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Novel Onium Salts. Synthesis and Characterization of the Difluoroammonium Cation, $NH_2F_2^+$

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The syntheses and properties of $NH_2F_2^+SbF_6^-$ and $NH_2F_2^+AsF_6^-$, the first known examples of difluoroammonium salts, are reported. The $NH_2F_2^+$ cation was characterized by ^{19}F and ^1H NMR and vibrational spectroscopy. At room temperature the $NH_2F_2^+$ salts are metastable and undergo spontaneous exothermic decomposition by HF elimination. Attempts were unsuccessful to prepare either NHF_3^+ salts by protonation of NF_3 at temperatures as low as −78° or fluorine-substituted ammonium salts by direct fluorination of $NH_4^+AsF_6^-$ in HF solution in the temperature range −78 to +25°.

Introduction

Recent studies in our laboratory demonstrated that several novel onium salts can be prepared by protonation of less acidic compounds in $HF-MF_5$ (M = Sb, As) solutions. Thus, protonation of H_2O and H_2S produced[1,2] the surprisingly stable $OH_3^+MF_6^-$ and $SH_3^+SbF_6^-$ salts, respectively. In this paper, we report on the protonation of HNF_2 and NF_3.

Whereas salts containing the NH_4^+ ion had been described already in the early part of the fourteenth century,[3] fluorine-substituted salts were unknown until 1965. Disproving earlier theoretical computations[4,5] that NF_4^+ salts should be thermodynamically unstable, these salts were synthesized[6,7] in 1965 and shown to be of high thermal stability. Since then, numerous papers dealing with NF_4^+ salts[8-18] and the thermally unstable NF_3^+ radical cation[17] have appeared. Of the mixed $NH_nF_{4-n}^+$ cations, the NH_3F^+ cation has previously been described,[19,20] but no data on the remaining two members in this series, i.e., $NH_2F_2^+$ and NHF_3^+, have been published. This is not surprising, since from comparison with the highly shock-sensitive HNF_2 molecule and its CsF adduct,[21] one might expect these more highly fluorinated mixed ammonium salts to be very susceptible to HF elimination. The adduct formation of HNF_2 with the Lewis acids BF_3, BCl_3, PF_5, and SO_2 has been studied[22] at −196° by infrared spectroscopy, but no evidence was found for ion formation. The thermal stability of these adducts was rather low with (in some cases irreversible) decomposition occurring at about −80°.

Experimental Section

Caution! Difluoramine is highly explosive[21] and protective shielding should be used during handling operations. The compound was always condensed at −142° and the use of a −196° bath should be avoided.[23] In the course of the present study five explosions of both $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$ in HF solution occurred, when these solutions were kept between −50 and +25° for extended periods of time. However, the appearance of the ruptured Kel-F or Teflon-FEP containers indicated pressure explosions (probably caused by HF elimination with N_2 formation and by the small ullage above the liquid phase) rather than rapid explosive decomposition. The rate of decomposition of these $NH_2F_2^+$ salt solutions varied strongly from sample to sample, indicating catalysis by trace impurities. The exothermic irreversible decomposition of solid $NH_2F_2^+$ salts appeared to proceed without explosion on a millimolar scale, provided the volume of the container was large enough to avoid overpressurization. When working with such solutions in containers with small ullage, we, therefore, recommend removing the volatile decomposition products by quick pumping at −78° every time before handling the sample.

The experimental techniques used in this study have previously been described.[1] Difluoramine was prepared from difluorourea.[24] Nitrogen trifluoride (99.9%, Rocketdyne) and $NH_4^+HF_2^-$ (Braun Chemical Co.) were used without further purification. Difluoramine was handled in a Pyrex, the other reactants in a Monel Teflon-FEP, vacuum system.

Preparation of $NH_2F_2^+AsF_6^-$. In a typical experiment, dry HF (50 mmol) and AsF_5 (1.74 mmol) were combined at −196° in a passivated (with ClF_3) thin-walled Kel-F capillary. The mixture was shortly warmed to room temperature to obtain a homogenous solution. Difluoramine (2.0 mmol) was added to the ampoule at −142°. The mixture was warmed to −78° and a white solid was formed which was completely soluble in the HF solvent at 20°. Unreacted NHF_2 and HF solvent were removed under dynamic vacuum between −78 and 0°, leaving behind 420 mg of a white solid. This weight is in excellent agreement with that (423 mg) expected for 1.74 mmol of $NH_2F_2^+AsF_6^-$.

