the absence and presence of additives (traces of F^-, H_2O, Lewis acids, etc.).

A considerable effort was directed toward the synthesis of compounds containing F_2NO^+ with oxidizing anions such as ClO_4^-, ClO_3^-, NO_3^-, etc., since such compounds would be expected to be highly energetic solid oxidizers. The general approach involved metathesis as exemplified by the generalized equation

$$F_2NO^+A^- + M^+ClO_4^- \xrightarrow{\text{solvent}} F_2NO^+ClO_4^- + M^+A^-$$

where A^- represents a Lewis acid ligand (AsF_6^-, SbF_6^-, or BF_4^-) and M^+ represents an alkali metal or other salt form of the desired oxidizing anion (usually perchlorate as shown). Various solvent media, such as HF, IF_5, or BrF_5, were employed.

These attempts were generally unsuccessful in that no compounds of the type $F_2NO^+ClO_4^-$ could be isolated from any of the reaction mixtures. Instead, when perchlorates were involved, the reaction products were identified as $FClO_3$ and FNO_2, possibly from decomposition of the desired compound or other interaction of the ions F_2NO^+ and ClO_4^- (*i.e.*, $F_2NO^+ + ClO_4^- \rightarrow FClO_3 + FNO_2$).

Similarly, combination of solutions containing F_2NO^+ and ClO_3^- or SO_3F^-, led to the formation of $FClO_2$ and SO_2F_2, respectively, along with FNO_2 in both cases.

In the earlier phases of the study, the reactions were thought to proceed *via* anion solvolysis, since it has been observed in separate experiments that ClO_4^- and ClO_3^- salts, for example, would yield $FClO_3$ and $FClO_2$, respectively, upon interaction with HF, IF_5, or BrF_5 in the presence of strong Lewis acids.[11] However, no SO_2F_2 could be formed from SO_3F^- in this manner, nor did ClO_4^- yield any $FClO_3$ when treated with BF_3 in HF, yet under similar conditions SO_2F_2 was formed by the reaction of F_2NO^+ and SO_3F^-, and $FClO_3$ was formed by the interaction of $F_2NO^+BF_4^-$ and ClO_4^-, in HF.

Analogous reaction products were observed in attempted metathesis reactions of $N_2F^+AsF_6^-$ with ClO_4^- and SO_3F^- in HF medium, namely, $FClO_3$ and SO_2F_2, respectively, along with N_2O.[12]

Acknowledgment.—This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contract No. DA-30-069-ORD-2638.

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The Difluoronitronium Cation, NF_2O^+

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Nitrogen oxide trifluoride forms white crystalline 1:1 adducts with the Lewis acids BF_3, AsF_5, and SbF_5. In addition to the 1:1 complex, BF_3 can form at $-126°$ a 2:1 adduct with NF_3O. The thermal stability of these complexes decreases in the order: $NF_3O\cdot SbF_5 > NF_3O\cdot AsF_5 > NF_3O\cdot BF_3 > NF_3O\cdot 2BF_3$. The dissociation pressure–temperature relation has been measured and thermodynamic data are calculated for the process $NF_3O\cdot BF_3(s) = NF_3O(g) + BF_3(g)$. Hydrolysis of $NF_3O\cdot AsF_5$ results in the formation of $NO_2^+AsF_6^-$. Infrared and Raman measurements show that $NF_3O\cdot SbF_5$, $NF_3O\cdot AsF_5$, $NF_3O\cdot BF_3$, and $NF_3O\cdot 2BF_3$ have the ionic structures $NF_2O^+SbF_6^-$, $NF_2O^+AsF_6^-$, $NF_2O^+BF_4^-$, and $NF_2O^+B_2F_7^-$, respectively. The NF_2O^+ cation (point group C_{2v}) has a structure similar to that of isoelectronic CF_2O. All fundamentals have been observed for NF_2O^+.

Introduction

Several independent disclosures have been made on the synthesis, properties, and chemistry of NF_3O.[1-5] In addition, one paper[6] dealing with the infrared spectrum and thermodynamic properties of NF_3O has been published.

