, respectively, we prefer their assignment to SiF_4 [13], which is the product expected for the thermal dissociation of a SiF_6^{2-} salt. It is important to note that no fragments due to $(CF_3)_3CO^-$ could be detected [1] for the white solid.

(5) The ^{19}F nmr spectrum of an HF solution of the product showed at room temperature only one exchange broadened resonance at ϕ=204 due to HF. On cooling to -80°C a singlet at ϕ=149 appeared which was assigned [1] to the $(CF_3)_3CO^-$ anion. However, for a tertiary perfluorobutoxy group a resonance around ϕ=70 should be expected [9, 10]. Furthermore, we cannot envision a mechanism which could provide for a rapid fluorine exchange between the covalent CF_3 groups and the HF solvent. On the other hand, the observed chemical shift and exchange characteristics are in line with expectations for a silicon fluoride. Unpublished work in this laboratory has shown that the SiF_6^{2-} anion is unstable in HF solution undergoing solvolysis according to $SiF_6^{2-} + 2HF \rightleftharpoons SiF_4 + 2HF_2^-$. The chemical shifts reported for SiF_4 in CCl_4 and SiF_6^{2-} in H_2O are ϕ=160 and 126, respectively, and acid was found to catalyze fluorine exchange between SiF_6^{2-} and F^- [14].

In summary, all the experimental data available for the reported [1] white solid are consistent with a hexafluorosilicate salt, such as $(NO)_2SiF_6$, but cannot be reconciled with the proposed composition $N_2F_5^+(CF_3)_3CO^-$.

Very recently, Stringham and Toy have also claimed [15] the synthesis of $N_2F_5^+BF_4^-$ by the photolytic reaction of N_2F_4 and BF_3 in the presence of fluorine below -100°C. Based on our experience, these reaction conditions are not likely to produce an $N_2F_5^+$ salt. Generally, compounds containing-NF_2 groups readily undergo fluorination to NF_3 during photolysis, followed by formation of NF_4^+ salts [16]. If the reaction is carried out in glass, formation of FNO is also possible, which can result in the formation of $NO^+BF_4^-$. Unpublished work in this laboratory has also shown that N_2F_4 does not form a stable adduct with BF_3 at temperatures as low as -78°C. At -78°C, an equimolar mixture of N_2F_4 and BF_3 is still liquid and can be transferred quantitatively from trap to trap. Therefore, the only solid products expected from the photolysis of N_2F_4-F_2-BF_3 mixtures in glass are NF_4BF_4 and BF_4^- salts of NO^+ or NO_2^+.

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APPENDIX E

Contribution from Rocketdyne, A Division of Rockwell
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On The Chemistry and Structure of $N_2F_3^+$ Salts

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Received . . . . .

Abstract

The novel $N_2F_3^+$ salt $N_2F_3SbF_6$ was prepared from N_2F_4 and SbF_5 in anhydrous HF solution. A metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 in HF produced N_2F_4 and the novel salt $N_2F_3SnF_5$. It was shown that N_2F_4 and BF_3 do not form a stable adduct at temperatures as low as -78°C. The vibrational and ^{19}F NMR spectra of the $N_2F_3^+$ cation were reexamined. All the experimental data are consistent with a planar structure of symmetry C_s for $N_2F_3^+$. The previously reported vibrational assignments, made on the basis of a nonplanar structure of symmetry C_1, are revised for 6 fundamental frequencies.

Introduction

The first report on the formation of a stable adduct between N_2F_4 and a Lewis acid was published[1] in 1965 by Ruff. He showed[1,2] that SbF_5, when treated with an excess of N_2F_4 in AsF_3 solution, produced, depending on the pressure of N_2F_4, either the 1:2 adduct $N_2F_4 \cdot 2SbF_5$ or the 1:3 adduct $N_2F_4 \cdot 3SbF_5$. Based on the observe ^{19}F NMR spectrum and an incomplete infrared spectrum, they assigned to $N_2F_4 \cdot 2SbF_5$ the ionic structure $N_2F_3^+Sb_2F_{11}^-$ with hindered rotation around the N-N bond in $N_2F_3^+$. In 1967, Young and Moy published[3] the syntheses of adducts between N_2F_4

and AsF_5. At -78°C and ambient temperature, the AsF_5: N_2F_4 combination ratios were reported to be 2.3 and 1.3 ± 0.2, respectively. In addition to an incomplete infrared spectrum and an unresolved ^{19}F NMR spectrum, the strongest lines of an x-ray powder diffraction pattern were given which was indexed on the basis of a cubic unit cell with $a = 10.8\text{Å}$. In the same year, Lawless published[4] a better resolved infrared spectrum of $N_2F_3AsF_6$, but no assignments were offered. In 1970, Qureshi and Aubke published[5] a paper dealing with the infrared and Raman spectra of solid $N_2F_3AsF_6$ and $N_2F_3Sb_2F_{11}$. With the exception of the N-N torsional mode, they observed and tentatively assigned all fundamental vibrations of $N_2F_3^+$ proposing a nonplanar structure of symmetry C_1.

Since $N_2F_3^+$ salts are of interest as burning aids in solid propellant NF_3-F_2 gas generator formulations[6], we have studied (i) the synthesis of $N_2F_3SbF_6$, (ii) the possibility of converting $N_2F_3SbF_6$ into "self-clinkering"[7] $N_2F_3^+$ salts by metathetical reactions,[8] and (iii) the vibrational spectra and structure of the $N_2F_3^+$ cation. The results of this study are summarized in this paper.

Experimental

Materials and Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3) Monel vacuum line equipped with Teflon-FEP U-traps and diaphragm valves. Pressures were measured with either a Heise Bourdon tube-type gage (0-1500 mm ± 0.1%) or a Validyne Model DM 56A pressure transducer. Non-volatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glovebox.

Arsenic pentafluoride and SbF_5 (Ozark Mahoning), N_2F_4 (Air Products), and BF_3 and SO_2 (Matheson) were purified by fractional condensation prior to use. The BrF_5 (Matheson) was treated with F_2 at 200°C and then purified by fractional condensation. The HF was dried as previously described[9]. The SnF_4 (Ozark Mahoning) was used as received. The preparation of Cs_2SnF_6 has previously been described.[7]

The infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer as dry powders pressed between AgBr or AgCl disks in a Wilks minipellet press. Raman spectra were recorded on a Cary Model 83 spectrometer using the 4880-Å exciting line and a Claassen filter[10] for the elimination of plasma lines. Polarization measurements for HF solutions in thin-walled KelF capillaries were carried out by method VIII, as described[10] by Claassen et al. The ^{19}F NMR spectra were recorded on a Varian Model EM 390 spectrometer at 84.6 MHz using Teflon-FEP sample tubes (Wilmad Glass Co.) and $CFCl_3$ as an external standard. Debye-Scherrer powder patterns were taken using a GE Model XRD-6 diffractometer with nickel-filtered copper K_α radiation.

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

Synthesis of $N_2F_3AsF_6$. A 30 ml stainless steel cylinder was loaded at -196°C with 22.8 mmol of AsF_5 and 26.8 mmol of N_2F_4. In a prechilled but empty dewar, the cylinder was allowed to warm slowly from -196°C to room temperature. Unreacted N_2F_4 (4.0 mmol) was recovered by pumping at ambient temperature. The weight (6.25 g) of the resulting white solid was in excellent agreement with that (6.25 g) calculated for 22.8 mmol of $N_2F_3AsF_6$. The compound, when prepared in this manner, always was slightly tacky, but hard. It was characterized by ^{19}F NMR and vibrational spectroscopy.

The N_2F_4 - BF_3 Systems. Equimolar amounts of N_2F_4 and BF_3, when combined at -78°C in a Teflon FEP ampule, did not form a solid. The liquid could be distilled at -78° to a colder trap without leaving any solid residue behind.

The N_2F_4 - SnF_4 System. A suspension of SnF_4 (4.68 mmol) in 4 ml of liquid HF in a Teflon-FEP ampule was pressurized with N_2F_4 (12.7 mmol) to a pressure of 900 mm. The mixture was stirred for 5 days at room temperature. Based on its vibrational spectra and chemical analysis, the white solid residue obtained upon removal of all material volatile at 25°C did not contain any $N_2F_3^+$.

Synthesis of $N_2F_3SnF_5$. Solid $N_2F_3SbF_6$ (6.48 mmol) and $CsSnF_6$ (3.24 mmol) were placed in a previously described Teflon-FEP apparatus, and approximately 2 ml of anhydrous HF was added. After stirring and shaking vigorously for 30 min at room temperature, some of the HF was removed under vacuum, and the mixture was cooled to -78°C. The solid and liquid phases were separated by pressure filtration, and the volatile products were removed by pumping at 25°C for 15 hours. The volatile material was separated by fractional condensation and consisted of the HF solvent and N_2F_4 (3.2 mmol). The filtrate residue (0.3 g) was shown by vibrational spectroscopy to contain the $N_2F_3^+$ and $(SnF_5^-)_n$ ions[1-5,7] as the main components, in addition to a small amount of SbF_6^-. The filter cake consisted mainly of $CsSbF_6$ with lesser amounts of $N_2F_3SnF_5$.

Attempts were unsuccessful to suppress N_2F_4 evolution in the above reaction by carrying out the entire metathesis at -78°C. Again N_2F_4 evolution and $N_2F_3SnF_5$ formation were observed.

Results and Discussion

Synthesis. For the metathetical synthesis of $N_2F_3^+$ salts using the $CsSbF_6$ process[8], $N_2F_3SbF_6$ was needed as a starting material. Although Ruff had studied[1,2] the interaction of N_2F_4 with SbF_5 in a solvent, such as AsF_3, he had obtained only the polyantimonates $N_2F_3Sb_2F_{11}$ and $N_2F_3Sb_3F_{16}$. We found that, if this reaction is carried out in HF solution using excess N_2F_4 at a pressure of about one atmosphere, $N_2F_3SbF_6$ can be obtained in quantitative yield and excellent purity according to:

$$N_2F_4 + SbF_5 \xrightarrow[\text{room temperature}]{\text{HF solution}} N_2F_3SbF_6$$

Similarly, no difficulty was encountered in preparing a well defined 1:1 adduct between N_2F_4 and AsF_5. In this case, no solvent was required and the yield was quantitative::

$$N_2F_4 + AsF_5 \xrightarrow{25°C} N_2F_3AsF_6$$

According to a previous report[3] by Young and Moy on the same system, the averaged composition of their adduct was $N_2F_4 \cdot 1.33AsF_5$ and, in the presence of HF as a solvent, the yield was only about 65%.

Boron trifluoride, which is a weaker Lewis acid than SbF_5 and AsF_5, does not form a stable adduct with N_2F_4 at temperatures as low as -78°C. Our attempts also failed to directly synthesize an $N_2F_3^+$ salt derived from SnF_4 by treatment of a SnF_4-HF suspension with N_2F_4. No N_2F_4 uptake occurred. This lack of reactivity cannot be due to insufficient acid strength of SnF_4 since metathesis in HF yields stable $N_2F_3SnF_5$ (see below). A more plausible explanation is that N_2F_4 is not a strong enough Lewis base to depolymerize SnF_4.

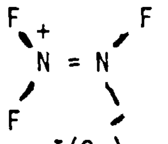
Since the direct synthesis of an adduct between N_2F_4 and SnF_4 was not possible, a metathetical reaction between $N_2F_3SbF_6$ and Cs_2SnF_6 was carried out in HF solution. The following reaction occurred:

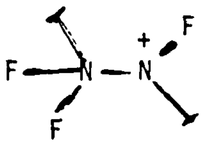
$$2N_2F_3SbF_6 + Cs_2SnF_6 \xrightarrow[\text{-78°C filtration}]{\text{HF solution}} 2CsSbF_6\downarrow + N_2F_3SnF_5 + N_2F_4$$

The $N_2F_3SnF_5$ salt is a white solid, stable at room temperature. It is considerably more soluble in HF than $CsSbF_6$, thus making the metathesis possible. Attempts were unsuccessful to prepare $(N_2F_3)_2SnF_6$ by modification of the above reaction conditions. This was somewhat unexpected in view of the fact that previously no difficulty was encountered in the preparation of the analogous $(NF_4)_2SnF_6$ salt from NF_4SbF_6 and Cs_2SnF_6 under similar reaction conditions.[7] It should be remembered, however, that the favored reaction product from the displacement reaction between NF_4BF_4 and SnF_4 in HF was NF_4SnF_5 and not $(NF_4)_2SnF_6$.[7] These results indicate that the reaction chemistry of SnF_4 and its anions in HF is rather complex and hard to predict without exact knowledge of the corresponding solvation and lattice energies of the possible products.

Vibrational Spectra. Figures 1-3 show the vibrational spectra of $N_2F_3SbF_6$, $N_2F_3AsF_6$, and $N_2F_3SnF_5$, respectively. The observed frequencies are listed in Tables I and II. The vibrational spectra of SbF_6^-,[5,6,11,12] AsF_6^-,[5,11,13,14] and $(SnF_5^-)_n$[7] are well known and can be assigned without difficulty (see Tables I and II), with the remaining bands being due to the $N_2F_3^+$ cation.

The $N_2F_3^+$ cation could possess either a planar structure of symmetry C_s(I) or a nonplanar structure of symmetry C_1 caused by


$I(C_s)$


$II(C_1)$

significant contributions from resonance structure II. The assignments previously made[5] by Qureshi and Aubke for $N_2F_3^+$ were based on symmetry C_1, although structure II is energetically considerably less favorable than I (one nitrogen possesses only six valence electrons) and is in poor agreement with the published NMR data[1,2] which show hindered rotation around the N-N bond up to at least 120°C. Symmetry C_1 had previously been chosen[4] because the highest Raman frequency observed for either solid $N_2F_3AsF_6$ or $N_2F_3Sb_2F_{11}$ occurred at about 1310 cm^{-1}. Since this frequency is considerably lower than expected[15,16] for an N=N double bond, significant contributions from II were assumed.[5]

As can be seen from Figures 1-3, the highest Raman band observed for all three $N_2F_3^+$ salts occurs at about 1520 cm^{-1}, thus confirming the original assignment[1-3] of the strong 1520 cm^{-1} infrared band to the N=N double bond stretching mode and eliminating the basis for Qureshi and Aubke's reassignment.[5] The previous failure to observe the 1520 cm^{-1} Raman band can be explained by its relatively low intensity and the low signal to noise ratio in the reported spectrum.[5]

Having established the identity of the N=N stretching mode, we can now proceed to test if the rest of the $N_2F_3^+$ spectrum is consistent with symmetry C_s. For $N_2F_3^+$ of C_s symmetry a total of 9 fundamental vibrations is expected of which 6 belong to species A' and 3 belong to A''. An approximate description of these 9 modes is given in Table III. All 9 modes should be infrared and Raman active, with a possible exception being the torsional mode ν_9 which is expected to be of very low Raman intensity. The three A" modes should result in depolarized Raman bands.

As can be seen from Table III, three NF stretching modes are expected, all belonging to species A' and occurring in the frequency range 900-1300 cm^{-1}. There are three very intense infrared bands in this region (see Figures 1 and 2), all of which have Raman counterparts. Of the three predicted NF stretching modes, the symmetric NF_2 stretch (ν_4) is expected to have the highest Raman intensity and the lowest depolarization ratio and, therefore, is assigned to the band at about 925 cm^{-1}. The reverse should hold true for the antisymmetric NF_2 stretching mode ν_2 which, therefore, is assigned to the band at about 1310 cm^{-1}. This leaves the assignment of the band at about 1127 cm^{-1} to the unique NF stretching mode ν_3, the frequency of which is similar to that of the NF stretch in N_2F^+[17].

For the assignment of the five deformation modes, the following five frequencies are available; 671, 516, 497, 344, and 310 cm^{-1}. Of these, the 516 and 310 cm^{-1} bands are clearly polarized in the Raman spectra and therefore must represent the two remaining A' modes. By comparison with the known frequencies of the NF_2[18] and CF_2[19] radicals, the 516 cm^{-1} band is assigned to the NF_2 scissoring mode ν_5, leaving the 310 cm^{-1} band for the unique FNN in plane deformation mode ν_6.

Of the remaining three fundamental frequencies, the 671 and 497 cm^{-1} ones exhibit reasonably intense depolarized Raman bands, whereas the 344 cm^{-1} one has been observed only in one Raman spectrum (Figure 1, Trace B) as an extremely weak band. In the infrared spectra, the 344 cm^{-1} fundamental is of medium intensity. These intensity relations identify the 344 cm^{-1} band as the N=N torsional mode. Of the two remaining frequencies, the 671 cm^{-1} fundamental is assigned to the antisymmetric and the 497 cm^{-1} fundamental to the symmetric $FNNF_2$ out of plane deformation. This assignment is based on that[20] of the related C_2F_4 molecule.

Numerous combination bands were observed in the infrared spectra. Their assignment is given in Table I and lends further support to the above assignments for the fundamental frequencies.

In summary, the vibrational spectra of the $N_2F_3^+$ ion are entirely consistent with our predictions for a planar model of symmetry C_s. All nine fundamentals were observed, with 6 of them being polarized and 2 of them being depolarized in the Raman spectra. As expected, the torsional mode is of very low Raman intensity. The double bond character of the NN bond in $N_2F_3^+$ is confirmed by the high frequencies of the NN stretching and the torsional mode.

NMR Spectra. The ^{19}F NMR spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ were recorded at 84.6 MHz in SO_2, BrF_5, SbF_5, and HF solution. The HF solvent was acidified with either AsF_5 or SbF_5 to suppress exchange between the solvent and the cation.[20,22] In HF, BrF_5 and SbF_5 solutions, exchange between the anions and the solvent was observed, however in SO_2 solution, separate signals were observed for AsF_6^- at ϕ 57 and SbF_6^- at ϕ 111 with the appropriate area ratios.

For $N_2F_3^+$, a typical ABX pattern with an area ratio of 1:1:1 was observed at about ϕ - 127, -154, and -187, respectively. The chemical shifts of these signals exhibited only little solvent and temperature dependence. Even at 150°C (SbF_5 solution), no averaging of the NF resonances was noticeable, indicating strongly hindered rotation about the N-N axis, as expected for a N=N double bond. These findings are in excellent agreement with the previous report by Ruff for $N_2F_3Sb_2F_{11}$ in SO_2 solution and the melt.

Our low-temperature spectra (-70 to -90°C) in either BrF_5 (see Figure 4) or acidified HF solutions were much better resolved than those obtainable for the SO_2 solution and thus permitted a more accurate determination of the three coupling constants. The A signal consisted of a sharp doublet of doublets with J_{AB} = 317 Hz, J_{AX} = 78 Hz, and a line width of about 8 Hz.. The B signal was again a doublet of doublets with J_{AB} = 317 Hz and $J_{BX} \sim 78$ Hz, but with significantly broader lines (line width of about 60 Hz). The X signal was a sharp 1:2:1 (J=78 Hz)triplet indicating very similar values of J_{AX} and J_{BX}. Our observed coupling constants significantly differ from those (J_{AB} = 379 Hz, J_{AX} = 81 Hz, J_{BX} = 45 Hz) previously reported[2] for a poorly resolved spectrum.

Assignment of ABX to the three fluorines in $N_2F_3^+$ can be made based on the following arguments. The two nitrogen atoms in $N_2F_3^+$ are not equivalent. The one possessing only one fluorine ligand is centered in an electrically less symmetric field thus making ^{14}N quadrupole relaxation more effective and causing line broadening. Consequently, the broadened B signal is assigned to the unique fluorine. Since for the related FN=NF, CF_2=NF, and substituted fluoroethylenes the cis coupling constants were found to be always significantly smaller than the trans ones,[23] A (J_{AB} = 317 Hz) should be trans and X (J_{BX} = 78 Hz) should be cis with respect to B. The resulting structure is shown in Figure 4. The observed coupling constants are similar to those observed for cis FN=NF (J = 99 Hz) and trans FN=NF (J = 322 Hz).[23]

X-Ray Powder Data. The x-ray powder patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ are given as supplementary material. Young and Moy have reported[3] the three strongest lines for $N_2F_3AsF_6$ and stated that the pattern can be indexed for a cubic unit cell with a = 10.8 Å. Although our data confirm the three previously reported lines,[3] our observed pattern cannot be indexed based on the previously given unit cell dimensions. In view of the nonspherical geometry of $N_2F_3^+$, a relatively small cubic unit cell would be very surprising for $N_2F_3AsF_6$.

Acknowledgement. We are indebted to Drs. L. R. Grant and W. W. Wilson for helpful discussions and to Mr. R. D. Wilson for experimental help. This work was supported in part by the Office of Naval Research and the U. S. Army Research Office.

Supplementary Material Available: Table IV, listing the observed x-ray powder diffraction patterns of $N_2F_3AsF_6$ and $N_2F_3SbF_6$ (1 page). Ordering information is given on any current masthead page.

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Table I. Vibrational Spectra of $N_2F_3AsF_6$ and $N_2F_3SbF_6$

Assignments for $N_2F_3^+$ in point group C_s	Obsd freq. cm^{-1}, and rel intens[a]						Assignments for MF_6^- in point group O_h
	$N_2F_3SbF_6$			$N_2F_3AsF_6$			
	Solid		HF Solution	Solid		HF Solution	
	IR	Raman	Raman	IR	Raman	Raman	
$\nu_1 + \nu_2$ (A') = 2829	2825vw			2820vw			
$\nu_1 + \nu_3$ (A') = 2649	2647vw			2643vw			
$2\nu_2$ (A') = 2614	2608vvw			2605vvw			
$\nu_1 + \nu_4$ (A') = 2447	2443vw			2440vw			
$\nu_2 + 2\nu_5$(A') = 2339	2343vw			2340vw			
$\nu_2 + \nu_4$ (A') = 2232	2227w			2223w			
$\nu_3 + \nu_4$ (A') = 2052	2050sh						
$\nu_2 + \nu_7$ (A") = 1978	1976w			1970w			
$2\nu_4$ (A') = 1850	1850vw			1846vw			
$\nu_3 + \nu_7$ (A") = 1798	1796vw			1795vw			
$\nu_3 + \nu_5$ (A') = 1643	1642vw			1639vw			
$\nu_2 + \nu_6$ (A') = 1617	1619sh			1617vvw			
$\nu_4 + \nu_7$ (A") = 1596	1599vvw			1596vvw			
ν_1 (A')	1522s	1522(0.1)	1522(0.1)p	1519s	1520(0.2)	1524(0.2)p	
$\nu_3 + \nu_6$ (A') = 1437	1436m	1424(0+)	1435(0+)	1432m	1430(0+)		
				1390vw			$\nu_1 + \nu_3$ (F_{1u})
$2\nu_7$ (A') = 1342	1343m			1340m			
ν_2 (A')	1310vs	1307(0.1)	1306(0.1)p	1307vs	1305(0.2)	1300(0.2)p	
$\nu_5 + 2\nu_9$ (A') = 1204	1210vw			1206vw			$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
$\nu_5 + \nu_7$ (A") = 1187	1189vw			1186vw			
ν_3 (A')	1127vs	1124(0.4)	1127(0.6)p	1128vw	1127(0.6)	1128(0.7)p	
$2\nu_5$ (A') = 1032	1033vvw			1032vvw			
$2\nu_8$ (A') = 994	998m	997(0.2)	1000(0.25)p	996m	997(0.3)	1001(0.3)p	
ν_4 (A')	925s	924(3.2)	927(6.1)p	923s	925(4.7)	929(5.9)p	
	755mw			826mw			$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
	670vs			699vs			ν_3 (F_{1u})
ν_7 (A")		670(0.9)	671(0.8)dp		671(0.9)	671(0.8)dp	
		656(10)	655(10)p		690(10)	689(10)p	ν_1 (A_{1g})
				620sh			$\nu_5 + \nu_6$ ($A_{1u} + E_u + F_{1u} + F_{2u}$)
		582(0.4) 566(1.1)	575(0.4)dp		581(1.3)	575(0.4)dp	ν_2 (E_g)
ν_5 (A')	515ms	514(0.8)	518(1.0)p	515ms	516(1.2)	516(0.9)p	
ν_8 (A")	497ms	496(0.5)	499(0.6)dp	496ms	497(1.1)	498(0.5)dp	
ν_9 (A")	345m	348(0+)		343ms			
ν_6 (A')		310(0.5)	310(0.6)p		310(0.9)	310(1.0)p	
	290vs			392s			ν_4 (F_{1u})
		280(2.4)	280(2.3)dp		374(3.6)	371(2.0)dp	ν_5 (F_{2g})

(a) Uncorrected Raman intensities

Table II. Vibrational Spectra of Solid $N_2F_3SnF_5$

Obsd freq. cm^{-1}, and rel intens		Assignment	
Ir	Raman	$N_2F_3^+$ (C_s)	$(SnF_5^-)_n$
1518s	1519(0.1)	ν_1(A')	
1428m		$\nu_3 + \nu_6$ (A')	
1341m		$2\nu_7$(A')	
1304vs	1304(0.1)	ν_2(A')	
1126vs	1127(0.5)	ν_3(A')	
986m	988(0.4)	$2\nu_8$(A')	
921vs	921(3.9)	ν_4(A')	
	670(1.1)	ν_7(A')	
635 610 s,br			Stretching modes
	604(10)		
	572(0.3)		
	512(2)	ν_5(A')	
490-450m,br	492(1)	ν_8(A")	Bridge stretching
	310(0.8)	ν_6(A')	
	228(1.3)		Deformation modes
	179(1.1)		

Table III. Fundamental Frequencies (cm^{-1}) of $N_2F_3^+$ and Their Assignment in Point Group C_s

Frequency	Assignment	Approximate Description of Mode
1522	A' ν_1	N=N stretch
1307	ν_2	antisym. NF_2 stretch
1127	ν_3	NF' stretch
925	ν_4	sym. NF_2 stretch
516	ν_5	δ sym NF_2 in plane
310	ν_6	δ $FNNF_2$ in plane
671	A" ν_7	δ asym $FNNF_2$ out of plane
497	ν_8	δ sym $FNNF_2$ out of plane
344	ν_9	N=N torsion

Table IV. X-Ray Powder Data for $N_2F_3AsF_6$ and $N_2F_3SbF_6$[a]

$N_2F_3AsF_6$		$N_2F_3SbF_6$	
d obsd	Int	d obsd	Int
5.42	vs	5.66	vs
4.95	vw	5.08	vw
4.70	vw	4.36	vs
4.47	s	3.72	vs
4.05	w	3.59	vw
3.75	vw	3.43	w
3.40	vs	2.83	mw
2.99	vw	2.69	mw
2.868	vw	2.505	w
2.715	m	2.380	mw
2.586	vw	2.176	w
2.519	vw	2.058	ms
2.310	m	2.031	w
2.199	vw	1.886	w
2.062	m	1.860	w
1.868	w		
1.831	w		
1.798	mw		
1.727	w		
1.696	w		
1.668	w		
1.606	w		
1.587	w		

(a) Cu K_α radiation and Ni filter

Diagram Captions

Figure 1. Vibrational spectra of $N_2F_3SbF_6$. Trace A, infrared spectrum of the solid as an AgBr disk. The broken line is due to absorption by the window material. Traces B and C, Raman spectrum of the solid recorded at two different recorder voltages with spectral slitwidths of 3 and 8 cm^{-1}, respectively. Traces D-H, Raman spectra of an HF solution recorded at different recorder voltages and spectral slitwidths (5 and 8 cm^{-1}) with incidident polarization parallel and perpendicular (p and dp stand for polarized and depolarized bands, respectively).

Figure 2. Vibrational spectra of $N_2F_3AsF_6$. For explanation, see caption of Figure 1.

Figure 3. Raman spectrum of solid $N_2F_3SnF_5$ recorded at two different recorder voltages.

Figure 4. ^{19}F NMR spectrum of $N_2F_3AsF_6$ in BrF_5 solution, recorded at -78°C and 84.6 MHz using $CFCl_3$ as external standard. The very broad background signal is due to rapidly exchanging BrF_5 and AsF_6^-. The inserts show the A, B, and X signals, all recorded with tenfold scale expansion, but with different recorder gain settings.

APPENDIX F

REACTIONS OF ELECTROPOSITIVE CHLORINE COMPOUNDS WITH FLUOROCARBONS

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I. Introduction

II. Chlorine Monofluoride

- A. Synthesis and Properties
- B. Chlorination
- C. Fluorination
    - 1. Non-oxidative Fluorination
    - 2. Oxidative Fluorination
- D. Chlorofluorination
    - 1. Addition
    - 2. Addition and Fluorination
    - 3. Cleavage of Bonds
    - 4. Summary

III. R_fOCl/SF_5OCl

- A. Syntheses and Properties
- B. Reactions
    - 1. General
    - 2. Oxidation
    - 3. Addition

IV. CF_3OOCl/SF_5OOCl

- A. Syntheses and Properties
- B. Reactions

V. Chlorine Fluorosulfate

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    - 1. Addition
    - 2. Substitution

VI. Chlorine Perchlorate

- A. Synthesis and Properties
- B. Reactions

I. INTRODUCTION

This review is concerned with the reactions of simple chlorine containing compounds of the general composition XCl in which the chlorine atom has electropositive character. The $X^{\delta-} - Cl^{\delta+}$ polarization of the XCl bonds arises from the combination of chlorine with a group of higher electronegativity. The compounds included for review are ClF, R_fOCl, SF_5OCl, CF_3OOCl, SF_5OOCl, $ClOSO_2F$, $ClOClO_3$, and $ClONO_2$. Except for chlorine monofluoride and chlorine nitrate, these compounds have all been discovered within the last fifteen years. Nevertheless during this relatively short period an extensive reaction chemistry has developed involving both inorganic and organic compounds. In particular, the incorporation of positive chlorine species in fluorocarbons and their reactions with fluorocarbons are often unique. This review was written because this area of investigation is most interesting and fruitful and since it has not previously been reviewed.

By virtue of the combination of chlorine with a highly electronegative substituent, all of these materials are medium to strong oxidizing agents. As a consequence of this, care in their handling and use is mandatory. On the other hand, it is this enhanced reactivity which promotes and makes interesting their reactions with the "inert" fluorocarbons.

II. CHLORINE MONOFLUORIDE

A. SYNTHESIS AND PROPERTIES

Chlorine monofluoride was first prepared in 1928 by Ruff and Ascher[1] by a thermal reaction of the elements. Because this reaction can be difficult to control, the alternate method of Schmitz and Schumacher[2] is commonly used to obtain ClF.

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

Recent detailed descriptions of this method are available for either flow[3] or static[4] conditions as well as flow conditions for the reaction of the elements.[5] The low m.p. (-156°C) and b.p. (-100°C) of ClF facilitate its manipulation in vacuum systems and permit contact and mixing under moderating effect of low temperature. Extensive reviews[6-8] have been published on the physical properties and general chemistry of ClF and other interhalogen fluorides.

Musgrave[9] has described early reactions of halogen fluorides with organic materials. Others[10-13] have touched on the subject but have been more concerned with systems leading to the addition of the elements of XF (X=Cl, Br, I) to organic substrates. The reagents used in the latter reactions are generally not the interhalogen fluorides themselves but rather mixtures of X and F sources such as N-halosuccinimide and HF. The reactions of ClF surveyed in these monographs attest to its oxidizing character and vigorous nature.

Based on the observed reaction chemistry and the common acceptance of fluorine as the most electronegative element, it was a consensus that the direction of the polarization in chlorine monofluoride is $Cl^{\delta+} - F^{\delta-}$. Recently, however, this concept was disputed by Ewing et al[14] who, based on Zeeman effect measurements, concluded that the sign of the electric dipole in the molecule should be $Cl^{\delta-} - F^{\delta+}$. Shortly after this report, Hartree-Fock calculation by Greene[15] and ESCA results of Carroll and Thomas[16] were published which supported the classical electropositive chlorine concept for ClF. At about the same time, some of the original authors of the Zeeman investigation reexamined[17] their results. While no error in the experimental data was found it was concluded that the marginal nature of the Zeeman dipole measurements was insufficient to prove the direction of the dipole, and that the measurement should be repeated under higher resolution conditions. The ESCA experiments fulfill this need and it is safe to say that the polarity in ClF is as expected. The reactions of ClF with fluorocarbons, which reflect this polarity, are divided by type and summarized in the following paragraphs.

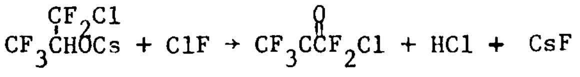
B. CHLORINATION

Reactions of ClF which have most often been used to attain chlorination of a substrate are those involving alkali metal salts, -OH, and -CH functions. In the case of salts the formation of the alkali metal fluoride provides an effective driving force for the reaction. This method provided the first synthesis of the perfluoroalkyl hypochlorites CF_3OCl[18] and $(CF_3)_3COCl$[19].

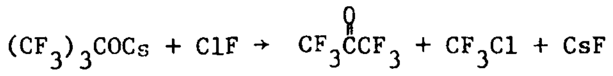
$$KOCF_3 + ClF \xrightarrow{-78^\circ C} KF + CF_3OCl$$

Assurance that only the salt and not its decomposition products COF_2 and KF reacted, was achieved by conducting the above reaction at a temperature of -78°C at which no decomposition of the $KOCF_3$ starting material is possible. The class of R_fOCl compounds, which are themselves positive chlorine species, will be discussed in detail later.

Cesium salts obtained as by-products in fluorocarbon ester reactions were identified by treatment with ClF[20].



$$CF_3\overset{CF_2Cl}{\overset{|}{C}}HOCs + ClF \rightarrow CF_3\overset{O}{\overset{\|}{C}}CF_2Cl + HCl + CsF$$



$$(CF_3)_3COCs + ClF \rightarrow CF_3\overset{O}{\overset{\|}{C}}CF_3 + CF_3Cl + CsF$$

Here one would have expected an alkyl hypochlorite to form. That it was not observed might be due to lack of controlled reaction conditions causing decomposition of the hypochlorites to the products shown. A simple chlorination was noted[20] for the trifluoromethyl sulfinate salt.

$$CF_3SO_2Cs + ClF \rightarrow CF_3SO_2Cl + CsF$$

Another effective driving force resulting in chlorination is the formation of HF. Several -OH compounds have thereby been converted to the corresponding hypochlorites[20].

$$ROH + ClF \xrightarrow{25°C} ROCl + HF$$

$$R = (CF_3)_3C\text{-}, (CF_3)_2CH\text{-}, (CF_3)_2CCH_3\text{-}, CF_3CH_2\text{-}$$

However, perfluoropinacol gave only degradation products while t-butyl alcohol reacted explosively. From the successful cases it was concluded that one CF_3 group in the α position is all that is necessary to allow preparation of the hypochlorite from the alcohol. Peroxy hydrogens can also be substituted by chlorine using ClF[21].

$$CF_3OOH + ClF \xrightarrow{-111°C} CF_3OOCl + HF$$

No O-O bond cleavage was observed and thus no CF_3OCl formed. The reported stability of the compound at 25° has not been experienced by others[22] although it is sufficiently stable to be synthetically useful as will be shown later. Quite recently DesMarteau[23] has utilized this reaction path to prepare and isolate for the first time, perfluoroacyl hypochlorites.

$$R_fCO_2H + ClF \xrightarrow{\text{low T}} R_fCO_2Cl + HF$$
$$R_f = CF_3, C_3F_7$$

As expected the compounds have low thermal stability. In addition they are explosive. Displacement of hydrogen from carbon need not occur if a more reactive site is available in the substrate as in the case of the alcohols described above. Lacking the presence of a more reactive group, however, stepwise substitution of H by Cl can occur[24].

