SOME REACTIONS OF THE BINARY FLUORIDES OF XENON: THE SYNTHESIS OF THE FIRST XENON-NITROGEN BOND

by

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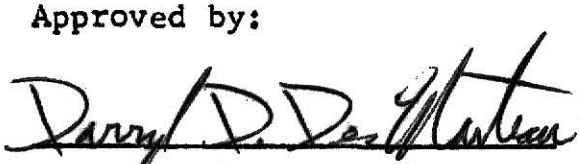

Major Professor

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I. INTRODUCTION

A. Historical Background

Although the first paper on noble gas compounds was in error[1], it prompted other workers[2] to consider the possibility of compounds from Group VIII. In a remarkable prediction, Pauling[3] suggested that the compounds KrF_6, XeF_6, and salts of Xenic acid, H_4XeO_6 would be stable. In 1933, the year of Pauling's prediction, Yost[4,5] actually used the method recognized today as good preparative procedure for synthesis of XeF_2. Yost failed to find any product, however, perhaps because of the small scale used.

Nearly thirty years later Bartlett[6] opened the door to xenon compounds with his announcement in 1962 of $Xe^+PtF_6^-$. Shortly thereafter Malm[7] and co-workers first synthesized XeF_4, while a German group[8] were the first to prepare XeF_2. The three binary fluorides have been used as starting materials by a number of workers to produce oxides and oxy salts by metathesis reactions with strong acids. Although salts are now known for ligands such as $OClO_3^-$, OSO_2F^-, $OSO_2CF_3^-$[9], $OTeF_5^-$[10], $OSeF_5^-$[11], and $OC(O)CF_3^-$[12], as well as adducts of these compounds with AsF_5, RuF_5, or SbF_5, until now all xenon compounds contained xenon bonded to either fluorine or oxygen.

Malm and Appelman[13] have written a review of the literature to 1969, and Holloway[14] has written a book on the compounds of xenon, as have others. The reader is referred to these sources for futher review of previous work as well as a summary of the various clathrates which are known.

This work is concerned with general trends in the reactions of xenon fluorides and introduces the first compound containing a xenon-nitrogen bond, $FXeN(SO_2F)_2$. The work[15] has been the subject of articles in Science News[16], Chem and Engineering News[17], and Scientific American[18].

B. Equipment

Most of the operations described in the following text involve use of a vacuum line. The particular set up in the line I have used is relatively simple. It is a double manifold system, one made of Pyrex glass with three T joints connected through a 4mm Kontes K-826500-0004 glass-Teflon valve to a Pyrex 10/30 T female outlet; the other manifold was made of 1/4 inch stainless steel cut to allow three T joints made with Universa Valves, 6V71UL4AT. The manifolds were connected to form a loop in both posterior and anterior ends by Kel-F tubing which allows a certain degree of flexibility. On the posterior end of the loop, connections were made to an accurate pressure gauge, the Wallace

and Tiernan 62A-4D-0800X. The anterior of the loop was brought through an 8mm Kontes K-826600-0008 glass-Teflon tap to a removable base center tube trap always kept at liquid nitrogen temperature to protect the pump from harmful vapors. Just after the cold trap was a Hastings thermo-conductivity pressure gauge capable of indicating pressures of less than one micron. Next was another 8mm Kontes valve which could isolate the diffusion pump from the cold trap. My diffusion pump was hand made by the university glass blower and filled with Halocarbon 11-21 oil. The dimensions were taken from a commercial single stage Eck & Krebs pump. Another 8mm Kontes valve separated the diffusion pump from the mechanical pump, a Precision Scientific Vactorr 150. Standard operating pressure of this system is less than one micron.

There is additional equipment necessary to work with xenon fluorides. In my case these items are detachable since there are so few inlets to the manifold. First, a soda lime scrubber is needed to reduce fluorine and remove it before the gas can attack the pump. The scrubber is a Pyrex tube loaded with soda lime, capable of being connected to the metal manifold on one end through flexible copper tubing and fitted with a 10/30 male Kontes joint on the other. Another detachable item is an air drier. This is a long tube filled with three inches of anhydrous $CaSO_4$, a glass wool plug, and four inches of P_2O_5. The end was connected

by Tygon tubing to a 10/30 male Kontes joint. Finally, two Kel-F U traps, of 1/4 and 3/8 inch diameter tubing are necessary to trap volatile condensables produced by reactions.

Reactors were made of three different materials. Two stainless steel bombs were used. The larger was a 25ml Nupro 316-25cc vessel fitted with a Universa 3V-81UL4 valve. The other, which is used only for preparation of XeF_6, is a 4cc Monel reactor equipped with a high pressure valve, the Autoclave Engineers 30VM-4071. The working pressure of this valve is 15,000 psi. The glass reactors were all hand blown and shaped to the most convenient form as stated in the specific experimental section. Finally, the most frequently used reactors were made from Kel-F tubing and fitted with a Hoke 1212G4 stainless steel or monel valve. These Kel-F reactors are made in the following manner:

The plastic is ordered in 1/4 and 3/8 inch outside diameter tubes from Fluorocarbon Company, Pine Brook, New Jersey. The 1/4 inch tubing is necessary to fit into the Hoke valve and usually the 3/8 inch tubing must be lightly drilled to allow a snug fit between the two tubes. After this fit is made, the sealing can be done by using a Pyrex ℠ 12/30 female joint as a mold. With a small, very soft flame the exterior of this mold is gently warmed until the Kel-F turns transparent. Sealing is done by pushing the tubes lightly in the mold, taking care not to close off the

bore of the smaller tube. To seal the bottom of the reactor, make a test tube from the narrowest glass tubing in which the Kel-F will fit and again use this as a mold to seal the plastic. The open end of the Kel-F should carefully be filed down so as to remove any burrs. Connections to the valve are made with Teflon ferrules.

Occasionally Kel-F must be shaped for other purposes, such as making traps or to make connections to the vacuum line. Bending is done by twirling the plastic over a heat gun, just as you would turn glass over a torch. Make the bend and quench the plastic under cold water. If this quenching is not done the Kel-F will straighten as it cools.

C. Standard Methods

The nature of the xenon fluorides is such that some word of introduction into methods of handling them is in order. Since xenon has a high molecular weight (131 a.m.u.) it is not surprising that even the covalent compounds have low vapour pressures[14] at room temperature. This fact, plus their high reactivity to give con-condensables makes it necessary to transfer xenon fluorides through a short connection, repeatedly opening and closing the necessary valves to assure a high vacuum. After transferring into the reactor, trapped at liquid nitrogen temperature, the xenon fluoride can be moved to the bottom of the tube by letting it warm, then, with the nitrogen cooling only the very tip

of the reactor, striking the solid ring of compound with two wrenches to break the ring and allowing the reactent to fall to the bottom. Giving this solid a quick pump to the line removes traces of impurities. The reactor is then taken to a balance and weighed.

If the other reactant is also of low volatility, such as $HN(SO_2F)_2$, it must be transferred to a vessel through a short connection and weighed by trial and error until the desired amount is obtained. Then it can be added to the xenon fluoride through the short connection. If solvent is desired it can now be added to the reactants.

If solvents are used, there must be some care taken in their selection, since although texts list XeF_2 as a mild fluorinating agent, in the presence of HF it becomes much more active, even being able to strip off Cl_2 from Freon 11 ($CFCl_3$). Freon 12, anhydrous HF, and BrF_5 have been found to be inert enough for use.

Although XeF_2 can be put into glass, there is no guarantee that a new compound, if formed, would be stable to glass, therefore all reactions with XeF_2 are carried out in Kel-F. Certainly XeF_6 should not be put in glass and stringent care must be taken to completely exclude moisture from both XeF_6 and XeF_4. If this is not done, one can form the highly explosive XeO_3[13].

Once the reactants are loaded in the Kel-F tube, the reaction is started at the lowest temperature the investigator

thinks reaction might begin. Then the bath is allowed to warm slowly, the reactor constantly monitored for signs of reaction. Since the product, if formed, might not be stable at elevated temperatures, the reaction is stopped as soon as possible and the isolation of product is started.

Monitoring and primary analysis on this work was done using a Perkin-Elmer 337 Infrared Spectrometer. Non-volatile or low volatile residuals could be checked using the Jasco R-300 Raman Spectrometer with an Argon 5145 nm laser source (Spectra-Physics 164). Power was normally 150-250 mWatts although this laser is capable of an output of 800 mWatts.

D. Basic Tenets

An advantage one has in working with xenon fluorides is that they are reactive enough that disappointments from mixing reactants and discovering that no reaction has taken place is rare indeed. However, man's vanity is sufficient that he is not content with just reacting species, he wants the reactions to go in a predictable manner. To this extent there are some general trends which should be pointed out.

First of all, one needs a highly electronegative ligand. Fluorine itself, of course, is the most highly electronegative element, and since the analogous xenon-chloride compounds are not known at room temperature, it is apparent that we should be concerned with those ligands whose group electro-

negativity is higher than chlorine.

We consider acids as likely moieties since subsequent elimination of HF is thermodynamically favourable, the bond energy of HF being one of the strongest ones known[19]. Since we are assuming that it is necessary to have a highly electronegative ligand, it naturally follows that the acid we choose should be a strong one. This helps us from a kinetic standpoint and here we have a crucial point. We need a reaction which is kineticly favourable so as to allow product formation at a feasible rate even at low enough temperatures so as to enhance the thermodynamic stability of the product. Once the product is formed it must be stable enough to allow isolation. If we are using an acid and eliminating HF we need to be able to have it warm to perhaps -30° or so to be able to pull off the HF. The low temperatures used can be a hinderance when one considers that the reactant may be a solid at these temperatures. Solid-solid reactions do not have as good a chance for synthesis, probably due to local heat generated at the solid-solid interface from an exothermic reaction; this heat may be sufficient to decompose the product.