For the preparation of the NMR samples, an excess of AsF_5 was used and not pumped off to suppress exchange between the cation and the HF solvent.

Decomposition of $NH_2F_2^+AsF_6^-$. A sample of solid $NH_2F_2^+AsF_6^-$, contained in a Teflon-FEP ampoule, was allowed to warm slowly from −78 to +20°. After about 20 min at 20°, the solid started to melt and spontaneously decomposed with gas and heat evolution (*caution*!). The decomposition products were separated by fractional condensation and identified by infrared spectroscopy or mass spectroscopy. The main constituents were AsF_5, HF, and N_2, in addition to some NF_3 and *trans*-N_2F_2.

Preparation of $NH_2F_2^+SbF_6^-$. In a typical experiment, SbF_5 (1.70 mmol) and dry HF (150 mmol) were combined at −196° in a passivated Teflon-FEP ampoule. The mixture was warmed to 25° to obtain a homogenous solution. Difluoramine (2.02 mmol) was added to the ampoule at −142° and the mixture was warmed to −78°. A white solid formed when the starting materials melted. On warm-up toward 0°, the solid completely dissolved in the excess HF. The unreacted NHF_2 and the HF solvent were pumped off between −45 and 0° leaving behind a white solid residue (499 mg). This weight agrees well with that (493 mg) expected for 1.70 mmol of $NH_2F_2^+SbF_6^-$.

Decomposition of $NH_2F_2^+SbF_6^-$. A sample of $NH_2F_2^+SbF_6^-$ (1.70 mmol), when kept at 25° for about 1 hr, underwent spontaneous exothermic decomposition with melting and gas evolution. The decomposition products, volatile at −78°, consisted of N_2 (0.56 mmol) and NF_3 containing a small amount of *trans*-N_2F_2 (0.58 mmol total). The residue (~410 mg; weight calculated for 1.70 mmol of $HF \cdot SbF_5$ 402 mg) was warmed to 25° under dynamic vacuum. A small amount of white solid stable at 25° was obtained which, based on its infrared spectrum, contained some $N_2F_3^+SbF_6^-$.

NF_3–HF–SbF_5 System. To a homogenized (see above) mixture of SbF_5 (1.93 mmol) and HF (150 mmol) in a Teflon-FEP ampoule was added NF_3 (3.52 mmol) at −196°. The mixture was kept at −78° for 16 hr. No evidence for adduct formation between NF_3 and HF–SbF_5 at −78° was detected, and the NF_3 starting material was recovered from the mixture at −78°.

$NH_4^+AsF_6^-$–HF–F_2 System. Ammonium bifluoride (2.79 mmol) was placed in a Teflon-FEP ampoule and 20 ml of liquid anhydrous HF was added at −78°. To the clear solution was added AsF_5 (3.0 mmol) resulting in the formation of white solid $NH_4^+AsF_6^-$. This solid was only sparingly soluble in HF, even at 25°. The ampoule was pressurized with 1 atm of F_2 at −78° and the contents of the ampoule were agitated for 1 hr at −78°. No pressure decrease (expected for F_2 consumption with HF formation) was observed. The ampoule was kept at each of the temperatures −45, −23, 0, and 25° for 1 hr with agitation, but again no F_2 uptake was observed.

Results and Discussion

Synthesis and Properties. The observed material balances show that protonation of NHF_2 in HF–MF_5 (M = As, Sb) solutions proceeds according to

$$NHF_2 + HF + MF_5 \rightarrow NH_2F_2^+MF_6^-$$

The resulting difluoroammonium salts are white crystalline solids. They are stable at −50° but at room temperature tend to undergo spontaneous exothermic decomposition with melting and gas evolution. In our study, the longest time period during which a solid $NH_2F_2^+$ salt could be kept at room temperature without decomposition was about 0.5 hr. The HF solutions of these salts appear to be reasonably stable at room temperature; however, their stability varied strongly from sample to sample indicating some catalytic effect of by-products or impurities. Precautionary measures for handling these compounds are given in the first paragraph of the Experimental Section.