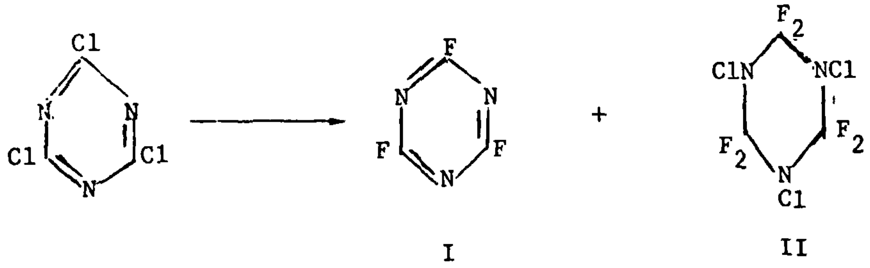
$$CF_3SCH_2CH_2SCF_3 + ClF \rightarrow CF_3SCHClCH_2SCF_3 + CF_3SCCl_2CH_2SCF_3 + HF$$

In this relatively uncontrolled experiment, one and two chlorines were substituted onto the same carbon indicating a preferential reactivity. This specificity is further demonstrated by the fact that the sulfur is not affected even though sulfur is often attacked and oxidized by ClF in similar compounds[24]. Aromatic hydrocarbons have been studied by Gambaretto and Napoli[5]. Using stoichiometric quantities, monochloro substitution products were obtained in all cases with yields ranging from 60-80%. Benzene gave chlorobenzene, and toluene produced 2-and 4-chlorotoluene in a 2:1 ratio. Styrene reacted primarily via ClF addition to the olefin side chain, but this was succeeded by limited substitution in the para position only. These aromatic chlorinations are indicative of a directed electrophilic attack. In these instances as in others, carefully selected reaction conditions, such as solvents, diluents, and low temperature, resulted in controlled specific chlorine substitution reactions. Furthermore, in all the preceding examples ClF reacted exclusively as a positive chlorine material.

C. FLUORINATION

1. Non-oxidative Fluorination

Relatively few cases have been reported in which ClF acts simply as a fluorine substituting agent. One process involving fluorination as a significant pathway is the conversion of cyanuric chloride to the fluoride[25].



Pure ClF produced 43% I and 17% II,while pure ClF_3 gave only I but in the same yield. Presumably the nitrogen line pairs increase the negative character of the ring chlorine thus facilitating its combination with $Cl^{\delta+}$ and replacement with fluorine. Perhaps a more plausible explanation for the above reaction is the stepwise addition of ClF across a C=N double bond, followed by Cl_2 elimination. Product II could then be obtained from I by a repeated ClF addition. The analogous reactions were observed for the addition of ClF to nitriles (see Sec. II,D,1.).

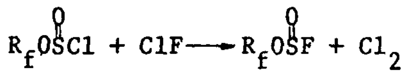
Although not exclusively a fluorination process, the action of ClF on tetrachlorobutadiene has been shown[26] to be partially of that nature.

$$\mathrm{ClCH{=}CClOCl{=}CHCl} \xrightarrow{\mathrm{ClF}} \mathrm{ClCF_2CFClCFClCF_2Cl} \qquad 15\% \qquad \mathrm{I}$$

$$\mathrm{Cl_2CFCFClCFClCFCl_2} \qquad 25\% \qquad \mathrm{II}$$

$$\mathrm{C_4F_5Cl_5} \qquad 50\% \qquad \mathrm{III}$$

Most probably ClF addition to the double bonds occurred, followed by HF or HCl elimination, followed by further ClF addition. As a net result, fluorination, chlorination, and chlorofluorination all occurred, but the former was dominant. For comparison, $\mathrm{ClF_3}$ gave similar products but the amounts of II and III were reversed as would be anticipated in view of its higher fluorine values. The displacement of chlorine from fluoroalkyl chlorosulfites to furnish the fluorosulfite has been reported[27].



$$\mathrm{R_fO\overset{O}{\overset{\|}{S}}Cl + ClF \longrightarrow R_fO\overset{O}{\overset{\|}{S}}F + Cl_2}$$

$$\mathrm{R_f = CF_3CH_2\text{-},\ (CF_3)_2CH\text{-},\ (CF_3)_2CCH_3\text{-}}$$

This halogen exchange could not be effected by NaF or KF even at 120°C. Side reactions were not encountered and the fluoroalkyl fluorosulfites were found to have very good thermal stability. All of the foregoing reactions are examples for the replacement of chlorine by fluorine.

2. Oxidative Fluorination

During studies on lower valent sulfur and nitrogen containing fluorocarbons, Shreeve and coworkers have made very skillful use of ClF reactions. Some of their early work has been summarized[28]. Basically, it has been shown that ClF is capable of effecting stepwise oxidation of S(II) to S(IV) and S(VI) without large amounts of C-S bond cleavage. Generally, this is achieved through careful reaction temperature control, but sometimes the nature of substituents on sulfur is the dominant factor in determining the final oxidation state of sulfur in the product. Although these are multistep fluorination reactions and probably involve intermediate S-Cl moieties, these have not been observed until the S (VI) stage is attained as in R_fSF_4Cl.

The first report[29] of this kind of fluorination used a -78°C reaction temperature which resulted in exclusive conversion of S(II) to S(IV).

$$R_fSR'_f + 2ClF \rightarrow R_fSF_2R'_f$$

$$R_f = CF_3- \qquad R'_f = CF_3-,\ CF_3CF_2-,\ CF_3CF_2CF_2-$$

Yields were greater than 90% and no C-S bond breakage was noted. In contrast, when conventional fluorinating agents (AgF_2, CoF_3, F_2) were employed, only C-S scission and degradation products were obtained. The use of ClF at higher temperatures resulted in additional oxidation[30,31] furnishing S(VI) derivatives. However, these reactions were now accompanied by significant amounts of C-S bond cleavage.

$$CF_3SCF_3 + ClF \rightarrow CF_3SF_4CF_3\ (48\%) + CF_3SF_4Cl\ (25\%)$$

$$CF_3SCF_2CF_3 + ClF \rightarrow CF_3SF_4CF_2CF_3\ (13\%) + CF_3SF_4Cl\ (13\%)$$

$$CF_3CF_2SF_4Cl\ (31\%)$$

Interestingly, these S(VI) compounds with pseudooctahedral geometry were found by nmr to be mixtures of cis and trans isomers. These reactions yielded the first examples of the cis isomers since previously published electrochemical methods[32] provide only the trans isomer. Also, if the substrate for the ClF reaction does not belong to the R_fSR_f type but has one R_f replaced by -Cl, $-SCF_3$[31], or R[33,34] then again only the trans isomer is formed.

$$R_fSCl + ClF \rightarrow R_fSF_4Cl \ (55\%)$$

$$R_f = CF_3-, C_2F_5-, n-C_3F_7-, n-C_4F_9-$$

$$R_fSSR_f + ClF \rightarrow R_fSF_4Cl \ (25-75\%)$$

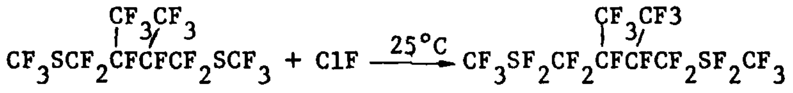
$$R_f = CF_3-, C_2F_5-$$

$$CF_3SR + ClF \rightarrow CF_3SF_4R \ (70\%)$$

$$R = CH_3-, C_2H_5-$$

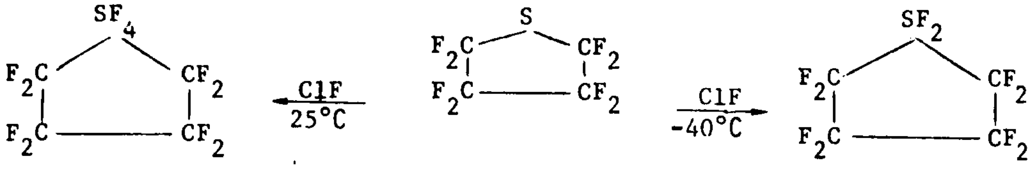
$$CF_3SCH_2SCF_3 + ClF \rightarrow CF_3SF_4CH_2SF_4CF_3 \ (30\%) + CF_3SF_4CH_2F \ (15\%)$$

For the R_fSCl and R_fSSR_f cases there were observed varying amounts of R_fSF_5 products formed by the displacement of Cl by F in R_fSF_4Cl. While in the R_fSR_f—ClF reaction the intermediate S(IV) products could be isolated, R_fSR and ClF were found to give hexavalent sulfur only, even at low temperature and with less than stoichiometric amounts of ClF. Thus the presence of the alkyl group promotes considerably the case of oxidation of the sulfur central atom by this electrophilic reagent. Somewhat at variance with these results are the findings of Haran and Sharp[24] that are shown by the equation.



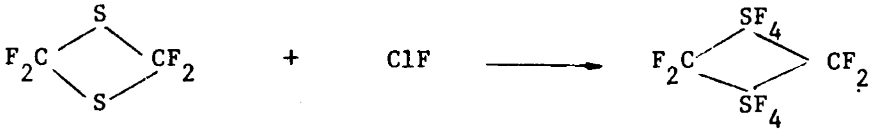
$$CF_3SCF_2\overset{CF_3}{C}F\overset{CF_3}{C}FCF_2SCF_3 + ClF \xrightarrow{25°C} CF_3SF_2CF_2\overset{CF_3}{C}F\overset{CF3}{C}FCF_2SF_2CF_3$$

Both sulfur atoms were oxidized but only to S(IV) despite excess quantities of ClF being present. In addition, the reluctance of the sulfur to participate in this reaction is reflected by the fact that 75% of the starting material remained unreacted. Apparently there is an increasing tendency to resist oxidation as the bulkiness of the fluoroalkyl part of the molecule increases. More examples are needed to verify this trend. Cyclic perfluoroalkyl sulfides are also capable of stepwise oxidative fluorination with chlorine monofluoride[35].



(63%) (74%)

Again only temperature control is required to produce either a S(IV) fluoride or a S(VI) fluoride in good yield. Similar results were obtained for the room temperature reaction of perfluoro -1,3 - dithietane and perfluoro -1,4 - dithietane[35].



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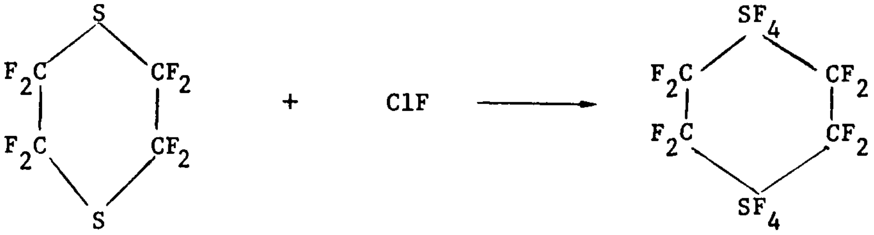


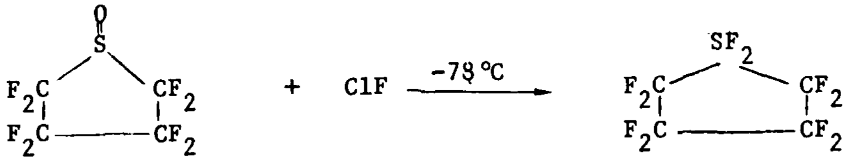
(32%)

Unfortunately no low temperature experiments were carried out with the dithietanes, but it is to be expected that at lower temperature the sulfur IV fluoride analogous of these compounds could be prepared. Once more, it should be noted that in all the fluorination reactions examined involving cyclic or acyclic disulfides, the only products isolated were those in which both sulfur atoms are in the same oxidation state, S(IV) or S(VI). This is characteristic for ClF since other oxidizing agents are capable of forming molecules containing sulfur in two different oxidation states. In particular, m-chloroperbenzoic acid has exhibited selectivity in its oxidizing action[34].

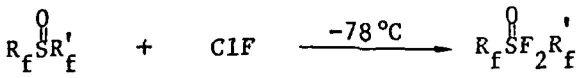
$$CF_3SCH_2SCF_3 + 2\ \underset{\text{I}}{ClC_6H_4CO_3H} \xrightarrow{25°C} CF_3SCH_2S(O)CF_3(99\%)$$

$$CF_3SCH_2SCF_3 + \text{excess I} \xrightarrow{25°C} CF_3SCH_2S(O)CF_3(80\%) + CF_3SCH_2SO_2CF_3(20\%)$$

Of the available sulfur atoms only one reacts giving a sulfoxide or a sulfone. This reagent does not oxidize bis-perfluoroalkyl sulfides. Sulfoxides are susceptible to oxidative fluroination and several examples have been reported[35,36].



(94%)



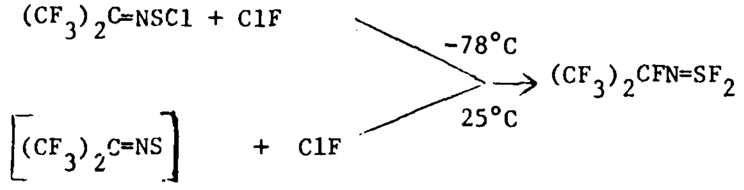
$$R_f\overset{O}{S}R_f' + ClF \xrightarrow{-78°C} R_f\overset{O}{S}F_2R_f' \quad (75\text{-}82\%)$$

$R_f = CF_3-, C_2F_5-$ $R_f' = CF_3-, C_2F_5-$

Obviously, the fluorination of the sulfoxides is a very facile process as reflected by the low temperature conditions employed and the high yields realized. In fact, higher temperatures lead to C-S bond breaking. It appears that doubly bonded oxygen on sulfur compared to two fluorines enhances appreciably the oxidation from S(IV) to S(VI) by providing increased electron density at the sulfur. This parallels the results for electron donating alkyl substituents on sulfur[34].

The identification and characterization of the various sulfur II, IV, and VI fluorides and oxyfluorides is generally quite precise.
This is due to the ^{19}F nmr chemical shifts characteristic for the various

species containing sulfur in different oxidation states. The application of this important tool to these systems has been summarized by Shreeve[28]. A final instance of oxidative fluorination of fluorocarbons via ClF has been described for chloro(hexafluoroisopropylidenimino)sulfur(II) and bis(hexafluoroisopropylidenimino)disulfide[37].



In each case sulfur II is oxidized to sulfur IV fluoride by what is effectively a 1, 3 addition of fluorine accompanied by a double bond shift and the cleavage of either an S-Cl or S-S linkage. Many other fluorinating agents (e.g. NF_3O, AgF_2, CsF, but not KF) also gave the same fluorination product from the corresponding sulfenyl chloride. Once more, electron donating groups bonded to sulfur are seen to promote oxidative fluorination.

D. CHLOROFLUORINATION

1. Addition

Saturation of multiple bonds by the addition of ClF represents the most common usage of ClF. Usable multiple bond systems include: C=C, C=O, C=S, S=N, C=N, and C≡N. Some of these reactions require catalysis but most do not. Normally a directed polar addition occurs in high yield but exceptions to this rule are also known. In this section we will be concerned only with simple additions. Systems that also undergo fluorination or extensive bond cleavage will be discussed separately. The use of solvents and cooling permits good conversion of ethylene derivatives to the corresponding ClF adducts without attack on hydrogen[5].

$$\mathrm{ClCH{=}CH_2} \xrightarrow{\mathrm{ClF}} \mathrm{ClFCHCH_2Cl} \qquad (72\%)$$

$$\mathrm{ClCH{=}CHCl} \longrightarrow \mathrm{ClFCHCHCl_2} \qquad (75\%)$$

$$\phi\mathrm{CH{=}CH_2} \longrightarrow \phi\mathrm{FCHCH_2Cl} \qquad (80\%)$$

Markovnikov addition was observed in each case. With butadiene a variety of chlorine fluoride additions ensued[5] attributed to a 1,2 Markovnikov addition as a first step followed by an only partially directed second addition.

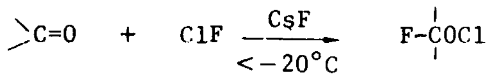
$$\mathrm{CH_2{=}CHCH{=}CH_2} \xrightarrow{\mathrm{ClF}} \mathrm{ClCH_2CHFCH{=}CH_2} \xrightarrow{\mathrm{ClF}} \mathrm{ClCH_2CHFCHClCH_2F} \quad (69\%)$$

$$+$$

$$\mathrm{ClCH_2CHFCHFCH_2Cl} \quad (31\%)$$

The intermediate is an allylic type olefin and reactions of other allyl substrates were shown also to give mixed Markovnikov and anti-Markovnikov ClF addition products. Calculated electronegativity values for R in the $\mathrm{RCH{=}CH_2}$ compounds were used by Gambaretto and Napoli to explain the various observed proportions of the different adducts. Boguslovskaya, et al[38] also carried out a study of ClF additions to R-allyl type compounds, correlating the nature of R- with the direction of addition. In all cases mixed adducts were found but in varying amounts. Moldavskii et al[39], as part of a study on perfluoropropene reactivity, showed that ClF forms exclusively i-$\mathrm{C_3F_7Cl}$, the Markovnikov predicted product in greater than 90% yield. Thus with the exception of allylic precursors, the reported ClF additions are overwhelmingly directed electrophilic additions.

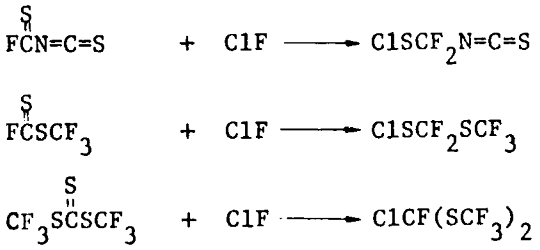
Carbonyl groups are not affected by ClF alone. However, in the presence of Lewis bases, such as CsF, they are attacked readily to generate fluorocarbon hypochlorites.



$$\gt C{=}O \quad + \quad ClF \xrightarrow[<-20^\circ C]{CsF} F{-}\overset{|}{\underset{|}{C}}OCl$$

This mode of addition was discovered at nearly the same time by three groups[18,40-42]. The French workers' efforts[42] were limited to CF_3OCl which was first found by them as a secondary product in the reaction of COF_2 and ClF_3 on alumina. Compounds prepared by the base catalysis[18,40,41] were: CF_3OCl, C_2F_5OCl, $i\text{-}C_3F_7OCl$, $ClCF_2CF(CF_3)OCl$, and $ClO(CF_2)_5OCl$. The intermediacy of R_fO^- species is established in these systems and is wholly analogous to the preceding discovery[43] of base catalyzed fluorination of carbonyls to give R_fOF products. The induced polarity of the C=O bond together with the fixed dipole of ClF allows only a directed addition to give $F\overset{|}{\underset{|}{C}}{-}OCl$. In fact, the same net addition was also reported by Fox and coworkers[44] when strong Lewis acids, such as HF,BF_3, or AsF_5, were present. It was postulated that acid catalysis promoted hypochlorite formation through interaction of the acid with ClF thereby increasing the ClF polarity and reactivity toward carbonyl groups. However, polarization of the carbonyl bond according to $\overset{\delta+}{C}{-}\overset{\delta-}{\underline{\overline{O}}}|\rightarrow AsF_5$ cannot be ruled out as an alternative explanation. The interesting chemistry of these hypochlorites will be discussed later.

Thiocarbonyl groups would appear to be ideal candidates for additions of ClF. However, only one report of such interaction has appeared[45], the reported reactions being:



$$F\overset{\overset{S}{\|}}{C}N{=}C{=}S \quad + \quad ClF \longrightarrow ClSCF_2N{=}C{=}S$$

$$F\overset{\overset{S}{\|}}{C}SCF_3 \quad + \quad ClF \longrightarrow ClSCF_2SCF_3$$

$$CF_3S\overset{\overset{S}{\|}}{C}SCF_3 \quad + \quad ClF \longrightarrow ClCF(SCF_3)_2$$

Catalysts were not required to convert the thiocarbonyl to a sulfenyl chloride. Also, sulfide links and other unsaturation in the starting materials were unaffected by the ClF. Polar additions of ClF to $\overset{VI}{S}{=}N$ bonds have been studied by Yu and Shreeve[46].

$$CF_3SF_3{=}NCF_3 + ClF \longrightarrow CF_3SF_4NClCF_3$$

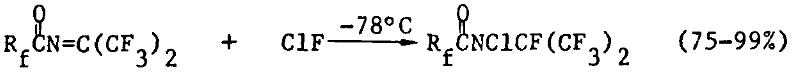
Cesium fluoride may be used to promote this addition, but is not essential. When the double bond involves tetravalent sulfur and nitrogen, ClF causes cleavage (see below). Numerous compounds containing C=N linkages have been investigated with respect to ClF additions. Without exception, these additions are polar and result in saturation of the C=N bond without its rupture. For example, fluorinated isocyanates react as shown[47]:

$$R_fN{=}C{=}O \quad + \quad ClF \longrightarrow R_fNClCFO \ (60\text{-}90\%)$$

$$R_f{=}CF_3\text{-},CF_3CO\text{-},FCO\text{-},Cl\text{-}$$

These products are generated at room temperature or below and have typical chloramine reactivity, i.e. with HCl, chlorine is eliminated and the amine formed. Other positive chlorine species, such as Cl_2O and CF_3OCl, are unreactive toward the isocyanates.

Fluorocarbon imines have been extensively studied by Shreeve and coworkers. Acylimines[48], haloimines[49], and alkylimines[50,51] all add ClF without C-N bond cleavage.



$$R_f\overset{O}{\overset{\|}{C}}N{=}C(CF_3)_2 \quad + \quad ClF \xrightarrow{-78°C} R_f\overset{O}{\overset{\|}{C}}NClCF(CF_3)_2 \quad (75\text{-}99\%)$$

$$R_f{=}CF_3\text{-},C_2F_5\text{-}$$

$$XN{=}CR'R \quad + \quad ClF \xrightarrow{-20°C} XNClCFR'R \quad (60\text{-}80\%)$$

$$R{=}CF_3\text{-},Cl,F \qquad R'{=}CF_3\text{-},Cl,F \qquad X{=}Cl,F,\text{-}N{=}CRR'$$

The directed polar additions found do not usually require the presence of a catalyst, such as CsF, to take place unless the imino carbon is peralkylated. Then a catalyst may be necessary. If the product chloroamine also has a chlorine bound to the adjacent carbon it can be dechlorinated readily to give a new imine.

$$\mathrm{ClCF{=}NF} \xrightarrow{\mathrm{ClF}} \mathrm{ClCF_2NFCl} \xrightarrow{-\mathrm{Cl_2}} \mathrm{CF_2{=}NF} \xrightarrow{\mathrm{ClF}} \mathrm{CF_3NFCl} \not\longrightarrow -\mathrm{Cl_2}$$

Typical alkylimine systems are shown in the equation.

$$\mathrm{RN{=}CR'R''} \quad + \quad \mathrm{ClF} \longrightarrow \mathrm{RNClCFR'R''} \qquad (70\text{–}95\%)$$

$$\mathrm{R{=}CF_3{-}, (CF_3)_2CF{-}} \qquad \mathrm{R'{=}CF_3{-}, F{-}} \qquad \mathrm{R''{=}CF_3{-}}$$

An example[46] of an imine which even under stringent conditions does not react without a catalyst with ClF is illustrated.

$$\overset{70^\circ \quad 10\ \mathrm{hr.}}{\not\longleftarrow} \quad \mathrm{CF_3SF_4N{=}CFCF_3} \quad + \quad \mathrm{ClF} \xrightarrow[25^\circ\mathrm{C}]{\mathrm{CsF}} \mathrm{CF_3SF_4NClCF_2CF_3} \qquad (100\%)$$

It is also noteworthy that the SF_4-N bond is retained under these conditions while certain SF_4-C or SF_4-Cl substrates[31] are subject to significant fluorinative cleavage under milder conditions. Previously, the simultaneous fluorination and chlorofluorination of cyanuric chloride with ClF[25] had been described. More recently, it has been demonstrated[52] that cyanuric fluoride is an excellent precursor to the same chlorofluorination product.

$$\mathrm{(FCN)_3} \quad + \quad \mathrm{3ClF} \longrightarrow \mathrm{(F_2CNCl)_3} \qquad (90\%)$$

Quite unexpectedly this triazacyclohexane was found to serve as a mild fluorinating agent in several cases, being reduced to $(FCN)_3$ and Cl_2. It is very rare that C-F bonds function as active fluorine sources.

In addition to the many C=N additions cited above it is also well established that nitriles can add ClF[53].

$$R_fCN + 2ClF \longrightarrow R_fCF_2NCl_2 \qquad (65\text{-}76\%)$$

$$R_f = CF_3-,\ C_2F_5-,\ ClCF_2-,\ -CF_2-$$

These additions were carried out in the temperature range of 0 to -78°C and no mono ClF adduct could be detected, even when less than a stoichiometric amount of ClF was used. This is caused by the fact that this intermediate imine, -CF=NCl, is more reactive toward ClF than the nitrile itself. Cyanogen chloride behaves similarly, but the chloroamine spontaneously dechlorinates[54].

$$ClCN \xrightarrow{ClF} ClCF_2NCl_2 \xrightarrow[\Delta,\ \text{Fast}]{25^\circ\text{C, slow}} Cl_2 + CF_2{=}NCl$$

In contrast to this is the thermolysis[53] of the R_fNCl_2 compounds which require a higher temperature, 200°C, and results in the formation of the azo compounds $R_fN{=}NR_f$.

2. Addition and Fluorination

In the addition reactions of ClF occasionally fluorination was also observed and could not be precluded. These limited cases generally involve imino type unsaturation[51].

$$\not\xleftarrow{\text{no CsF}} CF_3CCl_2N{=}C(CF_3)_2 + ClF \xrightarrow{CsF} CF_3CF_2NClCF(CF_3)_2$$

This product is the result of a series of ClF additions and Cl_2 eliminations promoted by CsF. One of the corresponding intermediates has been isolated for the related imine.

$$\mathrm{CF_3CCl{=}NCF(CF_3)_2 \xrightarrow[\text{no CsF}]{\text{ClF}} CF_3CF{=}NCF(CF_3)_2}$$

$$\mathrm{CF_3CCl{=}NCF(CF_3)_2 \xrightarrow[\text{CsF}]{\text{ClF}} CF_3CF_2NClCF(CF_3)_2}$$

Thus the ability to lose $\mathrm{Cl_2}$ from $\mathrm{>CCl{-}NCl{-}}$ groups plays a dominant role in these cases. Less easily explained is the following azine-ClF reaction[49].

$$\mathrm{(CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \xrightarrow[\text{no CsF}]{\text{ClF}} (CF_3)_2CFN{=}NCCl(CF_3)_2}$$

$$\mathrm{(CF_3)_2C{=}N{-}N{=}C(CF_3)_2 \xrightarrow[\text{CsF}]{\text{ClF}} (CF_3)_2CFN{=}NCCl(CF_3)_2}$$

$$+$$

$$\mathrm{(CF_3)_2CFN{=}NCF(CF_3)_2}$$

Without CsF, a 1,4-chlorine fluoride addition occurs whereas with CsF a displacement of Cl by F is also encountered. The yield of the latter reaction varied but could not be completely suppressed. Furthermore, CsF and ClF could not be made to give the fluorinated products using the 1,4- ClF adduct as a starting material.

3. Cleavage of Bonds

While the preceding ClF addition schemes involved little or no bond breaking, there are numerous systems in which bond cleavage is the main result of the action of ClF. For example, treatment of KSCN at -30°C gives a variety of products, but none of these retains an S-C bond[55].

$$\mathrm{KSCN + ClF \longrightarrow SF_5Cl,\ CF_3NCl_2,\ SF_6,\ CF_3N{=}NCF_3}$$

In like manner, sulfinyl amines do not generate any N-S derivatives[56,57].

$$RN{=}S{=}O + ClF \rightarrow RNCl_2 + SOF_2$$

$$R{=}CF_3\text{-},\ FSO_2\text{-}$$

When ClNSO is subjected to ClF, nitrogen trichloride is a likely intermediate, although it was not isolated[58].

$$ClNSO \xrightarrow{ClF} NCl_3 \quad + \quad SOF_2 \longrightarrow 1.5Cl_2 + 0.5N_2$$

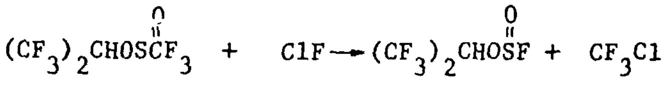
It was always observed that S(IV)-N bonds did not survive the action of ClF. This also appears to hold true for iminosulfur difluorides[56].

$$R_fN{=}SF_2 + ClF \rightarrow R_fNCl_2 + SF_4$$

$$R_f{=}FCO\text{-},\ CF_3CO\text{-},\ CF_3\text{-},\ i\text{-}C_3F_7\text{-},\ F_2SNCF_2CF_2\text{-}$$

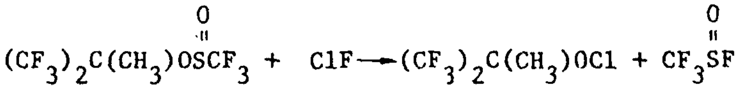
Efforts failed to isolate a mono adduct retaining the N-S linkage.

In the discussion of sulfide-ClF reactions, the important bond cleavage reactions of R_fSSR_f and R_fSR_f have been mentioned. Sulfinyl esters show at least two different bond breaking paths[20]:



$$(CF_3)_2CHO\overset{\overset{O}{\|}}{S}CF_3 \quad + \quad ClF \rightarrow (CF_3)_2CHO\overset{\overset{O}{\|}}{S}F \quad + \quad CF_3Cl$$

and



$$(CF_3)_2C(CH_3)O\overset{\overset{O}{\|}}{S}CF_3 \quad + \quad ClF \rightarrow (CF_3)_2C(CH_3)OCl \quad + \quad CF_3\overset{\overset{O}{\|}}{S}F$$

Because this particular process was not studied in much detail, it is not possible to define the conditions favoring either an S-O bond breakage to furnish an hypochlorite or an S-C bond fission to produce a sulfinyl fluoride. A synthetically useful C-O cleavage reaction brought about by ClF was reported for fluorocarbonyl trifluormethyl peroxide[22].

$$CF_3OOCF + ClF \xrightarrow[-78^\circ C]{ClF} COF_2 + CF_3OOCl \quad (88\%)$$

This procedure simplifies the synthesis of CF_3OOCl by elimination of the previously required intermediate step of hydrolyzing CF_3OOCFO to CF_3OOH.

4. Summary

It is evident from the above discussion that ClF has recently been successfully exploited in a variety of fluorocarbon reactions. The high reactivity of ClF under a wide range of conditions generally results in good to excellent yields of specific products. Quite often these are unattainable by other means. It is likely that similar judicious applications of ClF to other yet unexplored cases will provide interesting and useful results.

III. R_fOCl/SF_5OCl

The close relationship between the fluorocarbon hypochlorites and pentafluorosulfur hypochlorite permits a joint discussion of their chemistry.

A. SYNTHESES AND PROPERTIES

The earliest reported syntheses of R_fOCl were base catalyzed ClF additions to carbonyl functions[18,41]. Although not widely tested, Cl_2O was also used as a positive chlorine source to prepare the trifluoromethyl derivative[41].

$$COF_2 + Cl_2O \xrightarrow[-20^\circ C]{CsF} CF_3OCl + [CsOCl]$$

The base catalyzed chlorofluorination process was also applied to thionyl tetrafluoride.[41,59]

$$SOF_4 + ClF \xrightarrow[-20^\circ C]{CsF} SF_5OCl$$

This is directly related to Ruff and Lustig's fluorination procedure[60] for the synthesis of SF_5OF. Soon after the original reports, acid catalysis was shown to be effective in this hypochlorite formation[44]. Subsequently, the reaction of ClF and certain alcohols opened yet another route to fluorocarbon hypochlorites[19]. All of these R_fOCl

syntheses have been described in the preceding ClF reactions sections. Fluorocarbon hypochlorites and SF_5OCl are colorless liquids and gases. Volatility is related to molecular weight and is consistent with typical covalent fluorocarbons. For example, CF_3OCl has a b.p. of -46°C and SF_5OCl has a b.p. of 9°C. The thermal stability of the simpler compounds decreases rapidly from that of CF_3OCl in the following order: $CF_3OCl >> C_2F_5OCl > i\text{-}C_3F_7OCl \sim SF_5OCl$. When an α fluorine is not present as in the ROH derived hypochlorites[19], $(CF_3)_3COCl, CH_3C(CF_3)_2OCl, (CF_3)_2CHOCl$, etc.; then they are reported to be stable to at least 80°C. The hypochlorites are all susceptible to hydrolysis which is one of the major problems in utilizing them.

B. REACTIONS

1. General

The R_fOCl and SF_5OCl chemistry encompasses both radical and polar reactions. As part of the characterization of these compounds, the influence of UV photolysis was examined.

$$2\ CF_3OCl \xrightarrow{h\nu} CF_3OOCF_3 + Cl_2$$

$$2\ SF_5OCl \xrightarrow{h\nu} SF_5OOSF_5 + Cl_2$$

The high yields (90%)[18,61] of these peroxide forming processes render them useful for preparing these compounds. For CF_3OCl the photolysis has been studied under matrix conditions[62]. Longer chain R_fOCl with α fluorines give only degradation products attributed to rapid decomposition of the R_fCF_2O radicals. When the alkoxy radicals are stabilized by some special structural feature, then again peroxides can be obtained via photolysis[63].

$$CH_3C(CF_3)_2OCl \xrightarrow[\text{quartz}]{h\nu} CH_3C(CF_3)_2OOC(CF_3)_2CH_3 \quad (90\%)$$

$$(CF_3)_3COCl \xrightarrow[h\nu,\ \text{quartz}]{-78°C} (CF_3)_3COOC(CF_3)_3 \quad (30\%)$$

Other radical combinations are also known,[18,59] e.g. with NF_2 to produce CF_3ONF_2 and SF_5ONF_2. A reaction directly associated with the positive chlorine nature of the hypochlorites is the increased tendency to combine with negative chlorine. Seppelt has exploited this property as illustrated[64,65].

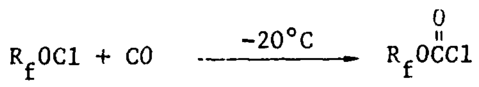
$$CF_3OCl + HCl \xrightarrow[\text{solv.}]{-120°C} CF_3OH + Cl_2$$

$$SF_5OCl + HCl \xrightarrow{-95°C} SF_5OH + Cl_2$$

Trifluoromethyl alcohol is the first example of an isolated primary perfluoroalcohol which have always been considered as nonexistent owing to their ready loss of HF. The thermal stability of CF_3OH is greater than that of SF_5OH (dec. at -20° vs. -60°C) even though the former's decomposition is thermodynamically more favored. This has been explained in terms of the longer intramolecular H--- F distances in CF_3OH compared to that in SF_5OH.

2. Oxidation

Spontaneous insertion of carbon monoxide into the OCl bond of these hypochlorites occurs in a near quantitative manner[66]. This is formally an oxidation of the carbon.



$$R_fOCl + CO \xrightarrow{-20°C} R_fO\overset{\overset{O}{\|}}{C}Cl$$

R_f=CF_3-,C_2F_5-,i-C_3F_7-,SF_5-,$(CF_3)_3C$-,$(CF_3)_2CH$-,etc.