A final requirement for the chosen reactant is that it must be resistant to oxidation. The potential for Xe (II)$\rightarrow$Xe(0) being 2.64 volts[13], i.e. XeF_2 is a very strong oxidizing agent, therefore, it is essentially necessary for all components in the ligand substrate to be

in as high an oxidation state as possible. It is also helpful, if the ligand is substituted, that it be substituted with fluorine; this eliminates the likely possibility that XeF_2 will be spent in fluorinating the substrate, especially if HF is present.

In trying to meet all the above recommendations, it becomes apparent that the number of likely moieties is indeed quite small. Lastly, one must bear in mind the possibility that the likely decomposition products might be thermodynamicly so stable relative to the synthesized product that whenever any product is formed it might react spontaneously to give the undesired decomposition.

II. EXPERIMENTAL

A. Starting Materials

1. Preparation of XeF_2

The synthesis of XeF_2 involves a modification of the method of Streng and Streng[20]. A one-liter round bottom Pyrex flask had a sidearm with a Kontes 4mm stopcock blown onto it. The top of the flask also was fitted with a Kontes 4mm stopcock and a 3/8 inch piece of glass tubing. The small section of tubing allowed connection of the vessel to the metal manifold.

The bulb was dried by washing with water and three portions of acetone, which was subsequently removed by the vacuum provided by a water aspirater. After connection to the manifold, final traces of water were removed by admitting fifty mm pressure of ClF_3 into the vessel and reevacuating.

A 2:1 excess of xenon was admitted as follows. One atmosphere of xenon was condensed in the sidearm and isolated from the bulb by closing the sidearm stopcock. Then one atmosphere of fluorine was bled into the bulb and the bulb closed off from the manifold.

While the fluorine remaining in the manifold was being discarded through the soda lime scrubber, the condensed

xenon was allowed to warm until it liquified. The sidearm stopcock was then opened to allow the xenon to flow into the main section of the bulb. The bulb was then placed in sunlight and the bottom cooled in ice. The reaction was allowed to continue for five days.

One end of a Kel-F U trap was connected to the vacuum line, the other end connected to another Kel-F U fitted at both ends with Hoke valves and made especially for collection and storage of XeF_2. The other end of the storage U was connected by a short Kel-F U to the bulb and all U traps evacuated. The storage trap was cooled to -78° and the connecting trap was held at liquid nitrogen temperature to collect excess xenon. Any unreacted fluorine was discarded through the scrubber.

The xenon collected can be hydrolysed to remove SiF_4, BF_3, and other impurities, dried, and used in later preparations of XeF_2. The reason for using an excess of xenon is to prevent formation of higher fluorides of xenon and hence eliminate the possibility of producing XeO_3.

2. Preparation of XeF_6[21-24]

In a four cc metal bomb equipped with an Autoclave Engineers High pressure valve capable of holding 15,000 psi, two millimoles of xenon and forty millimoles of fluorine were loaded and the reactor sealed off. Heating tape was

wrapped around the vessel with a thermocouple inserted and the reaction was allowed to run for five days at a temperature of 230°.

Collection of XeF_6 is done in the same manner as XeF_2 except that the arm of the storage tube is sealed off with a torch. XeF_6 forms nearly colourless crystals; if any liquid can be seen in the storage vessel it should immediately be destroyed with a heavy stream of KI solution. The liquid is probably $XeOF_4$, caused by water leaking in and hydrolysing the XeF_6. Further leakage could produce XeO_3. Long term storage of XeF_6 at room temperature is difficult, even in Kel-F, due to the attack of XeF_6 on the material, causing it to form cracks.

3. Preparation of N_2O_5

First anhydrous HNO_3 must be made as concentrated as possible[25]. This is most easily done by doubly distilling concentrated HNO_3 from two volumns of fuming sulfuric acid under vacuum. The receiving vessel was chilled to zero degrees during these distillations.

The anhydrous HNO_3 was then frozen at -78° in a three-neck ₹ round bottom flask equipped with a ringsealed nozzle in one arm, used for bubbling in dry O_2. The other arm was connected to a center-tube trap held at -78°. The trap outlet was connected to a mineral oil bubbler used to

measure O_2 flow. While the acid remained frozen, the middle neck was opened and P_2O_5 was layered evenly over the surface. First granular P_2O_5 was added and shaken to spread, then powdered P_2O_5 was admitted and also shaken to make a homogeneous layer of perhaps one cm. After this addition the center neck was stoppered. When the acid warmed enough to liquify, the O_2 was turned on at a rate of about one cc/sec. The HNO_3 bubbles off through the layered P_2O_5 which dehydrates it to form gaseous N_2O_5 which is then collected in the -78° trap.

4. Preparation of Anhydrous HNO_3

When completely anhydrous HNO_3 was needed for a reaction, it was prepared by adding the stoichiometric amount of N_2O_5 to a weighed amount of water in vacuo. This mixture was allowed to react as slowly as possible at the coolest temperature to hinder production of N_2O_4. The small amount of N_2O_4 produced was removed by quickly opening and closing the stopcock to the vacuum line.

5. Preparation of SF_5OSO_2F

SF_5OF (22 moles) and SO_2 (47 mmoles) were condensed into a 45 cc metal bomb[26]. The reactants were frozen and the bomb evacuated. It was then placed into a 40° oven for 20 hours

after which the products were separated by traps held at -95° and -196°. The product, collected at -95°, was a colourless liquid which had an experimental molecular weight of 230 (theoretical: 226). The yield was nearly 13 mmoles.

6. Preparation of Anhydrous $HClO_4$

The method of Smith[27] was used to prepare the reagent. About 20 mls of 72% perchloric acid were slowly added to 100 g of anhydrous $Mg(ClO_4)_2$ in a 300 ml round bottom flask. The flask was connected to a center-tube trap cooled to -78° which was linked to the vacuum line and the assembly evacuated to less then one torr. Gentle heat was applied to the still pot and the anhydrous acid was collected at -78° and used without further purification. It was stored in glass at -78°.

7. Preparation of HPF_4

The method used was that of Holmes and Storey[28]. Ten mmoles of H_3PO_3, ground to a fine powder, was placed in a Kel-F reactor. Then 1.4 g of anhydrous HF were condensed on top and the reactor was placed into a -50° bath for 1 1/4 hours. The mixture was then fractionated three times through an all Kel-F system using two U traps linked

end to end. The first trap was cooled to -95°, the second to -135°. The product, collected in the -135° trap, was checked by infrared until no more HF could be seen. Storage was not necessary, as the product was used immediately in a subsequent reaction.

8. Preparation of CF_3SH

In a 25 ml stainless steel reactor were loaded 7.15 g (30 mmoles) of HgF_2 and 4.5 g (60 mmoles) of CS_2[29]. The bomb was evacuated and then sealed off and heated for 5 hours between 230-40°. After cooling, the resulting mixture was washed and filtered with excess CS_2, the by-product of HgS caught on the filter paper. The CS_2 was then evaporated, and the product, $Hg(SCF_3)_2$, dried to a white crystalline solid. The yield was over 3 g.

The solid was then put into a 100 ml round bottom glass reactor and the bulb evacuated[30]. Then 0.75 g of anhydrous HCl were condensed in and the reaction allowed to proceed for two days at room temperature. The reactor was then taken to the vacuum rack where the mixture was fractionated through traps held at -60°, -150°, and -196°. The product from the -150° trap was then refractionated until the ir showed it was clear of HCl. Storage was done in glass covered with foil at room temperature.

9. Preparation of HNF_2

Although on a much smaller (and hence much safer) scale, the procedure used here is the method of Colburn[31].

Three ml of thiophenol was put into a 300 ml round bottom flask equipped with a sidearm, and the flask was evacuated. Then six mmoles of tetrafluorohydrazine were condensed into the bulb and the mixture was sealed off and heated at 45-50° for four hours. It was then taken to the vacuum rack and fractionated through traps held at -78°, -120°, and -196°, the product catching in the -120° trap (very near its freezing point). The ir matched the literature spectrum[32]. The HNF_2 so produced was transferred to a center tube trap, again condensing at -120°, and stored as a gas at room temperature.

10. Preparation of $HN(SO_2F)_2$

In a one liter round bottom flask fitted with a drying tube were placed 97 g of H_2NSO_3H (1 mole) and 420 g of PCl_5(2 moles). The solid mixture was heated at 100° for 10 hours, during which time the reactants liquified and HCl was driven off. After the gas evolution ceased the bulb was brought to the vacuum line and $OPCl_3$ was distilled off at a reduced pressure of 20 torr and a bath temperature of 80°. The residual oil[33], Cl_3PNSO_2Cl, was trans-

ferred to a small, 3-neck round bottom flask and 71 mls of chlorosulfonic acid were added. A ring sealed ₹ joint was inserted in one neck to permit a slow sweep of dry nitrogen through the flask while the reactants were heated to a temperature of 80°. The other arm of the flask was connected to a center-tube trap, held at -78°, to collect the evolved $OPCl_3$. The other end of the center-tube trap was connected through a P_2O_5 drying tube to a water aspirator. The reaction was allowed to continue for 8 hours, after which the bath temperature was raised to 120° and the distillation was continued for thirty minutes more. The residual oil was then distilled at a reduced pressure of 0.03 torr with the product, $HN(SO_2Cl)_2$, coming over at a temperature of 55°. Upon standing overnight the $HN(SO_2Cl)_2$ completely crystallized. The acid chloride was then fluorinated[34] by melting it and mixing it with 200 mls of AsF_3 which had been freshly dried by distilling from NaF and two volumes of concentrated sulfuric acid. This was done in a plastic bottle which was quickly capped with a reflux condenser and drying tube. The mixture was then refluxed for four hours, after which time the bottle was fitted with a distillation head and the $AsCl_3$ and excess AsF_3 were distilled off. The residue was transferred to a small glass apparatus and the $HN(SO_2F)_2$ was distilled off at 78° under a full dynamic vacuum. The product was purified with three 10 ml portions of Freon 11 by fractional

crystallization. The compound was checked and found to be pure by fluorine nmr. It was stored in a glass vessel at room temperature.