The main products in the decomposition of these $NH_2F_2^+MF_6^-$ salts are N_2, NF_3, and some *trans*-N_2F_2, in addition to the expected HF and MF_5. The fact that *trans*-N_2F_2 shows little tendency to complex with MF_5 under the given reaction conditions, agrees with previous[25] studies. The observation of only small amounts of *trans*-N_2F_2 but approximately equimolar amounts of N_2 and NF_3 as main products indicates the principal decomposition mode

$$3NH_2F_2^+MF_6^- \rightarrow 3MF_5 + 6HF + N_2 + NF_3$$

The formation of small amounts of *trans*-N_2F_2 might indicate that N_2F_2 is an intermediate in the above decomposition mode; however, previous decomposition studies[21] on N_2F_2 gave no evidence for a disproportionation according to

$$3N_2F_2 \rightarrow 2N_2 + 2NF_3$$

This difference in the decomposition products might be due to the exothermicity of the $NH_2F_2^+MF_6^-$ decomposition causing the formation of excited intermediates. The observed instability of $NH_2F_2^+$ salts toward HF elimination is not surprising. Thus, NHF_2 and its CsF adduct are known[21] to decompose explosively.

The stability of the mixed $NH_nF_{4-n}^+$ fluoroammonium cations decreases with decreasing *n*. Thus, NH_3F^+ is relatively stable,[19,20] $NH_2F_2^+$ is of very marginal stability, and no evidence was found in this study for the existence of a $NHF_3^+SbF_6^-$ salt at temperatures as low as −78°. Since the NH_3F^+ and $NH_2F_2^+$ cations are reasonably stable, particularly in HF solution at low temperatures, the direct fluorination of $NH_4^+AsF_6^-$ by F_2 in HF solution was studied over the temperature range −78 to +25°. However, no fluorination of $NH_4^+AsF_6^-$ was observed under these conditions indicating a significant activation energy for this reaction.

Table I. ^1H (δ) and ^{19}F (φ) NMR Shifts[a] (ppm) and HF Spin–Spin Coupling Constant (*J*, Hz) of $NH_2F_2^+$ Compared to Those of Closely Related Species

	NH_4^+ [b]	NH_3F^+ [c]	$NH_2F_2^+$	NF_4^+ [d]	NHF_2 [e]
δ	−6.3	−10.3 d[f]	−14.2 t		−7.2 t
φ		110.8 q	−11.6 t	−213.5	6 d
J_{HF}		44	34		24

[a] Measured for $NH_2F_2^+AsF_6^-$ in HF solution at −40° relative to external TMS and $CFCl_3$, respectively. [b] References 1 and 26. [c] Reference 19. [d] References 10 and 12. [e] Reference 27. [f] Key: d, doublet; t, triplet; q, quartet.

Nuclear Magnetic Resonance Spectra. The ^{19}F and ^1H NMR spectra of $NH_2F_2^+AsF_6^-$ were recorded for HF solutions acidified by AsF_5 to suppress exchange between the cation and the HF solvent. The results are summarized in Table I and compared to the data previously reported for the related species NH_4^+,[1,26] NH_3F^+,[19] NF_4^+,[10,12] and NHF_2.[27] As can be seen, the observed chemical shifts and the hydrogen–fluorine spin–spin coupling constant of $NH_2F_2^+$ are in excellent agreement with those known for the closely related species. Furthermore, the observed multiplicities (1:2:1 triplets) in both the ^1H and the ^{19}F spectra confirm that the species contains two hydrogen and two fluorine atoms. The components of the triplets were relatively broad and their line widths did not significantly decrease with decreasing temperature in the range −30 to −60°. This indicates that the line broadening is due to ^{14}N quadrupole relaxation and not to an exchange process. In addition to the $NH_2F_2^+$ signal, the proton spectrum showed a singlet at δ −8.6 due to HF and the fluorine spectrum exhibited a singlet at φ 173 for rapidly exchanging HF, AsF_6^-, and AsF_5. For a sample of $NH_2F_2^+SbF_6^-$ in unacidified HF, separate signals were observed for the SbF_6^- anion[1,28] and HF at φ 126 and 194.5, respectively.