The capability of NF_3O to form adducts with strong Lewis acids has been recognized by all three groups[1-6] investigating this compound. Thus, Fox and coworkers[4] reported the existence of 1:1 adducts between NF_3O and AsF_5 or SbF_5. They suggested the ionic structures $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$, respectively, for these adducts based on ^{19}F nmr and incomplete infrared data. Similarly, Bartlett and coworkers[5] reported the existence of the complex $NF_3O\cdot AsF_5$. They also proposed the ionic structure $NF_2O^+AsF_6^-$ based on incomplete infrared data. Some of the chemistry of the $NF_3O\cdot BF_3$ adduct has been developed in showing that this adduct can add at low temperature

[1] W. Maya (Rocketdyne), U. S. Patent 3,320,147 (1967).

[2] D. Pilipovich (Rocketdyne), U. S. Patent 3,346,652 (1967).

[3] W. B. Fox and J. S. MacKenzie, U. S. Patent 3,323,866 (1967).

[4] W. B. Fox, J. S. MacKenzie, N. Vanderkooi, B. Sukornick, C. A. Wamser, J. R. Holmes, R. E. Eibeck, and B. B. Stewart, *J. Am. Chem. Soc.*, **88**, 2604 (1966).

[5] N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, 213 (1966).

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the elements of fluorine to olefinic double bonds.[2,7] In this paper we wish to report some of the data obtained for these NF_3O adducts by the Rocketdyne group. These data include the characterization of the adducts and the complete infrared spectrum of the NF_2O^+ cation.

Experimental Section

Materials and Apparatus.—The materials used in this work were manipulated in a well-seasoned 304 stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke Inc., 4251 F4Y). Arsenic pentafluoride (from Ozark-Mahoning Co.), BF_3 (from The Matheson Co., Inc.), and NF_3O (prepared at Rocketdyne by glow discharge[1] of a mixture of N_2, O_2, and F_2) were purified by fractional condensation. Antimony pentafluoride (from Ozark-Mahoning Co.) was purified by vacuum distillation at ambient temperature. Hydrogen fluoride (from The Matheson Co., Inc.) was purified by removing all volatiles at −196° and exposing the residue at ambient temperature for 12 hr to a fluorine pressure of 2 atm, followed by removal of all volatiles at −196° *in vacuo*. The purities of the starting materials were determined by measurements of their vapor pressures and infrared spectra. Owing to their hygroscopic nature, materials were handled outside the vacuum system in the dry nitrogen atmosphere of a glove box.

For the dissociation pressure measurements the $NF_2O^+BF_4^-$ complex was prepared in a Teflon FEP U trap being directly connected to a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Pressures were read with a cathetometer (to an accuracy of ±0.2 mm) and the temperature of the cooling bath was determined with a copper–constantan thermocouple. To be certain that an equilibrium existed at each temperature reading, a sample of the gas above the solid complex was pumped off and a constant pressure was reestablished. True equilibrium existed at a given temperature if the pressures, before and after the pumping off procedure, were identical. Equilibrium pressures were always approached from below a given temperature. The best fit of log P *vs.* T^{-1} (in °K) was obtained by the method of least squares.

The infrared spectra were recorded on a Beckman Model IR-7 with CsI interchange and a Perkin-Elmer Model 337 spectrophotometer in the ranges 700–200 and 4000–400 cm^{-1}, respectively. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The low-temperature spectra of $NF_3O \cdot xAsF_5$ and $NF_3O \cdot xBF_3$ were taken by preparing the complexes on the internal window (cooled with liquid nitrogen) of an infrared cell. The body of this cell was made from Pyrex glass, all windows being AgCl. Screw-cap metal cells with AgCl windows and Teflon FEP gaskets were used for obtaining the spectrum of $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$ as a dry powder at ambient temperature.

The Raman spectrum of solid $NF_2O^+AsF_6^-$ was recorded using a Spectra-Physics Model 125 laser as a source of ∼80 mW of exciting light at 6328 Å and a Baird Type 1310 interference filter (45-Å half-width). The scattered light was analyzed with a Spex Model 1400 double monochromator, a photomultiplier cooled to ∼−25°, and a dc ammeter. Pyrex-glass tubes (7-mm o.d.) with a hollow inside glass cone for variable sample thicknesses were used as sample containers.

