SYNTHESIS, CHARACTERIZATION AND PROPERTIES
OF SOME
XENONIUM(II) SALTS CONTAINING Xe-O AND Xe-N BONDS

By
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ABSTRACT

This Thesis describes the syntheses and spectroscopic characterization of noble-gas compounds containing xenon(II)-nitrogen and xenon(II)-oxygen bonds in solution by multinuclear magnetic resonance (multi-NMR) and in the solid state by low-temperature Raman spectroscopy.

The key synthetic approach for the preparation of novel xenon(II) compounds containing xenon-nitrogen and xenon-oxygen bonds involved the HF elimination reactions of XeF$_2$ with the AsF$_6^{-}$ salts of several protonated oxygen and nitrogen bases in HF and BrF$_5$ solvents at low temperatures. In particular, CF$_3$C(OH)NH$_2^{+}$AsF$_6^{-}$, F$_5$TeNH$_3^{+}$AsF$_6^{-}$, and FO$_2$SNH$_3^{+}$AsF$_6^{-}$ reacted with XeF$_2$ by HF elimination to give CF$_3$C(OXeF)NH$_2^{+}$AsF$_6^{-}$, F$_5$TeN(H)-Xe$^{+}$AsF$_6^{-}$ and FO$_2$SN(H)-Xe$^{+}$AsF$_6^{-}$. The latter two salts are examples of a rare class of compounds in which xenon(II) is directly bonded to formally $sp^3$-hybridized nitrogen atoms. Their characterization in solution by multi-NMR was facilitated by preparing the xenon compounds with $^{15}$N-enriched (99.5 atom %) starting materials, i.e., F$_5$TeNH$_3^{+}$AsF$_6^{-}$ and FO$_2$SNH$_3^{+}$AsF$_6^{-}$. This allowed for the observation of the one-bond $^{129}$Xe-$^{15}$N scalar couplings in the $^{129}$Xe and $^{15}$N NMR spectra.

The salts, CF$_3$C(OH)NH$_2^{+}$AsF$_6^{-}$, F$_5$TeNH$_3^{+}$/AsF$_6^{-}$, and FO$_2$SNH$_3^{+}$/AsF$_6^{-}$, were prepared for the first time, and were characterized in the solid state by Raman spectroscopy, and in solution by $^{13}$C, $^{19}$F, $^1$H and $^{125}$Te NMR spectroscopy. The assignments of the Raman spectra of F$_5$TeNH$_3^{+}$/AsF$_6^{-}$ and FO$_2$SNH$_3^{+}$/AsF$_6^{-}$ were facilitated by recording the spectra of the natural abundance and 99.5 atom % $^{15}$N-enriched salts, resulting in $^{14}$/ $^{15}$N isotopic shifts for bands that involved vibrational motions of the nitrogen centers.

The compounds, F$_5$TeN(H)-Xe$^{+}$/AsF$_6^{-}$ and CF$_3$C(OXeF)NH$_2^{+}$/AsF$_6^{-}$, were isolated in the solid state and characterized by low-temperature Raman spectroscopy. Assignment of the Raman
bands associated with the vibrational motions of the nitrogen atom in $F_2TeN(H)-Xe^+AsF_6^-$ were facilitated by recording the Raman spectrum of the $^{15}N$-enriched compound and observing the $^{14}/^{15}N$ isotopic shifts. The compound, $FO_2SN(H)-Xe^+AsF_6^-$, was too unstable to be isolated from solution and therefore was not characterized by Raman spectroscopy.

The compounds, $CF_3C(OXeF)NH_2^+AsF_6^-$, $F_2TeN(H)-Xe^+AsF_6^-$ and $FO_2SN(H)-Xe^+AsF_6^-$, were characterized in solution by use of $^{129}Xe$, $^{125}Te$, $^{15}N$, $^{19}F$, $^1H$ and $^{13}C$ NMR spectroscopy. The assignment of the $^1H$ NMR resonances for $CF_3C(OH)NH_2^+$ and $CF_3C(OXeF)NH_2^+$ were facilitated by performing two dimensional heteronuclear ($^1H-^{19}F$) NOESY experiments, providing the first use of this technique in noble-gas chemistry.

The decomposition of $F_2TeN(H)-Xe^+AsF_6^-$ in HF and BrF$_5$ solvents has been studied in detail, primarily by $^{19}F$ NMR spectroscopy. The primary decomposition product, $F_5TeNF_2$, results from nucleophilic fluorination of $F_2TeN(H)-Xe^+$, and has been characterized for the first time by use of $^{15}N$ and $^{19}F$ NMR spectroscopy. The compound, $F_5TeNF_2$, was shown to react with $F_5TeNH_3^+AsF_6^-$ in AsF$_5$-acidified HF to give FN≡N$^+$AsF$_6^-$ and TeF$_6$ by $^{19}F$ NMR spectroscopy.
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<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>FEP</td>
<td>perfluoroethylene / perfluoropropylene copolymer</td>
</tr>
<tr>
<td>INEPT</td>
<td>insensitive nuclei enhanced by polarization transfer</td>
</tr>
<tr>
<td>IP</td>
<td>ionization potential</td>
</tr>
<tr>
<td>Kel-F</td>
<td>chlorotrifluoroethylene polymer</td>
</tr>
<tr>
<td>LCAO</td>
<td>linear combination of atomic orbitals</td>
</tr>
<tr>
<td>NOESY</td>
<td>nuclear Overhauser effect spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PFA</td>
<td>perfluoroalkoxy polymers</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>SA</td>
<td>shielding anisotropy</td>
</tr>
<tr>
<td>Teflon (PTFE)</td>
<td>tetrafluoroethylene polymer</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>rocking motion (vibrational spectroscopy)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>in-plane bend (vibrational spectroscopy)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>chemical shift in ppm from a reference compound (NMR spectroscopy)</td>
</tr>
<tr>
<td>$\pi$</td>
<td>out-of-plane bend (vibrational spectroscopy)</td>
</tr>
<tr>
<td>$\rho_r$</td>
<td>rocking motion (vibrational spectroscopy)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>torsional motion (vibrational spectroscopy)</td>
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<tr>
<td>$\nu$</td>
<td>stretching motion (vibrational spectroscopy)</td>
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<td>$\varpi$</td>
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An extra special thanks is due to my parents, Joe and Ethel Whalen, who gave of themselves without reservation so that I could grow and develop. Their love is the foundation upon which my life has been built.
To realize that our knowledge is ignorance,
This is a noble insight.
To regard our ignorance as knowledge,
This is mental sickness.
Only when we are sick of our sickness
Shall we cease to be sick.
The Sage is not sick, being sick of sickness;
This is the secret of health.

——— Tao Teh Ching
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CHAPTER 1

INTRODUCTION

GENERAL BACKGROUND

The potential for the Group VIII (18) elements of the Periodic Table to form compounds with other elements had been debated since the discovery of argon in 1894 by Ramsay and Rayleigh. Early attempts to isolate compounds of Group VIII elements, also known as the noble gases and "inert" gases, were unsuccessful. In particular, shortly after the discovery of argon, Moissan attempted to form a noble-gas compound by reaction of argon and elemental fluorine without success. Berthelot claimed to have formed a compound of helium with carbon disulfide and benzene by combining these materials in an electric discharge. However, R.J. Strutt was unable to repeat this result. Researchers such as Oddo and von Antröpp were proponents of noble-gas reactivity, and argued on the basis of periodic trends in valence and ionization potentials, that krypton and xenon should form compounds with the most electronegative element, fluorine. Kossel also predicted the existence of a xenon and a krypton fluoride. Pauling noted that main-group oxoacids could be seen as consisting of a central atom surrounded by as many oxygens as could fit around it. From the consideration of ionic radii, he reliably predicted coordination numbers of the central atom of a series of main-group oxoacids, including that of antimony acid, H$_3$Sb(OH)$_6$, with which the paper dealt ostensibly. On the basis of this simple argument, Pauling predicted coordination numbers of four and six for krypton and xenon, respectively, proposed the formula H$_4$XeO$_6$ for xenic acid, and predicted that salts of the form
Ag₂XeO₆ and AgH₂XeO₆ might be isolable. With the encouragement of Pauling, Yost and Kaye¹ attempted in 1932 and 1933 to react xenon and fluorine in an electric discharge, but no xenon fluorides were isolated.⁹ By the mid-1930's, the electronic theory of valence, particularly as first proposed by Lewis¹⁰ and Kossel,⁷ was recognized for rationalizing much of the chemical behavior of the elements. A key principle of this theory was that the noble-gas valence-electron configuration was the configuration to which most elements tended in their chemical bonding. Since the theory proposed by Lewis and Kossel rationalized most of the known chemical behavior of the elements, examples of chemical species which violated the noble-gas configuration by having more than an octet of valence electrons, so-called hypervalent species, such as Te(OH)₆ and IO(OH)₆, were considered as exceptions to the theory. This theory predicted unreactivity of the noble-gases resulting from the stability of the noble-gas valence-electron configuration. This concept was reinforced by the repeated failures to combine the noble-gases chemically with other elements, particularly those of Yost and Kaye;¹⁹ no further attempts to form compounds with the noble-gases were made until the 1960's.

In 1962, Bartlett¹¹,¹² successfully oxidized xenon gas with PtF₆, resulting in a salt, then formulated as "Xe⁺PtF₅⁻", demonstrating for the first time that it was possible to form noble-gas compounds. Shortly after the isolation of "Xe⁺PtF₆⁻", the first covalent derivatives of xenon were isolated and characterized, namely XeF₂,¹³ XeF₄,¹⁴ and XeF₆,¹⁵ from the reactions of xenon and elemental fluorine. There are several synthetic routes to oxides and oxofluorides of xenon. Examples are XeO₃,¹⁶ (Xe (VI)), XeOF₄,¹⁷ and XeO₂F₂,¹⁸ (Xe(VI)), and XeOF₂,¹⁹ (Xe(IV)). No xenon(II) oxides have been isolated and characterized. Several excellent reviews detailing the developments in the chemistry of the noble gases up to 1992 are available.²⁰-²⁶

The bulk of synthetic xenon chemistry to date involves xenon in the +2 oxidation state, and
the present Thesis is involved primarily with the chemistry of xenon(II) as well.

(A) **REPLACEMENT OF F IN XeF₂ WITH ELECTRONEGATIVE POLYATOMIC ANIONS**

The thermodynamic stability of the xenon fluorides with respect to the elements is derived from the high electron affinity (-333 ± 0.4 kJ mol⁻¹)²⁷ and small size of the fluorine atom, as can be seen in a thermochemical cycle for XeF₂ in the gas phase.²⁸ The experimentally determined exothermicity of equation (1.1)²⁹ can be rationized by summing equations (1.2) through (1.6), where I(Xe) is the first ionization potential of xenon,²⁸ EP is the electron pair energy for

\[
\text{Xe(g) + 2 F(g) \rightarrow F-Xe-F (g)} \quad \Delta H = -272 \text{ kJ mol}^{-1} \quad (1.1)
\]

\[
\text{Xe(g) \rightarrow Xe^+} \quad I(\text{Xe}) = 1176 \text{ kJ mol}^{-1} \quad (1.2)
\]

\[
\text{Xe}^+(g) + F(g) \rightarrow \text{Xe-F}^+(g) \quad \text{EP} = -201 \text{ kJ mol}^{-1} \quad (1.3)
\]

\[
F(g) \rightarrow F(g) \quad E(F) = -335 \text{ kJ mol}^{-1} \quad (1.4)
\]

\[
\text{Xe-F}^+(g) + F \rightarrow \text{F-Xe}^+\text{F} \quad \Delta H(\text{electrostatic}) \quad (1.5)
\]

\[
\text{F-Xe}^+\text{F} \leftrightarrow \text{F-Xe-F}^+ \quad \text{resonance energy} \quad (1.6)
\]

XeF⁺³⁰ and E(F) is the electron affinity of fluorine. The reaction represented by equation (1.1)
is exothermic because the large ionization potential of xenon is countered by the large electron affinity of fluorine and the sum of the EP, \(\Delta H\) (electrostatic) and resonance energy terms, which all favor a chemically bound species. The sum of the last two terms is \(-912 \text{ kJ mol}^{-1}\) since all other values are known. The small size of the fluorine atom contributes to a large value of \(\Delta H\) (electrostatic), and the electronegativity of fluorine also ensures that F-Xe\(^+\)F\(^-\) is stable with respect to F-Xe and F, and that Xe-F\(^+\) is stable with respect to Xe and F\(^+\).

The thermochemical data above indicate that ligands which are capable of replacing fluorine in XeF\(_2\) must be highly electronegative. It should be noted that \(\Delta H\) (electrostatic) will be less favorable for any atom or ligand group which replaces fluorine, because of the increase in size and the 1/r dependence of the electrostatic energy. Electron pair bonds [cf., EP above] involving fluorine are among the most energetically favorable bonds known, and replacement of fluorine with another ligand group is expected to lower the exothermicity of the electron pair energy (EP). These factors are well illustrated for XeCl\(_2\)(g), which is an unstable species that has been observed only at low temperatures by Mössbauer\(^{31,32}\) and matrix isolation infrared spectroscopy.\(^{33,34}\) The lower expected EP value for XeCl\(^+\) than XeF\(^+\) is reflected in the bond energies for ICl and IF (240 and 280 kJ mol\(^{-1}\), respectively).\(^{35,36}\) Further, the chlorine atom and chloride ion are much bigger than their fluorine counterparts,\(^{36}\) so that \(\Delta H\) (electrostatic) is less exothermic than in the fluoride case. Although the electron affinity of chlorine is 12 kJ mol\(^{-1}\) greater than for fluorine,\(^{35}\) all other terms are less favorable for chlorine than fluorine. Bartlett\(^{28}\) has shown that the chlorine analog of equation (1.1) is approximately 142 kJ mol\(^{-1}\) less favorable than for fluorine, in agreement with the instability of XeCl\(_2\).

In the context of the above argument it is apparent that a polyatomic ligand, \(L\), which is capable of replacing fluorine in XeF\(_2\) to give isolable derivatives, FXeL and XeL\(_2\), must be highly
electronegative. The conjugate bases of several strong oxygen and nitrogen acids are capable of replacing fluoride in XeF₂. Although the large electron affinities of these polyatomic groups favor stable species, their large sizes significantly reduce ΔH(electrostatic); for this reason, the ligand derivatives of XeF₂ are kinetically stable rather than thermodynamically stable. Decomposition, which is often explosive, occurs near room temperature in most cases.²⁰

Several strong oxoacids are capable of replacing F⁻ in XeF₂ in HF elimination reactions represented by equations (1.7) and (1.8). In general, isolation of pure products requires low reaction temperatures and removal of the evolved HF under vacuum.

\[
\text{XeF}_2 + \text{HL} \rightarrow \text{F-Xe-L} + \text{HF} \quad (1.7)
\]

\[
\text{XeF}_2 + 2 \text{HL} \rightarrow \text{L-Xe-L} + 2 \text{HF} \quad (1.8)
\]

The fluorosulfate anion, FSO₃⁻, is highly electronegative and is capable of stabilizing xenon(II). The mono- and bis-fluorosulfate derivatives of xenon(II) were synthesized²⁸,³⁷,³⁸ from the reaction of fluorosulfuric acid with XeF₂ as shown in equations (1.9) and (1.10).

\[
\text{XeF}_2 + \text{HSO}_3\text{F} \xrightarrow{-75 \degree\text{C}} \text{FXeOSO}_2\text{F} + \text{HF} \quad (1.9)
\]

\[
\text{XeF}_2 + 2 \text{HSO}_3\text{F} \xrightarrow{-75 \degree\text{C}} \text{Xe(OSO}_2\text{F})_2 + \text{HF} \quad (1.10)
\]

Other strong oxoacids which have yielded covalent derivatives of xenon(II) are HNO₃,²³ HClO₄,²⁸,³⁷ HSO₃CF₃,²⁸ and HOC(O)CF₃.³⁹⁻⁴¹ Xenon(II) derivatives containing the ligands,
OIOF$_4$\textsuperscript{42} and -OPOF$_2$\textsuperscript{43} are not isolated from the reactions of XeF$_2$ with the parent acids. The mono- and bis- derivatives are formed according to equations (1.11) and (1.12).

$$\text{XeF}_2 + x \text{F}_2\text{O}_3\text{F}_4 \xrightarrow{\text{CFCl}_3, -22 \, ^\circ \text{C}} x \text{P(O)}\text{F}_3 + F_{2-x}\text{Xe(OPOF}_2)_x$$  \hspace{1cm} (1.11)

\(x = 1 \text{ or } 2\)

$$\text{XeF}_2 + (\text{IO}_2\text{F}_3)_2 \xrightarrow{\text{SO}_2\text{ClF}} \text{F}_{2-x}\text{Xe(OIOF}_4)_x + \text{IOF}_3 + x/2 \text{ O}_2$$  \hspace{1cm} (1.12)

\(x = 1 \text{ or } 2\)

Mono- and bis- xenon(II) derivatives of the ligands -OSeF$_5$\textsuperscript{44,45} and -OTeF$_5$\textsuperscript{41,46-51} have been studied extensively. The -OTeF$_5$ group is exceeded only by fluorine and oxygen in its ability to stabilize the various oxidation states of xenon. This is attributed to its high effective group electronegativity resulting from the inductive effect of five fluorines on tellurium\textsuperscript{52} and is demonstrated by the existence of moderately stable -OTeF$_5$ analogues of XeF$_4$,\textsuperscript{51} XeOF$_4$\textsuperscript{53} and XeF$_6$.\textsuperscript{53} Salts of Xe-OTeF$_5$\textsuperscript{+} with AsF$_6$\textsuperscript{54,55} and Sb$_2$F$_{11}$\textsuperscript{54} anions are known: XeOTeF$_5$\textsuperscript{+}AsF$_6$\textsuperscript{-} is prepared from the fluoride abstraction reaction of FXeOTeF$_5$ with AsF$_3$, and XeOTeF$_5$\textsuperscript{+}Sb$_2$F$_{11}$\textsuperscript{-} is prepared by displacement of AsF$_6$\textsuperscript{-} upon dissolving XeOTeF$_5$\textsuperscript{+}AsF$_6$\textsuperscript{-} in SbF$_5$,\textsuperscript{54} followed by removal of SbF$_5$ and AsF$_5$ under vacuum. The salt, XeOSeF$_5$\textsuperscript{+}AsF$_6$\textsuperscript{-}\textsuperscript{26} has also been prepared by fluoride abstraction from FXeOSeF$_5$ using the strong Lewis fluoroacid, AsF$_3$. Owing to the high electronegativities of the F$_5$TeO- and F$_5$SeO- groups, which approach that of fluorine, the Lewis acidities of the Xe-L$^+$ cations (L = F$_5$TeO- and F$_5$SeO-) also approach that of XeF$^+$ [see Section (B)]. This has been demonstrated by the formation of adduct cations upon reaction of oxidatively
resistant nitrogen bases with XeOMF$_5^+$AsF$_6^-$ (M = Te, Se)$_{26}$ as shown in equation (1.13). All of the adducts are unstable at room temperature except s-C$_3$F$_3$N$_2$N-XeOMF$_5^+$AsF$_6^-$ (M = Se, Te).

\[ \text{XeOMF}_5^+\text{AsF}_6^- + \text{D} \rightarrow \text{D-XeOMF}_5^+\text{AsF}_6^- \]  \hspace{1cm} (1.13)

(D = s-C$_3$F$_3$N$_2$N, F$_3$S=N, CH$_3$C=N, C$_3$F$_3$N)

The number of nitrogen acids which undergo HF elimination reactions with XeF$_2$ is far less than the number of oxygen acids. The strong nitrogen acid, HN(SO$_2$F)$_2$, reacts with XeF$_2$ in a fashion which is analogous to that of the oxygen acids discussed above. The first Xe-N bonded species, FXeN(SO$_2$F)$_2$, was synthesized and partially characterized in 1974 by LeBlond and DesMarteau. Complete characterization by use of X-ray crystallography by Sawyer et al.$^{57}$ followed. Since then the bis- compound Xe[N(SO$_2$F)$_2$]$_2$$^{58,59}$ and the cations XeN(SO$_2$F)$_2^+$ and F[XeN(SO$_2$F)$_2$]$_2^+$ $^{58,59,60}$ have been characterized. The utility of the -N(SO$_2$F)$_2$ ligand to form stable bonds to xenon arises from the highly electron withdrawing groups bonded to nitrogen, resulting in a ligand which is resistant to oxidative fluorination. The compounds FXeN(SO$_2$F)$_2$ and Xe[N(SO$_2$F)$_2$]$_2$ were synthesized according to equation (1.14). The ligand transfer reagent, (CH$_3$)$_3$SiN(SO$_2$CF$_3$)$_2$, prepared as in equation (1.15), was used to prepare Xe[N(SO$_2$CF$_3$)$_2$]$_2$ in a (CH$_3$)$_3$SiF elimination reaction with XeF$_2$ [equation (1.16)].$^{61}$ The first reported xenon-nitrogen

\[ x \text{HN(SO}_2\text{F)}_2 + \text{XeF}_2 \xrightarrow{\text{CF}_2\text{Cl}_2, 0^\circ\text{C}} x \text{HF} + \text{F}_{2-x}\text{Xe[N(SO}_2\text{F)}_2]_x} \]  \hspace{1cm} (1.14)

(x = 1 or 2)
\[
\text{CH}_3\text{SiH} + (\text{CF}_3\text{SO}_2)\text{NH} \rightarrow (\text{CH}_3\text{SiN(SO}_2\text{CF}_3)_2 + \text{H}_2 \quad (1.15)
\]

\[
2 (\text{CH}_3\text{SiN(SO}_2\text{CF}_3)_2 + \text{XeF}_2 \rightarrow \text{Xe[N(SO}_2\text{CF}_3]_2 + 2 (\text{CH}_3\text{SiF}} \quad (1.16)
\]

adduct with a Lewis acid possessed the stoichiometry \(\text{FXeN(SO}_2\text{F}_2\text{)}\text{AsF}_5\) and was postulated to have the ionic formulation \(\text{XeN(SO}_2\text{F}_2\text{)}^+\text{AsF}_6^-\) [see equation (1.17)], although it was not isolated.\(^{58}\) Subjecting the salt to dynamic vacuum at room temperature resulted in the isolation of the \(\text{AsF}_6^-\) salt of the bridging cation, \(\text{FXeN(SO}_2\text{F}_2\text{)}\text{AsF}_6\) according to equation (1.18). The species \(\text{XeN(SO}_2\text{F}_2\text{)}^+\text{AsF}_6^-\) was later isolated, although it is thermally unstable at room temperature.\(^{60}\) A crystal structure of \(\text{XeN(SO}_2\text{F}_2\text{)}^+\text{Sb}_3\text{F}_{16}^-\) was obtained\(^{60}\) using crystals grown after dissolving \(\text{FXeN(SO}_2\text{F}_2\text{)}\text{AsF}_6^-\) in \(\text{SbF}_5\) solvent [equation (1.19)].

\[
2 \text{XeN(SO}_2\text{F}_2\text{)}^+\text{AsF}_6^- \rightarrow \text{FXeN(SO}_2\text{F}_2\text{)}^+\text{AsF}_6^- + \text{AsF}_5 \quad (1.18)
\]

\[
\text{FXeN(SO}_2\text{F}_2\text{)}^+\text{AsF}_6^- + 3 \text{SbF}_5 \rightarrow 2 \text{XeN(SO}_2\text{F}_2\text{)}^+\text{Sb}_3\text{F}_{16}^- + \text{AsF}_5 \quad (1.19)
\]
(B) **LEWIS ACIDITY AND OXIDATITIVE FLUORINATING ABILITY OF THE XeF⁺ CATION**

The valence bond and molecular orbital descriptions of XeF₂ indicate semi-ionic Xe-F bonds, with considerable negative charge on the fluorine atoms; the charge distribution may be described as \(\text{F}^{3-}\text{Xe}^{4+}\text{F}^{-}\). The valence-bond description of XeF₂ incorporates the notion of Xe-F bond polarity through the resonance contributions \(\text{F-Xe}^+\text{F}^- \leftrightarrow \text{F}^+\text{Xe-F}^-\). Owing to the Xe-F bond polarity, XeF₂ behaves as a fluoride ion donor towards many strong Lewis acids, yielding compounds of the form \(\text{XeF}_2\alpha\text{MF}_5\) \((\alpha = 1/2, 1, \text{or} 2; \text{MF}_5 = \text{Lewis acid})\). The compounds cannot be given a purely ionic formulation (i.e., \(\text{XeF}^+\text{M}_\alpha\text{F}_{5\alpha+1}^-\)) since fluorine bridges between xenon and a fluorine of the "anion" indicate covalent character in the bonding. Single crystal X-ray diffraction studies of these adducts reveal that the bridging Xe-F bond lengths increase with decreasing lengths of the terminal Xe-F bonds and increasing fluoride ion acceptor ability of \(\text{MF}_5\), indicating increased ionic character. For example, in \(\text{XeF}_2\text{RuF}_5\), the terminal Xe-F and bridging Xe-F bond lengths are 1.87(2) and 2.18(2) Å, respectively. The corresponding bond lengths in \(\text{XeF}_2\text{SbF}_5\) are 1.84 and 2.35 Å. The latter has the shortest terminal Xe-F bond length for an adduct of XeF₂, providing the closest approximation to a salt of XeF⁺. This is a result of the very weak basicity of the \(\text{Sb}_2\text{F}_{11}^-\) anion.

The Raman and infrared spectra of solid adducts of XeF₂ with Lewis acids complement the crystal data. They are best interpreted in terms of ionic formulations \(\text{XeF}^+\text{MF}_6^-\) and \(\text{XeF}^+\text{M}_2\text{F}_{11}^-\), but modes associated with the bridging Xe-F and M-F stretches and F-Xe-F bends confirm the presence of fluorine bridges. In the case of \(\text{XeF}^+\text{MF}_6^+\), the number of bands and selection rules for the infrared and Raman spectra indicate a symmetry lower than \(O_h\), resulting in part from the fluorine bridge interaction with XeF⁺.
Fluorine bridging of the XeF\(^+\) cation, to a fluorine of a weakly basic fluoroanion indicates that XeF\(^+\) has substantial Lewis acid character. Schrobilgen et al.\(^{26}\) have exploited the Lewis acid character of XeF\(^+\) by reacting XeF\(^+\)AsF\(_6\)\(^-\) with various oxidatively resistant nitrogen bases (D), resulting in Xe-N bonds [see equation (1.20)]. Because of the strong oxidizing power of XeF\(^+\)

\[
D + \text{XeF}^+\text{AsF}_6^- \rightarrow \text{D-XeF}^+\text{AsF}_6^-
\]

(estimated electron affinity 10.9 eV)\(^{26}\), only oxidatively resistant bases form stable adduct cations with XeF\(^+\). Nitrogen bases whose first adiabatic ionization potentials are greater than or equal to the electron affinity of XeF\(^+\) are often resistant to oxidation by XeF\(^+\), allowing the isolation of D-XeF\(^+\)AsF\(_6\)\(^-\) at low temperatures. The first example of a nitrogen base to form an adduct with XeF\(^+\) was HCN, whose first adiabatic ionization potential has been determined to be 13.80 eV from photoionization studies.\(^{70}\) In addition, a series of nitriles RC≡N form the adducts RC≡N-XeF\(^+\)AsF\(_6\)\(^-\), which have been characterized in solution (R = H, CH\(_3\), CH\(_2\)F, C\(_2\)H\(_5\), C\(_2\)F\(_5\), C\(_3\)F\(_7\) and C\(_6\)F\(_5\))\(^{71-73}\) and in the solid state (R = H, Me).\(^{71-73}\) A detailed study which expands the ligand series has been carried out.\(^{74}\) The general synthesis for these adducts involves the reaction of XeF\(^+\)AsF\(_6\)\(^-\) or Xe\(_2\)F\(_3\)\(^+\)AsF\(_6\)\(^-\) with the appropriate nitrile as shown in equations (1.21) and (1.22), resulting in the first examples of xenon bonded to an sp-hybridized nitrogen atom.

\[
\text{HF} \quad \begin{align*}
\text{XeF}^+\text{AsF}_6^- + \text{RC≡N} & \rightarrow \text{RC≡N-XeF}^+\text{AsF}_6^- \\
-20 \text{ to } -10 \, ^\circ\!\!\mathrm{C}
\end{align*}
\]

\[
\text{HF} \quad \begin{align*}
\text{Xe}_2\text{F}_3^+\text{AsF}_6^- + \text{RC≡N} & \rightarrow \text{RC≡N-XeF}^+\text{AsF}_6^- + \text{XeF}_2 \\
-20 \text{ to } -10 \, ^\circ\!\!\mathrm{C}
\end{align*}
\]
The fluoro(perfluoropyridine)xenon(II) cations, 4-RC₅F₄N-XeF⁺ (R = F or CF₃) have been formed in HF solvent according to equation (1.23) and equilibria (1.24) and (1.25) at -30 to -20 °C. An alternative synthesis involves the reaction of 4-RC₅F₄NH⁺AsF₆⁻ with XeF₂ in BrF₅ and HF solvents at -30 °C as in equation (1.25). As expected, the equilibrium favors a larger proportion of the xenon(II) cation in BrF₅ solvent, enabling the salts to be isolated by removal of the BrF₅ solvent under vacuum at -30 °C. The first adiabatic ionization potential of C₅F₅N (10.08 ± 0.05 eV) is approximately the same as that of the electron affinity of XeF⁺, in accordance with the criterion for a stable adduct. The first ionization potential (11.50 eV) of s-trifluorotriazine, s-C₃F₃N₃ and the existence of C₅F₅N-XeF⁺AsF₆⁻ suggested that the adduct s-C₃F₃N₂N-XeF⁺ should also exist. This compound has been synthesized according to equation (1.26) by the reaction of XeF⁺AsF₆⁻ with excess s-trifluorotriazine at room temperature for three hours followed by removal of excess s-C₃F₃N₃ under vacuum. The resulting salt is unique in that it is the only salt of the series which is stable indefinitely at room temperature.

\[
\text{XeF}^+\text{AsF}_6^- + s\text{-C}_3\text{F}_3\text{N}_3 \longrightarrow s\text{-C}_3\text{F}_3\text{N}_2\text{N-XeF}^+\text{AsF}_6^- \quad (1.26)
\]
The ligand, \( F_3S\equiv N \) (first IP, 12.50 eV),\(^{77}\) was also allowed to react with \( XeF^+ AsF_6^- \) in \( BrF_5 \) solvent at \(-60^\circ C\), giving the adduct \( F_3S\equiv N-XeF^+ \),\(^{26}\) which has been characterized by \( ^{19}F \) and \( ^{129}Xe \) NMR spectroscopy at \(-60^\circ C\) [equation (1.27)]. Solvolysis of \( F_3S\equiv N-XeF^+ AsF_6^- \) occurs at \(-20^\circ C\) in HF solvent and results in addition of HF across the S-N triple bond, followed by HF elimination to give \( F_4S= N-Xe^+ \) [equation (1.28)]. The expected intermediate cation, \( F_4S=N(H)-XeF^+ \), that results from HF addition to \( F_3S=N-XeF^+ \), is not observed. Addition of HF across the S-N double bond of \( F_4S=N-Xe^+ \) results in the \( F_5S(N(H))-Xe^+ \) cation, which is the first example of an \( sp^3 \)-hybridized nitrogen bonded to xenon [equation (1.29)].

\[
\begin{align*}
F_3S\equiv N + XeF^+ AsF_6^- & \xrightarrow{BrF_5} F_3S\equiv N-XeF^+ AsF_6^- \\
\text{-60 }^\circ \text{C} & \\
F_3S\equiv N-XeF^+ + HF & \xrightarrow{\text{HF}} [F_4S= N(H)-Xe-F^+] \xrightarrow{\text{HF}} F_4S= N-Xe^+ \\
& \quad (1.27) \\
& \quad (1.28)
\end{align*}
\]

\[
F_4S= N-Xe^+ + HF \xrightarrow{\text{HF}} F_5S(N(H))-Xe^+ \\
(1.29)
\]

The only known examples of krypton-nitrogen bonds arise from the reaction of \( HC\equiv NH^+ AsF_6^- \) with \( KrF_2 \) in \( BrF_5 \) solvent at \( ca. -60^\circ C \), resulting in \( HC\equiv N-KrF^+ AsF_6^- \);\(^78\) and from the reaction of the adducts \( R_2C= N-AsF_5 \) (\( R_2= CF_3, C_2F_5, n-C_3F_7 \)) with \( KrF_2 \) in \( BrF_5 \) solvent at \( ca. -60^\circ C \), resulting in \( R_2C= N-KrF^+ AsF_6^- \).\(^71\) The krypton cations are acid-base adducts, similar to the xenon(II) cations discussed above. The estimated electron affinity of \( KrF^+ \) (13.2 eV)\(^{26}\) is greater than \( XeF^+ \) (see above), indicating that it is a stronger oxidizer. As expected, the nitrile adducts with \( KrF^+ \) are less thermally stable than the xenon(II) analogs.

The oxidative fluorinating power of \( XeF^+ \) is well established. Bartlett and Sladky\(^79\) noted
that XeF₂ was incapable of oxidizing I₂ in acetonitrile solution, but addition of trace amounts of the Lewis acids SO₂, HF, or BF₃ resulted in the immediate oxidation of I₂ to IF₅, with formation of xenon gas. This suggested that XeF⁺ was formed from the interaction of the Lewis acid with XeF₂ [equation (1.30)], and that the oxidizing ability of XeF⁺ greatly surpassed that of XeF₂.

\[
A + XeF_2 \rightleftharpoons AF^- + XeF^+ \quad (1.30)
\]

\[(A = \text{Lewis acid})\]

Since the work of Bartlett and Sladky,⁷⁹ salts of XeF⁺ have been used as chemical reagents to oxidatively fluorinate other species. The reaction of XeF⁺MF₆⁻ (M = As, Sb) with a variety of reagents in HF solvent at low temperatures (ca. -80 to -40 °C) has demonstrated the oxidative fluorinating ability of the XeF⁺ cation, as well as its significant Lewis acid strength. The reaction of XeF⁺MF₆⁻ with sulfur(II) species such as the disulfides CF₃S-SCF₃,⁸⁰ CF₃S-SCH₃⁸⁰ and CH₃S-SCH₃,⁸⁰ resulted in MF₆⁻ salts of the thermally unstable fluorosulfonium cations according to equation (1.31). The sulfanes (C₆F₅)₂S,⁸¹ CF₃SCH₂,⁸² (CH₃)₂S,⁸²,⁸³ CF₃SH⁸⁴ and CH₃SH⁸⁴ are likewise oxidatively fluorinated by XeF⁺MF₆⁻, resulting in thermally unstable MF₆⁻ salts of fluorosulfonium cations [equation (1.32)]. It is interesting that the reaction of the sulfanes [sulfur(IV)] (CF₃)ₙSF₄₋⁸⁵ (n = 0 - 2) with XeF⁺MF₆⁻ in HF solvent resulted in fluoride abstraction rather than oxidative fluorination, indicating the strong Lewis acid strength of the XeF⁺ cation [equation (1.33)].⁸⁵ The fluoride transfer was attributed to the weak axial S-F bonds in the

\[
R-S-S-R' \ XeF^+MF_6^- \longrightarrow RS-S(F)R'^+MF_6^- + Xe \quad (1.31)
\]


\[
R{-}S{-}R' + XeF^+MF_6^- \rightarrow R{-}(F)R^+MF_6^- + Xe \tag{1.32}
\]

\[
(CF_3)_nSF_{4-n} + XeF^+MF_6^- \rightarrow (CF_3)_nSF_{3-n}^+MF_6^- + XeF_2 \tag{1.33}
\]

sulfuranes\textsuperscript{85} and their resulting fluoride ion donor ability. The XeF\textsubscript{2} produced is a substantially weaker oxidative fluorinator than XeF\textsuperscript{2} and is incapable of oxidatively fluorinating the compounds \((CF_3)_nSF_{4-n} (n = 0 \text{ - } 2)\). In the case of CF\textsubscript{3}S(O)F, a labile fluoride is not present, and reaction with XeF\textsuperscript{+}MF\textsubscript{6} results in oxidative fluorination to give CF\textsubscript{3}S(O)F\textsubscript{2}+MF\textsubscript{6}\textsuperscript{0}.\textsuperscript{85} It was postulated that the xenon-oxygen bonded species, CF\textsubscript{3}S(OxeF)F\textsuperscript{+}MF\textsubscript{6}, is an intermediate which decomposes by transfer of "F\textsuperscript{+}" to sulfur with elimination of xenon gas. A similar adduct cation, Cl\textsubscript{2}S-XeF\textsuperscript{+}, has been proposed as an intermediate in the oxidative fluorination reaction of SCl\textsubscript{2} by XeF\textsuperscript{+}MF\textsubscript{6}\textsuperscript{-}\textsuperscript{86} at low temperature [equation (1.34)]. Evidence for such an intermediate has been provided by the

\[
Cl_2S + XeF^+ \rightarrow [Cl_2S-XeF^+] \rightarrow Cl_2S-F^+ + Xe \tag{1.34}
\]

low-temperature isolation of \((CF_3)\textsubscript{2}SO-XeF^+\text{SbF}_6^-\) from HF solvent, which indeed contains a xenon-oxygen bond.\textsuperscript{85} Oxidative fluorination of H\textsubscript{2}O\textsuperscript{87} and H\textsubscript{2}S\textsuperscript{88} by XeF\textsuperscript{+}MF\textsubscript{6} in HF at low temperatures (ca. -78 °C) results in the salts H\textsubscript{2}OF\textsuperscript{+}MF\textsubscript{6} and H\textsubscript{2}SF\textsuperscript{+}MF\textsubscript{6}, respectively. The oxidative fluorination of H\textsubscript{2}O at low temperature, in spite of its high ionization potential (12.6 eV),\textsuperscript{89} demonstrates the powerful oxidative fluorinating ability of XeF\textsuperscript{+}MF\textsubscript{6}. Oxidative fluorination of AsCl\textsubscript{3} with XeF\textsuperscript{+}AsF\textsubscript{6} in HF solvent at -78 °C also resulted in the isolation of AsCl\textsubscript{3}F\textsuperscript{+}AsF\textsubscript{6}.\textsuperscript{90}

As discussed above, there is a growing number of examples of the use of XeF\textsuperscript{+} as an
oxidative fluorinating agent, and there is now a large number of salts of adduct cations, D-XeF⁺⁺, where D is a nitrogen base.²⁶ Although Minkwitz⁸⁶ has postulated an adduct cation Cl₂S-XeF⁺⁺ as an intermediate in the oxidative fluorination of SCl₂ by XeF⁺⁺MF₆⁻, there are no reported examples of an isolated and definitively characterized salt of an adduct cation, D-XeF⁺⁺, which decomposes by oxidative fluorination of the base [equation (1.35)]. Further work is required to establish the existence of D-XeF⁺⁺ cations as intermediates in the oxidative fluorination of bases.

\[
D\text{-}XeF^{++}\text{MF}_6^- \longrightarrow D\text{-}F^{++}\text{MF}_6^- + Xe
\]  
\[(M = As, Sb)\]  

(C) SPECIES CONTAINING XENON-CARBON BONDS

The first reported example of a xenon-carbon bonded species was Xe(CF₃)₂, which was prepared from the reaction of XeF₂ with plasma generated CF₃ radicals.⁹¹ The resulting waxy solid, assumed to be Xe(CF₃)₂, decomposes with a half-life of ca. 30 minutes at room temperature according to equation (1.36). Characterization of the material claimed to be Xe(CF₃)₂ is incomplete and the synthesis has not been confirmed.

\[
\text{Xe(CF}_3\text{)}_2 \longrightarrow \text{XeF}_2 + \text{C}_n\text{F}_m
\]  

The stability of cations containing xenon-carbon bonds was established by determination of the xenon-carbon bond energy of CH₃-Xe⁺ in the gas phase by ion cyclotron resonance. The Xe-C bond energy was determined to be 180 ± 33 kJ mol⁻¹⁹² and more recently, 231 ± 10 kJ mol⁻¹.⁹³ These values are similar to those observed for the Xe-F bonds of XeF₂ (132 kJ mol⁻¹)⁹⁴
and XeF\(^+\) (201 kJ mol\(^{-1}\)),\(^{94}\) indicating that isolation of salts containing cations with xenon-carbon bonds is feasible.

A number of structurally well-characterized compounds containing Xe-C bonds are, in fact, now known. In all cases they occur as colorless salts of xenonium cations, R-Xe\(^+\) (R = fluorophenyl or alkynyl group). The formation of the pentfluorophenylxenon(II) cation, \(\text{C}_6\text{F}_5\text{Xe}^+\), in \(\text{CH}_2\text{Cl}_2\) (-30 °C) and CH\(_3\)CN (0 °C) solutions, with the anions B(\(\text{C}_6\text{F}_5\)\(_2\)F\(^-\)), B(\(\text{C}_6\text{F}_5\)\(_2\)F\(_2\)\(^-\)) and B(\(\text{C}_6\text{F}_5\)\(_3\))F\(_3\)\(^-\) has been established.\(^{95-100}\) The salts are typically formed by the reaction of XeF\(_2\) with the ligand transfer reagent, B(\(\text{C}_6\text{F}_5\)\(_2\)), in methylene chloride solvent [equation (1.37)]. The X-ray crystal structure of [CH\(_3\)C≡N-XeC\(_6\)F\(_5\)]\(^+\) [\(\text{C}_6\text{F}_5\)\(_2\)BF\(_2\)]\(^-\), isolated from acetonitrile solution, shows that the xenon atom of C\(_6\)F\(_5\)-Xe\(^+\) is weakly coordinated to the nitrogen atom of a CH\(_3\)C≡N

\[
\text{XeF}_2 + \text{B(}\text{C}_6\text{F}_5\text{)}_3 \rightarrow \text{Xe-C}_6\text{F}_5^+\text{B(}\text{C}_6\text{F}_5\text{)}_2\text{F}_2^- \quad (1.37)
\]

molecule (Xe-N, 2.681(8) Å; Xe-C, 2.092(8) Å).\(^{100}\) The salt decomposes slowly at 14 °C. Reaction of [CH\(_3\)C≡N-Xe-C\(_6\)F\(_5\)]\(^+\) [\(\text{C}_6\text{F}_5\)\(_2\)BF\(_2\)]\(^-\) with AsF\(_5\) in CH\(_3\)CN solution results in [CH\(_3\)C≡N-Xe-C\(_6\)F\(_5\)]\(^+\)AsF\(_5\)\(^-\). Solutions of this compound in CH\(_3\)CN are stable for up to one day at room temperature.\(^{97}\) The reactions of XeF\(_2\) with the boron ligand transfer reagents B(m-C\(_5\)F\(_3\)C\(_6\)H\(_4\))\(_3\) and B(p-F\(_5\)C\(_6\)H\(_4\))\(_3\) in \(\text{CH}_2\text{Cl}_2\) solution at -45 to -50 °C result in the formation of the white solids [m-C\(_5\)F\(_3\)C\(_6\)H\(_4\)Xe]\(^+\)[m-C\(_5\)F\(_3\)C\(_6\)H\(_4\)BF\(_3\)]\(^-\);\(^{96}\) and [p-F\(_5\)C\(_6\)H\(_4\)Xe]\(^+\)[(p-F\(_5\)C\(_6\)H\(_4\))\(_2\)BF\(_2\)]\(^-\).\(^{96}\) The former compound is stable for up to one hour in CH\(_3\)CN at -41 °C, whereas the latter compound decomposes below -40 °C when attempting to dissolve it in the coordinating solvent, CH\(_3\)CN.