Vibrational Spectra. The low-temperature infrared and Raman spectra of the solids and the Raman spectra of HF solutions have been recorded for both $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$. The observed spectra are shown in Figures 1 and 2, and the observed frequencies and their assignment are listed in Table II. The assignments were made by comparison with those[29] of isoelectronic CH_2F_2. As can be seen from the Raman spectra of the HF solutions, the $NHF_2 \cdot MF_5$ adducts are ionic and exhibit the bands characteristic for octahedral AsF_6^- [30–32] and SbF_6^-.[31–33] In the solid state, site symmetry and crystal field effects, in addition to distortion due to anion–cation interactions,[1] cause a splitting of many bands.[1,31,33–35] In the absence of crystal structural data, no attempt will be made in the following discussion to analyze thoroughly these solid-state effects. An $NH_2F_2^+$ cation of symmetry C_{2v} (see below) already possesses nine fundamentals, the maximum number expected for a five atomic species. Consequently, the cation bands should be affected only by crystal field effects but not by symmetry lowering. Since the assignment of the anion bands (see Table II) is straightforward, we will discuss only that of the cation bands.

An XH_2F_2 species of symmetry C_{2v} possesses nine fundamentals classified as $4 A_1 + A_2 + 2 B_1 + 2 B_2$. All of these should be active in both the infrared and Raman spectra, except for the A_2 mode which should only be Raman active. The Raman spectrum of $NH_2F_2^+AsF_6^-$ in HF solution (Figure 1, traces C, D, E) readily permits the assignment of the three fundamentals involving mainly motions of the NF_2 group, since the relative Raman intensities of the NH_2 modes are very low. After subtraction of the three anion bands, we are left with three reasonably intense bands at 1064, 1039, and 534 cm^{-1}. Of these, the ones at 1064 and 534 cm^{-1} are polarized and, therefore, represent the symmetric NF_2 stretch and the NF_2 scissoring mode of species A_1, respectively. The remaining depolarized Raman band at 1039 cm^{-1} must then be due to

Table II. Vibrational Spectra of $NH_2F_2^+AsF_6^-$ and $NH_2F_2^+SbF_6^-$ Compared to That of CH_2F_2

	Obsd freq (cm^{-1}) and rel intens[b]								
	$NH_2F_2^+AsF_6^-$			$NH_2F_2^+SbF_6^-$			Assignment (point group)[c]		
	Solid		HF soln	Solid		HF soln			
CH_2F_2[a]	Ir	Ra	Ra	Ir	Ra	Ra	XH_2F_2 (C_{2v})	MF_6^- (O_h)	Approx description of mode
	2963 mw			2980 vw			$2\nu_7$ and		
	2941 mw			2935 w			ν_1 or ν_5 +		
3014	2913 m			2890 mw			lattice modes		
	2885 m			2790 vs			ν_6 (B_1)		$\nu_{as}(XH_2)$
	2836 m			2696 w					
	2784 m								
2948	2657 s			2637 ms			ν_1 (A_1)		$\nu_{sym}(XH_2)$
1508	1557 s			1543 ms			ν_2 (A_1)		$\delta_{sciss}(XH_2)$
1435	1474 s			1487 ms			ν_8 (B_2)		$\delta_{wag}(XH_2)$
1178	1185 vw			1176 vw			ν_7 (B_1)		$\delta_{rock}(XH_2)$
1113	1073 m 1065 m	1073 sh 1062 (4.5)	1064 (2.7) p	1066 m 1055 sh	1062 (2.3) 1052 (1)	1062 m	ν_3 (A_1)		$\nu_{sym}(XF_2)$
1090	1038 s 1020 w	1041 (3.2)	1039 (0.6) dp	1036 s	1037 (1.9)	1039 w	ν_9 (B_2)		$\nu_{as}(XF_2)$
	720 vw 682 ms			705 vw				ν_3 (F_{1u})	$\nu_{as}(MF_6)$
		714 (9.6) 674 (10)	683 (10) p	680 s 652 m 626 ms 610 mw	671 (10) 639 (8.4)	650 vs		ν_1 (A_{1g})	ν_{sym} in phase (MF_6)
	597 m 547 s	569 (4.9)	570 (0.5) dp	602 mw 550 m	566 (1.9) 539 (0.9)			ν_2 (E_g)	ν_{sym} out of phase (MF_6)
528	532 m	533 (3.1)	534 (0.8) p	528 s	524 (1.3)		ν_4 (A_1)		$\delta_{sciss}(XF_2)$
	414 m 391 vs			360 m 280 vs				ν_4 (F_{1u})	$\delta_{as}(MF_6)$
	376 w 369 w	369 (7.0)	366 (1.4) dp		276 (4.9)			ν_5 (F_{2g})	$\delta_{sym}(MF_6)$
	300 s	290 (1.1) br 216 (0+)			238 (0.4) 103 (2.3)				Lattice vibrations or XH· · ·FM str

[a] Reference 29. [b] Uncorrected Raman intensities. [c] Assignments for the anions bands are made for octahedral symmetry, although in the solid state the actual symmetry is obviously lower.