11. Preparation of $ClN(SO_2F)_2$

Several attempts were made to prepare the chloro compound by the method of Ruff[35]. None of these attempts, however, yielded the desired product. This particular compound was considered very desirable as it would be primarily covalent, both Cl and $N(SO_2F)_2$ possessing high electronegativity. A comparison between this essentially covalent compound and an ionic one (such as $CsN(SO_2F)_2$) would give an indication if the $FXeN(SO_2F)_2$ is more ionic or covalent.

It was then necessary to synthesis the chloro compound by a new method. Knowing that formation of HF is highly favourable thermodynamicly and that the ClF has a partially positive Cl from electronegativity considerations, it was felt that a simple reaction between $HN(SO_2F)_2$ and ClF should produce the desired result.

In a Kel-F reactor were condensed 1.82 mmoles $HN(SO_2F)_2$ and a slight excess of ClF. The reaction was then held at -78° for two days after which time the reaction mixture was transferred into a glass vessel containing powdered NaF (to remove the HF). It then was fractionated twice through

glass U traps held at -20°, -78°, -196°. The product was held in the -78° trap. The sample gave a molecular weight of 213 (calc. 215) and melted at -55° (lit. -52).

The fluorine nmr, taken in $CFCl_3$, gave a chemical shift of -54.7 (lit. -57.9). The difference may be due to the fact that Ruff took the nmr in CH_2Cl_2 solvent, and $ClN(SO_2F)_2$ may react with methylene chloride to yield Cl_2 and $H_2Cl_{2-x}N(SO_2F)_2$ $_2$. Ruff himself, in another paper[36], has mentioned the tendency of the $N(SO_2F)_2$ ligand to react with chlorides. In that paper he corrected some data which he had previously published. The correction was necessary because of this reaction. Gas phase infrared and liquid phase Raman spectra were also taken.

12. Prepararion of $CsN(SO_2F)_2$[34]

Into a 250 ml round bottom flask was added about 15 g of $HN(SO_2F)_2$ which was quickly frozen by a -78° bath. Then 50 ml of ice cold water were added and the mixture was allowed to warm slowly to room temperature. Cs_2CO_3 was added in small portions until indicator paper showed that the solution was neutral. The water was then removed by vacuum. The crude solid remaining was dissolved in 200 ml of hot absolute ethanol. The solution, while still hot, was suction filtered. This solution was boiled down to about 50 ml and cooled. The filtered product was dryed under vacuum.

B. Reactions

1. $XeF_2 + N_2O_5$

This was an attempt to synthesis the Xe (II) nitrate, producing NO_2F as a by-product. Xenon difluoride (1 mmole) was placed in a Kel-F reaction vessel along with 1 mmole of N_2O_5, and Freon 11 was added as solvent. The vessel was then warmed very slowly from -78° up to room temperature. The only identified product was oxygen, obtained from the decomposition of N_2O_5 to N_2O_4. XeF_2 remained as a solid in the bottom of the reactor.

2. $XeF_2 + HNO_3$

This was a continuation of the earlier work reported by Eisenberg and DesMarteau[37] in which they observed unstable coloured solids when using nitric acid mixed with nitrogen dioxide. In that paper they posed the possibility of an unstable intermediate of $FXeNO_3$. It was hoped that if pure nitric acid were used (or from the N_2O_5 reaction mentioned above) that this nitrate salt would be stable enough to permit isolation.

In a Kel-F reactor were loaded 0.818 mmoles XeF_2 and 0.812 mmoles of HNO_3. The reactor was placed in a bath at -60° and allowed to warm very slowly to room temperature.

The products indicate the reaction followed the equation:

$$XeF_2 + 2\ HNO_3 \quad Xe + 1/2\ O_2 + 2\ HF + N_2O_5$$

There was also some N_2O_4 present, undoubtedly due to some decomposition of N_2O_5.

3. $XeF_6 + HNO_3$

There are examples where the xenon (VI) compounds are more stable than the corresponding xenon (II) salts[38]. Since we could not isolate any xenon (II) nitrate, the thought was that perhaps the F_5XeNO_3 would be stable. Condensed into a Kel-F reactor were .669 mmoles XeF_6 and .662 mmoles HNO_3. The reaction was run from -35° to -10° over a span of 19 hours. Xenon (.096 mmoles) and NO_2F (.335 mmoles) were observed. The reaction was allowed to continue to +3° for another 22 hours. More xenon and NO_2F were observed. XeF_6 remained in the reactor. The overall reaction is:

$$XeF_6 + 6\ HNO_3 \longrightarrow Xe + 3\ O_2 + 6\ NO_2F + 6\ HF$$

4. $XeF_2 + SF_5OSO_2F$

The xenon (II) salts of $HOSeF_5$ and $HOTeF_5$ have already been prepared by Seppelt[11] and Sladky[10]. Seppelt found

that the selenium compound was remarkably stable, finally decomposing at better than 100 degrees. Since the corresponding acid of sulfur, SF_5OH, is not known, it was thought that XeF_2 might cleave the SF_5OSO_2F to form the analogous salt and the very stable SO_2F_2. This is supported by Ruff's paper on sulfur oxyfluoride derivatives where he demonstrated that fluoride ion attacks SF_5OSO_2F to give the SF_5O anion and SO_2F_2. According to group trends in the periodic table, the $FXeOSF_5$ ought to be at least as stable as the corresponding orthotellurate.

We condensed 1.08 mmoles of XeF_2 into a Kel-F reactor, followed by the appropriate amount of SF_5OSO_2F. The vessel was started at -105° and allowed to warm slowly to room temperature. Finally it was warmed at +37 for 12 hours in an oven. Only trace amounts of xenon were observed over this time span.

Some HF was added to the mixture to serve as a solvent and the vessel was allowed to sit for 30 minutes at room temperature.

The only volatiles ever observed in this mixture were slight amounts of xenon and SF_5OSO_2F. There was a weight loss of XeF_2 corresponding to .027 mmoles of Xe.

Apparently there is a sufficiently high activation barrier to reaction that if one were to supply enough heat to cause a reaction, in all probability that heat would be sufficient to cause any product to be unstable.

5. $XeF_6 + SF_5OSO_2F$

Since there was no reaction with XeF_2, it was thought that perhaps the analogous reaction would produce results with the more reactive XeF_6. There are indications that the octahedral xenon (VI) salts[36] are at least as stable as the corresponding xenon (II) salts, and it is also known[14] that XeF_6 is essentially $XeF_5^+F^-$ and may be sufficiently nucleophilic to cause cleavage of SF_5OSO_2F mentioned earlier. Xenon hexafluoride (.352 mmoles) was loaded in the Kel-F reactor followed by .352 mmoles SF_5OSO_2F. The mixture was started at -78°, warming to ambient temperature over a 22 hour period. The reactor was then heated in a +40° oven for about 4 hours. No reaction occurred during this period so the reactor was returned to the oven and heated to 70° for 6 hours. Even at this temperature the only observed components were the starting materials.

6. $XeF_2 + (CF_3)_2NOH$

The XeF_2 (1.24 mmoles) was loaded into a Kel-F reactor followed by a stoichiometric amount of $(CF_3)_2NOH$, obtained from Professor J. M. Shreeve. The reactor was placed in a -78° bath and allowed to warm slowly. The reaction begins at about -40° and is complete at -20°. Whether there is an unstable intermediate formed or not is unknown. The products of the reaction make such an intermediate plausible by

anology with reactions of HSO_3F and $HN(SO_2F)_2$:

$$XeF_2 + (CF_3)_2NOH \longrightarrow FXeON(CF_3)_2 + HF$$

$$2\ FXeON(CF_3)_2 \longrightarrow Xe + XeF_2 + [(CF_3)_2NO]_2$$

Isolation of such an intermediate, if it should exist, at least by this solid-solid reaction, is no simple task. Intense colour, indicative of free radicals is apparent at the outset of the reaction. Perhaps if a suitable solvent, allowing reaction at a lower temperature could be found, then one might have a chance of producing such a compound.

7. $XeF_2 + SF_5OOH$

As mentioned earlier, the acid SF_5OH is not known at the present time. The hydroperoxide, SF_5OOH, has been synthesized and it was hoped that its use as reactant might produce an OSF_5 or $OOSF_5$ salt. The SF_5OOH was made by Dr. DesMarteau[40].

A Kel-F reactor was charged with .738 mmoles of XeF_2 and .738 mmoles of SF_5OOH. The reactor was held at -78° to -70° for a period of 18 hours. The volatiles were pumped off and collected at -70°, and then analyzed. Some (.029 mmoles) xenon was observed but the essential products showed a decomposition of the SF_5OOH according to:

$$SF_5OOH \xrightarrow{XeF_2} OSF_4 + 1/2\ O_2 + HF$$

The XeF_2 undoubtedly serves as an active catalyst; perhaps the initial step is the elimination of HF and subsequent reformation of XeF_2.

8. $XeF_6 + HClO_4$

This was thought to have an extremely good chance of working since the Xe(II) salt was already known[9]. The Kel-F reactor was charged with 0.953 mmoles XeF_6 and 0.907 mmoles of $HClO_4$. It was then started at -111° and allowed to warm eventually to ambient temperature, the reaction being stopped on several occasions to sample the volatile components. When the sample fractions are added up the reaction is seen to follow the equation:

$$2\ XeF_6 + 6\ HClO_4 \rightarrow 2\ Xe + 6\ HF + 3\ O_2 + 6\ FClO_3$$

Apparantly the reactivity of XeF_6 is sufficient to fluorinate the perchlorate group rather than form a stable salt.

9. $XeF_2 + HPF_4$

In a Kel-F trap was condensed 0.829 XeF_2 and a stoichiometric amount of HPF_4. The reactor was then held at -111° for 5 hours. Since there was no apparent change, the reaction

was allowed to warm to -78°, and held at this temperature for 3 more hours. Finally the reactor was allowed to warm very slowly to room temperature. Solid began disappearing at -78° and reaction was complete after warming to room temperature. Ir analysis of the volatiles showed that the reaction follows the equation:

$$XeF_2 + HPF_4 \longrightarrow Xe + HF + PF_5$$

PF_5 is a stable compound, probably so stable that if any intermediate of the nature $FXePF_4$ is formed, it instantly is converted to Xe and PF_5.