Debye–Scherrer powder patterns were taken using a Phillips Norelco instrument, Type No. 12046, with copper Kα radiation and a nickel filter. Samples were sealed in Lindeman glass tubes (∼0.3- and ∼0.5-mm o.d.).

Preparation of $NF_2O^+AsF_6^-$.—In a typical experiment NF_3O (64.2 mmol) and AsF_5 (42.7 mmol) were combined at −196° in a U trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 760 mm, the mixture was cooled again to −196°. This procedure was repeated several times until the reaction was complete. Unreacted NF_3O (21.4 mmol) was removed by distillation at 0°. Therefore, AsF_5 (42.7 mmol) had reacted with NF_3O (42.8 mmol) in a mole ratio of 1:1.002, producing the complex $NF_2O^+AsF_6^-$.

Preparation of $NF_2O^+SbF_6^-$.—Antimony pentafluoride (93.6 mmol) was transferred in the glove box to a Kel-F trap containing a Teflon-coated, magnetic stirring bar. The trap was connected to the vacuum line and 30 ml of liquid HF was condensed into the trap at −196°. The contents of the trap were warmed to ambient temperature and stirred until all of the SbF_5 had dissolved in the HF. This trap was connected to a second trap by means of flexible Teflon tubing. The second trap contained liquid NF_3O (171 mmol) at −95°. The trap containing the SbF_5–HF solution was inverted and the SbF_5–HF solution was slowly added to the liquid NF_3O at −95° with shaking. The mixture was kept for 16 hr at −78°. Subsequently, the HF solvent and excess NF_3O were removed by vacuum distillation at 25°. Weighing of the trap, empty and after complex formation, indicated an NF_3O to SbF_5 combining ratio of 1:1.09.

Preparation of $NF_2O^+BF_4^-$ and $NF_2O^+B_2F_7^-$.—In a typical experiment, NF_3O (51.4 mmol) and BF_3 (12.8 mmol) were combined at −196° in a U trap. The mixture was allowed to warm up slowly until melting and reaction occurred. When the pressure inside the trap reached 1000 mm, the mixture was cooled again to −196°. This procedure was repeated several times until the reaction was complete. Unreacted NF_3O (45.0 mmol) was recovered by distillation at −126° and identified by its infrared spectrum. Therefore, BF_3 (12.8 mmol) had reacted with NF_3O (6.4 mmol) in a mole ratio of 2:1.00, producing the complex $NF_2O^+B_2F_7^-$.

Warming of the solid to −94.5° resulted in a pressure of about 180 mm. Removal of the volatiles at −94.5° yielded 6.4 mmol of BF_3, contaminated by a very small amount of NF_3O. Hence, NF_3O and BF_3 had combined in a 1:1 mole ratio, producing the complex $NF_2O^+BF_4^-$.

Similarly, synthesis of the complex $NF_2O^+B_2F_7^-$ was achieved when an excess of BF_3 (51.4 mmol) was combined with NF_3O (6.4 mmol) at −196°. Removal of unreacted BF_3 was very slow at −126°. Complete removal of the excess BF_3 could be achieved at −112°; however, at this temperature a small amount of NF_3O was also transferred. The amount of volatiles (38.7 mmol) was measured by keeping the trap (in which the volatiles had been collected) at −78° during expansion of the gas into a measured volume and by correcting the observed pressure for the known dissociation pressure of $NF_2O^+BF_4^-$ at −78° (see Results). Infrared measurements on the gas showed that it contained less than 0.1% of NF_3O. Hence, NF_3O (6.4 mmol) had combined with BF_3 (12.7 mmol) in a mole ratio of 1:1.98, producing the complex $NF_2O^+B_2F_7^-$.

Infrared measurements showed that the gas phase in equilibrium with solid $NF_2O^+BF_4^-$ at temperatures −78.6 to −54.1° consisted of NF_3O and BF_3 in a 1:1 mole ratio. (Intensities of NF_3O and BF_3 peaks always corresponded to those of an equimolar mixture.)