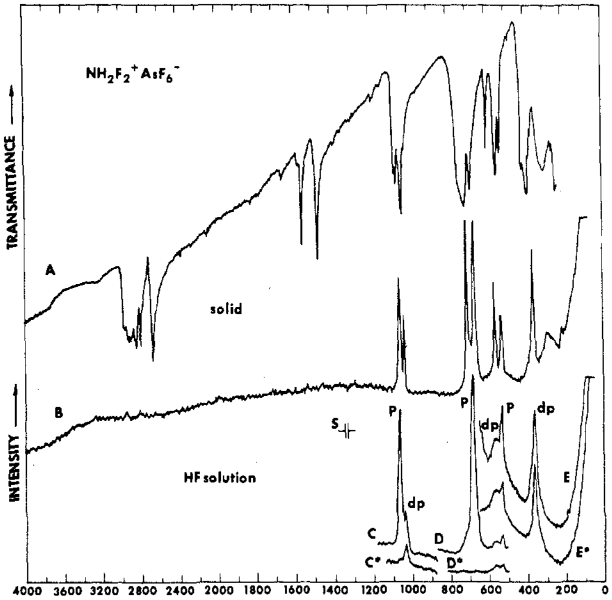

Figure 1. Vibrational spectra of $NH_2F_2^+AsF_6^-$. Trace A: infrared spectrum of the solid as a dry powder between CsI disks, recorded at −196°. Trace B: Raman spectrum of the solid suspended in HF at −70°. Traces C, D, and E: Raman spectrum of an HF solution, recorded at 25° at three different recorder voltages. Traces marked by an asterisk were recorded with the incident polarization perpendicular. P, dp, and S indicate polarized and depolarized bands and spectral slit width, respectively. For the Raman spectra, the 4880-Å exciting line of an Ar ion laser was used, the sample containers being Teflon-FEP or Kel-F tubes.

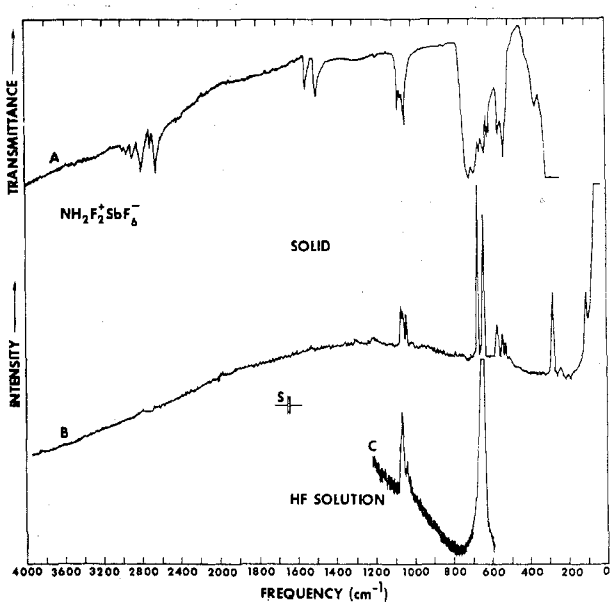

Figure 2. Vibrational spectra of $NH_2F_2^+SbF_6^-$. Trace A: infrared spectrum; bands due to impurities or decomposition products were deleted. Traces B and C: Raman spectra. Recording conditions were identical with those of Figure 1. Trace C is incomplete owing to sudden self-destruction of the sample during the recording of the spectrum.

the antisymmetric NF_2 stretch, ν_9 (B_2).

Identification of the NH_2 modes is possible from the infrared spectra where these modes are expected to be appreciably intense. In the frequency region of the NH_2 stretching modes (2500–3500 cm^{-1}), $NH_2F_2^+SbF_6^-$ exhibits two medium strong bands at 2790 and 2637 cm^{-1} which are assigned, by analogy with CH_2F_2,[29] to the antisymmetric and the symmetric NH_2 stretch, respectively. In addition to these bands, several weaker bands were observed, some of which can be attributed to combination bands (see Table II), probably in Fermi resonance with ν_1 and ν_5. In the infrared spectrum of $NH_2F_2^+AsF_6^-$, the splitting of these bands is even more pronounced. Similar splittings have previously been observed[29] for the CH_2 stretching modes of isoelectronic CH_2F_2. The assignment of these infrared bands to the NH_2 stretching modes is confirmed by the observation of a broad Raman band of very low intensity at about 2800 cm^{-1} for the HF solution of $NH_2F_2^+$-AsF_6^-.