The most stable xenonium salt presently known is [Xe(2,4,6-F\(_3\)C\(_6\)H\(_3\))]\(^+\) [BF\(_4\)]\(^-\);\(^{98}\) which is prepared by the reaction of B(\(\text{C}_6\text{H}_2\text{F}_3\))\(_3\)thf and XeF\(_2\) in the presence of BF\(_3\)O(CH\(_3\))\(_2\) in \(\text{CH}_2\text{Cl}_2\) solution.
at -40 °C. It is stable for up to 21 days at room temperature in dry air and hydrolyzes slowly over 7 days in aqueous CH₂C≡N solution. Examples of alkynyl xenonium tetrafluoroborates are known and are prepared by reaction of lithium acetylides or triphenylsilyl acetylenes with XeF₂ and BF₃·O(CH₃)₂ at low temperatures (-78 to -40 °C) in CH₂Cl₂ solvent.¹⁰¹ The known alkynyl derivatives are (CH₃)₂C·C≡C·Xe⁺BF₄⁻, (CH₃)₂Si·C≡C·Xe⁺BF₄⁻, CH₂CH₂·C≡C·Xe⁺BF₄⁻ and CH₃CH₂CH₂·C≡C·Xe⁺BF₄⁻; all of these species decompose in solution or as solids below 0 °C,¹⁰¹ but none have been characterized in the solid state.

It is interesting to note that, of all the known species containing xenon-carbon bonds, no neutral species of the form R-Xe-F have been characterized (R = fluoroaryl or alkynyl). This may be rationalized by considering the semi-ionic nature of the bonding in hypervalent compounds of the form R-Xe-F, which is best described in valence-bond terms by the resonance contributors R⁺·Xe-F⁺ ↔ R-Xe⁺·F⁻;¹⁰² the relative weightings of each contributor depends on the electronegativities of F and R. The carbon ligands used to form the cations R-Xe⁺ are undoubtedly among the least electronegative ligands which have ever been used as ligands with xenon. For this reason, the resonance contribution, R-Xe⁺·F⁻, essentially accounts for the bonding. Confirmation of the ionic character of the Xe-F bonds in solution is provided by the absence of observed one-bond ^¹²⁹Xe-¹⁹F scalar couplings attributable to Xe-F linkages in the ^¹⁹F and ^¹²⁹Xe NMR spectra. As well, the ^¹²⁹Xe NMR chemical shifts (ca. -3760 ppm for C₆F₅·Xe⁺ in acetonitrile solution)⁹⁵,⁹⁶ are the most shielded for chemically bound xenon.⁹⁵-¹⁰⁰ This is consistent with an ionized Xe-F bond and an Xe-C bond of high covalent character, since the ^¹²⁹Xe chemical shifts of xenon(II) compounds containing Xe-N, Xe-O and Xe-F bonds are known to decrease (i.e., become more shielded) with increasing ionic character of the Xe-F bond.²⁶,¹⁰³,¹⁰⁴
(D) PURPOSE AND GENERAL SYNTHETIC STRATEGIES UNDERPINNING THE PRESENT WORK

The overall purpose of the present work is to extend the chemistry of the noble gases and, more specifically, to prepare and characterize compounds containing novel covalent bonds between xenon and nitrogen or oxygen. One route to Xe-N bonded species is through the interaction of XeF⁺AsF₆⁻ with selected nitrogen bases in solution. Given the oxidizing strength of XeF⁺, nitrogen bases were selected on the basis of their resistance to oxidation.²⁶ It was found that nitrogen bases whose first adiabatic ionization potentials (IP₁), when known, were greater than or equal to the estimated electron affinity of XeF⁺ (10.9 eV), were often resistant to oxidative attack by XeF⁺ at low temperatures. This method of base selection preceded the successful preparation of AsF₆⁻ salts of the adduct cations RC≡N-XeF⁺, (R = alkyl,²²,²⁴ fluoroalkyl,⁷¹,²²,²⁴ C₆F₅,²²,²⁴ H²²,²⁴), C₃F₃N₂N-XeF⁺,⁷¹ and the pyridine adducts, C₃F₃N-XeF⁺ ⁷⁴,⁷⁵ and 4-CF₃C₂F₄N-XeF⁺.⁷⁴,⁷⁵ All of these cations involve ligands in which the nitrogen atoms bonded to xenon are formally sp- or sp²-hybridized. Except for the partially characterized salt, F₂SN(H)-Xe⁺AsF₆⁻,²⁶ there are no known examples of formally sp²-hybridized nitrogen bonded to xenon(II). In the present study, the AsF₆⁻ salts of several cations containing Xe-N and Xe-O bonds have been prepared and characterized; the atoms directly bonded to xenon in the novel cations are formally sp²-hybridized, contributing significantly to the chemistry of xenon(II). The importance of ligand electronegativity in stabilizing compounds of xenon(II) was discussed in Section (A) of this Chapter. The synthesis of xenon compounds in which the ligand atom bonded to xenon is sp²-hybridized is significant because the electronegativity of a ligand group decreases as the %s character of the valence hybrid orbitals decreases.¹⁰⁵ Thus the ligands studied in the present work, namely CF₃C(O)NH₂, F₅TeNH₂ and FO₂SNH₂, are among the least electronegative nitrogen- or
oxygen-donor ligands to ever form compounds with xenon(II). The low electronegativity of these ligands is reflected in the thermal instability of the resulting xenon(II) compounds, which are among the least stable xenon(II) derivatives known.

The ligands studied in the present work, namely, CF₃C(O)NH₂, F₅TeNH₂ and FO₂SNH₂, are isoelectronic with the strong oxoacids, CF₃C(O)OH, F₅TeOH and FO₂SOH, all of which form xenon(II) compounds [see Section (A)] which are stable at or near room temperature. Trifluoroacetamide, CF₃C(O)NH₂, was chosen as a potential base for adduct formation with XeF⁺ on the basis of its first adiabatic ionization potential (10.77 eV),¹⁰⁶ which is similar to the estimated electron affinity for XeF⁻ (10.9 eV),²⁶ so that it might be resistant to oxidative attack by the noble-gas cation. The IP₁-values of F₅TeNH₂ and FO₂SNH₂ are not known; their potential as ligands in novel xenon(II) compounds is based solely on the electronic similarity of these ligands to F₅TeOH and FO₂SOH. Although CF₃C(O)NH₂, F₅TeNH₂ and FO₂SNH₂ are not strong acids, it was possible to protonate these species, either in situ from the reaction with HF acidified with an equimolar amount of XeF⁺AsF₆⁻ [equations (1.38) and (1.39)], or from the reaction with excess AsF₅ in HF, to give the isolable salts, CF₃C(OH)NH₂⁺AsF₆⁻, F₅TeNH₂⁺AsF₆⁻ and FO₂SNH₂⁺AsF₆⁻ [equation (1.40)]. Ammonium cations generated in situ [equations (1.38) and (1.39)] or isolated as AsF₆⁻ salts [equation (1.40)], react with XeF₂ by HF elimination to give

\[
\text{XeF}^+\text{AsF}_6^- + \text{HF} \rightleftharpoons \text{XeF}_2 + \text{H}_2\text{F}^+\text{AsF}_6^- \quad (1.38)
\]

\[
\text{H}_2\text{F}^+\text{AsF}_6^- + D \rightleftharpoons \text{DH}^+\text{AsF}_6^- + \text{HF} \quad (1.39)
\]

\[ (D = \text{CF}_3\text{C(O)}\text{NH}_2, \text{F}_5\text{TeNH}_2, \text{FO}_2\text{SNH}_2) \]
Xe-N and Xe-O bonded cations, and are analogous to the reactions of strong oxoacids with XeF₂ [equation (1.7)]. The oxygen ligands CF₃C(O)O⁻, F₅TeO⁻ and FO₂SO⁻ are more electronegative than the analogous nitrogen ligands CF₃C(O)NH₂, F₅TeN(H)⁻ and FO₂SN(H)⁻, which have been used as ligands in compounds of xenon(II) in the present work. A comparison of the xenon(II)-oxygen derivatives with the novel xenon(II) compounds prepared in this Thesis provides the material for a systematic study of the effect of ligand electronegativity on the bonding and stability of compounds containing Xe(II)-O and Xe(II)-N bonds.
CHAPTER 2

EXPERIMENTAL SECTION

(A) VACUUM TECHNIQUES

(i) Vacuum Systems and Inert Atmosphere Systems

The compounds used in the course of this work are moisture sensitive or were used as precursors for moisture sensitive materials. It was therefore necessary to rigorously dry all precursors and apparatus. All manipulations were carried out under rigorously anhydrous conditions in glass or metal vacuum systems or in the oxygen and moisture free (< 0.1 ppm) inert nitrogen atmosphere of a Vacuum Atmospheres Model DLX drybox. The drybox was equipped with a cryogenic well which was cooled to -196 °C for the manipulation of thermally unstable materials under anhydrous conditions. Volatile reagents and solvents were manipulated by vacuum transfer using two vacuum lines. Volatile materials which were noncorrosive towards glass in the absence of water such as organic solvents [e.g., CH₂Cl₂, CHCl₃, (CH₃CH₂)₂O], F₅TeOH and S₂O₃F₂ were manipulated using a vacuum line constructed of Pyrex with grease-free 6-mm J. Young glass stopcocks equipped with FEP barrels (Figure 2.1). Volatile materials which attack glass, such as HF and BrF₅ solvents, were manipulated by vacuum transfer on a vacuum line constructed from nickel and 316 stainless steel valves and fittings (Autoclave Engineers, Inc.), Teflon, FEP, and Kel-F (Figure 2.2). Pressures were measured at ambient temperature using an
Figure 2.1  Glass vacuum line; (A) mercury manometer, (B) dry nitrogen inlet, (C) liquid nitrogen trap, (D) grease-free glass 6-mm J. Young stopcock with FEP barrel.
Figure 2.2 Metal vacuum line; (A) outlet to liquid nitrogen and charcoal traps followed by a two stage direct drive rotary vacuum pump (Edwards, E2M8) - hard vacuum, (B) outlet to soda lime and liquid nitrogen traps followed by a two stage direct drive rotary vacuum pump (Edwards, E2M8) - rough vacuum, (C) dry nitrogen inlet, (D) fluorine inlet, (E) 0 - 1500 Torr Bourdon gauge (F) MKS Model PDR-5B pressure transducers (0 - 1100 Torr), (G) MKS Model PDR-5B pressure transducer (0 - 1 Torr), (H) 3/8-in. 316 SS high pressure valve (Autoclave Engineers, 30VM6071), (I) 316 SS tee, (J) 316 SS cross, (K) 316 SS L, (L) nickel connectors
MKS Model PDR-5B power supply and digital readout in conjunction with pressure transducers having inert wetted surfaces constructed of Inconel. Two transducers of different dynamic pressure ranges were used, 0 to 1100 Torr and 0 to 1 Torr. The pressures were accurate to ± 0.5% of scale.

Vacuum on the glass line and metal line was attained by using Edwards two stage E2M8 direct drive high vacuum pumps. Two vacuum pumps were used on the metal vacuum line: one, a roughing pump, was used for the removal and disposal of volatile reactive fluorinated compounds by pumping through and entrapment on a bed of soda lime, which consisted of a copper tube (ca. 60 cm length, 15 cm dia.) packed with soda lime absorbent (Fisher Scientific, 4-8 mesh). The second vacuum pump provided the high vacuum source for the manifold (ca. $10^{-4}$ Torr). In the construction of the glass and metal vacuum lines, traps cooled to -196 °C were attached immediately before the vacuum pumps to prevent the passage of condensible volatile materials into the pumps.

(ii) **Preparative Apparatus and Sample Vessels for Raman and NMR Spectroscopy**

All synthetic procedures were performed in apparatus constructed from 304 and 316 stainless steel, glass, Kel-F or FEP. Stainless steel cylinders (Whitey) of 40 mL volume equipped with 316 stainless steel valves (Whitey ORM 2) were used in preparations requiring high pressures. Prior to use, these vessels were passivated by treatment with ca. 800 Torr of fluorine gas overnight, followed by vacuum removal of all volatiles at room temperature. Vessels constructed from glass were dried under vacuum on a glass vacuum line for at least 12 h prior to use. Sample preparations involving materials which attack glass were carried out in tubes fashioned from lengths of ¼-in. (7 mm), ¼-in. (14 mm), and ¼" (21 mm) o.d. FEP tubing (Furon) which were heat sealed at one end and heat-flared (45° SAE) at the other. The tubes were then
attached to Kel-F valves encased in aluminum housings by flare fittings. All vessels constructed in this way were dried by first pumping on a glass vacuum line for at least 5 h followed by passivation on a metal vacuum line with ca. 800 Torr of fluorine gas overnight. All volatiles were then removed under vacuum, and the vessel pressurized with 760 Torr of dry N₂ gas.

Nuclear magnetic resonance (NMR) spectra were recorded on samples prepared in FEP tubes (9-mm and 4-mm o.d.). The 9-mm o.d. FEP NMR tubes were fabricated from lengths of 3/8-in. (9.5-mm) o.d. FEP tubing by reducing their diameter to 9-mm o.d. in a heated brass cylindrical form with mechanical pressure. One end of the tube was heat-sealed by pushing it into the end of a thin-walled 10-mm o.d. glass NMR tube previously heated in a Bunsen flame. The other end was heat flared (45° SAE) for direct attachment to a Kel-F valve. The 4-mm o.d. FEP tubing had one end heat scaled by pushing the tube into the end of a thin-walled 5-mm o.d. NMR tube and the other end was heat flared (45° SAE) for direct attachment to a Kel-F valve. The sample tubes used for recording the NMR spectra were heat scaled using a small diameter nichrome wire resistance furnace.

Raman spectra at room temperature were recorded on samples in Pyrex melting point capillaries. Before use, the melting pointing capillaries were heated under dynamic vacuum for 24 h at 200 °C and then stored in a dry nitrogen-filled drybox where they were loaded with the appropriate materials. The ends of the loaded melting point capillaries were filled with Kel-F grease before removal from the drybox. The capillaries were then immediately sealed using a miniature oxygen-natural gas torch. Raman spectra at low temperatures were recorded on samples in FEP or glass tubes. FEP tubes of 7-mm or 4-mm o.d. were heat-sealed at one end and heat flared at the other end (45° SAE) for direct attachment to Kel-F valves. The tubes were fluorinated as above prior to addition of solid materials. Glass tubes for low temperature Raman spectroscopy
were constructed from medium wall 3-mm o.d. glass tubes that were heat sealed at one end and
glassblown onto ca. 5-cm lengths of ¼-in. o.d. glass tubing on the other end. The ¼-in. o.d. end
of each glass tube was attached to a 4-mm J. Young glass stopcock with a Teflon barrel and dried
overnight under high vacuum. The appropriate materials were loaded into each tube in a drybox,
followed by heat sealing below the stopcock using an oxygen-natural gas torch.

Vessels were attached to vacuum lines using Teflon, FEP and/or Kel-F adaptors. All
tubing was connected using ¼-in. Teflon unions (Swagelok) and Teflon compression fittings (back
and front ferrules, Hoke Controls). The fluoroplastic valves and connectors have been described
in greater detail elsewhere.107

(B) PREPARATION AND PURIFICATION OF STARTING MATERIALS

(i) HF, BrF₅ and SO₂ClF Solvents

Hydrogen fluoride and BrF₅ solvents were transferred on a metal vacuum line through all
fluoroplastic connections. Anhydrous hydrogen fluoride (Harshaw Chemical Co.) was purified by
treatment with 5 atm. of F₂ gas in a nickel can for a period of 1 month, converting residual water
to HF and O₂ gas. The anhydrous HF was then vacuum distilled into a dry Kel-F storage vessel
equipped with a Kel-F valve and stored at room temperature until used. Hydrogen fluoride was
transferred into reaction vessels by vacuum distillation on a metal vacuum line through
connections constructed of Teflon, Kel-F and FEP as shown in Figure 2.3.

Bromine pentafluoride (Ozark-Mahoning Co.) was purified as described earlier,107 and
stored over dry KF in a ¾-in. o.d. Kel-F storage tube equipped with a Kel-F valve. Bromine
pentafluoride solvent was transferred into reaction vessels by vacuum distillation on a metal line
through connections constructed of Teflon, Kcl-F and FEP as shown in Figure 2.4.

Sulfuryl chloride fluoride, SO$_2$ClF (Aldrich) was purified according to the literature method$^{108}$ and stored over KF in a glass vessel equipped with a 6-mm glass J. Young stopcock equipped with a glass barrel. Transfers of SO$_2$ClF were performed under vacuum using a vacuum line and tubing constructed of glass as shown in Figure 2.5. Fluorine-19 NMR indicated the presence of a trace of SO$_2$F$_2$ impurity ($\delta^{19}$F) = 32.4 ppm) in the solvent.

(ii) CHCl$_3$, CH$_2$Cl$_2$, (CH$_3$CH$_2$)$_2$O, CH$_3$C= N and CF$_2$ClCF$_2$Cl Solvents

Chloroform, CHCl$_3$ (Caledon Reagent Grade), CH$_2$Cl$_2$ (Caledon Reagent Grade) and CD$_2$Cl$_2$ (Isotech Inc.) were dried by combining the solvent with Davison Type 3A molecular sieves (Fisher Scientific) for 3 days followed by vacuum distillation into a dry glass bulb equipped with a 4-mm glass J. Young stopcock equipped with a Teflon barrel. The molecular sieves were dried under dynamic vacuum for 24 h at 120 °C prior to use as a drying agent.

Acetonitrile, CH$_3$C= N (Caledon HPLC Grade) was purified according to the literature procedure.$^{109}$

Diethyl ether (Fisher Scientific) was refluxed over sodium wire with benzophenone indicator under a dry nitrogen atmosphere until the solution turned blue (ca. 2 h). Refluxing was continued for an additional 10 h, and the ether was then distilled under atmospheric pressure onto fresh sodium wire in a glass vessel equipped with a greaseless 6-mm glass J. Young stopcock equipped with a Teflon barrel. After several days, the ether was vacuum distilled into a similar vessel which had been previously dried under vacuum.

Freon-114, CF$_2$ClCF$_2$Cl (Aldrich), was purified according to the literature method$^{110}$ and was transferred under vacuum using all glass apparatus.
Figure 2.3 Apparatus for the storage and vacuum transfer of anhydrous HF solvent: (A) 250 mL Kel-F HF container equipped with a Kel-F valve, (B) Kel-F Y-connector, (C) FEP tube reactor, (D) Kel-F valve with aluminum casing.
Figure 2.4  Apparatus for the storage and vacuum transfer of BrF$_5$ solvent; (A) ¼-in. o.d. Kel-F storage vessel containing BrF$_5$ over KF, (B) Kel-F Y-connector, (C) FEP tube reactor, (D) Kel-F valve in aluminum casing.
Figure 2.5  Apparatus for the storage and vacuum transfer of SO$_2$ClF solvent; (A) 250 mL glass bulb equipped with a 6-mm glass J. Young stopcock with glass barrel containing SO$_2$ClF over KF, (B) glass Y-connector, (C) FEP tube reactor, (D) 6-mm J. Young glass stopcock with FEP barrel, (E) Kel-F valve with aluminum casing.
(iii) **Purification of SbF₅ and Preparation of AsF₅ and TeF₆**

Antimony pentafluoride, SbF₅ (Ozark-Mahoning Co.) was purified by the literature method¹¹¹ and stored in a glass vessel. Subsequent transfers of SbF₅ were performed using an all glass syringe in the inert atmosphere of a glove bag which had been previously purged with dry nitrogen for 12 h.

Arsenic pentafluoride was prepared according to the literature method¹¹² by the fluorination of AsF₃¹¹³ in a nickel can. The AsF₅ was distilled into a nickel storage cylinder from which it was used without further purification.

Tellurium hexafluoride was prepared from the fluorination of TeF₄, which was prepared according to the literature method,¹¹⁴ in a monel reactor using a 50 mol% excess of elemental fluorine under autogeneous pressure at 250 °C for 4 h. Crude TeF₆ was purified by condensation onto a dry sample of NaF in a stainless steel Whitey cylinder at -196 °C and stored at room temperature for several days prior to use.

(iv) **Preparation of XeF₂ and XeF⁺AsF₆⁻**

Xenon difluoride was prepared from elemental xenon and fluorine by the thermal method described in the literature.¹¹² The salt XeF⁺AsF₆⁻ was prepared from the reaction of XeF₂ and AsF₅ in HF solvent as described earlier.¹⁷³ Both reagents were stored in Kel-F tubes in the inert nitrogen atmosphere of a dry box. All transfers of the solids XeF⁺AsF₆⁻ and XeF₂ were made from their Kel-F storage vessels inside the drybox.

(v) **Preparation of F₅TeOH, B(OTeF₅)₂, As(OTeF₅)₅, and Xe(OTeF₅)₂**

Pentafluoroorthotelluric acid, F₅TeOH,¹¹⁵ B(OTeF₅)₂,¹¹⁶ As(OTeF₅)₅,¹¹⁷ and
Xe(OTeF$_5$)$_2$ were prepared and purified according to the literature procedures. The compounds, B(OTeF$_5$)$_3$ and As(OTeF$_5$)$_5$, were stored in an FEP tube and a PFA jar, respectively, in the inert nitrogen atmosphere of a drybox, and transfers of the solids were performed inside the drybox. The compound, Xe(OTeF$_5$)$_2$, was stored at -78 °C in a ½-in. o.d. FEP vessel equipped with a Kel-F valve under ca. 1300 Torr of dry nitrogen gas. Transfers of Xe(OTeF$_5$)$_2$ into reaction vessels was done in the inert nitrogen atmosphere of a drybox. The compound, F$_5$TeOH, was stored in a ½-in. o.d. FEP vessel equipped with a Kel-F valve back-filled with ca. 1300 Torr of dry nitrogen gas at room temperature. Transfers of F$_5$TeOH were carried out by vacuum sublimation in an all glass apparatus.

(vi) Preparation of CF$_3$C(OH)NH$_2$·AsF$_6$·

In a typical purification procedure, 1.2860 g (11.377 mmol) of 2,2,2-trifluoroacetamide (Aldrich) was purified by recrystallization from 224 g of anhydrous CHCl$_3$ in one arm of an H-vessel (Figure 2.6). The arms of the H-vessel were constructed from 2.5-cm o.d. medium wall glass tubing. The arms of the H-vessel were separated by a medium porosity sintered glass frit. The crystals were isolated by filtration through the frit followed by drying under dynamic vacuum for 12 h at room temperature; 0.6255 g (48.6% yield) of CF$_3$C(O)NH$_2$ was isolated, indicating some degree of volatility of the compound at room temperature.

The salt, CF$_3$C(OH)NH$_2$·AsF$_6$·, was prepared from the reaction of CF$_3$C(O)NH$_2$ and AsF$_5$ in HF solvent according to equations (2.1) and (2.2)

\[
\text{CF}_3\text{C(O)NH}_2 + (x + 1) \text{HF} \longrightarrow \text{CF}_3\text{C(OH)NH}_2^+\text{F(HF)}_x^-
\] (2.1)
\[
\text{CF}_3\text{C(OH)NH}_2^+\text{F(HF)}_x^- + \text{AsF}_5 \rightarrow \text{CF}_3\text{C(OH)NH}_2^+\text{AsF}_6^- + x \text{HF}
\] (2.2)

In a typical preparation of CF$_3$C(OH)NH$_2^+$AsF$_6^-$, CF$_3$C(O)NH$_2$ (1.2708 g, 11.242 mmol) was loaded into a ½-in. o.d. FEP tube attached to a Kel-F valve and dissolved in 4 mL of anhydrous HF at -78 °C, giving a yellow solution. Arsenic pentafluoride was metered from a nickel storage can into a dry 0.4005 L preweighed glass bulb. The AsF$_5$ was condensed onto the CF$_3$C(O)NH$_2$ solution at -196 °C. Weighing of the glass bulb before and after the transfer indicated that 2.5086 g (14.764 mmol) of AsF$_5$ was condensed onto the frozen solution. Warming to -78 °C resulted in a dark orange precipitate and a yellow supernatant. The precipitate dissolved on warming to -50 °C, resulting in a colorless solution. The solvent was removed in vacuo at -42 °C leaving a white microcrystalline material. After pumping for 0.5 h at -42 °C and 3.5 h at -10 °C, 3.3820 g of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ (99.3% yield) was recovered. Decomposition with liquefaction was observed after one month at room temperature, however indefinite storage without decomposition was possible at -78 °C. The salt was stored in the reaction vessel at -78 °C under ca. 1300 Torr of dry nitrogen gas. Transfers of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ were carried out directly from the storage vessel inside a nitrogen-filled drybox.

(vii) **Preparation of the First-Stage Graphite Intercalate C$_{10}$AsF$_5$**

Graphite powder was intercalated with AsF$_5$ using a modified version of the method described by Chun-Hsu et al.$^{118}$ Graphite rod (Ultra Carbon; Spectrographic analysis grade) was ground to a fine powder with a mortar and pestle and dried by heating under vacuum at 150 °C for 24 h. In a nitrogen-filled glove bag, 0.9003 g (74.96 mmol carbon) of the graphite powder was
Figure 2.6  Glass H-vessel; (A) arm of H-vessel constructed from 2.5-cm o.d. medium wall Pyrex glass, (B) Teflon-coated magnetic stir bar, (C) 6-mm J. Young glass stopcock with FEP barrel, (D) medium porosity sintered glass frit, (E) 3/4-in. o.d. glass tubing.
loaded into a passivated ½-in. o.d. FEP tube equipped with a Kel-F valve. Approximately 1500 Torr of AsF₅ gas was expanded from its nickel storage container into the manifold of the metal vacuum line and the reaction vessel containing the graphite powder (-196 °C). With constant agitation of the reaction vessel, the absorption of AsF₅ by the graphite was monitored by observing the pressure in the manifold. Complete absorption of the AsF₅ was observed upon warming the sample to ambient temperature after ca. 10 min. The partially intercalated graphite was blue in color and the volume had increased. This procedure was repeated until no more AsF₅ was absorbed by the graphite. The blue powder was pumped for ca. 1 min. at room temperature to remove any unreacted AsF₅. The sample was then placed under static vacuum and the pressure was monitored. No increase in pressure was observed, indicating the absence of a significant amount of unreacted AsF₅. The mass of the resulting blue powder (2.1398 g) corresponded closely to that expected for a quantitative preparation of C₁₀AsF₅ (2.1740 g). The C₁₀AsF₅ was stored under ca. 1000 Torr of dry nitrogen gas and was used without further characterization.

(viii) Preparation of trans-N₂F₂ and Investigation of cis-trans-N₂F₂ Isomerization at Low Temperature in AsF₅-Acidified HF Solvent

The trans-isomer of difluorodiazone, N₂F₂ was selectively prepared without the formation of a detectable amount of the cis-isomer from the reaction of N₂F₄ and the first stage graphite intercalate C₁₀AsF₅ using the method of Munch and Selig¹¹⁹ according to equation (2.3). In a nitrogen-filled glove bag, 0.3969 g (1.368 mmol) of C₁₀AsF₅ was transferred to a vessel constructed from a fluorinated ½-in. o.d. FEP tube equipped with a Kel-F valve.

\[ \text{C}_{10}\text{AsF}_5 + \text{N}_2\text{F}_4 \rightarrow \text{C}_{10}\text{AsF}_7 + \text{trans-N}_2\text{F}_2 \]

(2.3)
Tetrafluorohydrazine, N₂F₄ (1.312 mmol) was expanded into the manifold of a metal vacuum line and condensed onto the C₁₀AsF₅ at -196 °C. The reaction vessel was slowly warmed to room temperature with periodic agitation. The vessel was allowed to sit for 2 days with periodic shaking. The vessel was pumped under dynamic vacuum at -196 °C. The trans-N₂F₂ produced in this manner was allowed to remain over the AsF₅ intercalated graphite at room temperature. Transfers of trans-N₂F₂ were carried out by allowing the gas to expand from the reaction vessel at room temperature into the manifold of a metal vacuum line. The trans-N₂F₂ was then condensed into the appropriate reaction vessel at -196 °C. The purity of the trans-N₂F₂ was confirmed from the ¹⁹F NMR spectrum at room temperature in Freon-114 solvent (ca. 0.5 M), and consisted of the characteristic AA'XX' spectrum centered at δ(¹⁹F) = 92.2 ppm, as expected. The ¹⁹F NMR resonance of the cis- isomer of N₂F₂ was not observed at ca. δ(¹⁹F) = 133.7 ppm, indicating the selectivity of the reaction.

The possibility of AsF₅-assisted isomerization of trans-N₂F₂ in HF was investigated at low temperature. The trans-isomer of N₂F₂ was expanded into the volume calibrated manifold (0.019 L) of a metal vacuum line at ambient temperature. Using the ideal gas approximation and the measured pressure, the quantity of trans-N₂F₂ in the manifold was determined to be 0.0882 mmol. The contents of the manifold was condensed into a 4-mm FEP tube containing approximately 0.4 mL of HF at -196 °C. Arsenic pentafluoride (0.808 mmol) was likewise expanded into the manifold and condensed into the FEP sample tube at -196 °C. The tube was warmed to -20 °C, whereupon a clear colorless solution was formed. The sample was kept at -20 °C for 5 min., and was then heat sealed at -196 °C under dynamic vacuum. Only trans-N₂F₂, HF and AsF₆⁻ were observed in the ¹⁹F NMR spectrum at -37 °C, indicating that cis/trans-N₂F₂ isomerization did not occur under these conditions.
(ix) **Purification of Ammonia**

Ammonia gas, NH₃ (Canadian Liquid Air, Ltd. or Matheson) was condensed from a gas cylinder into an ammonia drying tube at -78 °C containing freshly cut sodium metal (0.3 - 0.4 g; BDH Chemicals). Liquid ammonia (100 - 200 mL) was stored at -78 °C in a dry ice-acetone bath for at least one week prior to use. Transfers of ammonia gas directly from the storage vessel were performed under vacuum using all glass apparatus.

(x) **Preparation of ¹⁵N-Enriched (99.5 atom %) Ammonia**

The apparatus shown in Figure 2.7, which was modified from the literature,¹²² was dried under vacuum for 12 h and back-filled with nitrogen gas. Nitrogen-15 enriched NH₃ was prepared according to equation (2.4). A solution of 99.5 atom % ¹⁵NH₄Cl (1.2083 g; MSD Isotopes or Isotech, Inc.) in 10 mL of distilled water was prepared and pipetted into the round bottom flask of the apparatus. The apparatus was sealed using ½-in. Teflon unions (Swagelok) as shown in Figure 2.7 and the pressure above the solution was decreased to 450 Torr of dry nitrogen with the U-trap immediately following the reflux column cooled to -196 °C. The stopcock immediately following the -196 °C U-trap was closed and the aqueous solution was gently heated with a heat gun to initiate gentle reflux, which slowly leached the KOH pellets (13.47 g) situated on platform B directly above the reaction flask into the solution, whereupon ¹⁵NH₃ gas was evolved from the aqueous solution and collected in the U-trap at -196 °C. After the reflux subsided, additional NH₃

\[
¹⁵NH₄Cl + xs KOH \xrightarrow{H₂O} KCl + ¹⁵NH₃
\]  

(2.4)
Figure 2.7  Glass ammonia generator: (A) Approximately 50 mL round bottom flask, (B) platforms with 3-3.5 mm diameter holes to support KOH pellets, (C) condenser, (D) 3/8-in. Teflon unions (Swagelok) equipped with 3/8-in. Teflon compression fittings (Swagelok), (E) sections of 3/8-in. o.d. glass tubing, sealed at one end, (F) 6-mm glass J. Young stopcock with FEP barrel, (G) 1/4-in. Teflon unions (Swagelok) equipped with 1/4-in. Teflon compression fittings (Swagelok), (H) 120 or 300 mL glass flask.
gas was liberated from the aqueous solution by cooling the solution to -78 °C and evacuating the vessel by quickly opening and closing the stopcock immediately following the 196 °C U-trap. Warming the solution until liquefaction resulted in condensation of additional \(^{15}\text{NH}_3\) gas into the -196 °C U-trap. This was repeated until condensation of additional \(^{15}\text{NH}_3\) was no longer observed in the -196 °C U-trap. The U-trap was warmed to -78 °C and the \(^{15}\text{NH}_3\) was slowly condensed over ca. 3 h under static vacuum into a second U-trap at -196 °C. The second trap was warmed to -78 °C and the \(^{15}\text{NH}_3\) was condensed under static vacuum into a preweighed 120 mL glass bulb at -196 °C. The glass bulb was warmed to room temperature and weighed; 0.3949 g of \(^{15}\text{NH}_3\) was isolated (98.83 % yield).

(xi) Preparation of 99.5 atom % \(^{15}\text{N}\) Enriched \([\text{CH}_3\text{Si}]_2\text{NH}\)

The method of Sauer,\(^{123}\) was modified for the synthesis of \([\text{CH}_3\text{Si}]_2^{15}\text{NH}\) from \(^{15}\text{NH}_3\) gas and \((\text{CH}_3)_2\text{SiCl}\) using Freon-114 as solvent, according to equation (2.5)

\[
3^{15}\text{NH}_3 + 2(\text{CH}_3)_2\text{SiCl} \longrightarrow [(\text{CH}_3)_2\text{Si}]_2^{15}\text{NH} + 2^{15}\text{NH}_4\text{Cl}
\]  

(2.5)

Chlorotrimethylsilane (Aldrich) was purified by vacuum distillation into a dry glass bulb equipped with a grease-free 4-mm glass J. Young stopcock equipped with a Teflon barrel. By vacuum distillation, 1.6144 g (14.86 mmol) of \((\text{CH}_3)_2\text{SiCl}\) was transferred into a dry glass H-vessel equipped with a medium porosity sintered glass frit between the two arms of the vessel (Figure 2.6). Freon-114 (16.3 g) was distilled onto the \((\text{CH}_3)_2\text{SiCl}\) at -196 °C. A clear colorless solution resulted on warming to room temperature. Nitrogen-15 enriched \(\text{NH}_3\) (0.3949 g, 21.92 mmol) was vacuum transferred onto the frozen solution of \((\text{CH}_3)_2\text{SiCl}\) and Freon-114 (-196 °C). The vessel
was allowed to warm slowly to ambient temperature with stirring. Upon liquefaction of the solvent, a white precipitate formed. After stirring for 7 days, the contents of the arm containing the white precipitate was cooled to -60 °C. With the other arm at -60 °C, the mixture was filtered, giving a clear colorless filtrate. The white precipitate was washed three times by repeated back-distilling of solvent (with the appropriate arms of the vessel at -40 and -60 °C) followed by filtration as above. The bulk of the solvent was back-distilled onto the residue after the last filtration, and the resulting clear liquid was distilled through a one-piece glass dual-trap apparatus (Figure 2.8), with the U-traps cooled to -40 and -196 °C. Pure [(CH$_3$)$_3$Si]$_2^{15}$NH was collected in the -40 °C U-trap (1.0345 g, 87.2 % yield). The $^1$H NMR parameters are similar to those reported by Cowley et al.$^{124}$ (neat liquid at 25 °C): δ($^1$H) = -0.61 ppm (CH$_3$), $^2$J($^1$H-$^{29}$Si) = 6.6 Hz, δ($^1$H) = 0.52 ppm (NH), $^1$J($^1$H-$^{15}$N) = 63.1 Hz. The -196 °C trap contained freon-114 (CF$_2$ClCF$_2$Cl), (CH$_3$)$_3$SiCl, and a trace of [(CH$_3$)$_3$Si]$_2^{15}$NH.

(xii) **Preparation of F$_5$TeNHSi(CH$_3$)$_3$**

The compound, F$_5$TeNHSi(CH$_3$)$_3$, was prepared using the method of Seppelt et al.$^{125}$ with modifications, according to equation (2.6). In a typical preparation, [(CH$_3$)$_3$Si]$_2$NH

$$\text{TcF}_6 + [(\text{CH}_3)_3\text{Si}]_2\text{NH} \rightarrow \text{F}_5\text{TeNHSi}[(\text{CH}_3)_3 + (\text{CH}_3)_3\text{SiF} \quad (2.6)$$

(1.79946 g, 11.149 mmol; Aldrich) was vacuum distilled into a 40 mL Whitey 304 stainless steel cylinder equipped with a Whitey ORM 2 valve, cooled to -196 °C. The cylinder was passivated with fluorine gas (ca. 1000 Torr) prior to use. Tellurium hexafluoride was expanded into the volume calibrated (0.019 L) manifold of a metal vacuum line equipped with a 1.976 L nickel
Glass dual U-trap apparatus; (A) glass H-vessel (see Figure 2.6), (B) ¼-in. Teflon unions (Swagelok) equipped with ¼-in. Teflon compression fittings (Swagelok), (C) 6-mm glass J. Young stopcock with FEP barrel, (D) 304 SS 40 mL cylinder (Whitey) equipped with a 316 SS valve (Whitey ORM 2).
ballast can at ambient temperature (total volume, 1.995 L). The pressure of TeF₆ was converted
to moles using the ideal gas approximation. A total pressure of 134 Torr (14.4 mmol) of TeF₆ was
transferred into the cylinder, which was cooled to -196 °C. The cylinder was allowed to warm
slowly to ambient temperature and then shaken mechanically for 1 week. Excess TeF₆ and
(CH₂)₃SiF were pumped off at -50 °C. After no vapor pressure was detected, the cylinder was
warmed to room temperature and subjected to vacuum distillation using a one-piece glass dual U-
trap apparatus (Figure 2.8); the first trap (-30 °C) contained 2.365 g (68.2 % yield) of pure
F₅TeNHSi(CH₂)₃ (checked by ¹⁹F and ¹H NMR). The explosive cis-F₂Te[N(H)Si(CH₂)₃]₂ is often a minor product in the synthesis, was not observed in the ¹⁹F NMR spectra. The
second trap (-196 °C) contained (CH₂)₃SiF, [(CH₂)₃Si]₂NH, and some products which were not
identified.

Seppelt¹²⁵ noted that the successful synthesis of F₅TeNHSi(CH₂)₃ free from significant
amounts of explosive cis-F₂Te[N(H)Si(CH₂)₃]₂ required that the stainless steel reaction vessel be
rinsed with concentrated nitric acid between runs and the reaction be carried out at room
temperature. In the present work, concentrated hydrochloric acid was substituted for nitric acid
as the rinsing agent.

(xiii) Preparation of F₅TeNH₂ and F₅Te¹⁵NH₂

The compounds, F₅TeNH₂ and F₅Te¹⁵NH₂, were prepared by a modification of the
published synthesis.¹²⁵ Typically [(CH₂)₃Si]₂NH (0.7485 g, 4.637 mmol; Aldrich) and TeF₆
(6.056 mmol) were combined in a 40 mL Whitey 304 stainless steel cylinder for 1 week followed
by vacuum distillation of all volatiles at -50 °C, as outlined above for the preparation of
F₅TeNHSi(CH₂)₃. The compound, F₅TeNHSi(CH₂)₃, was allowed to react with HF in an
\((\text{CH}_3)_2\text{SiF}\) elimination reaction according to equation (2.7). Anhydrous HF (0.1705 g, 8.505 mmol) was transferred by vacuum distillation into the cylinder at -196 °C. The cylinder was allowed to warm to ambient temperature and was mechanically agitated overnight. Volatiles were removed under vacuum at -78 and at -40 °C. The cylinder was warmed to 40 °C and the remaining material was sublimed under vacuum into a ¼-in. o.d. FEP vessel cooled to -196 °C. A sticky white solid was isolated, identified by \(^{19}\text{F}\) NMR spectroscopy as \(\text{F}_2\text{TeNH}_2\) (0.5688 g; 51.41% yield).\(^{125}\)

The synthesis of \(\text{F}_5\text{Te}^{15}\text{NH}_2\) was identical to that of \(\text{F}_2\text{TeNH}_2\), except that 99.5 atom % \(^{15}\text{N}\) enriched \(((\text{CH}_3)_2\text{Si})_2\text{NH}\) was used in the preparation of the former. The \(^{15}\text{N}\) enriched \(((\text{CH}_3)_2\text{Si})_2\text{NH}\) isolated in the -40 °C U-trap [see Section (B), Part (xi)] was condensed into the 40 mL stainless steel vessel attached to the dual trap apparatus depicted in Figure 2.8. The remainder of the procedure for the preparation of \([^{15}\text{N}]\text{F}_5\text{TeNH}_2\) was identical to that for \(\text{F}_5\text{TeNH}_2\). The compounds, \(\text{F}_5\text{TeNH}_2\) and \(\text{F}_5\text{Te}^{15}\text{NH}_2\), were stored in FEP tubes inside the drybox. Transfers of the reagents were made from the FEP storage vessels inside the drybox.

(xiv) Preparation of \(\text{F}_5\text{TeNH}_3^{+}\text{AsF}_6^{-}\) and \(\text{F}_5\text{Te}^{15}\text{NH}_3^{+}\text{AsF}_6^{-}\)

The salt, \(\text{F}_5\text{TeNH}_3^{+}\text{AsF}_6^{-}\), was prepared from the reaction of \(\text{F}_5\text{TeNH}_2\) with excess AsF\(_3\) in anhydrous HF solvent according to equations (2.8) and (2.9). In a typical preparation,

\[
\text{F}_5\text{TeNH}_2 + (x + 1) \text{HF} \rightarrow \text{F}_5\text{TeNH}_3^{+}\text{F(HF)}_x^{-} \tag{2.8}
\]
\[ F_2\text{TeNH}_2^+\text{F(HF)}_x^- + \text{AsF}_5 \rightarrow F_2\text{TeNH}_2^+\text{AsF}_6^- + x \text{HF} \quad (2.9) \]

1.1873 g (4.9758 mmol) of \( F_2\text{TeNH}_2 \) was placed in a \( \frac{1}{8} \)-in. o.d. FEP tube which was flared (45° SAE) and connected by means of compression fittings to a Whitey ORM 2 316 stainless steel valve. Anhydrous HF (4 mL) was distilled onto the \( F_2\text{TeNH}_2 \) (-196 °C). Warming to -78 °C resulted in a colorless solution. Arsenic pentafluoride (6.1 mmol) was condensed onto the frozen solution at -196 °C. Warming to -55 °C resulted in a colorless solution. Excess \( \text{AsF}_5 \) was removed under vacuum at -78 °C. The HF solvent was removed under vacuum at -40 °C until 2.0442 g of a white powder remained (96% yield), with no detectable vapor pressure at this temperature. The salt, \( F_2\text{TeNH}_2^+\text{AsF}_6^- \), is stable indefinitely under anhydrous conditions at room temperature and hydrolyzes rapidly in the presence of water.