Hydrolysis of $NF_2O^+AsF_6^-$.—A thin film of solid $NF_2O^+AsF_6^-$ condensed on the internal, cold window of the low-temperature infrared cell was exposed briefly to atmospheric moisture. The sample was allowed to warm up to ambient temperature and after 4 hr all volatiles were removed by pumping. The infrared spectrum of the white, solid residue left on the internal window was identical with that of a sample of $NO_2^+AsF_6^-$.

Results

Syntheses.—Nitrogen oxide trifluoride and AsF_5 when mixed, produce the 1:1 complex $NF_2O^+AsF_6^-$, a white crystalline solid. Quantitative synthesis clearly indicates a 1:1 combining ratio. Similarly, the addition of SbF_5 (dissolved in HF) to an excess of liquid

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[7] The chemistry of NF_3O adducts is rather interesting. Reactions in addition to the cited fluorination are known and are the subject of a forthcoming paper by D. Pilipovich, R. D. Wilson, and W. Maya.

NF_3O at −95° resulted in the 1:1 complex, $NF_2O^+SbF_6^-$. The combination of NF_3O with BF_3 at −126° produced the 1:2 complex $NF_2O^+B_2F_7^-$. Quantitative synthesis clearly indicates a 1:2 combining ratio. This ratio was found independent of using either NF_3O or BF_3 in excess. The 1:2 complex $NF_2O^+B_2F_7^-$ loses 1 mol of BF_3 at −95° to produce the 1:1 complex $NF_2O^+BF_4^-$. Quantitative synthesis and infrared measurements on the gas phase above the solid complex support the 1:1 combining ratio.

Thermochemical Properties.—The complex $NF_2O^+SbF_6^-$ has no detectable dissociation pressure at 25°. The corresponding arsenic compound $NF_2O^+AsF_6^-$ has no detectable dissociation pressure at 0°, but exhibits a dissociation pressure of 4 mm at 22.1°. The 1:2 adduct $NF_3O \cdot 2BF_3$ has no detectable dissociation pressure at −126°, but shows a dissociation pressure of about 180 mm at −94.5°. For the 1:1 adduct $NF_2O^+BF_4^-$ the following dissociation pressure data were observed [temperature (°C), pressure (mm)]: −93.90, 1.8; −78.63, 12.5; −73.13, 24.0; −64.28, 63.0; −57.39, 123.5; −54.06, 166.0. A plot of log P_{mm} *vs.* T^{-1} (in °K) for the heterogeneous equilibrium $NF_2O^+BF_4^-(s) = NF_3O(g) + BF_3(g)$ is a straight line. The equation $\log P_{\text{mm}} = 11.1025 - (1944.88/T)$ represents these dissociation data in the temperature range −93.9 to −54.1°. By extrapolation, a dissociation pressure of 1 atm was obtained at −36.61°. At 25° the dissociation pressure amounts to 37,680 mm. From the slope of the log P_{mm} *vs.* T^{-1} curve $\Delta H_d{}^{\circ}$ [8] = 17.80 kcal mol^{-1} was found. From $\Delta F^{\circ}_T = -RT \ln Kp$ (atm), a free energy change, $\Delta F^{\circ}_{298} = 3.804$ kcal mol^{-1}, and from $\Delta S^{\circ}_T = (\Delta H^{\circ} - \Delta F^{\circ}_T)T^{-1}$, an entropy change, $\Delta S^{\circ}_{298} = 72.45$ cal deg^{-1} mol^{-1}, were found for the dissociation process at 25°. A heat of formation of $NF_2O^+BF_4^-(s)$, $\Delta H_f{}^{\circ}{}_{298} = 323$ kcal mol^{-1}, was calculated based upon $\Delta H_f{}^{\circ}{}_{298}[NF_3O(g)]^9 = -33$ kcal mol^{-1} and $\Delta H_f{}^{\circ}{}_{298}[BF_3(g)]^{10} = -271.6$ kcal mol^{-1}.