10. $XeF_2 + CF_3SH$

Again the hope here was to eliminate HF and bond xenon to sulfur. Unfortunately the sulfur proved far too susceptible to oxidation.

XeF_2 (.855 mmoles) was condensed into the Kel-F reactor and CF_3SH (.855 mmoles) condensed on top of it. The reaction was started at -140° and eventually warmed to room temperature. After nearly one hour at room temperature a reaction began to set in, finally leaving only some liquid present in the bottom of the tube. A great deal of CF_3SH was still present in the reactor, the reaction following the equation:

$$CF_3SH + 4\ XeF_2 \longrightarrow 4\ Xe + HF + SF_6 + CF_4$$

Although the reaction did not give the desired compound, it does make for an interesting example of the fluorinating potency of XeF_2.

11. $XeF_2 + HNF_2$

Since the reaction with $HN(SO_2F)_2$ produced a xenon compound, it was thought that HNF_2 was a likely prospect to react in an analogous manner. In a Kel-F tube were placed 1.48 mmoles of XeF_2 and then 1.26 mmoles of HNF_2 were condensed in on top of it. Freon 12 was added to cover the solid and the reaction ran for 10 hours at zero degrees. A purple drop of N_2F_4 was seen floating on top of the Freon. Quickly withdrawing the solvent and checking the infrared and Raman of the residuals showed that only XeF_2 was left. Presumably the reaction is exactly analogous to the $HN(SO_2F)_2$ reaction:

$$XeF_2 + HNF_2 \longrightarrow HF + [FXeNF_2]$$

$$[FXeNF_2] \longrightarrow 1/2\ Xe + 1/2\ XeF_2 + 1/2\ N_2F_4$$

This reaction was tried several times at colder temperatures but no evidence for the intermediate was found. It seems

reasonable to assume that the compound is indeed formed, but that it is so unstable as to be unisolable. If a different synthetic method was used, perhaps then the compound could be obtained. It seems here that a temperature high enough to cause reaction is also sufficient to cause decomposition.

12. $XeF_2 + HN(SO_2F)_2$

In a Kel-F reactor were placed 2.66 mmoles of XeF_2 and 1.18 mmoles of $HN(SO_2F)_2$, the acid trapped in a ring some distance above the XeF_2. Freon 12 was added to cover the reactants and the vessel was placed in an ice bath. Both reactants are solids at this temperature, but after 24 hours no more acid was visible in the tube. The reactants then were kept at zero degrees for three more days, after which time the reactor was connected to the vacuum line and the volatiles were pumped off as quickly as possible without bumping the remaining white solid out of the reactor. Purification of the compound is achieved by pumping directly on the sample for at least thirty minutes. The product, $FXeN(SO_2F)_2$, is a white solid of very low vapour pressure at room temperature, decomposing very slowly at ambient temperature.

The compound has also been made in anhydrous HF, the yields being much poorer since HF is known to accelerate

the decomposition. Freon 11 has also been used as a solvent. The problem with Freon 11 is that it is not sufficiently impervious to fluorination by an XeF_2/HF mixture, chlorine gas being evolved. Further discussion of the synthetic methods tried are contained in the "Discussion" section.

13. Decomposition of $FXeN(SO_2F)_2$

A purified sample of $FXeN(SO_2F)_2$ (.55 mmoles) still contained in the Kel-F reactor was plunged into a hot water bath at +75° and held there for five minutes. The volatiles from the reaction showed only Xe (.56 mmoles) at -78° (no volatiles at -196°, volatiles from -78° having no ir spectrum). When room temperature infrareds were taken, first the dimer, $[N(SO_2F)_2]_2$, was observed, and then, by condensing sample into the arm of the infrared cell, XeF_2 was seen. The decomposition can be written as:

$$2\ FXeN(SO_2F)_2\ (0.43\ \text{mmoles}) \xrightarrow{75^\circ}$$

$$Xe\ (0.22\ \text{mmoles}) + [N(SO_2F)_2]_2\ (.022\ \text{mmoles}) + XeF_2\ (0.22\ \text{mmoles})$$

The separation of XeF_2 from the dimer is difficult. Once the initial xenon was removed the residual mixture was hydrolysed to determine xenon trapped as XeF_2. In a separate experiment, the residuals were not hydrolysed and ir spectra were taken.

These spectra showed the presence of both dimer and XeF_2. Further, hydrolysis of the initial salt yields the quantitative amount of xenon.

14. $FXeN(SO_2F)_2 + SbF_5$

It is known that many xenon compounds form adducts of the type: $FXeA + SbF_5 \rightarrow AXe^+SbF_6^-$ with SbF_5 and AsF_5. Attempts to form this salt failed, cleaving the anion and causing sufficient heat to decompose the rest of the sample. Trials were run both neat and in CF_2Cl_2, giving similar results.

Typically, 0.663 mmoles of the purified $FXeN(SO_2F)_2$, still in the reactor tube, had added to it excess SbF_5, which had been distilled from NaF, and was placed in a bath at $+5.5^o$ (the melting point of SbF_5 is 6^o). As the SbF_5 melted, it slowly moved down the walls of the reactor until it hit the solid in the bottom. Reaction was immediate, turning yellow, then colourless, and smoking. When the volatiles were analyzed 0.10 mmoles of non-condensables (probably N_2) and 0.40 mmoles of SO_2F_2 along with 0.54 mmoles of xenon were observed. Other attempts with the SbF_5 produced non-condensables (N_2) to SO_2F_2 in the ratio of 1:4 (SO_2F_2 is difficult to separate from xenon), however, the amount of xenon given off is not in a constant ratio with these other two. The dimer $[N(SO_2F)_2]_2$ was seen in

the residuals along with the excess SbF_5. There are probably two reactions occurring:

$$(1)\quad 2\ FXeN(SO_2F)_2 \longrightarrow Xe + XeF_2 + [N(SO_2F)_2]_2$$

$$(2)\quad 2\ FXeN(SO_2F_2)_2 \xrightarrow{SbF_5} 2\ Xe + N_2 + 4\ SO_2F_2$$

In (2) we have the basic reaction which was under study. There is apparently enough heat evolved during the reaction, however, to cause the equation (1), the decomposition, to become important. XeF_2 left behind is in the form of $F_3Xe_2^+SbF_6^-$, as identified by Raman spectroscopy.[41]

TABLE I

Summary of Reactions

Reactant	Reactant	Conditions	Products
XeF_2	N_2O_5	-78° to 25° Freon 11 2 da	O_2, N_2O_4
XeF_2	HNO_3	-60° to 25° 2 da	Xe, 1/4 O_2, HF, 1/2 N_2O_5, HNO_3
XeF_6	HNO_3	-35° to 3° 41 hrs	Xe, 1/2 O_2, NO_2F, HF
XeF_2	SF_5OSO_2F	-105° to 37° 3 da	No reaction
XeF_6	SF_5OSO_2F	-78° to 40° 3 da	No reaction

Reactant	Reactant	Conditions	Products
XeF_2	$(CF_3)_2NOH$	-78° to -20° 2 da	HF, 1/2 Xe, 1/2 XeF_2, 1/2 $[(CF_3)_2NO]_2$
XeF_2	SF_5OOH	-78° to -70° 18 hrs	XeF_2, HF, SOF_4, 1/2 O_2
XeF_6	$HClO_4$	-111° to 25° 3 da	2/3 XeF_6, 1/3 Xe, HF, 1/2 O_2, $FClO_3$
XeF_2	HPF_4	-111° to 25° 12 hrs	Xe, HF, PF_5
XeF_2	CF_3SH	-140° to 25° 2 da*	3/4 CF_3SH, Xe, 1/4 HF, 1/4 SF_6, 1/4 CF_4

* Reaction occurred only after 1 hr at 25°.

Reactant	Reactant	Conditions	Products
XeF_2	HNF_2	0° 10 hrs Freon 12	HF, 1/2 Xe, 1/2 XeF_2, 1/2 N_2F_4
XeF_2	$HN(SO_2F)_2$	0° 4 da Freon 12	$FXeN(S)_2F)_2$, HF

III. DISCUSSION

Back in the introduction a list of criteria were proposed for the selection of likely ligands for the bonding with xenon fluorides. Let me summarize those preliminary ideas:

1) High group electronegativity
2) Strong acids
3) Lowest possible reaction temperature
4) Avoid solid-solid reactions
5) Resistance to oxidation
6) Resistance to fluorination
7) Unlikely side reactions

By referring to the experimental section we can examine the validity of the above concepts. In the reaction of N_2O_5 we failed to have a compound which was a strong acid and apparently had a favourable side reaction to produce decomposition of N_2O_5. Likewise, side reaction with the nitric acid is more favourable to produce N_2O_5 than it is to produce $FXeNO_3$. One surprising aspect of this reaction is that no NO_2F is made even though HF is present. This is in light of the reported work of Johnston and Woolfolk[42] who found fluorination of NO_2 by XeF_2 when the reaction is allowed to continue for a long length of time. We found

that XeF_6 is of sufficient fluorinating strength, however, yielding quantitative amounts of NO_2F.

The thermodynamic considerations of the strong acids is borne out more clearly by the reaction, or rather the non-reaction, of XeF_2 with SF_5OSO_2F. I would hesitate to say that this experiment is a failure, however, since the number of inert solvents for use with xenon fluorides is discouragingly small. While I'm on the subject of solvents let me mention that although Freon 12 was used in the $FXeN(SO_2F)_2$ preparation, it is obvious that XeF_2 is at best very sparingly soluble in it. Recently, however, Dr. DesMarteau discovered that the extremely reactive XeF_6 is very soluble in Freon 12. The list of solvents for XeF_6 is minimal.

The selection of $(CF_3)_2NOH$ was a good one. The difficulty is that it is not a sufficiently strong acid to allow production of HF at a low enough temperature so as to permit isolation of what must be an unstable intermediate. Practical difficulties occur because the reactants are solids at the temperature where reaction sets in. This violates point (4).