The preparation of \( F_2\text{Te}^{15}\text{NH}_3^+\text{AsF}_6^- \) was identical to that described for \( F_2\text{TeNH}_3^+\text{AsF}_6^- \) using \( F_2\text{Te}^{15}\text{NH}_2 \) as the starting material. The salts were stored at room temperature in \( \frac{1}{8} \)-in. or \( \frac{1}{4} \)-in. o.d. FEP tubes inside a nitrogen-filled drybox. Transfers of the salts were made directly from the storage vessels inside the drybox.

(xv) Preparation of \( F_2\text{TeNH}_3^+\text{As(OTeF}_2)_6^- \)

In a \( \frac{1}{4} \)-in. o.d. FEP tube equipped with a Kel-F valve, \( F_2\text{TeOH} \) (0.09635 g, 0.4021 mmol) was combined with \( \text{As(OTeF}_2)_5 \) (0.49494 g, 0.39037 mmol) and \( F_2\text{TeNH}_2 \) (0.10858 g, 0.45504 mmol) at -196 °C. The solvent, \( \text{SO}_2\text{ClF} \), was vacuum distilled onto the reagents at -196 °C, giving a clear colorless solution on warming to -78 °C (ca. 0.7 M). The \( \text{SO}_2\text{ClF} \) solvent was removed at -32 °C under vacuum, leaving a sticky white precipitate. A finely divided white powder resulted on further vacuum pumping at -45 °C for 2 h.
(xvi) Sulfur trioxide

Sulfur trioxide, SO$_3$ (Sulfan B: Allied Chemical) was heated to ca. 65 $^\circ$C for 2 h to effect depolymerization.$^{126}$ The liquified SO$_3$ was then poured into a dry evacuated round bottom flask equipped with a greaseless 6-mm glass J. Young stopcock equipped with a Teflon barrel and used without further purification.

(xvii) Preparation of S$_2$O$_5$F$_2$

The anhydride of fluoroosulfuric acid, S$_2$O$_5$F$_2$, was prepared, with modification, using the method of Gillespie and Rothenbury,$^{127}$ by the reaction of excess SO$_3$ with SbF$_5$. The reactions were conducted in the vessel depicted in Figure 2.9. Two 3/8-in. o.d. FEP tubes were sealed at one end and fused to lengths of ¼-in. o.d. FEP tubing. The tubes were joined using a ¼-in. Teflon T-piece union (Swagelok) with Teflon compression fittings (Swagelok). A Kel-F valve was attached as shown in Figure 2.9. In a typical preparation, SbF$_5$ (12.0880 g, 0.0557713 mol) was syringed into the FEP tube to be attached at 90° to the Kel-F valve inside a dry nitrogen-filled glove bag. Sulfur trioxide (ca. 16 mL) was vacuum sublimed through an all glass apparatus into the FEP tube to be attached at 180° to the Kel-F valve. The SbF$_5$ was gently heated with a heat gun and poured onto the SO$_3$ at 50 $^\circ$C. After 5 h at 50 $^\circ$C with intermittent shaking, a clear liquid below a white solid resulted. The liquid was vacuum distilled into a dry ¼-in. o.d. FEP tube equipped with a Kel-F valve containing approximately an equal volume of H$_2$SO$_4$ (>99%, Fisher Scientific) to remove excess SO$_3$. The white solid, reported to consist mainly of antimony oxides,$^{127}$ did not
Figure 2.9  FEP T-vessel for preparation of $\text{S}_2\text{O}_3\text{F}_2$; (A) 3/8-in. o.d. FEP tubing, heat-scaled at one end, (B) 3/8-in. Teflon T (Swagelok) equipped with Teflon 3/8-in. compression fittings (Swagelok), (C) 3/8-in. FEP tubing drawn down to 3/16-in. o.d. using a Bunsen flame for attachment by a flare fitting (45° SAE) to a Kel-F valve, (D) Kel-F valve in aluminum casing.
transfer under vacuum. Two liquid phases resulted after 1 h at 55 °C. Some white solid (assumed
to be SO₂) was observed at the interface of the two liquids. After mixing intermittently at 55 °C
for several hours, the volatile contents of the tube were vacuum distilled onto a second
approximately equal volume of >99% H₂SO₄. After mixing at 55 °C for several hours, the white
solid at the liquid interface had dissolved, leaving two liquid phases. The volatile layer (low
density phase) was vacuum distilled into a dry ¼-in. o.d. FEP tube equipped with a Kel-F valve
and shown to be pure S₂O₅F₂ (8.3798 g; 33% yield based on SbF₅) from the gas phase infrared
spectrum¹²⁸ (3 Torr pressure, 1 dm pathlength, AgCl windows).

(xviii) Preparation of 99.5 atom% ¹⁵N Enriched FO₂SNH₂

The compound, FO₂S¹⁵NH₂, was prepared by the reaction of ¹⁵NH₃ and S₂O₅F₂¹²⁹
at low temperature in diethyl ether solvent according to equation (2.10). In a typical preparation,

\[
2 ^{15} \text{NH}_3 + S_2O_5F_2 \rightarrow FO_2S^{15}NH_2 + ^{15} \text{NH}_4 ^+SO_3F^- \quad (2.10)
\]

S₂O₅F₂ (3.9559 g, 21.722 mmol) was vacuum distilled into an arm of a glass H-vessel (Figure
2.6). Diethyl ether (34 mL) was vacuum distilled onto the S₂O₅F₂ at -196 °C. A colorless solution
resulted on warming to room temperature. Under static vacuum, 99.5 atom % ¹⁵N enriched NH₃
(0.7890 g, 43.80 mmol) was condensed into the empty arm of the H-vessel at -196 °C. Both arms
of the H-vessel were cooled to -78 °C for 3 days. The arm containing the ether/S₂O₅F₂ solution
was warmed to -60 °C and the arm containing the ¹⁵NH₃ was warmed to -45 °C. The middle
stopcock was opened and with constant stirring by means of a magnetic stir bar and intermittent
opening and closing of the middle stopcock, the ¹⁵NH₃ had essentially completely reacted after
ca. 0.5 h, as indicated by the almost complete consumption of the pool of liquid $^{15}$NH$_3$ in the
-45 °C arm. This was accompanied by the development of a white precipitate in the ether solution.
The ether solution was then frozen at -196 °C to condense any unreacted $^{15}$NH$_3$ gas into the arm
containing the frozen ether solution, and the middle stopcock was closed. The ether solution was
warmed to -60 °C for an additional 0.5 h with constant stirring. The empty arm of the H-vessel
was cooled to -78 °C, and with the arm containing the ether solution at room temperature, the
middle stopcock was opened and the ether solution was filtered through the medium porosity
sintered glass frit; however, filtration was slow. It was necessary to slightly warm the frit with
a heat gun to prevent freezing of the FO$_2$S$^{15}$NH$_2$ (m.p., 8 °C)$^{129}$ upon evaporation of the diethyl
ether from the frit. Filtration required ca. 2 h to complete. The white precipitate was washed by
back-distilling diethyl ether into the arm. This was facilitated with a -78 / 25 °C temperature
gradient. After washing the precipitate, four additional filtrations and washings were performed
using the conditions described above. After an additional filtration, the ether solution was pipetted
into a one-piece glass distillation vessel (Figure 2.10) in a dry nitrogen-filled glove bag. Most of
the diethyl ether was removed under vacuum at 0 °C, leaving a yellow viscous liquid. The liquid
was distilled under static vacuum while heating the liquid gently with a heat gun and cooling the
distillate receptacle to -196 °C. A clear liquid distillate was isolated, leaving behind a solid yellow
residue. The distillate was then pumped at 0 °C for 2 h under dynamic vacuum, and redistilled
at room temperature under dynamic vacuum in a micro-distillation apparatus (Figure 2.11);
0.6859 g of a colorless liquid was isolated. $^1$H NMR (CD$_3$C=H solution): doublet of doublets,
$\delta$(H) = 6.79 ppm, $^1$J(H-15N) = 86.7 Hz, $^3$J(H-19F) = 6.1 Hz. Multiplets at $\delta$(H) = 1 - 5 ppm
indicated the presence of residual organic material (ca. 5 - 10%). $^{19}$F NMR: triplet of doublets,
$\delta$(F) = 56.78 ppm, $^2$J(H=19F,15N) = 2.7 Hz, $^3$J(F=19F,1H) = 6.3 Hz. The Raman spectrum (neat
Figure 2.10  Glass distillation apparatus used to fractionate \( \text{FO}_2\text{SNH}_2 \) and \( ^{15}\text{N} \)-enriched \( \text{FO}_2\text{SNH}_2 \); (A) 250 mL round bottom flask, (B) Teflon-coated magnetic stir bar, (C) entrance for stir bar after annealing of glass apparatus (now sealed), (D) 6-mm glass J. Young stopcock with FEP barrel, (E) \( \frac{1}{4} \)-in. o.d. glass tubing, (F) receptacle arm tapered to allow removal of distillate by pipet.
liquid) was similar to the infrared spectrum of FO$_2$SNH$_2$ with residual organic impurities containing ether groups. Raman bands of impurity (relative intensities): 2991.9 (5.2), 2952.4 (10.0), 2941.8 (6.2), 2910.6 (2.3), 2885.7 (2.3), 2735.0 (0.4), 1458.1 (1.7), 1449.2 (1.6), 1104.2 (1.6), 1074.8 (1.2), 1061.4 (0.6), 1050.3 (0.3), 689.0 (0.6), 658.9 (0.4), 594.8 (0.7), 577.3 (0.9), 408.1 (1.5), 395.0 (2.1), 336.3 cm$^{-1}$ (3.1). Multiple distillations did not remove the residual organic impurity.

(xix) Preparation of FO$_2$SNH$_2$

Natural abundance FO$_2$SNH$_2$ was prepared according to equations (2.11) and (2.12)

$$\text{ClO}_2\text{SNCO} + \text{NaF} \rightarrow \text{NaCl} + \text{FO}_2\text{SNCO} \quad (2.11)$$

$$\text{FO}_2\text{SNCO} + \text{H}_2\text{O} \rightarrow [\text{FO}_2\text{SN(H)(C)(O)OH}] \xrightarrow{\Delta} \text{FO}_2\text{SNH}_2 + \text{CO}_2 \quad (2.12)$$

In a typical preparation, chlorosulfuryl isocyanate, ClO$_2$SNCO (14.0027 g; Aldrich) was pipetted into a 250 mL glass distillation vessel (Figure 2.10) in a dry nitrogen-filled glove bag. Dry acetonitrile (50 mL) was vacuum distilled onto the ClO$_2$SNCO at -196 °C. A clear solution resulted at room temperature, which turned pale yellow after 1 h. Dry NaF (4.4496 g; J.T. Baker) was added to the solution under a dry nitrogen atmosphere with stirring by means of a magnetic stir bar. The solution immediately became intense yellow. The vessel was closed and the reaction mixture was heated at 70 °C for 2.5 h. The contents of the vessel were frozen at -78 °C and 1.782 g of distilled water was added to the empty arm of the reaction vessel with a pipet.
Figure 2.11  Glass micro-distillation apparatus used to fractionate \( \text{FO}_2\text{SNH}_2 \): (A) 50 mL round bottom flask, (B) Teflon coated stir bar, (C) 4-mm glass J. Young stopcock with FEP barrel, (D) \( \frac{1}{4} \)-in. o.d. glass tubing, (E) condenser, (F) thermocouple inlet for temperature determination, (G) B19 ground glass joint, lubricated with Apiezon "N" grease, (H) \( \frac{1}{4} \)-in. Teflon unions (Swagelok) equipped with \( \frac{1}{4} \)-in. Teflon compression fittings (Swagelok), (I) glass tapered receiving tubes.
With both arms of the vessel cooled to -78 °C, the reaction vessel was evacuated. The acetonitrile solution was cooled to -196 °C and the arm containing the water was warmed to room temperature. The water sublimed to the walls immediately above the frozen acetonitrile solution, where it immediately froze. The vessel was back-filled with approximately 760 Torr of nitrogen gas and the arm of the vessel containing the reagents was allowed to slowly warm to room temperature. The pressure of the system was monitored by leaving the vessel open to the mercury manometer of a glass vacuum line. As the water melted, immediate bubbling with an increase in pressure of 10 Torr occurred each time a drop of water was added to the stirred yellow reaction mixture. The pressure increase resulting from the evolution of CO₂ gas upon decomposition of the unstable carbamic acid, FO₂SN(H)C(O)OH, according to equation (2.12), was released by opening the stopcock to the vacuum line until the total pressure of the reaction vessel was reduced to ca. 760 Torr. Shortly after the addition of the water was complete, the large increases in pressure ceased. The pressure was monitored and occasionally adjusted to ca. 760 Torr while the solution was heated to 70 °C with constant stirring for 2 h. No significant increase in pressure was observed during this time. The vessel was cooled to 0 °C and most of the CH₃CN solvent was removed under dynamic vacuum. After ca. 1 h, a yellow mixture of liquid and solid material remained. The empty arm of the vessel was cooled to -196 °C while under static vacuum and the yellow material was gently warmed with a heat gun. A colorless liquid distillate was collected, leaving behind a yellow powder. The colorless distillate was redistilled under dynamic vacuum at room temperature using the micro-distillation apparatus depicted in Figure 2.11. Pure FO₂SNH₂ (4.3908 g, 45% yield based on FO₂SNCO) was obtained. ¹H NMR (neat liquid): δ(¹H) = 5.41 ppm (singlet). ¹⁹F NMR (neat liquid): 56.52 ppm (singlet). The FO₂SNH₂ was stored in a ¾-in. o.d. FEP vessel in the drybox. Transfers of FO₂SNH₂ were carried out by pipetting the colorless
liquid directly from the FEP storage vessel inside the drybox.

(xx) Preparation of Natural Abundance and $99.5 \% ~^{15}\text{N}-\text{Enriched} ~ \text{FO}_2\text{SNH}_2^{+}\text{AsF}_6^{-}$

The natural abundance and $99.5 \% ~^{15}\text{N}-\text{enriched}$ salts, $\text{FO}_2\text{SNH}_2^{+}\text{AsF}_6^{-}$, were prepared from the reaction of $\text{AsF}_5$ with $\text{FO}_2\text{SNH}_2$ or $\text{FO}_2\text{S}^{15}\text{NH}_2$ in HF solvent at $-40$ °C (equation (2.13))

$$
\text{FO}_2\text{SNH}_2 + \text{HF} + \text{AsF}_5 \longrightarrow \text{FO}_2\text{SNH}_2^{+}\text{AsF}_6^{-} \quad (2.13)
$$

In a typical preparation, natural abundance $\text{FO}_2\text{SNH}_2$ (0.3056 g, 3.084 mmol) was pipetted into a $\frac{1}{4}$-in. o.d. FEP tube equipped with a Kel-F valve. Approximately 0.6 mL of anhydrous HF was condensed onto the $\text{FO}_2\text{SNH}_2$ at $-196$ °C. Warming to $-78$ °C resulted in a clear colorless solution. The contents of the tube were cooled to $-196$ °C and 3700 Torr of $\text{AsF}_5$ was expanded into the manifold of a metal vacuum line (manifold volume $\approx$ ca. 19 mL). The $\text{AsF}_5$ was condensed into the tube at $-196$ °C (3.8 mmol $\text{AsF}_5$ transferred using the ideal gas approximation). Upon warming to $-78$ °C with constant agitation of the reaction tube, a white precipitate formed with a colorless supernatant. The HF was pumped off at $-40$ °C over 2 h, resulting in a finely divided white powder (0.7923 g; 88.91% yield).

(C) PREPARATION OF THERMALLY UNSTABLE XENON-NITROGEN AND XENON-OXYGEN BONDED CATIONS

The xenon-nitrogen bonded cations $\text{FO}_2\text{SN(H)-Xe}^{+}$ and $\text{F}_5\text{TeN(H)-Xe}^{+}$ were prepared by combining stoichiometric amounts of $\text{FO}_2\text{SNH}_2$ or $\text{F}_5\text{TeNH}_2$ with $\text{XeF}^{+}\text{AsF}_6^{-}$ in HF solvent at $-196$ °C followed by warming to -50 to -30 °C to effect reaction and dissolution. Alternatively,
the xenon-nitrogen bonded cations $\text{FO}_2\text{SN(H)-Xe}^+$ and $\text{F}_5\text{TeN(H)-Xe}^+$ and the xenon-oxygen bonded cation $\text{CF}_3\text{C(OXeF)NH}_2^+$ were prepared by combining the hexafluoroarsenate salts of the protonated ligands, namely $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$. $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ and $\text{CF}_3\text{C(OH)NH}_2^+\text{AsF}_6^-$ with stoichiometric amounts of XeF$_2$ in BrF$_5$ solvent at -196 °C followed by warming to -65 to -50 °C to effect reaction and dissolution. The cation $\text{F}_5\text{TeN(H)-Xe}^+$ was also prepared by combining stoichiometric amounts of $\text{F}_5\text{TeNH}_3^+\text{As(OTeF}_2)_6^-$ and Xe(OTeF$_2$)$_2$ in SO$_2$ClF solvent at -196 °C followed by warming to -60 °C to effect reaction and dissolution. The xenon-nitrogen and xenon-oxygen bonded cations were characterized in solution by $^{129}\text{Xe}$, $^{15}\text{N}$, $^{19}\text{F}$, $^1\text{H}$, $^{125}\text{Te}$ and $^{13}\text{C}$ NMR spectroscopy and in the solid state by Raman spectroscopy.

(i) Preparation and Isolation of $\text{CF}_3\text{C(OXeF)NH}_2^+\text{AsF}_6^-$

Solid samples of $\text{CF}_3\text{C(OXeF)NH}_2^+\text{AsF}_6^-$ were prepared and characterized by low-temperature Raman spectroscopy. In a typical preparation, 0.1987 g (1.758 mmol) $\text{CF}_3\text{C(O)NH}_2$ was dissolved in ca. 1 mL of anhydrous HF at -50 °C in a prefluorinated reaction vessel constructed from a 1/4-in. o.d. FEP tube equipped with a Kel-F valve. The tube was cooled to -196 °C and 0.5970 g (1.760 mmol) of XeF$_2$AsF$_6^-$ was added. The sample was warmed to -50 °C with agitation, whereupon approximately 95% of the white solid material dissolved. The supernatant was pale yellow. It was necessary to remove the HF solvent under vacuum very slowly to prevent precipitation of the $\text{CF}_3\text{C(OH)NH}_2^+\text{AsF}_6^-\cdot\text{XeF}_2\cdot\text{nHF}$ adduct [see Part (iii) of this Section]. The sample was slowly pumped under dynamic vacuum, reducing the solvent volume by ca. 75% after 3 h. At this point all of the solid dissolved, and the solution was pale yellow. After a further 3 h of pumping under dynamic vacuum, a free flowing white powder remained. The Raman spectrum indicated the presence of solvated HF from the broad peaks at
3150, 3175, and 3299 cm\(^{-1}\), assignable to HF hydrogen bonded to the amido group. This assignment was made by analogy with bands at 3250, 3393 and 3526 cm\(^{-1}\) observed in the infrared spectrum of CF\(_3\)C(O)NH\(_2\) and HF condensed on a CsI window at 12 K.\(^{125}\) The HF was removed by pumping at -50 °C for 14.5 h using a glass vacuum line and an intermediate copper U-trap (-196 °C) for HF trapping. Removal of HF was confirmed by the absence of the peaks attributable to hydrogen bonded HF in the low temperature Raman spectrum.

(ii) Preparation of NMR Samples of CF\(_3\)C(OXeF)NH\(_2\)\(^{+}\)AsF\(_6\)\(^{-}\)

The CF\(_3\)C(OXeF)NH\(_2\)\(^{+}\) cation was characterized in BrF\(_5\) solution by \(^1\)H, \(^{13}\)C, \(^{19}\)F and \(^{129}\)Xe NMR spectroscopy. The salt, CF\(_3\)C(OH)NH\(_2\)\(^{+}\)AsF\(_6\)\(^{-}\), (0.01668 g, 0.05504 mmol) was transferred into a 4-mm o.d. FEP tube; the tube was cooled to -196 °C and XeF\(_2\) (0.00985 g, 0.0582 mmol) was added. Bromine pentafluoride (0.3 mL) was condensed onto the walls of the tube above the reagents at -196 °C. The BrF\(_5\) slowly melted upon warming the tube to -60 °C. After agitating for approximately 10 min. at -55 °C, a pale yellow solution resulted. A similar procedure was followed using a 9-mm o.d. FEP tube, and the amounts of reagents were 0.13405 g (0.44250 mmol) CF\(_3\)C(OH)NH\(_2\)\(^{+}\)AsF\(_6\)\(^{-}\), 0.0840 g (0.496 mmol) XeF\(_2\) and 1.7 mL of BrF\(_5\). The tubes were heat sealed under dynamic vacuum at -196 °C and stored at this temperature prior to recording their NMR spectra at -60 to -50 °C.

(iii) Preparation and Isolation of CF\(_3\)C(OH)NH\(_2\)\(^{+}\)AsF\(_6\)\(^{-}\)XeF\(_2\) \(\times\) HF

In a typical preparation, CF\(_3\)C(OH)NH\(_2\)\(^{+}\)AsF\(_6\)\(^{-}\) (0.0919 g, 0.303 mmol) and XeF\(_2\) (0.0516 g, 0.305 mmol) were combined in a 4-mm o.d. FEP tube at -196 °C and dissolved in ca. 0.4 mL of anhydrous HF at -50 °C, following the same procedure as was used in the preparation of
CF₃C(OXeF)NH₂⁺AsF₆⁻ [see Part (i) of this Section]. Alternatively, the reaction of equimolar amounts of CF₃C(O)NH₂ and XeF⁺AsF₆⁻ resulted in the isolation of the same product. The solvent was rapidly pumped off at -50 °C, resulting in the isolation of a free flowing white powder after 1 h. The Raman spectrum (-160 °C) was consistent with the formulation CF₃C(OH)NH₂⁺AsF₆⁻·XeF₂·xHF. The sample was further pumped for 28 h at -50 °C using a glass vacuum line with an intermediate copper U-trap (-196 °C). The Raman spectrum (-160 °C) was still consistent with the formulation, CF₃C(OH)NH₂⁺AsF₆⁻·XeF₂·xHF. Anhydrous HF was then condensed onto the white solid at -196 °C, giving a pale yellow solution after periodic agitation for 15 min at -50 °C (0.55 mL volume). After slow removal of the solvent under dynamic vacuum for 4 h, a white free flowing powder was isolated. The low temperature Raman spectrum was consistent with the formulation CF₃(OXeF)NH₂⁺AsF₆⁻.

(iv) Preparation and Isolation of F₅TeN(H)⁺Xe⁺AsF₆⁻ and [¹⁵N]F₅TeN(H)⁺Xe⁺AsF₆⁻.

A typical preparation involved combining XeF₂ (0.0660 g, 0.390 mmol) and F₅TeNH₂⁺AsF₆⁻ (0.1716 g, 0.3995 mmol) in a 4-mm o.d. FEP tube fused to a ¼-in. (7-mm) o.d. T-piece with a Kel-F valve (Figure 2.12). The 4-mm o.d. tube was maintained at -196 °C to prevent reaction of the solids. Anhydrous HF (0.5 mL) was vacuum distilled onto the reagents, resulting in a colorless solution at -40 °C. The solution was warmed to -36 °C, resulting in a pale yellow solution after 5 minutes. The yellow color is attributed to the formation of the F₅TeN(H)⁺Xe⁺ cation in solution. Alternatively, stoichiometric amounts of XeF⁺AsF₆⁻ and F₅TeNH₂ combined in HF solvent as described above result in the generation of the F₅TeN(H)⁺Xe⁺ cation in solution. After 40 minutes, a deposit of orange crystals with a pale yellow supernatant was present. The sample was cooled to -40 °C, resulting in the precipitation of more crystals of the
Figure 2.12  FEP vessel for isolation of \( \text{F}_2\text{TeN(H)-Xe\text{AsF}_6} \): (A) 4-mm o.d. FEP tube sealed at one and heat-fused to \( \frac{1}{4}\)-in. (7-mm) o.d. FEP tubing at the other, (B) \( \frac{1}{4}\)-in. (7-mm) o.d. FEP tubing, (C) T connection formed by heat-fusing three \( \frac{1}{4}\)-in. o.d. FEP tubes, (D) end heat-sealed, (E) Kel-F valve in aluminum casing.
same morphology and color after 10 minutes. Samples were not cooled below -40 °C since pale yellow and white crystalline materials began to precipitate. The 4-in. o.d. FEP T-piece was cooled to -78 °C, and the yellow supernatant was decanted into the 4-in. o.d. tube. Care was taken to prevent warming of the orange crystals above -40 °C, since decomposition occurred. Both ends of the FEP apparatus were cooled to -196 °C, and the tube containing the supernatant was separated from the apparatus using a heat seal. The crystalline precipitate was pumped on at -50 °C for 20 h using a glass vacuum line with an intermediate copper U-trap cooled to -196 °C to remove any remaining HF solvent. Raman spectra were obtained by insertion of the 4-mm o.d. reaction vessel containing the yellow-orange solid directly into the laser beam at low temperature. Violent photodegradation occurred on a sample using a 514.5-nm laser power of 250 mW with the sample at -140 °C. Routine spectra were obtained without decomposition at -160 to -165 °C using laser powers of ≤ 210 mW.

Attempts to mount crystals of F₅TeN(H)-Xe⁺AsF₆⁻ in glass or quartz capillaries at low temperature failed due to their thermal instability; rapid decomposition occurred above -30 °C.

Identical procedures were used for the preparation and characterization of the F₅TeN(H)-Xe⁺AsF₆⁻ and [¹⁵N]F₅TeN(H)-Xe⁺AsF₆⁻ salts.

(v) Preparation of NMR Samples of F₅TeN(H)Xe⁺AsF₆⁻ and [¹⁵N]F₅TeN(H)Xe⁺AsF₆⁻

Identical conditions were used to prepare NMR samples of F₅TeN(H)-Xe⁺AsF₆⁻ and [¹⁵N]F₅TeN(H)-Xe⁺AsF₆⁻ for characterization by ¹⁹F, ¹H, ¹²⁵Te, ¹²⁹Xe and ¹⁵N NMR spectroscopy. Samples for NMR in HF solvent typically were prepared by combining stoichiometric amounts of F₅TeNH₂ (0.02567 g, 0.1076 mmol) with XeF⁺AsF₆⁻ (0.03630 g, 0.1070 mmol) in a 4-mm o.d. FEP tube at -196 °C, followed by vacuum distillation of HF (ca.
0.2 mL) into the tube. A sample prepared in a 9-mm o.d. FEP tube typically contained 0.1428 g (0.5984 mmol) of F₅TeNH₂ and 0.2010 g (0.5926 mmol) of XeF⁺AsF₆⁻ combined with ca. 1.5 mL of HF solvent. The tubes were sealed under vacuum at -196 °C, and warming to -35 °C for ca. 50 minutes effected reaction and dissolution, resulting in pale yellow solutions which often contained white and yellow crystalline precipitates. Spectra were typically run at temperatures between -45 and -32 °C. Samples of identical composition were prepared by combining similar molar quantities of F₅TeNH₃⁺AsF₆⁻ and XeF₂ in HF solvent under the same conditions.

Samples for NMR spectroscopy in BrF₅ solvent were prepared by combining at -196 °C similar molar amounts of F₅TeNH₃⁺AsF₆⁻ and XeF₂ as used in the preparations of the 4- and 9-mm o.d. FEP samples in HF solvent (see above, this Section). Approximately 0.3 and 1.5 mL volumes of BrF₅ solvent were then vacuum distilled into the 4-mm and 9-mm o.d. FEP tubes, respectively, at -196 °C. After sealing under dynamic vacuum at -196 °C, the tubes were warmed to -40 °C for 10 min., resulting in pale yellow solutions. NMR spectra were run at temperatures between -58 and -44 °C. Complete decomposition of the BrF₅ solutions of F₅TeN(H)-Xe⁺ had occurred after several hours at -44 °C, as determined by ¹⁹F NMR spectroscopy, resulting in pale purple colored solutions.

(vi) Attempted Preparation of NMR Samples of F₅TeN(H)-Xe-F

(a) Reaction of XeF₂ and F₅TeNH₂. Xenon difluoride (0.01570 g, 0.09274 mmol) and F₅TeNH₂ (0.02074 g, 0.08692 mmol) were combined at -196 °C in a 4-mm. o.d. FEP tube equipped with a Kel-F valve. Sulfuryl chlorofluoride solvent was distilled in at -196 °C and the tube was heat sealed under dynamic vacuum. The sample was warmed to -25 °C, whereupon the XeF₂ remained undissolved, and ¹⁹F NMR indicated no F₅Te- group present except that of
F₅TeNH₂. Warming to -12 °C resulted in dissolution of the XeF₂ to give a colorless solution. Fluorine-19 NMR indicated the presence of unreacted F₅TeNH₂ and XeF₂. No change in the ¹⁹F NMR spectrum was observed after warming the sample to 0 °C for 10 minutes. The absence of TeF₆ in the ¹⁹F NMR indicated that no fluorination of the F₅TeNH₂ by the solvent or XeF₂ occurred in this temperature range. Further warming of the sample was not attempted.

(b) Reaction of F₅TeNHSi(CH₃)₃ and XeF₂. The compound F₅TeNHSi(CH₃)₂ (0.05346 g, 0.1076 mmol) was pipetted into a 4-mm o.d. FEP tube equipped with a Kel-F valve. The tube was cooled to -196 °C and XeF₂ (0.01898 g, 0.1121 mmol) was added. Sulfuryl chlorofluoride solvent was distilled into the tube at -196 °C, and the tube was heat sealed under vacuum as above. The ¹⁹F NMR spectrum indicated no reaction upon warming to -12 °C, and resulted in a colorless solution. The absence of TeF₆ and (CH₃)₂SiF in the ¹⁹F NMR spectrum indicated that F₅TeNHSi(CH₃)₃ was stable to fluorination by XeF₂ and the solvent at -12 °C. Further warming of the sample was not attempted.

(vii) Preparation of NMR Samples of F₅TeN(H)Xe⁺As(O'TeF₃)₆⁻ in SO₂ClF Solvent

In a typical preparation, 0.11810 g (0.067637 mmol) of F₅TeNH₅⁺As(O'TeF₃)₆⁻ was loaded into a 4-mm o.d. FEP tube equipped with a Kel-F valve. The vessel was cooled to -196 °C and 0.03902 g (0.06413 mmol) of Xe(O'TeF₃)₂ was added. Sulfuryl chloride fluoride solvent was vacuum distilled into the vessel at -196 °C. The FEP tube was heat sealed under dynamic vacuum at -196 °C followed by warming to -78 °C, which resulted in a clear colorless solution (ca. 0.2 M). The ¹⁹F, ¹H, and ¹²⁹Xe NMR spectra were initially obtained at -61 °C. Although the solution was initially colorless at this temperature, after 2 h the solution became pale yellow in color. Exchange in the F-on-Te(VI) region complicated the interpretation of the ¹⁹F NMR spectra;
however, cooling to -115 °C substantially slowed the exchange without precipitation of the reagents, allowing the assignment of most of the resonances.

(viii) Preparation of NMR Samples of FO₂SN(H)-Xe⁺AsF₆⁻ and [¹⁵N]FO₂SN(H)-Xe⁺AsF₆⁻

The FO₂SN(H)-Xe⁺ cation was generated in BrF₅ solvent and characterized by ¹²⁹Xe, ¹⁹F, and ¹H NMR spectroscopy. Samples were typically prepared by combining 0.0563 g (0.195 mmol) of FO₂SNH₃⁺AsF₆⁻ and 0.0377 g (0.223 mmol) of XeF₂ at -196 °C in a 4-mm o.d. FEP tube equipped with a Kel-F valve. Bromine pentafluoride was vacuum distilled onto the reagents at -196 °C and the sample tube was sealed under vacuum at -196 °C. Warming to -56 °C resulted in the formation of a pale yellow solution (ca. 1 M). Dissolution of the XeF₂ crystals required agitation for ca. 10 min. at this temperature. NMR spectra were recorded at -58 to -60 °C. Samples in 9-mm o.d. FEP tubes were prepared by combining 0.1219 g (0.4218 mmol) of FO₂SNH₃⁺AsF₆⁻ and 0.0713 g (0.421 mmol) of XeF₂ in BrF₅ solvent (ca. 0.27 M) under identical conditions.

(D) NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

(i) Instrumentation

All NMR spectra were recorded unlocked (field drift < 0.1 Hz h⁻¹) with the use of Bruker AC-200 (4.6975 T), AC-300 (7.0463 T), and AM-500 (11.7440 T) spectrometers equipped with Aspect 2000 or 3000 computers.

Spectra were recorded on samples in heat sealed 9-mm o.d. or 4-mm o.d. FEP NMR tubes as described below. The FEP sample tubes were placed inside 10-mm o.d. or 5-mm o.d. Wilmad
precision thin wall glass NMR tubes before being placed in the probe of the NMR spectrometer.

The $^{129}$Xe, $^{15}$N, $^{125}$Te and $^{13}$C NMR spectra were recorded at 11.7440 T in 9-mm o.d. FEP sample tubes (HF, BrF$_3$ and SO$_2$ClF solvents) using a 10-mm VSP probe (broad-banded over the frequency range 23 - 202 MHz) tuned to 139.051 ($^{129}$Xe), 50.698 ($^{15}$N), 157.795 ($^{125}$Te) or 125.760 ($^{13}$C) MHz, respectively. Xenon-129 and $^1$H NMR spectra of the FO$_2$SN(H)-Xe$^+$ and F$_3$TeN(H)-Xe$^+$ cations were also recorded at 7.0463 T in 9-mm FEP tubes (HF solvent) on a 10-mm VSP probe (broad-banded over the frequency range 14 - 121 MHz) tuned to 83.445 ($^{129}$Xe) and 300.144 MHz ($^1$H) to reduce SA broadening effects which are observed at 11.7440 T. Fluorine-19 (470.599 MHz) and proton (500.138 MHz) spectra were generally recorded at 11.7440 T in 4-mm o.d. FEP tubes (HF, BrF$_3$ and SO$_2$ClF solvents) using a 5-mm dual $^1$H/$^{19}$F probe, except for the $^1$H NMR spectra of F$_3$TeNH$_2$ and [N$_5$F$_3$TeNH$_2$, which were recorded at 4.6975 T (200.133 MHz) in 4-mm o.d. FEP sample tubes (CD$_2$Cl$_2$ solvent) using a 5-mm $^1$H probe.

Xenon-129 NMR spectra at 11.7440 T were recorded using 16 - 64 K data points with a spectral width of 50 - 100 kHz and with acquisition times of 0.333 - 0.164 s and data point resolutions of 3.0 - 6.1 Hz/pt (1500 - 21,000 scans). Xenon-129 NMR spectra recorded at 7.0463 T were acquired using 8 K data points with a spectral width of 8474 Hz, an acquisition time of 0.483 s and a data point resolution of 2.1 Hz/pt (19,573 scans). Fluorine-19 NMR spectra were recorded using 1 - 64 K data points with spectral width settings of 2 - 125 kHz, acquisition times of 0.256 - 0.262 s, and data point resolutions of 3.8 - 3.9 Hz/pt (4500 - 11,000 scans). Carbon-13 NMR spectra were recorded using 32 K data points, a spectral width of 50 kHz, an acquisition time of 0.328 s, and a data point resolution of 3.1 Hz/pt (11,475 - 57,000 scans). Proton spectra at 11.7440 T were recorded using 16 - 32 K data points, spectral widths of 10 kHz, acquisition times of 1.638 - 0.820 s and data point resolutions of 0.61 - 1.22 Hz/pt (200 - 400 scans). Proton
NMR spectra at 4.6975 T were recorded using 4 - 32 K data points, spectral widths of 3 - 5 kHz, acquisition times of 0.684 - 1.638 s and data point resolutions of 0.3 - 1.5 Hz/pt (140 - 230 scans). Nitrogen-15 NMR spectra were recorded using 32 K data points, a spectral width of 25 kHz, an acquisition time of 0.655 s and a data point resolution of 1.52 Hz/pt (300 - 500 scans). Tellurium-125 NMR spectra were recorded using 32 - 64 K data points, a spectral width range 25 - 50 kHz, an acquisition time of 0.333 - 0.655 s, and a data point resolution of 1.5 - 3.0 Hz/pt (7000 - 40,850 scans).

Proton-fluorine heteronuclear 2D NOESY spectra of CF$_3$C(OH)NH$_2$AsF$_6$ and CF$_3$C(OXeF)NH$_2$AsF$_6$ in BrF$_5$ solvent were recorded in the absolute value mode using the pulse sequence reported by Yu and Levy.$^{136}$ Spectra were acquired in 16 scans for each of the 128 free induction decays that contained 2K data points in F2 ($^{19}$F dimension) over a 5 kHz spectral width. The $^{19}$F 90° pulse width was 14.3 µs while the $^1$H 90° pulse width through the decoupler channel was 9.0 µs. A 1.0 s relaxation delay was employed between acquisitions. A mixing time of 0.25 s was used. Zero-filling in the F1 ($^1$H) dimension produced a 1K x 2K data matrix with a digital resolution of 7.1 Hz/pt in F2 and 3.5 Hz/pt in F1. During 2D Fourier transformation, a sine-bell squared window function shifted by $\pi/2$ was applied to both dimensions. The transformed data were not symmetrized.

Xenon-129 INEPT spectra of [$^{15}$N]F$_2$TeN(H)-XeAsF$_6$ in HF solvent were recorded at 83.468 MHz using a 10 mm VSP probe (broad-banded over the frequency range 14 - 121 MHz). The spectra were acquired over a 15 kHz spectral width in 2K data points (0.682 s acquisition time and a data point resolution of 1.5 Hz/pt). Spectra were obtained using the INEPT pulse sequence with a $^{129}$Xe 90° pulse width of 14.0 µs. The $^1$H 90° pulse width through the decoupler channel was 20.0 µs. The fixed delay in the INEPT pulse sequence ($0.25\{1/[J^{129}\text{Xe}^-\text{H}]\}$) was
0.01086 s with a relaxation delay of 1.0 s. The free induction decays were zero-filled to 8K data points and processed using Gaussian multiplication for resolution enhancement (line broadening, 2.5; Gaussian broadening, 0.35) before Fourier transformation.

Pulse widths corresponding to bulk magnetization tip angles of -90° were 18 (11.7440 T) and 14 (7.0463 T) (129Xe), 1 (19F), 6 (13C) and 5 (11.7440 T) and 7 μs (4.6975 T) (1H). Line broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data point resolutions or the natural line widths of the resonances. All line shape functions were Lorentzian unless specified, where the free induction decays were multiplied by Gaussian functions for resolution enhancement on Fourier transformation. No relaxation delays were applied except for 15N, where relaxation delays of 20 - 120 s were applied.

The respective nuclei were referenced externally to neat samples of XeOF₄ (129Xe), CFCl₃ (19F), natural abundance CH₂NO₂ (15N), Te(CH₂)₂ (125Te) and (CH₃)₄Si (13C and 1H) at 30 °C. Positive chemical shifts were assigned to resonances occurring to high frequency of the reference substance.

For variable temperature measurements, samples were kept cold (-196 or -78 °C) until immediately prior to their placement in the NMR probe. They were generally warmed only enough to liquify and solubilize the contents and were then quickly placed in the precooled probe. Prior to data accumulation, the tubes were allowed to equilibrate in the probe for periods of several minutes while spinning. Temperatures were periodically checked by placing a copper constantan thermocouple into the sampling region of the probe. Temperatures were considered to be accurate to within ±1 °C.
(ii) **NMR Sample Preparation**

All NMR samples were prepared in sample tubes constructed from 4-mm and 9-mm o.d. FEP tubes. Low volatility compounds such as XeF₂, XeF⁺AsF₆⁻, F₅TeNH₂, F₅TeNH₃⁺AsF₆⁻, FO₂SNH₂, FO₂SNH₃⁺AsF₆⁻, CF₃C(O)NH₂ and CF₃C(OH)NH₂⁺AsF₆⁻ were transferred into preweighed FEP sample tubes inside the dry box. The FEP sample tubes were cooled to -196 °C inside the drybox using a cryowell cooled with liquid nitrogen from the outside of the drybox prior to combining reactive reagents. The FEP sample tubes were rapidly removed from the drybox and placed inside a -78 °C temperature bath prior to addition of solvent. The solvents HF and BrF₅ were vacuum distilled into the FEP sample tubes through all fluoroplastic connections using a metal vacuum line. Solvents which do not attack glass in the absence of water vacuum distilled into the reaction tubes using all glass connections.

FEP sample tubes were sealed by immersing the sample in liquid nitrogen and causing the tube to collapse under dynamic vacuum by heating with a small cylindrical electrical tube furnace near the top of the sample tube. The FEP tubes were inserted into thin-walled glass Wilmad NMR tubes prior to placement in the probe of the NMR spectrometer.