Hydrolysis of $NF_2O^+AsF_6^-$.—Careful hydrolysis of $NF_2O^+AsF_6^-$ resulted in the formation of a white solid residue. The infrared spectrum of the solid showed four absorptions at 2360 (ms), 697 (vs), 598 (ms), and 400 (m) cm^{-1}, respectively. When solid $NF_2O^+AsF_6^-$ is added to excess water, the hydrolysis proceeds violently.

X-Ray Powder Data.—Debye–Scherrer powder patterns were obtained for $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$. The patterns of both compounds were too complex to allow determination of the crystal system and lattice parameters. The pattern obtained for $NF_2O^+AsF_6^-$ possibly contained some of the stronger lines characteristic for $NO_2{}^+AsF_6$.[11]

Vibrational Spectra.—Figures 1 and 2 show the infrared spectrum of the solids $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$, respectively. These spectra were recorded using the dry-powder technique. The observed frequencies are listed in Table I and are compared with those reported for isoelectronic CF_2O.[12,13] Figure 3 shows the low-temperature infrared spectrum of solid $NF_3O \cdot xAsF_5$. The latter spectrum was obtained by admitting at 25° an equimolar amount of gaseous NF_3O and AsF_5 at a total pressure of about 4 mm into the cell. Subsequently, cooling of the internal window by liquid nitrogen was started. As soon as the first visible, solid deposit had formed on the internal window, pumping on the sample was started to avoid deposition of unreacted starting materials. The absence of solid AsF_5 in the spectrum can be readily established by comparison with the spectrum previously reported[14] for this compound. Below 800 cm^{-1} a remarkable frequency shift and appearance of additional bands were observed in the spectrum (shown in Figure 3) when compared to that of Figure 1. Warming the sample (deposited on the internal cold window) to about 10° under pumping followed by cooling resulted in spectra resembling closely that shown in Figure 1. Low-temperature spectra were

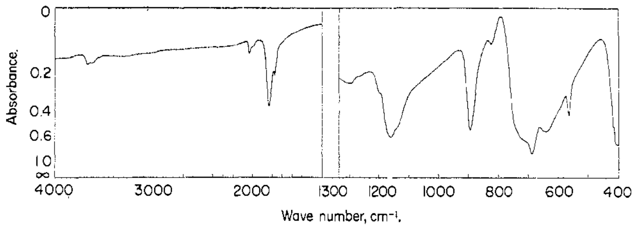

Figure 1.—Infrared spectrum of $NF_2O^+AsF_6^-$ as a dry powder.

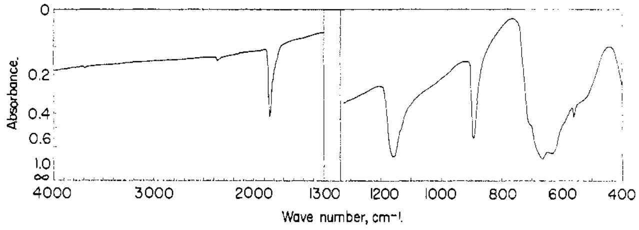

Figure 2.—Infrared spectrum of $NF_2O^+SbF_6^-$ as a dry powder.

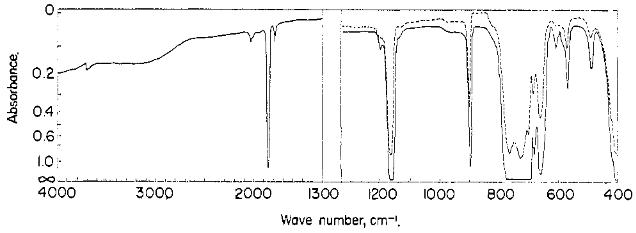

Figure 3.—Low-temperature infrared spectra of $NF_3O \cdot xAsF_5$ at two different concentrations.

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[8] It is not strictly correct to infer that the measured heat of reaction for the dissociation process equals the thermodynamic heat of dissociation. This would only be appropriate if the complex were in the gas phase or if the heat of sublimation of the complex were zero. However, for convenience, $\Delta H_d{}^{\circ}$ will be used throughout the text to mean the heat of reaction of a complete dissociation process of the type: complex(s) = gas + gas.