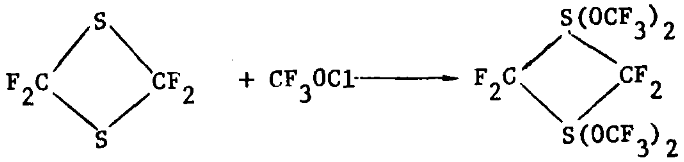
Hypofluorites undergo this reaction only with activation, while the best known alkyl hypochlorite, $(CH_3)_3COCl$, does not react with CO to 80°C Fluorocarbon hypochlorites add directly to SO_2 at room temperature or below[19,66]. Excellent yields of the corresponding chlorosulfate are obtained by inserting the sulfur of the SO_2 molecule into the OCl bond.

$$R_fOCl + SO_2 \longrightarrow R_fOSO_2Cl$$

$$R_f = CF_3-, i-C_3F_7-, (CF_3)_3C-, (CF_3)_2CH-, CH_3C(CF_3)_2-, CF_3CH_2-$$

This represents a formal oxidation of S(IV) to S(VI). Under the influence of UV light CF_3OCl has been found to oxidize bis(trifluoromethyl)sulfide and tetrafluoro—1,3—dithietane[67].

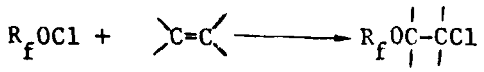
$$CF_3SCF_3 + CF_3OCl \xrightarrow[20\ hr.]{UV} (CF_3)_2S(OCF_3)_2$$



However, the duration of the described experiment seems incompatible with CF_3OCl being the active agent in this oxidation of S(II) to S(IV). Thus, CF_3OCl under UV irradiation decomposes rapidly to CF_3OOCF_3 and Cl_2. Therefore, unless the oxidation of S(II) to S(IV) occurs quickly it would appear that CF_3OOCF_3 alone, or assisted by Cl_2, must be the oxidizing agent.

3. Addition

The addition of R_fOCl to olefins has been investigated by several groups[39,68,69]. Rapid reaction was generally noted.



$$R_fOCl + >C=C< \longrightarrow R_fOC-CCl$$

$R_f = CF_3-$ Olefin = $CF_2=CF_2$, $CH_2=CH_2$, $CF_2=CFCl$, $CH_2=CHCl$, $CF_2=CH_2$, $CF_3CF=CF_2$, $CF_3OCH=CH_2$, $CFCl=CFCl$

$R_f = i\text{-}C_3F_7-$ Olefin = $CF_2=CF_2$

$R_f = (CF_3)_3C-$ Olefin = $CF_2=CF_2$, $CH_2=CH_2$

$R_f = SF_5-$ Olefin = $CF_2=CF_2$, $CH_2=CH_2$

Except for $CF_2=CFCl$, $CF_3CF=CF_2$, and $CF_3OCH=CH_2$ one product only was formed in these directed additions. That product was the one predicted on the basis of the chlorine from R_fOCl adding to the most electronegative carbon of the C=C bond. Where total direction was not possible the ratio of isomers obtained (if reported) was:

$$6\ CF_3OCFClCF_2Cl : 5\ CF_3OCF_2CFCl_2$$

and

$$7\ CF_3OCF_2CFClCF_3 : 3\ ClCF_2CF(OCF_3)CF_3$$

If the addition was allowed to proceed without moderation, some evidence for dimers and oils was noted[68], thus indicating that R_fOCl is capable of inducing radical chain processes. The high yields (90%) and facile, yet controllable reactions experienced with these systems are contrary to those found for similar CF_3OF[70] and SF_5OF[71] additions which are extremely difficult to control. As would be expected the fluorocarbon ether products, especially the perhalofluorinated ones have outstanding thermal stability[69]. Additional 1:1 adducts of olefins and both CF_3OCl and SF_5OCl have been made and a comparison of their properties is being conducted[72]. Because of their desirable properties, these adducts should be a fertile area for investigation. Of all the olefins examined[69], only $CF_3CF{=}CFCF_3$ failed to react along with the butyne, $CF_3C{\equiv}CCF_3$. One additional report on the addition of CF_3OCl to a double bond has appeared[73].

$$C_2F_5N{=}CF_2 + CF_3OCl \rightarrow [C_2F_5NClCF_2OCF_3] \longrightarrow C_2F_5NClCF_3 + COF_2$$

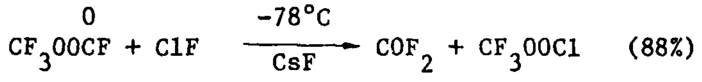
Decomposition of the adduct is surprising. By way of comparison, CF_3OF participates in this reaction only at 250°C and then only to form the fluorinated product, $C_2F_5NFCF_3$.

IV. CF_3OOCl/SF_5OOCl

A. SYNTHESES AND PROPERTIES

Chloroperoxytrifluoromethane has been prepared by two methods.

$$CF_3OOH + ClF \xrightarrow{-111^\circ C} HF + CF_3OOCl \quad (95\%)$$

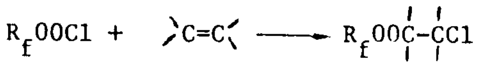


$$CF_3OO\overset{O}{\overset{\|}{C}}F + ClF \xrightarrow[CsF]{-78^\circ C} COF_2 + CF_3OOCl \quad (88\%)$$

The former method[21] was used for the original synthesis of the compound and gives a purer product. The second route[22] presumably proceeds via formation of CF_3OOCF_2OCl which decomposes eliminating COF_2 to furnish CF_3OOCl. Some dispute as to the stability of this pale yellow liquid (b.p. -20°) has arisen. While Ratcliffe, et al. claimed that the compound was stable for prolonged periods at 25°C, Walker and DesMarteau reported only a few hours half life at that temperature. Recently, the molecular structures of CF_3OOCl and the related CF_3OOH and CF_3OOF have been determined using gas phase electron diffraction[74]. For the chloro compound, steric CF_3---- Cl interactions occur giving rise to two distinct conformers. The synthesis of SF_5OOCl was accomplished[75] by reactions analogous to those cited above for CF_3OOCl. The starting materials have been reported; SF_5OOH[76] and SF_5OOCFO[77]. Pentafluorosulfur peroxyhypochlorite was obtained in 70% yield from the hydroperoxide and 90% yield from the fluoroacylperoxide. It is a straw yellow liquid with an extrapolated boiling point of 26.4°C but is decomposes rapidly at 22°C.

B. REACTIONS

The primary reaction mode of these R_fOOCl compounds is the rupture of the terminal hypochlorite bond. Both CF_3OOCl[22] and SF_5OOCl[78] add readily to olefins below 0°C to form peroxides.

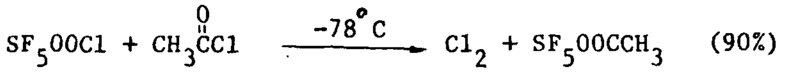


$$R_fOOCl + \rangle C{=}C\langle \longrightarrow R_fOO\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}Cl$$

$R_f = CF_3-$, SF_5- Olefin$=C_2H_4$, C_2F_4, C_2F_3Cl, CF_2CH_2, CF_2CCl_2,

CFHCHCl, <u>cis</u>-CFHCFH

Yields vary and are usually higher for the CF_3- compound. Normally, where isomers are possible, only one product is formed in agreement with a directed, electrophilic addition. Smaller quantities of R_fO ethers are also obtained. The R_fO ether products are believed[78] to arise from reaction of R_fOCl, a decomposition product of R_fOOCl, with the olefins. The fluorocarbon peroxides that are formed are colorless liquids, stable at 22°C. Perfluoro-2-butyne did not react with CF_3OOCl and neither CF_3OOCl nor SF_5OOCl reacted with perfluoropropene or perfluorocyclopentene. Earlier[21], it was shown that, unlike R_fOCl type materials, the R_fOOCl moieties do not insert CO or SO_2 into the O–Cl bond. Peroxyesters can be prepared from SF_5OOCl (and SF_5OOH) via acyl halide reactions[77] as shown by the following example:



$$SF_5OOCl + CH_3\overset{\overset{O}{\|}}{C}Cl \xrightarrow{-78^\circ C} Cl_2 + SF_5OOCCH_3 \quad (90\%)$$

This peroxyester is an ambient temperature stable compound, as are others prepared from SF_5OOH. Clearly, these chloroperoxides behave as positive chlorine species and are useful for the synthesis of many new peroxy derivatives.

V. CHLORINE FLUOROSULFATE

A. SYNTHESIS AND PROPERTIES

Chlorine fluorosulfate was first prepared[79] by Gilbreath and Cady according to:

$$Cl_2 + S_2O_6F_2 \xrightarrow{125^\circ C} 2\ ClOSO_2F \quad (100\%)$$

More recently, a more convenient procedure was developed[80,81] using the readily available SO_3 as a starting material.

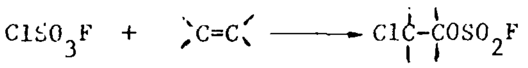
$$ClF + SO_3 \longrightarrow ClOSO_2F \quad (98\%)$$

Chlorine fluorosulfate is a pale yellow liquid (b.p. 43°C) which on standing or handling becomes red presumably due to the formation of some ClO_2SO_3F. It is stable at room temperature and has been stored in stainless steel for more than a year without significant decomposition. Nonetheless, it is an extremely reactive material with a host of substrates.

B. REACTIONS

1. Addition

At the time of its discovery, $ClOSO_2F$ (or $ClSO_3F$) was shown to add to olefinic double bonds, i.e. $CF_2=CF_2$[70]. Since then, these and similar reactions of $ClSO_3F$ have been studied by Moldavskii[39] and mainly by Fokin and coworkers[82,83].



$$ClSO_3F + \rangle C{=}C\langle \longrightarrow ClC{-}COSO_2F$$

Olefins= C_2F_4, CFClCFCl, C_2F_3Cl, C_3F_6, $(CF_3)_2C{=}CF_2$, C_2Cl_4

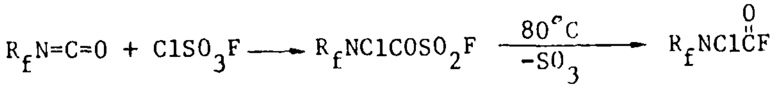
Except for C_2F_3Cl where two isomers were noted, only one product was obtained following Markovnikov's rule. The order of reactivity with $ClSO_3F$ was: $C_2F_4 < CFCl{=}CFCl \sim CF_2{=}CFCl < CF_3CF{=}CF_2 < (CF_3)_2C{=}CF_2$. Although this order of reactivity is similar to that observed for nucleophilic reagents, it was speculated[82] that the high electrophilicity of $ClSO_3F$ and the formation of isomers with C_2F_3Cl are in keeping with an electrophilic mechanism. Numerous other double bonds are also attacked by $ClSO_3F$. For example imines react at low temperature[73,84].

$$C_2F_5N{=}CF_2 + ClSO_3F \xrightarrow{-78°C} C_2F_5NClCF_2OSO_2F$$

$$FN{=}C(NF_2)_2 + ClSO_3F \xrightarrow{-78°C} FNClC(NF_2)_2OSO_2F$$

In contrast HSO_3F must be heated to react with $C_2F_5N{=}CF_2$ and $S_2O_6F_2$ does not react at all[73]. These N-chloro compounds are stable at ambient temperature and are the only products, as expected for a directed polar addition.

Fluorinated isocyanates add $ClSO_3F$ according to:[47]



$$R_fN{=}C{=}O + ClSO_3F \longrightarrow R_fNClCOSO_2F \xrightarrow[-SO_3]{80°C} R_fNCl\overset{O}{\overset{\|}{C}}F$$

$R_f{=}CF_3{-}$, F-

Chlorine monofluoride adducts were similarly prepared[47] but other positive chlorine containing molecules, such as Cl_2O, CF_3OCl, ClNCO, and $ClNSF_2$, did not react. For ClNSO, the $ClSO_3F$ additions[58] were also analogous to those of ClF.

$$2\ ClN{=}S{=}O + 4\ ClSO_3F \longrightarrow 3\ Cl_2 + N_2 + 2\ SO(OSO_2F)_2$$

Only 2:1 addition was possible, and the intermediate NCl_3 decomposed to the elements. Most unusual is the ease with which $ClSO_3F$ adds to hexafluorobenzene below 20 C to give 1:1, 2:1, and 3:1 adducts depending on the stoichiometry employed[85],

$$C_6F_6 + ClSO_3F \longrightarrow C_6F_6Cl(OSO_2F) + C_6F_6Cl_2(OSO_2F)_2 + C_6F_6Cl_3(OSO_2F)_3$$

Peroxydisulfuryl difluoride behaves similarly. Both compounds give a para adduct in the 1:1 addition, as demonstrated by hydrolysis to 4-chloropentafluoro-2,5-cyclohexadiene-one and fluoranil, respectively. These benzene adducts have good thermal stability and are high boiling liquids. Further details on their properties are lacking. The triple bond of nitrile groups also adds $ClSO_3F$ in a 1:1 manner[85].

$$FC(NO_2)_2CN + ClSO_3F \longrightarrow FC(NO_2)_2C(OSO_2F){=}NCl$$

If a cyano salt is involved,both chlorination and addition occur.

$$MC(NO_2)_2CN + 2\ ClSO_3F \longrightarrow MSO_3F + ClC(NO_2)_2C(OSO_2F){=}NCl$$

It should be remembered that -C≡N and ClF reacted only in a 1:2 stoichiometry[53].

2. Substitution

Fokin and coworkers investigated the replacement of chlorine and iodine by fluorosulfate in selected fluorocarbon halides using $ClSO_3F$[87].

$$CFCl_2CFCl_2 + ClSO_3F \xrightarrow{40^\circ C} CFCl_2CFClOSO_2F$$

$$CF_2ClCFCl_2 + ClSO_3F \xrightarrow{50^\circ C} CF_2ClCFClOSO_2F \quad (84\%)$$

$$2\ CF_2Cl_2 + 3\ ClSO_3F \xrightarrow{80^\circ C} CF_2Cl(OSO_2F)\ (37\%) + CF_2(OSO_2F)_2 \quad (29\%)$$

$$CF_3I + ClSO_3F \xrightarrow{20^\circ C} CF_3OSO_2F \quad (83\%)$$

Catalysis by HSO_3F was found to be necessary for these reactions to proceed. In general, facile stepwise substitution of chlorine in $-CFCl_2$ groups was observed. However, the method seemed restricted inasmuch as $CF_3CFClCF_2Cl$ was reported to be unreactive up to 100°C. Nevertheless in our experience[88] the Cl in $-CF_2Cl$ groups can be replaced as shown by:

$$ClCF_2CF_2Cl + ClSO_3F \xrightarrow{130^\circ C} ClCF_2CF_2OSO_2F \quad (90\%)$$

The terminal Cl in $CF_3CFClCF_2Cl$ has also been replaced by $-SO_3F$ using $ClSO_3F$ and a small amount of Br_2 as a catalyst[88]. Bromo compounds, as expected, react more readily and some typical examples are:

$$C_2F_5Br + ClSO_3F \xrightarrow{25^\circ C} C_2F_5OSO_2F \quad (96\%)$$

$$BrCF_2CF_2CF_2Br + ClSO_3F \xrightarrow{25^\circ C} CF_2(CF_2OSO_2F)_2 \quad (50\%)$$

In none of these cases was the presence of HSO_3F necessary to attain the desired reaction. Acid salts and acids interact with $ClSO_3F$ in an expected manner, but the isolation of the unusual CF_3CO_2Cl intermediate was surprising[88].

$$CF_3CO_2H + ClSO_3F \longrightarrow CF_3CO_2Cl \longrightarrow CF_3Cl + CO_2$$

As already mentioned above, the same compound has only recently been reported by DesMarteau[23] using ClF as the source of positive chlorine.

VI. CHLORINE PERCHLORATE

A. SYNTHESIS AND PROPERTIES

Chlorine perchlorate is easily prepared by the action of $ClSO_3F$ on certain perchlorate salts[89].

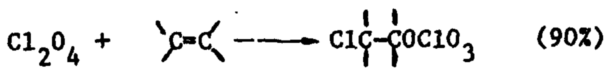
$$MClO_4 + ClSO_3F \xrightarrow{<-20^\circ C} MSO_3F + ClOClO_3 \quad (90\%)$$

$$M = Cs^+,\ NO_2^+$$

Chlorine monofluoride has been used in place of $ClSO_3F$ but yields were very low and unreliable. Chlorine perchlorate ($ClOClO_3$ or Cl_2O_4) is a pale yellow liquid (extrapolated b.p. 44.5°C) with only limited stability at room temperature. It and nearly all of its covalent derivatives are shock sensitive. Consequently, they should always be treated with the respect appropriate for potential explosives. As a member of the class of compounds known as chlorine oxides, it is unusual because it is the only one containing chlorine in two different oxidation states i.e. +I and +VII.

B. REACTIONS

When examined with fluorocarbon olefins, reaction occurred rapidly at low temperature in a 1:1 mole ratio providing colorless liquid products[90,91].



$$Cl_2O_4 + \ \rangle C{=}C\langle \ \longrightarrow ClC{-}COClO_3 \quad (90\%)$$

$$C_2F_4,\ C_2F_3Cl,\ CFClCFCl,\ C_3F_6,\ CF_2{=}CFCF{=}CF_2$$

The terminal Cl-O bond of $ClOClO_3$ was always cleaved during these reactions. The mono-adduct of perfluorobutadiene decomposed explosively and spontaneously at ambient temperature. All the other compounds exhibit good to excellent (100°C) thermal stability. One isomer only was noted in all cases. For C_3F_6, this was the Markovnikov predicted product, $CF_3CFClCF_2OClO_3$, while for C_2F_3Cl it was the anti-Markovnikov compound, $ClCF_2CFCl(OClO_3)$. This is unexplained and different from $ClSO_3F$[81] and SF_5OOCl[75] which gave a mixture of isomers, and from CF_3OOCl[22] which gave only the expected $Cl_2CFCF_2OOCF_3$. Aromatic fluorocarbons add Cl_2O_4 at low temperature[92], much as they do $ClSO_3F$[85], confirming the close relationship of these two hypochlorites. Some minor differences, however, appear to occur since a 1:2, but not a 1:3, addition product is formed.

$$C_6F_6 + 2\ Cl_2O_4 \longrightarrow C_6F_6Cl_2(OClO_3)_2$$

$$C_6F_5Cl + 2\ Cl_2O_4 \longrightarrow C_6F_5Cl_3(OClO_3)_2$$

Both products are cyclohexenes and, based on nmr, only one isomer is obtained in each case. They are colorless, viscous liquids. With C_6F_5Br a more complex reaction was observed entailing addition and ring opening. The exact nature of the product has not been determined. Various fluorocarbon halides have been found to react with Cl_2O_4 resulting in a displacement of the halide by a perchlorate group[91]. In saturated fluorocarbon chlorides, primary and secondary chlorines in either mono or dichloro groups did not react. Trichlorofluoromethane did react, but gave COFCl and Cl_2O_7 as primary products. Bromine compounds were more susceptible to attack, as shown.

$$BrCF_2CF_2Br + Cl_2O_4 \xrightarrow{-25\,^\circ C} BrCF_2CF_2OClO_3 \quad (11\%)$$

$$CF_3CFBrCF_2Br + Cl_2O_4 \xrightarrow{0\,^\circ C} CF_3CFBrCF_2OClO_3 \quad (45\%)$$

$$(CFBrCF_2Br)_2 + Cl_2O_4 \xrightarrow{-25\,^\circ C} (CFBrCF_2OClO_3)_2 \quad (90\%)$$

Geminal bromines, when substituted, led to decomposition products. If the bromine is on a carbon adjacent to a perfluorogroup, no substitution ensued. Fluorocarbon iodides reacted vigorously with Cl_2O_4 as shown.

$$2R_fI + 4Cl_2O_4 \longrightarrow (R_f)_2\ I^{+}I(ClO_4)_4^{-} \longrightarrow 2R_fOClO_3 + 2\,[IClO_4]$$

$$R_f = CF_3-,\ C_2F_5-,\ i\text{-}C_3F_7-,\ ICF_2CF_2-,\ C_6F_5-$$

With $C_7F_{15}I$, $i\text{-}C_3F_7I$, and C_6F_5I the intermediate salt was isolated and characterized[91]. Thermal decomposition of the heptane salt afforded $C_7F_{15}OClO_3$, but the isopropyl and the aromatic compounds exploded before they could give the simple covalent perchlorate. These conversions of R_fI to R_fOClO_3 were high yield processes. The only other known route to fluorocarbon perchlorates, which does not involve the halogen perchlorates, is the reaction of alcohols and alkoxides with Cl_2O_7, wherein the products normally were not isolated[93].

VI. CHLORINE NITRATE

A. SYNTHESIS AND PROPERTIES

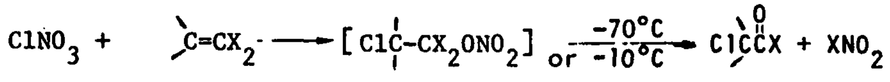
Originally chlorine nitrate was prepared from either Cl_2O or ClO_2 with NO_2 or N_2O_5[94]. To avoid the use of the hazardous chlorine oxides, the following alternate synthesis was developed[95].

$$ClF + HNO_3 \xrightarrow{-78^{\circ}C} HF + ClNO_3 \qquad (90\%)$$

Commercial anhydrous nitric acid may be used. The formed $ClNO_3$ ($ClONO_2$) is a pale yellow liquid (b.p. 23°C) which undergoes slow decomposition at ambient temperatures, but which may be stored indefinitely at -40°C or lower.

B. REACTIONS

Only one report on the addition of $ClNO_3$ to unsaturated fluorocarbons has appeared[96].



X=F, Cl

The vigorous reaction of $ClNO_3$ with these olefins necessitated dilution with solvents. When two halogens were on the nitrate carbon, the illustrated low temperature decomposition occurred. This instability has discouraged further work on fluorocarbon nitrates.

As part of a study on halogen nitrates[97], the system $CF_3I-ClNO_3$ was examined with the following results.

$$CF_3I + 2ClNO_3 \xrightarrow{-45^\circ C} Cl_2 + CF_3I(ONO_2)_2 \xrightarrow{25^\circ C} COF_2, CF_3I, N_2O_5, \text{etc.}$$

Thus, as with Cl_2O_4, an intermediate oxidized iodo derivative is generated first. Unlike the perchlorate case however, this does not decompose to a stable R_fNO_3, but degrades as shown. Naumann and coworkers have studied these processes more carefully[98], isolating the $CF_3I(ONO_2)_2$ intermediate and obtaining still another intermediate which they did not isolate.

$$CF_3I + ClNO_3 \longrightarrow CF_3ICl(ONO_2) \xrightarrow{<-20^\circ C} CF_3I(ONO_2)_2$$

A thorough, controlled decomposition scheme was worked out for the dinitrato moiety above -20°C involving intermediates, such as CF_3IO and CF_3IO_2. The overall decomposition equation is:

$$10\ CF_3I(NO_3)_2 \longrightarrow 5\ CF_3I + 5\ COF_2 + 10\ N_2O_5 + I_2 + IF_5 + I_2O_5$$

Raman spectroscopic characterization of $CF_3I(NO_3)_2$, $C_6F_5I(NO_3)_2$, and related compounds has been reported[99]. Even though $ClNO_3$ has been available for a number of years, it has not been extensively investigated with respect to fluorocarbons. This might be explained by the apparent instability of the products.

VIII. SUMMARY

Most of the known reaction chemistry of electropositive chlorine compounds can be rationalized in terms of either addition of Cl-X across multiple bonds or oxidative addition to atoms, such as iodine or sulfur in their lower oxidation states. The observed variety of the final reaction products can be explained by a multitude of secondary reactions which can involve either eliminations, further additions, or degradations. The observed reactions are easily moderated and controlled, and only rarely no reaction was encountered. The $Cl^{\delta+}-X^{\delta-}$ polarity of the Cl-X bond in these compounds was demonstrated by the "directed" nature of many of the reactions. The strong electrophilic character of these compounds was also evident. Because of the great reactivity of these compounds and the limited amount of work done so far in this area, there are many opportunities for future fruitful research.

IX. ACKNOWLEDGEMENT

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Vibrational Spectra and Force Fields of the Tetrafluorooxohalate (V) Anions, ClF_4O^-, BrF_4O^-, and IF_4O^-

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Abstract

Improved syntheses are described for BrF_4O^- and IF_4O^- salts, and their vibrational spectra are reported. The spectra of $CsBrF_4O$ are simpler than those previously reported for $KBrF_4O$ and thus allow more reliable assignments. For comparison, the low-temperature Raman spectrum of $CsClF_4O$ has also been recorded. Normal coordinate analyses have been carried out for the ClF_4O^-, BrF_4O^-, and IF_4O^- anions and are compared to those of the structurally related $HalF_4^-$ anions and $HalF_5$ molecules and those of XeF_4, XeF_4O, and XeF_5^+.

Introduction

The existence of $KBrF_4O$, a salt containing a novel bromine oxyfluoride anion, has recently been reported both by Bougon and coworkers[1] and Gillespie and Spekkens.[2] It was obtained either by the reaction[1] of

$KBrO_3$ with a large excess of BrF_5 at 80°C in the presence of F_2 or by the reaction[2] of $KBrF_6$ with $KBrO_3$ in CH_3CN solution. Both methods have drawbacks. Although Bougon's method[1] can yield a pure product, the course of the reaction is difficult to control and frequently $KBrF_4$ is obtained as the only product (see below). Gillespie's method[2] produces a mixture of $KBrF_2O_2$ and $KBrF_4O$ which must be separated by numerous extractions with CH_3CN. In view of these difficulties, an improved synthetic method for the synthesis of BrF_4O^- was desirable.

Although the crystal structure of $CsIF_4O$ has been reported[3], only a small amount of the material had been obtained accidentally during unsuccessful attempts to crystallize $CsIF_6$ from CH_3CN solution. Furthermore, products containing mixtures of MIF_4O and MIF_2O_2 salts have been prepared[4] by the interaction of MIO_3 or MIO_2F_2 with IF_5 or by the controlled hydrolysis of MIF_6 in CH_3CN. However, no suitable method for the preparation of pure MIF_4O has previously been reported.

The vibrational spectra of these $HalF_4O^-$ anions were also of interest. For IF_4O^- only spectra of mixtures of IF_4O^- and $IF_2O_2^-$ salts were known[4], and for $KBrF_4O$ the previously reported[1,2] Raman spectra exhibited more bands than permitted for an isolated six atomic species. Interionic dynamic coupling was suggested[1] to account for the large number of bands observed for $KBrF_4O$. However, in view of their similar relative intensities, the bands occurring in the 530 - 390 cm^{-1} region could not be reliably assigned.

In this paper we report improved syntheses for BrF_4O^- and IF_4O^-

salts and their vibrational spectra which allow more reliable assignments for these ions. These assignments are supported by normal coordinate analyses of 12 structurally closely related species.

Experimental Section

Materials. Bromine pentafluoride (Matheson Co.) was treated with 35 atm of F_2 at 200°C for 24 hours prior to its use. Fluorine (Rocketdyne) was passed through a NaF scrubber for removal of HF. The akali metal perbromates[5] and $CsClF_4O$[6] were prepared as previously described. Potassium bromate (A. R. Baker) was used as received. Iodine pentafluoride was purified by distillation and I_2O_5 was prepared from I_2 and HNO_3. The KF was dried by fusion in a platinum crucible.

Apparatus. Volatile materials were manipulated in a well-passivated (with ClF_3 and BrF_5) 304 stainless steel vacuum line equipped with Teflon FEP U traps and bellows-seal valves. Pressures were measured with a Heise Bourdon tube-type gauge (0-1500 mm ± 0.1%). Nonvolatile materials were handled outside of the vacuum system in the dry nitrogen atmosphere of a glove box.

Infrared spectra were recorded on Perkin-Elmer Model 283 and 577 spectrophotometers. For gases a Monel cell with AgCl windows was used. The spectrum of $CsBrF_4O$ was recorded as a dry powder between AgBr windows in the form of a pressed disk. The pressing operation was carried out using a Wilks minipellet press. The spectrum of KIF_4O was recorded as a Nujol mull between CsI windows. Raman spectra were recorded on Cary Model 82 and 83 spectrometers using the 4880 Å exciting line, a Claassen filter[7] for the elimination of plasma lines, and melting point capillaries or Kel F tubes as sample containers. For the low-temperature spectra a previously described[8] device was used.

Synthesis of KIF_4O. A mixture of KF and I_2O_5 in a mol ratio of 5:1 was treated with a large excess of IF_5 for one hour at 25°. Volatile products were pumped off, first at 25°, then at 100°. The white crystalline residue was identified by elemental and spectroscopic analyses as KIF_4O. Anal. Calcd for KIF_4O: K, 15.2; I, 49.2. Found: K, 15.1; I, 49.0.

Syntheses of BrF_4O^- Salts. In a typical experiment, $CsBrO_4$ (2.044 mmol) was placed into a sapphire reaction tube (1/2" o.d., 12" long, Tyco) which contained a Teflon coated magnetic stirring bar and was attached to a valve through a Swagelok compression fitting using a Teflon front and a Steel back ferrule. Bromine pentafluoride (14.1 mmol) and F_2 (2.4 mmol) were added at -78°C. The mixture was stirred at 25° for 30 hours and then cooled to -196°C. The products volatile at 196°C were pumped off and those volatile at 25°C were separated by fractional condensation through a series of traps kept at -64, -95, and -196°C, respectively. Based on their infrared and Raman spectra, they consisted of $FBrO_2$, BrF_5, and $FBrO_3$, respectively. Based on its infrared and Raman spectrum, the white solid residue (623 mg) consisted of $CsBrF_4O$ (weight calcd for 2.044 mmol of $CsBrF_4O$ is 623 mg). Similar results were obtained when the reaction was carried out at 70°C. However, if the reaction was carried in the absence of F_2, the conversion of $CsBrO_4$ to $CsBrF_4O$ was very low, even after prolonged heating to 80°. The influence of HF on this reaction was also studied. The addition of 5 mol percent (based on $MBrO_4$) HF did not produce significant amounts of BrF_4O^- in the reaction of $CsBrO_4$ with BrF_5 in the absence of F_2 at 25 to 50°.

For the $KBrO_4$-BrF_5-F_2 reaction system, when studied in the same manner as described above for $CsBrO_4$, higher reaction temperature were required. For example, at 45°C for 19 hours, essentially all of the $KBrO_4$ starting material was recovered unchanged. Heating of the starting materials to 80°C for 95 hours resulted in a conversion of $KBrO_4$ to $KBrF_4O$ of about 70 percent.

A sample of $KBrF_4O$ was also prepared from $KBrO_3$ and BrF_5 by closely following the procedure published[1] by Bougon. However, when the reaction conditions or the scale of the reaction were slightly modified, several experiments produced $KBrF_4$ in almost quantitative yield, even when the BrF_5 was prefluorinated with 35 atm of F_2 at 200°. No evidence was found for the formation of significant amounts of $FBrO_3$ in these reactions.

The $CsClF_4O$-ClF_3 System. A weighed sample of $CsClF_4O$ in a ten fold excess of ClF_3 was stirred for 24 hours at 25°C. The volatile products were pumped off and consisted of unreacted ClF_3 and ClF_3O. Based on its weight and vibrational spectra,[9] the white solid residue consisted exclusively of $CsClF_4$.

Results and Discussion

Synthesis of XF_4O^- Salts. The reaction of I_2O_5 with a large excess of IF_5 in the presence of a stoichiometric amount of KF affords essentially pure KIF_4O in a one step reaction according to:

$$I_2O_5 + 3IF_5 + 5KF \longrightarrow 5KIF_4O$$

This synthesis is based on the previous report[10] of Aynsley et al. that the reaction of I_2O_5 with IF_5 produces IF_3O.

The KIF_4O prepared in this manner is a white, crystalline solid. It is stable up to about 200°C and hydrolyzes according to:

$$KIF_4O + 2H_2O \longrightarrow KIO_3 + 4HF$$

Attempts were unsuccessful to synthesize K_2IF_5O by changing the $KF-I_2O_5$ ratio in the above synthesis. Based on its vibrational spectra, the resulting product was shown to be $KIF_4O \cdot KF$.

For the synthesis of BrF_4O^- salts, the reactions of $MBrO_4$ with F_2 in BrF_5 solution were found to be most reproducible. Whereas $CsBrO_4$ is fluorinated even at ambient temperature, the reaction of $KBrO_4$ requires heating to about 80°. Although the formation of BrF_4O^- salts in these reactions was shown to be reproducible and quantitative, the amount of the volatile by-products $FBrO_2$ and $FBrO_3$ varied and was never sufficient to account for all the missing oxygen. The remaining oxygen was probably in the form of O_2 which was pumped off at -196° together with the unreacted F_2. Furthermore, it is remarkable that under the given conditions the reactions did not proceed in the absence of F_2. This implies that F_2 participates in these reactions and does not merely serve the purpose of suppressing a possible reduction of BrF_5 to BrF_3,as was previously suggested[3] for the bromate - BrF_5 system. It was also shown that contrary to a previous report on the $KBrO_3$ - BrF_5 system, the addition of small amounts of HF did not significantly catalyze the $CsBrO$ - BrF_5 reaction between 20-50°.

Although the reaction of $KBrO_3$ with BrF_5 to $KBrF_4O$ which was previously reported[1] by Bougon and coworkers was successfully duplicated in our laboratory, it was difficult to accomplish. Frequently, quantitative conversion to $KBrF_4$ was obtained. Since the BrF_5 used in our experiments had been thoroughly prefluorinated with F_2 at 200°C, it could not have contained sufficient BrF_3 for a quantitative displacement reaction, such as

$$KBrF_4O + BrF_3 \longrightarrow KBrF_4 + BrF_3O.$$

That such a displacement reaction of $HalF_4O^-$ by $HalF_3$ can indeed proceed quantitatively,was demonstrated in this study for the following system:

$$CsClF_4O + ClF_3 \longrightarrow CsClF_4 + ClF_3O$$

In view of the possibility of such a displacement reaction and the known[11] thermal instability of BrF_3O, the presence of a small amount of BrF_3 might be sufficient to catalyze the decomposition of BrF_4O^- to BrF_4^- according to:

$$\begin{tikzcd}
BrF_4O^- + BrF_3 \arrow[rr] & & BrF_4^- + BrF_3O \arrow[dl, "\Delta T"] \\
& BrF_3 + 1/2\ O_2 \arrow[ul] &
\end{tikzcd}$$

Our finding that BrF_4^- can be readily formed in this system confirms the original report[12] by Schmeisser and Pammer, but is inconsistent with the recent report[2] of Gillespie and Spekkens.

From a mechanistic point of view, the reactions of BrF_5 with BrO_3^- or BrO_4^- are very interesting since they involve an oxygen-fluorine exchange.

Based on the observed quantitative yields of BrF_4O^-, a free radical mechanism involving the addition of oxygen atoms to bromine fluorides is extremely unlikely. Furthermore, the increased reactivity of the thermally more stable $CsBrO_4$ relative to that of $KBrO_4$ suggests an alkali-metal salt catalyzed reaction. A mechanism involving the addition of BrF_5 or BrF_6^- across a Br=O double bond of BrO_4^- or BrO_3^- followed by $FBrO_3$ or $FBrO_2$ elimination with BrF_4O^- formation appears plausible, but requires additional experimental support.

Vibrational Spectra. Vibrational spectra were recorded for KIF_4O, $CsBrF_4O$, $KBrF_4O$, and $CsClF_4O$. The spectra of KIF_4O (see Figure 1 and Table 1) are in fair agreement with those[4] previously assigned to the MIF_4O part of MIO_2F_2 - MIF_4O mixtures, except for the relative intensities of the 280 and 365 cm^{-1} infrared bands. This discrepancy is caused by the fact[4] that $IO_2F_2^-$ possess a strong infrared band at 360 cm^{-1}.