(E) **RAMAN SPECTROSCOPY**

(i) **Instrumentation**

Raman spectra were recorded on a Jobin-Yvon Mole S-3000 triple spectrograph system equipped with a 0.32-m prefILTER, adjustable 25-mm entrance slit, and a 1.00-m monochromator. Holographic gratings were used for the prefILTER (600 grooves mm⁻¹, blazed at 500 nm) and monochromator (1800 grooves mm⁻¹, blazed at 550 nm) stages. The 514.5-nm line of an Ar⁺ ion
laser was used for excitation of the samples. The spectra of microcrystalline samples of CF$_3$C(O)NH$_2$, F$_5$TeNH$_3$AsF$_6$, [\(^{15}\)N]F$_5$TeNH$_3$AsF$_6$, FO$_2$SNH$_2$ and [\(^{15}\)N]FO$_2$SNH$_2$, which were sealed in a baked-out Pyrex melting point capillaries, were recorded at ambient temperature. The Raman spectra of the microcrystalline salts CF$_3$C(OH)NH$_2$AsF$_6$, CF$_3$C(OXeF)NH$_2$AsF$_6$, CF$_3$C(OH)NH$_2$AsF$_6$-xHF (in 9-mm or 6-mm o.d. FEP tubes), F$_5$TeN(H)XeAsF$_6$ and [\(^{15}\)N]F$_5$TeN(H)XeAsF$_6$ (in 4-mm o.d. FEP tubes), FO$_2$SNH$_3$AsF$_6$ and [\(^{15}\)N]FO$_2$SNH$_3$AsF$_6$ (in 3-mm medium wall glass tubes) were recorded at -160 to -165 °C in the macro-sample chamber of the instrument. The low temperatures were achieved by flowing dry nitrogen gas, chilled by passing through a 50 L tank of liquid nitrogen, along the outside of the sample tube, which was mounted vertically in an open-ended unsilvered glass Dewar jacket (Figure 2.13). The angle between the sample tube and the laser beam was 90° and Raman scattered radiation was observed at 90° to the incident laser beam and at 90° to the sample tube. The temperature was measured using a copper-constantan thermocouple (error ± 0.8 °C). The spectra were recorded by signal averaging using a Spectraview-2D CCD detector equipped with a 25-mm chip (1152 x 298 pixels). The laser powers measured at the samples were 90 (CF$_3$C(OXeF)NH$_2$AsF$_6$, and CF$_3$C(O)NH$_2$). 190 (CF$_3$C(OH)NH$_2$AsF$_6$), 120 (CF$_3$C(OH)NH$_2$AsF$_6$-xHF), 240 (F$_5$TeNH$_2$ and [\(^{15}\)N]F$_5$TeNH$_2$), 260 (F$_5$TeNH$_3$AsF$_6$ and [\(^{15}\)N]F$_5$TeNH$_3$AsF$_6$), 210 (F$_5$TeN(H)XeAsF$_6$ and [\(^{15}\)N]F$_5$TeN(H)XeAsF$_6$), 240 (FO$_2$SNH$_2$ and [\(^{15}\)N]FO$_2$SNH$_2$) and 260 mW (FO$_2$SNH$_3$AsF$_6$ and [\(^{15}\)N]FO$_2$SNH$_3$AsF$_6$). Slit settings corresponded to a resolution of 0.5 - 1 cm$^{-1}$. A total of 20 - 30 reads having 10 - 40 s integration times were summed for each of the Raman spectra.

Unless otherwise specified, Raman frequencies involving $^{14}/^{15}$N isotopic studies are estimated to be accurate to ± 0.5 cm$^{-1}$. As a result $^{14}/^{15}$N isotopic shifts less than 0.5 cm$^{-1}$ in the
Figure 2.13  Apparatus for low temperature Raman spectroscopy; (A) Kel-F valve flare-sealed (45° SAE) onto FEP tube, (B) rubber septum, (C) unsilvered glass vacuum jacket, (D) copper-constantan thermocouple, (E) glass ball and socket joint, (F) steel mount for adjustment of the sample tube in the laser beam, (G) cold nitrogen gas stream (\(\gtrsim -170 \, ^\circ C\)) generated by passing room temperature nitrogen gas into a 50 L tank of liquid nitrogen.
Raman spectra of the natural abundance and 99.5 atom% $^{15}$N enriched samples of $\text{F}_5\text{TeNH}_2$, $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$, $\text{F}_5\text{TeN(H)Xe}^+\text{AsF}_6^-$, $\text{FO}_2\text{SNH}_2$ and $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ were considered to be insignificant. The Raman spectra of natural abundance and 99.5% $^{15}$N-enriched samples of a given compound were recorded on the same day using identical conditions in order to minimize systematic errors.

Raman spectra obtained in FEP sample tubes contained lines resulting from the FEP sample tube. The frequencies and intensities of the Raman lines at -154 °C are: 203 (0.2), 278 (0.6), 294 (4.5), 309 (0.9), 381 (3.6), 387 (2.6), 579 (1.3), 598 (0.3), 734 (10.0), 752 (0.9), 1217 (1.2), 1310 (1.6) and 1385 (3.3) cm$^{-1}$. The prominence of these lines in the Raman spectra depended on the scattering efficiency of the sample and where the laser beam was focussed. In the present work, lines arising from FEP have been subtracted out of the spectra reported in the Tables but not in the Figures.

The Raman spectrometer was calibrated using the 1018.3 cm$^{-1}$ line of vacuum distilled neat liquid indene in a sealed glass melting point capillary at ambient temperature.$^{137}$

(ii) **Raman Sample Preparation**

The Raman sample vessels constructed from $\frac{3}{4}$-in. (7-mm) o.d. FEP tubing were heat sealed at one end by pushing the tube into the end of a flame heated piece of glass tubing that had been previously stretched to approximately 0.5-mm at one end using an oxygen torch. Vessels constructed from 4-mm o.d. tubing were heat sealed similarly at one end by pushing the end into a flame heated 5-mm thin-walled glass NMR tube. The other ends of the Raman vessels were heat flared (45° SAE) for direct attachment to a Kel-F valve. All Raman sample vessels were pressurized with dry nitrogen gas (ca. 1300 Torr) at -78 °C prior to obtaining the Raman spectrum.
at -160 to -165 °C. Low-temperature Raman samples of materials which do not attack glass were run in vessels constructed of 3-mm o.d. medium wall glass tubing. The tubing was flame sealed at one end and attached to a length of 1/4-in. o.d. glass tubing at the other. The tubing was then attached using a 1/4-in. Teflon union (Swagelok) with Teflon compression fittings (Swagelok) to a glass 4-mm J. Young stopcock equipped with a Teflon barrel. The vessel was vacuum dried and flamed out. Samples were loaded into the tube inside the dry box. The loaded 3-mm o.d. vessels were then flame sealed under vacuum while cooling the sample to -78 or -196 °C. The Raman spectra were obtained directly on the samples contained in the sealed glass tubes at -160 to -165 °C. Samples run at room temperature were loaded into glass melting point capillaries in the drybox and plugged with Kel-F grease. The capillaries were then removed from the drybox and immediately sealed with an oxygen-natural gas microtorch. The sample tubes were stored at -78 °C prior to running the Raman spectra.
CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF CF$_3$C(OXeF)NH$_2^+$ AND CF$_3$C(OH)NH$_2^+$AsF$_6^-$ AND CF$_3$C(OH)NH$_2^+$AsF$_6^-XeF$_2$ x HF SALTS USING MULTI-NMR AND RAMAN SPECTROSCOPY

INTRODUCTION

The noble-gas cations NgF$^+$ (Ng = Xe, Kr) have long been known to exhibit Lewis acid character in their salts with weakly fluorobasic anions such as AsF$_6^-$, SbF$_6^-$ and Sb$_2$F$_{11}^-$ where the NgF$^+$ cation interacts with the fluoroanion in the solid state by means of a fluorine bridge.\textsuperscript{21} Recently, the Lewis acidities of NgF$^+$ (Ng = Kr, Xe) cations have been exploited to synthesize novel adduct cations containing Xe-N and Kr-N bonds.\textsuperscript{26,71-73,75,78} A variety of oxidatively resistant organic nitrogen bases have now been shown to form adducts with XeF$^+$, including hydrogen cyanide,\textsuperscript{72,73} alkynitriles,\textsuperscript{72} perfluorobenzenenitrile,\textsuperscript{72} perfluoroalkynitriles,\textsuperscript{71,72} perfluoropyridines\textsuperscript{75} and s-trifluorotriazine.\textsuperscript{71} Adducts of the strong oxidant cation, KrF$^+$, with hydrogen cyanide\textsuperscript{78} and perfluoroalkyl nitriles,\textsuperscript{71} have also been stabilized at low temperatures to give the R$_{F}$C≡N-KrF$^+$ (R$_{F}$ = CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$) and HC≡N-KrF$^+$ cations, and provide the only examples of Kr-N bonds presently known. The Ng-N bonds in the cations have been shown by $^{19}$F and $^{129}$Xe NMR spectroscopy to have high degrees of ionic character.\textsuperscript{26,73} The ability of a base to resist oxidation by the strongly oxidizing NgF$^+$ cations correlates well with the first adiabatic ionization potential (IP$_1$) of the nitrogen base. It has
been shown that a base having an IP\textsubscript{1}-value that is similar to or greater than the estimated electron affinities of XeF\textsuperscript{+} (10.9 eV) and KrF\textsuperscript{+} (13.2 eV) may be sufficiently resistant to oxidation by NgF\textsuperscript{+} to form kinetically stable Ng-N bonds at low temperatures.\textsuperscript{26}

Where possible, the general preparative strategy has been straightforward and has entailed the interaction of the appropriate base with an NgF\textsuperscript{+} salt in HF solvent. In instances where the protonated form of the base predominates in HF solvent, or when the base is readily oxidized by the noble-gas cation, NgF\textsubscript{2} is allowed to react with the oxidatively more resistant protonated nitrogen base cation in the strongly oxidizing solvent, BrF\textsubscript{5}. Equilibrium displacement of HF from the protonated base by the difluoride occurs to a significant extent in BrF\textsubscript{5} solvent at the low temperatures usually required to stabilize the adduct cations. These synthetic approaches are illustrated by the NgF\textsuperscript{+} adducts of HC≡N. Hydrogen cyanide (IP\textsubscript{1} = 13.80 eV)\textsuperscript{138} forms the adduct cation HC≡N-XeF\textsuperscript{+} upon reaction of HC≡N with XeF\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} or Xe\textsubscript{2}F\textsubscript{3}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} in HF solution at -20 to -10 \textdegree C,\textsuperscript{72,73} whereas the powerful oxidizing ability of KrF\textsuperscript{+} requires the reaction of HC≡NH\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} with KrF\textsubscript{2} in BrF\textsubscript{5} solvent near the melting point of the solvent to prepare the krypton analog, HC≡N-KrF\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}.\textsuperscript{78} A third synthetic approach, which also avoids the use of the strong oxidant NgF\textsuperscript{+} cations, is exemplified by the perfluoroalkyl nitriles R\textsubscript{F}C≡N (R\textsubscript{F} = CF\textsubscript{3}, C\textsubscript{2}F\textsubscript{5}, n-C\textsubscript{3}F\textsubscript{7}) and relies upon the reaction of the adducts R\textsubscript{F}C≡N-AsF\textsubscript{5} and KrF\textsubscript{2} to form the R\textsubscript{F}C≡N-NgF\textsuperscript{+} (Ng = Kr, Xe) adduct cations at low temperatures in BrF\textsubscript{5} solvent.\textsuperscript{71}

Oxygen electron-pair donors have not been investigated to any significant extent as bases towards NgF\textsuperscript{+} cations. Only one example of a cation containing the O-Xe-F linkage, namely (CF\textsubscript{3})\textsubscript{2}S=O-XeF\textsuperscript{+}, has been reported.\textsuperscript{85} This cation was prepared by reaction of the sulfurane, (CF\textsubscript{3})\textsubscript{2}S=O, with XeF\textsuperscript{+}SbF\textsubscript{6}\textsuperscript{-} in HF at -65 \textdegree C over a 12 h period; the solid decomposes explosively above -78 \textdegree C if mechanically shocked. The present work describes the second example of an
adduct cation containing the O-Xe-F linkage, namely, CF$_3$C(OXeF)NH$_2^+$ and its characterization in the solid state by low-temperature Raman spectroscopy and in solution by $^{19}$F, $^1$H, $^{13}$C and $^{129}$Xe NMR spectroscopy.

RESULTS AND DISCUSSION

(A) SYNTHESIS AND ISOLATION OF CF$_3$C(OH)NH$_2^+$AsF$_6^-$·XeF$_2$·xHF,

CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ AND CF$_3$C(OH)NH$_2^+$AsF$_6^-$

The first adiabatic ionization potential of 2,2,2-trifluoroacetamide (10.77 eV)$^{106}$ is similar to the estimated electron affinity of the XeF$^+$ cation (10.9 eV)$^{73}$ suggesting that it is potentially resistant to oxidation by XeF$^+$ under suitable solvent conditions and at low temperature, enabling an Xe-O bonded adduct cation to be formed.

The CF$_3$C(OXeF)NH$_2^+$ cation results from the HF elimination reaction of the conjugate acid of CF$_3$C(O)NH$_2$, namely CF$_3$C(OH)NH$_2^+$, with XeF$_2$. The strong electrophilic characters of XeF$^+$ and BrF$_5$ solvent and nucleophilicities of the oxygen and nitrogen base sites were mitigated by protonation of CF$_3$C(O)NH$_2$ under superacid conditions by reaction of the amide with excess AsF$_5$ in HF solvent. Upon removal of the solvent, CF$_3$C(OH)NH$_2^+$AsF$_6^-$ was isolated as a white microcrystalline powder in quantitative yield according to equation (3.1), and underwent slow decomposition at room temperature.

\[
\text{CF}_3\text{C(O)NH}_2 + \text{AsF}_5 \xrightarrow{\text{HF}, \text{-50}^{\circ}\text{C}} \text{CF}_3\text{C(OH)NH}_2^+\text{AsF}_6^- \quad (3.1)
\]
\[
\begin{align*}
\text{CF}_3\text{(OH)NH}_2^+\text{AsF}_6^- + \text{XeF}_2 & \xrightarrow{\text{BrF}_5} \text{CF}_3\text{(OXeF)NH}_2^+\text{AsF}_6^- + \text{HF} \\
& \text{at -62 to -55 }^\circ\text{C} \\
\text{CF}_3\text{(O)NH}_2 + \text{XeF}^+\text{AsF}_6^- & \xrightarrow{\text{HF}} \text{CF}_3\text{(OH)NH}_2^+\text{AsF}_6^- + \text{XeF}_2 \\
& \text{at -50 }^\circ\text{C}
\end{align*}
\]

The salt \(\text{CF}_3\text{(OH)NH}_2^+\text{AsF}_6^-\) was characterized in solution by multi-NMR using \(\text{BrF}_5\) as solvent at low temperature. The slow reaction of the \(\text{CF}_3\text{(OH)NH}_2^+\) cation with \(\text{BrF}_5\) solvent at -55 \(^\circ\text{C}\) is indicated by the presence of broad resonances at \(\delta(\text{H}) = 5.2, 3.3\) and 2.6 ppm in the \(^1\text{H}\) NMR spectrum, which likely result from the rapidly exchanging H-on-N environments of \(\text{NH}_4^+, \text{N}_2\text{H}_4\) and \(\text{HN}_3\). A doublet at \(\delta(\text{H}) = 5.1\) ppm \([J(\text{H}-\text{F}) = 535 \text{ Hz}]\) indicated the presence of HF.

Combining stoichiometric amounts of \(\text{CF}_3\text{(OH)NH}_2^+\text{AsF}_6^-\) with \(\text{XeF}_2\) in \(\text{BrF}_5\) solvent at -62 to -55 \(^\circ\text{C}\) [equation (3.2)] resulted in the formation of the xenon cation, \(\text{CF}_3\text{(OXeF)NH}_2^+.\) The HF elimination reaction represented by equation (3.2) is directly analogous to the reaction of \(\text{CF}_3\text{(O)OH}\) and \(\text{XeF}_2\) to give the neutral species \(\text{CF}_3\text{(O)XeF}.\) \(\text{F}^{19}\) and \(\text{Xe}^{129}\) NMR spectra show that the reaction between \(\text{CF}_3\text{(O)NH}_2^+\) and \(\text{XeF}^+\text{AsF}_6^-\) does not proceed to any measurable extent in anhydrous HF solvent owing to solvolysis of the reagents; \(\text{XeF}^+\) is a strong fluoride ion acceptor in HF solvent and \(\text{CF}_3\text{(O)NH}_2\) is protonated according to equation (3.3). However, slow removal of HF solvent at -50 \(^\circ\text{C}\) under dynamic vacuum displaces equation (3.2) toward the right, yielding a pale yellow viscous solution which, after continued pumping, yielded \(\text{CF}_3\text{(OXeF)NH}_2^+\text{AsF}_6^-\) as a white microcrystalline solid. The \(\text{Xe}^{129}\) and \(\text{F}^{19}\) NMR spectra of solutions of this material in \(\text{BrF}_5\) solvent (-60 \(^\circ\text{C}\)) confirm the presence of the
CF$_3$C(OXeF)NH$_2^+$ cation. In the solid state, CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ decomposes rapidly with gas evolution and liquefaction at temperatures approaching 0 °C. In contrast, rapid removal of HF solvent from a solution of XeF$^+$AsF$_6^-$ and CF$_3$C(O)NH$_2$ under dynamic vacuum at -50 °C results in immediate precipitation of the solvated adduct, CF$_3$C(OH)NH$_2^+$AsF$_6^-$XeF$_2$ as white powder [equation (3.4)]; no CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ was observed in the solid by Raman spectroscopy. Elimination of HF from CF$_3$C(OH)NH$_2^+$AsF$_6^-$XeF$_2$ as HF did not occur after pumping under dynamic vacuum for 28 h at -50 °C; however, redissolution of the adduct in HF at -50 °C followed by slow removal of the solvent under vacuum resulted in the isolation of pure CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ [see Section (D), below]. The adduct, CF$_3$C(OH)NH$_2^+$AsF$_6^-$XeF$_2$ as HF, is considered to be an intermediate in the HF elimination reaction of CF$_3$C(OH)NH$_2^+$ and XeF$_2$.

Although several examples of HF elimination reactions involving XeF$_2$ and acids, HL, are known (L = FO$_2$SO$^-$, $^{37-39,140}$ CF$_3$O$_2$SO$^-$, $^{140}$ CH$_3$O$_2$SO$^-$, $^{140}$ F$_5$TeO$^-$, $^{41,46-48,115,141,142}$ F$_5$SeO$^-44$, ClO$_3$O$^-$, $^{140}$ CF$_3$(O)O$^-$, $^{39,41}$ and (FSO$_2$)$_2$N$^-$, $^{56-60}$), CF$_3$C(OH)NH$_2^+$AsF$_6^-$XeF$_2$ as HF, represents the first reported instance of the isolation of an intermediate in an HF elimination reaction involving XeF$_2$.

(B) **CHARACTERIZATION OF CF$_3$C(OH)NH$_2^+$AsF$_6^-$ BY $^1$H, $^{13}$C AND $^{19}$F NMR SPECTROSCOPY AND BY TWO DIMENSIONAL ($^1$H-$^1$H) NOESY EXPERIMENTS**

Since the CF$_3$C(OXeF)NH$_2^+$ cation is in equilibrium with CF$_3$C(OH)NH$_2^+$ in BrF$_5$ solvent
[equation (3.2)], unambiguous NMR characterization of the CF$_3$C(OXeF)NH$_2^+$ cation required a detailed NMR study of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ in BrF$_5$ solution. Although CF$_3$C(O)NH$_2$ is potentially an ambident base, the $^1$H NMR spectrum of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ in BrF$_5$ solvent at -55.4°C (Figure 3.1) confirms that protonation occurs exclusively at the oxygen and that the oxygen site is more basic (cf. resonance Structures 3.1 and 3.2).
Figure 3.1 $^1$H NMR spectrum (500.138 MHz) at -55.4 °C of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ (0.25 M) in BrF$_5$ solvent; (A) proton on oxygen of the protonated carbonyl group, (B) two singlets of equal intensity arising from the chemically inequivalent amido protons, (C) HF.
Previous work has shown that amides are protonated at oxygen in strong acid and superacid media.\textsuperscript{143-149} The $^1$H NMR resonance of the protonated carbonyl group of the CF$_3$C(OH)NH$_2^+$ cation is a singlet at $\delta$($^1$H) = 11.61 ppm, $\Delta v_{1/2} = 20$ Hz, in agreement with the value reported for the protonated carbonyl group of the FC(OH)NH$_2^+$ cation ($\delta$($^1$H) = 11.07 ppm, HSO$_3$F/SO$_2$ solution at -80 °C).\textsuperscript{149} Similar $^1$H chemical shifts have been reported for O-protonated acetamide ($\delta$($^1$H) = 10.72 ppm, -80 °C),\textsuperscript{145} formamide ($\delta$($^1$H) = 10.81 ppm, -85 °C),\textsuperscript{145} and benzamide ($\delta$($^1$H) = 10.14 ppm, -85 °C)\textsuperscript{144} in HSO$_3$F solvent. The NH protons of the CF$_3$C(OH)NH$_2^+$ cation are inequivalent on the NMR time scale (Figure 3.1), giving two broad singlets ($\Delta v_{1/2} = 61$ Hz) of equal intensity at 8.75 and 8.38 ppm. The large line widths are primarily attributed to residual one-bond scalar coupling between the protons and $^{14}$N (I = 1). The chemical inequivalence of the NH protons is attributed to hindered rotation about the C-N bond, and is consistent with the large barriers to C-N bond rotation found for neutral [$^{15}$N]CF$_3$C(O)NH$_2$ in dioxan ($E^\ddagger = 76.5 \pm 2.9$ kJ mol$^{-1}$) and methyl propyl ketone ($E^\ddagger = 77.8 \pm 2.5$ kJ mol$^{-1}$) solvents.\textsuperscript{150} Oxygen coordination of amides has been shown to substantially increase the barrier to rotation about the C-N bond by increasing the C-N double bond character relative to that of the free amide.\textsuperscript{143} Examples of increases in C-N bond rotational barriers resulting from O-coordination have been extensively studied by NMR spectroscopy and include O-protonation of dimethyl formamide, N-methyl formamide and N-methyl acetamide in 100% H$_2$SO$_4$,\textsuperscript{146} and O-coordination of BF$_3$ in sym- and unsym-dimethylureas\textsuperscript{151} and of BX$_3$ in tetramethylurea ($X = Br, Cl, F$).\textsuperscript{152} In all cases, resonance structures can be drawn, representing "amide-like" linkages containing C-N double bonds which dominate the bonding when oxygen is coordinated to a Lewis acid. Resonance Structure 3.2 represents $\pi$-donation from nitrogen to carbon, and is expected to be the dominant contributing structure for the CF$_3$C(OH)NH$_2^+$ cation [see Section (E) below]. Hindered rotation in protonated
primary amides in acidic solution has been observed in a variety of acidic media and at different temperatures by $^1$H NMR spectroscopy. The relative shieldings of the amido proton resonances in the CF$_3$C(OH)NH$_2^+$ cation cannot be unambiguously assigned by comparison with previously reported examples.$^{153}$ However, definitive assignments of the amido protons in the CF$_3$C(OH)NH$_2^+$ cation were obtained from a two-dimensional heteronuclear ($^1$H-$^{19}$F) NOESY experiment performed on a sample of CF$_3$C(OH)NH$_2^+$ AsF$_6^-$ dissolved in BrF$_5$ solvent at -58.9 ºC (Figure 3.2). A correlation was observed between the $^{19}$F NMR resonance of the CF$_3$ group and both the low-frequency proton-on-nitrogen resonance and the proton-on-oxygen resonance. This experiment utilizes the nuclear Overhauser effect (nOe), which results from a through-space dipolar interaction between nuclei.$^{154}$ This effect rapidly diminishes with internuclear distance, so that correlations are only observed for nuclei which are close to one another. The presence of a correlation between the CF$_3$ group and the low-frequency proton-on-nitrogen resonance indicates that this $^1$H resonance arises from the proton cis to the CF$_3$ group (cf. resonance Structures 3.1 and 3.2). A correlation is also observed between the proton-on-oxygen resonance and the fluorine resonance of the CF$_3$ group, indicating that intermolecular exchange involving the proton on oxygen is slow relative to dipolar relaxation induced by the fluorine atoms of the CF$_3$ group. The $^{19}$F NMR spectrum of the CF$_3$C(OH)NH$_2^+$ cation in BrF$_5$ solvent at -55.4 ºC consisted of a singlet at -75.6 ppm assigned to the CF$_3$ resonance. A value of $^4J(^{19}$F-$^1$H) = 1.8 Hz was observed by Akiyama et al.$^{155}$ for the scalar coupling between the NH proton trans to the carbonyl group and the fluorines of the CF$_3$ group in CF$_3$C(O)NH$_2$ at -40 ºC in tetrahydrofuran, using $^{19}$F NMR spectroscopy. The large line width ($\Delta v_{1/2} = 32$ Hz) observed in the $^{19}$F NMR spectrum of the CF$_3$C(OH)NH$_2^+$ cation precluded resolution of the $^4J(^{19}$F-$^1$H) scalar coupling. The quadrupole collapsed $^{19}$F NMR resonance of the AsF$_6^-$ anion occurs at -60.7 ppm ($\Delta v_{1/2} = 284$ Hz), as
Figure 3.2 Heteronuclear $[^1\text{H} \ (500.138 \ \text{MHz}) - ^{19}\text{F} \ (470.599 \ \text{MHz})]$ NOESY spectrum at -58.9 °C of CF$_3$C(OH)NH$_2$AsF$_6^-$ (0.48 M) in BrF$_5$ solvent; one-dimensional $^1\text{H}$ and $^{19}\text{F}$ NMR spectra are displayed along the vertical and horizontal axes, respectively; (A) proton on oxygen environment of the protonated carbonyl group, (B) amido proton trans to the CF$_3$ group, (C) amido proton cis to the CF$_3$ group, (D) fluorine on carbon environment of the CF$_3$C(OH)NH$_2^+$ cation. The continuous horizontal line of peaks running through the two-dimensional plot is an axial peak artifact along F1 = 0.$^{182}$
null
previously observed for AsF$_6^-$ in BrF$_5$ solvent at low temperature.$^{73}$ The carbon-13 spectrum of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ (-56.2 °C) in BrF$_5$ solvent consists of two binomial quartets at $\delta$(13C) = 166.2 $^{2}J$(13C-19F) = 46 Hz and at 114.0 ppm $^{1}J$(13C-19F) = -284 Hz, which are assigned to the COH and CF$_3$ resonances, respectively, and are similar to those reported for related compounds containing the CF$_3$C(O)- moiety.$^{156}$

(C) CHARACTERIZATION OF CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ BY $^{1}$H, 13C, 19F AND 129Xe NMR SPECTROSCOPY AND BY TWO-DIMENSIONAL ($^{1}$H-19F) NOESY EXPERIMENTS

The structure of the CF$_3$C(OXeF)NH$_2^+$ cation was established in solution by $^{1}$H, 13C, 19F and 129Xe NMR spectroscopy, and is consistent with resonance Structures 3.3 and 3.4.

The 129Xe NMR spectrum of the CF$_3$C(OXeF)NH$_2^+$ cation consists of a doublet centered at -1578 ppm (-53.0 °C, BrF$_5$ solvent) arising from $^{1}J$(129Xe-19F) = 5991 Hz, in the region expected for xenon(II) covalently bonded to fluorine (Figure 3.3). The magnitude of $^{1}J$(129Xe-19F) is comparable to other directly bonded 129Xe-19F couplings.$^{103,104,108}$ The XeF$_2$ triplet is also present [$\delta$(129Xe) = -1572 ppm; $^{1}J$(129Xe-19F) = 5651 Hz] and is consistent with equation (3.2).

In the 19F NMR spectrum, a singlet at $\delta$(19F) = -183.1 ppm with a satellite doublet [$^{1}J$(19F-129Xe) = 6012 Hz] is assigned to the F-on-Xe(II) of the CF$_3$C(OXeF)NH$_2^+$ cation (Figure 3.4). The 19F resonance centered at -187.5 ppm with accompanying 129Xe satellites [$^{1}J$(129Xe-19F) = 5650 Hz] is assigned to XeF$_2$. A doublet centered at -193.1 ppm [$^{1}J$(19F-1H) = 534 Hz] is assigned to HF formed according to equation (3.2). The 19F NMR resonance of the CF$_3$ group of the CF$_3$C(OXeF)NH$_2^+$ cation consists of a singlet at $\delta$(19F) = -74.4 ppm (-54.0 °C, BrF$_5$ solvent). The CF$_3$ group of the CF$_3$C(OH)NH$_2^+$ cation occurs at $\delta$(19F) = -75.6 ppm. Integration of the
$^{129}$Xe NMR spectrum and F-on-Xe(II) region of the $^{19}$F NMR spectrum gave values of 0.29 and 0.30$^{157}$ for the ratio $[\text{CF}_3\text{C(OXeF)}\text{NH}_2]^+/[\text{XeF}_2]$ (initial molar ratios were $\text{CF}_3\text{C(OH)}\text{NH}_2^+\text{AsF}_6^-$ /$\text{XeF}_2 = 0.892$ and 0.946; initial [XeF$_2$] = 0.29 and 0.20 M), respectively. Integration of the CF$_3$ group resonances gave a value of 0.32$^{157}$ for the ratio $[\text{CF}_3\text{C(OXeF)}\text{NH}_2]^+/[\text{CF}_3\text{C(OH)}\text{NH}_2^+]$ (initial molar ratio $\text{CF}_3\text{C(OH)}\text{NH}_2^+\text{AsF}_6^-$/XeF$_2 = 0.946$; initial [XeF$_2$] = 0.20 M), in good
Figure 3.3 $^{129}\text{Xe}$ NMR spectrum (139.051 MHz) at -53.0 °C of CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ (0.26 M) and XeF$_2$ (0.29 M) dissolved in BrF$_5$ solvent; (A) doublet arising from the one-bond coupling $^{1}J(^{129}\text{Xe}-^{19}\text{F})$ in the CF$_3$C(OXeF)NH$_2^+$ cation, (B) triplet arising from the one-bond coupling $^{1}J(^{129}\text{Xe}-^{19}\text{F})$ in XeF$_2$. 
Figure 3.4 $^{19}\text{F}$ NMR spectrum (470.599 MHz) at -54.0 °C of
CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ (0.18 M) and XeF$_2$ (0.19 M) dissolved in
BrF$_5$ solvent; only the F-on-Xe(II) region is shown; (A)
CF$_3$C(OXeF)NH$_2^+$ cation, (B) singlet arising from the fluorine
environment of XeF$_2$, (C) HF. Lower case letters denote $^{129}$Xe
satellites.
agreement with values obtained from the $^{129}$Xe NMR spectrum and from the $^{19}$F NMR spectrum of the F-on-Xe(II) region.

The $^{13}$C NMR spectrum of the CF$_3$C(OXeF)NH$_2^+$ cation (-59.4 °C, BrF$_5$ solvent) consisted of two binomial quartets at -165.7 ppm [$^2J^{13}$C-$^{19}$F] = 42 Hz] and at -113.7 ppm [$^1J^{13}$C-$^{19}$F] = 285 Hz], which were assigned to the CO and CF$_3$ carbons, respectively. Satellites arising from $^2J^{13}$C-$^{129}$Xe, were not observed in the $^{13}$C NMR spectrum due to a low signal-to-noise ratio.

The $^1$H NMR spectrum of an equimolar mixture of CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ and XeF$_2$ in BrF$_5$ solvent at -55.0 °C (Figure 3.5) was consistent with equation (3.2). The two broad peaks of equal intensity at 7.88 and 7.71 ppm were assigned to the chemically inequivalent proton-on-nitrogen resonances of the CF$_3$C(OXeF)NH$_2^+$ cation arising from hindered rotation about the C-N bond. This is consistent with an O-Xe-F linkage, since an N-Xe-F linkage would result in free rotation about the C-N bond, and the observation of only one proton-on-nitrogen resonance in the $^1$H NMR spectrum. The proton-on-oxygen resonance of the CF$_3$C(OH)NH$_2^+$ cation was observed at 12.04 ppm, and was deshielded by 0.41 ppm relative to that of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ in BrF$_5$ solvent at the same temperature (Figure 3.1). The two equal-intensity singlets at 8.48 and 8.39 ppm were assigned to the amido protons of the CF$_3$C(OH)NH$_2^+$ cation (Figure 3.5); the separation of the peaks is 135 Hz less than that observed for pure CF$_3$C(OH)NH$_2^+$AsF$_6^-$ in BrF$_5$ solvent (Figure 3.1), and is consistent with partial coalescence of the amido protons of the CF$_3$C(OH)NH$_2^+$ cation arising from proton exchange between the CF$_3$C(OH)NH$_2^+$ cation and HF, which is present in the system according to equation (3.2). Exchange was confirmed by recording the $^1$H NMR spectrum of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ in the presence of HF (1.83 molar equivalents of anhydrous HF in BrF$_5$ solvent at -57.6 °C). Complete collapse of the proton-on-nitrogen resonance to a broadened singlet resulted [8($^1$H) = 8.59 ppm,
Figure 3.5 $^1$H NMR spectrum (500.138 MHz) at -55.0 °C of CF$_3$C(OH)NH$_2^+$ AsF$_6^-$ (0.18 M) and XeF$_2$ (0.19 M) dissolved in BrF$_5$ solvent; (A) proton on oxygen of CF$_3$C(OH)NH$_2^+$, (B) protons on nitrogen of CF$_3$C(OH)NH$_2^+$, (C) protons on nitrogen of CF$_3$C(OXeF)NH$_2^+$, (D) HF.
Figure 3.6 Heteronuclear $[^1\text{H} (500.138 \text{ MHz})-^{19}\text{F}(470.599 \text{ MHz})]$ NOESY spectrum at -57.6 °C of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ (0.35 M) and XeF$_2$ (0.38 M) dissolved in BrF$_5$ solvent; portions of the one-dimensional $^1$H and $^{19}$F NMR spectra are displayed along the vertical and horizontal axes, respectively; (A) and (B) are the proton on nitrogen resonances of CF$_3$C(OH)NH$_2^+$, (C) and (D) are the protons on nitrogen which are cis and trans to the CF$_3$ group, respectively, in CF$_3$C(OXeF)NH$_2^+$, (E) CF$_3$ group resonance of CF$_3$C(OXeF)NH$_2^+$, (F) CF$_3$ group resonance of CF$_3$C(OH)NH$_2^+$. 
\[ \Delta \nu_{1/2} = 88 \text{ Hz} \] with retention of the proton-on-oxygen resonance \([\delta(\text{H}) = 11.68 \text{ ppm}]\). Coalescence of the amido proton peaks can arise from two possible mechanisms: deprotonation to give the amidic acid, \(\text{CF}_3\text{C(OH)=NH}^-\) [equation (3.5)], and N-protonation to give the \(\text{CF}_3\text{C(OH)NH}_3^{2+}\) dication [equation (3.6)]. Both equilibria would account for retention of the

\[
\text{CF}_3\text{C(OH)=NH}_2^+ + \text{HF} \rightleftharpoons \text{CF}_3\text{C(OH)=NH}^- + \text{H}_2\text{F}^- \quad (3.5)
\]

\[
\text{CF}_3\text{C(OH)=NH}_2^+ + 2 \text{HF} \rightleftharpoons \text{CF}_3\text{C(OH)-NH}_3^{2+} + \text{HF}_2^- \quad (3.6)
\]

proton-on-oxygen resonance. Equation (3.5) can be discounted since the amidic acid mechanism has been shown to be inhibited by strong acid (\(\text{H}_2\text{SO}_4\)), and contributes to proton exchange only in dilute aqueous acid.\(^{147}\) The transient diprotonated cation, \(\text{CF}_3\text{C(OH)-NH}_3^{2+}\) [equation (3.6)], could undergo free rotation about the C-N bond, resulting in partial collapse of the amido proton doublet with retention of the proton on oxygen resonance.

The protons on nitrogen of \(\text{CF}_3\text{C(OXeF)NH}_2^+\) were assigned by performing a two-dimensional heteronuclear \(^1\text{H}-^{19}\text{F}\) NOESY experiment in \(\text{BrF}_3\) solvent at -57.6 °C (Figure 3.6). A correlation was observed between the \(^{19}\text{F}\) NMR resonance of the \(\text{CF}_3\) group and the high-frequency \([\delta(\text{H}) = 7.88 \text{ ppm}]\) proton on nitrogen resonance of the \(\text{CF}_3\text{C(OXeF)NH}_2^+\) cation, implying that the high-frequency \(^1\text{H}\) NMR resonance arises from the proton cis to the \(\text{CF}_3\) group (trans to the OXeF group). It is interesting that the relative shieldings of the proton-on-nitrogen resonances for the \(\text{CF}_3\text{C(OXeF)NH}_2^+\) cation are opposite to those observed for the \(\text{CF}_3\text{C(OH)NH}_2^+\) cation. The change in relative shieldings may result from differences in electronic anisotropy resulting from the different moieties bonded to oxygen in the \(\text{CF}_3\text{C(OXeF)NH}_2^+\) and
CF$_3$C(OH)NH$_2^+$ cations. The CF$_3$ group in the CF$_3$C(OH)NH$_2^+$ cation correlates with both the cis and trans protons of the amido group (Figure 3.6). This is attributed to insufficient resolution of the partially coalesced proton on nitrogen resonances for the CF$_3$C(OH)NH$_2^+$ cation resulting from exchange with HF (see above).

(D) CHARACTERIZATION OF CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$ BY LOW-TEMPERATURE RAMAN SPECTROSCOPY

Assignments for the CF$_3$C(OXeF)NH$_2^+$ cation (Table 3.1 and Figure 3.7) were based on the Raman spectra of CF$_3$C(O)NH$_2$ and related compounds containing the O-Xe-F linkage.$^{41,42,85,140,158}$ Assignments for the AsF$_6^-$ anion were made by comparison with those of XeF$^+$AsF$_6^-$,$^{158}$ HO=NXeF$^+$AsF$_6^-$,$^{73}$ and O$_2^+$AsF$_6^-$.$^{159}$

Evidence for the O-Xe-F linkage is provided by the characteristic bands arising from O-Xe-F stretching and bending fundamentals. Five bands are observed in the $\nu$(Xe-O) and $\nu$(Xe-F) regions. The intense bands at 543 and 530 cm$^{-1}$ are assigned to $\nu$(Xe-F) by comparison with the assigned Xe-F stretches in related xenon(II) compounds: FO$_2$SOXeF (539, 532, 527, 521 cm$^{-1}$),$^{158}$ cis- and trans-F$_4$OIOXeF (527 cm$^{-1}$),$^{42}$ F$_3$TeOXeF (520 cm$^{-1}$),$^{41}$ CF$_3$O$_2$SOXeF (534 cm$^{-1}$),$^{140}$ and (CF$_3$)$_2$S=OXeF$^+$SbF$_6^-$ (552 cm$^{-1}$).$^{85}$ The bands at 508, 502 and 476 cm$^{-1}$ are assigned to $\nu$(Xe-O) by comparison with the assigned Xe-O stretches in FO$_2$SOXeF (434 cm$^{-1}$),$^{158}$ cis- and trans-F$_4$OIOXeF (488, 438 cm$^{-1}$),$^{42}$ F$_3$TeOXeF (457 cm$^{-1}$),$^{41}$ CF$_3$O$_2$SOXeF (369 cm$^{-1}$),$^{140}$ and (CF$_3$)$_2$S=OXeF$^+$SbF$_6^-$ (494 cm$^{-1}$).$^{85}$ The splitting of the v(Xe-F) and v(Xe-O) bands may result from vibrational coupling of two or more cations in the unit cell (factor-group splitting), but cannot be confirmed without knowledge of the crystal structure of CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$. Site-symmetry effects can be eliminated as the source of the splitting since the highest possible point-
Figure 3.7  Raman spectrum of microcrystalline CF$_3$C(Ox)NH$_2$H$^+$AsF$_6^-$ (-165 °C) recorded in an FEP sample tube using 514.5-nm excitation. Asterisks (*) denote FEP sample tube lines.
group symmetry for the $\text{CF}_3\text{C(OXeF)}\text{NH}_2^+$ cation is $C_2$, which does not possess any degenerate irreducible representations. Similar band splittings for modes assigned to $\nu(\text{Xe-F})$ are observed in the Raman spectra of $\text{HC}=$N-XeF$^+$AsF$_6^-$, $^{73} \text{FO}_2\text{SOXeF},^{158}$ and XeF$^+$MF$_6^-$ salts ($M = \text{Ru, Pt, Ir}$).$^67$ It is interesting to compare the $\nu(\text{Xe-O})$ and $\nu(\text{Xe-F})$ stretching modes of the $\text{CF}_3\text{C(OXeF)}\text{NH}_2^+$ cation with those of the (CF$_3)$_2S=O-XeF$^+$ cation, since these are the only reported examples of cations containing the O-Xe-F linkage. The $\nu(\text{Xe-F})$ and $\nu(\text{Xe-O})$ Raman bands in the structurally related (CF$_3)$_2S=O-XeF$^+$ cation were observed at 552 and 494 cm$^{-1}$, respectively.$^85$ The average of the bands assigned to $\nu(\text{Xe-O})$ for the $\text{CF}_3\text{C(OXeF)}\text{NH}_2^+$ cation, 495 cm$^{-1}$, is very similar to $\nu(\text{Xe-O})$ in the (CF$_3)$_2S=O-XeF$^+$ cation, and the average of the bands assigned to $\nu(\text{Xe-F})$ for the $\text{CF}_3\text{C(OXeF)}\text{NH}_2^+$ cation, 536 cm$^{-1}$, is 16 cm$^{-1}$ lower than $\nu(\text{Xe-F})$ for the (CF$_3)$_2S=O-XeF$^+$ cation. Raman spectroscopic trends in the terminal Xe-F stretches of xenon(II) compounds indicate a more ionic Xe-F bond in the $\text{CF}_3\text{C(OXeF)}\text{NH}_2^+$ cation than in the (CF$_3)$_2S=O-XeF$^+$ cation [see Section (G) of this Chapter]. The bands at 141 and 292 cm$^{-1}$ are assigned to the O-Xe-F and C-O-Xe bending modes, respectively. Comparable values for $\delta$(O-Xe-F) and $\delta$(X-O-Xe) are observed in structurally related xenon(II) compounds containing the O-Xe-F linkage.$^{41,42,85,140,158}$

The band at 3335 cm$^{-1}$ in the Raman spectrum of $\text{CF}_3\text{C(OXeF)}\text{NH}_2^+$AsF$_6^-$ is assigned to an NH stretching mode. Two bands are usually observed in the vibrational spectra of primary amides arising from the symmetric and asymmetric NH$_2$ stretches.$^{160}$ Although peaks observed at 3174 and 3337 cm$^{-1}$ can be assigned to $\nu_{\text{sym}}$(NH$_2$) and $\nu_{\text{asym}}$(NH$_2$), respectively, in the Raman spectrum of solid trifluoroacetamide,$^{161}$ it is not possible to assign the NH stretch of $\text{CF}_3\text{C(OXeF)}\text{NH}_2^+$AsF$_6^-$ to a particular symmetry species since the bands observed in this region for O-complexed amides are often not directly comparable to the bands of the free amide.$^{162,163}$ The out-of-plane wag of the NH$_2$ group, $\omega$(NH$_2$), is assigned to the band at 672 cm$^{-1}$ by
comparison with CF$_3$C(O)NH$_2$ (666 cm$^{-1}$), and the frequency increase (6 cm$^{-1}$) is attributed to
O-coordination of CF$_3$C(O)NH$_2$ to the XeF$^+$ cation and an attendant increase in C-N double bond
correct character. This mode is observed at 639 cm$^{-1}$ in matrix isolated CF$_3$C(O)NH$_2$, and complexation
with HF by bridging of the HF molecule between oxygen and an NH proton results in an increase
of 17 cm$^{-1}$. The fundamental arising from the torsional motion of the NH$_2$ group, $\tau$(NH$_2$), is
tentatively assigned to the band at 810 cm$^{-1}$ by analogy with solid CF$_3$C(O)NH$_2$ (796 cm$^{-1}$). The
increase in $\tau$(NH$_2$) (14 cm$^{-1}$) is attributed to an increase in C-N double bond character
resulting from O-coordination. The rocking motion fundamental, $\gamma$(NH$_2$), is not observed in the
Raman spectrum of CF$_3$C(OXeF)NH$_2$ $^+$AsF$_6^-$, but is observed as a weak band at 1199 cm$^{-1}$ in the
Raman spectrum of solid CF$_3$C(O)NH$_2$. The band at 1623 cm$^{-1}$ has been assigned primarily
to the in-plane bending mode, $\delta$(NH$_2$), which is 6 cm$^{-1}$ lower than that observed for CF$_3$C(O)NH$_2$.
This mode is relatively insensitive to complexation, as observed for several primary amides and
their HF complexes.