The reaction of SF_5OOH was hopefully to form an $-OOSF_5$ compound of xenon. Unfortunately, the sulfur oxyfluorides are well known for their stability. Presumably the thermodynamics of the mixture strongly favour the production of OSF_4.

The xenon(II) perchlorate has already been characterized by Bartlett[9]. In his paper he made no mention of the xenon(VI) salt and our intent was to produce such a species, due to the high stability of the xenon(VI) salts[37] as mentioned earlier. The fluorinating effect of XeF_6 is too great to product this salt and the products are only HF and $FClO_3$. Conversely, the perchlorate anion is not stable enough toward degradative fluorination. This is point (6).

The reaction of HPF_4 was an attempt to bond xenon to phosphorus. As with the sulfur oxyfluorides, phosphorus pentafluoride is a remarkably stable species. Thermodynamicly, point (7) is violated and the result is the reduction of Xe(II) to Xe(0).

Point (5), resistance to oxidation, is admirably demonstrated by the annihilation of the CF_3S anion, sulfur being oxidized all the way up to +6. This is a good example for showing the interrelationship of these basic points. Sulfur is fluorinated only after the reaction is raised to room temperature, HF is eliminated and the stable SF_6 is the result.

The HNF_2 reaction is analogous to the imido process; in my opinion the $FXeNF_2$ is too likely a product to be discounted. A variation on the method used, solvent used, or reaction with XeF_6 is likely to be fruitful. One reason for this conclusion is that although NF_3 is unreactive, it is considered to be so through kinetic, as opposed to thermo-

dynamic reasons[19,43]. The fact that tetrafluorohydrazine, rather than trifluoroammine, is formed gives some evidence supporting this thought. Characterization of such a compound would indeed be useful, the calculation and assignment of xenon-nitrogen parameters would be much simpler.

Finally, we come to the reaction that produced the first compound containing a xenon-nitrogen bond. It was not known if the imidodisulfuryl fluoride would be sufficiently resistant to fluorination to allow a simple metathesis reaction to take place. And, in fact, when reaction is attempted neat, at room temperature, substantial quantities of SO_2F_2 are liberated. Since the acid does not melt until +17°, reaction must be run at a relatively high temperature. We have found that at zero degrees for several days reaction does proceed to give the desired product in yields of approximately 90%. When HF is used as a solvent, reaction can be run at lower temperatures and for shorter lengths of time, but the yields are not as high. It is thought the reason for this is that HF has the unfortunate effect of accelerating decomposition of the salt. Freon 11 was also used as a solvent and product can be obtained, but, as mentioned earlier, XeF_2 in the presence of HF becomes a potent fluorinating agent. The result is that when some reaction has taken place, and HF produced, the XeF_2/HF mixture is capable of fluorinating the solvent to produce CF_2Cl_2 and liberating Cl_2 gas. This does not really impede

the reaction, except from the standpoint that some XeF_2 is wasted in fluorination. Best results were obtained using Freon 12 as a solvent, if it can be thought of a such, the XeF_2 and $HN(SO_2F)_2$ not being very soluble at this temperature. Removal of solvent is done as quickly as possible to avoid effective concentration of HF and the product obtained is a coarse white to very pale yellow solid having very low volatility at 25°. The excess XeF_2 used in reaction is removed by pumping for at least thirty minutes under a dynamic vacuum. Considerable weight uptake is direct evidence for the formation of the compound.

Since $FXeN(SO_2F)_2$ has a high molecular weight (330) it is not surprising that it has almost negligible volatility at room temperature. The compound can be sublimed, with considerable decomposition, by heating the bottom of the reactor at 40-45° and cooling the upper portion of the tube with ice, all the while pulling a dynamic vacuum. Sublimation should be used only if the investigator is willing to lose at least 90% of the product. We have found that if the reactor is heated to 65° the compound is completely decomposed in five minutes.

The bulk of the evidence in the structure of the compound comes from nmr and Raman spectroscopy. Infrared spectra were attempted but the quality of this spectrum is very poor and is suspect in any case, there being a real possibility of compound reaction with the AgCl windows of the cell.

Photocopies of the actual nmr and Raman spectra are included in the appendix.

If the $FXeN(SO_2F)_2$ is indeed bonded to nitrogen, then we would expect two basic peaks in the fluorine nmr with area ratios of 1:2. The smaller peak will certainly be split into a ratio of nearly 1:6:1 since xenon has an isotope, Xe^{129} with I=1/2, present in an abundance of 26.4%. Xe^{129} will cause the main peak to be lowered to about 0.75 of its value if it was not coupled. The reason why 75% of the main peak is not split is because the other xenon isotopes do not cause splitting. The spin of Xe^{129} causes the remaining 0.25 of the intensity to be divided equally into two satellites, each with a ratio of 0.125, compared to the original. The final ratios, then, are 0.125:0.750: 0.125 or 1:6:1. This smaller peak, split into a triplet has a chemical shift of 127 ppm upfield from external $CFCl_3$ and a coupling constant of 5600 Hz. The very large coupling constant is not unusual for xenon compounds[44,45] and the magnitude (5600 Hz) compares favourably with that of XeF_2 (5690 Hz). In a recent paper[46], Gillespie has suggested that the magnitude of these numbers is an indication of the ionic-covalent character of the species. This empirical argument holds that ionic xenon (II) salts tend to have higher chemical shifts and higher coupling constants. From these figures the salt $FXeOSO_2F$ would be considered to be a species more ionic than the so-called "semi-ionic" XeF_2[47],

while the $FXeOSeF_5$ would be considered more covalent. By comparison of chemical shifts for $FXeN(SO_2F)_2$ and $FXeOSeF_5$ (+127 and +142 respectively) and of the coupling constants (5600 Hz and 5650 Hz) we see that $FXeN(SO_2F)_2$ is best considered as an example of a covalent xenon salt. Further evidence for covalency comes from the fact that the larger peak (at ϕ=-57.7) is also split into a triplet with the ratio of 1:6:1, due again to coupling of the fluorines on the sulfur to Xe^{129}. This would occur only in a molecule with a large covalent character, and is, in fact, the first instance where such long-range coupling has been observed in any xenon compound.

The Raman spectra of $FXeN(SO_2F)_2$ closely resembles other compounds which contain the $N(SO_2F)_2$ ligand. One may make tentative band assignments based on analogous compounds, but these assignments should indeed be viewed as tentative, since the lower regions of the spectra are quite crowded with peaks, the $N(SO_2F)_2$ moiety itself leading to 21 bands in C_s symmetry.

Certain bands are easily assigned. In HSO_3F the S-O symmetric and asymmetric stretching frequencies have been assigned as 1084 and 1285 cm^{-1} respectively[48], both of these frequencies have been observed to increase in more covalent molecules. In $FXeN(SO_2F)_2$ we have assigned 1450 and 1428 cm^{-1} as the asymmetric and 1218 and 1205 as the symmetric stretches. These characteristic bands are split

into doublets because the S-O groups can vibrate in-phase or out-of-phase.

The S-F stretches and bends are also readily identified, being relatively intense and occurring at rather unique frequencies. Again, in the SO_3F anion[48], the value is lower by about 100 cm^{-1} in the ionic compounds than in the covalent ones. In the cesium salt the bands at 729 and 748 cm^{-1} are assigned to the S-F stretch, while in the $FXeN(SO_2F)_2$ these values increase to 798 and 832 cm^{-1}. The S-F bends shift very little according to the ionic-covalent character, staying within the 450-500 cm^{-1} range.

The region from 500-650 cm^{-1} is characterized by four weak absorptions which are assigned to the SO_2 rocking and bending modes. Two other weak absorptions near 420 cm^{-1} and 340 cm^{-1} are assigned to the in-phase and out-of-phase SO_2 twisting modes. This same pattern of weak absorptions has been assigned in the same manner by Gillespie[49] in the spectrum of $S_2O_5F_2$, and by both Bartlett[50] and Gillespie[41] in separate papers on the spectrum of $FXeOSO_2F$.

In his paper on $S_2O_5F_2$[49], Gillespie showed the compound, which may be written as $O(SO_2F)_2$, has C_s symmetry. This compound, when compared with our structures, allows assignment of the NS_2 stretches and bend. In $S_2O_5F_2$ Gillespie assigned a weak band at 814 cm^{-1} as the asymmetric stretch and an intense polarized band at 323 cm^{-1} as the symmetric stretch. We have weak absorptions (depolarized)

in the liquids) occurring near 900 cm^{-1} and intense polarized bands near 340 cm^{-1} which we assign as asymmetric and symmetric stretches accordingly. Our assignments near 290 cm^{-1} for the bends is higher than Gillespie's, but is necessary because these are the lowest intense polarized peaks common to the compounds.

In the xenon compound there are several intense peaks in the lowest range of the spectrum which do not occur in the other $N(SO_2F)_2$ species. These are assigned to the vibrational modes containing xenon and closely fit the assignments made for xenon (II) fluorosulfates[41,50]. The assignment of 386 cm^{-1} for the xenon-nitrogen stretch is the most tentative of the assignments, there, of course, being no analogous xenon compounds for comparison. The region seems plausible if one assumes there is a roughly linear relationship as the bridging atom is substituted, since in XeF_2 the xenon-fluorine stretch is 497 cm^{-1} and in the oxy salts the xenon-oxygen stretch is lowered by about 50 or 60 cm^{-1} to near 435 cm^{-1}. A subsequent lowering of another 50 cm^{-1} would put us in this area, a region where SO_2 twisting modes would be the only other probable assignment.