The vibrational spectra of $CsBrF_4O$ are shown in Figure 2. The spectra of $KBrF_4O$ were in excellent agreement with those[1,2] previously reported and, hence, are not reiterated. Surpirsingly, the vibrational spectra of $CsBrF_4O$ significantly differed from those of $KBrF_4O$. Since in the $HalF_4$ stretching frequency region the room temperature Raman spectrum of $CsBrF_4O$ was more similar to that[13] of $CsClF_4O$ than to that[1,2] of $KBrF_4O$, we have also reexamined the Raman spectrum of $CsClF_4O$ (see Figure 3).

By analogy with the previous report[2] on $KBrF_4O$, it was found that cooling of the samples resulted in much better resolved Raman spectra.

The observed frequencies of $CsBrF_4O$ and $CsClF_4O$ are summarized in Table I. Attempts to obtain the Raman spectrum of $CsBrF_4O$ in anhydrous HF solution failed owing to the following displacement reaction:

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

The observed spectrum was in excellent agreement with that recently reported[11] for BrF_3O.

The previously reported[1,2] Raman spectra of $KBrF_4O$ are very complex and contain more bands than expected for an isolated six atomic species. Furthermore, the relative intensities of many bands are too similar to allow conclusive assignments. In view of these complications and in the absence of additional structural data on BrF_4O^-, the proposed[1,2] C_{4v} structure for BrF_4O^- had to be considered tentative, although very likely. Consequently, a detailed analysis of the simpler $CsBrF_4O$ spectrum and its comparison with those of ClF_4O^- and IF_4O^- were expected to provide additional support for the proposed C_{4v} model.

Assignments for BrF_4O^-. For an isolated BrF_4O^- anion of symmetry C_{4v} nine fundamental vibrations should be observed. These are classified as $3A_1 + 2B_1 + B_2 + 3E$. All nine modes should be Raman active, whereas only the A_1 and E modes should be infrared active. For a solid salt, such as $CsBrF_4O$, the actual site symmetry of the anions is expected to be lower than C_{4v}. This symmetry lowering can cause a splitting of the E modes into their degenerate components and violations of the above given selection rules. Furthermore, if the unit cell contains more than one anion, the number of internal modes can increase by a factor Z, where Z is the number of anions per unit cell. Based on the tentative unit cell dimensions reported[1] by Bougon for $KBrF_4O$, Z is estimated to be about 32. Assuming that $CsBrF_4O$ has a similar crystal structure, each mode could be split into many components. However, only a much lower number of bands are usually observed since these correlation splittings are relatively small and usually do not exceed 1 to 2% of the mode frequency.

Assignments for BrF_4O^- can be made by comparison with the known vibrational spectra of the structurally related species ClF_4O^-[13], ClF_4^-[9], ClF_5[14-17], BrF_4^-[18], BrF_5[14,16], IF_4^-[19], IF_5[14,16], XeF_4[19,20], XeF_4O[14], and XeF_5^+[21]. All these species are pseudo octahedral with an approximately square planar XF_4 group. A summary of the frequencies of their fundamental vibrations is given in Table 2.

Based on its high frequency and relative intensity, the Br=O stretching mode ν_1 (A_1) must be assigned to the band at 930 cm^{-1}. Of the remaining bands the symmetric in phase BrF_4 stretching mode ν_2 (A_1) should be the most intense Raman band and by comparison with the known assignments for ClF_4^-, ClF_4O^-, BrF_4^-, IF_4^-, and IF_4O^- should have a frequency in the vicinity of about 500 cm^{-1}. It therefore must be assigned to the Raman band at 500 cm^{-1}. The symmetric out of phase BrF_4 stretching mode ν_4 (B_1) should be the second most intense Raman band and, by comparison with the known frequencies of the closely related BrF_4^- anion (see Table 2), is predicted to occur about 80 cm^{-1} below ν_2 (A_1). Consequently, this mode must be assigned to the band at about 417 cm^{-1}. The last stretching mode, the antisymmetric BrF_4 stretch, ν_7 (E), is expected to result in a very strong and broad infrared band in the 450 to 550 cm^{-1} frequency region. Such an infrared band has been observed (see Figure 2) and is consequently assigned to ν_7.

In the Raman spectrum, there are three bands at 482, 471 and 444 cm^{-1}, respectively, which are assigned to the degenerate ν_7 (E) mode for the following reasons. Their frequencies are too high for a deformation mode and differ by too much from those of the nondegenerate ν_2 and ν_4 modes in order to be accounted for by correlation splittings of the latter. The splitting of ν_7 into three components can be explained by Fermi resonance (see below).

The assignments for the BrF_4O^- deformation modes can be made by comparison with those of BrF_5 and BrF_4^-. In this type of molecule, the umbrella deformation mode ν_3 (A_1) always results in a very intense infrared band and, consequently, is assigned to the strong infrared band at 301 cm^{-1}. Then the 236 and 178 cm^{-1} bands must be due to the symmetric and the antisymmetric in plane XF_4 deformation modes, ν_6 (B_2) and ν_9 (E), respectively, with ν_6 (see Table 2) always having the higher frequency. The $OBrF_4$ deformation mode, ν_8 (E) is assigned to the remaining Raman bands at 421, 401, and 390 cm^{-1} which show the expected counterparts of medium intensity in the infrared spectrum. The last yet unassigned deformation mode is the antisymmetric out of plane XF_4 deformation ν_5 (B_1). This mode is expected to be of very low intensity and usually is not observed for similar species. Of the compounds listed in Table 2, it has only been observed for XeF_5^+ at 261 cm^{-1}. Since the related ν_3 (A_1) mode of XeF_5^+ exhibits a frequency higher by 53 cm^{-1} than that of ν_3 of BrF_4O^-, the frequency of ν_5 of BrF_4O^- might be expected to occur around 210 cm^{-1}. A careful inspection of the Raman spectrum of $CsBrF_4O$ shows indeed a very weak band at 205 cm^{-1} which is therefore assigned to ν_5 (B_1) of BrF_4O^-. The two bands at 80 and 62 cm^{-1}, respectively, observed in the Raman spectrum of $CsBrF_4O$ occur at too low a frequency for internal BrF_4O^- vibrations and must be assigned to lattice modes.

The splittings, best observed in the low temperature Raman spectrum of $CsBrF_4O$, can be readily accounted for by assuming a splitting into two components for each of the three doubly degenerate E modes. The additional splittings observed for ν_7 and ν_8 can be readily explained by Fermi resonance of ν_7 and ν_8 with the E mode combination bands ($\nu_3 + \nu_9$) and ($\nu_6 + \nu_9$), respectively. Similarly the splitting observed for ν_3 might be explained by Fermi resonance with a combination band of a lower frequency mode and a lattice vibration. Since bromine contains two naturally occurring isotopes (^{79}Br and ^{81}Br) in almost equal abundance, we have computed the approximate isotopic splittings to be expected for BrF_4O^-. In all cases the computed isotopic splittings were considerably smaller than those observed and the relative intensities did not exhibit the correct 1:1 ratio. Consequently, the observed splittings cannot be attributed to the bromine isotopes.

The assignments proposed for $CsBrF_4O$ are summarized in Tables 1 and 2 . When compared to the related compounds of Table 2, these assignments for BrF_4O^- result in very satisfactory frequency trends. Additional support for the assignments comes from the results of a normal coordinate analysis (see below).

Based on the above assignments for $CsBrF_4O$, the previously reported [1,2] vibrational spectrum of $KBrF_4O$ can be reassigned in the following manner: 930 (ν_1); 529 (ν_2); 506, 486, 481, 459 (ν_7); 434 (ν_4); 421, 409, 399 (ν_8); 314 (ν_3); 248, 239 (ν_6); 196, 184, 161 (ν_9).

Assignments for ClF_4O^- and IF_4O^-. The assignments previously proposed[13] for ClF_4O^- have been confirmed by this study. In view of the low-temperature splittings observed for BrF_4O^-, we have examined the low-temperature Raman spectrum of $CsClF_4O$ for similar effects. In general, the assignments for chlorine fluorides are more difficult than those of the corresponding bromine and iodine compounds. This is caused by a well documented[22] overlap of the frequency ranges of the stretching and the deformation modes. This frequently results in coincidences of fundamental vibrations and, if they belong to the same symmetry species, in their mixing.

Although the room temperature Raman spectra of $CsBrF_4O$ (see Figure 2) and $CsClF_4O$ (see Figure 3) in the $HalF_4$ stretching frequencies region appear at first glance to be quite analogous, this first impression is somewhat misleading. For ClF_4O^-, the antisymmetric ClF_4 stretching mode ν_7 has a frequency considerably higher than those of the two symmetric stretching modes ν_2 and ν_4, whereas for BrF_4O^- the frequency of ν_7 falls in between those of ν_2 and ν_4. Therefore, for ClF_4O^- the bands belonging to ν_7 are well isolated and can be assigned with confidence. The remaining assignment of the ClF_4O^- spectrum has previously been discussed in detail[13] and, therefore, is not reiterated.

For IF_4O^-, the assignments[4] proposed by Milne and Moffett have been adopted, except for ν_9 (E). This mode results in a very weak and broad Raman band. Based on frequency correlations with related molecules and force constant arguments, a frequency of about 140 cm^{-1} appears more plausible than the value of 124 cm^{-1} previously proposed.[4]

Table 2 lists the frequencies of 12 species containing an approximately square planar XF_4 group. The given assignments are all consistent with each other, thus rendering any gross misassignments for any of these species highly unlikely. The trends observed within this group of 12 species will be discussed in terms of their force constants (see below) rather than in terms of their frequencies since the frequencies of some of the modes are strongly influenced by the mass of the central atom.

Force Constants. The plausibility of the above assignments for the XF_4O^- anions was examined by computations of modified valence force fields and by their comparison with those of the structurally related XF_4 and XF_5 species. The required potential and kinetic energy metrics were computed by a machine method[23] using the geometries listed in Table 3. For BrF_4O^- and ClF_4O^- the exact geometries are unknown and therefore idealized bond angels of 90° were assumed. The bondlengths of BrF_4O^- were estimated by comparison with those known for the related species BrF_4^-,[24] BrF_5,[25] and BrO_4^-.[26] For ClF_4O^- the previous estimates[13] were adopted. For IF_4O^- the exact geometry is known[3]. Since the observed OIF bond angle of 89° is very close to the 90° estimates used for ClF_4O^- and BrF_4O^- and since the OXeF bond angle in $XeOF_4$ was found to be larger than 90° (91.8°),[27] we have also used a 90° bond angle for IF_4O^-. This simplifies the computations and makes the resulting force fields more comparable. The force constant definitions used are those[14] of Begun et al. Literature values, for which the deformation coordinates had been weighted by unit (1 Å) distance, were converted back to unweighted values to allow a better comparison. The force constants were adjusted by trial and error, assuming the simplest possible modified valence force field, to give an exact fit between the observed and computed frequencies. The potential energy distribution showed that for the XF_4O^- anions all the vibrations were highly characteristic (99-100 per cent), except for the E block. However, introduction of small F_{78} terms resulted in the E block vibrations also becoming highly characteristic (91 per cent or higher). The resulting force fields are summarized in Table 4.

As can be seen from Table 4 the force constants are all very reasonable. A few very minor deviations can be readily explained. For example f_{rr} of BrF_4^- appears somewhat high. This is caused by using for the antisymmetric stretching mode the relatively low frequency value of 478 cm^{-1} observed for the solution spectrum.[19] For the solid, the band due to this vibration is extremely broad[18] with its band center being closer to 500 cm^{-1}. If this higher frequency value is chosen, f_{rr} of BrF_4^- becomes more similar to those of BrF_4O^- and BrF_5. Similarly for the lighter central atoms, the off-diagonal symmetry force constants in the E block become more important, thus increasing the uncertainties in these numbers which were obtained from underdetermined force fields.

General Trends. Inspection of Table 4 reveals the following trends. Whereas the values of the XF stretching force constants are either similar (within the XF_4^- series) or increase in the direction $Cl < Br < I$ (for XF_4O^- and XF_5), the XO stretching force constant in ClF_4O^- is much higher than those in both BrF_4O^- and IF_4O^-. Since the values of the XO force constants within the ClO_4^-, BrO_4^-, IO_4^- series (8.24, 6.05, 5.90 mdyn/Å)[28] exhibit the same trend, this seems to reflect a general characteristic of XO bonds. In the XO_4^- series the central X atom does not possess any free valence electron pair or fluorine ligands, and therefore no special resonance or bonding effects should be invoked. The bond weakening effect of a formal negative charge in the anions and the bond strengthening effect of a positive charge in the cations are as expected. The negative charge increases the $X^{\delta+}$—$F^{\delta-}$ polarity of the XF_4 bonds, thus weakening them. The reverse is true for a positive charge. This effect can also account for most of the observed increase in the force constants when going from an iodine species to the corresponding isoelectronic xenon species which differ by one formal charge.

A comparison of the XF_4^- - XF_4O^- pairs for each halogen shows that for X being chlorine, an oxygen substituent releases electron density to the more electronegative ClF_4 group, thus increasing the polarity of the ClF_4 bonds and decreasing the Cl-F stretching force constant. For X being bromine, there is little change in the X-F stretching force constant indicating comparable electronegativities for oxygen and the BrF_4 group.

For X being iodine, oxygen becomes more electronegative than the IF_4 group, thus withdrawing electron density from IF_4 and increasing the covalency of the IF_4 bonds.

The XF_4 deformation constants f_α show the expected trend. With decreasing size of the central atom, the mutual repulsion among the ligands increases and the bonds become more difficult to deform. The FXO angle deformation constant, f_β, does not appear to change significantly when going from chlorine to iodine. However, for a given halogen atom, f_β appears to follow the same trends exhibited by the corresponding XF_4 stretching force constants, f_r.

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Diagrams Captions

Figure 1. Vibrational Spectra of KIF_4O. Upper trace, infrared spectrum of a Nujol mull between CsI windows; lower trace, Raman spectrum. The band marked by an asterisk is due to Nujol. The numbers 1-9 designate the assignments to the corresponding fundamentals.

Figure 2. Vibrational Spectra of $CsBrF_4O$. Upper trace, infrared spectrum of the dry powder in an AgBr disk. The broken line indicates absorption due to the window material. Lower traces, Raman spectra recorded at different temperatures and gain settings with a spectral slit width of 2 cm^{-1}.

Figure 3. Raman spectra of $CsClF_4O$ recorded at different temperatures and gain settings with a spectral slit width of 2 cm^{-1}.

TABLE 1. VIBRATIONAL SPECTRA OF KIF$_4$O, CsBrF$_4$O and CsClF$_4$O and Assignments for CsBrF$_4$O obsd Frequencies, cm^{-1}, and Relative Intensities[a]

KIF$_4$O		CsBrF$_4$O			CsClF$_4$O	
IR	RA	IR	RA		RA	
			25°	-120°	25°	-120°
885s	887(10)	934 vs	931 (4.8)	929(5.5)ν_1	1223(0.3)	1228(0.4)
540 sh	540(5.8)		500(10)	499(10) ν_2	1213 sh	1215 sh
480 vs				482(2.9)ν_7	1200(0.6)	1202(0.7)
	478(2.3)	570-460 vs	472(4.4)	471(4.2)ν_7	1189(0.2)	1191(0.4)
383 m	381(1.3)		444(3)	444(3.2)ν_7		1182 sh
366 mw	368(1)			421(5.9)ν_8		605(0.2)
279 ms	283(0.3)		413(6.8)	417(7.9)ν_4	585(0.6)	588(0.9)
	224(0.5)	399 } m	400 sh	401(2.7)ν_8	556(0.3)	559(0.5)
	140(0+)	389		390(1.5)ν_8	465 sh	470(5)
		301 vs	299(1.5)	303(1.6)ν_3	455(10)	459(9)
				291(0.2)ν_3		452(10)
		240 sh	236(1.7)	234(2.1)ν_6		435(0.3)
			218 sh	225 sh ν_6		419 sh
			202(0+)	205(0.2)ν_5	412(2.4)	414(3.5)
			178(0.5)	179(0.5)ν_9	395 sh	395(1.2)
				164(0.2)ν_9		370 sh
				80	353(5.5)	358(6.6)
				62		345(5)
					335 sh	334(3.7)
						320 sh
						290 sh
					276(0.5)	278(0.6)
						258(0.2)
						215 sh
						200 sh
					196(1.0)	194(1)
						185 sh
					82	89
					70	73

(a) uncorrected Raman intensities (peak heights)

TABLE 2. A COMPARISON OF THE FREQUENCIES [cm^{-1}] OF THE FUNDAMENTAL VIBRATIONS OF THE $HalF_4O^-$ ANIONS WITH THOSE OF SIMILAR MOLECULES AND IONS

APPROXIMATE DESCRIPTION OF MODE FOR XF_4Y in POINT GROUP C_{4v}	ClF_4O^-	ClF_4^-	ClF_5	BrF_4O^-	BrF_4^-	BrF_5	IF_4^-	IF_4O^-	IF_5	XeF_4	XeF_4O	XeF_5^+
A_1 ν_1 $\nu(XY)$	1203	-	708	930	-	682	-	887	710	-	926	679
ν_2 $\nu sym XF_4$	456	505	539	500	523	587	522	537	616	543	576	625
ν_3 δsym out of plane XF_4	339	425	495	302	317	369	271	279	318	291	294	355
B_1 ν_4 νsym out of phase XF_4	356	417	480	417	449	535	455	480	604	502	527	610
ν_5 $\delta asym$ out of plane XF_4				205								261
B_2 ν_6 δsym in plane XF_4	278	288	375	235	246	312	195	219	276	235	233	300
E ν_7 $\nu asym$ XF_4	578	590	725	505	478	644	448	482	631	586	608	652
ν_8 δYXF_4	414	-	484	395	-	415	-	374	372	-	361	410
ν_9 $\delta asym$ in plane XF_4	194		299	179	[183]	237		140	200		161	218

TABLE 3. ASSUMED MOLECULAR PARAMETERS FOR ClF_4O^-, BrF_4O^-, AND IF_4O^-

	ClF_4O^-	BrF_4O^-	IF_4O^-
R, Å (axial)	1.42	1.56	1.72
r, Å (equatorial)	1.75	1.88	1.965
β, deg ∢ OXF	90	90	90
α, deg ∢ FXF	90	90	90

TABLE 4. COMPARISON OF THE SYMMETRY AND INTERNAL FORCE CONSTANTS[a] OF 12 SPECIES CONTAINING AN APPROXIMATELY SQUARE PLANAR XF_4 GROUP USING THE ASSIGNMENTS AND FREQUENCY VALUES OF TABLE 2

	ClF_4O^-	ClF_4^- [b]	ClF_5 [c]	BrF_4O^-	BrF_4^- [b]	BrF_5 [c]	IF_4^- [b]	IF_4O^-	IF_5 [c]	XeF_4 [b]	XeF_4O [d]	XeF_5^+ [e]
A_1 $F_{11} = f_R$	9.38	-	3.51	6.70	-	4.02	-	6.56	4.82	-	7.08	4.35
$F_{22} = f_r + 2f_{rr} + f_{rr}'$	2.33	2.853	3.24	2.80	3.06	3.81	3.052	3.23	4.22	3.302	3.60	4.38
$F_{33} = f_\beta + 2f_{\beta\beta} + f_{\beta\beta}'$	0.415	0.630	1.20	0.470	0.577	0.805	0.514	0.575	0.72	0.597	0.601	0.875
B_1 $F_{44} = f_r - 2f_{rr} + f_{rr}'$	1.38	1.946	2.59	1.95	2.258	3.21	2.319	2.58	4.08	2.822	3.11	4.17
$F_{55} = f_\beta - 2f_{\beta\beta} + f_{\beta\beta}'$				0.682								0.764
B_2 $F_{66} = f_\alpha - 2f_{\alpha\alpha} + f_{\alpha\alpha}'$	0.216	0.232	0.389	0.154	0.169	0.271	0.106	0.134	0.217	0.155	0.152	0.260
E $F_{77} = f_r - f_{rr}'$	1.81	1.86	2.43	1.91	1.794	2.97	1.755	2.01	3.39	3.048	3.16	3.65
$F_{88} = f_\beta - f_{\beta\beta}'$	0.494	-	0.772	0.386	-	0.635	-	0.444	0.526	-	0.418	0.595
$F_{99} = f_\alpha - f_{\alpha\alpha}'$	0.157		0.382	0.142	0.143	0.249		0.091	0.192		0.122	0.232
$F_{78} = f_{r\beta} - f_{r\beta}'$	0.246	-	0.185	0.128	-		-	0.087	-	-	-	-
f_R	9.38	-	3.51	6.70	-	4.02	-	6.56	4.82	-	7.08	4.35
f_r	1.838	2.13	2.674	2.142	2.227	3.24	2.221	2.458	3.77	3.055	3.258	3.968
f_{rr}	0.238	0.23	0.161	0.213	0.20	0.15	0.183	0.163	0.035	0.120	0.123	0.053
f_{rr}'	0.028	0.27	0.244	0.232	0.433	0.27	0.466	0.447	0.38	0.007	0.098	0.318
f_α [f]	0.187	~0.2	0.385	0.148	0.156	0.260	~0.1	0.113	0.205	~0.13	0.137	0.246
f_β [g]	0.46	~0.6	0.98	0.428	~0.5	0.720	~0.46	0.510	0.623	~0.49	0.509	0.735

(a) all values in mdyn/Å

(b) data from ref. 19

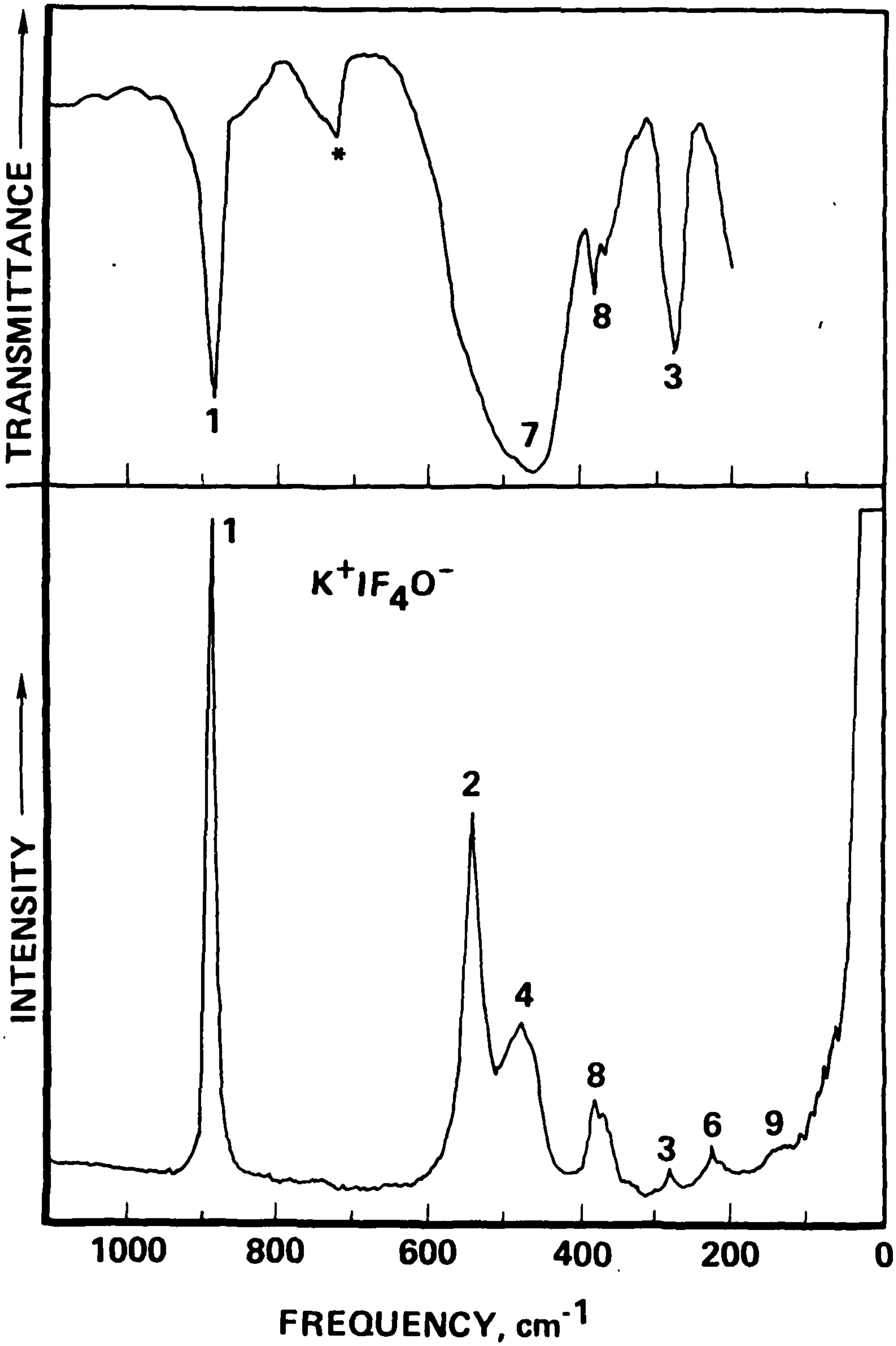
(c) data from ref. 16

(d) data from ref. 14

(e) data from ref. 21, values of f_{rr} and $f_{rr'}$ in Table 5 of ref. 21 should be exchanged

(f) assuming $f_{\alpha\alpha} = 0$

(g) assuming $f_{\beta\beta} = 0$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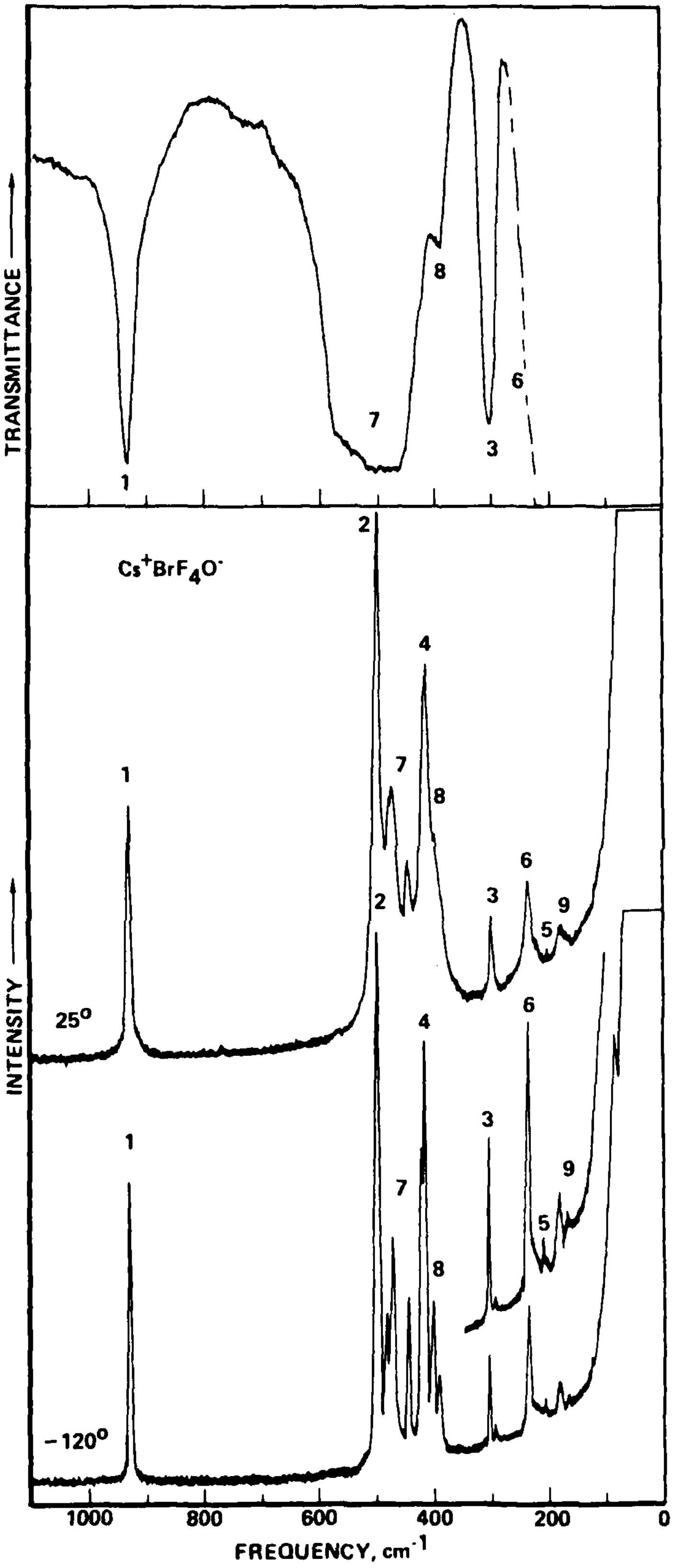
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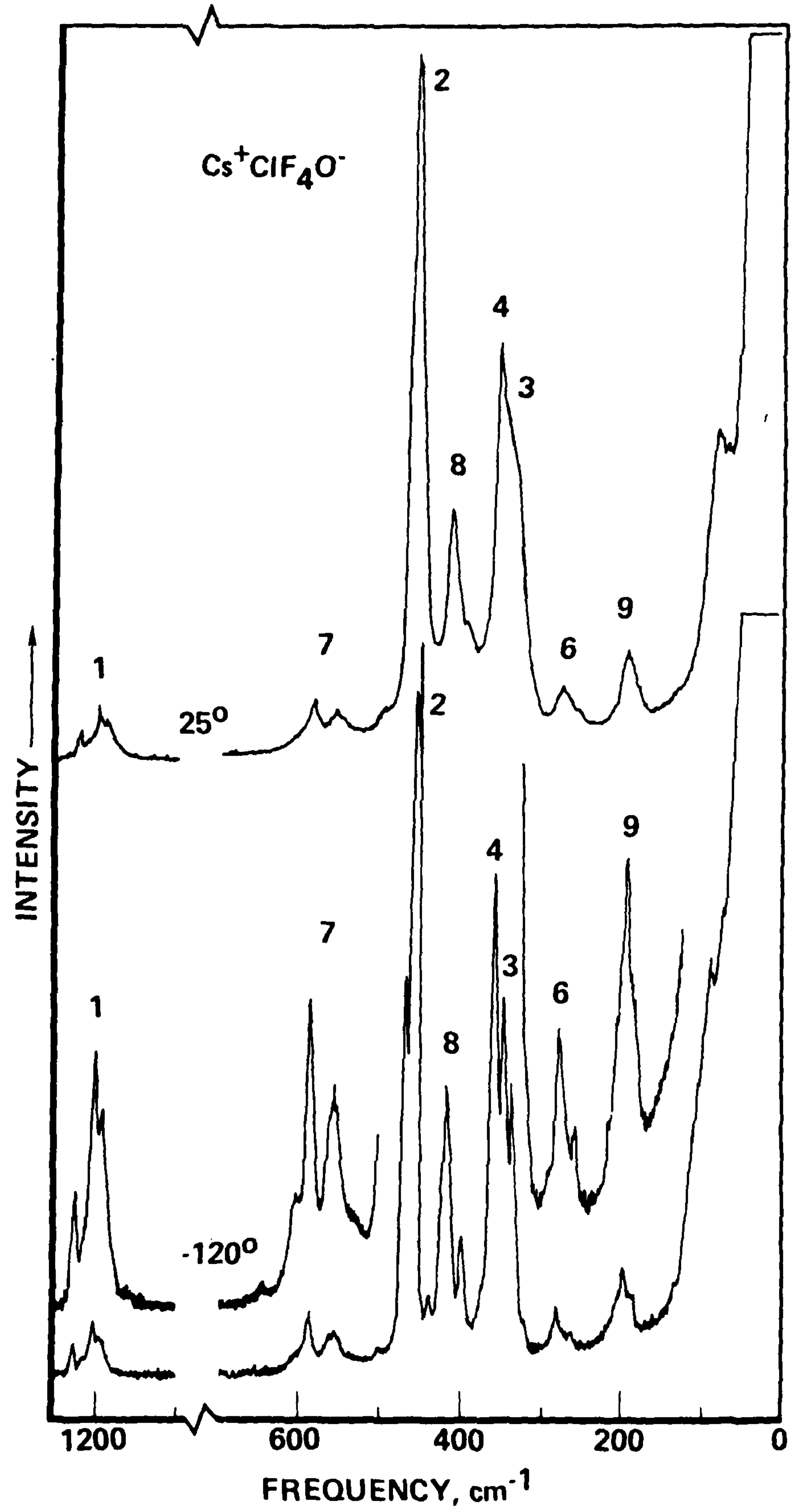

$Cs^+ClF_4O^-$
INTENSITY
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3
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1200
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FREQUENCY, cm^{-1}

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APPENDIX H

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

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Abstract

The infrared spectra of gaseous, solid, and matrix isolated BrF_3O and the Raman spectra of solid and liquid BrF_3O and of its HF and $FClO_3$ solutions are reported. Nine fundamental vibrations were observed, and some ^{79}Br - ^{81}Br isotopic shifts were measured in Ne, Ar, and N_2 matrices. These data support a pseudo trigonal bipyramidal structure of symmetry C_s with two fluorine atoms at the apexes and one fluorine, one oxygen, and one localized free electron pair at the remaining corners. A modified valence force field was computed using the isotopic data. The results show that the equatorial BrF bond (f_R = 3.51 mdyn/Å) is significantly stronger than the two axial BrF bonds (f_r = 2.93 mdyn/Å), and that the bond order of the BrO bond is close to two (f_D = 7.68 mdyn/Å). The vibrational and ^{19}Fnmr spectra show that in the liquid and solid state BrF_3O is associated through the axial fluorine atoms. Thermodynamic properties were computed for BrF_3O in the range 0-2000°K.

Introduction

The synthesis of the novel bromine oxyfluoride BrF_3O has recently been reported [1] by Bougon and Bui Huy. Based on incomplete vibrational spectra, a structure of symmetry C_s was proposed[1] for BrF_3O. In this paper, the results of a detailed investigation and analysis of the vibrational and ^{19}Fnmr spectra of this interesting compound are given which confirm the previously proposed structure.

Experimental Section

Bromine trifluoride oxide was prepared, as previously described,[1] from $KBrF_4O$ and O_2AsF_6 by a displacement reaction in BrF_5. The starting materials $KBrF_4O$ and O_2AsF_6 were obtained by literature methods.[2,3] The vacuum lines, spectrometers, instruments, and sampling techniques, used at C.E.N. have previously been described.[4,5]

At Rocketdyne, the BrF_3O was prepared in a passivated sapphire reactor which was connected through a small volume Teflon FEP U trap to a stainless steel Teflon FEP vacuum system. The crude BrF_3O was collected in this U trap by fractional condensation at -20°and was further purified by briefly pumping off the more volatile components at 0°. The U trap was incorporated into the matrix isolation apparatus so that the diluent gas could be swept through the trap into the matrix isolation inlet system. The length and diameter of the matrix inlet tube were kept at a minimum to avoid decomposition of the BrF_3O. The mole ratio of diluent to sample was controlled by the temperature and hereby the vapor pressure of BrF_3O in the U trap. In order to avoid extensive decomposition of BrF_3O, rapid deposition rates were required. The matrix isolation experiments were carried out at 3.6°K using CsI windows and an apparatus previously described.[6,7] A Perkin Elmer Model 283 spectrometer was used which was calibrated by comparison with standard gas calibration points.[8,9] The reported frequencies and isotopic shifts are believed to be accurate to ± 1 and ± 0.1 cm^{-1}, respectively.