The bands at 1543, 1562 and 1745 cm$^{-1}$ result from the $v$(CO) and $v$(CN) stretching modes.
Although vibrational coupling of these modes is likely, $v$(CO) is formally assigned to the bands
at 1543 and 1562 cm$^{-1}$ (Table 3.1) following the method of assignment for amidium salts, which are electronically similar to the CF$_3$C(OXeF)NH$_2$ $^+$ cation. The CO stretching frequency is
expected to be lower than that of uncomplexed CF$_3$C(O)NH$_2$ because the double-bond character
of the C-O linkage is significantly reduced upon O-coordination. This implies dominance of
resonance Structure 3.4 in the bonding of the CF$_3$C(OXeF)NH$_2$ $^+$ cation. Correspondingly, the C-N
stretch is expected to increase significantly and is assigned to the band at 1745 cm$^{-1}$, which is
close to the observed range for $v$(CN) in the infrared spectra of O-protonated and O-alkylated
amides (ca. 1600 - 1730 cm$^{-1}$). Unambiguous evidence for the reversal of $v$(CO) and $v$(CN)
frequencies upon O-protonation of amides has been provided by Cook,\textsuperscript{167} who compared the infrared spectra of N-acyltrialkylammonium halides and O-protonated N,N-dicyclohexylacetamide hydrohalide salts. Since the former are isoelectronic with the hypothetical N-protonated amides, a direct comparison of the infrared spectra of these salts with those of the neutral compounds aided in the assignment of the $v$(CO) and $v$(CN) bands. Following previously published assignments,$^{161}$ the bands at 1706 and 1460 cm$^{-1}$ in the Raman spectrum of CF$_3$C(O)NH$_2$ are assigned to $v$(CO) and $v$(CN), respectively. When compared to CF$_3$C(OXeF)NH$_2^+\text{AsF}_6^-$, these values show a decrease in $v$(CO) of 154 cm$^{-1}$ and an increase in $v$(CN) of 285 cm$^{-1}$ in the xenon cation. Similar values of $v$(CO) and $v$(CN) have been reported from the infrared spectra of protonated amides; for example, $v$(CO) for the O-protonated salt of N,N-dimethylacetamide, CH$_3$C(OH)N(CH$_3$)$_2^+\text{SbCl}_5^-$,\textsuperscript{165} is observed at 1401 cm$^{-1}$ and that of N,N-dimethylacetamide vapor is observed at 1651 cm$^{-1}$ [$\Delta v$(CO) = 250 cm$^{-1}$],\textsuperscript{168} whereas the value of $v$(CN) increases to 1680 cm$^{-1}$ (average of three bands) upon O-protonation of N,N-dimethylacetamide,\textsuperscript{165} compared to 1492 cm$^{-1}$ for the amide vapor [$\Delta v$(CO) = 188 cm$^{-1}$].\textsuperscript{168} An incomplete report of the infrared spectrum of CF$_3$(O)NH$_2^+$BF$_3$ provides a value of 1760 cm$^{-1}$ for $v$(CO).\textsuperscript{169} If CF$_3$(O)NH$_2^+$BF$_3$ is indeed O-bonded, it is likely that $v$(CO) has been misassigned in light of the well established trends noted above for $v$(CO) and $v$(CN).

The in-plane (δ) and out-of-plane (γ) OCN bends are tentatively assigned to the peak at 596 cm$^{-1}$ by analogy with CF$_3$C(O)NH$_2$,\textsuperscript{161} assuming that they are similar in the CF$_3$C(OXeF)NH$_2^+$ cation.

The CF$_3$ group modes of CF$_3$C(OXeF)NH$_2^+$ are assigned by analogy with those in Raman spectrum of solid CF$_3$C(O)NH$_2$: 1073 [$v_{\text{sym}}$(CF$_3$)], 747 [$\delta_{\text{sym}}$(CF$_3$)], 523 [$\delta_{\text{asym}}$(CF$_3$)] and 432, 419 cm$^{-1}$ [$\gamma$(CF$_3$)]. The symmetric stretch, $v_{\text{sym}}$(CF$_3$), is not observed in the Raman spectra of
CF$_3$C(O)NH$_2$ and CF$_3$C(OXeF)NH$_2$\(^+\), but is observed at 1340 cm\(^{-1}\) in the infrared spectrum of CF$_3$C(O)NH$_2$.\(^{161}\) The symmetric stretch of the CF$_3$ group is not observed in the Raman spectrum of the CF$_3$C(OXeF)NH$_2$\(^+\) cation, because it is too weak and/or because it coincides with an FEP sample tube band at 1384 cm\(^{-1}\).

A total of 21 bands are assigned to the AsF$_6$\(^-\) anion, and are derived from the six normal modes for AsF$_6$\(^-\) under $O_h$ point symmetry.\(^{170}\) Since only three bands ($v_1(A_{1g})$, $v_2(E_g)$, and $v_5(F_{2g})$) are Raman active for $O_h$ symmetry, a reduction of anion symmetry is apparent. A symmetry of $C_{2v}$ or $C_3$ would account for the observation of 15 normal modes, since all mode degeneracies would then be removed. The apparent reduction in anion symmetry may result in part from a low site symmetry for the AsF$_6$\(^-\) anion in the unit cell, or from a true distortion of the molecular geometry of the anion due to hydrogen bonding interactions with the protons of the cation, as observed in the SbF$_6$\(^-\) and AsF$_6$\(^-\) salts of OH$_3$\(^+\),\(^{171}\) SH$_3$\(^+\),\(^{172}\) and NF$_2$H$_2$\(^+\).\(^{173}\) The observation of more than 15 bands is attributed to intermolecular vibrational coupling within the crystallographic unit cell. This is likely since low site symmetry alone cannot account for the splitting of the non-degenerate $v_1(A_{1g})$ mode for AsF$_6$\(^-\) (647, 683 cm\(^{-1}\)). A crystal structure is required, however, to confirm these assignments (factor group analysis).

(E) CHARACTERIZATION OF CF$_3$C(OH)NH$_2$\(^+\)AsF$_6$\(^-\) BY LOW-TEMPERATURE RAMAN SPECTROSCOPY

The assignments for the Raman spectrum of CF$_3$C(OH)NH$_2$\(^+\)AsF$_6$\(^-\) were made by analogy with those of CF$_3$C(O)NH$_2$\(^+\)\(^{161}\) and CF$_3$C(OXeF)NH$_2$\(^+\)AsF$_6$\(^-\) (Table 3.1 and Figure 3.8). The $v$(CO) and $v$(CN) modes are assigned to the bands at 1519 and 1767 cm\(^{-1}\), indicating greater double-bond character for the C-N bond than for the C-O bond and are similar to those of CF$_3$C(OXeF)NH$_2$\(^+\).
Table 3.1. Raman Frequencies\(^a\) and Assignments for CF\(_3\)C(O)NH\(_2\), CF\(_3\)C(OH)NH\(_2\)\(^+\)AsF\(_6\)\(^-\), CF\(_3\)C(OH)NH\(_2\)\(^+\)AsF\(_6\)\(^-\)\(\times\)XeF\(_2\)\(\times\)HF, and CF\(_3\)C(OXeF)NH\(_2\)\(^+\)AsF\(_6\)\(^-\).

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<th>CF(_3)C(OH)NH(_2)(^+)AsF(_6)(^-)(\times)XeF(_2)(\times)HF(^c)</th>
<th>CF(_3)C(OXeF)NH(_2)(^+)AsF(_6)(^c)</th>
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<td>398 (0.8)</td>
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<td>379 (14)</td>
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<td>273 (6)</td>
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<td>502 (34)</td>
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<td>432 (8)</td>
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<td>409 (0.3)</td>
<td>$\nu_5(AsF_6)^b$</td>
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<td>385 (14)</td>
<td>$\delta(CO\text{xe})$</td>
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<tr>
<td>379 (14)</td>
<td>$\gamma(C-C)$</td>
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<td>292 (12)</td>
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<td>255 (10)</td>
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<td>lattice modes</td>
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</table>

Notes:
- $^b$ indicates the assignment for $\nu_4(AsF_6)$.
Table 3.1 (continued)

aValues in parentheses denote relative intensities; sh denotes a shoulder. bRecorded at room temperature in a glass sample tube; this work. Assignments have been taken from ref. (161). cRaman spectra were recorded in FEP sample tubes at -165 °C. Raman lines due to the FEP sample tube have been omitted from the table unless overlap with a sample tube band is likely. Data are given for the spectra depicted in Figures 3.7 - 3.9. dThe symmetries of the N-H stretches cannot be assigned from the available data. eThe broadness of the $v_{\text{asym}}(\text{NH}_2)$ and $v_{\text{sym}}(\text{NH}_2)$ bands is attributed, in part, to hydrogen bonding involving solvated HF. fBands not observed in the Raman spectrum. gBand may overlap with an FEP sample tube band. hNotation provided for the fundamental modes of the AsF$_5^-$ anion is that for $O_h$ symmetry. The splitting of degenerate modes may be attributable to low site symmetry in the solid state or vibrational coupling within the unit cell. iThe band assigned to the $\delta(\text{COXe})$ bend in the CF$_3\text{C(OXeF)NH}_2^+$ cation is coincident with an FEP band at 292 cm$^{-1}$. This is indicated by the increased intensity of this band relative to the most intense FEP band at 734 cm$^{-1}$. 
Figure 3.8  Raman spectrum of microcrystalline CF$_3$C(OH)NH$_2^+$AsF$_6^-$ (-165 °C) recorded in an FEP sample tube using 514.5-nm excitation. Asterisks (*) denote FEP sample tube lines. A dagger (†) denotes an artifact characteristic of the instrument.
The bands attributed to \( \omega(\text{NH}_2) \) (670 cm\(^{-1}\)), \( \tau(\text{NH}_2) \) (806 cm\(^{-1}\)) and \( \gamma(\text{NH}_2) \) (1197 cm\(^{-1}\)) are also similar to those observed in the Raman spectra of CF\(_3\)C(O)NH\(_2\) and CF\(_3\)C(OXeF)NH\(_2\)^+AsF\(_6\)^-. A band attributable to \( \delta(\text{NH}_2) \) was not observed, and is likely the result of the inherent low Raman intensity of this band.\(^{174}\)

The band at 1276 cm\(^{-1}\) has been tentatively assigned to \( \delta(\text{OH}) \) of the protonated carbonyl group. Infrared spectra of the related salts CH\(_3\)C(OH)NH\(_2\)^+X^- (X = SbCl\(_6\), NO\(_3\), Cl),\(^{162}\) [CH\(_3\)C(OH)NH\(_2\)^+]\(^2\)X\(^2\)- (X = SnCl\(_6\), PtCl\(_6\))\(^{162}\) and CH\(_3\)C(OH)N(CH\(_3\))\(^2\)X^- (X = Cl, Br, I, SbCl\(_6\))\(^{165}\) exhibit bands at 1333-1368 and 1040-1192 cm\(^{-1}\), respectively, which are assigned to \( \delta(\text{OH}) \). Bands attributable to \( \gamma(\text{OH}) \) and \( \nu(\text{OH}) \), which, like \( \delta(\text{NH}_2) \), usually have very low Raman intensities,\(^{174}\) and were too weak to be observed.

Seven bands have been assigned to the AsF\(_6\)^- anion, as opposed to three bands expected for AsF\(_6\)^- with \( O_h \) symmetry. Again, hydrogen bonding between cation and anion, as in the salt, CF\(_3\)C(OXeF)NH\(_2\)^+AsF\(_6\)^-, may contribute to symmetry lowering of the anion. Low site symmetry in the solid may also give rise to the splitting of the \( \nu_5 \) band and observation of \( \nu_3 \) (720 cm\(^{-1}\)) and \( \nu_6 \) (251 cm\(^{-1}\)), both of which are formally Raman forbidden for octahedral XY\(_6\) species.\(^{170}\) All bands are assigned except \( \nu_4 \) (ca. 420 cm\(^{-1}\)). This can be accounted for by considering the low intensity of this band in the Raman spectrum of HC≡NXeF^+AsF\(_6\)^-\(^{73}\) combined with the presence of bands in this region due to the FEP sample tube.

(F)  CHARACTERIZATION OF CF\(_3\)C(OH)NH\(_2\)^+AsF\(_6\)^-XeF\(_2\)-XHF BY LOW-TEMPERATURE RAMAN SPECTROSCOPY

A white microcrystalline powder precipitates upon rapid removal of the HF solvent under vacuum from a solution containing stoichiometric amounts of CF\(_3\)C(O)NH\(_2\) and XeF^+AsF\(_6\)^-, or
Figure 3.9  Raman spectrum of microcrystalline CF$_3$C(OH)NH$_2$$^+$AsF$_6$-XeF$_2$-xHF
(-165 °C) recorded in an FEP sample tube using 514.5-nm excitation.
Asterisks (*) denote FEP sample tube lines. A dagger (†) denotes an artifact characteristic of the instrument.
CF₃C(OH)NH₂⁺AsF₆⁻ and XeF₂. The Raman spectroscopic results (Table 3.1 and Figure 3.9) are consistent with the formulation CF₃C(OH)NH₂⁺AsF₆⁻•XeF₂•xHF. The Raman spectrum resembles that expected for a mixture of polycrystalline XeF₂ and CF₃C(OH)NH₂⁺AsF₆⁻. However, the average of the very intense peaks at 511 and 515 cm⁻¹, assigned to ν₈(Xe-F) of XeF₂ incorporated in the adduct, is 17 cm⁻¹ higher in frequency than the symmetric Xe-F stretch for polycrystalline XeF₂ (495 cm⁻¹). The interaction of XeF₂ with fluoroacids as in XeF⁺AsF₆⁻, XeF⁺Sb₂F₁₁⁻ and XeF₂•XeF₅⁺AsF₆⁻ results in elongation of one Xe-F bond (Xe--F bridge bond) in complexed XeF₂, accompanied by a shortening of the remaining (terminal) Xe-F bond. This results in bands which are assignable to a bridging Xe--F stretch and a terminal Xe-F stretch, that are lower and higher in frequency, respectively, than ν₈(Xe-F) (496 cm⁻¹) and ν₉(Xe-F) (547 cm⁻¹) in uncoordinated XeF₂, from which they are formally derived. The latter mode is Raman forbidden for XeF₂ under D₃h point symmetry. The absence of a relatively intense band assignable to ν₉(Xe-F) at approximately 550 cm⁻¹ in the Raman spectrum of CF₃C(OH)NH₂⁺AsF₆⁻•XeF₂•xHF indicates that the Xe-F bonds in coordinated XeF₂ are essentially symmetric. The frequency of ν₈(Xe-F) is also inconsistent with an XeF₂ molecule containing significantly different Xe-F bond lengths (see above). The observation of two peaks for ν₈(Xe-F) is attributed to vibrational coupling of XeF₂ molecules within the unit cell of CF₃C(OH)NH₂⁺AsF₆⁻•XeF₂•xHF. By analogy with known adducts containing symmetric XeF₂, it is probable that the fluorine ligands of XeF₂ interact with the positive centers of the CF₃C(OH)NH₂⁺ cation in the adduct CF₃C(OH)NH₂⁺AsF₆⁻•XeF₂•xHF, namely the hydroxyl and amido protons, through hydrogen bonding. Structures 3.5 - 3.7 illustrate possible hydrogen bonding interactions of XeF₂ and CF₃C(OH)NH₂⁺ in which the local molecular point symmetry of XeF₂ does not deviate significantly from D₃h.
Further evidence for the assigned structure of the solvate CF$_3$C(OH)NH$_2^+$AsF$_6^-$XeF$_2$-$\gamma$HF was obtained by comparing bands in the amide region of the Raman spectrum with those of CF$_3$C(O)NH$_2$ and CF$_3$C(OH)NH$_2^+$AsF$_6^-$. The bands at 1767 and 1549 cm$^{-1}$ are assigned to $\nu$(CN) and $\nu$(CO), respectively. This is consistent with an increase of 262 cm$^{-1}$ for $\nu$(CN) and a decrease of 157 cm$^{-1}$ for $\nu$(CO) relative to CF$_3$C(O)NH$_2$ and with the changes in C-N and C-O bond order anticipated upon O-protonation of amides. The bands at 1262 and 1232 cm$^{-1}$ are assigned to the bending mode, $\delta$(OH), and are similar to the value assigned for CF$_3$C(OH)NH$_2^+$AsF$_6^-$ (1276 cm$^{-1}$). As in the Raman spectrum of CF$_3$C(OH)NH$_2^+$AsF$_6^-$, modes arising from $\nu$(OH) and $\gamma$(OH) are presumably too weak to be observed. Evidence for solvation by HF is provided by the presence of a broad band at 3090 cm$^{-1}$ which is assigned to $\nu_{sym}$(HF), and is similar to that observed in the infrared spectra of hydrogen-bonded complexes of HF with CF$_3$C(O)NH$_2$.$^{164}$

A total of 17 bands are attributed to the AsF$_6^-$ anion, and have been assigned using arguments similar to those already presented for CF$_3$C(OH)NH$_2^+$AsF$_6^-$ and CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$. 

(G) **NATURE OF THE BONDING IN CF$_3$C(OXeF)NH$_2^+$**

The bonding in the CF$_3$C(OXeF)NH$_2^+$ cation can be assessed using trends for xenon(II) compounds that are well established from Raman and NMR spectroscopy. Previous NMR studies of xenon(II) derivatives containing XeF groups bonded to oxygen or fluorine have shown that the $^{19}$F and $^{129}$Xe NMR parameters can be used to assess the relative covalent characters of the Xe-O, Xe-F bridge and terminal Xe-F bonds in compounds of the type F-Xe-L (L = ligand atom).$^{26,103,104,108}$ In general, as the ionic character of the Xe-L bond increases, the covalent character of the terminal Xe-F bond increases, increasing the formal charge on xenon. This trend
is paralleled by increasing values of $\delta^{(129}\text{Xe})$ and $1^{J(129}\text{Xe}^{19}\text{F}}$, and decreasing values of $\delta^{(19}\text{F})$ for the terminal Xe-F group. The pattern observed in the $^{19}\text{F}$ and $^{129}\text{Xe}$ NMR spectra is complemented by measurements of $\nu(\text{Xe-F})$ provided by Raman spectroscopy, which signify increased covalent character of the Xe-F bond with shifts to higher frequency, and vice versa.\textsuperscript{26}

Table 3.2 lists the relevant NMR and Raman spectroscopic data for the $\text{CF}_3\text{C(OXeF)NH}_2^+$ cation and some related Xe-O, Xe-N and Xe—F bonded compounds of Xe(II) arranged in approximate order of increasing ionic character of the Xe-F bond. Xenon difluoride and XeF$^+\text{Sb}_2\text{F}_{11}^-$, in which the XeF$^+$ cation is fluorine bridged to the weakly fluorobasic Sb$_2$F$_{11}^-$ anion,\textsuperscript{69} provide the upper and lower limits, respectively, of the terminal Xe-F bond ionic character. The charge distribution for XeF$_2$ may be represented as F$^{12-}\text{Xe}^{12+}\text{F}^{12-}$, indicating a high degree of Xe-F bond ionic character.\textsuperscript{179} The low basicity of the Sb$_2$F$_{11}^-$ anion in XeF$^+\text{Sb}_2\text{F}_{11}^-$ provides the closest approximation to a free XeF$^+$ cation, where the Xe-F bond order approaches one. Consistent with the valence bond Structures 3.8 and 3.9, the degree of Xe-F bond ionic character in $\text{L-Xe-F}$ depends upon the basicity of the ligand $\text{L}$.\textsuperscript{26} As can be inferred from

\begin{align*}
\text{L-Xe}^+\text{F} & \longleftrightarrow \text{L-Xe-F}^+ & \longleftrightarrow & \text{L}^- \text{Xe}^{2+} \text{F} \\
3.8 & & 3.9 & & 3.10
\end{align*}

\begin{align*}
\text{L-Xe}^{2+}\text{F} & \longleftrightarrow \text{L Xe-F}^+ & \longleftrightarrow & \text{L Xe}^{2+}\text{F} \\
3.11 & & 3.12 & & 3.13
\end{align*}

$^{19}\text{F}$ and $^{129}\text{Xe}$ NMR shielding trends, the magnitude of $1^{J(19}\text{F}^{129}\text{Xe})$ and terminal Xe-F stretching frequencies (Table 3.2), the Xe-O bond in the $\text{CF}_3\text{C(OXeF)NH}_2^+$ cation is significantly more
Table 3.2. Comparison of Chemical Shifts, One Bond Xe-F Coupling Constants and ν(Xe-F) of Some L-Xe-F Derivatives

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<tr>
<th>Species</th>
<th>ν(Xe(_2)F(_2))^b cm(^{-1})</th>
<th>(^1)J((^{129})Xe-(^{19})F), Hz</th>
<th>(^\delta)((^{129})Xe)^c ppm</th>
<th>(^\delta)((^{19})F)^d ppm</th>
<th>T, °C</th>
<th>ref</th>
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<td>F(_{10})Sb(<em>2)F(</em>{11})—XeF(_2)(^e)</td>
<td>619</td>
<td>7230</td>
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<td>-290.2</td>
<td>23</td>
<td>66,69,108,111</td>
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<td>F-Xe—F—F—Xe-F(^f)</td>
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<td>6740</td>
<td>-1051</td>
<td>-252.0</td>
<td>-62</td>
<td>69,108,111</td>
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<td>(CP(_3))(_2)S=OXeF(_4)SbF(_6)(^-)</td>
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<td>6343</td>
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<td>72,73</td>
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<td>6020</td>
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<td>5991</td>
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<td>5932</td>
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<td>71</td>
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<td>cis-F(_4)OIOXeF(^-)</td>
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<td>5803</td>
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<td>F(_2)TeOXeF(^d)</td>
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\(^a\) NMR Parameters: \(^b\) cm\(^{-1}\) \(^c\) ppm \(^d\) ppm \(^e\) \(^f\) \(^g\) \(^h\) \(^i\) \(^j\) \(^k\)
Table 3.2 (continued)

*Spectra were recorded in BrF₃ solvent unless otherwise indicated. The NMR parameters of the XeF group, in particular δ(¹²⁹Xe), are very sensitive to solvent and temperature conditions; it is therefore important to make comparisons in the same solvent medium and at the same or nearly the same temperature. Table entries refer to the terminal fluorine on the xenon atom.  

bVibrational data refers to terminal Xe-F stretches.  

cReferenced with respect to the neat liquid XeOF₄ at 30 °C.  

dReferenced with respect to the neat liquid CFCl₃ at 30 °C.  

NMR parameters recorded in SbF₅ solvent.  

fδ(¹⁹F) measured in anhydrous HF solvent at -10 °C.  

NMR parameters measured in HF solvent.  

This work.  

iδ(¹⁹F) measured in SO₂ClF solvent at -40 °C.  

jNMR parameters measured in SO₂ClF solvent.  

kNMR parameters measured in SO₂ClF solvent at -50 °C.  

Vibrational spectrum obtained using infrared spectroscopy in acetonitrile solvent at ambient temperature. NMR parameters obtained in CD₃CN solvent at -30 °C.
covalent than those of the Xe-N bonded cations $F_3S\equiv N\cdot XeF^+$, $HC\equiv N\cdot XeF^+$ and $CH_2C\equiv N\cdot XeF^+$, which have been shown to have highly ionic Xe-N bonds.\textsuperscript{26} Based on $J_{\text{Xe}^{129}-\text{F}}^{\text{199}}$ and $\nu(XeF)$, the Xe-F bond in the $CF_2C(OXeF)NH_2^+$ cation is more ionic than the Xe-F bond in $(CF_3)\_2S=O\cdot XeF^+$, implying a more covalent Xe-O bond in the former cation. The $\delta(^{129}\text{Xe})$ values are, however, opposite in direction to the trend established above, but the difference in the solvents and temperatures used, and the large influence that these factors are known to have on the $^{129}\text{Xe}$ NMR chemical shifts of Xe(II) compounds,\textsuperscript{103,108} renders this parameter unreliable for assessing Xe-F bond ionicity in the present case. One possible factor contributing to the ionic character of the Xe-O bonds in the $(CF_3)\_2S=O\cdot XeF^+$ and $CF_3C(OXeF)NH_2^+$ cations is the formal hybridization on oxygen. In general, a greater $s$-contribution to the hybridization of the ligand donor atom is expected to increase its effective electronegativity,\textsuperscript{105} resulting in a more ionic Xe-L bond. This is illustrated in the series of cations containing Xe-N bonds, where the Xe-N bonds in cations containing formally $sp$-hybridized nitrogen (e.g., $F_3S\equiv N\cdot XeF^+$, $RC\equiv N\cdot XeF^+$) are consistently more ionic than the Xe-N bonds in the cations containing formally $sp^2$-hybridized nitrogen (e.g., $CF_3C_2F_4\cdot XeF^+$, $C_2F_5\cdot XeF^+$, $s-C_3F_3N_2\cdot XeF^+$). The oxygen of the $(CF_3)\_2S=OXeF^+$ cation is formally $sp^2$-hybridized, whereas resonance Structure 3.4 for the $CF_3C(OXeF)NH_2^+$ cation indicates $\pi$-donation from nitrogen to carbon, which effectively lowers the $s$-contribution to hybridization on oxygen so that it is intermediate between $sp^2$ and $sp^3$, resulting in a more covalent Xe-O bond in the $CF_3C(OXeF)NH_2^+$ cation. It is also apparent from Table 3.2 that cationic L-Xe-F\textsuperscript{+} compounds exhibit spectroscopic properties which are consistent with more ionic Xe-L bonds than the structurally analogous neutral compounds. This can be rationalized using a simple valence bond description. Resonance Structures 3.8 - 3.10 represent the bonding in the neutral molecules L-Xe-F, whereas 3.11 - 3.13 represent the corresponding cationic species L-Xe-
F⁺. For the neutral species L-Xe-F, resonance Structure 3.10 contributes least to the bonding as a result of the dipositive charge on xenon. The relative weights of 3.8 and 3.9 depend on the group electronegativity of the ligand L, with a greater contribution from Structure 3.8 for lower electronegativity of L. For the L-Xe-F⁺ cations, resonance Structures 3.11 and 3.13 have reduced weights relative to 3.12 as a result of the high charge localization. Thus, resonance Structure 3.12, which represents a purely ionic interaction of the ligand L and XeF⁺, is expected to dominate the bonding in CF₃C(OXeF)NH₂⁺ and related O- and N-bonded xenon(II) cations.
CHAPTER 4

CHARACTERIZATION AND COMPARISON OF THE BONDING IN F₅TeNH₃ AND F₅TeNH₃⁺AsF₆⁻ USING ¹⁹F NMR AND RAMAN SPECTROSCOPY

INTRODUCTION

(A) REVIEW OF THE SYNTHESIS, CHARACTERIZATION AND BONDING OF THE ACIDS F₅XO⁻ AND THE SALTS M⁺OXF₅⁻ (X = S, Se, Te)

The ligands F₅XO⁻ (X = S, Se, Te) are bulky, highly electronegative and are second only to fluorine in their ability to stabilize high oxidation states of metals and nonmetals.¹²,¹³³,¹³⁴ The first compounds containing the F₅XO⁻ group were prepared from the direct fluorination of the chalcogens in the elemental state or the oxides, yielding hypofluorites F₅XOF (X = S,¹³⁵ Se¹³⁶), peroxides F₅XO-OXF₅ (X = S,¹³⁷ Se¹³⁸) and F₅TeOTeF₅.¹³⁸ The synthetic potential of the F₅XO-group increased dramatically in 1964 with the discovery of the acid, HOTeF₅¹³⁹ from the reaction of BaTeO₄ with HSO₃F in an attempt to prepare TeC₂F₂ by analogy with the preparation of SeO₂F₂ from BaSeO₄ and HSO₃F.¹⁴⁰ Failure to prepare TeO₂F₂ in this way reflects the propensity of hexavalent tellurium to adopt coordination number six.¹² The compound HOTeF₅ is best prepared according to equation (4.1)

\[ \text{Te(OH)}_6 + 5 \text{HSO}_3\text{F} \rightarrow 5 \text{H}_2\text{SO}_4 + \text{HOTeF}_5 \]  \hspace{1cm} (4.1)
The preparation of HOSeF$_5$, first reported in 1972 by Seppelt, involves the reaction of SeO$_2$F$_2$ and HF with an increase in coordination number of selenium(VI) according to equation (4.2), which illustrates the tendency for coordination numbers four and six to exist in the same system for hexavalent selenium.

$$3 \text{SeO}_2\text{F}_2 + 4 \text{HF} \rightarrow 2 \text{HOSeF}_5 + \text{H}_2\text{SeO}_4$$

(4.2)

In contrast to SeO$_2$F$_2$, SO$_2$F$_2$ is extremely inert showing no tendency to increase its coordination number to six. The preparation of HOSF$_5$ therefore requires a more indirect route, involving the reaction of SOF$_4$ with ClF to give the hypochlorite ClOSF$_5$ as an intermediate, followed by reaction with HCl (equation 4.3).

$$\text{SOF}_4 + \text{ClF} \xrightarrow{\text{CsF}} \text{ClOSF}_5 \xrightarrow{\text{HCl}} \text{HOSF}_5$$

(4.3)

The thermal stabilities of HOSF$_5$, HOSeF$_5$ and HOTeF$_5$ vary considerably:

$$\text{HOSF}_5 \xrightarrow{-60 \degree \text{C}} \text{HF} + \text{SOF}_4$$

(4.4)

$$\text{HOSeF}_5 \xrightarrow{290 \degree \text{C}} \text{HF} + \frac{1}{2} \text{O}_2 + \text{SeF}_4$$

(4.5)

$$\text{HOTeF}_5 \xrightarrow{>310 \degree \text{C}} \text{HF} + (\text{TeOF}_4)_n + \text{TeF}_4 + \text{TeF}_6 + \ldots$$

(4.6)
Below -60 °C, HOSF$_5$ is only kinetically stable with respect to reduction of coordination number, limiting its use as a synthetic reagent. The selenium analog, HOSeF$_5$, decomposes at 290 °C with reduction of selenium from the +6 to the +4 oxidation state. The tendency to undergo reduction is reflected in the powerful oxidizing power of HOSeF$_5$. As a result, HOSeF$_5$ is the strongest oxidizer among the three HOXF$_5$ compounds. The high thermal decomposition temperature of HOTeF$_5$ and the uncharacteristic distribution of products indicates the stability of hexacoordinate tellurium (VI) with respect to reduction of coordination number and oxidation state. Thus, most of the chemistry of the F$_5$XO- ligand has involved HOTeF$_5$ as the starting material. The chemistry of the F$_5$SeO- ligand is less extensive, and few examples of the F$_5$SO- ligand are known owing to the instability of HOSF$_5$.

The inductive effect resulting from the accumulation of fluorine atoms results in high group electronegativities for the F$_5$XO- ligands, enabling them to stabilize high oxidation states that are only otherwise stabilized by the most electronegative element, fluorine. Examples include W(OTeF$_5$)$_6$, U(OTeF$_5$)$_6$, O=Xe(OTeF$_5$)$_4$, Br(OSeF$_5$)$_3$, and Kr(OTeF$_5$)$_2$. Several methods have been used to establish the electronegativities of the F$_5$TeO- and F$_5$SeO-groups relative to fluorine and the other halogens. The $^1$H NMR chemical shift of the methyl protons of CH$_3$OSeF$_5$ relative to those of CH$_3$X (X = F, Cl, Br, I) has indicated that the F$_5$SeO-group has an electronegativity which is greater than that of fluorine. Although the electronegativity of the F$_5$TeO- group relative to fluorine has been debated, the weight of evidence indicates that fluorine is more electronegative. Using the difference in the $^1$H NMR chemical shifts of the methyl and methylene protons in the compounds CH$_3$CH$_2$X (X = OTeF$_5$, F, Cl, Br, I), a value of 3.88 has been obtained for the electronegativity of the F$_5$TeO- group, as compared to 3.98 for fluorine (Pauling scale). A study involving $^{127}$I and $^{129}$Xe Mössbauer and
\(^{129}\)Xe and \(^{125}\)Te NMR spectroscopic measurements on a series of xenon and iodine compounds containing F and \(\text{F}_2\text{TeO}^-\) as ligands also indicate that the electronegativity of the \(\text{F}_2\text{TeO}^-\) group is less than that of fluorine.\(^{181}\)

As expected from the high electronegativity of the \(\text{F}_2\text{TeO}^-\) and \(\text{F}_2\text{SeO}^-\) groups, the compounds \(\text{HOTeF}_5\) and \(\text{HOSeF}_5\) are strong acids. The acid strength of \(\text{HOTeF}_5\) has been found to lie between those of \(\text{HNO}_3\) and \(\text{HCl}\) by spectrophotometric measurements in acetic acid solution.\(^{200}\) The high acidity is also reflected in the large variety of known \(\text{F}_2\text{XO}^-\) salts.\(^{52}\) Salts of the \(\text{F}_2\text{XO}^-\) anions (\(X = \text{Tc}, \text{Se}\)) may be obtained directly from \(\text{HOTeF}_5\) and \(\text{HOSeF}_5\) by reaction with nitrogen bases (equations (4.7) and (4.8)).\(^{201-204}\)

\[
\text{HOTeF}_5 + D \rightarrow D^+\text{OTeF}_5^- \tag{4.7}
\]

\((D = \text{C}_2\text{H}_5\text{N}, \text{NH}_3, \text{C}_{14}\text{H}_{18}\text{N}_2, \text{N(CH}_2\text{CH}_3)_3)\)

\[
\text{HOSeF}_5 + D \rightarrow D^+\text{OSeF}_5^- (D = \text{NH}_3) \tag{4.8}
\]

The salts \(\text{NR}_4^+\text{OTeF}_5^- (R = \text{CH}_3, \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)\) have been prepared from the \(\text{HCl}\) elimination reaction of \(\text{HOTeF}_5\) with \(\text{NR}_4\text{Cl}\). Alkali metal derivatives of \(\text{F}_2\text{TeO}^-\) may be prepared from \(\text{HOTeF}_5\) and \(\text{MCl} (M = \text{K, Rb, Cs})\) with the evolution of \(\text{HCl}\).\(^{201,206}\) Syntheses of the analogous \(\text{M}^+\text{OSeF}_5^-\) salts requires the use of \(\text{MF} (M = \text{Li, Na, K, Rb, Cs})\) producing \(\text{HF}\) since chloride is oxidized by selenium(VI), giving chlorine gas. The salts, \(\text{Na}^+\text{OXF}_5^- (X = \text{Se, Te})\)\(^{207}\) may be prepared from the reaction of a siloxane \(\text{R}_3\text{OSi-OXF}_5\) with \(\text{NaOSiR}_3\) [equation (4.9)] and \(\text{Li}^+\text{OTeF}_5^-\)\(^{207}\) is prepared from the reaction of \(\text{LiOCH}_3\) and \(\text{HOTeF}_5\) [equation (4.10)]. Other derivatives include \(\text{NO}_2^+\text{OSeF}_5^-\)\(^{208}\) and \(\text{NO}^+\text{OTeF}_5^-\)\(^{209}\) which both have covalent formulations.
\[ R_2Si-OF_5^- + NaOSiR_3 \rightarrow Na^+OF_5^- + R_2SiOSiR_3 \quad (X = Se, Te) \]  
(4.9)

\[ HOTeF_5 + LiOCH_3 \rightarrow HOCH_3 + Li^+OTeF_5^- \]  
(4.10)

in the gas phase, and the salt Ag\(^+\)OTeF_5\(^-\);\(^{206}\) for which a partially covalent interaction between the cation and anion has been observed in acetonitrile solution. Because of the instability of HOSF_5 above -60 \(^\circ\)C,\(^{192,193}\) salts of the OSF_5\(^-\) anion can not be prepared from the parent acid. The salt, Cs\(^+\)OSF_5\(^-\), is prepared from the addition reaction of CsF and SOF_4.\(^{210,211}\)

The OXF_5\(^-\) anions all exhibit molecular geometries having \(C_{4v}\) point symmetry in solution and in the solid state. Structural characterization of these anions has been obtained by \(^{19}\)F NMR spectroscopy, which exhibits typical AB_4 spectra, and infrared and Raman spectroscopy. Because of orientational disorder resulting from the essentially spherical shape of the OXF_5\(^-\) anions and the similarities of the covalent and van der Waals radii of oxygen and fluorine atoms, the salts are not suitable for detailed single crystal X-ray analysis. Only one salt F_3XO\(^-\) salt, namely [1,8-bis(dimethylamino) naphthalenium]OTeF_5\(^-\), has been published in which the oxygen and fluorine atoms are not disordered.\(^{202}\)

The wealth of vibrational and \(^{19}\)F NMR spectroscopic data on compounds containing F_3XO- groups has made it possible to compare the bonding in F_3XO-M (X = S, Se, Te) compounds as M is varied.\(^{52,53,84}\) It has been noted that increasing ionic character of the O-M bond results in a strengthening of the O-X bond, and a weakening of the X-F bonds. Further, the axial X-F bond is weakened more than the equatorial X-F bonds, a well established "trans effect". This is adequately illustrated by comparing the acids HOXF_5 (M = H) with salts of the form
M$^{+}$OXF$_5^-$, where the ionic characters of the M-O bonds in the latter compounds are significantly greater than in the former. Table 4.1 lists the $^{19}$F NMR and vibrational data for HOXF$_5$ and the OXF$_5^-$ anions (X = S, Se, Te). As shown in the vibrational data, deprotonation of the acids HOXF$_5$ to give OXF$_5^-$ results in a lowering of the v(X-F$_{ax}$) and v$_{sym}$(X-F$_{eq}$) stretching frequencies and an increase in the v(XO) stretching frequencies. The axial X-F stretches are decreased more than the equatorial X-F stretching frequencies, consistent with the expected changes in bond strengths described above. The X-O bond orders in the F$_5$XO$^-$ anions have been estimated from the force constants obtained from normal coordinate calculations to lie between one and two for X = Se$^{206}$ and Te$^{206}$ an S-O bond order of 1.5 has been calculated for the F$_5$SO$^-$ anion.$^{210}$ Structural evidence for partial double bond in the F$_5$TeO$^-$ is present in the single crystal X-ray structure of $[1,8$-(dimethylamino)naphthalenium]$^+$OTeF$_5$. $^{202}$ where the Te-O bond length [1.803(3) Å] is significantly shorter than a Te-O single bond (cf., Te(OH)$_6$, Te-O = 1.908(1) Å).$^{211}$ The X-O bond orders are indicative of partial double bonds resulting from π-donation from oxygen to the F$_5$X- group. Valence bond theory has been used by several authors (c.f., resonance Structures 4.1 - 4.3) to represent the bonding in the OXF$_5^-$ anions (X = S, Se, Te)$^{205,210,213,214}$ without explicitly identifying the orbitals on the hypervalent chalcogen center which accept π-electron density from oxygen. The weaker axial X-F bonds are represented by greater weighting of resonance Structure 4.3. Strauss et al. have stated that vacant d-orbitals on the chalcogen center function as acceptor orbitals for the π-electron density from oxygen (d$_\pi$-p$_\pi$ bonding).$^{203}$ Oberhammer and Seppelt$^{215}$ also provide evidence for d$_\pi$-p$_\pi$ bonding in the oxides F$_5$XOXF$_5$ (X = S, Se, Te) from the energetically unfavorable eclipsed geometries of the equatorial fluorine ligands, the nearly constant X-O-X bond angles (ca. 140°) and the short X-O bond lengths. With regard to the bonding in the OXF$_5^-$ anions, Seppelt$^{215}$ has stated that resonance Structures 4.1 -
Table 4.1. Comparison of Raman and $^{19}$F NMR Spectroscopic Data for the Acids F$_5$XOH and Some of the Salts, [M]$^+[F_5XO]^-$

(X = S, Se, Te).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Raman Frequencies, cm$^{-1}$</th>
<th>$^{19}$F NMR Chemical Shifts, ppm</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu(X$-$F_{ax}$)</td>
<td>$\nu_{sym}(X$-$F_{eq}$)</td>
<td>$\nu(X$-$O)$</td>
</tr>
<tr>
<td>F$_5$TeOH</td>
<td>735</td>
<td>685</td>
<td>735</td>
</tr>
<tr>
<td>[N(n-Bu)$_4$]$_2$OTeF$_5$-$^d$</td>
<td>576</td>
<td>645</td>
<td>867</td>
</tr>
<tr>
<td>N(CH$_3$)$_4$OTeF$_5$-$^e$</td>
<td>583, 650</td>
<td>583, 650</td>
<td>868</td>
</tr>
<tr>
<td>F$_5$SeOH $^f$</td>
<td>625</td>
<td>685</td>
<td>753</td>
</tr>
<tr>
<td>K$^+$/OTeF$_5$-$^g$</td>
<td>559</td>
<td>649</td>
<td>919</td>
</tr>
<tr>
<td>F$_5$SOH $^h$-$^l$</td>
<td>610, 635</td>
<td>761</td>
<td>-</td>
</tr>
<tr>
<td>Cs$^+$/OSF$_5$-$^j$</td>
<td>722</td>
<td>697</td>
<td>1153</td>
</tr>
</tbody>
</table>
Table 4.1 (continued)

\(^a\) Raman spectra were performed on the neat compounds at ambient temperatures unless otherwise specified. \(^b\) \(^{19}\)F NMR spectra were recorded at ambient temperatures unless otherwise specified and positive (negative) chemical shifts are deshielded (shielded) relative to CFCl\(_3\) standard. \(^c\) \(\delta_A\) and \(\delta_B\) refer to the axial and equatorial \(^{19}\)F NMR resonances, respectively. \(^d\) \(^{19}\)F NMR spectra recorded in CH\(_2\)Cl\(_2\) solvent. \(^e\) \(^{19}\)F NMR spectra recorded in CH\(_2\)C≡N solvent at -10 °C. \(^f\) \(^{19}\)F NMR spectra recorded in CH\(_2\)C≡N solvent. \(^g\) Raman spectra recorded in CH\(_2\)C≡N solvent. \(^h\) Raman spectra recorded at -160 °C. \(^i\) \(^{19}\)F NMR spectra recorded at -70 °C in CHCl\(_2\)F solvent. \(^j\) \(^{19}\)F NMR spectra recorded in DMSO solvent.
4.3 imply hyperconjugation. This is a misnomer since hyperconjugation implies donation of electron density from a σ orbital to a π* orbital. In these anions, negative hyperconjugation\(^{216}\) may contribute significantly to the bonding, where π electron density from the p-orbitals on oxygen donate electron density into σ* orbitals of the F\(_5\)Te- group. Recent SCF ab initio calculations using natural population analysis\(^{216}\) on molecules containing hypervalent main-group centers such as CH\(_2\)SO\(_2\)Cl, F\(_3\)CO\(^-\) and the hypothetical F\(_3\)TeC\(^-\) anion indicate that the primary acceptor orbitals on the hypervalent centers are σ*, constructed mainly from valence s and p orbitals and that valence d orbitals play only a minor role. The lengthening of the X-F bonds (X = S, Se, Te) upon deprotonation of HOXF\(_5\) to give OXF\(_5\)^- is predicted, since π\(_O\) → σ*(X-F) donation increases the population of X-F antibonding orbitals. The "trans effect" described above indicates that π\(_O\) → σ*(X-F\(_{ax}\)) > π\(_O\) → σ*(X-F\(_{eq}\)), which may be confirmed by performing the appropriate calculations.