The spectrum of $FXeN(SO_2F)_2$ has one band which is unique. This is an incredibly intense spike at 504 cm^{-1} and is readily assigned as the Xe-F stretch. All known compounds which contain a xenon-fluorine bond have such an

TABLE II

Band Assignments of some $N(SO_2F)_2$ Containing Compounds

$CsN(SO_2F)_2$	$ClN(SO_2F)_2$	$HN(SO_2F)_2$	$N(SO_2F)_{2-2}$	$FXeN(SO_2F)_2$	
1363 (18)	1490 (13)	1492 (7)	1506 (14)	1450 (5)	SO_2 asym str
	1470 (10)	1480 (8)	1485 (12)	1428 (4)	
1216 (100)	1250 (2)	1247 (100)	1261 (100)	1218 (10)	SO_2 sym str
1173 (7)	1245 (100)	1218 (11)	1225 (31)	1205 (3)	
845 (12)	922 (4)	913 (5)	918	881 (4)	NS_2 asym str
748 (32)	836 (20)	838 (6)	843	832 (10)	SF str
729 (75)	805 (5)	808 (52)	864 (50)	(819)? (5)	
				798 (90)	
568 (17)	567 (6)	638 (8)		656 (4)	SO_2 rocks and bends
524 (25)	552 (5)	563 (3)	670?	581 (<1)	
	539 (6)	558 (4)	552	559 (<1)	
	514 (4)	518 (8)	520?	549 (1)	
				504 (100)	XeF str

Explanation of Table II:

Assignments for observed frequencies in certain compounds containing the $-N(SO_2F)_2$ ligand. Relative intensities are given in parantheses with the strongest band given the value of 100. Underlined wavenumbers are taken from infrared spectra.

$CsN(SO_2F)_2$	$ClN(SO_2F)_2$	$HN(SO_2F)_2$	$N(SO_2F)_{2-2}$	$FXeN(SO_2F)_2$	
490 (13)	504 (14)	482(5)	506 (7)	478 (1)	SF bend
466 (17)	479 (4)	468 (7)	475 (11)	467 (1)	
426?	438 (2)	417 (1)	434?	435 (1)	SO_2 twist
	652 (46)	3430	675 (78)	386 (2)	NX str
362 (40)	378 (45)	333 (40)	327 (25)	337 (4)	NS_2 symstr
333 (13)	315 (3)	378 (1)	316 (11)	308 (1)	SO_2 twist
294 (29)	283 (21)	285 (16)	295 (31)	287 (6)	NS_2 bend
	310 (42)			214 (45)	NX bend
				180 (6)	N XeF bend
				130 (27)	SNXe bend
	220 (6)		260 (32)	110 (27)	SNX torsion
	128 (1)	170 (2)			NS_2 scissors

intense absorption. Gillespie has related this stretching frequency to bond length[41], the higher frequencies being shorter bonds and more ionic compounds. The nmr has strongly implied the covalent nature of $FXeN(SO_2F)_2$, and so we should expect a low value for this stretching frequency in the Raman. In fact, the value of 504 cm^{-1} is the lowest reported absorbance next to XeF_2 and $FXeOSeF_5$.

The Raman and nmr spectra, included in the appendix and listed in Table II with band assignments, show not only the presence of the $N(SO_2F)_2$ ligand, but provide strong evidence that the compound does indeed contain the first bond between xenon and nitrogen, that bond giving a moiety which is best thought of as essentially covalent in nature.

It is hoped that the publication of this new salt, with its xenon-nitrogen bond, will cause increased interest and activity in the chemistry of xenon compounds. We now know that xenon can be bound to nitrogen; perhaps the near future holds compounds containing bonding with sulfur and others.

What the field needs is a new general technique. The binary fluorides can be made directly from the elements. The salts have all been made by metathesis reactions of the binary fluorides with strong acids. As more compounds are synthesized, and our understanding of the nature of noble gas chemistry is increased, we hope that a general trend in these compounds will allow some fundamental new synthetic

procedure to emerge. The area is only twelve years old. This is still only the beginning.

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APPENDIX

Explanation of figure A-1.

Fluorine nmr spectrum of $FXeN(SO_2F)_2$ taken in BrF_5 at -40°.

Explanation of Figure A-2:

Raman spectrum of the ionic Cesium salt. The calibration is cm^{-1} difference from the Rayleigh line.

THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE.

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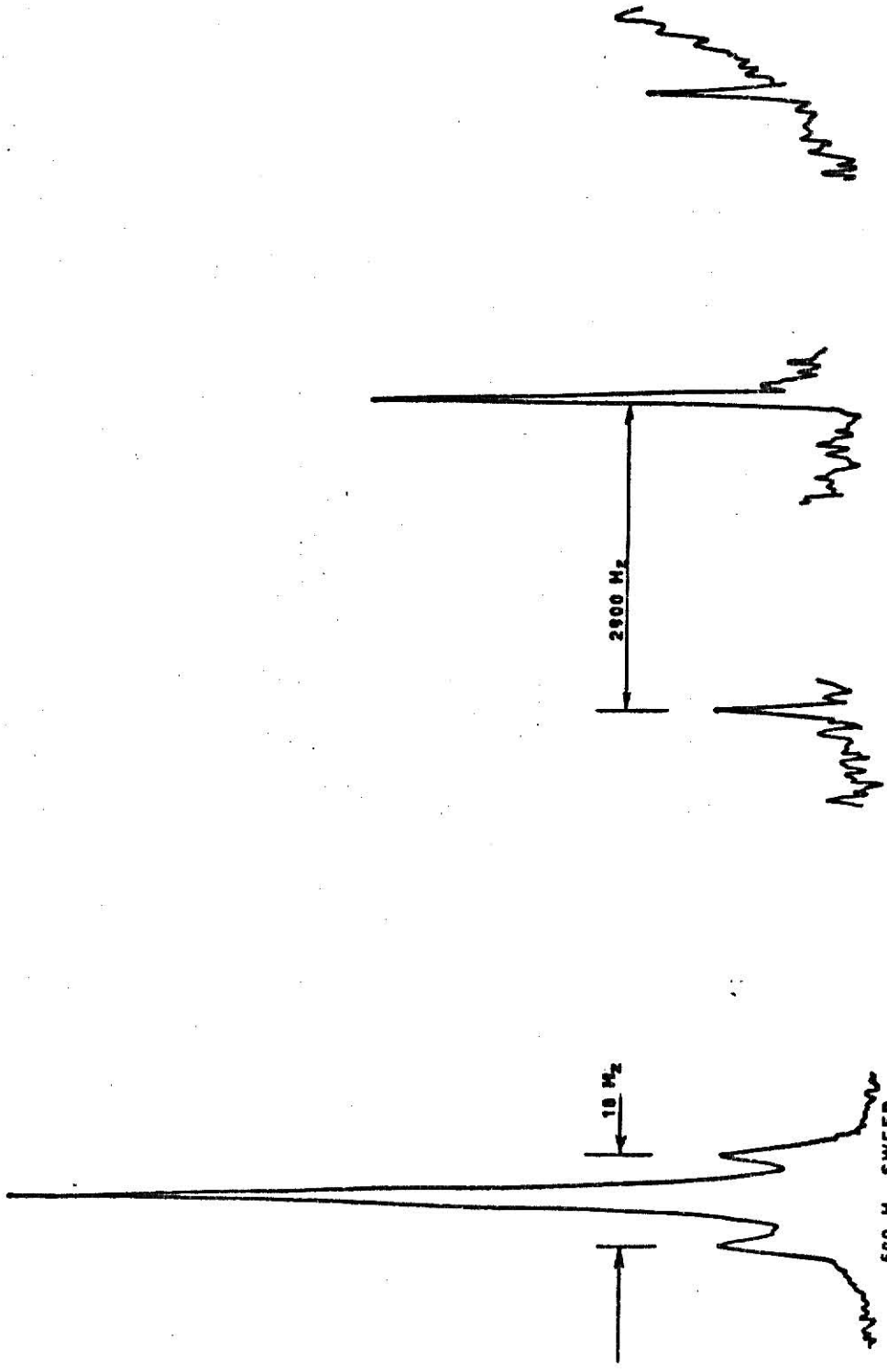
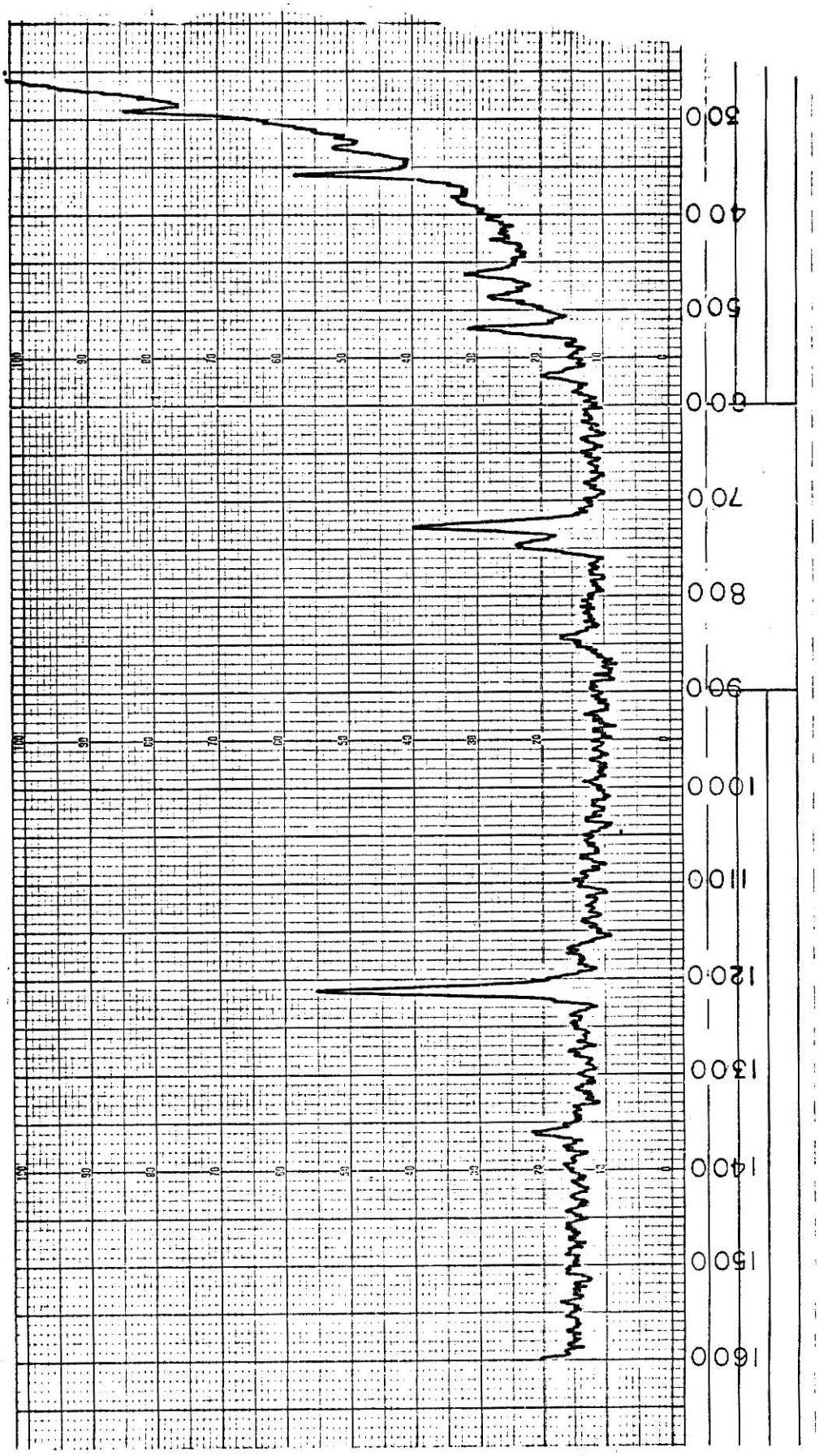