The recording of infrared spectra of gaseous BrF_3O was found difficult due to rapid attack of the AgCl or AgBr windows. Since the attack of the AgBr windows was very rapid, they were protected by a 1 mm thick polyethylene sheet. To assure that the observed bands were indeed belonging to BrF_3O, the cell was periodically evacuated and refilled with fresh BrF_3O. One of the decomposition products found in the infrared cell was BrF_3.

The concentrated solution of BrF_3O in HF was obtained by dissolving a sample of $CsBrF_4O$ in a thin walled 6 mm o.d. Kel F capillary in anhydrous HF.

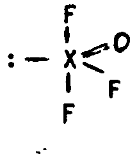
When the HF was added the following displacement reaction occurred in quantitative yield:[10]

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

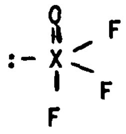
The Raman spectra of this solution were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line. A Claassen filter was used to eliminate plasma lines.[11] Polarization measurements were carried out by Method VIII as described by Claassen et al.[11]

Results and Discussions

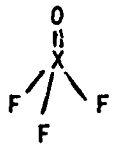
As previously discussed[12] in detail for ClF_3O, a monomeric halogen trifluoride oxide molecule theoretically could possess one of the following three structures:



I (C_s)



II (C_s)



III (C_{3V})

It has previously been shown[12] that ClF_3O has structure I, and the same arguments also hold for BrF_3O. Thus, the observed number of fundamental vibrations, the Br isotopic shifts, the infrared gas band contours, and relative band intensities and frequencies all rule out structures II and III. The following paragraphs can therefore be limited to a discussion of the experimental data in terms of structure I.

Infrared Spectrum of the Gas. Figure 1 shows the infrared spectrum of gaseous BrF_3O. Due to the low vapor pressure and low thermal stability of BrF_3O, only the five most intense infrared bands were observed in the gas phase. Figure 2 shows the band contours of four of these bands with scale expansion under higher resolution conditions. From the estimated (see below) geometry of BrF_3O, the three rotational constants were computed to be A=0.189, B=0.119, and C=0.086 cm^{-1}. Based on these values, the infrared band contours of BrF_3O should be intermediate between those of sets 25 and 24 in the tables of Ueda and Shimanouchi.[13] The band at 601 cm^{-1} shows a PR branch separation of about 17 cm^{-1} (see Figure 2), in excellent agreement with the 17 cm^{-1} estimate[13] for an A-type band. This confirms the assignment of this band to the antisymmetric axial FBrF stretching mode, ν_7 (A''). For this mode, the change of dipole moment occurs along the axis with the smallest moment of inertia. The second band for which a well defined band contour was observed is the BrO stretching mode, ν_1 (A'), at 995 cm^{-1}. This band does not exhibit well defined P and R branches, as expected[13] for a blend of the B and C type.

Infrared Spectra of Matrix Isolated BrF_3O. Due to the limited availability of gas phase data and the tendency of BrF_3O to associate in the liquid and solid state (see below), it was important to obtain matrix isolation spectra. Furthermore, these spectra were expected to yield information about the nature of the association of BrF_3O. Since for the closely related BrF_3[14] and $FBrO_2$[15] molecules pronounced and unpredictable matrix effects and splittings were observed, the spectra of BrF_3O were recorded in three different matrix materials, i.e. Ne, Ar, and N_2. A survey scan of BrF_3O in N_2 is shown in Figure 3, trace A. Spectra of BrF_3O in Ne, Ar, and N_2, recorded with scale expansion and under high resolution conditions, are given in Figures 4-7, together with the observed frequencies. As can be seen, the matrix data confirm the presence of the five bands observed in the gas phase spectra. Two additional fundamental vibrations were observed at about 400 and 250 cm^{-1}, in agreement with the Raman data (see below). By analogy with previous reports[14,16] on matrix isolated BrF_3, the BrF_3O spectra exhibited pronounced matrix frequency shifts and splittings. As for BrF_3[14] and $FBrO_2$[15], a Ne matrix was found to give for most bands the simplest spectrum and the frequency values closest to those observed for the gas phase.

The matrix spectra exhibit, in addition to site and bromine isotopic splittings (see below), bands due to associated BrF_3O. Most of these are marked by a P in Figure 4-7. Their assignment to associated BrF_3O was confirmed by variation of the matrix ratio, controlled diffusion experiments and the recording of the spectrum of neat solid BrF_3O at 3.6°K (see trace B of Figure 3). Their interpretation will be discussed later.

Reliable determination of the bromine isotopic shifts (bromine has two natural isotopes, ^{79}Br and ^{81}Br, of about equal abundance) was important for the assignments and force field computations. Whereas matrix splittings depend on the matrix material, the isotopic splittings should be matrix independent and be observable in all three matrix materials.

In a Ne matrix, monomeric BrF_3O appears to occupy only one matrix site, as evidenced by the observation of a single isotopic doublet for ν_1, ν_2, and ν_7 (see Figures 4-7). The splittings observed for ν_3, ν_8, and ν_5 in Ne are too large for bromine isotopes and also were not observed for the Ar and N_2 matrices which contained much less associated BrF_3O. Consequently, one of the two bands in each of these pairs is attributed to associated BrF_3O.

In Ar or N_2 matrices, monomeric BrF_3O occupies at least two different matrix sites. When the site symmetry splittings are of the same magnitude as the bromine isotopic splittings, the two central lines will coincide and the bands can have the appearance of a triplet with a more intense central component. Typical examples for such apparent triplets are the bands at about 580 cm^{-1} in Ar and at about 998 and 618 cm^{-1} in N_2. The observed and computed ^{79}Br - ^{81}Br isotopic shifts will be given and discussed in the force field section. The doublet at 985.6 and 982.9 cm^{-1}, observed for the N_2 matrix (see Figure 4, lower trace), exhibits a splitting (2.7 cm^{-1}) too large for either ν_1 (2.25 cm^{-1}) or an N_2 site splitting, but has about the right frequency separation (2.9 cm^{-1}) for the bromine isotopes in the combination band ($\nu_7 + \nu_8$) and, therefore, is assigned in this manner.

Raman Spectra. Raman spectra of BrF_3O were recorded for the solid at -180 and -30°C (Figure 3, traces C and D), for the liquid at 20°C, and HF solutions at high and low concentrations (Figure 8, traces A, B, and C). The spectra of the solid, liquid, and HF solution agree well with each other, except for the symmetric axial FBrF stretching mode, ν_3 (A'), which, due to association effects (see below), shows varying degrees of splitting and frequency shifts to lower frequencies. The infrared spectra (see above) had shown seven of the nine fundamental vibrations, expected[12] for BrF_3O of symmetry C_S. The remaining two fundamental vibrations are readily identified from the Raman spectra and have frequencies of about 200 and 330 cm^{-1}. Polarization measurements were carried out for the concentrated HF solution (traces B, Figure 8) and show the number of polarized and depolarized bands expected for model I (6A' + 3A'').

Assignments. Assignment of the 9 fundamental vibrations observed for BrF_3O are straight forward. By analogy with ClF_3O[12], model I of symmetry C_S should possess 6A' and 3A'' modes, all being infrared and Raman active. In the Raman spectrum, only the A' modes should be polarized. The experimental observations are in agreement with these predictions.

Of the six fundamental vibrations in species A', three should be stretching modes involving the Br=O, the equatorial BrF, and the axial FBrF band , respectively. The Br=O stretching mode should have a significantly higher frequency than the BrF modes and, therefore, is assigned to the band at about 1000 cm^{-1}. The equatorial BrF stretching mode should have a higher frequency and infrared intensity and a significantly larger $^{79}Br - ^{81}Br$ isotopic splitting than the symmetric axial FBrF stretch. Consequently, these two modes are assigned to the bands at 625 and 531 cm^{-1}, respectively.

For the assignment of the three A' deformation modes, three polarized Raman bands at about 350, 240, and 200 cm^{-1} are available. The three deformation modes can be approximately described as an equatorial FBrO scissoring motion and as two axial FBrF bending motions. Since only one of these three involves the doubly bonded oxygen ligand, it should have the highest frequency and is assigned to the 350 cm^{-1} fundamental. The two remaining fundamentals belong to the two axial FBrF bending modes. Since they are highly mixed (see below), their identity will be discussed in the force constant section.

There are three fundamental vibrations in species A'' with frequencies of about 600, 390, and 330 cm^{-1} available for assignment to the antisymmetric axial FBrF stretch and the equatorial FBrO wagging and torsion motions. Based on its high frequency, large ^{79}Br - ^{81}Br isotopic splitting, and high infrared and low Raman intensity, the 600 cm^{-1} fundamental must be assigned to the antisymmetric axial FBrF stretching mode. Assignments for the two remaining deformation modes are made on the basis of their relative infrared intensities. The torsional mode should be of much lower intensity than the wagging mode and is therefore assigned to the 330 cm^{-1} fundamental. This leaves the 390 cm^{-1} fundamental for assignment to the wagging mode. The bands observed below 130 cm^{-1} in the Raman spectrum of solid BrF_3O have frequencies too low for internal modes and also were not observed for either the liquid or HF solutions. Consequently, they are assigned to lattice vibrations.

The above assignments are summarized in Table 1 and compared to those previously reported for ClF_3O[12] and BrF_3.[14, 16, 17] As can be seen, the agreement is excellent, thus lending additional support to our assignments. The decrease in the frequencies of the HalF stretching vibrations on oxygen addition is caused by the following effect. These halogen fluorides are more electronegative than oxygen. Consequently, an added oxygen ligand releases electron density to the rest of the molecule. This increases the $\overset{\delta-}{F}-\overset{\delta+}{Hal}$ polarity of these bonds and hereby weakens them.

Force Constants. A normal coordinate analysis was carried out for BrF_3O to support the above assignments. The potential and kinetic energy metrics were computed by a machine method.[18] The geometry assumed for this computation was $D(BrO)=1.56\mathring{A}$, $R(BrF')=1.72\mathring{A}$, $r(BrF)=1.81\mathring{A}$, $\alpha(OBrF')=120°$, $\beta(OBrF)=\gamma\ (F'BrF)=90°$, based on the observed[19] geometry for BrF_3 and an extrapolation between BrO bond length and stretching frequency, similar to that[20] used for ClO bonds, using the data published for BrO_4^- [21,22]

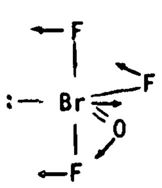
and $FBrO_3$.[23,24] In the absence of structural data for BrF_3O, we assumed an idealized geometry with 90 and 120°bond angles. However, based on the known increase in mutual repulsion within the series $F < O <$ free electron pair, the true geometry of BrF_3O is expected to show a F'BrO bond angle of less than 120° and a slightly bent axial FBrF group. The latter prediction is also supported by the observation of the symmetric axial BrF_2 stretching mode as a weak band in the infrared spectrum of gaseous BrF_3O. The symmetry coordinates used for BrF_3O were identical to those previously given[12] for ClF_3O, except for interchanging S_3 and S_4. The bending coordinates were weighted by unit (1Å) distance.

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. The observed $^{79}Br - ^{81}Br$ isotopic shifts were used as additional constraints, and the most simple force field was chosen which exactly duplicated these shifts. The computed force constants are listed in Table II. Uncertainty estimates are difficult to make. However, numerical experiments indicate that the uncertainties in the valence force constants should not exceed 0.1 mdyn/Å.

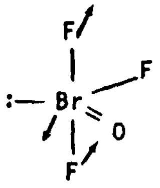
As can be seen from Table II, the observed frequencies and isotopic shifts can be accurately duplicated by a force field which, except for F_{56} and F_{78}, is diagonal. In the A' block, a small value was required for F_{78} in order to be able to fit the isotopic shift observed for ν_7. The introduction of a nonzero value for F_{78} also resulted in the PED becoming significantly more characteristic. In the A' block, a relatively large value was required for F_{56} in order to be able to fit ν_5 and ν_6. However, the remaining fundamentals were little influenced by the value of F_{56}.

The potential energy distribution (see Table II) shows that all fundamentals are highly characteristic, except for ν_5 and ν_6 which correspond to approximately equal mixtures of F_{55} and F_{66}. More information on the nature of ν_5 and ν_6 can be obtained from the eigenvector matrix L. Its important elements for ν_5 and ν_6 are: ν_5, $-0.006\ S_4$, $0.133\ S_5$, $-0.119\ S_6$, and ν_6, $-0.034\ S_4$, $0.057\ S_5$, $0.081\ S_6$. By analogy with ClF_3O[12], ν_6 and ν_5

correspond to a symmetric and an antisymmetric combination, respectively, of the symmetry coordinates S_6 and S_5. As shown by the following stick diagram,



ν_6



ν_5

ν_6 can be visualized as a symmetric bending motion of the two axial fluorine atoms in a plane containing the linear FBrF group and the free valence electron pair of bromine. The ν_5 fundamental can be considered as the corresponding bending motion perpendicular to this plane. As shown by the stick diagram, ν_6 also contains a significant contribution from the equatorial scissoring coordinate S_4.

The force constants of greatest interest are the stretching force constants since they are a direct measure for the strength and covalent character of the various bonds. A comparison of the stretching force constants of BrF_3O with those of similar molecules and ions is given in Table III. As can be seen, the value of the BrO stretching force constant is in good agreement with our expectations for a BrO double bond. The general trend of the BrO stretching force constants listed in Table III is similar to that observed for chlorine oxyfluorides.[25] The force constant increases with increasing fluorine substitution, oxidation state, and formal charge of the central atom. Consequently, it is not surprising that BrF_3O exhibits the highest f_D value of the listed compounds. The only presently known bromine oxyfluoride, expected to have a higher f_D value, is the BrF_2O^+ cation which has a BrO stretching frequency of about 1050 cm^{-1}.[26-28]

The BrF stretching force constants of BrF_3O are similar to those of BrF_3, although somewhat lower due to the electron density releasing effect of the oxygen substituent (see above). The difference between the equatorial and the axial BrF stretching force constant of BrF_3O is significantly larger than their estimated uncertainties (see above). This indicates that the equatorial BrF bond is significantly stronger than the two axial ones. The same effect has previously been observed for ClF_3O and was explained [12] by significant contributions from semiionic three-center four-electron p σ bonds [29-31] to the axial bonds.

Nmr Data. ^{19}F nmr spectra were recorded for the neat liquid at 10° and for $FClO_3$ solutions of two different concentrations in the temperature range 10 to -40° (see Table IV). By analogy with ClF_3O,[25,32,33] only a single line signal was observed. However, it has been shown [34] by relaxation time measurements that ClF_3O contains two different kinds of fluorines with a chemical shift separation of 50 ppm. The observation of a single line signal was attributed to rapid exchange.[34] Consequently, the observation of a single line signal for BrF_3O might be explained in a similar manner and should not be used as an argument against the above proposed model of symmetry C_s.

The signal observed for BrF_3O was shifted to higher field with both decreasing temperature and increasing concentration. Both trends indicate that the resonance for associated BrF_3O (see below) occurs upfield from that of monomeric BrF_3O.

Association in the Liquid and Solid Phase. The physical properties of BrF_3O, i.e. its relatively high melting and boiling point and low vapor pressure, indicate association in the liquid and solid phase. This was experimentally confirmed by vibrational and nmr spectroscopy. By analogy with the findings for the similar pseudo-trigonal bipyramidal molecules BrF_3, SF_4, ClF_3,[14,35] and ClF_3O,[12] it can be shown that condensed BrF_3O is associated through fluorine bridges. The bromine atom achieves pseudo-hexacoordination by accepting an axial fluorine atom of another BrF_3O molecule as a fourth equatorial ligand.

As expected [12] for this type of association, the axial FBrF stretching frequencies are shifted to significantly lower frequencies, whereas the BrO and the equatorial BrF stretch are only little affected. Thus, the Raman spectra of the neat liquid and of HF solutions of BrF_3O (see Figure 8) show that the band due to the symmetric axial FBrF stretching mode has decreased in frequency by 30-80 cm^{-1} and has become very broad. The Raman spectrum of a 2×10^{-2} molar solution of BrF_3O in $FClO_3$ at -10° has also been recorded. However, in this relatively unpolar solvent, the monomer concentration is high, as evidenced by νsym FBrF having a freqquency of 527 cm^{-1}. For the BrO and the equational BrF stretching mode, frequencies of 996 and 619 cm^{-1}, respectively, were observed which are also close to those of the corresponding gas phase values.

For neat solid BrF_3O (see Figure 3, traces B-D) association predominates, as expected. [12] For the symmetric FBrF stretching mode, only a weak Raman band occurred in the monomer region at 526 cm^{-1}, but a series of bands was observed at 511, 480, 457, and 447 cm^{-1} with increasing relative intensities which show infrared counterparts of medium intensities. Furthermore, the infrared frequency of the antisymmetric FBrF stretching mode has decreased by about 60 cm^{-1}, relative to the gas phase value.

The above conclusions were further corroborated by the results from the matrix isolation study. In addition to the bands due to monomeric BrF_3O, new bands were observed, particularly in the Ne spectra. These new bands had frequencies similar to those of neat solid BrF_3O and, therefore, are assigned to associated BrF_3O. In agreement with previous findings [12] for ClF_3O, the bands due to associated BrF_3O were observed on the high frequency sides of $\nu(Br=O)$ and $\nu(BrF')$ and the low frequency side of ν_{as} (FBrF) (see Figures 4 and 5, bands marked by P). For νsym (FBrF), the bands due to associated BrF_3O at 490 and 470 cm^{-1} (trace A, Figure 3) exhibited a large shift to lower frequencies and were more intense than that of the corresponding monomer band at 524 cm^{-1}. The higher intensities of the 490 and 470 cm^{-1} bands do not imply the presence of more associated than monomeric BrF_3O, but are mainly due to a larger change of dipole moment involved in these modes. The ratio of monomer to oligomer can better be judged from the relative intensities of bands, such as ν(BrO), which do not participate in the bridge formation. In Figure 3, trace A, the appropriate bands are 998 cm^{-1} (monomer) and the shoulder on its high frequency side (oligomer).

It should be noted that the spectra of neat liquid or solid BrF_3O did not show any evidence for bands due to BrF_2O^+ [26-28] or BrF_4O^- [2,10,36]. This rules out extensive self-ionization according to $2BrF_3O \rightleftharpoons BrF_2O^+BrF_4O^-$.

Additional support for the proposed association stems from the ^{19}F nmr spectra of BrF_3O which by analogy with those [26,34] of ClF_3O show an upfield shift with increasing concentration and decreasing temperature, conditions which favor association. For ClF_3O, the axial fluorine signal is observed [34] at higher field than that due to the equatorial fluorine. Since the axial fluorine bond is weaker than the equatorial one, an upfield shift is indicative of bond weakening, i.e. association.

Thermodynamic Properties. The thermodynamic properties of BrF_3O were computed with the molecular geometry given above and the vibrational frequencies of Table II, assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation.[37] These properties are given for the range 0-2000°K in Table V.

Conclusion. Except for the ^{19}F nmr data, which in the absence of relaxation time measurements[34] are inconclusive, all the data observed for BrF_3O are in excellent agreement with the predictions made for Model 1 of symmetry C_s. Whereas gaseous, matrix isolated, and $FClO_3$ dissolved BrF_3O is mainly monomeric, liquid, solid, and HF dissolved BrF_3O shows pronounced association involving bridging through the axial fluorine atoms.

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Diagram Captions

Figure 1. Infrared spectrum of gaseous BrF_3O at 5 mm pressure. The window material used above 450 cm^{-1} was AgCl and below 450 cm^{-1} was AgBr protected by a 1 mm thick polyethylene sheet. The broken lines indicate absorption due to the window material.

Figure 2. Infrared band contours recorded for gaseous BrF_3O with 10 fold scale expansion under higher resolution conditions.

Figure 3. Vibrational spectra of solid BrF_3O. Trace A, infrared spectrum of BrF_3O in a N_2 matrix (MR ~ 1000:1), recorded at 3.6°K using CsI windows. Trace B, infrared spectrum of neat BrF_3O, recorded at 3.6°K using CsI windows. Traces C and D, Raman spectra of neat BrF_3O recorded at -180 and -30°, respectively. The parts of the -30° spectrum, not shown in this figure, closely resembled those of Trace C.

Figure 4. Infrared spectra of matrix isolated BrF_3O (ν_1 region), recorded at 3.6°K with 20 fold scale expansion under higher, resolution conditions. The upper, middle and lower trace were recorded for Ne, Ar, and N_2 matrices, respectively. (MR ~ 1000:1). Bands due to monomeric and to associated BrF_3O are marked by M and P, respectively.

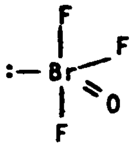
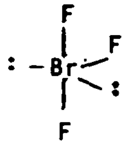
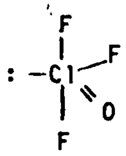
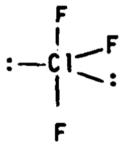
Figure 5. Infrared spectra of matrix isolated BrF_3O (ν_4 and ν_5 region). The ν_2 band in N_2 matrix was recorded for a thicker sample.

Figure 6. Infrared spectra of matrix isolated BrF_3O (ν_7 and ν_8 region).

Figure 7. Infrared spectra of matrix isolated BrF_3O (ν_4 and ν_5 region). The ν_4 and ν_5 bands in N_2 and the ν_5 band in Ar were recorded for a thicker sample.

Figure 8. Raman spectra of liquid BrF_3O. Trace A, neat liquid. Traces B, concentrated HF solution with the incident polarization parallel and perpendicular; P and DP indicate polarized and depolarized bands, respectively. Trace C, dilute HF solution.

Table 1. Vibrational Spectra[a] of BrF_3O Compared to Those of BrF_3^b, ClF_3O^c, and ClF_3^b

Observed frequencies, cm^{-1}, and relative intensities[d]								Assignment for XF_3O in Point Group C_s		Approximate Description of Mode
										
IR	RA[g]	IR	RA	IR	RA	IR	RA			
995s	1008s,p	-		1224s	1222(1.5)p	-		A'	ν_1	$\nu(X{=}O)$
625s	619vs,p	675s	675s,p	692s	694(2.6)p	751s	752s,p		ν_2	$\nu(XF_{equat})$
531mw	502vs,p	552w	552vs,p	481m	482(10)p	530m	529vs,p		ν_3	$\nu sym(F_{ax}XF_{ax})$
345ms	350m,p	-		491ms	489(1)	-			ν_4	$\delta sciss(OXF_{equat})$
240m[e]	235w	242	233w,p	318m	319(0.1)	328	329w,p		ν_5	$\delta sciss\ (F_{ax}XF_{ax})$ in $F\ddot{X}F$ plane
	198mw,p	242		230mw	224(0.4)p	328			ν_6	$\delta sciss\ (F_{ax}XF_{ax})$ out of $F\ddot{X}F$ plane
601vs		614vs	612 vvw	676vs		702vs		A''	ν_7	$\nu as\ (F_{ax}XF_{ax})$
397mw[f]	394mw,dp	350vw		501m	500(1)	442w	431w,dp		ν_8	$\delta wag\ (OXF_{equat})$
	330sh,dp	-		412w	414(0.2)dp	-			ν_9	$\tau(OXF_{equat})$

(a) all frequencies are gas phase values except as noted
(b) data from ref 17
(c) data from ref 12
(d) uncorrected Raman intensities
(e) Ne matrix value
(f) neat solid
(g) conc. HF solution

Table II. Observed Frequencies, Symmetry Force Constants,[a] Computed and Observed ^{79}Br - ^{81}Br Isotopic Shifts, and Potential Energy Distribution[b] for BrF_3O

		Frequency, cm^{-1}	Symmetry Force Constants		Isotopic Shifts, cm^{-1} $\Delta\nu$ comp	$\Delta\nu$ obsd	PED
A'	ν_1	995	$F_{11} = f_D$	7.68	2.28	2.25	$99\ F_{11}$
	ν_2	625	$F_{22} = f_R$	3.51	1.54	1.5	$97\ F_{22}$
	ν_3	531	$F_{33} = f_r + f_{rr}$	3.16	0		$100\ F_{33}$
	ν_4	345	$F_{44} = f_\alpha$	1.21	1.01		$93\ F_{44}$
	ν_5	236	$F_{55} = f_\beta + f_{\beta\beta'}$	1.70	0.54		$91\ F_{55} - 63\ F_{56} + 70\ F_{66}$
	ν_6	201	$F_{66} = f_\gamma + f_{\gamma\gamma'}$	1.62	0.30		$45\ F_{66} + 25\ F_{56} + 24\ F_{55}$
			$F_{56} = f_{\beta\gamma'} + f_{\beta\gamma''}$	0.65			
A''	ν_7	601	$F_{77} = f_r - f_{rr}$	2.70	2.68	2.7	$98\ F_{77}$
	ν_8	394	$F_{88} = f_\beta - f_{\beta\beta'}$	1.23	0.23		$98\ F_{88}$
	ν_9	330	$F_{99} = f_\gamma - f_{\gamma\gamma'}$	1.15	0.21		$96\ F_{99}$
			$F_{78} = f_{r\beta} - f_{r\beta'}$	0.2			

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

(b) Percent contributions. Contributions of less than 9% to the PED are not listed.

Table III. Stretching Force Constants (mdyn/Å) of BrF_3O Compared to Those of Similar Molecules

	BrO_3^-[a]	BrO_4^-[b]	BrF_4O^-[c]	$FBrO_2$[d]	BrF_3O	BrF_3[e]	BrF_5[f]	ClF_3O[g]	ClO_4^-[b]	ClF_3[h]
f_D (XO)	5.28	6.05	6.70	6.76	7.68	-	-	9.37	8.24	-
f_R (XF')	-	-	-	-	3.51	4.07	4.02	3.16	-	4.19
f_r (XF)	-	-	2.14	2.25	2.93	3.10	3.24	2.34	-	2.70
f_{rr}	-	-	0.21	-	0.23	0.31	0.15	0.26	-	0.36

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

(b) ref 22

(c) ref 10

(d) E. J. Baran, Spectrosc. Letters, 9, 323 (1976)

(e) ref 16

(f) K. O. Christe, E. C. Curtis, C. J. Schack, and D. Pilipovich, Inorg. Chem., 11, 1679 (1972)

(g) ref 12

(h) ref 14

Table IV. ^{19}Fnmr Spectra of Neat BrF_3O and in $FClO_3$ Solution

		Chemical Shift[a], ppm			
Temperature (°C)	+ 10	-10	-20	-30	-40
Neat Liquid	- 165.2				
2.3 Molar Solution	- 165.2	-163.2	-161.4	-160.8	-160.2
2.5 x 10^{-2} Molar Solution		-169.7	-169.5	-168.9	-167.2

(a) using $CFCl_3$ as external standard

Table V. Thermodynamic Properties for BrF_3O

T,°K	C_p°	$H^\circ - H_o^\circ$	$-(F^\circ - H_o^\circ)/T$	S°
0	0.	0.	0.	0.
100	10.871	0.872	30.788	59.512
200	16.448	2.255	37.595	68.868
298.15	19.830	4.050	62.543	76.127
300	19.878	4.087	62.627	76.250
400	21.852	6.182	66.809	82.264
500	23.032	8.431	70.416	87.278
600	23.775	10.774	73.591	91.548
700	24.265	13.178	76.427	95.252
800	24.603	15.622	78.988	98.516
900	24.845	18.095	81.322	101.428
1000	25.023	20.589	83.466	104.055
1100	25.157	23.098	85.448	106.447
1200	25.261	25.619	87.291	108.641
1300	25.343	28.150	89.012	110.666
1400	25.409	30.688	90.627	112.547
1500	25.462	33.231	92.147	114.301
1600	25.506	35.780	93.584	115.946
1700	25.543	38.332	94.945	117.494
1800	25.574	40.888	96.239	118.955
1900	25.600	43.447	97.471	120.338
2000	25.623	46.008	98.648	121.652

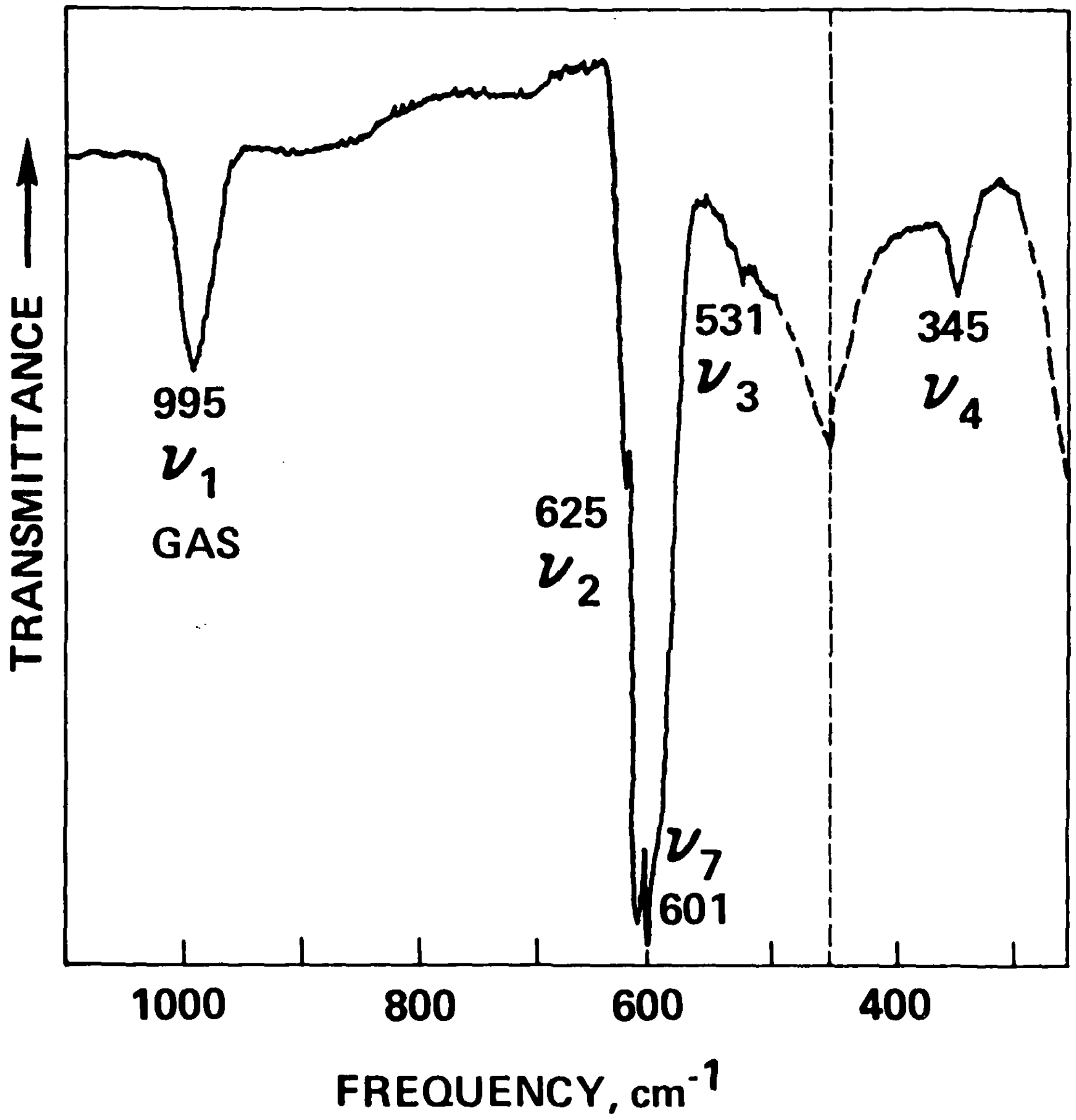

TRANSMITTANCE
995
ν_1
GAS
625
ν_2
ν_7
601
531
ν_3
345
ν_4
1000
800
600
400
FREQUENCY, cm^{-1}

FIG. 1

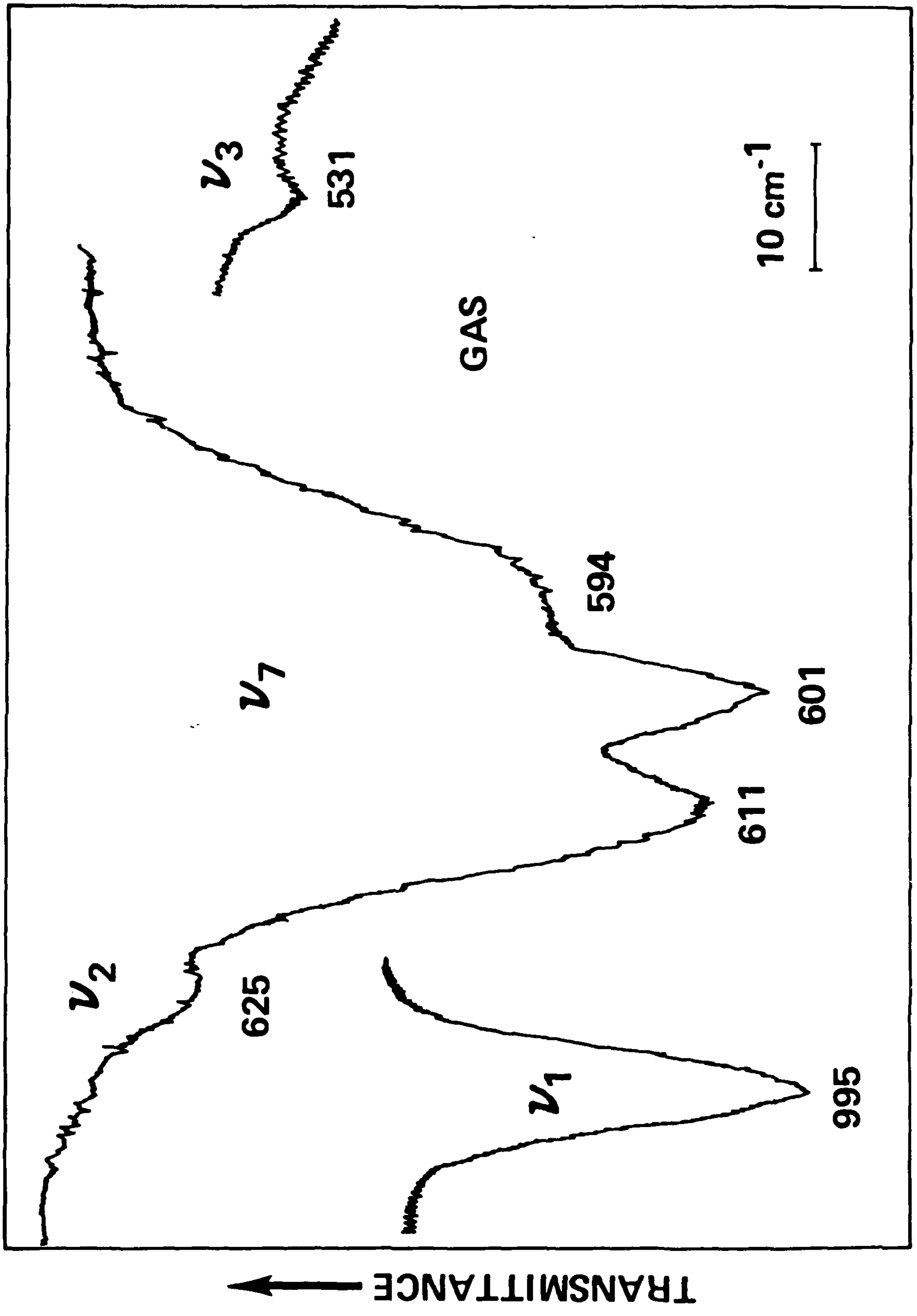
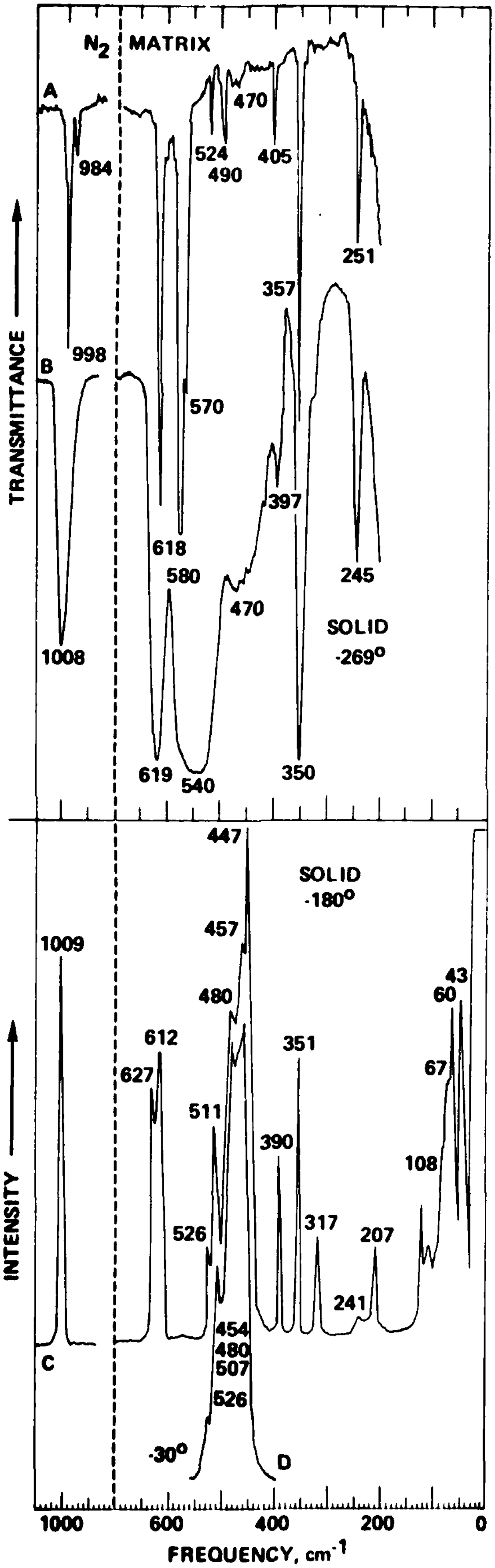