An explanation for the observed behavior of the \(^{19}\)F NMR chemical shifts (Table 4.1) of the HOXF\(_5\) / OXF\(_5\)^- pairs (X = S, Se, Te) cannot be made with certainty, but may be related to the effect of negative hyperconjugation discussed above. Table 4.1 illustrates that both the axial and
equatorial fluorine resonances of the OXF$_5^-$ anions are deshielded relative to those of the acids, HOXF$_5$. In particular the axial fluorine resonances are deshielded by 18 to 25 ppm (X = Te), 38 ppm (X = Se) and 66 ppm (X = S). The equatorial resonances are deshielded by 4 to 10 ppm (X = Te), 14 ppm (X = Se), and 30 ppm (X = S). This qualitatively resembles the trend observed in the X-F force constants derived from the vibrational data, where the axial X-F bond is affected more by changes in the X-O bond order, which has been attributed to $\pi_O \rightarrow \sigma^*(X-F)$ negative hyperconjugation. In the presence of a magnetic field, mixing of lower energy orbitals with higher unoccupied orbitals, which are termed "excitations", results in paramagnetic currents which may deshield (negative paramagnetic contribution) or shield (positive paramagnetic contribution) the nucleus.\textsuperscript{218,219} It is possible that the population of the $\sigma^*(X-F)$ orbitals resulting from negative hyperconjugation deshields the fluorine nuclei by altering the paramagnetic circulations involving $\sigma^*(X-F)$ as the higher energy orbital. Further speculation is unwarranted without a detailed knowledge of the electronic states of the OXF$_5^-$ anions.

(B) SYNTHESIS AND CHARACTERIZATION OF F$_5$XNH$_2$ (X = S, Te)

The chemistry of the nitrogen analogues, F$_5$XNH$_2$ (X = S, Se, Te), is less developed than that of the oxygen acids HOXF$_5$ (X = S, Se, Te). Although preceded by several examples of $\alpha$-fluoro secondary amines $R_fNH_R'_f$ where $R_f$ and $R'_f$ have been either perfluoroalkyl or pentafluorosulfur groups,\textsuperscript{221-225} the preparation of the $\alpha$-fluoro primary aminosulfur(VI) pentafluoride was first reported in 1965, by Clifford and Duncan\textsuperscript{226} by addition of HF across the SN triple bond of F$_3$S=N [equation (4.11)].

\[
F_3S=N + 2 HF \rightarrow F_5SNH_2 \tag{4.11}
\]
The compound $\text{F}_5\text{SNH}_2$ dissociates slowly at room temperature and more rapidly at 45 °C to give HF and $\text{F}_3\text{S}≡\text{N}$. However, $\text{F}_5\text{SNH}_2$ is much more stable than $\text{F}_5\text{SOH}$, which decomposes to give SOF$_4$ and HF at -60 °C.$^{192,193}$ As a result, the chemistry of $\text{F}_5\text{SNH}_2$ has been investigated to a greater extent. In spite of the electron withdrawing effect of the $\text{F}_5\text{S}$- group, $\text{F}_5\text{SNH}_2$ has some degree of basic character, since 1:1 adducts are formed with PF$_5$ and BF$_3$ that are both stable at room temperature.$^{227}$

Of the heavier analogues, i.e., $\text{F}_5\text{SeNH}_2$ and $\text{F}_5\text{TeNH}_2$, only the latter is known. The preparation of $\text{F}_5\text{TeNH}_2$ was preceded by the preparation of the dialkylamino derivatives, $\text{F}_5\text{TeN(CH}_3)_2$. $^{228,229}$ $\text{F}_5\text{TeN(CH}_2\text{CH}_3)_2$. $^{229}$ and $\text{F}_5\text{TeN(C}_6\text{H}_5)$. $^{229}$ These species were prepared from the appropriate dialkylaminotrimethylsilane and TeF$_6$ in silicon-nitrogen cleavage reactions [equation (4.12)]. The thermodynamic driving force for the reactions is the formation of the very strong Si-F bond. The primary amine, $\text{F}_5\text{TeNH}_2$, $^{230}$ was prepared in 1973 in a two-step silicon-nitrogen cleavage reaction [equations (4.13) and (4.14)]. Aminotellurium(VI) pentafluoride, as expected by analogy with HOTeF$_5$, exhibits no tendency to undergo HF elimination or reduce its

$$\text{R}_2\text{NSi(CH}_3)_3 + \text{TeF}_6 \longrightarrow \text{R}_2\text{NTeF}_5 + \text{FSi(CH}_3)_3$$  
(4.12)

strong Si-F bond. The primary amine, $\text{F}_5\text{TeNH}_2$, $^{230}$ was prepared in 1973 in a two-step silicon-nitrogen cleavage reaction [equations (4.13) and (4.14)]. Aminotellurium(VI) pentafluoride, as expected by analogy with HOTeF$_5$, exhibits no tendency to undergo HF elimination or reduce its

$$\text{TeF}_6 + (\text{CH}_3)_3\text{SiNHSi(CH}_3)_3 \longrightarrow \text{F}_5\text{TeNHSi(CH}_3)_3 + (\text{CH}_3)_3\text{SiF}$$  
(4.13)

$$\text{F}_5\text{TeNHSi(CH}_3)_3 + \text{HF} \longrightarrow \text{F}_5\text{TeNH}_2 + (\text{CH}_3)_3\text{SiF}$$  
(4.14)
coordination number at ambient temperatures, and decomposes only when heated to 150 °C.

Unlike the sulfur analogues, cis-disubstituted products may be produced in the preparation of the compounds F₅TeNR'R' [R, R' = alkyl; R = H, R' = Si(CH₃)₂]. Of the alkyl derivatives studied, only the reaction of (CH₃)₃SiN(CH₃)₂ with TeF₆²²⁸,²²⁹ produces a stable cis-disubstituted product, namely cis-F₄Te[N(CH₃)₂]₂, which is formed along with F₅TeN(CH₃)₂. In the preparation of F₅TeNHSi(CH₃)₂ cited above, reaction conditions must be carefully controlled to prevent the formation of cis-F₄Te[NHSi(CH₃)₂]₂, which is known to be explosive.²³⁰,¹²₅ The formation of cis-F₄Te[NHSi(CH₃)₂]₂ is believed to be favored for kinetic reasons since the trans isomer, being less sterically hindered, should be thermodynamically more stable.¹²₅

The basicity of the nitrogen center in F₅TeNH₂ was investigated by attempting to prepare adducts with the Lewis acids AsF₅ and BF₃.²³⁰ A 1:1 adduct is formed with AsF₅ which is stable at room temperature, whereas the 1:1 adduct formed with the weaker Lewis acid, BF₃, decomposes reversibly above -60 °C. The fact that the F₅TeNH₂·BF₃ adduct is less thermally stable than F₅SNH₂·BF₃ (stable at room temperature)²²⁷ has been interpreted as an indication of the weaker basicity of F₅TeNH₂ relative to that of F₅SNH₂. The electron withdrawing power of the F₅Te-group results in some acid character for F₅TeNH₂, however, it is only marginally acidic. In contrast to the strong acid HOTeF₅,²⁵² no definite products result from the reaction of F₅TeNH₂ and nitrogen bases such as pyridine and triethylamine.²³⁰ No reaction is observed between F₅TeNH₂ and CsF, rather an unstable salt assumed to be Cs⁺NHTeF₅⁻ is isolated according to equation (4.15).²³⁰ The resulting Cs⁺NHTeF₅⁻ salt decomposes in most solvents, and has exploded

\[
F₅TeNHSi(CH₃)₂ + CsF \rightarrow Cs⁺NHTeF₅⁻ + (CH₃)₃SiF \tag{4.15}
\]
in the laser beam of a Raman spectrometer.\textsuperscript{230}

The weaker basicity of the nitrogen lone pair in $F_5TeNH_2$ relative to that in $F_2SNH_2$ was attributed by Seppelt\textsuperscript{230} to result from $Te-N \ p_\pi-d_\pi$ bonding. As mentioned above for the $\text{OXF}_5^- \ anions$, the acceptor orbitals may largely consist of $\sigma^*(Te-F_{ax})$ and $\sigma^*(Te-F_{eq})$ antibonding orbitals, with only a minor contribution from vacant $d$-orbitals. In describing the bonding in $F_5TeNH_2$, a direct comparison can be made with the $\text{OTeF}_5^-$ anion [Section (A) of this Chapter]. Protonation of $F_5TeNH_2$ to give the acid cation, $F_5TeNH_3^+$, is expected to result in a reduction in the $Te-N \pi$-bonding and a strengthening of the $Te-F$ bonds, by analogy with the changes in bonding which occur upon protonation of the $\text{OTeF}_5^-$ anion.

The present Chapter investigates the synthesis and characterization of $F_5TeNH_2$ and the corresponding novel acid cation, $F_5TeNH_3^+$, as the $\text{AsF}_6^-$ salt to investigate the effect of protonation of $F_5TeNH_2$ on the bonding of the $F_5TeN^-$ group, using $^{19}F$ and $^1H$ NMR and Raman spectroscopy. The salt, $F_5TeNH_3^+\text{AsF}_6^-$, has been characterized for the first time by Raman spectroscopy and $^{19}F$, $^{15}N$, $^1H$ and $^{125}Te$ NMR spectroscopy.

RESULTS AND DISCUSSION

(A) \textbf{PREPARATION AND ISOLATION OF F$_5$TeNH$_2$, F$_5$TeNH$_3^+$AsF$_6^-$ AND THE 99.5 \% $^{15}N$-ENRICHED ANALOGS}

Aminotellurium(VI) pentafluoride, $F_5TeNH_2$, was prepared according to the method of Seppelt [equations (4.13) and (4.14)].\textsuperscript{125,230} The amine is a volatile white solid at room temperature, subliming easily under vacuum, and is consistent with the physical properties observed by Seppelt.\textsuperscript{230} The physical properties of $F_5TeNH_2$ are similar to those observed for
F₅TeOH, also a volatile solid at room temperature, and are consistent with the essentially spherical structures of these molecules. The 99.5% ¹⁵N enriched compound was prepared using a similar procedure, however, [¹⁵N]hexamethyldisilazane was prepared from ¹⁵N enriched NH₄Cl [equations (4.16) and (4.17)].

\[ ^{15}\text{NH}_4\text{Cl} + \text{KOH} \longrightarrow ^{15}\text{NH}_3 + \text{KCl} + \text{H}_2\text{O} \]  \hspace{1cm} (4.16)

\[ 3\, ^{15}\text{NH}_3 + 2\, (\text{CH}_3)_2\text{SiCl} \longrightarrow 2\, ^{15}\text{NH}_4\text{Cl} + [(\text{CH}_3)_2\text{Si}]_2^{15}\text{NH} \]  \hspace{1cm} (4.17)

Identical procedures were used for the preparation of the salts F₅TeNH₃⁺AsF₆⁻ and [¹⁵N]F₅TeNH₃⁺AsF₆⁻ from the amines, F₅TeNH₂ and [¹⁵N]F₅TeNH₂. The basicity of F₅TeNH₂ was previously demonstrated from the formation of the 1:1 adducts F₅TeNH₂·BF₃ and F₅TeNH₂·AsF₅ by reaction of F₅TeNH₂ and the Lewis acid in CH₂Cl₂.²³⁰ Only the adduct with the stronger Lewis acid, namely, F₅TeNH₂·AsF₅, is stable with respect to dissociation into the starting materials at room temperature. In light of the stability of this adduct, the ability of F₅TeNH₂ to behave as a protic base in HF/AsF₅ superacid solution (Hₒ = -20)²³¹ was investigated. The compound, F₅TeNH₂, was dissolved in HF solvent at -78 °C. A 20 mole % excess of AsF₅ was condensed onto the frozen solution at -196 °C. On warming to -78 °C, a white precipitate formed which was isolated after removal of the solvent and excess AsF₅ at -55 °C under vacuum. The resulting white powder has been shown by mass balance, multinuclear NMR spectroscopy in solution and Raman spectroscopy in the solid state to be F₅TeNH₃⁺AsF₆⁻, formed according to equation (4.18) in near quantitative yield (96%). The salt hydrolyses very
\[ F_5\text{TeNH}_2 + HF + \text{AsF}_5 \xrightarrow{-78 \text{ to } -55^\circ C} F_5\text{TeNH}_3^+\text{AsF}_6^- \]  

(4.18)

rapidly in the presence of air, but can be stored indefinitely at room temperature under a dry nitrogen atmosphere.

(B) CHARACTERIZATION OF F$_5$TeNH$_2$ IN THE SOLID STATE BY LOW TEMPERATURE RAMAN SPECTROSCOPY

The low temperature Raman spectra of natural abundance and 99.5 atom % $^{15}$N-enriched F$_5$TeNH$_2$ were obtained at -160 °C, both of which are microcrystalline solids at this temperature. Figure 4.1 illustrates the Raman spectrum of F$_5$TeNH$_2$ and the $^{14/15}$N isotopic shifts in the Raman spectra of F$_5$TeNH$_2$ and [${^{15}}$N]F$_5$TeNH$_2$ are shown in Figure 4.2, and the frequencies are listed in Table 4.2, along with those of the related F$_5$TeOF, F$_5$TeO$^-$ and F$_5$TeOH compounds. Although F$_5$TeNH$_2$ was characterized by infrared and Raman spectroscopy in methylene chloride solution in the paper which reported the original synthesis,\textsuperscript{230} a more thorough assignment of the bands is presented here. This has been facilitated by observing the $^{14/15}$N isotopic shifts of bands which arise from modes that involve the motion of the nitrogen atom by comparison of the Raman spectra of natural abundance F$_5$TeNH$_2$ (99.63% $^{14}$N) and 99.5 atom % $^{15}$N-enriched F$_5$TeNH$_2$. The isotopic shifts, $\Delta\nu(^{14/15}N)$, are given as the difference in the frequencies (cm$^{-1}$), $\nu(^{14}N)$ - $\nu(^{15}N)$. Isotopic shifts are often quoted as the ratio $\Delta\lambda(^{14/15}N)/\lambda(^{14}N)$ as defined in references (73) and (232), where $\lambda$ refers to a normal mode. This convention has not been used here, however, since the likely occurrence of vibrational coupling prevents the direct assignment of each band in the Raman spectra to a particular vibrational mode of F$_5$TeNH$_2$ (see below).

A total of 3N - 6 = 21 normal modes are expected for F$_5$TeNH$_2$. There are several
Figure 4.1  Raman spectrum of solid natural abundance F$_5$TeNH$_2$ recorded at -160 °C by use of 514.5-nm excitation.
Figure 4.2  Raman spectra of solid natural abundance (lower traces) and 99.5 atom % $^{15}$N-enriched (upper traces) $F_5TeNH_2$ recorded at -160 °C by use of 514.5-nm excitation; (a) 150 - 800 cm$^{-1}$ region and (b) 1000 - 1050, 1450 - 1550 and 3250 - 3400 cm$^{-1}$ regions.
b

INTENSITY, cps s⁻¹ x 100

Δν, cm⁻¹

1000 1500 3300 3400

x 4

x 2

x %

x %
Table 4.2. Vibrational Frequencies and Assignments for F$_5$TeNH$_2$ and $[^{15}$N$]$F$_5$TeNH$_2$, and Comparison with F$_5$TeOF, F$_5$TeO$^-$, F$_5$TeOH$^a$

<table>
<thead>
<tr>
<th>F$_5$TeOF$^b$</th>
<th>F$_5$TeO$^-$$^c$</th>
<th>F$_5$TeOH$^e$</th>
<th>F$_5$TeNH$_2$$^g$</th>
<th>$[^{15}$N$]$F$_5$TeNH$_2$$^g$</th>
<th>$\Delta v (^{14/15}$N$)^h$</th>
<th>Assgnt and Approx Mode Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>721 (1.6)</td>
<td>584 (30)</td>
<td>735</td>
<td>582.7 (10)</td>
<td>572.9 (10)</td>
<td>-9.8</td>
<td>$A_1$ $\nu_{1}$, $\nu$(Te-F$<em>{ax}$) sym $[\nu</em>{1} + \nu_{3}]$</td>
</tr>
<tr>
<td>669 (10)</td>
<td>652 (100)</td>
<td>685</td>
<td>619.6 (8.42)</td>
<td>619.4 (7.62)</td>
<td>0</td>
<td>$\nu_{2}$, $\nu_{sym}$(TeF$_4$)</td>
</tr>
<tr>
<td>613 (3.8)</td>
<td>868 (47)</td>
<td>735</td>
<td>761.0 (1.03)</td>
<td>752.9 (0.59)</td>
<td>-8.1</td>
<td>$\nu_{3}$, $\nu$(Te-X) asym $[\nu_{1} + \nu_{3}]$</td>
</tr>
<tr>
<td>301 (0.5)</td>
<td>319$^d$</td>
<td>319</td>
<td>300.7 (3.36)</td>
<td>298.8 (2.76)</td>
<td>-1.9</td>
<td>$\nu_{4}$, $\delta_{sym}$(TeF$_4$) umbrella</td>
</tr>
<tr>
<td>660 (0.3)</td>
<td>584 (30)</td>
<td>652</td>
<td>628.6 (sh)</td>
<td>628.0 (sh)</td>
<td>-0.6</td>
<td>$B_1$ $\nu_{5}$, $\nu_{sym}$(TeF$_4$) out-of-phase</td>
</tr>
<tr>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>n.o.</td>
<td>-0.3</td>
<td>$\nu_{6}$, $\delta_{eckes}$(TeF$_4$)</td>
</tr>
<tr>
<td>309 (1.0)</td>
<td>283 (6)</td>
<td>733.5$^f$</td>
<td>326.8 (2.06)</td>
<td>326.5 (1.75)</td>
<td>-0.6</td>
<td>$B_2$ $\nu_{7}$, $\Delta_{eckes}$(TeF$_4$) in-plane</td>
</tr>
<tr>
<td>738 sh</td>
<td>636$^d$</td>
<td>689.1 (7.14)</td>
<td>680.4 (4.38)</td>
<td>681.0 (3.98)</td>
<td>-0.6</td>
<td>$B_2$ $\nu_{8}$, $\nu_{sym}$(TeF$_4$)</td>
</tr>
<tr>
<td>325 sh</td>
<td>346 (6)</td>
<td>336.8 (2.29)</td>
<td>336.6 (1.91)</td>
<td>336.6 (1.91)</td>
<td>-0.2</td>
<td>$\nu_{9}$, $\delta$(TeF$_4$)</td>
</tr>
<tr>
<td>309-325</td>
<td>328 (40)</td>
<td>286.7 (2.41)</td>
<td>283.1 (2.27)</td>
<td>283.1 (2.27)</td>
<td>-3.6</td>
<td>$\nu_{10}$, $\delta$(XeF$_4$)</td>
</tr>
<tr>
<td>279 (0.2)</td>
<td>196 (3)</td>
<td>210.4 (0.21)</td>
<td>194.6 (0.46)</td>
<td>194.6 (0.31)</td>
<td>0</td>
<td>$\nu_{11}$, $\delta_{asym}$(TeF$_4$)</td>
</tr>
</tbody>
</table>

$^{a}$ C$_{4v}$

$^{b}$ C$_{s}$

$^{c}$ A$^*$ $\nu_{12}$, $\nu_{sym}$(NH$_2$)

$^{d}$ 3280.1 (0.28) 3275.8 (0.25) -4.3

$^{e}$ 3297.2 (7.58) 3292.9 (5.72) -4.3
<table>
<thead>
<tr>
<th>Frequency</th>
<th>Wavenumber</th>
<th>refractive index</th>
<th>( \nu_{14} ), ( \delta(\text{NH}_2) )</th>
<th>( \nu_{13} ), ( \delta_{\text{sym}}(\text{SNH}) )</th>
<th>( \Lambda^{\prime} ) ( \nu_{15} ), ( \nu_{\text{asym}}(\text{NH}_2) )</th>
<th>( \nu_{16} ), ( \delta_{\text{asym}}(\text{SNH}) )</th>
<th>lattice modes and/or hydrogen-bonding interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1514.2 (0.10)</td>
<td>1509.3 (0.12)</td>
<td>-4.9</td>
<td>( \nu_{14} ), ( \delta(\text{NH}_2) )</td>
<td>( \nu_{13} ), ( \delta_{\text{sym}}(\text{SNH}) )</td>
<td>( \Lambda^{\prime} ) ( \nu_{15} ), ( \nu_{\text{asym}}(\text{NH}_2) )</td>
<td>( \nu_{16} ), ( \delta_{\text{asym}}(\text{SNH}) )</td>
<td></td>
</tr>
<tr>
<td>1028.4 (0.16)</td>
<td>1024.8 (0.13)</td>
<td>-3.6</td>
<td>( \nu_{14} ), ( \delta(\text{NH}_2) )</td>
<td>( \nu_{13} ), ( \delta_{\text{sym}}(\text{SNH}) )</td>
<td>( \Lambda^{\prime} ) ( \nu_{15} ), ( \nu_{\text{asym}}(\text{NH}_2) )</td>
<td>( \nu_{16} ), ( \delta_{\text{asym}}(\text{SNH}) )</td>
<td></td>
</tr>
<tr>
<td>3385.3 (1.65)</td>
<td>3376.1 (1.28)</td>
<td>-9.2</td>
<td>( \nu_{14} ), ( \delta(\text{NH}_2) )</td>
<td>( \nu_{13} ), ( \delta_{\text{sym}}(\text{SNH}) )</td>
<td>( \Lambda^{\prime} ) ( \nu_{15} ), ( \nu_{\text{asym}}(\text{NH}_2) )</td>
<td>( \nu_{16} ), ( \delta_{\text{asym}}(\text{SNH}) )</td>
<td></td>
</tr>
<tr>
<td>719.3 (0.17)</td>
<td>717.6 (0.11)</td>
<td>-1.7</td>
<td>( \nu_{14} ), ( \delta(\text{NH}_2) )</td>
<td>( \nu_{13} ), ( \delta_{\text{sym}}(\text{SNH}) )</td>
<td>( \Lambda^{\prime} ) ( \nu_{15} ), ( \nu_{\text{asym}}(\text{NH}_2) )</td>
<td>( \nu_{16} ), ( \delta_{\text{asym}}(\text{SNH}) )</td>
<td></td>
</tr>
</tbody>
</table>

41.2 (0.75) | 42.0 (0.35) | \( \nu_{14} \), \( \delta(\text{NH}_2) \) | \( \nu_{13} \), \( \delta_{\text{sym}}(\text{SNH}) \) | \( \Lambda^{\prime} \) \( \nu_{15} \), \( \nu_{\text{asym}}(\text{NH}_2) \) | \( \nu_{16} \), \( \delta_{\text{asym}}(\text{SNH}) \) |

67.5 (0.23) | 67.5 (0.31) | \( \nu_{14} \), \( \delta(\text{NH}_2) \) | \( \nu_{13} \), \( \delta_{\text{sym}}(\text{SNH}) \) | \( \Lambda^{\prime} \) \( \nu_{15} \), \( \nu_{\text{asym}}(\text{NH}_2) \) | \( \nu_{16} \), \( \delta_{\text{asym}}(\text{SNH}) \) |

91.0 (0.14) | 91.0 (0.16) | \( \nu_{14} \), \( \delta(\text{NH}_2) \) | \( \nu_{13} \), \( \delta_{\text{sym}}(\text{SNH}) \) | \( \Lambda^{\prime} \) \( \nu_{15} \), \( \nu_{\text{asym}}(\text{NH}_2) \) | \( \nu_{16} \), \( \delta_{\text{asym}}(\text{SNH}) \) |
Table 4.2 (continued)

aData obtained from Raman spectra unless otherwise specified. Assignments for the modes of the F$_5$TeX groups have made assuming C$_{4v}$ symmetry using the mode species descriptions from ref (233). All frequencies are reported in cm$^{-1}$. bRef (233); liquid at -55 °C. cRef (205); solid N(CH$_3$)$_4$O$^+$TeF$_5^-$ at 25 °C. $\nu_1$ and $\nu_2$ have been described as antisymmetric and symmetric combinations of $\nu_{sym}(TeF_4)$ and $\nu(Te-F_{ax})$, respectively. dObtained from the infrared spectra at 25 °C. eRefs (220) and (203); Raman spectrum of the liquid, recorded at room temperature. fObtained from the gas phase infrared spectrum, ref (220). gThis work; Raman spectra recorded at -150 °C using 154.4-nm excitation. hIsotopic shifts $\Delta\nu(^{14}N/^{15}N) = \nu(^{15}N) - \nu(^{14}N)$, where the frequencies of the bands $\nu$ are given in cm$^{-1}$. 
possibilities for the molecular point symmetry. In the presence of a planar nitrogen center, which may result from Te-N π bonding, $C_{2v}$ point symmetry is expected if the NH$_2$ group is staggered or eclipsed with respect to the equatorial fluorines of the F$_5$Te- group. A pyramidal nitrogen center would result in $C_s$ point symmetry for the staggered and eclipsed conformations. All modes are Raman active under these symmetry designations. Due to the large difference in mass of the atoms in the F$_5$TeN- and -NH$_2$ groups, the vibrational frequencies associated with these two moieties are well separated from each other. As a result, it is possible to assign the modes of each moiety separately, allowing for the comparison of the vibrational modes of each moiety with those of simpler molecules. Precedent for this approximation was established in the assignment of the vibrational spectra of F$_5$TeOCl and F$_5$TeOF.$^{233}$

All bands attributable to the F$_5$TeN- group have been successfully assigned to the $3N - 6 = 15$ normal modes under $C_{4v}$ point group symmetry to provide direct comparison with the large body of published vibrational data for the F$_5$TeX group ($X = O,^{205,206}$ OH,$^{220}$ OF,$^{233}$ OCl,$^{233}$ and Cl$^{234}$). Comparisons are made with F$_5$TeO-, F$_5$TeOF, F$_5$TeOH in Table 2. Under $C_{4v}$ symmetry, the normal modes belong to the irreducible representations $4A_1 + 2B_1 + B_2 + 4E$ and are shown in Figure 4.3, all of which are Raman active.

The bands at 582.7 and 761.0 cm$^{-1}$ both have large isotopic shifts, and therefore have contributions from the Te-N stretching mode. The bands are tentatively assigned to the symmetric and asymmetric ν(N-Te-F$_{ax}$) stretching modes ($ν_1 + ν_3$), respectively. This assignment is in accord with the rule of thumb that an asymmetric stretch is usually higher in frequency than the associated asymmetric stretch. As expected in the Raman, the intensity of the symmetric stretch is greater than that for the asymmetric stretch (see Table 4.2). The strong coupling of the $ν_1$ and $ν_3$ modes supports Seppelt’s hesitation to make a distinction between the Te-F and Te-N stretching
Figure 4.3  Normal modes for pseudo-octahedral species, $XY_5Z$, of $C_{4v}$ point symmetry.
vibrations in the original assignment of the infrared and Raman spectra for $\text{F}_5\text{TeNH}_2$ in methylene chloride solution.\textsuperscript{230} Strong coupling of $\nu_1$ and $\nu_3$ was observed in the calculation of a modified valence force field for the analogous $\text{F}_5\text{SO}^-$ anion.\textsuperscript{210} The range of frequencies assigned to Te-N stretching modes for the related dialkylamino derivatives $\text{F}_5\text{TeNR}_2$ (538 - 629 cm$^{-1}$)\textsuperscript{229} is in agreement with the present study. The $^{14/15}\text{N}$ isotopic shift of the band at 300.7 cm$^{-1}$ [$\Delta\nu^{14/15}\text{N} = -1.9$ cm$^{-1}$] indicates that this band arises from the symmetric umbrella motion (out of plane bend) of the equatorial fluorines, $\delta_{\text{sym}}(\text{TeF}_4)$, since this mode undoubtedly couples with $\nu($Te-N), as observed in the vibrational spectra of $\text{F}_5\text{TeOX}$ (X = Cl, F).\textsuperscript{233} The isotopic dependence of the band at 286.7 cm$^{-1}$ [$\Delta\nu^{14/15}\text{N} = -3.6$ cm$^{-1}$] in the Raman spectrum of $\text{F}_5\text{TeNH}_2$ provides evidence for its assignment to the $\delta($NTeF$_4$) mode. The frequency is also similar to those observed for $\text{F}_5\text{TeOF}$ (309 - 325 cm$^{-1}$),\textsuperscript{233} and $\text{F}_5\text{TeO}^-$ (328 cm$^{-1}$).\textsuperscript{205,206} The assignments of bands to $\nu_{\text{sym}}(\text{TeF}_4)$ ($A_1$) and $\nu_{\text{asym}}(\text{TeF}_4)$ (E) have been made on the basis of intensity, since $\nu_{\text{sym}}(\text{TeF}_4)$ is consistently the most intense band in the Raman spectra of $\text{F}_5\text{TeCl},$\textsuperscript{234} $\text{F}_5\text{TeOF},$\textsuperscript{233} and $\text{F}_5\text{TeOCl}$,\textsuperscript{233} and the assumption that an asymmetric stretch is in general higher in frequency than the corresponding symmetric stretch. The $\nu_{\text{asym}}(\text{TeF}_4)$ (E) band is split, and may result from vibrational coupling of adjacent molecules within the unit cell of the microcrystalline solid, or from site symmetry effects in the solid state, since the Raman spectrum for $\text{F}_5\text{TeNH}_2$ in CH$_2$Cl$_2$ solution,\textsuperscript{230} where solid state interactions are alleviated, exhibits a single band at 684 cm$^{-1}$, the average of the solid state bands attributed to $\nu_{\text{asym}}(\text{TeF}_4).$ The small isotopic shifts of both of the bands attributed to $\nu_{\text{asym}}(\text{TeF}_4)$ [$\nu^{14/15}\text{N} = -0.6$ cm$^{-1}$] are assumed to result from vibrational coupling with the $\delta($NTeF$_4$) mode of the same symmetry (E).

The assignment of bands to $\nu_7$ [$\delta_{\text{sciss}}(\text{TeF}_4)$ in plane], $\nu_9$ [$\delta(\text{FTeF}_4)$] and $\nu_{11}$ [$\delta_{\text{asym}}(\text{TeF}_4)$] is straightforward by comparison with $\text{F}_5\text{TeOF},$\textsuperscript{233} $\text{F}_5\text{TeOH},$\textsuperscript{220} and $\text{F}_5\text{TeO}^-$,\textsuperscript{205,206} since these
bands are relatively constant for different substituents X in F₅TeX compounds, as shown in Table 4.2.

The band attributed to the v_{sym}(TeF₄) mode of B₁ symmetry (v₂) exhibits a small ¹⁴/¹⁵N isotopic shift (Δv¹⁴/¹⁵N = -0.6 cm⁻¹). The accuracy of the isotopic shift is dubious, however, since the band is observed as a shoulder on the more intense band at 619.6 cm⁻¹. Under C₄ᵥ point group symmetry, this mode is not expected to couple with v(Te-N) (v₃) or δ(NTeF₄) (v₁₀) because it does not belong to the E or A₁ irreducible representations. This selection rule for vibrational coupling of modes, and thus for the observation of isotopic dependences, may not apply since the true point group symmetry of F₅TeNH₂ is C₂ᵥ or Cₛ (see above) and the assumption of C₄ᵥ symmetry is only an approximation applied to the F₅TeN- group. If one considers that C₂ᵥ and Cₛ are subgroups of C₄ᵥ, correlation tables indicate that v_{sym}(TeF₄) may couple with v(Te-N) or δ(NTeF₄). For example, the irreducible representation of symmetry E, assignable to δ(NTeF₄) under C₄ᵥ point group symmetry correlates with A' + A'' under Cₛ. The mode v_{sym}(TeF₄) belongs to the B₁ irreducible representation under C₄ᵥ, which correlates with A' under Cₛ, allowing it to couple with δ(NTeF₄). Similarly, v(Te-N) belongs to the A' irreducible representation under Cₛ point group symmetry. Under C₂ᵥ point group symmetry, v_{sym}(TeF₄) may couple with v(Te-N) since they both belong to the A₁ irreducible representation.

As shown in Table 4.2, the frequencies of the bands attributed to Te-F stretching modes in F₅TeNH₂, in particular v(Te-Fₐₓ) [cf., symmetric combination of v₁ + v₃], are significantly lower than those of F₅TeOH and F₅TeOF. The Te-F stretching frequencies are, however, similar to those of the F₅TeO⁻ anion. The lowering of these bands relative to their equivalents in F₅TeOH has been attributed, by analogy with IOF₅, to an increase in donation of electron density from oxygen to tellurium, which increases the ionic character, and thus weakens the Te-F bonds.
discussed in Section (A) of this Chapter, a more accurate model may involve donation of \( \pi \)-electron density from oxygen to \( \sigma^* (\text{Te-F}) \) orbitals in \( \text{F}_3\text{TeX}^- \). Population of these antibonding orbitals accounts for the weakening of the Te-F bonds. The weakness of the axial Te-F bond compared to the equatorial Te-F bonds may result from the fact that \( \pi_{O} \rightarrow \sigma^* (\text{Te-F}_{ax}) > \pi_{O} \rightarrow \sigma^* (\text{Te-F}_{eq}) \). Resonance Structures 4.4 - 4.6 may be proposed for \( \text{F}_5\text{TeNH}_2 \), which are analogous to those proposed to describe the bonding in the \( \text{F}_5\text{TeO}^- \) anion\(^{206} \) [see Section (A) of this Chapter]. Greater weighting of resonance Structure 4.6 reflects the weaker axial Te-F bond.

\[
\begin{array}{c}
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\hline
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\end{array}
\quad \Rightarrow \quad
\begin{array}{c}
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\hline
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\hline
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\hline
\text{F} \quad \text{F} \\
\text{Te} \quad \text{F} \quad \text{F} \\
\text{F} \quad \text{N} \quad \text{H} \\
\end{array}
\]

etc.

4.4 4.5 4.6

A band attributable to \( \nu_6, \delta(\text{TeF}_4) \) is not observed in the Raman spectrum of \( \text{F}_5\text{TeNH}_2 \), presumably owing to an inherently low intensity and is likewise too weak to be observed in the vibrational spectra of \( \text{F}_5\text{TeCl}, \text{F}_5\text{TeOCl}, \text{F}_5\text{TeOF}, \text{F}_5\text{TeOH}, \text{F}_5\text{IO}^{236} \) and \( \text{F}_5\text{TeO}^- \).\(^{206} \) A value of 275 cm\(^{-1} \) has been estimated for \( \text{F}_5\text{IO}^{236} \) from an infrared combination band. A value of \( \nu_6 \) for \( \text{F}_5\text{TeCl} \) (199.1 cm\(^{-1} \)) has been calculated from the force constants obtained using the Wilson F'/G matrix method.\(^{234} \)

The \( 3N - 6 = 6 \) modes for the TeNH\(_2\) group may be assigned to the irreducible representations \( 4A' + 2A'' \) under \( C_5 \) point group symmetry assuming a nonplanar nitrogen...
geometry, or to $3A_1 + B_1 + 2B_2$ under $C_2v$, point group symmetry for a planar nitrogen center. The latter may result from $N \rightarrow Te \pi$-donation, by analogy with amides, where substantial $N \rightarrow C \pi$-donation results in a planar nitrogen center.\textsuperscript{237} By analogy with a vibrational study of aniline,\textsuperscript{232} it is possible to estimate the degree of the planarity of the nitrogen center from the $^{14/15}N$ isotopic frequency dependence of the bands associated with the NH$_2$ group on the HNH bond angle ($\theta$). The quantitative dependence of the isotopic shift on the HNH bond angle ($\theta$) is derived from the isotopic dependence of the $G$ matrices for $^{14}N$ and $^{15}N$ aniline which are calculated for different geometries of the NH$_2$ group.\textsuperscript{232} The degree of vibrational coupling of the symmetric and asymmetric stretching modes of the NH$_2$ group with other vibrational modes in aniline is negligible,\textsuperscript{232} and therefore the bands assignable to the $v_{\text{sym}}$(NH$_2$) and $v_{\text{asym}}$(NH$_2$) modes are more reliable than the other bands assigned to the NH$_2$ group for estimating $\theta$, since these latter bands may have contributions from several modes. Assuming similar vibrational purity of the bands assigned to $v_{\text{sym}}$(NH$_2$) and $v_{\text{asym}}$(NH$_2$) in F$_5$TeNH$_2$, Table 4.3 compares observed values of $\Delta \lambda/\lambda^0$ for $v_{\text{sym}}$(NH$_2$) and $v_{\text{asym}}$(NH$_2$) with calculated values of $\Delta \lambda/\lambda^0$ as a function of $\theta$, for [$^{14}N$]F$_5$TeNH$_2$ and [$^{15}N$]F$_5$TeNH$_2$. The results do not indicate a rigorously planar nitrogen center, where $\theta = 120^\circ$, since there is not a close correspondence of the calculated and observed values of $\Delta \lambda/\lambda^0$ for $v_{\text{sym}}$(NH$_2$) and $v_{\text{asym}}$(NH$_2$) [see Table 4.3]. This provides evidence against a pure Te-N $\pi$-bond of bond order 2, which would result in a planar nitrogen center. Possibly a Te-N bond order of less than two is present, as has been observed from calculation of X-O force constants for IOF$_5$, F$_5$TeO$^-$ and F$_5$ScO$^-$.\textsuperscript{206} In addition, $\pi_N \rightarrow \sigma^*$ negative hyperconjugation as a mechanism for $\pi$-donation from nitrogen to the F$_5$Te- group does not require a planar nitrogen geometry. This has been illustrated in geometric optimizations for FCH$_2$NH$_2$.\textsuperscript{238} which indicate maximum negative hyperconjugation when the plane defined by the NH$_2$ group is 144.6$^\circ$ with
Table 4.3. Calculated and Observed $^{14/15}\text{N}$ isotopic shifts, $\Delta\lambda/\lambda^0$, of $\nu_{\text{sym}}(\text{NH}_2)$ and $\nu_{\text{asym}}(\text{NH}_2)$ for $\text{F}_5\text{TeNH}_2$.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Planar$^b$ (0 = 120°)</th>
<th>Planar$^b$ (0 = 107°)</th>
<th>Pyramidal$^b$ (0 = 109.5°)</th>
<th>Observed $\Delta\lambda/\lambda^0$</th>
<th>$\nu_{\text{sym}}(\text{NH}<em>2)$ $\nu</em>{\text{asym}}(\text{NH}_2)$</th>
<th>Frequency, (cm$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordinate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$^{14}\text{N}\text{F}_5\text{TeNH}_2$ $^{15}\text{N}\text{F}_5\text{TeNH}_2$</td>
<td></td>
</tr>
<tr>
<td>$\nu_{\text{sym}}(\text{NH}_2)$</td>
<td>-0.00230</td>
<td>-0.00322</td>
<td>-0.00304</td>
<td>-0.00261</td>
<td></td>
<td>3297.2</td>
</tr>
<tr>
<td>$\nu_{\text{asym}}(\text{NH}_2)$</td>
<td>-0.00645</td>
<td>-0.00566</td>
<td>-0.00582</td>
<td>-0.00543</td>
<td></td>
<td>3385.3</td>
</tr>
</tbody>
</table>

$^a\Delta\lambda/\lambda^0 = [\lambda^{(\text{15}\text{N})} - \lambda^{(\text{14}\text{N})}]/\lambda^{(\text{14}\text{N})}$; $\lambda = 4\pi^2e^2c^2\nu^2$, where $c$ = velocity of light. Values for $\Delta\lambda/\lambda^0$ were calculated from G matrices in ref (232). $^b\theta$ = HNH bond angle. $^c$This work; frequencies obtained from Raman spectra of $^{14}\text{N}\text{F}_5\text{TeNH}_2$ and $^{15}\text{N}\text{F}_5\text{TeNH}_2$ recorded at -150 °C using 514.5-nm excitation.
respect to the N-C bond axis, indicating a pyramidal nitrogen geometry.

The bands attributable to the TeNH₂ group have therefore been assigned under the modes of C₂ symmetry as shown in Table 4.2 (v₁₂ to v₁₉). One of the A' modes has been omitted since it is the same mode as v₁ [v(Te-N)] of the F₅TeN⁻ group. All modes associated with the TeNH₂ group exhibit ¹⁴/¹⁵N isotopic shifts. The band associated with δ(TeNH) has been assigned by comparison to the infrared spectrum of F₅TeOH (1023.8, 1014.8 cm⁻¹).²²⁰ Comparison with the infrared spectrum of matrix isolated FNH₂²³⁹ and aniline in dilute solution²³² allowed for the assignments of v_sym(NH₂), v_asym(NH₂), δ_sym(SNH), and δ(NH₂). The ¹⁴/¹⁵N isotopic dependence and the process of elimination allowed for assignment of the band at 719.3 cm⁻¹ in the Raman spectrum of F₅TeNH₂ to the wagging mode, ω(NH₂), referred to as v₁₆ [δ_asym(SNH)] in Table 4.4, which occurs at 700 cm⁻¹ in the infrared spectrum of liquid aniline.²³²

Bands observed at 91.0, 67.5 and 41.2 cm⁻¹ exhibit no measurable shifts on ¹⁵N substitution and have been assigned to hydrogen bonding and/or lattice modes.