^{19}F nuclear magnetic resonace spectrum of $FXe\,N(SO_2F)_2$ in BrF_5 at -40^0 showing ^{129}Xe -F coupling of 18 and 5600 Hz. Upper satellite is superimposed on 40 k Hz sideband of BrF_5.

Explanation of Figure A-3:

Raman spectrum of the acid starting material. This sample fluoresces, which causes the baseline to rise. The break in the spectrum is caused by lowering the baseline.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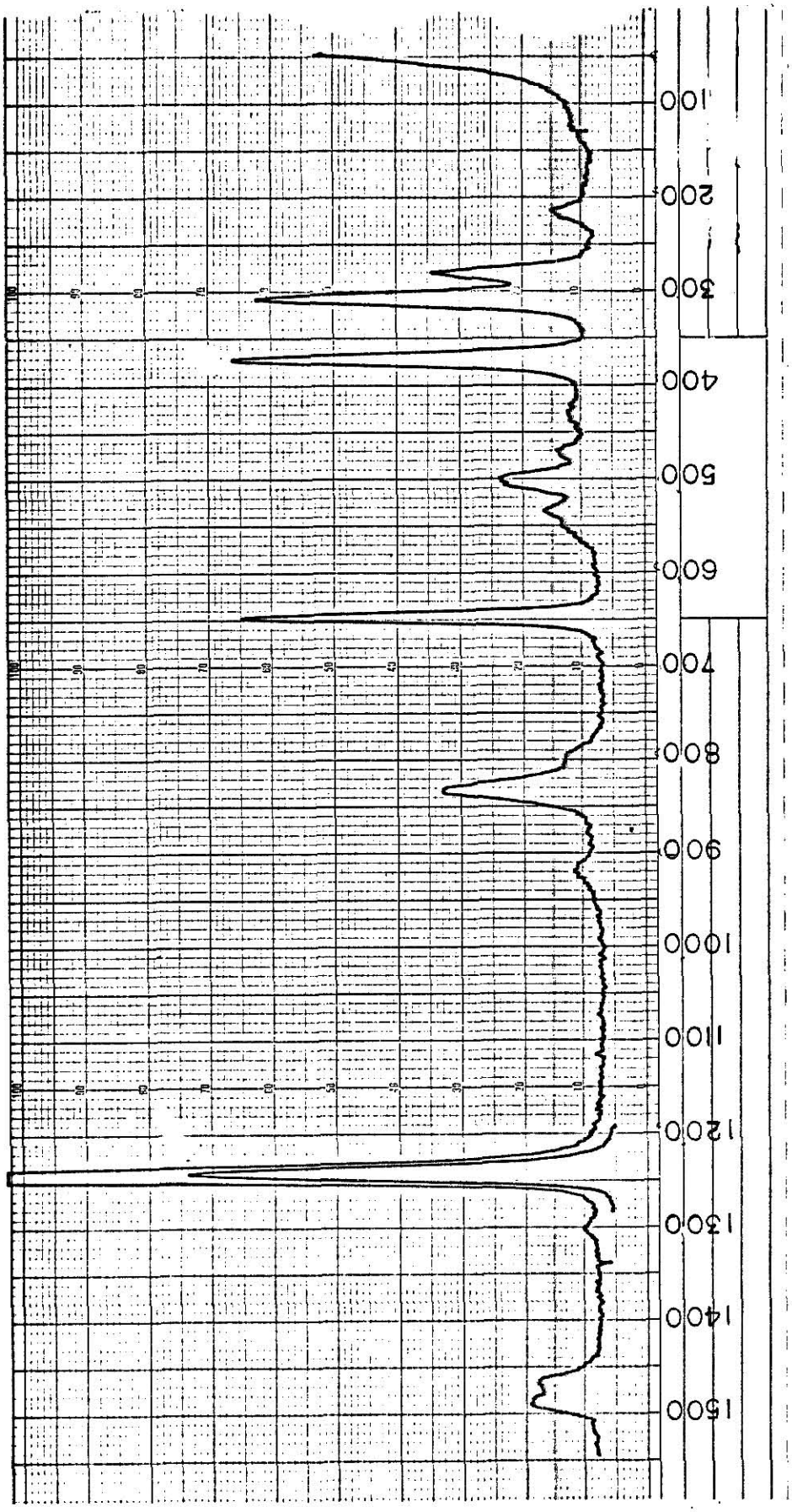
$CsN(SO_2F)_2$

Explanation of Figure A-4:

Raman spectrum of the covalent Chlorine compound. The gain was reduced to show the shape of the band at 1242 cm^{-1}.

Explanation of Figure A-5:

The gain was increased in this Raman spectrum to show the presence of weaker absorptions.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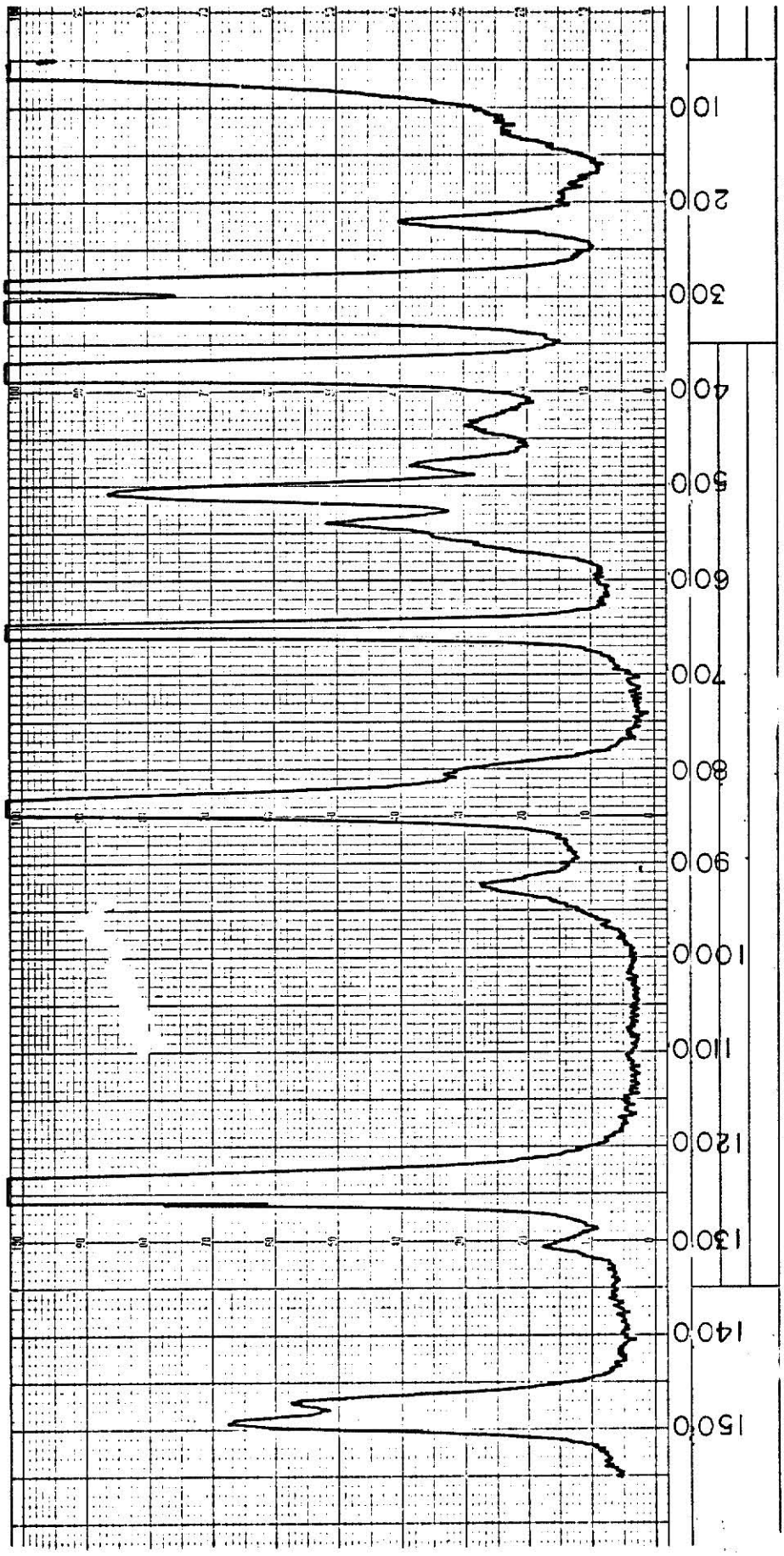
$ClN(SO_2F)_2$