[9] J. Q. Weber of our laboratories estimated this value by comparison with bond energies of known N–F and N–O–F containing compounds.

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Table I

Vibrational Spectra of $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$ and Their Assignments Compared with Those of CF_2O

Obsd freq, cm^{-1}				Assignment (point group)	
	$NF_2O^+AsF_6^-$				
CF_2O Infrared	Infrared	Raman	$NF_2O^+SbF_6^-$ Infrared	NF_2O^+ or CF_2O (C_{2v})	AsF_6^- or SbF_6^- (O_h)
3851 w	3706 w		3702 vw	$2\nu_2$ (A_1)	
2195 w	2055 w			$\nu_1 + \nu_4$ (B_1)	
1928 ms	1858 ms	1863 (0+)	1862 ms	$\nu_{x=0}$, ν_2 (A_1)	
1907 w, sh	1791 w		1790 w, sh	$2\nu_1$ (A_1)	
	1300 w, br				$\nu_2 + \nu_3$ ($F_{1u} + F_{2u}$)
	1201 w				
1249 vs	1162 s	1169 (0+)	1163 s	$\nu_{asym\ XF_2}$, ν_4 (B_1)	
	1135 w, sh		1135 w, sh	$2\nu_5$ (A_1)	
965 s	898 ms	902 (4)	897 ms	ν_1 (A_1)	
	827 w				$\nu_2 + \nu_6$ ($F_{1u} + F_{2u}$)
774 ms	720 ms, sh		715 m, sh	$\delta_{out\ of\ pl}$, ν_6 (B_2)	
	692 vs		673 vs		ν_3 (F_{1u})
		689 (10)			ν_1 (A_{1g})
626 m	645 m	634 (1)	647 m, sh	$\delta_{asym\ in\ pl}$, ν_5 (B_1)	
		584 (2)			ν_2 (E_g)
584 m	569 mw, br	573 (2)	569 mw	$\delta_{sym\ in\ pl}$, ν_3 (A_1)	
	392 m				ν_4 (F_{1u})
		373 (2)			ν_5 (F_{2g})

also recorded on solid $NF_3O \cdot xBF_3$ samples (see Figure 4). In addition to bands characteristic for NF_2O^+ and $B_2F_7^-$,[15,16] those characteristic for solid BF_3[17] were always present. Attempts to remove the excess BF_3 resulted in the simultaneous removal of the complex itself. The spectrum of a typical mixture showed absorptions at the following wave numbers (cm^{-1}): 1855 m, 1420 s, br, 1340 mw, 1220 m, br, 1165 vs, 1150–950 s, br, 899 ms, 884 w, 836 ms, 735 m, br, 650 m, sh, 630 s, br, 570 m, 551 w, 528 mw, 520 mw, 472 m, 455 w. Figure 5 shows the Raman spectrum of solid $NF_2O^+AsF_6^-$. The observed frequencies are listed in Table I.

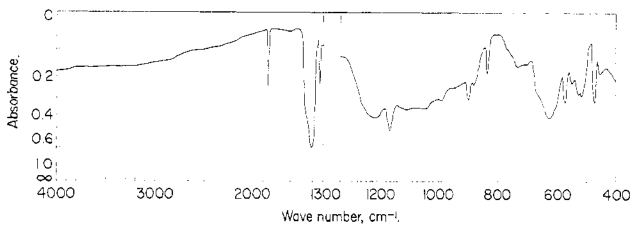

Figure 4.—Low-temperature infrared spectrum of $NF_3O \cdot xBF_3$.

Discussion

Synthesis and Properties. The preparation of $NF_2O^+AsF_6^-$ presents no difficulties since the two starting materials, NF_3O and AsF_5, have a common liquid phase. In the case of the corresponding SbF_6^- salt, HF was chosen as a solvent owing to the low boiling point (−85°) of NF_3O[2] and high melting point (7°) of SbF_5. In this manner NF_3O can always be kept in excess and the formation of undesirable polymeric anions,[18,19] such as $Sb_2F_{11}^-$, can be avoided. For the synthesis of $NF_2O^+B_2F_7^-$ the use of excess NF_3O is advisable, since excess NF_3O can be removed from the solid adduct more easily than excess BF_3. The fact that only the 1:2 adduct is formed at −126°, even if a large excess of NF_3O is used in its preparation, is unexpected, since at −95° the 1:1 adduct is more stable than the 1:2 adduct.