ν_2
625
ν_1
995
611
601
ν_7
594
GAS
ν_3
531
10 cm^{-1}
FREQUENCY
TRANSMITTANCE

FIG 2



N$_2$
MATRIX
A
984
524
490
470
405
251
998
B
570
618
357
397
245
580
470
1008
SOLID
-269°
619
540
350
TRANSMITTANCE
447
SOLID
-180°
1009
457
480
612
43
60
627
351
67
511
390
108
526
317
207
241
454
480
507
526
C
-30°
D
INTENSITY
1000
600
400
200
0
FREQUENCY, cm^{-1}

FIG. 3

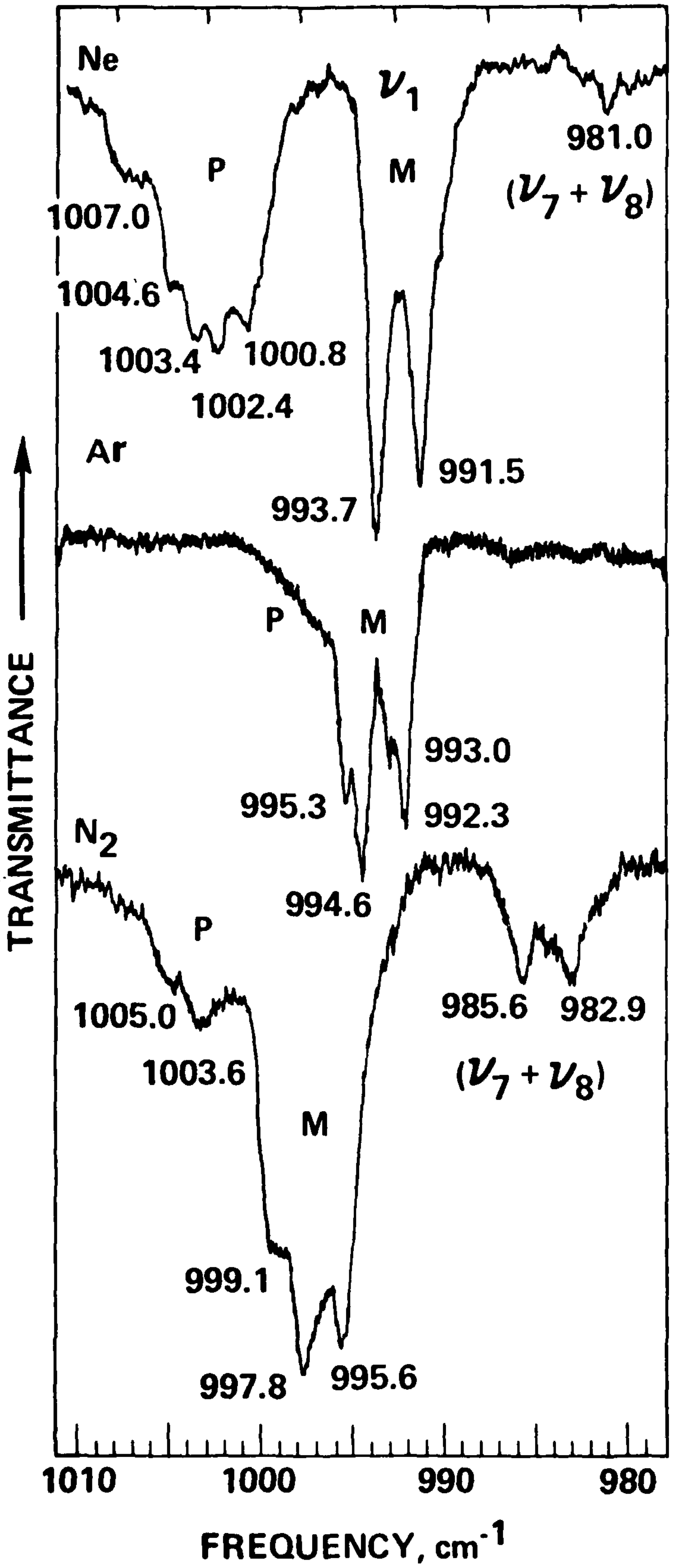
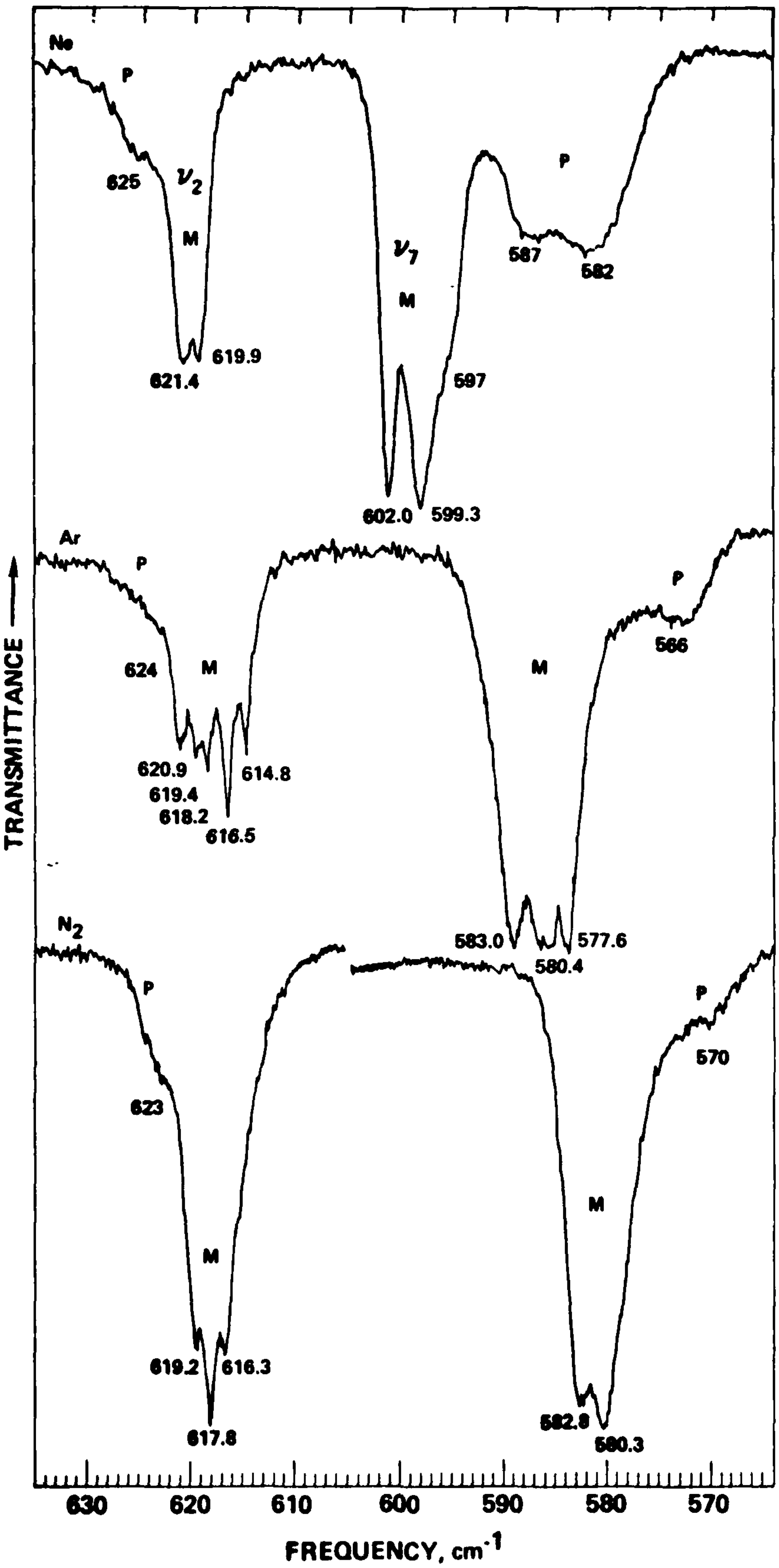

Ne
ν_1
P
M
1007.0
1004.6
1003.4
1002.4
1000.8
993.7
991.5
981.0
$(\nu_7 + \nu_8)$
Ar
P
M
995.3
994.6
993.0
992.3
N_2
P
1005.0
1003.6
M
999.1
997.8
995.6
985.6
982.9
$(\nu_7 + \nu_8)$
TRANSMITTANCE
1010
1000
990
980
FREQUENCY, cm^{-1}

FIG. 4



Ne
P
625
ν_2
M
621.4
619.9
ν_7
M
602.0
599.3
597
P
587
582
Ar
P
624
M
620.9
619.4
618.2
616.5
614.8
M
583.0
580.4
577.6
P
566
N2
P
623
M
619.2
617.8
616.3
M
582.8
580.3
P
570
TRANSMITTANCE
630
620
610
600
590
580
570
FREQUENCY, cm-1

FIG. 5

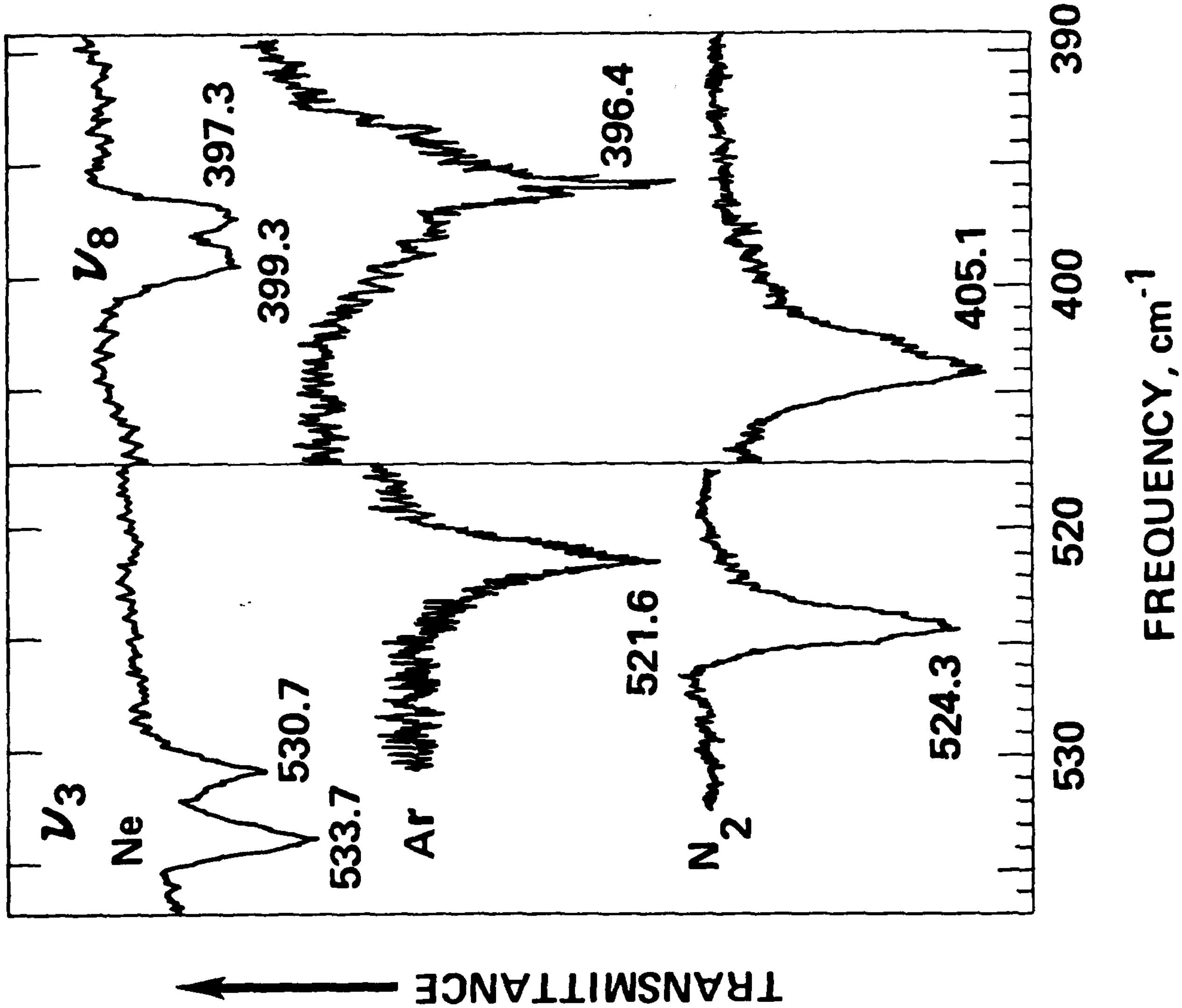

ν_3
Ne
533.7
530.7
Ar
521.6
N_2
524.3
ν_8
399.3
397.3
396.4
405.1
530
520
400
390
FREQUENCY, cm^{-1}
TRANSMITTANCE

FIG 6

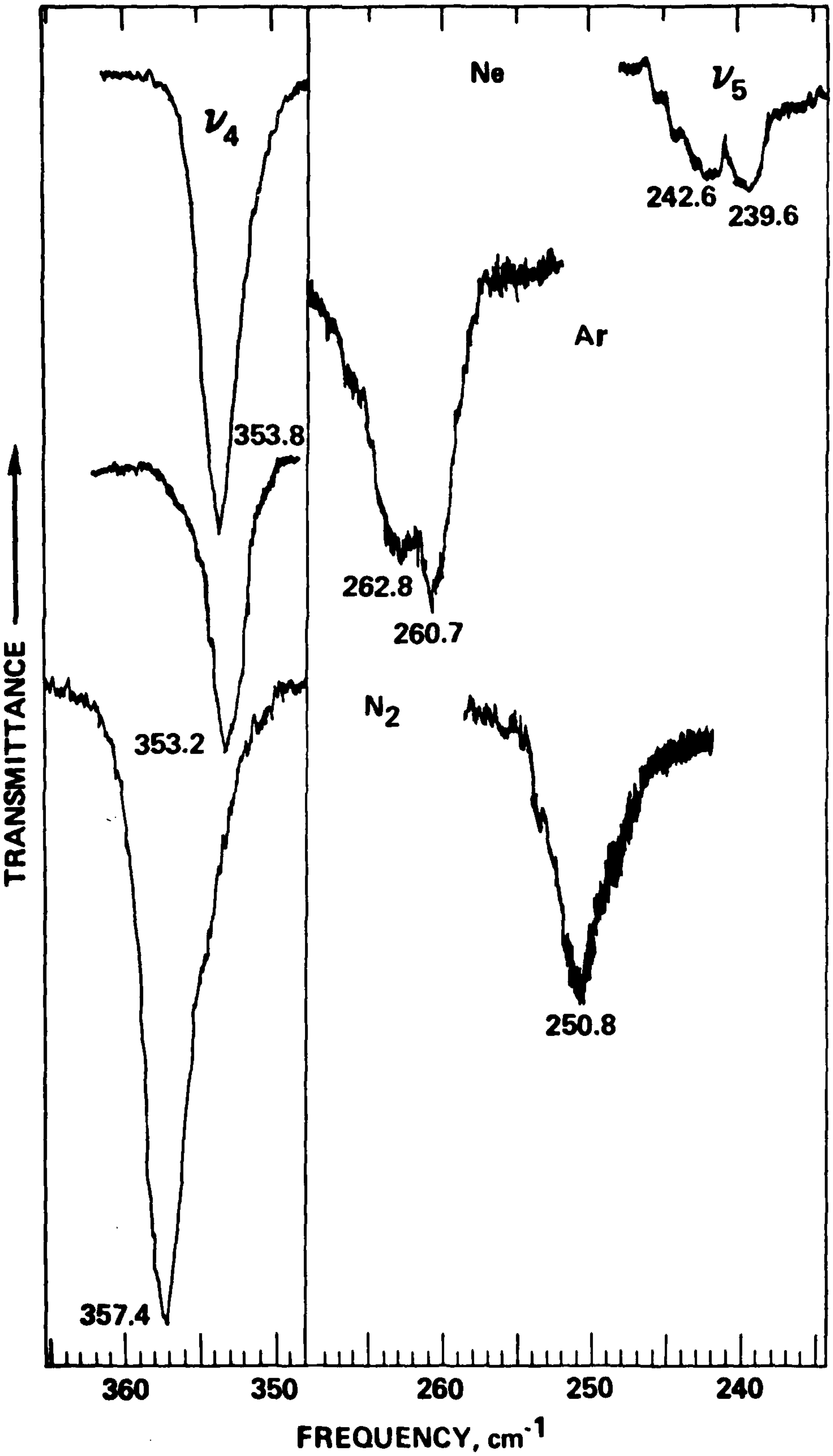
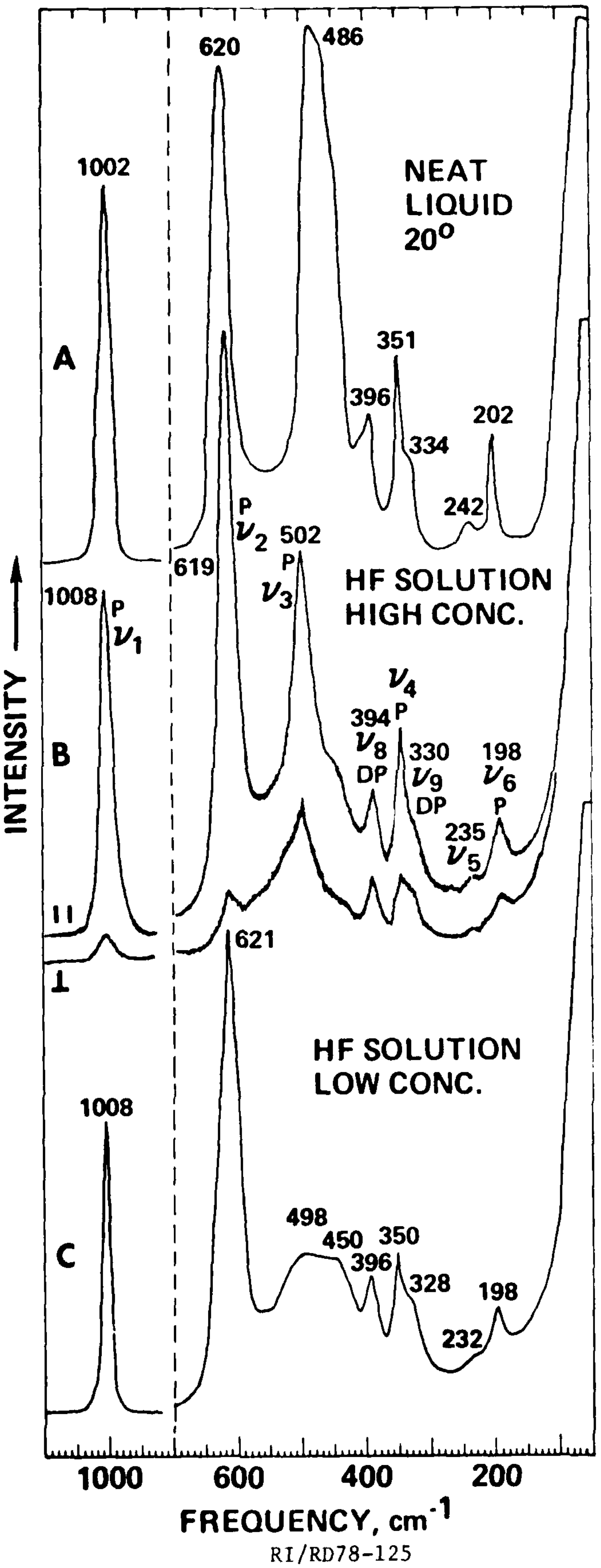

Ne
ν_4
ν_5
242.6
239.6
Ar
353.8
262.8
260.7
353.2
N$_2$
250.8
357.4
TRANSMITTANCE
360
350
260
250
240
FREQUENCY, cm^{-1}

FIG. 7



620
486
1002
NEAT LIQUID 20°
A
351
396
334
202
242
P
ν2
502
P
ν3
619
HF SOLUTION HIGH CONC.
1008
P
ν1
INTENSITY
ν4
P
394
ν8
DP
330
ν9
DP
198
ν6
P
B
235
ν5
||
⊥
621
HF SOLUTION LOW CONC.
1008
498
450
350
396
328
C
198
232
1000
600
400
200
FREQUENCY, cm⁻¹

FIG. 8

Contribution from Rocketdyne, A Division of
Rockwell International, Canoga Park, California 91304,
and M.A.N., Neue Technologie, D-8000
Muenchen, W. Germany

Bromyl Fluoride. Vibrational Spectra, Force Field, and Thermodynamic Properties

Karl O. Christe*, E. C. Curtis, and Eberhard Jacob

Abstract

Infrared spectra are reported for $FBr^{18}O_2$ in the gas phase and for $FBr^{16}O_2$ in Ne, N_2, and Ar matrices at 3.6°K. Isotopic shifts were measured for ^{79}Br-^{81}Br and ^{16}O-^{18}O and were used for the computation of a valence force field. Thermodynamic properties were computed for $FBrO_2$ and $FClO_2$ in the range 0-2000°K.

Introduction

Bromyl fluoride was first synthesized by Schmeisser and Pammer[1,2] in 1955. Because of its low thermal stability and high reactivity, this compound had been only poorly characterized and was not further studied until 1975. In 1975, Gillespie and Spekkens published[3] the Raman spectra of solid and liquid $FBrO_2$ and proposed a monomeric pyramidal structure, similar to that[4] of $FClO_2$. Using the Raman frequencies reported[3] for liquid $FBrO_2$, Baran calculated[5] a modified valence force field and mean amplitudes of vibration for $FBrO_2$, assuming all bond angles to be 108°. Very recently, Jacob succeeded[6] in obtaining good gas phase infrared spectra for $FBrO_2$. In spite of the fact that gaseous $FBrO_2$ possesses a half life of only 30 minutes at 15°C. He also prepared a sample of $FBr^{18}O_2$ and reported preliminary infrared data for the gas and for the neat and the argon matrix isolated solid. Although the oxygen isotopic shifts were measured, no ^{79}Br-^{81}Br isotopic shifts were given.

In this paper, we report higher resolution spectra and oxygen and bromine isotopic shifts for gaseous and for Ne, N_2, and Ar matrix isolated $FBrO_2$. In view of the interest[3,5] in the nature of bonding in $FBrO_2$, a new force field computation appeared warranted, particularly since the previously used[5] frequencies significantly differ from those of gaseous $FBrO_2$ and since the previously assumed[5] geometry of $FBrO_2$ was only a crude estimate. Furthermore, the availability of both oxygen and bromine isotopic shifts offered a unique opportunity to test the value of such additional data for the refinement of force fields for compounds, such as bromine oxyfluorides.

Experimental Section

The samples of $FBrO_2$ used for recording the gas phase spectra were prepared, as previously described,[6] by low-temperature co-condensation of BrF_5 and H_2O. The infrared spectra of gaseous $FBrO_2$ were recorded at 15°C on a Perkin Elmer Model 325 spectrophotometer in the range 4000-290cm^{-1} using a nickel cell with AgBr windows attached to an external mirror system (optical path length 110cm).

The samples of $FBrO_2$ used for the matrix isolation study were obtained as a by-product during a spectroscopic study[7] of BrF_3O. The spectrometer and handling have been previously described.[7]

Results and Discussion

Infrared Spectra of Gaseous $FBrO_2$. A survey infrared spectrum of gaseous $FBr^{18}O_2$ is shown in Figure 1. The corresponding spectrum of $FBr^{16}O_2$ has previously been reported.[6] Figures 2 and 3 show the band contours of each band recorded under higher resolution conditions and scale expansion.

The observed gas phase frequencies of $FBrO_2$ are compared in Table 1 to those[3,6] previously reported for the liquid and the solid. As can be seen from Table 1, the gas phase frequencies significantly deviate from those of liquid and solid $FBrO_2$, indicating some degree of association in the condensed phases. The BrF stretching mode, ν_2 (A'), exhibits the most pronounced frequency change ($-62cm^{-1}$) on going from the gas to the solid, whereas the mean frequency change of the two BrO_2 stretching modes, ν_1 (A') and ν_5 (A''), is only $-17cm^{-1}$. This indicates that association takes place mainly through the fluorine ligands. Preferential association through fluorine ligands has previously also been demonstrated[7] for BrF_3O.

Infrared Spectra of Matrix Isolated $FBrO_2$. In order to obtain unambiguous bromine isotopic shifts (bromine contains two naturally occuring isotopes, ^{79}Br and ^{81}Br, of almost equal abundance) for $FBrO_2$, the infrared spectra of matrix isolated $FBr^{16}O_2$ were recorded at 3.6°K. Since for the related BrF_3O[7] and BrF_3[8] molecules, pronounced and unpredictable matrix effects and splittings were observed, the spectra of $FBrO_2$ were recorded in three different matrix materials, i.e. Ne, N_2, and Ar. The observed spectra, recorded under higher resolution conditions with 20 fold scale expansion are shown in Figure 4. The observed frequencies are listed in Table 1.

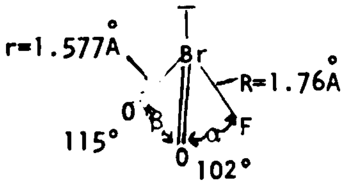
By analogy with previous reports on matrix isolated BrF_3[8,9] and BrF_3O[7], the $FBrO_2$ spectra exhibited pronounced matrix frequency shifts. As for BrF_3[8] and BrF_3O[7], a Ne matrix was found to give the best results and frequency values very close to those found for the gas phase (see Table 1). Association effects were most pronounced in the Ar matrix.

Assignments and Determination of Isotopic Shifts. The assignments for $FBrO_2$ in point group C_s are straightforward and are well supported by Raman polarization data[3], ^{18}oxygen isotopic shifts[6], and by comparison with the spectra of the closely related $FClO_2$[10] and SeO_2F^-[3] species. They are listed in Table 1 and require no further comment.

For the determination of the $^{16}O-^{18}O$ isotopic shifts in $FBrO_2$, the gas phase anharmonic infrared frequencies listed in Table I were used. However for compounds exhibiting such large isotopic shifts, anharmonicity corrections of these shifts are important for force field calculations. Unfortunately, no experimental data are available for $FBrO_2$ to permit reliable anharmonicity corrections. However for RuO_4, which possesses a central atom of a mass similar to that of Br and exhibits comparable $^{16}O-^{18}O$ isotopic shifts, anharmonicity corrections were estimated [11] to be about 1.4 and 0.5 cm^{-1} for the $^{16}O-^{18}O$ isotopic shifts of the ν_3 stretching and the ν_4 deformation modes, respectively. Assuming similar correction values for $FBrO_2$, the magnitude of the expected anharmonicity corrections obviously is significantly larger than the 0.1 cm^{-1} uncertainty in the values of the observed anharmonic frequencies. Therefore, we have treated the observed anharmonic oxygen isotopic shifts in the following normal coordinate analysis as the lower limit and have used 1.6 and 1.0 cm^{-1} larger shifts as the upper limits for the stretching modes ν_1 and ν_5 and the deformation mode ν_3, respectively. As will be shown below, the force field analysis supports this choice.

For the bromine isotopic shifts, anharmonicity corrections are much less of a problem due to the smallness (0-3cm^{-1}) of these shifts. Therefore, possible anharmonicity corrections for these shifts should not exceed the measured uncertainties (± 0.1cm^{-1}) of these shifts. The best values for the isotopic shifts are listed in the last two columns of Table 1. The agreement between the bromine isotopic shifts observed for gaseous $FBrO_2$ and those observed for the matrix isolated species is generally good if one takes into consideration that the Q branch bandcontours of ν_1 and ν_2 are distorted on the P branch side by hot bands and that for ν_5 a double Q branch is observed for each bromine isotope.

Force Field Computations. A normal coordinate analysis was carried out for $FBrO_2$ to obtain more reliable force constants for this interesting molecule and to examine the usefulness of isotopic shifts for such an analysis. The potential and kinetic energy matrices were computed by a machine method.[12] The following geometry was



assumed for this computation, based on the known geometries of $FBrO_3$[13], $FClO_3$[14], and $FClO_2$[4] and an extrapolation between BrO bond length and stretching frequency, similar to that[15] used for ClO bonds, using the data published for $FBrO_4^-$[16,17] and $FBrO_3$[13,18]. This geometry appears more likely than that (α = β = 108°, r = 1.63Å) chosen[5] by Baran for his computation.

The symmetry coordinates used for $FBrO_2$ were identical to those previously given[10] for $FClO_2$, except for the correction of the obvious typographical error in the factor of S_4. The bending coordinates were weighted by unit (1Å) distance.

The force constants were adjusted by trial and error with the aid of a computer to give an exact (0.1 cm^{-1}) fit between all observed and computed frequencies. The observed ^{79}Br-^{81}Br and ^{16}O-^{18}O isotopic shifts were used as additional constraints. We will first discuss our choice of a force field for the A'' block since it contains only one stretching and one deformation mode.

The force constants of F_{55} and F_{66} were computed as a function of F_{56}. The resulting curves are shown in Figure 5. We have also computed the bromine and oxygen isotopic shifts over the same range of F_{56} and have plotted their values in Figure 5. The observed isotopic shifts, $\Delta Br\nu_5 \pm 0.1$ cm^{-1} and $\Delta O\nu_5 + 1.6$ cm^{-1} (see above discussion of anharmonicity corrections), were used to define the probable range of the force constants. The values thus obtained are given in Figure 5 and Table II. Figure 5 demonstrates the importance of the anharmonicity corrections for $\Delta O\nu_5$, i.e. a better overlap with the $\Delta Br\nu_5$ force field constraint, as previously demonstrated[19] by McDowell and Goldblatt for OsO_4. Furthermore, it shows that the preferred force field closely corresponds to F_{66} being a minimum, a condition previously shown [19,20] to be a good approximation to the General Valence Force Field values for similar weakly coupled systems.

For the A' block of $FBrO_2$ the problem of defining a preferred force field is more difficult since this block contains two stretching and two deformation modes. Numerical experiments showed that only three of the six off-diagonal symmetry force constants were essential for fitting the isotopic data. These three off-diagonal constants were F_{13}, F_{24}, and F_{34}, with F_{13} and F_{34} being more important than F_{24}. This result is in good agreement with the previous findings[10] for the related $FClO_2$ molecule and is not surprising in view of the fact that G_{13}, G_{24}, and G_{34} are the major off-diagonal G matrix terms in the A' block. It was also shown that the variation of F_{13}, F_{24}, and F_{34} strongly influenced only the corresponding diagonal terms. This relative independence of the interaction constants permitted us to examine each of them separately. The results of these computations were again summarized in graphical form and are presented in Figures 6-8. In this manner, the values of F_{13}, F_{24}, and F_{34}, required to duplicate all the observed isotopic data, were determined. These three interaction constants were then combined in a single force field, and a satisfactory fit of the isotopic data could be achieved with only minor adjustments. The resulting force field is given in Table II. The computed oxygen shifts were intentionally kept slightly larger than the observed ones to leave some room for any future anharmonicity corrections.

Figures 6 and 7, dealing with the stretch-bend interaction constants F_{13} and F_{24}, respectively, are analogous to Figure 5, which has been discussed above in detail for the A'' block, and therefore do not require any further comment. Figure 8 shows the dependence of the two diagonal bending constants F_{33} and F_{44} on the bend-bend interaction constant F_{34}. In order to be able to fit the observed oxygen shift of ν_3, either a rather large positive or a small negative value is required for F_{34}. Of these two possibilities, the former is preferred, since it results in more plausible force constants. For F_{34} = 0.2, the potential energy distribution (PED) is essentially 100 percent characteristic (F_{44} = minimum), whereas for the extremal values of F_{34}, ν_3 and ν_4 become about even mixtures of F_{33} and F_{44}. The moderate amount of mixing obtained for ν_3 and ν_4 in our preferred force field (see Table II) is not surprising in view of their similar frequencies and motions involved. The remainder of the PED (see Table II) is highly characteristic and supports the approximate description ot the modes given in Table II.

A comparison of the internal force constants of $FBrO_2$ with those previously reported[5] by Baran is given in Table III. As can be seen, the two force fields significantly differ, particularly for f_R and $f_{\alpha\beta}$. Our results show that the BrF bond in $FBrO_2$ is significantly stronger than previously assumed[5].

Comparison with Similar Compounds and Bonding in $FBrO_2$. A comparison of the $FBrO_2$ stretching force constants with those of other bromine oxides, fluorides, and oxyfluorides is given in Table IV. The BrF stretching force constants are separated into two groups. In the f_R group, the BrF bonds contain significant contributions from semi-ionic 3 center -4 electron bonding, whereas in the f_R' group, the BrF bonds are largely covalent. The spread within each group is caused by secondary effects, such as formal charge (anion, neutral molecule, cation), degree of fluorine substitution, and oxidation state of the central atom. These effects have previously been discussed[21,22] in length for the corresponding chlorine compounds and appear to be also applicable to the bromine compounds of Table IV, although for the latter they are somewhat less pronounced. This is caused by the fact that the larger bromine central atoms are more polarizable than chlorine, hereby causing the two types of bonds to become less distinct.