(C) CHARACTERIZATION OF F₅TeNH₂ AND [¹⁵N]F₅TeNH₂ IN SOLUTION BY ¹⁹F AND ¹H NMR SPECTROSCOPY

The ¹⁹F NMR spectrum for F₅TeNH₂ was investigated in CD₂Cl₂ solvent at 30 °C, and is similar to that reported by Seppelt.²³⁰ The C₄ᵥ point symmetry of the F₅TeN⁻ group is apparent from the characteristic AB₄ pattern, where δ_A = -37.3, and δ_B = -41.2 ppm. The two-bond coupling constant ²J(¹⁹F_A⁻¹⁹F_B) = 170 Hz. The couplings ¹J(¹⁹F_B⁻¹²⁵Te) = 3519, ¹J(¹⁹F_B⁻¹²³Te) = 2944, and ¹J(¹⁹F_A⁻¹²⁵Te) = 3284 Hz were also resolved. The couplings ¹J(¹⁹F_A⁻¹²³Te), ²J(¹⁹F_A⁻¹⁵N), ²J(¹⁹F_B⁻¹⁵N), ³J(¹⁹F_A⁻¹H) and ³J(¹⁹F_B⁻¹H) were not resolved in the ¹⁹F NMR spectrum of [¹⁵N]F₅TeNH₂. The ¹⁹F NMR spectra are consistent with observations made for
dialkylaminotellurium pentafluorides $\text{F}_5\text{TeNR}_2$ (R = $\text{CH}_3$, $^{228,229}\text{CH}_2\text{CH}_3$, $^{229}\text{C}_4\text{H}_8$) and $\text{F}_5\text{TeNH}_2$.

The $^1\text{H}$ NMR spectrum of $\text{F}_5\text{TeNH}_2$ in CD$_2$Cl$_2$ solvent at 30 °C (Figure 4.4a) exhibits a broad singlet ($\Delta v_{1/2} = 79$ Hz) centered at $\delta(^1\text{H}) = 4.30$ ppm, arising from the protons directly bonded to nitrogen. The large line width and the absence of any resolved couplings results from fast relaxation of $^1\text{H}$ due to interactions with the directly bonded quadrupolar $^{14}\text{N}$ nucleus (I = 1). The effects of quadrupolar broadening of the proton resonance are alleviated in the $^1\text{H}$ NMR spectrum of [$^{15}\text{N}$]$\text{F}_5\text{TeNH}_2$ in CD$_2$Cl$_2$ solvent at 30 °C (Figure 4.4b), and a doublet centered at $\delta(^1\text{H}) = 4.29$ ppm arising from $^1\text{J}(^1\text{H}-^{15}\text{N}) = 71$ Hz is observed (reduced coupling constant $^1\text{K}(\text{H-N}) = 5.8 \times 10^{20}$ NAm$^{-2}$m$^{-3}$). Each peak of the doublet is flanked by a low intensity satellite doublet arising from $^2\text{J}(^1\text{H}-^{125}\text{Te}) = 42$ Hz. The magnitude of $^1\text{J}(^1\text{H}-^{15}\text{N})$ is directly comparable to that observed for related R$^{15}\text{NH}_2$ compounds where R = (CF$_3$)$_2$P-, (CF$_3$)$_2$As-, CF$_3$S-. Several attempts have been made to arrive at an empirical relationship between the magnitude of $^1\text{J}(^1\text{H}-^{15}\text{N})$ and the 2s character in the nitrogen bonding orbitals with the aim of evaluating the hybridization at nitrogen. The fundamental assumption in attempting to correlate the magnitude of a directly bonded coupling constant with the nature of the bond hybridization is that the Fermi contact term is the dominant contribution to the coupling mechanism. This statement is usually assumed to be valid if one of the coupled nuclei is a proton. Equation (4.19) is a simplified expression for the Fermi contact contribution to the one bond $^{15}\text{N}$-$^1\text{H}$ coupling constant. Here

$$^1\text{J}(^{15}\text{N}-^1\text{H}) \propto \chi^{(15}\text{N}) \chi^{(1}\text{H})(\Delta \varepsilon)^{-1} (\alpha_N)^2 (\alpha_H)^2 |\psi_{N(2s)}(0)|^2 |\psi_{H(1s)}(0)|^2$$

(4.19)

$\chi^{(15}\text{N})$ and $\chi^{(1}\text{H})$ are the gyromagnetic ratios of the coupled nuclei, $\Delta \varepsilon$ is the average excitation
energy, $(\alpha_n)^2$ and $(\alpha_p)^2$ are the $s$ characters of the hybrid orbitals which make up the N-H bond, and the $|\psi(0)|^2$ terms represent the magnitudes of the indicated valence $s$ orbitals at the appropriate nuclei. Birnbaum et al.\textsuperscript{240} published an empirical equation (4.20) based on the

\[ \% \ s = 0.43|J^{15N\cdot 1H}| - 6 \]  

(4.20)

proportionality of $|J^{15N\cdot 1H}|$ and the $s$ characters of the hybrid orbitals which make up the N-H bond as shown in equation (4.19). This has been used to assess the hybridization at nitrogen (i.e., $s$ character of 0.0, 1.1, and 25.0 correspond to $sp^2$, $sp^3$ and $sp^4$ nitrogen valence orbital hybridizations, respectively). This information might in turn be used to assess the nature of the nitrogen-hydrogen bond. For example, an $sp^3$ valence orbital hybridization for nitrogen would agree a trigonal planar geometry and the presence of a filled $p$ orbital on nitrogen, with the possibility for a donation from nitrogen to the directly bonded hydrogen. Equation (4.20) was established originally from coupling constant data obtained from molecules with tetrahedral and trigonal planar nitrogen geometries.\textsuperscript{242} But has also been shown to be valid for linear species such as NCN$^\text{2+}$ and CH$_3$NH$_2$.\textsuperscript{137} Using equation (4.20), the observed value of $|J^{15N\cdot 1H}| = 71$ Hz for $F_2NH$ exhibits a $s$ character of 0.5 for the nitrogen valence hybrid orbitals, indicating that the nitrogen again is $sp^3$ hybridized. This would agree a tetrahedral nitrogen geometry and provide a method where there is no measurable $\Delta 
abla$ in $\phi_y$ remaining. In addition to assessing the applicability of equation (4.20) to the present example, using Coumary and Birnbaum's experimental results that $J$ is significantly different from that of lithium, based on the data available, it is not possible to determine the hybridization at nitrogen of $F_2NH$. From the magnitude of $|J^{15N\cdot 1H}|$, ...
and the presence or absence of $p_d$ bonding between nitrogen and tellurium cannot be commented upon.

(D) **CHARACTERIZATION OF $\text{F}_2\text{TeNH}_3^\cdot\text{AsF}_6^-$ AND $^{15}\text{N}\text{F}_2\text{TeNH}_3^\cdot\text{AsF}_6^-$ IN SOLUTION BY $^{19}\text{F}$, $^1\text{H}$, $^{15}\text{N}$, AND $^{125}\text{Te}$ NMR SPECTROSCOPY**

Bromine pentfluoride and anhydrous HF solvents were found to be suitable for obtaining the NMR spectra of $\text{F}_2\text{TeNH}_3^\cdot\text{AsF}_6^-$, and the parameters obtained from the multinuclear NMR spectra are listed in Table 4.4.

The $^1\text{H}$ NMR spectrum of $\text{F}_2\text{TeNH}_3^\cdot\text{AsF}_6^-$ in BrF$_3$ solvent at -53 °C (Figure 4.5a) consists of a broad singlet centered at 7.45 ppm ($\Delta v_{1/2} = 28$ Hz). The broadening and absence of resolved couplings results from the fast relaxation of the directly bonded quadrupolar nitrogen center ($I = 1$). The $^1\text{H}$ NMR spectrum of $^{15}\text{N}\text{F}_2\text{TeNH}_3^\cdot\text{AsF}_6^-$ in BrF$_3$ solvent at -56 °C (Figure 4.5b) illustrates a doublet arising from $^1J(\text{H}^\cdot{^{15}\text{N}}) = 76$ Hz (reduced coupling constant $^1K(\text{N-H}) = 6.2 \times 10^{20}$ $\text{NA}^{-2}\text{m}^{-3}$) centered at 7.43 ppm. The magnitude of the one-bond reduced N-H scalar coupling constant is comparable to that observed for similar compounds containing formally $sp^3$ hybridized, positively charged nitrogen centers (cf., $\text{NH}_3^\cdot\text{AsF}_6^-$: $^2J(\text{N-H}) = 6.2 \times 10^{20}$ $\text{NA}^{-2}\text{m}^{-3}$). $\text{CH}_2\text{NH}_3^\cdot\text{Cl}_2$: $^2J(\text{N-H}) = 6.2 \times 10^{20}$ $\text{NA}^{-2}\text{m}^{-3}$).

The $^{19}\text{F}$ NMR spectrum of the salt $\text{F}_2\text{TeNH}_3^\cdot\text{AsF}_6^-$ at -44 °C in BrF$_3$ solvent (Figure 4.6) consists of a typical $\text{AB}_2$ pattern confirming the $C_{2v}$ symmetry of the $\text{F}_2\text{TeN}^-$ group, where $\delta^{19}\text{F}_A = -55.0$ ppm and $\delta^{19}\text{F}_B = -39.2$ ppm. The parameters obtained from the $^{19}\text{F}$ NMR spectra are listed in Table 4.4. Assignments of the chemical shifts and coupling constants are made by analogy with $\text{F}_2\text{TeNH}_2$ (see above). The peak at -53.2 ppm results from TeF$_6$ and the broad resonance centered at -40 ppm is assigned to the AsF$_6^-$ anion. Broadening of this resonance
Figure 4.5 ¹H NMR spectra (500.138 MHz) of (a) natural abundance F₅TeNH₃⁺AsF₆⁻ (-53 °C; BrF₅ solvent) and (b) 99.5 atom % ¹⁵N-enriched F₅TeNH₃⁺AsF₆⁻ (-56 °C; BrF₅ solvent). Asterisks (*) denote ¹²⁵Te satellites.
Figure 4.6 $^{19}$F NMR spectrum (470.599 MHz) of natural abundance $\text{F}_2\text{TeNH}_3^+\text{AsF}_6^-$ in BrF$_5$ solvent (-44 °C); (A) resonance of equatorial fluorine atoms bonded to tellurium, (B) resonance of axial fluorine atom bonded to tellurium, (C) unidentified resonance, (D) TeF$_6^-$, (E) AsF$_6^-$; Asterisks (*) denote $^{125}$Te satellites.
is due to the rapid quadrupole relaxation of $^{75}$As ($I = 3/2$). The broad resonance at -52.0 ppm is attributed to a decomposition product, but the lack of coupling information prevents the assignment of this resonance. No additional couplings were observed in the $^{19}$F NMR spectrum of $[^{15}\text{N}]\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ in HF or BrF$_5$ solvents.

The $^{125}$Te NMR spectrum of $[^{15}\text{N}]\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ in HF solvent at -45.0 °C is shown in Figures 4.7a and 4.7b, and the $^{125}$Te NMR chemical shift ($\delta^{125}\text{Te} = 588$ ppm) is consistent with that expected for the F$_2$Te- group (cf., F$_2$TeOH, $\delta^{125}\text{Te} = 601$ ppm in CH$_3$C=NH solvent$^{248}$). All possible scalar couplings involving $^{125}$Te are observed, and are listed in Table 4.4. The $^{125}$Te NMR resonance is split into a doublet from the one-bond coupling $^1J(^{125}\text{Te}^{-19}\text{F}_A) = 3801$ Hz. Each line of the doublet is further split into a quintet from the scalar coupling of tellurium with four equivalent equatorial fluorines [$^1J(^{125}\text{Te}^{-19}\text{F}_B) = 3651$ Hz]. These couplings are consistent with those observed in the $^{19}$F NMR spectra. Each line of this multiplet is further split into a doublet of quartets from the scalar coupling of tellurium with nitrogen [$^1J(^{125}\text{Te}^{-15}\text{N}) = 48$ Hz] and with the three equivalent protons of the -NH$_3^+$ group [$^2J(^{125}\text{Te}^{-1}\text{H}) = 25$ Hz]. The magnitude of $^2J(^{125}\text{Te}^{-1}\text{H})$ is consistent with that observed for the same coupling in the $^1$H NMR spectrum of the F$_5$TeNH$_3^+$ cation. The observation of well defined quartets corresponding to the two-bond scalar coupling with the protons on nitrogen indicates that F$_5$TeNH$_3^+$ predominates in the highly acidic HF solvent.

The $^{15}$N NMR spectrum of $[^{15}\text{N}]\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ (Figure 4.8) at -40 °C in HF solvent consists of a quartet centered at -317.1 ppm. The quartet structure arises from the one-bond scalar coupling of nitrogen and the three equivalent protons [$^1J(^{15}\text{N}^{-1}\text{H}) = 76$ Hz]. The magnitude of the coupling is consistent with $^1J(^1\text{H}^{-15}\text{N})$ observed in the proton $^1$H NMR spectrum. Each line of the quartet is flanked by low intensity satellites arising from $^2J(^{15}\text{N}^{-125}\text{Te}) = 48$ Hz, which is
Figure 4.7  $^{125}$Te NMR spectrum (157.795 MHz) of 99.5 atom % $^{15}$N-enriched \( F_5\text{TeNH}_3^+\text{AsF}_6^- \) in HF solvent (−45 °C); (a) entire multiplet, dagger (†) denotes a peak of the \( \text{TeF}_6 \) multiplet (not shown in full), and (b) expansion of the central region of the multiplet attributed to \( F_5\text{TeNH}_3^+ \).
\( \delta_{125}\text{Te} \) (ppm from Te(\( \text{CH}_3 \))\(_2\))
Figure 4.8  $^{15}$N NMR spectrum (50.698 MHz) of 99.5 atom % $F_5TeNH_3^+AsF_6^-$ in HF solvent (-40 °C). Asterisks (*) denote $^{125}$Te satellites.
Table 4.4. $^{19}$F, $^1$H, $^{125}$Te and $^{15}$N NMR Chemical Shifts and Coupling Constants for $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ and $[^{15}\text{N}]\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$.

<table>
<thead>
<tr>
<th>Chemical Shifts (ppm)</th>
<th>Coupling Constants, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta(^{19}\text{F})$</td>
<td>$-55.6$ ((\delta_A))</td>
</tr>
<tr>
<td></td>
<td>$-30.2$ ((\delta_B))</td>
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<tr>
<td>$\delta(^1\text{H})$</td>
<td>7.45</td>
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<tr>
<td>$\delta(^{125}\text{Te})$</td>
<td>588</td>
</tr>
<tr>
<td>$\delta(^{15}\text{N})$</td>
<td>-317.1</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The $^{19}$F, $^1$H, $^{125}$Te, and $^{15}$N NMR spectra were referenced to external neat CFCl$_3$, (CH$_3$)$_4$Si, Te(CH$_3$)$_2$ and CH$_3$NO$_2$ at 30 °C, respectively, with positive (negative) shifts denoting high (low) frequency resonances with respect to the standards. $^b$Recorded at -44 °C in BrF$_5$ solvent. $^c$Recorded at -53 °C in BrF$_5$ solvent. $^d$Recorded at -45 °C in HF solvent. $^e$Recorded at -40 °C in HF solvent.
consistent with that observed in the $^{125}$Te NMR spectrum. The $^{15}$N NMR chemical shift is intermediate between those observed for NH$_4^+$AsF$_6^-$ in HF (-369.6 ppm)$^{244}$ and FNH$_3^+$O$_2$SCF$_3^-$ in HF (-252.1 ppm)$^{244}$. The trend in the $^{15}$N NMR chemical shifts is explained by an approximate formulation of the local paramagnetic term, restricted to electronic circulations on observed atom N bonded to other atoms [equation (4.21)]. In this equation, $\sigma_p^{NN}$ is the local paramagnetic

$$\sigma_p^{NN} = -\mu_0 \mu_B \langle r^3 \rangle_{2p} / 2\pi(\Delta B)[Q_{NN} + \Sigma Q_{NX} Q_{NX}]$$  \hspace{1cm} (4.21)$$

contribution to the shielding of nitrogen, and an increase in the absolute magnitude of $\sigma_p^{NN}$ deshields the nucleus; $\mu_0$ is the permeability of a vacuum, $\mu_B$ the Bohr magneton, and $\langle r^3 \rangle_{2p}$ the average radius of the valence p electrons on nitrogen. The $\Sigma Q$ term expresses the imbalance of electronic charge that allows the paramagnetic circulation in the magnetic field. The $Q_{NN}$ part depends on the 2p orbital populations on nitrogen, whereas $\Sigma Q_{NX}$ is a multiple bond term. The fact that the $^{15}$N NMR resonance of the FNH$_3^+$ cation is deshielded by 117 ppm relative to the NH$_4^+$ cation can be attributed to the $\sigma$ fluoro effect (electron withdrawal by the electronegative fluorine atom) which contracts the nitrogen 2p orbitals, increasing $\langle r^3 \rangle_{2p}$. Also, the substitution of one hydrogen in NH$_4^+$ with fluorine to give FNH$_3^+$ increases the $Q_{NN}$ term by reducing the valence orbital symmetry around nitrogen. Both of these effects increase the magnitude of the paramagnetic contribution to the nitrogen shielding ($\sigma_p^{NN}$) thus deshielding the nitrogen nucleus in FNH$_3^+$ relative to NH$_4^+$.$^{244}$ The less shielded $^{15}$N NMR resonance of the F$_5$TeNH$_3^+$ cation relative to NH$_4^+$ is expected following the same arguments as for the FNH$_3^+$ cation since the F$_5$Te- group is undoubtedly more electronegative than H. Although a subject of debate,$^{52}$ the larger body of evidence indicates that the group electronegativity of F$_5$TeO- is less than that of
fluorine. Although the group electronegativity of the $F_2Te^-$ group has not been estimated, by analogy with $F_2TeO^-$ the electronegativity of the $F_2Te^-$ group is probably less than that of fluorine. As a result, the $\sigma$ withdrawing effect of the $F_2Te^-$ group in the $F_2TeNH_3^+$ cation is assumed to be less than that of fluorine in the $FNH_3^+$ cation, resulting in a smaller $<r^2>_p$ term on nitrogen in the former and a smaller value of $\sigma_p^{NN}$.

(E) CHARACTERIZATION OF $F_2TeNH_3^+AsF_6^-$ AND $[^{15}NF_2TeNH_3^+AsF_6^-]$ IN THE SOLID STATE BY RAMAN SPECTROSCOPY

The ambient temperature Raman spectra of the white microcrystalline product isolated from the reaction of natural abundance $F_2TeNH_2$ with excess AsF$_5$ in HF solvent are shown in Figure 4.9. Figure 4.10 illustrates the regions of the Raman spectra of the natural abundance and 99.5 atom % $^{15}N$ enriched salts which exhibit $^{14}/^{15}N$ isotopic shifts and frequencies obtained from both Raman spectra are listed in Table 4.5.

The Raman spectra are consistent with the formation of $F_2TeNH_3^+AsF_6^-$ in the solid state. The $F_2TeNH_3^+$ cation is expected to give rise to $3N - 6 = 24$ normal modes. The lowest energy conformation, where the NH$_3$ protons are staggered with respect to the equatorial fluorines of the $F_2Te^-$ group, results in $C_2$ point symmetry for the $F_2TeNH_3^+$ cation. The modes of this point symmetry belong to the irreducible representations $14 A' + 10 A''$, and all are Raman and infrared active. In Table 4.5, the modes for the $F_2TeNH_3^+$ cation have been assigned by considering the $F_2TeN^-$ ($C_{4v}$) and $TeNH_3$ ($C_{3v}$) groups separately. This has been done primarily to allow for direct comparison of modes of the $F_2TeN^-$ group with the large body of vibrational data available for $F_2TeX^-$ compounds [see Section (B) of this Chapter]. This is reasonable since the infrared and Raman selection rules are not altered by this approximation, and the large frequency difference
Figure 4.9  Raman spectrum of natural abundance $F_3\text{TeNH}_3^+\text{AsF}_6^-$ recorded at ambient temperature by use of 514.5-nm excitation.
Figure 4.10  Raman spectra of natural abundance (lower trace) and 99.5 atom % $^{15}$N-enriched (upper trace) $F_2TeNH_3^+AsF_6^-$ recorded at ambient temperature by use of 514.5-nm excitation.
between modes of the $\text{F}_2\text{TeN}$- and $\text{-TeNH}_3$ groups minimizes vibrational coupling.

All $3N - 6 = 15$ modes of the $\text{F}_2\text{TeN}^-$ group of the $\text{F}_5\text{TeNH}_3^+$ cation have been assigned under $C_{4v}$ point symmetry. The large isotopic shift of the band at 566.5 cm$^{-1}$ [$\Delta v(\text{N}^{14/15}) = -15.7$ cm$^{-1}$] indicates that it may be assigned to $v(\text{Te-N})$ ($A_1$). Similarly, the band at 276.3 cm$^{-1}$ which also exhibits a large isotopic shift [$\Delta v(\text{N}^{14/15}) = -3.4$ cm$^{-1}$], is assigned to $\delta(\text{NTeF}_2)$ (E). Comparisons with the band attributable to $\delta(\text{OTeF}_2)$ in the vibrational spectra $\text{F}_5\text{TeOF}$ (309-325 cm$^{-1}$), $\text{F}_5\text{TeOCl}$ (316 cm$^{-1}$), and $\text{F}_5\text{TeO^-}$ (328 cm$^{-1}$) provide further evidence for the assignment.

The peaks at 730.2 and 682.2 cm$^{-1}$ are assigned to the $v(\text{Te-F}_{\text{ax}})$ and $v_{\text{sym}}(\text{TeF}_4)$ modes of $A_1$ symmetry by comparison with $\text{F}_5\text{TeOF}$, $\text{F}_5\text{TeCl}$, $\text{F}_5\text{TeOCl}$, and $\text{F}_5\text{TeOH}$.

The intensity of the peak at 682.2 cm$^{-1}$ also supports its assignment to $v_{\text{sym}}(\text{TeF}_4)$ since bands attributed to this mode are invariably the most intense in the Raman spectra of the related $\text{F}_5\text{TeX}$ compounds (Table 4.5). As expected, $\text{N}^{14/15}$ isotopic shifts are observed for the bands attributed to $v(\text{Te-F}_{\text{ax}})$ [$\Delta v(\text{N}^{14/15}) = -0.9$ cm$^{-1}$] and $v_{\text{sym}}(\text{TeF}_4)$ [$\Delta v(\text{N}^{14/15}) = -0.7$ cm$^{-1}$].

The assignment of all other modes associated with the $\text{F}_5\text{Te}$ group are made by analogy with related compounds (Table 4.5). An $\text{N}^{14/15}$ isotopic shift is observed for the band at 315.7 cm$^{-1}$ assigned to $v_4$, $\delta_{\text{sym}}(\text{TeF}_4)$, although the band overlaps with the peak assigned to $v_4$, $\delta_{\text{sym}}(\text{TeF}_4)$ at 320.4 cm$^{-1}$ in the Raman spectrum of $[\text{N}^{15}]\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$. Therefore the isotopic shift cannot be determined accurately. A mass dependence of the band attributed to $v_4$, $\delta_{\text{sym}}(\text{TeF}_4)$ has been observed in the Raman and infrared spectra of $\text{F}_5\text{TeOF}$ and $\text{F}_5\text{TeOCl}$, which has been attributed to vibrational coupling of $v(\text{Te-O})$, $v(\text{O-X})$ [$X = \text{Cl, F}$], and $v_{\text{sym}}(\text{TeF}_4)$.

The small $\text{N}^{14/15}$ isotopic shift [$\Delta v(\text{N}^{14/15}) = -0.7$ cm$^{-1}$] observed for the band attributed to $v_9$, $\delta(\text{FTeF}_2)$ (E) may result from coupling of the $v_9$ mode with $v_{10}$, $\delta(\text{NTeF}_2)$, which also belongs
Table 4.5. Raman Frequencies and Assignments for $\text{F}_2\text{TeNH}_3^+\text{AsF}_6^-$ and $[^{15}\text{N}]\text{F}_2\text{TeNH}_3^+\text{AsF}_6^-$ and the Related $\text{F}_2\text{TeOF}$, $\text{F}_2\text{TeOH}$ and $\text{F}_3\text{TeO}^-$

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<th>$\Delta v$(14/15N) b</th>
<th>approx mode description</th>
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</tr>
<tr>
<td>721 (1.6)</td>
<td>584 (30)</td>
<td>735</td>
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<td>669 (10)</td>
<td>652 (100)</td>
<td>685</td>
<td>682.9 (100)</td>
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<td>725</td>
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<td>319</td>
<td>315.7 (6.03)</td>
</tr>
<tr>
<td>660 (0.3)</td>
<td>584 (30)</td>
<td>652</td>
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<tr>
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<td>1396.0 (0.40)</td>
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<td>1405.7 (0.86)</td>
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<td></td>
<td>3110.1 (1.92)</td>
<td>3110.0 (1.75)</td>
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<tr>
<td></td>
<td>1539.7 (0.59)</td>
<td>1531.6 (0.59)</td>
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</tr>
</tbody>
</table>

Notes:
- "n.o." stands for "not observed".
- "sh" stands for "shoulder".
- "f" indicates a frequency measured using a different instrument.
- The table includes assignments for $v_{11}$, $v_{22}$, $v_{33}$, $v_{44}$, $v_{55}$, $\delta_{\text{sym}}(\text{TeF}_4)$, $\delta(\text{TeF}_4)$, $v_{10}$, $\delta_{\text{asym}}(\text{TeF}_4)$, $v_{12}$, $v_{13}$, $\delta_{\text{asym}}(\text{TeF}_4)$, $v_{14}$, and $v_{15}$.

Reference:
- "Raman Frequencies and Assignments for $\text{F}_2\text{TeNH}_3^+\text{AsF}_6^-$ and $[^{15}\text{N}]\text{F}_2\text{TeNH}_3^+\text{AsF}_6^-$ and the Related $\text{F}_2\text{TeOF}$, $\text{F}_2\text{TeOH}$ and $\text{F}_3\text{TeO}^-$" from a scientific paper.
<table>
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<tr>
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<td>(1.69)</td>
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<tr>
<td>689 sh</td>
<td></td>
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<td>593</td>
<td>(3.15)</td>
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<td>396</td>
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<tr>
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</table>
Table 4.5 (continued)

aData obtained from Raman spectra unless otherwise specified. Assignments for the modes of the F₅TeX groups have made assuming C₄ᵥ symmetry using the mode species descriptions from ref (233). Assignments for the NH₃ group of the F₅TeNH₃⁺ cation have been made under approximate C₃ᵥ symmetry. All frequencies are reported in cm⁻¹. bRef (233); liquid at -55 °C. cRef (205); solid N(CH₃)₄⁺OTeF₅⁻ at 25 °C. ν₁ and ν₂ have been described as antisymmetric and symmetric combinations of νₚₛₗₚ(TeF₄) and ν(Te-Fₐₓ), respectively. dObtained from the infrared spectra at 25 °C. eRefs (220) and (203); Raman spectrum of the liquid, recorded at room temperature. fObtained from the gas phase infrared spectrum, ref (220). gThis work; Raman spectra recorded at 25 °C using 154.4-nm excitation. hIsotopic shifts Δν(^15N) = ν(^15N) - ν(^14N), where the frequencies of the bands ν are given in cm⁻¹.
to the E symmetry species.

The band at 311.1 cm\(^{-1}\) assigned to \(v_7\), \(\delta_{\text{sciss}}(\text{TeF}_4)\) has an observed isotopic shift \([\Delta v^{14/15N} = -0.9 \text{ cm}^{-1}\)] that is forbidden under \(C_{dv}\) point symmetry since the symmetry species for \(v_7\) (B\(_2\)) is neither A\(_1\) nor E, which are the symmetry species for \(v_3\), \(v(\text{Te-N})\) and \(v_{10}\) \(\delta(\text{NTeF}_4)\), respectively. However, vibrational coupling of \(v_7\) and \(v_{10}\) is possible if one considers the point symmetry for the entire \(\text{F}_5\text{TeNH}_3^+\) cation (C\(_2\)). The E representation of the point group \(C_{dv}\) correlates with A' + A'' of the C\(_2\) point group. Likewise, the B\(_2\) representation in \(C_{dv}\) correlates with A' or A'' in C\(_2\). Under the lower point symmetry, the modes belong to the same representations, and thus can couple. Similarly, the observed isotopic shift \([\Delta v^{14/15N} = -0.8 \text{ cm}^{-1}\)] of the band assigned to \(v_8\), \(v_{\text{sym}}(\text{TeF}_4)\) (E) can be explained by vibrational coupling with \(v_3\), \(v(\text{Te-N})\) (A\(_1\)) since the A\(_1\) representation correlates with A' in C\(_2\).

As for \(\text{F}_5\text{TeNH}_2\), a band attributable to \(v_6\), \(\delta(\text{TeF}_4)\) is not observed in the Raman spectrum of \(\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-\), presumably owing to an inherently low intensity [see Section (B) of this Chapter].

All of the bands attributable to the \(\text{TeNH}_3\) group have been assigned to symmetry species of the \(C_{3v}\) point group. A total of \(3N - 6 = 9\) normal modes belonging to the irreducible representations 3 A\(_1\) + 3 E are expected under \(C_{3v}\) symmetry. One A\(_1\) mode \([v(\text{Te-N})]\) is the same as \(v_3\) of the \(\text{F}_5\text{TeN}\) group and is therefore not repeated. The remaining 2 A\(_1\) + 3 E modes and the corresponding bands \((v_{12}\) to \(v_{18}\)) observed in the Raman spectra of \(\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-\) are listed in Table 4.5.

The very broad bands at 3018 and 3110 cm\(^{-1}\) have been assigned to \(v_{12}\) \([v_{\text{sym}}(\text{NH}_2)]\) and \(v_{14}\) \([v_{\text{asym}}(\text{NH}_2)]\), from the expected NH stretching frequency range for compounds containing an \(\text{NH}_3^+\) group (3030 - 3130 cm\(^{-1}\)).\(^{249}\) It is noteworthy that the NH stretches for \(\text{F}_5\text{TeNH}_2\) occur
at considerable higher frequency [3280.1, 3297.2, 3385.3 cm$^{-1}$; see Section (B) of this Chapter]. This is consistent with the higher frequency range expected for neutral primary amines (3300 - 3500 cm$^{-1}$).$^{259}$ No significant $^{14/15}$N isotopic shifts are observed for the NH stretching vibrations. This has been attributed to the broadness of the bands, making the shifts undetectable.

The symmetric bend, $\delta_{\text{sym}}$(NH$_3$), has been assigned to the bands at 1396.9 and 1405.7 cm$^{-1}$, which exhibit $^{14/15}$N isotopic shifts of -5.7 and -5.9 cm$^{-1}$, respectively. The band assigned to $\nu_{15}$, $\delta_{\text{asym}}$(NH$_3$) is observed at 1539.7 cm$^{-1}$ and exhibits an $^{14/15}$N isotopic shift of -8.1 cm$^{-1}$. Assignment of $\nu_{\text{sym}}$(NH$_3$) and $\delta_{\text{asym}}$(NH$_3$) has been made by comparison with the vibrational spectra of salts of the F$^-$NH$_3$ cation$^{239}$ and FCH$_3$.$^{67}$

By comparison with F$_5$TeOH,$^{220}$ $\nu_{16}$ [$\delta_{\text{sym}}$(TeNH)] is expected to occur at approximately 1000 cm$^{-1}$. Since no bands are observed in this region, it is assumed that the band has a very weak Raman intensity. It is worth noting that $\delta$(TeOH) is too weak to be observed in the Raman spectrum of F$_5$TeOH; the band was observed in the infrared gas phase spectrum.

A total of 15 bands are assigned to the AsF$_5^-$ anion in the Raman spectrum of F$_5$TeNH$_3$ $^+$ AsF$_5^-$. For undistorted AsF$_5^-$, of $O_h$ point symmetry, only three Raman-active bands are expected. The bands have been assigned to the modes of $O_h$ point symmetry in Table 4.5 although a reduction in symmetry is apparent. Possible sources of deviation from $O_h$ point symmetry are solid state effects such as a low site-symmetry in the solid and intermolecular vibrational coupling, which gives rise to factor group splitting; the effects of both may be predicted from a knowledge of the crystallographic unit cell. Also, interactions between cation and anion may result in an authentic distortion of the anion symmetry, such as the reduction of AsF$_5^-$ symmetry to $C_{4v}$ upon fluorine bridge formation with the XeF$_6^+$ $^{67,68}$ and KrF$_6^+$ $^{69}$ cations.

An anion site symmetry of $C_{2v}$ or lower, where all mode degeneracies are removed, would
result in the observation of all $3N - 6 = 15$ bands in the Raman spectrum, since no selection rules forbid the vibrational activity of any of the modes. It is possible that a low site-symmetry for the AsF$_6^-$ anion results from H-F hydrogen-bonding interactions with the F$_5$TeNH$_3^+$ cation. Christe et al.\textsuperscript{171} have explained the observation of $v_1$ through $v_5$ and the splittings of the bands in the Raman spectrum of OH$_3^+$AsF$_6^-$ at -120 °C in terms of weak H-F cation-anion interactions that dominate at low temperature in a rigid lattice containing AsF$_6^-$ anions in a non-octahedral field (i.e., a low site symmetry). The Raman spectrum at 25 °C resembles that for octahedral AsF$_6^-$; the weak cation-anion interactions are assumed to be overcome by thermal motion, thus resulting in an effective increase in the AsF$_6^-$ site symmetry. It is possible that the lattice in F$_5$TeNH$_3^+$AsF$_6^-$ is rigid at room temperature, resulting in a sufficiently low AsF$_6^-$ site-symmetry to account for the number of observed bands.

A reduction in AsF$_6^-$ site symmetry from $O_h$ to $C_{2v}$ or lower by weak cation-anion interactions or simply by the existence of a low site symmetry for AsF$_6^-$ in the solid state would result in the removal of all $O_h$ degeneracies. As seen in Table 4.5, the number of bands in the Raman spectrum of F$_5$TeNH$_3^+$AsF$_6^-$ which correlate with $v_2$ ($E_g$) and $v_5$ ($T_{2g}$) are greater than can be accounted for by simple removal of degeneracies through a reduction of AsF$_6^-$ symmetry. Intermolecular coupling may account for the additional splitting, and could possibly be confirmed by factor-group analysis if X-ray structural data were available.

(F) ASSESSMENT OF THE BONDING IN F$_5$TeNH$_2$ AND THE F$_5$TeNH$_3^+$ CATION USING RAMAN AND $^{19}$F NMR SPECTROSCOPY

In Table 4.6 the vibrational frequencies associated with the modes of the F$_5$TeX- groups in F$_5$TeNH$_2$ and the F$_5$TeNH$_3^+$ cation are compared with those of F$_5$TeOH and the F$_5$TeO$^-$ anion.
As can be seen, the trends observed in a comparison of the vibrational spectra of $\text{F}_5\text{TeOH}$ and $\text{F}_5\text{TeO}^-$ are also present in $\text{F}_5\text{TeNH}_2$ and the $\text{F}_5\text{TeNH}_3^+$ cation. The deprotonation of $\text{F}_5\text{TeOH}$ to give the $\text{F}_5\text{TeO}^-$ anion results in a shift to high frequency of $\nu(\text{TeO})$ by 133 cm$^{-1}$ resulting from an increase in the Te-O bond order. Accompanying the increase in $\nu(\text{TeO})$ is a decrease of the Te-F stretching modes. The largest effect is observed for $\nu(\text{Te-F})$, which is 151 cm$^{-1}$ lower for the $\text{F}_5\text{TeO}^-$ anion than for $\text{F}_5\text{TeOH}$. The weakening of the Te-F bonds and strengthening of the Te-O bond in the $\text{F}_5\text{TeO}^-$ anion (and similarly for $\text{F}_5\text{SeO}^-$ and $\text{F}_5\text{SO}^-$) relative to the parent acids has been attributed to donation of electron density from oxygen to the X-F bonds ($X = S, Se, Te$) as discussed in Section (A) of this Chapter. A close parallel is observed in a comparison of the Raman spectra of the acid/base pairs $\text{F}_5\text{TeOH/FSiO}^-$ and those of the $\text{F}_5\text{TeNH}_3^+$ cation and $\text{F}_5\text{TeNH}_2$. Deprotonation of the $\text{F}_5\text{TeNH}_3^+$ cation results in an increase in the Te-N bond order, which is reflected in the low value of $\nu_3$ [$\nu(\text{Te-N})$] for $\text{F}_5\text{TeNH}_3^+$ compared to the band at 761.0 cm$^{-1}$ in the Raman spectrum of $\text{F}_5\text{TeNH}_2$, which has a component from the Te-N stretching mode. This accompanied by an increase in the Te-F stretching force constants, particularly that for Te-F$_{ax}$. This is reflected in the high frequency of $\nu_1$ [$\nu(\text{Te-F}_{ax})$, 730.2 cm$^{-1}$, for $\text{F}_5\text{TeNH}_3^+$. Although strong vibrational coupling of the $\nu(\text{Te-N})$ and $\nu(\text{Te-F}_{ax})$ stretching modes prevents the assignment of $\nu(\text{Te-F}_{ax})$ to a particular band, it contributes strongly to the band at 582.7 cm$^{-1}$, which is significantly lower than the band assigned to $\nu(\text{Te-F}_{ax})$ in $\text{F}_5\text{TeNH}_3^+$. These observations are consistent with a close parallel in the bonding of the acid/base pairs $\text{F}_5\text{TeOH/FSiO}^-$ and $\text{F}_5\text{TeNH}_3^+/\text{F}_5\text{TeNH}_2$.

The $^{19}$F NMR spectra of $\text{F}_5\text{TeNH}_2$ and $\text{F}_5\text{TeNH}_3^+/\text{AsF}_6^-$ are shown in Figure 4.11 and the $^{19}$F NMR chemical shifts are listed in Table 4.7. As can be seen, protonation of $\text{F}_5\text{TeNH}_2$
Table 4.6. Vibrational Frequencies and Assignments for $F_5TeO^-$, $F_5TeOH$, $F_5TeNH_2$ and $F_5TeNH_3^+$

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<td></td>
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<td>$v_{2}$, $v_{\text{sym}}(\text{TeF}_4)$</td>
<td>sym $[v_1 + v_3]$</td>
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</table>

*Data obtained from Raman spectra unless otherwise specified. Assignments for the modes of the $F_5TeX$ group have made assuming $C_{5v}$ symmetry using the mode species descriptions from ref (233). Ref (233); liquid at -55 °C. Ref (234); liquid at ambient temperature. Ref (29); $N(CH_3)_4OTeF_5$ at 25 °C. $v_1$ and $v_2$ have been described as asymmetric and symmetric combinations of $v_{\text{sym}}(\text{TeF}_4)$ and $v(\text{Te-F}_{\text{ax}})$, respectively. *Obtained from the infrared spectra at 25 °C. Ref (220) and (203); Raman spectrum of the liquid, recorded at room temperature. *Obtained from the gas phase infrared spectrum. This work; recorded at -150 °C using 514.5-nm excitation. This work; recorded at ambient temperature using 514.5-nm excitation.
Table 4.7. $^{19}$F NMR Parameters for $\text{F}_5\text{TeNH}_2$ and $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$. 

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{19}$F NMR Chemical Shifts$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{F}_5\text{TeNH}_2$ $^b$</td>
<td>$\delta_A$ -37.8, $\delta_B$ -42.8</td>
</tr>
<tr>
<td>$\text{F}_5\text{TeNH}_3^+$ $^b$ $\text{AsF}_6^-$ $^c$</td>
<td>$\delta_A$ -55.6, $\delta_B$ -30.2</td>
</tr>
</tbody>
</table>

$^a$ $^{19}$F NMR spectra referenced with respect to neat external CFCl$_3$ at 30 °C. Negative chemical shifts indicate low frequency resonances with respect to CFCl$_3$. Recorded in BrF$_5$ solvent. $^b$ -44 °C, $^c$ -50 °C.
Figure 4.11  (a) $^{19}$F NMR spectrum (470.599 MHz) of $\text{F}_2\text{TeNH}_2$ in BrF$_5$ solvent (-44 °C); (A) multiplet assigned to the axial fluorine atom bonded to tellurium, (B) resonance of equatorial fluorine atoms bonded to tellurium, (C) TeF$_6$. (b) $^{19}$F NMR spectrum (470.599 MHz) of $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ in BrF$_5$ solvent (-50 °C); (A) resonance of equatorial fluorine atoms bonded to tellurium, (B) resonance of axial fluorine atom bonded to tellurium, (C) unidentified resonance, (D) TeF$_6$, (E) AsF$_6^-$; Asterisks (*) in both spectra denote $^{125}$Te satellites.
significantly alters the $^{19}F$ NMR shieldings of the axial and equatorial fluorines of the $F_5Te$- group. The axial fluorine resonance ($\delta_A$) is shielded by 18.5 ppm on protonation, whereas the equatorial resonance ($\delta_E$) is deshielded by 5.2 ppm. The greater shift for the axial fluorine resonance is consistent with the trans effect observed in the $^{19}F$ NMR spectra of the acid/base pairs $F_5XOH/F_5XO^{-}$ for $X = S, Se, Te$ [see Section (A) of this Chapter].

(G) **CONCLUSION**

The differences in bonding reflected in the Raman and $^{19}F$ NMR spectral parameters for the acid/base pair $F_5TeNH_3^+/F_5TeNH_2$ are analogous to those observed for $F_5TeOH$ and $F_5TeO^{-}$ anion. The Te-N bond order in $F_5TeNH_2$ is greater than in the $F_5TeNH_3^+$ cation, indicating some degree of $\pi$-donation from the lone pair on nitrogen to acceptor orbitals of the $F_5Te$- group, possibly $\sigma^*(Te-F)$. The presence of electron density in these antibonding orbitals reduces the strengths of the Te-F bonds. The greater weakening of the axial Te-F bond is attributed to the fact that $\pi_N \to \sigma^*(Te-F_{ax}) > \pi_N \to \sigma^*(Te-F_{eq})$. Protonation of the nitrogen in $F_5TeNH_2$ reduces the strength of the Te-N bond since the nitrogen lone pair is no longer available for Te-N $\pi$ bonding. The depopulation of the $\sigma^*(Te-F)$ orbitals results in an increase in the strength of the Te-F bonds.
CHAPTER 5

[PENTAFLUOROTELLURIUM(VI)AMIDO] XEONIUM(II) HEXAFLUOROARSENATE;

$F_5TeN(H)_2Xe^+AsF_6^-$

INTRODUCTION

While many examples of xenon bonded to oxygen or fluorine and of xenon bonded to other highly electronegative ligands through oxygen were synthesized immediately following the discovery of noble-gas reactivity, the decade had elapsed before an example with a ligating atom other than oxygen and fluorine, namely nitrogen, was synthesized, and two decades before the Xe-N bond in FXeN(SO$_2$F)$_2$ was definitively characterized in the solid state by X-ray crystallography and in solution by multinuclear magnetic resonance spectroscopy. Other imidodisulfurylfluoride derivatives containing Xe(II)-N bonds have since been characterized primarily by use of NMR spectroscopy, namely, Xe[N(SO$_2$F)$_2$]$_2$ F[XeN(SO$_2$F)$_2$]$_2^+$. XeN(SO$_2$F)$_2^+AsF_6^-$ and XeN(SO$_2$F)$_2^+SbF_6^-$ The compound Xe[N(SO$_2$CF$_3$)$_2$]$_2^+$ has also been prepared and characterized and is the most thermally stable of the imido derivatives of xenon.