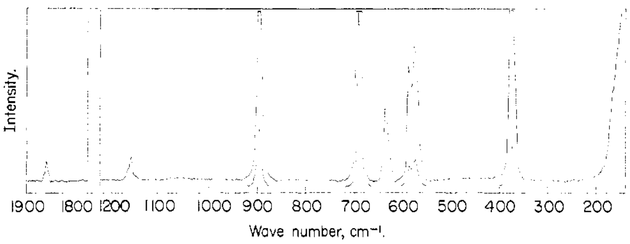

Figure 5.—Raman spectrum of solid $NF_2O^+AsF_6^-$.

The NF_3O–Lewis acid adducts are white, crystalline hygroscopic solids. Their thermal stability decreases with decreasing strength of the Lewis acid. The SbF_5 and the AsF_5 salt are quite stable and have been stored in a Teflon FEP container for several months without noticeable decomposition. They act as oxidizers and react violently with water. With a limited amount of water partial hydrolysis takes place according to

$$NF_2O^+AsF_6^- + H_2O \longrightarrow NO_2^+AsF_6^- + 2HF$$

The heat of dissociation,[8] 17.80 kcal mol^{-1}, obtained for $NF_2O^+BF_4^-$ is of the same order of magnitude as the values obtained for similar ionic complexes such as $ClF_2^+BF_4^-$ [20] (23.6 kcal mol^{-1}) and $NO^+ClF_2^-$ [21] (15.5 kcal mol^{-1}). Unfortunately, only an estimated value[9] was available for the heat of formation of NF_3O. Therefore, the $\Delta H_f°_{298}$ value of $NF_2O^+BF_4^-$ contains the possible error inherent in the estimated value of $\Delta H_f°_{298}$ of $NF_3O(g)$ used in our calculation.

Vibrational Spectra.—The 1:1 adducts between NF_3O and Lewis acids could be either fluorine- or oxygen-bridged coordination complexes or be ionic. The simplicity of the observed infrared spectra, the occurrence of the bands characteristic for AsF_6^- and SbF_6^-,

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(17) D. A. Dows, *J. Chem. Phys.*, **31**, 1637 (1959).
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and the strong frequency shift of the N–O stretching vibration (when compared to free NF_3O) to higher wave numbers suggest that the 1:1 adducts are ionic. Consequently, the NF_3O part of the adduct should be present in the form of NF_2O^+. Table I lists the observed frequencies for $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$ together with their assignments. The vibrations belonging to AsF_6^- and SbF_6^- will be discussed first, since they can be assigned more easily by comparison with similar complexes containing these anions. An octahedral anion of the type XF_6^- has O_h symmetry. The six normal modes of vibration are classified as $A_{1g} + E_g + 2\ F_{1u} + F_{2g} + F_{2u}$. Of these, only the two F_{1u} modes will be infrared active, while only the A_{1g}, E_g, and F_{2g} modes will be Raman active, provided that the selection rules are valid and that the octahedron is not distorted. The remaining F_{2u} mode is inactive in both the infrared and Raman spectra. By comparison with the vibrational spectra of $K^+AsF_6^-$,[22] $NF_4^+AsF_6^-$,[23] $ClF_2^+AsF_6^-$,[24] $Na^+SbF_6^-$,[25] $Li^+SbF_6^-$,[26] and $ClF_4^+SbF_6^-$,[27] the normal modes belonging to AsF_6^- and SbF_6^-, respectively, can be assigned without difficulty, the observed frequencies and intensities being in good agreement.