As far as $FBrO_2$ is concerned, it can be seen from Table IV that its stretching force constants do not fit too well the general trends of Table IV. A similar anomaly has previously been noted for $FClO_2$ and was explained by a weak highly polar $(p-\pi^*)$ σ bond.[22] The same explanation, i.e. bonding between a 2p electron of F and an antibonding π^* orbital of the BrO_2 radical can be invoked for $FBrO_2$.

Thermodynamic Properties. The thermodynamic properties of $F^{79}Br^{16}O_2$ were computed with the molecular geometry given above and the vibrational frequencies of Table II, assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation[23]. These properties are given for the range 0-2000°K in Table V. Since no thermodynamic data had previously been reported for $FClO_2$, we have also computed these properties for $F^{35}Cl^{16}O_2$ (see Table VI) using the previously published frequencies[10] and geometry.[4]

Conclusion. A force field has been computed for $FBrO_2$ using gas phase frequency values and bromine and oxygen isotopic shifts. It was shown that the most important force constants, f_{BrO} and f_{BrF}, can be determined with an accuracy of about 0.08 and 0.04 mdyn/Å, respectively. The importance of anharmonicity corrections for the oxygen shifts was demonstrated. In the absence of such anharmonicity corrections, the bromine isotopic shifts are more useful for defining the force field due to the smaller anharmonicity corrections required. The BrF bond in $FBrO_2$ (2.75 mdyn/Å) is considerably stronger than previously assumed (2.25 mdyn/Å)[5], but is still somewhat weaker than predicted by comparison with related bromine compounds. This weakening effect might be explained by assuming a polar sigma bond between a 2p electron of F and an antibonding π^* orbital of the BrO_2 radical.

Acknowledgement. One of us (KOC) is indebted to Drs. L. R. Grant, C. J. Schack, and W. W. Wilson for helpful discussions, and to the Office of Naval Research for financial support.

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Diagrams Captions

Figure 1. Survey infrared spectrum of gaseous $FBr^{18}O_2$ recorded at 15°C in a nickel cell equipped with AgBr windows with an optical path length of 110 cm^{-1}. The band marked by an asterisk is due to HF.

Figure 2. The band contours of ν_1, ν_2, and ν_3 of gaseous $FBr^{18}O_2$ recorded under higher resolution conditions with scale expansion. For ν_1 and ν_2 the frequencies of the ^{79}Br and ^{81}Br Q branch centers are marked. For ν_3, only the unresolved Q branch is shown at the same scale as that used for ν_1 and ν_2. The complete band envelope is shown at a 2.5 times compressed scale.

Figure 3. The band contour of ν_5 of gaseous $FBr^{18}O_2$ showing the double Q branches for both bromine isotopes.

Figure 4. Infrared spectra of Ne, N_2, and Ar matrix isolated $FBr^{16}O_2$, recorded at 3.6°K with 20 fold scale expansion under higher resolution conditions using CsI windows and a MR of ~1000:1.

Figure 5. Force constant display of the A'' block of $FBrO_2$ using the observed bromine ($2.7 \pm 0.1 cm^{-1}$) and oxygen ($42.4 + 1.6 cm^{-1}$) isotopic shifts as constraints. F_{55}, F_{66}, and F_{56} have units of mdyn/Å, mdyn Å/radian^2, and mdyn/radian, respectively. The rectangle of $\Delta O\nu_5$ marked by broken lines represents the observed anharmonic oxygen shift of $\nu_5 \pm 0.4cm^{-1}$, whereas the solid rectangle assumes the

observed anharmonic oxygen shift as the lower limit and a 1.6cm^{-1} higher, for anharmonicity corrected, value as the upper limit. The broken and the solid vertical lines indicate the plausible force constant ranges and the preferred force field, respectively.

Figure 6. Force constant display of the A' block. All off-diagonal constants were set zero, except for F_{13}. Only those diagonal constants are shown which were significantly influenced by changes in the interaction constant F_{13}. For additional explanation see caption of Figure 5.

Figure 7. Force constant display of the A' block showing the dependence of F_{22} and F_{44} on F_{24}. For additional explanation see captions of Figures 5 and 6.

Figure 8. Force constant display of the A' block showing the dependence of F_{33} and F_{44} on F_{34}.

TABLE I. VIBRATIONAL SPECTRA OF $FBrO_2$

Assignment in Point Group C_s	Observed Frequencies, cm^{-1}, and Relative Intensities																
	Infrared												Raman[b]			Anharmonic Isotopic Shifts, cm^{-1}	
	Gas				Matrix Isolated						Solid[a] -87°C		Solid -75°C	Liquid -10°C	BrF_5 Solution Room Temp.		
					Ne		N_2		Ar.								
	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79}Br^{18}O_2$	$F^{81}Br^{18}O_2$	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79}Br^{16}O_2$	$F^{81}Br^{16}O_2$	$F^{79,81}Br^{16}O_2$	$F^{79,81}Br^{18}O_2$	$F^{79,81}Br^{16}O_2$	$F^{79,81}Br^{16}O_2$	$F^{79,81}Br^{16}O_2$	[illegible]	[illegible]
$A'\nu_1$	921.0	919.5	876.3	874.8	921.6	920.1	922.3	920.8	914.8	913.3	918 vs	867	908(100)	908(100)p	916(100)p	44.7	1.5
ν_2	551.9	550.4	551.5	550.1	546.2	544.8	535.7	534.3	537.0	535.6	490 vs,br	486	524 sh 496(25) 487 sh	506(36)p		0.4	1.4
ν_3	385.8		370.4		386.8		391.2		384.0		387 ms	369	400 sh 386(10)	394(14)p		15.4	-
ν_4	~310		~296		-		-		-		305 mw	290	305(20) 294 sh	305(21)p		~14	-
$A''\nu_5$	978.9	976.2	936.5	933.7	976.2	973.6	971.2	968.6	967.2	965.6	947 vs,br	902	963(5) 940(20)	953(14)dp	962(8)dp	42.4	2.7
ν_6	-	-	-	-	-	-	-	-	-	-	276 271 mw	260	267(15)	271(16)dp		-	-

---

(a) Data from ref. 6
(b) Data from ref. 3

TABLE II. OBSERVED FREQUENCIES FOR $F^{79}Br^{16}O_2$, SYMMETRY FORCE CONSTANTS,[a] COMPUTED AND OBSERVED ^{16}O-^{18}O AND ^{79}Br-^{81}Br ISOTOPIC SHIFTS, AND POTENTIAL ENERGY DISTRIBUTION[b]

Assignment in Point Group C_s	Approximate Description of Mode	Frequency, cm^{-1}	Symmetry Force Constants		Isotopic Shifts, cm^{-1} Computed		Isotopic Shifts, cm^{-1} Observed		PED
					ΔO	ΔBr	ΔO	ΔBr	
A' ν_1	ν sym BrO_2	921.0	$F_{11} = fr + frr$	6.931 ± 0.095	45.23	1.56	44.7	1.5	$96F_{11}$
ν_2	ν BrF	551.9	$F_{22} = fR$	2.750 ± 0.04	0.31	1.40	0.4	1.4	$99F_{22}$
ν_3	δ sciss BrO_2	385.8	$F_{33} = f\beta$	1.453 ± 0.08	15.65	1.12	15.4		$76F_{33}$ $16F_{34}$
ν_4	δ sym $FBrO_2$	310	$F_{44} = f\alpha + f\alpha\alpha$	1.487 ± 0.08	11.74	0.52			$103F_{44}$ $37F_{33}$-41
			$F_{13} = fr\beta$	-0.40 ± 0.19					
			$F_{24} = fR\alpha$	0.095 ± 0.09					
			$F_{34} = f\alpha\beta$	0.49 ± 0.07					
A'' ν_5	ν asym BrO_2	978.9	$F_{55} = fr - frr$	7.037 ± 0.06	43.28	2.70	42.4	2.7	100 F_{55}
ν_6	δ asym $FBrO_2$	273	$F_{66} = f\alpha - f\alpha\alpha$	0.762 ± 0.004	7.21	0.33			100 F_{66}
			$F_{56} = fr\alpha - fr\alpha'$	0.14 ± 0.22					

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

(b) Percent contributions. Contributions of less than 9% to the PED are not listed.

TABLE III. INTERNAL FORCE CONSTANTS[a] OF $FBrO_2$ COMPARED TO THOSE OF REFERENCE 5

	This Work	Reference 5
f_r	6.984 ± 0.08	6.76
f_R	2.750 ± 0.04	2.25
f_{rr}	-0.05 ± 0.08	0
f_α	1.125 ± 0.04	1.090
f_β	1.453 ± 0.08	1.664
$f_{\alpha\alpha}$	0.363 ± 0.04	0.344
$f_{\alpha\beta}$	0.49 ± 0.07	0.01
$f_{R\alpha}$	0.095 ± 0.09	0.034
$f_{r\alpha}$	-0.07 ± 0.11	0
$f_{r\alpha}'$	+0.07 ± 0.11	0

(a) Units are identical to those of Table II.

TABLE IV. STRETCHING FORCE CONSTANTS (mdyn/Å) OF $FBrO_2$ COMPARED TO THOSE OF OTHER BROMINE COMPOUNDS

	BrO_3^{-}[a]	BrO_4^{-}[b]	BrF_4O^{-}[c]	BrF_4^{-}[d]	$FBrO_2$	$FBrO_3$[e]	BrF	BrF_3[f]	BrF_5[g]	BrF_2^{+}[h]	BrF_6^{+}[i]
fr (BrO)	5.28	6.05	6.70	-	6.98	6.92	-	-	-	-	-
fR (BrF)	-	-	2.14	2.23	2.75	-	-	3.10	3.24	-	-
fR' (BrF)	-	-	-	-	-	3.22	4.07	4.07	4.02	4.60	4.90

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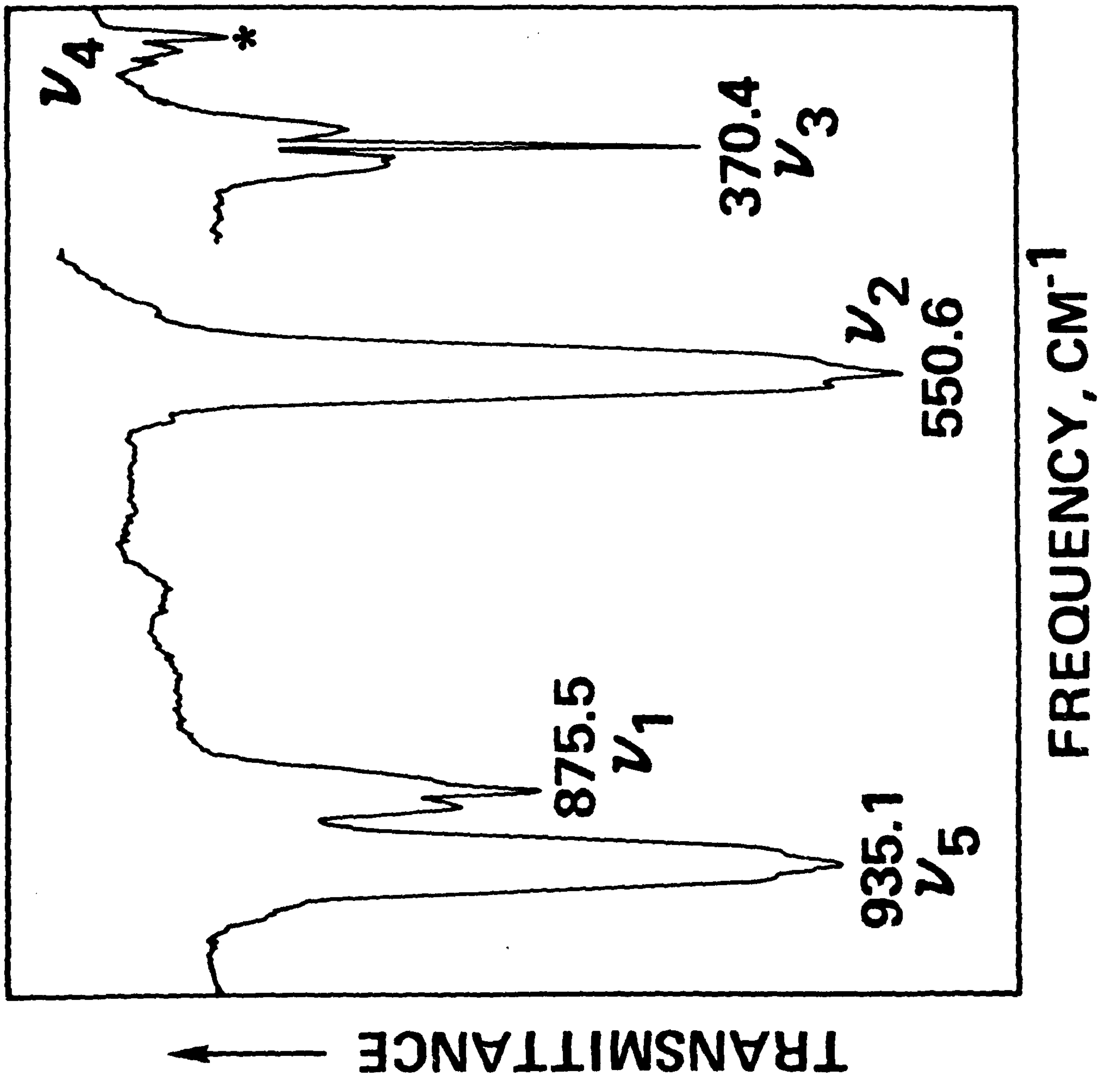
TABLE V. THERMODYNAMIC PROPERTIES FOR $F^{79}Br^{16}O_2$

T (DEG K)	C^0_P	$(H^0_T - H^0_0)$	$-(F^0_T - H^0_0)/T$	S^0_T
0	0	0	0	0
100	9.493	0.831	48.749	57.059
200	12.831	1.957	54.945	64.732
298.15	15.033	3.332	59.119	70.295
300	15.066	3.360	59.188	70.388
400	16.527	4.945	62.576	74.938
500	17.467	6.648	65.438	78.734
600	18.082	8.427	67.931	81.977
700	18.498	10.258	70.144	84.797
800	18.789	12.123	72.134	87.288
900	18.998	14.013	73.944	89.513
1000	19.154	15.921	75.603	91.523
1100	19.272	17.842	77.134	93.355
1200	19.363	19.774	78.557	95.036
1300	19.436	21.714	79.885	96.589
1400	19.494	23.661	81.130	98.031
1500	19.541	25.613	82.303	99.378
1600	19.580	27.569	83.410	100.640
1700	19.613	29.529	84.458	101.828
1800	19.640	31.491	85.455	102.950
1900	19.664	33.456	86.404	104.013
2000	19.684	35.424	87.310	105.022

TABLE VI. THERMODYNAMIC PROPERTIES OF $F^{35}Cl^{16}O_2$

T (DEG K)	C_P^0	$(H_T^0 - H_0^0)$	$-(F_T^0 - H_0^0)/T$	S_T^0
0	0.	0.	0.	0.
100	8.507	0.805	46.851	54.898
200	11.267	1.790	52.666	61.618
298.15	13.509	3.012	56.456	66.559
300	13.545	3.037	56.519	66.643
400	15.167	4.478	59.581	70.775
500	16.318	6.055	62.180	74.291
600	17.134	7.730	64.459	77.342
700	17.718	9.474	66.495	80.030
800	18.143	11.268	68.339	82.425
900	18.459	13.099	70.026	84.581
1000	18.699	14.958	71.581	86.539
1100	18.884	16.837	73.023	88.330
1200	19.030	18.733	74.368	89.979
1300	19.147	20.642	75.629	91.507
1400	19.241	22.562	76.814	92.930
1500	19.318	24.490	77.934	94.260
1600	19.382	26.425	78.993	95.509
1700	19.436	28.366	80.000	96.686
1800	19.481	30.312	80.958	97.798
1900	19.520	32.262	81.872	98.852
2000	19.554	34.216	82.747	99.854

FIGURE 1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ν_2
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ν_1
935.1
ν_5
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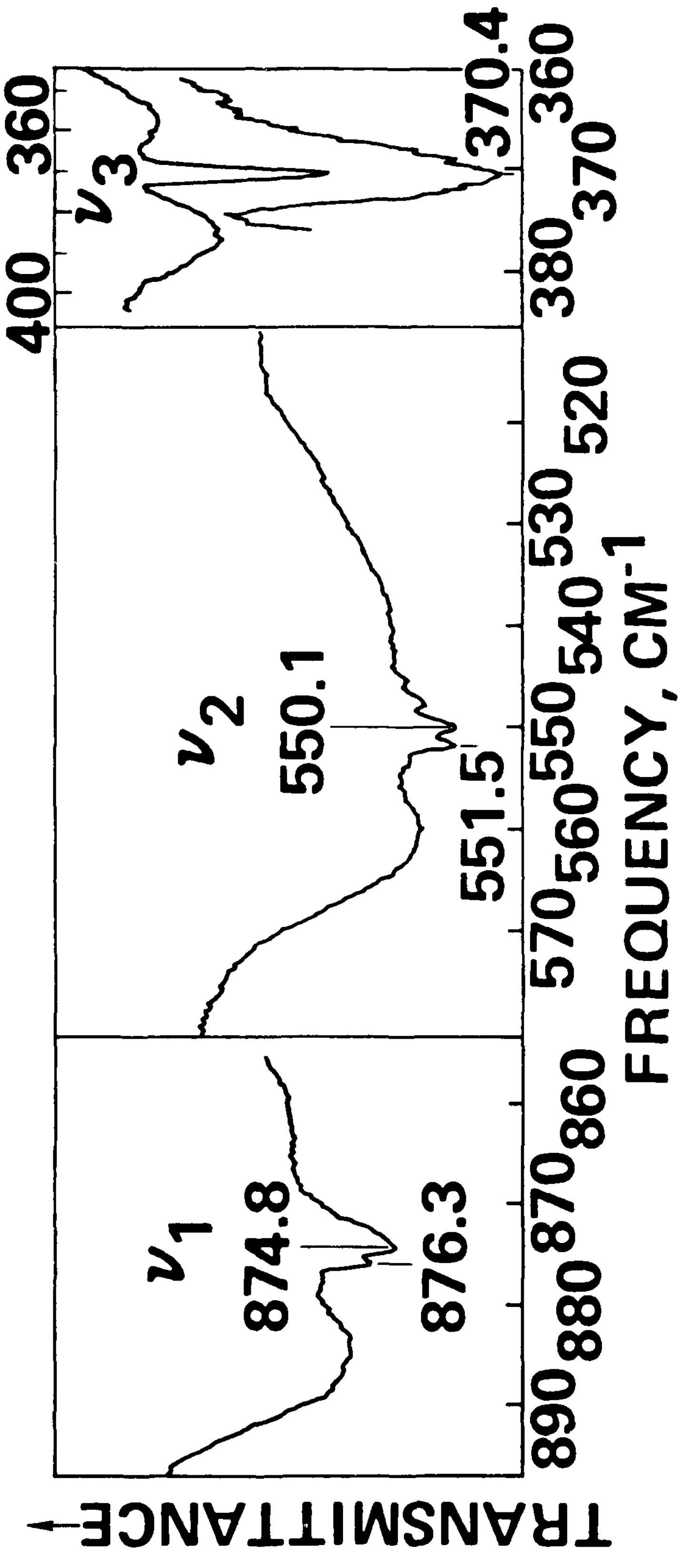
TRANSMITTANCE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ν_2
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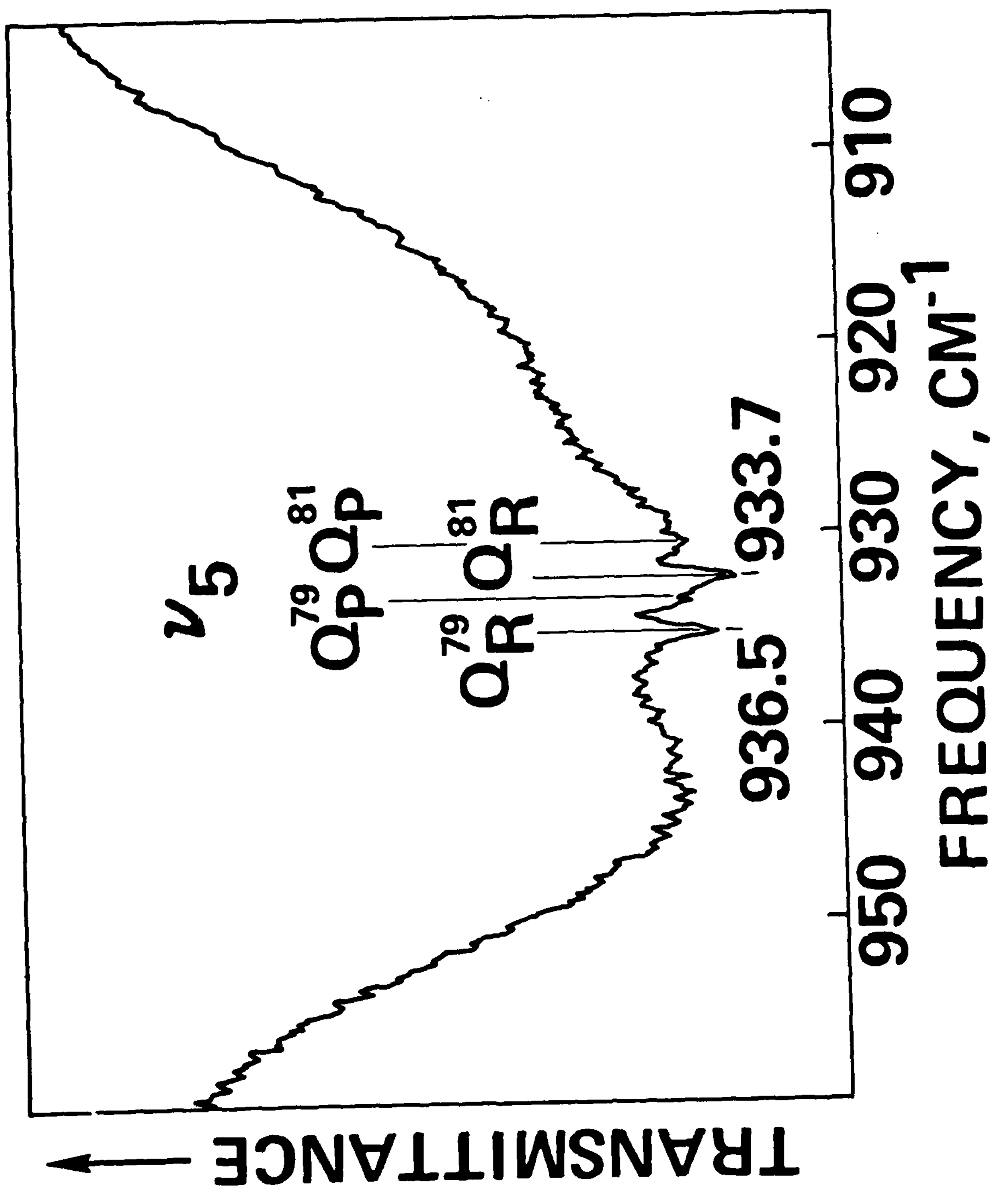
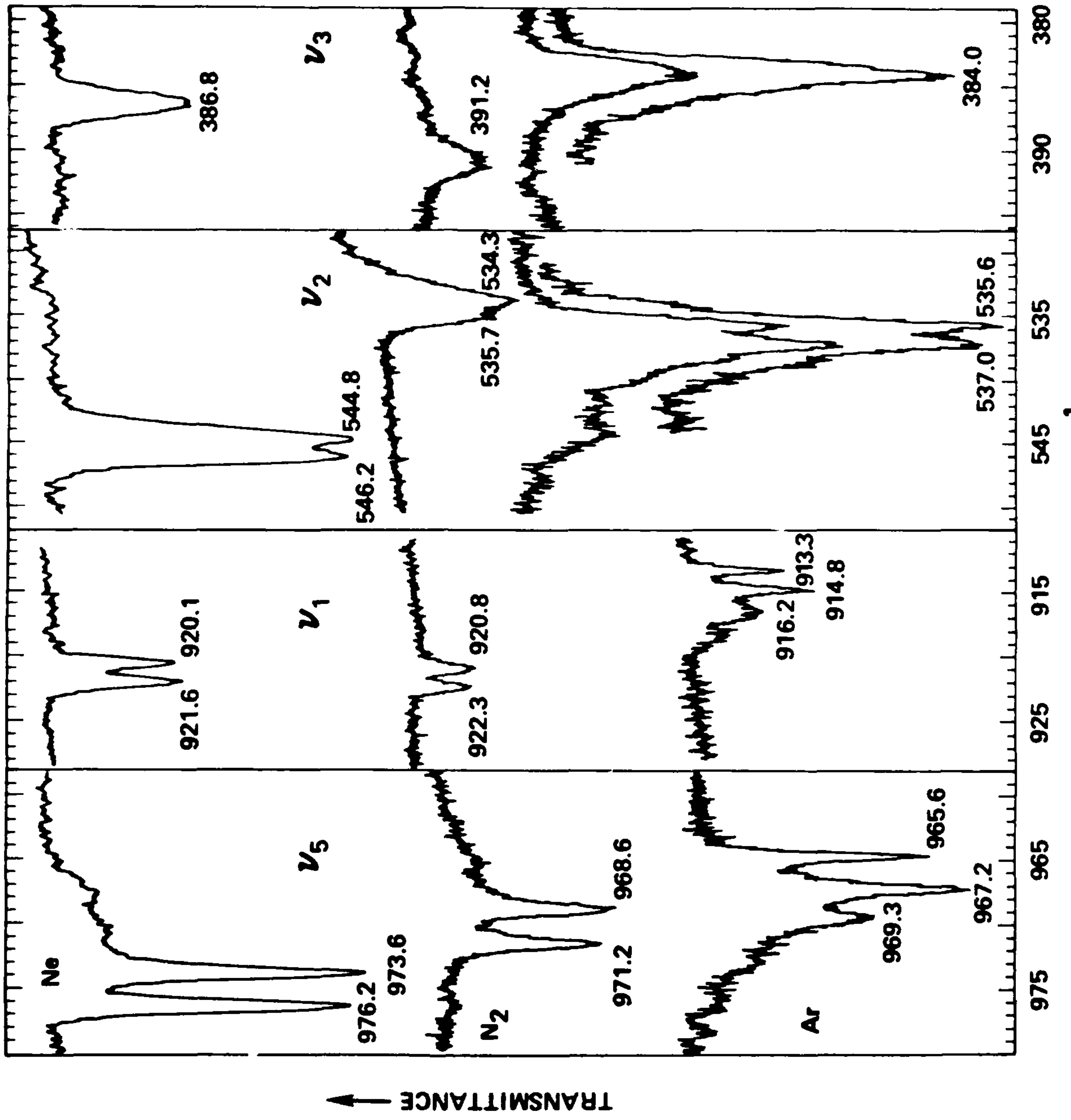
360
380
360
380
370
360


ν_5
$^{79}Q_P$ $^{81}Q_P$
$^{79}Q_R$ $^{81}Q_R$
936.5
933.7
950
940
930
920
910
FREQUENCY, CM^{-1}
TRANSMITTANCE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390
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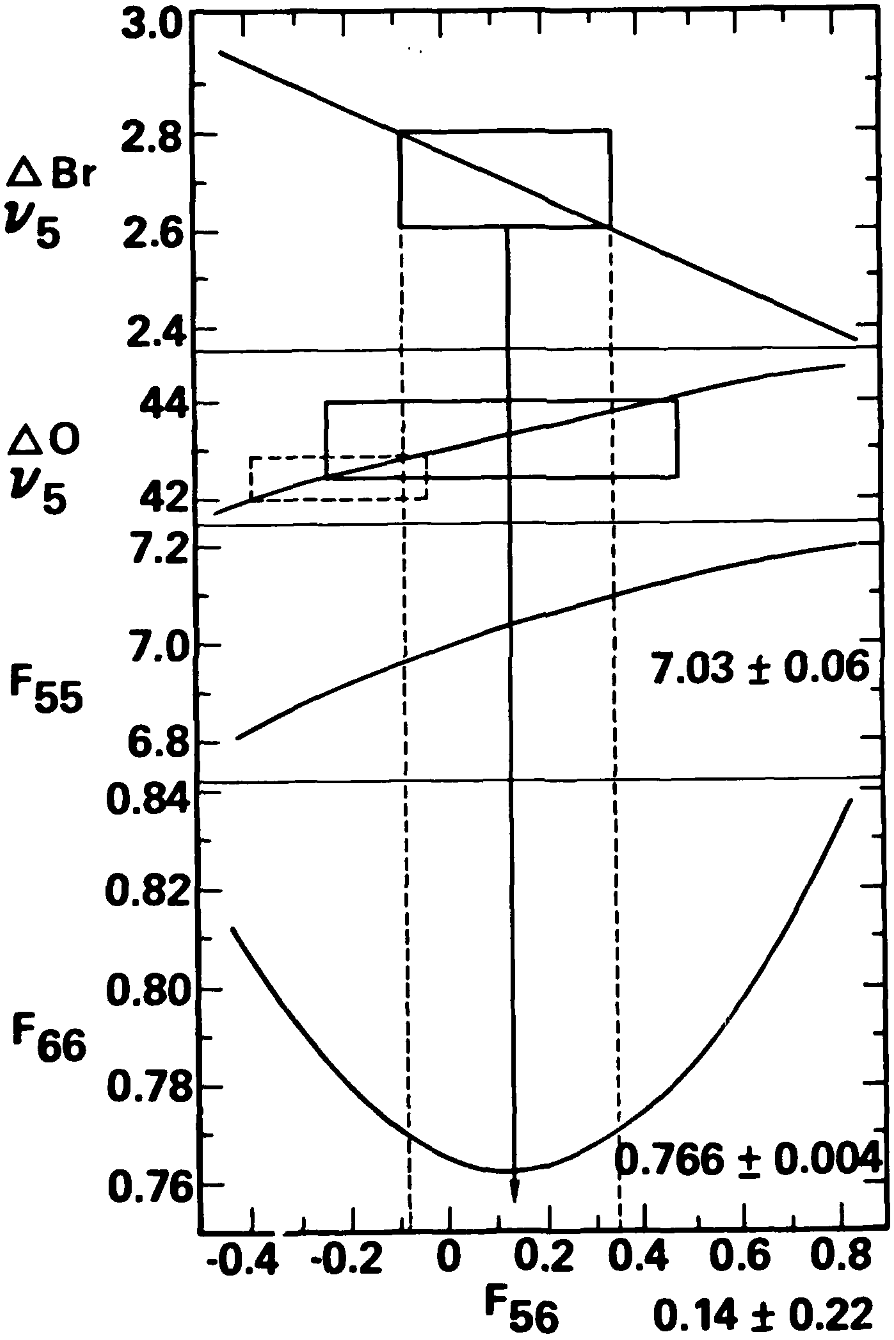
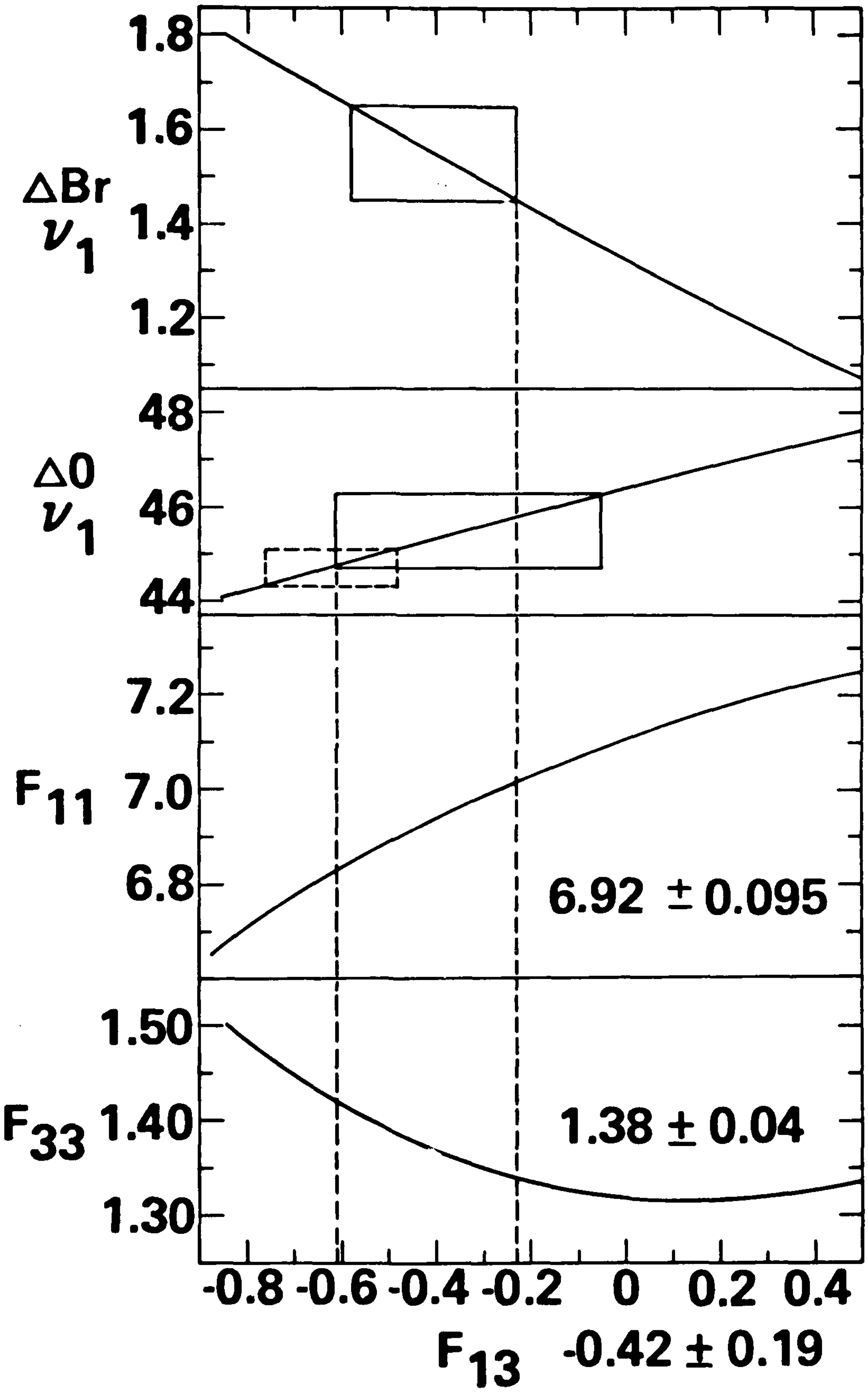
ν_2
ν_3
976.2
973.6
971.2
968.6
969.3
967.2
965.6
921.6
920.1
922.3
920.8
916.2
914.8
913.3
546.2
544.8
535.7
534.3
537.0
535.6
386.8
391.2
384.0