In the region of the NH_2 deformation modes (1700–1100 cm^{-1}) two intense sharp infrared bands were observed at about 1550 and 1480 cm^{-1}, respectively. Based on a comparison of their absolute and relative frequencies with those of CH_2F_2,[29] SiH_2Hal_2,[36] and GeH_2Hal_2,[37] they should represent the scissoring and the wagging deformations, respectively, of the NH_2 group. Comparison of their relative intensities with those of the above dihalohydrides is ambiguous. Whereas in the infrared spectrum of CH_2F_2 the CH_2 scissoring mode is of very low intensity, in the remaining molecules its intensity is similar to that of the wagging mode and very high. Assignment of the 1550- and 1480-cm^{-1} bands of $NH_2F_2^+$ to the NH_2 wagging and the rocking modes, respectively, and of a weak infrared feature at 1655 cm^{-1} to the NH_2 scissoring mode would result in an unreasonably high frequency for the rocking mode and in a too small frequency difference between the wagging and the rocking mode, provided that the NH_2 modes in $NH_2F_2^+$ are not strongly affected by NH···FM bridging between the cations and the anions. Adopting the above assignment of 1550 and 1480 cm^{-1} to the scissoring and wagging mode, respectively, we still have to locate the NH_2 rocking mode. By comparison with the other XH_2F_2 molecules,[29,36,37] we would expect this mode to have a frequency of about 1200 cm^{-1}. The infrared spectra of the $NH_2F_2^+$ salts show indeed a weak band at about 1180 cm^{-1} which is tentatively assigned to the NH_2 rocking mode. However, its relative infrared intensity is unexpectedly low. An alternate assignment for this mode exists by attributing one of the more intense components of the 1050-cm^{-1} band system to it. However, this alternative seems to us less satisfactory for the following reasons. The Raman spectra of the solids show the same splittings. Since the NH_2 modes are of very low intensity in the Raman spectrum (see above), these bands should belong to an NF_2 mode. Furthermore, by comparison with the frequencies of the scissoring and the wagging mode, a frequency of 1070–1020 cm^{-1} for the NH_2 rocking mode appears unreasonably low.

The torsion mode, ν_5 (A_2), should only be Raman active and be of low intensity. This explains our failure to detect this mode for $NH_2F_2^+$.

The spectra of the solid salts show, in addition to the splittings frequently observed[1,31,33–35] for MF_6^- salts, bands in the region 100–300 cm^{-1}. These bands were not observed for the Raman spectrum of $NH_2F_2^+AsF_6^-$ in HF solution and are rather broad. Therefore, they are attributed to lattice modes or cation–anion interaction through XH···FM bridges. Since the spectra of these solids were recorded at temperatures where the lattice is likely to become rigid, the observed phenomena are not surprising. A more detailed discussion of these effects has previously been given for OH_3^+ salts.[1]

The unknown frequency of ν_5 (A_2), the tentative assignment for the NH_2 deformation modes, the uncertainty in the frequencies of ν_6 (B_1) and ν_1 (A_1), and the importance of the off-diagonal terms in the **F** matrix of the CH_2F_2 general valence force field[29] do not justify a normal-coordinate analysis for $NH_2F_2^+$ at the present time.

Summary

The existence of 1:1:1 adducts between NHF_2, HF, and SbF_5 or AsF_5 was established by the observed material balances. The ionic structures, $NH_2F_2^+MF_6^-$, were established for these adducts by ^1H and ^{19}F NMR and vibrational spectroscopy. Seven or eight of the nine fundamentals, expected for a $NH_2F_2^+$ cation of symmetry C_{2v}, were observed. The nature of the products, resulting from the decomposition of these adducts, was briefly studied. With the exception of NHF_3^+, all of the fluoroammonium ions are now known.

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Registry No. HF, 7664-39-3; AsF_5, 7784-36-3; NHF_2, 10405-27-3; SbF_5, 7783-70-2; $NH_2F_2^+AsF_6^-$, 56533-30-3; $NH_2F_2^+SbF_6^-$, 56533-31-4.

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