The remaining bands observed in the spectra of both $NF_2O^+AsF_6^-$ and $NF_2O^+SbF_6^-$ complexes should be due to the NF_2O^+ cation. This cation is isoelectronic with CF_2O and, hence, can be expected to have a similar structure. Comparison of the spectrum of NF_2O^+ with that previously reported[12,13] for CF_2O (see Table I) shows that both the frequencies and relative intensities are very similar. Therefore, the assignments for NF_2O^+ were made for point group C_{2v}. All six fundamentals (classified as $3\ A_1 + 2\ B_1 + B_2$) should be infrared and Raman active and are assigned in analogy to those of CF_2O. The fact that ν_6 (B_2) was not observed in the Raman spectrum is not surprising and is due to its low relative intensity. In planar XY_3 the corresponding out-of-plane deformation mode is Raman inactive.

The low-temperature infrared spectrum of $NF_3O \cdot xAsF_5$ (see Figure 3) shows practically no frequency shifts for ν_1, ν_2, ν_3, and ν_4 of NF_2O^+ when compared to that obtained for the complex as a dry powder at 25° (see Figure 1). The bands at 664 and 729 cm^{-1} in the low-temperature spectrum agree reasonably well with the values assigned to ν_5 and ν_6, respectively, of NF_2O^+ in the dry powder spectrum (see Table I). However, the band, characteristic for ν_3 (F_{1u}) of AsF_6^- has a relatively low intensity in the low-temperature spectrum. Hence, it seems likely that the additional bands observed in the range 600–770 cm^{-1} and possibly also the band at 491 cm^{-1} are As–F vibrations and belong to polymeric anions, such as $As_2F_{11}^-$. This assignment is supported by the fact that warming of the sample (deposited on the cold window) close to ambient temperature under pumping, followed by cooling, resulted in the removal of AsF_5 and in a spectrum resembling closely that of Figure 1. Similarly, in the low-temperature infrared spectrum of the $NF_3O \cdot xBF_3$ complex the bands characteristic for NF_2O^+ (1855 (ν_2), 1165 (ν_4), 899 (ν_1), 735 (ν_6), 650 (ν_5), and 570 cm^{-1} (ν_3)) were present, in addition to those characteristic for $B_2F_7^-$ [15,16] (1220, 1150–950, and 836 cm^{-1}). The remaining bands can be assigned to solid BF_3[17] (1420, 1340, 630, and 472 cm^{-1}). Attempts to remove the solid BF_3 from the cold AgCl window without removing the complex itself were unsuccessful owing to the difficulties to control and maintain the temperature of the cold window closely. This is not surprising since in the synthesis of $NF_2O^+B_2F_7^-$ (see above) the same difficulty was encountered. Other structures, theoretically possible for a 1:2 complex between NF_3O and BF_3, such as $[BF_3 \leftarrow ONF_2]^+[BF_4]^-$ (NF_2O^+ being isoelectronic with CF_2O might be expected to exhibit donor properties toward Lewis acids similar to those of a carbonyl group[28]) can be ruled out based on the spectra. For a structure such as $[BF_3 \leftarrow ONF_2]^+[BF_4]^-$ one would expect to observe the bands characteristic for BF_4^- [24,29–31] and a strong frequency decrease of the N=O stretching vibration when compared to the free NF_2O^+ cation.

The infrared data reported in this paper agree well with those previously reported for some of the bands of $NF_2O^+SbF_6^-$ [4] and $NF_2O^+AsF_6^-$.[4,5] Furthermore, they confirm the ionic structures previously suggested[4,5] for these adducts.

Assignment of the four bands in the spectrum obtained for the hydrolysis product of $NF_2O^+AsF_6^-$ presents no difficulties. The bands at 697 and 400 cm^{-1} are assigned to ν_3 (F_{1u}) and ν_4 (F_{1u}), respectively, of AsF_6^-, whereas the bands at 2360 and 598 cm^{-1} are characteristic for ν_3 (Σ_u^+) and ν_2 (π_u), respectively, of NO_2^+.[32,33]

In summary, the vibrational spectra of the 1:1 adducts between NF_3O and Lewis acids are consistent with ionic structures containing the NF_2O^+ cation. All six fundamentals expected for NF_2O^+ were observed with proper frequencies and intensities. The low-temperature spectra are indicative of ionic structures containing the NF_2O^+ cation and dimeric anions.

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