Explanation of Figure A-6:

Raman spectrum of the dimer, obtained by the decomposition of $FXeN(SO_2F)_2$.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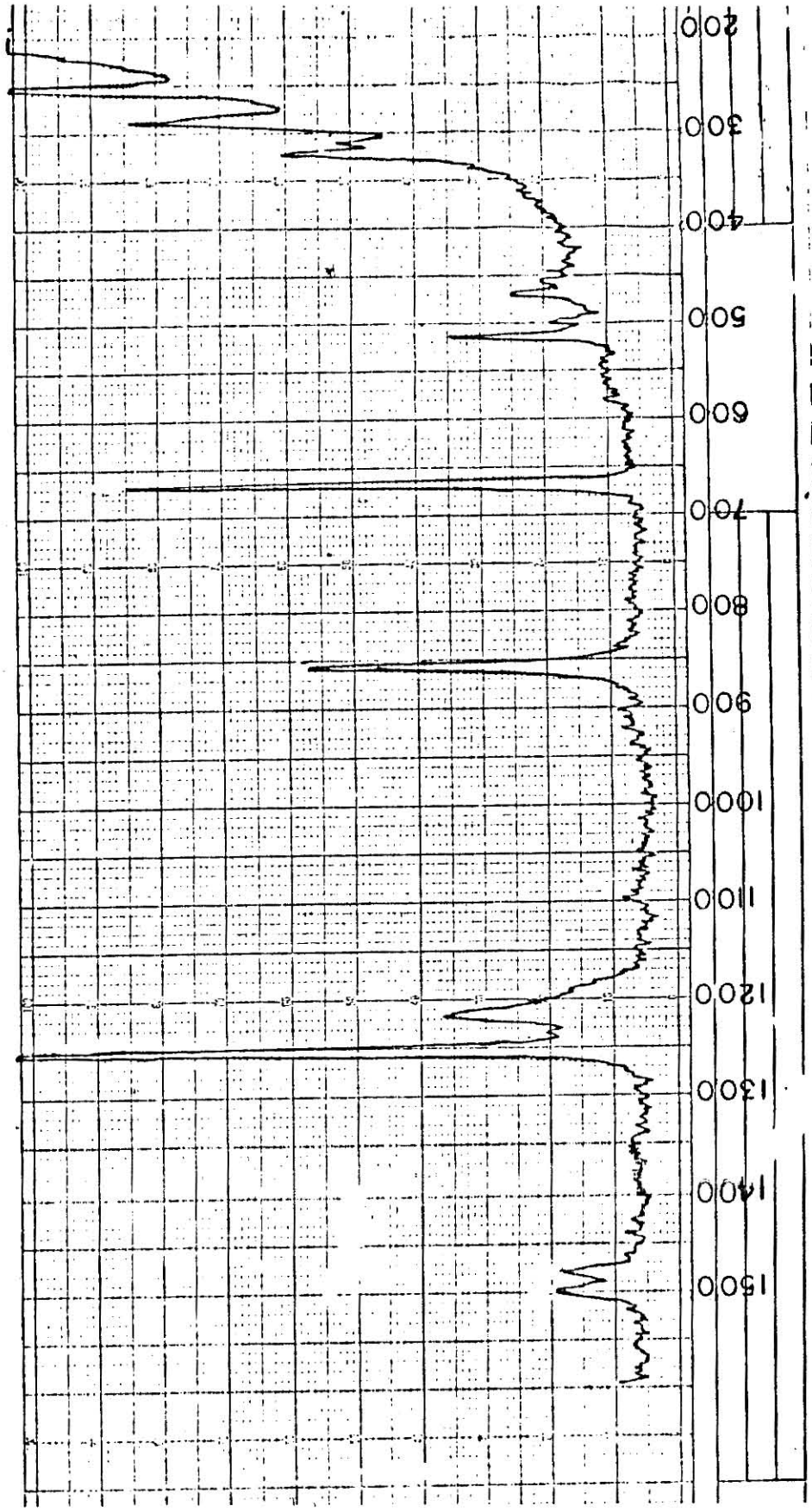
$ClN(SO_2F)_2$

Explanation of Figure A-7:

Raman spectrum of $FXeN(SO_2F)_2$. The gain has been adjusted to allow recording of the portion closer to the Rayleigh line. Notice how weak the band at 1222 seems by comparison with the peak at 504 cm^{-1}. The shoulder at 521 cm^{-1} is a laser line.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$[NiSO_2F]_2$

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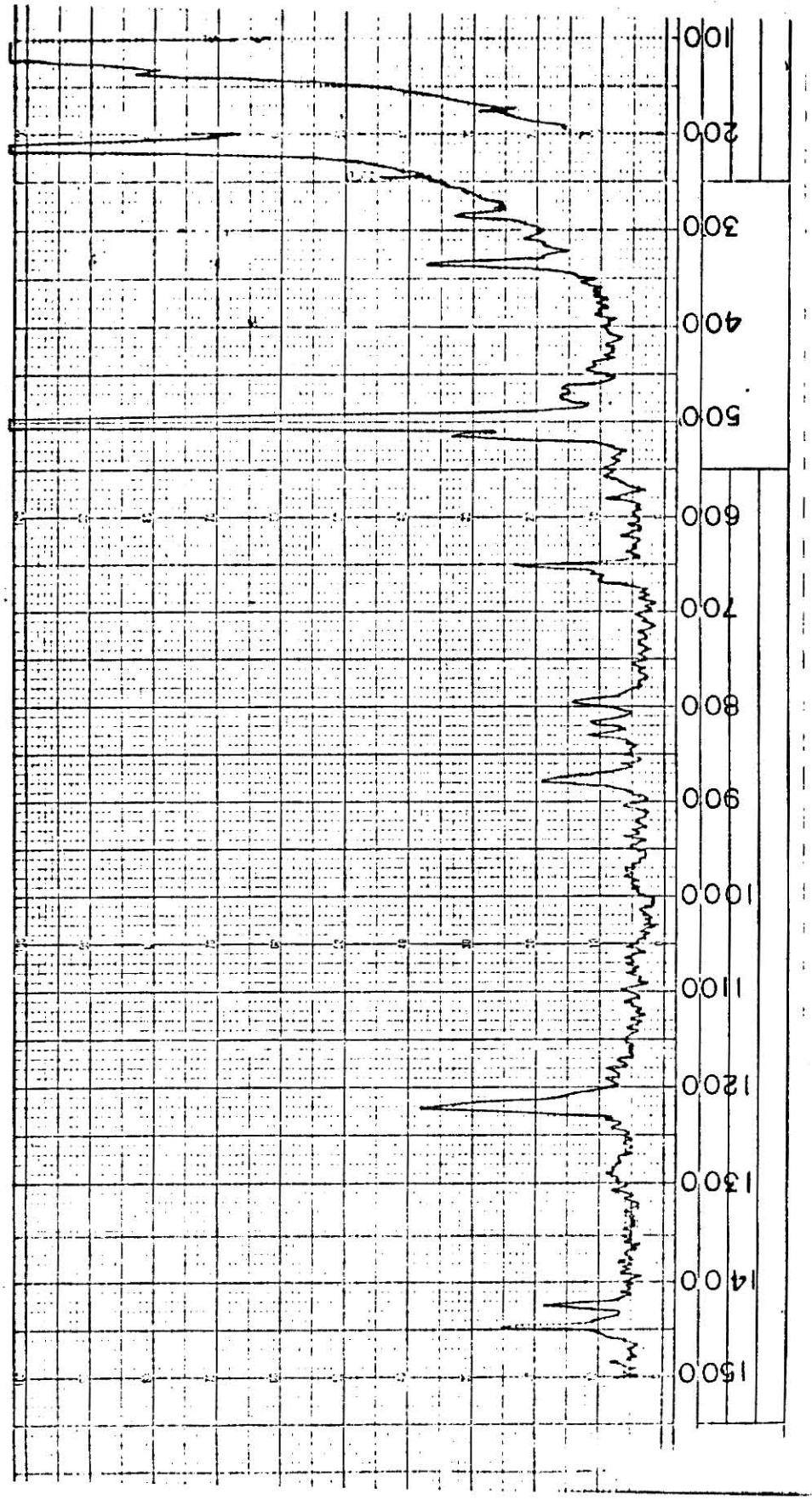
Finally, I would like to thank my wife, Babe, for her continued patience and support during this time.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$FXeNISO_2F_2$

SOME REACTIONS OF THE BINARY FLUORIDES OF XENON: THE SYNTHESIS OF THE FIRST XENON-NITROGEN BOND

by

ROBERT DALE LEBLOND
B.S., Michigan State University, 1969

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

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1974

The binary fluorides of xenon, which can be prepared directly from the elements, have been used as the starting materials for synthesizing the known salts of xenon. Since xenon dichloride is not stable under ambient temperatures while the difluoride is, it appears that any substituted ligands must have high group electronegativity. This concept, plus the fact that the salts are produced by metathesis reactions, have caused the number of known salts to be small.

There are certain techniques and special equipment necessary to do research in the area of rare gas compounds. For these reasons, a brief discussion of these problems is included in the introductory material.

Until now, the compounds of xenon have all contained xenon bonded to oxygen or fluorine. In addition to a number of unsuccessful attempts to synthesize new xenon compounds, this paper is concerned with the synthesis and characterization of the first compound to contain a xenon-nitrogen bond, $FXeN(SO_2F)_2$. Synthetic details for producing this new compound are related and a discussion is given to the spectroscopic data obtained. Characterization of this salt includes use of fluorine nmr, which is explained, and laser Raman spectroscopy. The Raman spectrum is compared with similar $N(SO_2F)_2$ compounds, both ionic and covalent in nature, and also compared with compounds also related spectroscopicly. From these spectra tentative band assign-

ments are given for the imidodisulfuryl compounds. The positions of certain of these peaks imply that this new compound is perhaps the most covalent xenon (II) species known.