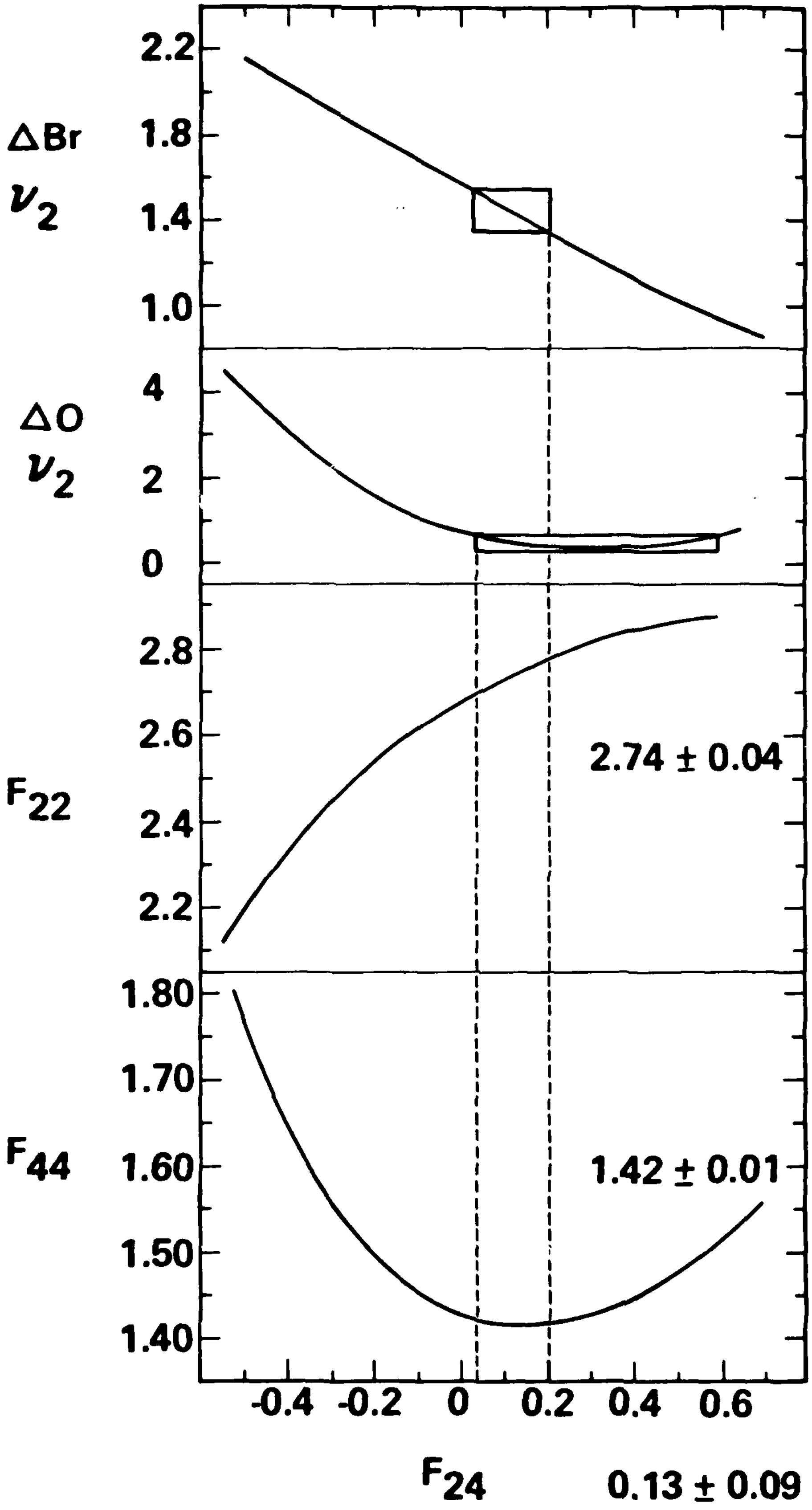
FIGURE 5


3.0
2.8
ΔBr
ν_5
2.6
2.4
44
ΔO
ν_5
42
7.2
7.0
F_{55}
7.03 ± 0.06
6.8
0.84
0.82
0.80
F_{66}
0.78
0.766 ± 0.004
0.76
-0.4
-0.2
0
0.2
0.4
0.6
0.8
F_{56}
0.14 ± 0.22



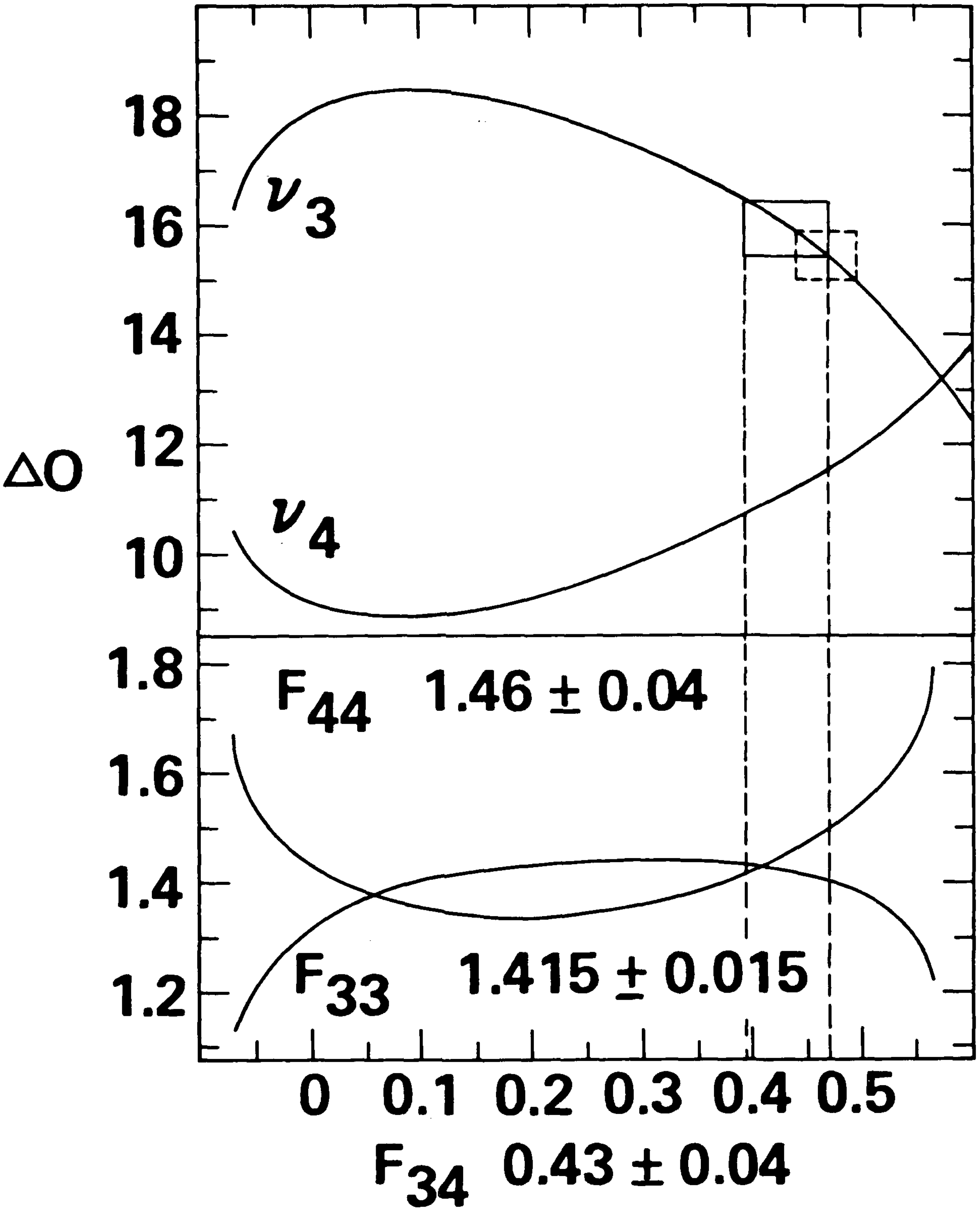
1.8
1.6
ΔBr
ν1
1.4
1.2
48
Δ0
ν1
46
44
7.2
F11
7.0
6.8
6.92 ± 0.095
1.50
F33
1.40
1.38 ± 0.04
1.30
-0.8
-0.6
-0.4
-0.2
0
0.2
0.4
F13
-0.42 ± 0.19

FIGURE 7



ΔBr
ν_2
2.2
1.8
1.4
1.0
ΔO
ν_2
4
2
0
F_{22}
2.8
2.6
2.4
2.2
2.74 ± 0.04
F_{44}
1.80
1.70
1.60
1.50
1.40
1.42 ± 0.01
-0.4
-0.2
0
0.2
0.4
0.6
F_{24}
0.13 ± 0.09

FIGURE 8


18
16
14
12
10
ΔO
ν_3
ν_4
1.8
1.6
1.4
1.2
F_{44} 1.46 ± 0.04
F_{33} 1.415 ± 0.015
0
0.1
0.2
0.3
0.4
0.5
F_{34} 0.43 ± 0.04

STABLE CHLORINE TRIFLUORIDE DIOXIDE

United States Patent [19]

Christe

[11] **4,038,374**

[45] **July 26, 1977**

[54] **STABLE CHLORINE TRIFLUORIDE DIOXIDE**

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

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

[21] Appl. No.: **714,458**

[22] Filed: **Aug. 16, 1976**

Related U.S. Application Data

[60] Continuation-in-part of Ser. No. 529,773, Dec. 5, 1974, abandoned, which is a division of Ser. No. 290,031, Sept. 18, 1972, Pat. No. 3,873,676.

[51] **Int. Cl.**^{2} **C01B 7/24**
[52] **U.S. Cl.** **423/466**; 423/462; 149/1
[58] **Field of Search** 423/462, 466

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Primary Examiner—Edward Stern
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

Chlorine trifluoride dioxide is disclosed for use as an oxidizer in formulating energetic compositions, such as propellants. The stable ClF_3O_2 is produced by reacting a $ClO_2F_2^+$ salt with a strong Lewis base at $-78°$ C.

1 Claim, No Drawings

STABLE CHLORINE TRIFLUORIDE DIOXIDE

The invention herein described was made in the course of or under a contract with the Department of Navy.

CROSS-REFERENCE TO RELATED APPLICATIONS

The application is a continuation-in-part of Ser. No. 529,773 filed, Dec. 5, 1974, now abandoned, and which was a division of Ser. No. 290,031, filed Sept. 18, 1972, and issued Mar. 25, 1975, as U.S. Pat. No. 3,873,676.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to compositions of matter and is particularly directed to chlorine trifluoride dioxide and a method of producing the same.

2. Prior Art

Energetic compositions of matter are useful in providing energy sources for rocket engines, guided missiles, auxiliary power units for aircraft, ordnance, demolition and the like. Such compositions conventionally are produced by mixing a fuel with an oxidizer. Obviously, the energy of such compositions results primarily from the oxidation of the fuel. Hence, it is desirable to provide a highly energetic oxidizing agnet. On the other hand, it is equally desirable that the oxidizing agent be a stable material, so as to prevent accidental or unintentional ignition or explosive decomposition of the composition. Numerous organic and inorganic compounds have been proposed heretofore for use as such oxidizing agents. However, it has been found that, as a general rule, stable compounds are low energy oxidizers and high energy oxidizers are unstable. Thus, although some useful oxidizing agents have been disclosed by the prior art, the search for a stable, high-energy, oxidizing material has continued. In recent years, studies have indicated that halogen oxyfluoride materials might provide a satisfactory oxidizing material. However, although empirical formulas may be stated for such materials and some of the properties of such materials may be predicted, the synthesis of these materials has proven to be extremely difficult and it is sometimes found that several materials, each having distinct structures and properties, are defined by a single empirical formula. Thus, U.S. Pat. No. 3,285,842 discloses a process for producing a material which was believed to have the empirical formula chlorine trifluride dioxide, ClF_3O_2, which the patent states to be a violet liquid which is unstable at tempertures above −71° C. It was subsequently shown, however, that this composition does not contain the chemical compound ClF_3O_2, but consists of a mixture of chlorine fluorides and oxygen fluorides (K. O. Christe, R. D. Wilson, and I. B. Goldberg, *J. Fluor-Chem.*, 7,543 (1976). This fact readily explains the great difference in physical and chemical properties between the composition and the novel composition disclosed in this invention. While it would be expected that the *previously claimed* composition would also be a highly energetic oxidizing agent, the lack of stability renders it unsafe for use in the production of propellants and the like.

Brief Summary and Objects of Invention

These disadvantages of the prior art are overcome with the present invention and a composition of matter is disclosed which based on its chemical structure truly is chlorine trifluride dioxide. It is sufficiently stable at +25° C and, hence, can be safely employed for manufacturing propellants and the like. In addition, a method is disclosed for producing chlorine trifluoride dioxide by reacting $ClF_2O_2^+ PtF_6^-$ with a strong lewis base at a temprature of about −78° C and separating the products of the reaction by distillation.

Accordingly, it is an object of the present invention to provide a new composition of matter having the chemical composition ClF_3O_2.

An additional object of the present invention is to provide a method of producing chlorine trifluoride dioxide.

A specific object of the present invention is to provide chlorine trifluoride dioxide by reacting $ClF_2O_2^+$ salts with nitryl fluoride at a temperature of about −78° C and separating the products of the reaction by distillation.

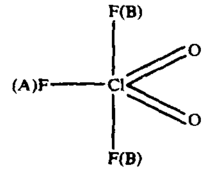
These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In that form of the present invention chosen for purposes of illustration, chlorine trifluoride dioxide has been produced by reacting a $ClF_2O_2^+$ salt, such as $ClF_2O_2^+PtF_6^-$, with a strong Lewis base at −78° C.

EXAMPLE 1

A sample of $ClO_2^+PtF_6^-$ containing about 10% of $ClF_2O_2^+PtF_6^-$ was treated at −78° C in a sapphire reactor with a large excess of FNO for several days. No material noncondensible at −196° C (i.e., F_2) was observed. The products, volatile at 25° C were removed and separated by fractional condensation through a series of traps kept at −126° C, −142° C, and −196° C. The −142° C fraction contained a novel compound which was identified by its infrared spectrum as ClF_3O_2. The observed frequencies are listed in Table 1 and are in excellent agreement with those expected for a trigonal bypyramidal structure of symmetry C_{2v}.



This structure was confirmed by ^{19}F nuclear resonance spectroscopy. The observed signal consisted of a typical AB_2 pattern centered at −413 ppm relative to the external standard $CFCl_3$. The F-F coupling constant was measured to be 443 Hz. The B_2 part of the AB_2 pattern occurs downfield from the A part, proving that the B_2 fluorine atoms occupy the two axial positions. Additional structural proof was obtained from the Raman spectrum of the gas and the liquid showing strong absorptions at 1096, 684, 548, 527, 493, 290, and 229 cm^{-1}. The molecular weight of the compound was confirmed by vapor density measurements (measured, 122; calculated, 124). These data establish beyond doubt (see K.O. Christe and R.D. Wilson, Inorg, Chem, 12, 1356 (1973) and K.O. Christe and E.C. Curtis, Inorg, Chem. 12, 2245 (1973) that contrary to the previous claim (U.S.P. 3,285,842) our novel composition has indeed the chemical composition ClF_3O_2.

Table I

Infrared Spectrum of ClF_3O_2 and its Tentative Assignment

Frequency (cm^{-1})	Intensity	Assignment for Point Group C_{2v}
1334	s	$\nu_{10}(B_2)$, $\nu as ClO_2$
1096	s	$\nu_1(A_1)$, $\nu sym ClO_2$
699	vs	$\nu_7(B_1)$, $\nu as ClF_2 Ax$
687	vs	$\nu_2(A_1)$, νClF
598	ms	$\nu_{11}(B_2)$, $\delta rock\ ClO_2$
543)		
532)	mw	$\nu_3(A_1)$ and $\nu_8(B_1)$

The solid residue obtained from the FNO displacement reaction showed the correct weight change expected for conversion into $NO^+PtF_6^-$. Its identity as $NO^+PtF_6^-$ was confirmed by infrared spectroscopy.

The chlorine trifluoride dioxide is white as a solid having a melting point of about −81.2° C and colorless as a liquid having a boiling point of about −21° C. It is marginally stable at 25° C. The observed stability and lack of color furthermore demonstrate that our product cannot be identical with the previously reported deeply violet and unstable $ClF.O_2F_2$ and ClF_3. O_2 addition compounds supposedly having the empirical composition ClF_3O_2.

EXAMPLE II

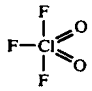
A sample $ClO_2^+PtF_6^-$ containing about 10% of $ClO_2F_2^+PtF_6^-$ was treated with a sufficient quantity of FNO_2 to maintain a liquid phase at −78° C in a stainless steel reactor up to 12 hours. This reaction yielded solid $NO_2^+PtF_3^-$ and gaseous ClF_3O_2 plus $FClO_2$. If desired, the chlorine trifluoride dioxide may then be separated by conventional distillation techniques, as in a multiplate distillation tower.

Small amounts of material were purified by combining the ClF_3O_2 and $FClO_2$ at −196° C with a small excess of BF_3. These materials were allowed to mix and warm to ambient temperature. This results in $ClF_2O_2^+BF_4^-$, which is stable, plus $ClO_2^+BF_4^-$, which has a dissociation pressure of 180 millimeters at 22° C and which can be removed by pumping. The $ClF_2O_2^+BF_4^-$ is then reacted with sufficient FNO_2 to maintain a liquid phase at −78° C for up to 12 hours. This reaction produced solid $NO_2^+BF_4^-$ plus gaseous ClF_3O_2 and FNO_2. The two gases may be pumped off and separated by passing the gases through a pair of traps maintained at −126° C and −196° C, respectively. The chlorine trifluoride dioxide will be caught in the −126° C trap.

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

What is claimed is:

1. A new composition of matter comprising of chlorine trifuloride dioxide, ClF_3O_2, having structure



having the infrared spectrum set forth in the following Table,

Table I

Infrared Spectrum of ClF_3O_2 and its Tentative Assignment

Frequency (cm^{-1})	Intensity	Assignment for Point Group C_{2v}
1334	s	$\nu_{10}(B_2)$, $\nu as ClO_2$
1096	s	$\nu_1(A_1)$, $\nu sym ClO_2$
699	vs	$\nu_7(B_1)$, $\nu as ClF_2 Ax$
687	vs	$\nu_2(A_1)$, νClF
598	ms	$\nu_{11}(B_2)$, $\delta rock\ ClO_2$
543)		
532)	mw	$\nu_3(A_1)$ and $\nu_8(B_1)$

and being a white solid which melts at about −81° C to a colorless liquid and boils at about −21 C and is stable up to about +25° C.

* * * * *

APPENDIX K

SYNTHESIS OF ANHYDROUS METAL PERCHLORATES

United States Patent [19]

Schack et al.

[11] **4,012,492**

[45] **Mar. 15, 1977**

[54] **SYNTHESIS OF ANHYDROUS METAL PERCHLORATES**

[75] Inventors: **Carl J. Schack**, Chatsworth; **Donald Pilipovich**, Agoura, both of Calif.

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

[22] Filed: **June 10, 1975**

[21] Appl. No.: **585,549**

[52] **U.S. Cl.** **423/472**; 423/476; 423/500

[51] **Int. Cl.^{2}** **C01B 7/02**; C01B 11/00; C01G 23/00; C01G 37/00; C01G 31/00

[58] **Field of Search** 423/476, 472, 500

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Primary Examiner—Edward Stern

Attorney, Agent, or Firm—R. S. Sciascia; Philip Schneider; Thomas McDonnell

[57] **ABSTRACT**

Preparation of titanium tetraperchlorate, vanadium perchlorate, and chromyl perchlorate by the reactions of chlorine perchlorate with the respective anhydrous metal chlorides at a temperature from about −45° C to about 20° C. These perchlorates are useful in compounding gas generating compositions.

5 Claims, No Drawings

SYNTHESIS OF ANHYDROUS METAL PERCHLORATES

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention pertains to the preparation of inorganic oxidizing salts and in particular to the preparation of anhydrous metal perchlorates.

2. Prior Art

Syntheses of anhydrous metal perchlorates have been restricted mainly to metals from Groups I and II. A few preparations have been reported for transition metal perchlorates as well as NO_2^+ and NH_4^+ complex perchlorates.

One method is known for the preparation of anhydrous titanium tetraperchlorate. This method proceeds by the reaction of anhydrous perchloric acid with anhydrous titanium tetrachloride. However the product is not pure as is evidenced by the data presented pertaining to the melting point, analysis, stability, yield, and polycrystalline form. A major disadvantage of the impurities in the product is the necessity of refrigeration. Other disadvantages of this synthesis are the scarcity, expense, and danger of anhydrous perchloric acid.

The known method for the preparation of chromyl perchlorate is through the reaction of chromyl chloride and dichlorine hexoxide. Although the reaction product is pure, the synthesis has the disadvantages which result from the scarcity, expense, and danger of anhydrous dichlorine hexoxide.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to form anhydrous metal perchlorates safely, quickly, and inexpensively.

Another object of this invention is to form anhydrous metal perchlorates in a high degree of purity.

These and other objects are achieved by a method which proceeds by the following reactions:

$$CrO_2Cl_2 + 2Cl_2O_4 - 2Cl_2 + CrO_2(ClO_4)_2$$

$$TiCl_4 + 4Cl_2O_4 - 4Cl_2 + Ti(ClO_4)_4$$

$$VOCl_3 + 3Cl_2O_4 - VO(ClO_4)_3 + 3Cl_2$$

and which occur at a temperature from −45° C to 20° C.

DETAILED DESCRIPTION OF THE INVENTION

Due to the strong oxidizing strength of the perchlorate group the method of the invention must proceed in vessels constructed from stainless steel, platinum, teflon, monel or similar non-oxidizable materials or coated therewith. The reaction is carried out at ambient pressure and at a temperature from about −45° C to about 20° C but preferably from −25° C to 0° C. Stirring is optional because the bubbling of the by-product chlorine through the reaction solution provides sufficient agitation. Completion of the reaction is determined preferably by monitoring the chlorine gas by-product. Generally the reaction is complete within 4 to 6 hours and the perchlorate product may then be collected.

Preferably, chlorine perchlorate is prepared by the method disclosed in U.S. Pat. No. 3,694,172 by Schack et al.

The reactants are added in stoichiometric amounts. Thus for the synthesis of chromyl perchlorate the reactants are added in a CrO_2Cl_2-to-Cl_2O_4 mole ratio of 1:2. For the synthesis of vanadium perchlorate, the reactants are added in a $VOCl_3$-to-Cl_2O_4 mole ratio of 1:3. It is preferred that an extra 5 to 10 mole percent of Cl_2O_4 is added in order to decrease the reaction time. Since water produces impurities in the perchlorate product, the reactants and the system should be anhydrous.

The reactants may be added in any order or in any rate. However the reactions are exothermic; so, measures must be taken to ensure that reaction temperature does not exceed about 20° C. According to a preferred embodiment of this invention the reactants are added to the reaction vessel in the solid state, thereby minimizing the vapors of the reactants.

This embodiment is utilized in Example I given hereinafter. It is understood that the examples are given by way of illustration and are not intended to limit the disclosure or the claims to follow in any way.

EXAMPLE I

Titanium tetrachloride (1.22 mmol) and $ClOClO_3$ (6.01 mmol) were combined at −196° in a 75 ml stainless steel cylinder and then gradually warmed to −25°. After several days, recooling to −196° showed no noncondensable gases were present. The contents of the reactor were separated by fractional condensation in a series of U-traps cooled to −78°, −112°, and −196°. Nothing was trapped at −78° while the −112° fraction consisted solely of unreacted Cl_2O_4 (1.17 mmol), and the −196° fraction was Cl_2 (4.88 mmol). The pale yellow solid residue left in the reactor weighed 0.525 g. The weight calculated for 1.22 mmol of $Ti(ClO_4)_4$ was 0.544 g and therefore the yield of $Ti(ClO_4)$ was 97 percent. Vacuum sublimation of the $Ti(ClO_4)_4$ was carried out in a Pyrex apparatus at 50°–60° using a −78° cold finger. The sublimed material was nearly colorless and had a m.p. with dec. of 101°–2°. Almost no residue remained unsublimed. Anal. Calcd. for $Ti(ClO_4)_4$: Ti, 10.75; ClO_4, 89.25. Found: Ti, 10.8; ClO_4, 87.9. A sample of $Ti(ClO_4)_4$ (0.242 mmol) was heated in a stainless steel cylinder for 4 hours at 115° followed by 1.5 hr. at 190°. This produced O_2 (1.705 mmol), Cl_2 (0.481 mmol), and a white solid residue of TiO_2 (0.241 mmol). All temperatures are in degrees Centigrade.

EXAMPLE II

Chromyl chloride (1.41 mmol) and $ClOClO_3$ (3.16 mmol) were reacted at −45° for several days in a stainless steel cylinder. After separation and identification, the volatile products found were CrO_2F_2 (0.18 mmol), Cl_2 (2.59 mmol), and Cl_2O_4 (0.66 mmol). The $CrO_2(ClO_4)_2$ (1.23 mmol) remained in the cylinder. The CrO_2F_2 probably arose through reaction of CrO_2Cl_2 with the ClF_3 passivated metal surfaces in the reactor and/or vacuum line during transfers. Anal., Calcd. for $CrO_2(ClO_4)_2$: ClO_4, 70.3. Found: ClO_4, 69.6. A sample of $CrO_2(ClO_4)_2$ (0.65 mmol) was pyrolyzed for 15 hrs at 110° producing Cl_2 (0.66 mmol), O_2 (2.21 mmol) and CrO_3 (0.65 mmol), m.p. 195°–7°, lit. 196°. All temperatures are in degrees Centigrade.

As can be seen from the examples, the method of this invention produces a highly pure anhydrous metal perchlorate without the use of the scarce and dangerous anhydrous perchloric acid or dichlorine hexoxide. The anhydrous titanium perchlorate has been stored at room temperature for over three months without degradation.

Obviously many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed and desired to be secured by Letters Patent of the United States is:

1. A method of preparing an anhydrous metal perchlorate which comprises admixing for at least 4 hours at a temperature from −45° C to 20° C an anhydrous metal chloride selected from the class consisting of titanium tetrachloride, chromyl chloride, and vanadium oxytrichloride with chlorine perchlorate in a metal chloride-to-chlorine perchlorate mole ratio which is 1:4 if titanium tetrachloride is selected, or is 1:2 if chromyl chloride is selected, or is 1:3 if vanadium oxytrichloride is selected, and recovering said anhydrous metal perchlorate.

2. A method of preparing an anhydrous metal perchlorate which comprises admixing for at least 4 hours at a temperature from −45° C to 20° C an anhydrous metal chloride selected from the class consisting of titanium tetrachloride, chromyl chloride, and vanadium oxytrichloride with chlorine perchlorate in a metal chloride-to-chlorine perchlorate mole ratio which is from 1:4.2 to 1:4.4 if titanium tetrachloride is selected, or is from 1:2.1 to 1:2.2 if chromyl chloride is selected, or is from 1:3.15 to 1:3.3 if vanadium oxytrichloride is selected, and recovering said anhydrous metal perchlorate.

3. The method of claim 2 wherein said anhydrous metal chloride is titanium chloride.

4. The method of claim 2 wherein said anhydrous metal chloride is chromyl chloride.

5. The method of claim 2 wherein said anhydrous metal chloride is vanadium oxytrichloride.

* * * * *

APPENDIX L

SYNTHESIS OF NITRYL PERCHLORATE

United States Patent [19]

Schack

[11] **4,026,996**

[45] **May 31, 1977**

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[54] **SYNTHESIS OF NITRYL PERCHLORATE**

[75] Inventor: **Carl J. Schack**, Chatsworth, Calif.

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

[22] Filed: **May 28, 1974**

[21] Appl. No.: **474,130**

[52] **U.S. Cl.** **423/386**
[51] **Int. Cl.²** **C01B 21/52**
[58] **Field of Search** 423/386, 476; 149/74, 149/75

[56] **References Cited**

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Primary Examiner—Earl C. Thomas
Attorney, Agent, or Firm—L. Lee Humphries; Robert M. Sperry

[57] **ABSTRACT**

An improved method of synthesizing nitryl perchlorate by oxidizing chlorine nitrate with ozone.

2 Claims, No Drawings

SYNTHESIS OF NITRYL PERCHLORATE

The invention herein described was made in the course of or under a contact or subcontract thereunder, (or grant) with the Department of the U.S. Navy.

BACKGROUND

1. Field of the Invention

This invention relates to solid oxidizers and is particularly directed to methods of producing nitryl perchlorate.

2. Prior Art

Nitryl perchlorate, $No_2^+ClO_4^-$, has been known for many years as a powerful oxidizer. Heretofore, the conventional method of producing nitryl perchlorate has required the reaction of chlorine dioxide, ClO_2, with nitrogen dioxide, NO_2, and ozone, O_3. Unfortunately, chlorine dioxide, in either the gaseous or liquid state, tends to explode for no apparent reason. Consequently, any operation which involves chlorine dioxide is hazardous to people, buildings and equipment.

SUMMARY OF THE INVENTION

These disadvantages of the prior art are overcome with the present invention and an improved method of producing nitryl perchlorate is provided which eliminates the use of chlorine dioxide, with its attendant hazards, yet provides good yields and easy purification.

The advantages of the present invention are preferably attained by providing a method of producing nitryl perchlorate by reacting chlorine nitrate, $ClNO_3$, with ozone.

Accordingly, it is an object of the present invention to provide improved methods of producing oxidizers.

Another object of the present invention is to provide an improved method of producing nitryl perchlorate.

An additional object of the present invention is to provide a safer method of producing nitryl perchlorate.

A further object of the present invention is to provide a method of producing nitryl perchlorate without the use of chlorine dioxide.

A specific object of the present invention is to provide a method of producing nitryl perchlorate by reacting chlorine nitrate with ozone.

These and other objects and features of the present invention will be apparent from the following detailed description.

DETAILED DESCRIPTION OF INVENTION

In that form of the present invention chosen for illustration, a method of producing nitryl perchlorate is proposed which calls for reacting chlorine nitrate with ozone. It should be understood that, as used herein, the terms "nitryl perchlorate" and "nitronium perchlorate" are synonymous.

Chlorine nitrate is a liquid which boils at 22° C and is easily prepared, following the teachings of U.S. Pat. No. 3,472,635, assigned to the present assignee. Chlorine nitrate is not hazardous and is relatively insensitive to physical shock.

Although chlorine nitrate is well-known, the reaction of the present invention is unexpected. Conventionally, ClO—X compounds react with ozone to give chloryl species; such as

$$ClOClO_3 + 2O_3 \rightarrow O_2ClOClO_3 + 2O_2 \qquad (1)$$

$$ClSO_3F + 2O_3 \rightarrow O_2ClOSO_2F + 2O_2 \qquad (2)$$

or it does not react at all, as in

$$CF_3OCl + O_3 \rightarrow \text{No reaction} \qquad (3)$$

The reaction of the present invention is

$$ClONO_2 +_3 \rightarrow NO_2^+CLO_4^- + 3O_2$$

This reaction has been observed to occur readily at temperatures as low as -78° C, in the presence of an inert fluorocarbon solvent, CF_3Cl, and at temperatures ranging from -45° C to ambient without a solvent. Conversions, using this method, have been as high as 89% and yields have been 100%. Moreover, the reactants, chlorine nitrate and ozone, and the by-product, oxygen, are gases; whereas the nitryl perchlorate is a solid. Consequently, purification is simple and the gases may be recovered and recycled.

EXAMPLE I

Chlorine nitrate (24.2 cm^3, 1.08 mmol) and CF_3Cl solvent (approximately 250 cm^3), were condensed into a 30 ml. stainless steel cylinder cooled to -196° C in a liquid nitrogen bath. Following that, ozone (72.6 cm^3, 3.24 mmol) was also condensed in at -196° C and the closed cylinder was warmed to and maintained at -45° C. After 42 hrs. the reaction cylinder was recooled to -196° C and the oxygen that had formed was measured (53.4 cm^3, 2.38 mmol) and pumped away. On warming the reaction to room temperature, the remaining products were separated by fractional condensation in U-traps cooled to -78°, -112°, and -196° C. Unreacted chlorine nitrate (7.6 cm^3, 0.34 mmol) was retained at -112° C. Unreacted ozone and the CF_3Cl solvent were trapped at -196° C. There remained in the cylinder, the white solid, nitryl perchlorate (107 mg, 0.74 mmol) which was readily dentified by its infrared spectrum and comparison to an authentic sample. The conversion of $ClNO_3$ to $NO_2^+ClO_4^-$ was 68.6% and the yield of $NO_2^+ClO_4^-$ based on the material reacted was essentially quantitative.

EXAMPLE II

A 30-ml. stainless steel cylinder was loaded successively with $ClNO_3$(23.2 cm^3, 1.03 mmol), CF_3Cl (approximately 480 cm^3), and O_3 (90.5 cm^3, 4.04 mmol) by condensing them in at -196° C. The reaction was allowed to proceed at -45° C for 72 hrs. At that time the oxygen now present was measured (106 cm^3, 4.73 mmol) and pumped away followed by all the other volatile materials. There remained in the cylinder the white solid $No_2^+ClO_4^-$ (133 mg, 0.92 mmol). The yield of nitryl perchlorate was 89%.

EXAMPLE III

Chlorine nitrate (16.4 cm^3, 0.73 mmol) and ozone (61.6 cm^3, 2.75 mmol) were separately condensed into a 30 ml. stainless steel cylinder cooled to -196° C in a liquid nitrogen bath. The cylinder was then kept at -45° C for 66 hrs. The products were separated by fractional condensation in a series of U-traps cooled to -78° C, -112°, and -196° C after removal of the by-product O_2 (49.2 cm^3, 2.20 mmol). Unreacted chlorine nitrate (7.8 cm^3, 0.35 mmol) and ozone (20.2 cm^3, 0.90 mmol) were the only other volatile species found. The solid product nitryl perchlorate (57 mg, 0.39 mmol) remained in the cylinder and was identified by its infrared spectrum. The conversion of $ClNO_3$ to $NO_2^+ClO_4^-$ was

53% and the yield based on the converted material was nearly quantitative.

EXAMPLE IV

Chlorine nitrate (20.4 cm³, 0.91 mmol), CF_3Cl (approximately 300 cm³) and ozone (72.0 cm³, 3.21 mmol) were condensed successively into a 30 ml. stainless steel cylinder cooled to -196° C. The closed cylinder was allowed to warm to ambient temperature, approximately 20° C, for 4 hours. The volatile materials were then pumped out of the cylinder leaving behind the white solid, nitryl perchlorate (111 mg, 0.76 mmol). The yield of $NO_2^+ClO_4^-$ was 84%.

EXAMPLE V

A 30 ml stainless steel cylinder was charged with $ClNO_3$ (24.6 cm³, 1.10 mmol), CF_3Cl (approximately 250 cm³), and O_3 (85.2 cm³, 3.80 mmol) by condensing them in at -196° C. The reaction was allowed to proceed at -78° C for 45 hours. By-product $_2$ (23.8 cm³, 1.06 mmol) was then measured and removed. Other volatile species were separated by fractional condensation. Unreacted $ClNO_3$ (17.5 cm³, 0.78 mmol) was recovered and the solid nitryl perchlorate formed was 45 mg, 0.31 mmol. The conversion of $ClNO_3$ to $NO_2^+ClO_4^-$ was 28% and the yield based on the converted material was nearly quantitative.

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

What is claimed is:

1. The method of synthesizing nitryl perchlorate comprising the step of:
   combining chlorine nitrate and ozone in the presence of an inert fluorocarbon solvent at a temperature in the range from about −78° C to about ambient.
2. The method of claim 1 wherein:
   said conbining step is performed in the presence of CF_3Cl.

* * * * *

APPENDIX M

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