More recently, the significant Lewis acidity of the XeF$^+$ cation, as seen from the propensity of XeF$^+$ to form fluorine bridges in the solid state, has been utilized to form species with Xe(II)-N bonds from the reaction of oxidatively resistant bases with the XeF$^+$ cation [equation (5.1)].
D: + XeF⁺ → D-XeF⁺  \hspace{1cm} (5.1)

Reactions of XeF⁺ with hydrogen cyanide,⁷²-⁷³ alkylnitriles,⁷² pentafluorobenzenenitrile,⁷² and perfluoroalkynitriles⁷¹,⁷² form the adduct cations RC≡N-Xe-F⁺. Perfluoropyridines⁷⁵ and s-trifluorotriazine⁷¹ likewise react with XeF⁺, resulting in cations in which xenon is bonded to a formally \( sp² \) hybridized nitrogen atom incorporated in the aromatic ring. With the exception of the adduct with s-trifluorotriazine, \( s\)-C₃F₇N₂N-XeF⁺,⁷¹ all of the adduct cations are only kinetically stable below room temperature.

More recently the krypton(II) adduct cations, HC≡N-KrF⁺⁷⁸ and \( R_F \)C≡N-KrF⁺ (\( R_F = CF₃, C₂F₅, n-C_3F₇ \))⁷¹ have also been characterized in this laboratory as the AsF₆⁻ salts, all of which are unstable above ca. -40 °C.

In the present paper the HF elimination reaction of XeF₂ with the novel ammonium salt \( F₅TeNH₃⁺AsF₆⁻ \) has been shown to result in the formation of the \( F₅TeN(H)\)-Xe⁺ cation, which represents the second example of xenon(II) bonded to a formally \( sp³ \) hybridized nitrogen. The first example, \( F₅SN(H)\)-Xe⁺, was formed by solvolysis of \( F₅S≡N\)-XeF⁺ in HF solvent.⁶ The salt, \( F₅TeN(H)\)-Xe⁺AsF₆⁻, has been characterized in the solid state by Raman spectroscopy and in solution by \( ^1H, ^{129}Xe, ^{125}Tc, ^{15}N, \) and \( ^{19}F \) NMR spectroscopy. Assignment of vibrational bands in the Raman spectra and elucidation of scalar couplings to nitrogen in the NMR spectra have been aided by preparation of \( ^{15}N \)-enriched (99.5 atom %) \( F₅TeN(H)\)-Xe⁺AsF₆⁻.
RESULTS AND DISCUSSION

(A) PREPARATION AND ISOLATION OF $F_5$TeN(H)-Xe$^{+}$AsF$_6^-$

The $F_5$TeN(H)-Xe$^{+}$ cation was prepared in solution by the reaction of stoichiometric amounts XeF$^+$AsF$_6^-$ and $F_5$TeNH$_2$ in anhydrous HF solvent with warming to -45 to -35 °C to effect reaction and dissolution. The base, $F_5$TeNH$_2$, was protonated in HF acidified with the strong Lewis fluoroacid, XeF$^+$AsF$_6^-$, according to equations (5.2) and (5.3). The ammonium cation $F_5$TeNH$_3^+$ underwent an HF elimination reaction with XeF$_2$, and produced the $F_5$TeN(H)-Xe$^{+}$ cation [equation (5.4)]. The salt, $F_5$TeNH$_3^+$AsF$_6^-$, which was prepared by reaction of $F_5$TeNH$_2$

$$\text{XeF}^+\text{AsF}_6^- + \text{HF} \rightarrow \text{XeF}_2 + \text{H}_2\text{F}^+\text{AsF}_6^-$$  \hspace{1cm} (5.2)

$$\text{F}_5\text{TeNH}_2 + \text{H}_2\text{F}^+\text{AsF}_6^- \rightarrow \text{F}_5\text{TeNH}_3^+\text{AsF}_6^- + \text{HF}$$  \hspace{1cm} (5.3)

$$\text{F}_5\text{TeNH}_3^+\text{AsF}_6^- + \text{XeF}_2 \rightarrow \text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^- + 2 \text{HF}$$  \hspace{1cm} (5.4)

with excess AsF$_5$ in HF solvent (Chapter 4), underwent an HF elimination reaction with XeF$_2$ according to equation (5.4) in both HF (-45 to -35 °C) and BrF$_5$ (-62 to -45 °C) solvents to give $F_5$TeN(H)-Xe$^{+}$AsF$_6^-$. The $F_5$TeNH$_3^+$ and $F_5$TeN(H)-Xe$^{+}$ cations were both observed in HF and BrF$_5$ solvents by $^1$H, $^{19}$F, $^{15}$N and $^{125}$Te NMR spectroscopy, which indicated that the HF elimination depicted in equation (5.4) was an equilibrium. The $F_5$TeN(H)-Xe$^{+}$ cation was completely decomposed after several hours in HF solution at -20 °C. Decomposition was rapid (ca. 1 minute) in HF solution at -1 °C and is discussed in Chapter 6.
A pale orange microcrystalline solid, which crystallized from anhydrous HF at -40 °C, was isolated by decanting the supernatant from the solid followed by pumping under vacuum for 20 h at -50 °C. The Raman spectrum of the solid (-165 °C) is consistent with $F_5\text{TeN(H)-Xe}^+\text{AsF}_5^-$ contaminated with $F_5\text{TeNH}_3^+\text{AsF}_5^-$, which arises according to equation (5.4), and $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$. The salt, $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$, is believed to result primarily from the reaction of $\text{XeF}_2$ and $\text{AsF}_5$ produced in the decomposition of $F_5\text{TeN(H)-Xe}^+\text{AsF}_6^-$ in HF solvent (see Chapter 6). The pale orange color of the solid, which is attributed to $F_5\text{TeN(H)-Xe}^+\text{AsF}_6^-$, decomposed rapidly at -30 °C.

The $F_5\text{TeN(H)-Xe}^+$ cation was also generated in $\text{SO}_2\text{ClIF}$ solution from the reaction of stoichiometric amounts of $F_5\text{TeNH}_3^+\text{As(OTeF}_5)_6^-$ and $\text{Xe(OTeF}_5)_2$ at -61 °C in an $\text{HOTeF}_5$ elimination reaction according to equation (5.5), which is directly analogous to the HF elimination reaction depicted in equation (5.4). The reagents were soluble down to -115 °C, because of the large size of the anion, resulting in low lattice energies for $F_5\text{TeN(H)-Xe}^+\text{As(OTeF}_5)_6^-$ and $F_5\text{TeNH}_3^+\text{As(OTeF}_5)_6^-$.

$$
F_5\text{TeNH}_3^+\text{As(OTeF}_5)_6^- + \text{Xe(OTeF}_5)_2 \rightleftharpoons F_5\text{TeN(H)-Xe}^+\text{As(OTeF}_5)_6^- + 2 \text{HOTeF}_5
$$

(B) CHARACTERIZATION OF NATURAL ABUNDANCE AND $^{15}$N-ENRICHED $F_5\text{TeN(H)-Xe}^+\text{AsF}_5^-$ by $^{129}\text{Xe}$, $^{125}\text{Te}$, $^{19}\text{F}$, $^{15}\text{N}$, AND $^1\text{H}$ NMR SPECTROSCOPY

Every element in the $F_5\text{TeN(H)-Xe}^+$ cation possesses at least one nuclide which is suitable for observation by NMR spectroscopy, namely, the spin-½ nuclei $^1\text{H}$, $^{15}\text{N}$, $^{125}\text{Te}$, $^{129}\text{Xe}$ and $^{19}\text{F}$, and the spin-1 nuclide $^{14}\text{N}$. The multinuclear magnetic resonance spectra in $\text{BrF}_5$ and HF solvents
for all five spin-1\textsubscript{2} nuclei are consistent with Structure 5.1 for the F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} cation in solution (see Table 5.1).

The $^{129}$Xe NMR spectra of natural abundance F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} consist of a broad singlet at -2840 ppm in HF solvent (-45.0 °C; Figure 5.1a) and at -2903 ppm in BrF\textsubscript{5} solvent (-48.3 °C). The absence of xenon-fluorine scalar coupling indicates that the Xe-F bond is ionized in solution [cf., XeF\textsubscript{2} (BrF\textsubscript{5} solvent, -52 °C): $^{1}J$(F-$^{129}$Xe) = 5621 Hz].\textsuperscript{71} The failure to observe the xenon-nitrogen scalar coupling is attributed to quadrupolar collapse resulting from fast relaxation of the $^{14}$N nucleus (I = 1). In prior studies of the imidodisulfurylfluoride derivatives of xenon(II), the low symmetry and resultant large electric field gradient (efg) at the $^{14}$N nucleus (I = 1) in the trigonal planar -N(SO\textsubscript{2}F\textsubscript{2})\textsubscript{2} group resulted in quadrupolar collapse of the xenon-nitrogen scalar couplings in FXeN(SO\textsubscript{2}F\textsubscript{2})\textsubscript{2}.\textsuperscript{57} XeN(SO\textsubscript{2}F\textsubscript{2})\textsubscript{2}+\textsuperscript{60} Xe[Na(SO\textsubscript{2}F\textsubscript{2})\textsubscript{2}]\textsubscript{2}.\textsuperscript{59} and F\textsubscript{2}XeN(SO\textsubscript{2}F\textsubscript{2})\textsubscript{2}+\textsuperscript{60} in SbF\textsubscript{5}, BrF\textsubscript{5}, and SO\textsubscript{2}ClF solvents. Nitrogen-15 enrichment (30%) facilitated the observation of the xenon-nitrogen scalar couplings. It was also necessary to prepare the $^{15}$N-enriched HC≡N-XeF\textsuperscript{+} cation to observe all possible scalar couplings.\textsuperscript{73} Similarly, the lone pair of electrons and the unsymmetrical geometry at the formally sp\textsuperscript{3}-hybridized nitrogen center in F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} results in a large efg at nitrogen, so that $^{14}$N undergoes rapid relaxation, which prevents the observation of scalar couplings to nitrogen. The Xe(II)-N scalar coupling, $^{1}J$(Xe-$^{15}$N), was observed on $^{15}$N-enrichment, confirming the xenon-nitrogen linkage.

The $^{129}$Xe NMR spectra of 99.5% $^{15}$N-enriched F\textsubscript{5}TeN(H)-Xe\textsuperscript{+}AsF\textsubscript{6}⁻ recorded at 11.7440 T consists of a doublet centered at -2840 ppm in HF solvent at -45.0 °C, $^{1}J$(Xe-$^{15}$N) = 138 Hz (Figure 5.1b), and at -2902 ppm in BrF\textsubscript{5} solvent at -45 °C, $^{1}J$(Xe-$^{15}$N) = 142 Hz. The magnitude of $^{1}J$(Xe-$^{15}$N) is comparable to directly bonded $^{129}$Xe-$^{15}$N scalar couplings of related xenon(II)-nitrogen bonded compounds such as (FO\textsubscript{2}S\textsubscript{2})\textsubscript{2}N-Xe\textsuperscript{+} (91.7 Hz)\textsuperscript{60} and
Xe F
\ N-Te-F^+
   \   \  \  
   \ F  F_F
   \_ F_F

5.1
Figure 5.1  
(a) $^{129}$Xe NMR spectrum (139.051 MHz) of natural abundance $F_2TeN(H)$-Xe$^+$AsF$_5^-$ in HF solvent (-45.0 °C) with an external magnetic field strength of 11.7440 T.

(b) $^{129}$Xe NMR spectrum (139.051 MHz) of 99.5% $^{15}$N-enriched $F_2TeN(H)$-Xe$^+$AsF$_5^-$ in HF solvent (-45.0 °C) with an external magnetic field strength of 11.7440 T.  
(c) $^{129}$Xe NMR spectrum (83.445 MHz) of 99.5% $^{15}$N-enriched $F_2TeN(H)$-Xe$^+$AsF$_5^-$ in HF solvent (-38.8 °C) with an external magnetic field strength of 7.0463 T.
Table 5.1

NMR Chemical Shifts and Spin-Spin Coupling Constants for the F$_3$TeN(H)-Xe$^+$ Cation.

<table>
<thead>
<tr>
<th>Chemical Shifts (ppm)$^a$</th>
<th>T. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^{(129\text{Xe})}$</td>
<td>-2841</td>
</tr>
<tr>
<td>(-2902)</td>
<td>-38.8</td>
</tr>
<tr>
<td>-2832$^b$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-45.0</td>
</tr>
<tr>
<td>$\delta^{(125\text{Te})}^c$</td>
<td>598</td>
</tr>
<tr>
<td></td>
<td>-61.2</td>
</tr>
<tr>
<td>$\delta^{(19\text{F})}^d$</td>
<td>-51.6 (-51.9) F$_{ax}$</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-31.2 (-44.0)</td>
</tr>
<tr>
<td>$\delta^{(15\text{N})}^c$</td>
<td>-268.0 (-266.3)</td>
</tr>
<tr>
<td></td>
<td>-40.0 (-45.0)</td>
</tr>
<tr>
<td>$\delta^{(1\text{H})}^c$</td>
<td>(6.90)</td>
</tr>
<tr>
<td></td>
<td>(-44.2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling Constants, Hz$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1J^{(129\text{Xe}-15\text{N})}$</td>
</tr>
<tr>
<td>$^1J^{(129\text{Xe}-1\text{H})}$</td>
</tr>
<tr>
<td>$^3J^{(129\text{Xe}-19\text{F}_{eq.})}$</td>
</tr>
<tr>
<td>$^1J^{(125\text{Te}-19\text{F}_{ax.})}$</td>
</tr>
<tr>
<td>$^1J^{(125\text{Te}-15\text{N})}$</td>
</tr>
<tr>
<td>$^1J^{(123\text{Te}-19\text{F}_{eq.})}$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>$^2J^{(129\text{Xe}-1\text{H})}$</td>
</tr>
<tr>
<td>$^2J^{(19\text{F}<em>{ax.}-19\text{F}</em>{eq.})}^d$</td>
</tr>
<tr>
<td>$^1J^{(125\text{Te}-19\text{F}_{ax.})}$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>$^1J^{(125\text{Te}-15\text{N})}$</td>
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<tr>
<td></td>
</tr>
</tbody>
</table>
Table 5.1 (continued)

a Samples were referenced externally at 30 °C with respect to the neat liquid references; XeOF₄ (¹²⁹Xe), (CH₃)₂Te (¹²⁵Te), CFCl₃ (¹⁹F), CH₃NO₂ (¹⁵N) and (CH₂)₄Si (¹H). A positive chemical shift denotes a resonance occurring to high frequency of the reference compound. The values in parentheses have been measured in BrF₅ solvent. All other values have been measured in HF solvent unless otherwise specified.

b Value obtained from the reaction of F₅TeNH₃+As(OTeF₃)₆⁻ and Xe(OTeF₃)₂ in SO₂ClF solvent.

c Obtained from a 99.5% ¹⁵N-enriched sample of F₅TeN(H)-Xe⁺AsF₆⁻.

d All ¹⁹F spectra in HF solvent displayed a broad saddle-shaped feature at ca. -68 ppm arising from the partially quadrupole collapsed ¹J(⁷⁵As-¹⁹F) of the octahedral AsF₆⁻ anion. In BrF₅ solvent, the resonance at ca. -68 ppm was completely quadrupole collapsed, resulting in a broad singlet. Values obtained from natural abundance samples of F₅TeN(H)-Xe⁺AsF₆⁻ in HF and BrF₅ solvents.
FO$_2$SN(H)-Xe$^+$ (107 Hz; see Chapter 8). The magnitude of the Xe-N scalar coupling is also discussed in Section (E) of this Chapter. Because of the large linewidth ($\Delta v_{1/2} = 80$ Hz) of each peak of the doublet, the long range couplings to xenon, namely, $^2J(^{129}$Xe-1H), $^2J(^{129}$Xe-125Te), $^3J(^{129}$Xe-19F$_{ax}$) and $^3J(^{129}$Xe-19F$_{eq}$), were not observed in the $^{129}$Xe NMR spectra of F$_3$Te$^{15}$N(H)-Xe$^+$ at 11.7440 T. The large linewidth presumably results from line broadening caused by shielding anisotropy (SA) relaxation of the $^{129}$Xe nucleus, which is field dependent and is significant for xenon. This is exemplified in the field dependence of the $^{129}$Xe linewidth for the 30% $^{15}$N-enriched (FO$_2$S)$_2$N-Xe$^+$ cation in SbF$_5$ solvent, which is proportional to the inverse of the spin-lattice relaxation time constant, $T_1$. At an external field strength of 5.8719 T, the linewidth of the $^{129}$Xe resonance for (FO$_2$S)$_2$N-Xe$^+$ was 139 Hz, and the $^{129}$Xe-15N scalar coupling was not resolved. However, at 2.3488 T, the linewidth was significantly reduced and the $^{129}$Xe-15N scalar coupling was resolved. The contribution to spin-lattice relaxation ($T_1$) arising from SA is inversely proportional to the square of the external magnetic field $B_o$ and is given by equation (5.6), where $\omega$ is the resonance frequency, $\gamma$ is the gyromagnetic ratio, $\tau_c$ is the molecular correlation time for isotropic tumbling in solution, and $\Delta \sigma$ refers to the anisotropy of the $^{129}$Xe shielding tensor. As $B_o$ increases, one can see that $T_1$ decreases. The relaxation rate ($1/T_1$) is therefore increased and the resonance line is broadened. As expected, the SA broadening of the $^{129}$Xe resonance for F$_3$TeN(H)-Xe$^+$ was significantly reduced at 7.0463 T in HF solvent at -38.8 $^\circ$C, as shown in Figure 5.1c. The $^{129}$Xe resonance is centered at $\delta(^{129}$Xe) = -2841.5 ppm and consists of a doublet of doublet of quintets. Figure 5.2b illustrates a resolution enhancement of
Figure 5.2  
(a) $^{129}$Xe NMR spectrum (83.445 MHz) of 99.5% $^{15}$N-enriched F$_2$TeN(H)-Xe$^+$AsF$_6^-$ in HF solvent (-38.8 °C) with an external magnetic field strength of 7.0463 T. (b) Resolution of $^{129}$Xe spectrum enhanced by application of a Gaussian function to the free induction decay before Fourier transformation.
the $^{129}\text{Xe}$ resonance obtained by the application of a Gaussian function to the free induction decay before Fourier transformation. The largest doublet splitting arises from $^1J(^{129}\text{Xe}-^{15}\text{N}) = 136$ Hz, which was the only resolved coupling in the $^{129}\text{Xe}$ NMR spectrum at 11.7440 T (Figure 5.1b). At 7.0463 T (Figure 5.2b), each line of the doublet is further split into a doublet arising from $^2J(^{129}\text{Xe}-^1\text{H}) = 24$ Hz. The quintet splitting arises from the scalar coupling of xenon with the four chemically equivalent equatorial fluorine atoms bonded to tellurium [$^3J(^{129}\text{Xe}-^{19}\text{F}_{\text{eq}}) = 6$ Hz]. The magnitude of $^3J(^{129}\text{Xe}-^{19}\text{F}_{\text{eq}})$ is smaller than that observed for the related $\text{F}_5\text{TeO-Xe}^+$ cation (18.5 Hz).$^{54} \text{F}_5\text{TeOXeF}$ (30 Hz)$^{141}$ and $\text{Xe(OTeF}_3)_2$ (31 Hz).$^{141}$ A coupling corresponding to $^2J(^{129}\text{Xe}-^{125}\text{Te})$ is not observed in the $^{129}\text{Xe}$ or the $^{125}\text{Te}$ NMR spectrum of $\text{F}_5\text{TeN(H)-Xe}^+$ (see below).

The scalar coupling of $^{129}\text{Xe}$ with the axial fluorine bonded to tellurium is not resolved. This coupling was also not resolved in the $^{129}\text{Xe}$ NMR spectra of $\text{F}_5\text{TeO-Xe}^+$, $^{54} \text{F}_5\text{TeO-XeF}$,$^{141}$ and $\text{Xe(OTeF}_3)_2$.$^{141}$ There is a potential ambiguity in the $^{129}\text{Xe}$ NMR spectrum of $\text{F}_5\text{TeN(H)-Xe}^+$ at 7.0463 T, since one could argue that the doublet splitting of 24 Hz assigned to $^2J(^{129}\text{Xe}-^1\text{H})$ may arise from $^3J(^{129}\text{Xe}-^{19}\text{F}_{\text{ax}})$ as opposed to $^2J(^{129}\text{Xe}-^1\text{H})$. However, the assignment of this coupling to $^2J(^{129}\text{Xe}-^1\text{H})$ was confirmed by an $^{129}\text{Xe}$,$^1\text{H}$ INEPT experiment,$^{252}$ with $^{129}\text{Xe}$ as the observed nucleus. In the $^1\text{H}$ pulse sequence, a fixed delay of (4J)$^{-1}$ was used in which $J$ is the magnitude of the coupling assigned to $^2J(^{129}\text{Xe}-^1\text{H})$. After completion of the INEPT experiment, the quintets of the $^{129}\text{Xe}$ resonance which are separated by $J$ Hz are out of phase (see Figure 5.3b). This indicates polarization transfer from $^1\text{H}$ to $^{129}\text{Xe}$ and confirms that the coupling of 24 Hz results from $^2J(^{129}\text{Xe}-^1\text{H})$ and not from $^3J(^{129}\text{Xe}-^{19}\text{F}_{\text{ax}})$.

The $^{15}\text{N}$ NMR spectrum of the 99.5 atom % $^{15}\text{N}$-enriched $\text{F}_5\text{TeN(H)-Xe}^+$ cation in HF solvent at -40 °C (Figure 5.4), consists of a doublet centered at -268.0 ppm, $^1J(^{15}\text{N}-^1\text{H}) = 62$ Hz. Satellite doublets are also observed, corresponding to $^1J(^{15}\text{N}-^{129}\text{Xe}) = 138$ Hz (natural abundance
Figure 5.3  
(a) $^{129}$Xe NMR spectrum (83.445 MHz) of 99.5% $^{15}$N-enriched $F_2TeN(H)$-$Xe^+$AsF$_6^-$ in HF solvent (-38.8 °C) with an external magnetic field strength of 7.0463 T. Resolution enhanced by Gaussian multiplication before Fourier transformation of the free induction decay.  
(b) $^{129}$Xe-1H INEPT of 99.5% $^{15}$N-enriched $F_2TeN(H)$-$Xe^+$AsF$_6^-$ in HF solvent at (-38.8 °C) with an external field strength of 7.0463 T. Resolution enhanced by applying a Gaussian function to the free induction decay before Fourier transformation.
Figure 5.4  $^{15}\text{N}$ NMR spectrum (50.698 MHz) of 99.5% $^{15}\text{N}$-enriched $\text{F}_2\text{TeN(H)-Xe'AsF}_6$ in HF solvent (-40.0 °C). Asterisks (*) denote $^{129}\text{Xe}$ satellites arising from $^{15}(^{15}\text{N},^{129}\text{Xe})$. The inner peak of each satellite doublet overlaps with a peak of the higher intensity doublet.
The inner peaks of each satellite doublet are coincident with the central doublet peaks and therefore are not observed. The scalar coupling $J^{15N-129Xe} = 138$ Hz was calculated by subtracting the $J^{15N-1H} = 62$ Hz from the frequency separation of the visible satellite peaks. A similar $15N$ NMR spectrum is observed in BrF$_5$ solvent at $-45^\circ$C centered at -266.3 ppm, $J^{15N-1H} = 62$ Hz, but because of insufficient signal-to-noise, the satellite peaks arising from $J^{15N-129Xe}$ were not observed. The $15N$ chemical shift is similar to those observed for the related $15N$ enriched compounds, FXeN(SO$_2$F)$_2$ (-247.9), $^{57}$ XeN(SO$_2$F)$_2$I (-232.5) and XeN(SO$_2$F)$_2^+$ (-243.0 ppm). $^{60}$ The $15N$ NMR resonance of the F$_5$TeN(H)-Xe$^+$ cation is significantly deshielded relative to the F$_5$TeNH$_3^+$ cation [$\delta^{15N} = -317.1$ ppm], which is present in samples containing the F$_5$TeN(H)-Xe$^+$ cation according to equation (5.4). The more deshielded $15N$ resonance observed for the F$_5$TeN(H)-Xe$^+$ cation is expected from examination of the factors contributing to the local paramagnetic shielding term for nitrogen, $\sigma_p^N$ [equation (5.7)]. $^{244}$ The greater inductive effect of the Xe$^+$ group is expected to increase the radial factor $\langle r^3 \rangle_{2p}$.

$$\sigma_p^N = -[\mu_B^2 \langle r^3 \rangle_{2p} \Sigma Q] / [2\pi(\Delta E)]$$  \hspace{1cm} (5.7)

lower the $\sigma^*$ LUMO relative to the nonbonding orbital on nitrogen, thus reducing $\Delta E$ for paramagnetic $n_N \rightarrow \sigma^*$ circulations, and increase $\Sigma Q$, the charge-imbalance term for the valence electrons of the nitrogen atom. All of these terms reinforce each other, thus contributing to an increase in the magnitude of $\sigma_p^N$, that deshields the nitrogen nucleus. In a comparison of HN(SO$_2$F)$_2$ and FXeN(SO$_2$F)$_2$, $^{57}$ the $^{15N}$ chemical shifts were observed to be almost the same (-249.2 and -250.4 ppm, respectively). Since inductive effects through the $\sigma$ framework predict a deshielding of FXeN(SO$_2$F)$_2$ relative to HN(SO$_2$F)$_2$, it was argued that since the nitrogen lone
pair of electrons is part of the π framework of the \(-\text{N(SO}_2\text{F)}_2\) group, \(\sigma_p^N\) is dominated by the deshielding of the nitrogen atom by the \(n_N \rightarrow \pi^*\) circulation of the nitrogen lone-pair electrons in \(\pi^*\) orbitals of the sulfur-nitrogen bonds. There is little influence from the inductive effects of XeF and H, which act primarily through the σ framework.\(^57\) In the present case, σ inductive effects appear to dominate. This is reasonable, since the absence of a free lone pair dictates that Te-N π-bonding is not possible for the \(\text{F}_5\text{TeNH}_3^+\) cation. It is possible that some degree of Te-N or Xe-N π-bonding contributes to the bonding in the \(\text{F}_5\text{TeN(H)}\)-Xe\(^+\) cation, which would deshield the nitrogen atom through \(n_N \rightarrow \pi^*\) circulations of the nitrogen atom lone-pair of electrons in \(\pi^*\) orbitals of the Te-N and Xe-N bonds. Evidence for Te-N π-bonding in \(\text{F}_5\text{TeNH}_2\) has been given in Chapter 4. Xenon-nitrogen π-bonding in the \(\text{F}_5\text{TeN(H)}\)-Xe\(^+\) cation is reasonable by analogy with the R-Xe\(^+\) cations (R = C\(_6\)F\(_5\),\(^95\)\(^99\) 2,4,6-F\(_3\)C\(_6\)H\(_2\),\(^98\) 2,6-F\(_2\)C\(_6\)H\(_3\),\(^253\) 2-FC\(_6\)H\(_4\),\(^253\) and 4-FC\(_6\)H\(_4\),\(^253\)), where the deshielding of the aryl fluorine \(^19\)F and aryl carbon \(^13\)C NMR resonances in the 2, 4 and 6 positions on the aryl ring was consistent with Xe-C π-bonding.\(^253\)

The \(^1\)H NMR spectrum of natural abundance \(\text{F}_5\text{TeN(H)}\)-Xe\(^+\) consists of a singlet at 6.90 ppm; no coupling to nitrogen is observed, as a result of the fast relaxation of the quadrupolar nitrogen nucleus (quadrupolar collapse), but a satellite doublet that arises from \(^2J(^1\text{H},^\text{125}\text{Te}) = 46\) Hz is observed (Figure 5.5a). The failure to observe the scalar coupling \(^2J(^1\text{H},^\text{129}\text{Xe})\) is attributed to SA broadening of the \(^{129}\text{Xe}\) satellites at the high field strength (11.7440 T) used to obtain the \(^1\)H NMR spectra. The one-bond proton-nitrogen coupling, \(^1J(^{15}\text{N},^1\text{H}) = 62\) Hz, is observed in the \(^1\)H NMR spectrum of the 99.5% \(^{15}\text{N}\)-enriched \(\text{F}_5\text{TeN(H)}\)-Xe\(^+\) cation in BrF\(_5\) solvent at -44.2 °C (Figure 5.5b). Satellite peaks arising from \(^2J(^1\text{H},^\text{125}\text{Te})\) are visible but not well resolved because of insufficient signal-to-noise.

The \(^{125}\text{Te}\) NMR spectrum of an equimolar mixture of 99.5% \(^{15}\text{N}\)-enriched \(\text{F}_5\text{TeNH}_2\) and
Figure 5.5 $^1$H NMR spectra (500.138 MHz) of (a) natural abundance (-55.5 °C) and (b) 99.5% $^{15}$N-enriched F$_2$TeN(H)-Xe*AsF$_6$ (-44.2 °C) in BrF$_5$ solvent. Asterisks (*) denote $^{125}$Te satellites arising from $^2J(^1$H-$^{125}$Te).
$\delta_{1H}$ (ppm from $(CH_3)_4Si)$
Figure 5.6  
(a) $^{125}$Te NMR spectrum (157.795 MHz) of equilibrium mixture resulting from the reaction of 99.5% $^{15}$N-enriched $\text{F}_2\text{TeNH}_3^\ast\text{AsF}_6^\ast$ and $\text{XeF}_2$ in HF solvent at -34.1 °C: (A) center of multiplet assigned to $\text{F}_2\text{TeNH}_3^\ast$, (B) center of multiplet assigned to $\text{F}_2\text{TeN(H)-Xe}^\ast$, (C) center of multiplet assigned to $\text{TeF}_6$. (b) $^{125}$Te NMR spectrum (157.795 MHz) of 99.5% $^{15}$N-enriched $\text{F}_2\text{TeN(H)-Xe}^\ast\text{AsF}_6^\ast$ in HF solvent at -34.1 °C; peaks labelled (A) are part of the multiplet assigned to $\text{F}_2\text{TeN(H)-Xe}^\ast$; an asterisk (*) denotes a peak of the $\text{TeF}_6$ multiplet; all other peaks arise from the $\text{F}_2\text{TeNH}_3^\ast$ multiplet. (c) Expansion of a portion of the $\text{F}_2\text{TeN(H)-Xe}^\ast$ multiplet; peaks labelled (A) and (B) arise from $\text{F}_2\text{TeNH}_3^\ast$ and $\text{TeF}_6$, respectively.
XeF\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} in HF solvent (-34.1 °C) is shown in Figure 5.6a. The \textsuperscript{15}N-enriched F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} cation is unambiguously assigned to the multiplet centered at 598 ppm, since the two other resonances, centered at 543 and 607 ppm, are attributable to TeF\textsubscript{6} and the \textsuperscript{15}N-enriched F\textsubscript{5}TeNH\textsubscript{3}\textsuperscript{+} cation (Chapter 4), respectively. The presence of the F\textsubscript{5}TeNH\textsubscript{3}\textsuperscript{+} cation in the \textsuperscript{125}Te spectrum is consistent with equation (5.4). A detailed analysis of the solution equilibria and decomposition of F\textsubscript{5}TeN(H)-Xe\textsuperscript{+}AsF\textsubscript{6} in HF and BrF\textsubscript{5} solvents will be discussed in Chapter 6. The \textsuperscript{125}Te NMR resonance of \textsuperscript{15}N-enriched F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} consists of a first order multiplet centered at 598 ppm (Figure 5.6b), and is consistent with Structure 5.1. The \textsuperscript{125}Te chemical shift is comparable to that observed for the isoelectronic F\textsubscript{5}TeO-Xe\textsuperscript{+} cation (576 ppm).\textsuperscript{54} The resonance is split into a quintet arising from \(J(\textsuperscript{125}Te-\textsuperscript{19}F_{\text{eq}}) = 3766 \text{ Hz}\). Referring to the expansion in Figure 5.6c, a doublet splitting arises from \(J(\textsuperscript{125}Te-\textsuperscript{19}F_{\text{ax}}) = 3578 \text{ Hz}\), and two further doublet splittings arise from \(J(\textsuperscript{125}Te-\textsuperscript{15}N) = 333 \text{ Hz}\) and \(J(\textsuperscript{125}Te-\textsuperscript{1}H) = 46 \text{ Hz}\). As expected, \(J(\textsuperscript{125}Te-\textsuperscript{129}Xe)\) is not observed, because of the relatively low receptivity of \textsuperscript{125}Te (2.24 x 10\textsuperscript{-3})\textsuperscript{254} and \textsuperscript{129}Xe (5.69 x 10\textsuperscript{-3})\textsuperscript{254} relative to \(\textsuperscript{1}H\), and the low concentration of \textsuperscript{15}N-enriched F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} in solution.

The \textsuperscript{19}F NMR spectrum of the F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} cation in HF solvent at -31.2 °C and in BrF\textsubscript{5} solvent at -44.0 °C each consist of a typical AX\textsubscript{4} pattern and the spectral parameters are listed in Table 5.1. The axial fluorine resonance is split into a quintet at -51.6 ppm in HF solvent (-51.9 ppm in BrF\textsubscript{5}) arising from the two-bond scalar coupling to the four chemically equivalent equatorial fluorine atoms bonded to tellurium [\(2J(\textsuperscript{19}F_{\text{ax}}-\textsuperscript{19}F_{\text{eq}}) = 166 \text{ Hz}\)]. The equatorial fluorine resonance is likewise split into a doublet centered at -43.4 ppm in HF (-43.2 ppm in BrF\textsubscript{5}). Of the four possible couplings to \textsuperscript{125}Te, only \(J(\textsuperscript{19}F_{\text{eq}}-\textsuperscript{125}Te) = 3767 \text{ Hz}\) (HF or BrF\textsubscript{5} solvent) is observed because of the low concentration of the F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} cation in solution. The observation of \(J(\textsuperscript{19}F_{\text{eq}}-\textsuperscript{125}Te)\) confirms that the AX\textsubscript{4} pattern arises from the F\textsubscript{5}TeN(H)-Xe\textsuperscript{+}
cation, since the same coupling is observed in the $^{125}$Te NMR spectrum of $F_5TeN(H)$-$Xe^+$ (see above). The scalar coupling, $^1J(^{19}F\text{eq},^{125}Te) = 3113$ Hz, is also resolved from satellite peaks which flank the $^{19}F\text{eq}$ resonance. Long range scalar couplings to $^{129}Xe$, $^1H$ and $^{15}N$ were not observed in the $^{19}F$ spectra of natural abundance or $99.5\%$ $^{15}N$-enriched $F_5TeN(H)$-$Xe^+$AsF$_6^-$ ions. A resonance attributable to the AsF$_6^-$ anion is observed at ca. -68 ppm in the $^{19}F$ spectra in HF solvent (-40 °C). The resonance is saddle-shaped ($\Delta v_{1/2} = 2588$ Hz) because of the partially quadrupole-collapsed scalar coupling $^1J(^{75}As,^{19}F)$. In BrF$_5$ (-60 °C) solvent a similar $^{19}F$ resonance is observed for the AsF$_6^-$ anion, without a saddle-shaped structure ($\Delta v_{1/2} = 617$ Hz).

Resonances arising from the $F_5TeNH_3^+$ cation are also observed in the $^{19}F$, $^{125}Te$, and $^1H$ NMR spectra in HF and BrF$_5$ solvents and are consistent with equation (5.4). In a sample that had initial XeF$_2$ and $F_5TeNH_3^+$AsF$_6^-$ concentrations of 0.38 and 0.36 M, respectively, in BrF$_5$ solution, the relative concentrations $[F_5TeNH_3^+] : [F_5TeN(H)-Xe^+]$ were determined to be 1.0 : 1.2 in the $^{19}F$ NMR spectrum recorded at -60 °C after warming the sample -40 °C for 10 minutes. In HF solvent at -33.3 °C, the same ratio was determined to be 1.0 : 0.3 with initial XeF$_2$AsF$_6^-$ and $F_5TeNH_2$ concentrations of 0.71 M. The lower relative amount of $F_5TeN(H)$-$Xe^+$ in HF solvent is reasonable since the presence of excess HF is expected to drive the HF elimination reaction depicted in equation (5.4) towards the starting materials. The observation of XeF$_2$ in the $^{19}F$ and $^{129}Xe$ spectra is also consistent with equation (5.4). The XeF$_2$ resonance in the $^{19}F$ NMR spectrum in BrF$_5$ solvent (-58 °C) is observed at -184.1 ppm [$^1J(^{19}F,^{129}Xe) = 5621$ Hz]. A doublet assignable to HF is observed at -192.8 ppm [$^1J(^{19}F,^1H) = 527$ Hz]. The observation of scalar couplings in the $^{19}F$ NMR spectrum indicate that XeF$_2$ and HF are not undergoing fast intermolecular exchange in BrF$_5$ solution at this temperature. In HF solvent at -41 °C, the $^{19}F$ NMR resonance of XeF$_2$ is observed at -199.7 ppm, similar to the value of
-199.6 ppm for pure XeF$_2$ in HF at -68 °C,$^{111}$ and is significantly broadened ($\Delta v_{1/2} = 386$ Hz). The presence of XeF$_2$ is consistent with solvolysis of XeF$^+$AsF$_6^-\cdot$ according to equation (5.2). The absence of peaks in the $^{19}$F NMR spectra assignable to F$_5$TeNH$_2$ (see Chapter 4) or XeF$^+$ indicated that the reactions represented by equations (5.2) and (5.3) went essentially to completion in HF solvent. The absence of solid material in the sample was also consistent with solvolysis of XeF$^+$AsF$_6^-\cdot$ represented by equation (5.2), since it was reported to be insoluble in HF at low temperatures.$^{111}$

(C) CHARACTERIZATION OF F$_5$TeN(H)-Xe$^+$As(OTeF$_3_2_\cdot$ IN SO$_2$ClF SOLVENT BY $^{129}$Xe AND $^{19}$F NMR SPECTROSCOPY

The reaction of equimolar amounts of the salt F$_5$TeNH$_2^+$As(OTeF$_3_2_\cdot$ and Xe(OTeF$_3_2$)$_2$ in SO$_2$ClF solvent at -61.2 °C resulted in a complex equilibrium mixture. The $^{129}$Xe NMR spectrum consisted of two singlets assignable to Xe(OTeF$_3_2$)$_2$ [$\delta^{129}$Xe = -2271 ppm; $\Delta v_{1/2} = 126$ Hz] and the F$_5$TeN(H)-Xe$^+$ cation [$\delta^{129}$Xe = -2832 ppm; $\Delta v_{1/2} = 61$ Hz]. No long range couplings, such as $^3J$(Xe-1F$_{ax}$), $^3J$(Xe-1F$_{eq}$), and $^2J$(Xe-1H), were resolved for either compound. In a sample having initial Xe(OTeF$_3_2$)$_2$ and F$_5$TeNH$_2^+$As(OTeF$_3_2$)$_2$ concentrations of 0.23 and 0.24 M, respectively, integration of the $^{129}$Xe NMR resonances indicates a ratio [Xe(OTeF$_3_2$)$_2$] : [F$_5$TeN(H)-Xe$^+$] of 1.7 : 1.0.

The $^{19}$F NMR spectrum (470.599 MHz) indicated rapid exchange of F$_5$TeO- and F$_5$TeN-groups at -61.2 °C, that prevented analysis of the spectrum. Cooling to -115.4 °C resulted in substantial slowing of the exchange on the $^{19}$F NMR time scale as shown in Figure 5.7. The doublet at $\delta^{(19)}$F = -30.73 ppm (A) and the quintet at $\delta^{(19)}$F = -52.57 ppm (K) are assigned to the equatorial and axial fluorine resonances of F$_5$TeNH$_2^+$, respectively [$^2J$(F$_{eq}$-1F$_{ax}$) = 163
\(^{19}\text{F NMR spectrum (470.599 MHz)}\) of the equilibrium mixture resulting from the reaction of \(\text{F}_5\text{TeNH}_3^+\text{As(OTeF}_5\text{)_6}\) and \(\text{Xe(OTeF}_2\text{)_2}\) recorded at -115.4 °C in \(\text{SO}_2\text{ClF}\) solvent: (A) equatorial fluorine atom peaks of \(\text{F}_5\text{TeNH}_3^+\), (a) \(^{125}\text{Te}\) satellites, (B) equatorial fluorine atom peaks of two unidentified \(\text{F}_5\text{Te}\)- groups, (b) \(^{125}\text{Te}\) satellites, (C) unidentified species, (D) equatorial fluorine atom peaks of \(\text{F}_5\text{TeN(H)-Xe}\), (E) equatorial fluorine atom peaks of \(\text{As(OTeF}_5\text{)_6}\), (F) second order \(\text{AB}_4\) spectrum of \(\text{As(OTeF}_5\text{)_6}\), (f) \(^{125}\text{Te}\) satellites, (G) equatorial fluorine atom peaks of \(\text{Xe(OTeF}_2\text{)_2}\), (H) equatorial fluorine atom peaks of \(\text{HOTeF}_3\), (b) \(^{125}\text{Te}\) satellites, (I) axial fluorine atom peaks of \(\text{As(OTeF}_5\text{)_6}\), (J) \(\text{TeF}_6\), (i) \(^{125}\text{Te}\) satellites, (K) axial fluorine atom peaks of \(\text{F}_5\text{TeNH}_3^+\).
Hz. Doublets at -38.55 (D), -38.65 (E), -45.48 (G) and -47.28 (H) ppm are assignable to the equatorial fluorines of $\text{F}_5\text{TeN(H)}\cdot\text{Xe}^+$, $\text{As(OTeF}_3)_5^{255}$ $\text{Xe(OTeF}_3)_2^{255}$ and $\text{HOTeF}_5^{255}$ respectively. The quintet at -48.02 ppm (I) is assigned to the axial fluorines of $\text{As(OTeF}_3)_5^{255}$ The axial fluorine resonances of $\text{HOTeF}_5$ (ca. -44.5 ppm)$^{255}$ and $\text{Xe(OTeF}_3)_2$ (ca. -41.5 ppm)$^{255}$ are obscured by the $\text{AB}_4$ pattern of $\text{As(OTeF}_3)_6^-$ at ca. -44 ppm$^{110}$ (F) and several unidentified exchange-broadened species in the region from -39 to -44 ppm. The singlet at -51.6 ppm (J) exhibiting $^{125}\text{Te}$ satellites (j) is assigned to $\text{TeF}_6$ and is expected to overlap with the low intensity resonance of the axial fluorine atom of $\text{F}_5\text{TeN(H)}\cdot\text{Xe}^+$ (ca. -52 ppm). The species present in solution are consistent with the $\text{HOTeF}_5$ elimination reaction represented by equation (5.5). The presence of $\text{As(OTeF}_3)_5$ is not attributed to dissociation of $\text{As(OTeF}_3)_6^-$ according to equation (5.8) since there is no evidence for $\text{OTeF}_5^-$ or the bridged species, $\text{H(OTeF}_3)_2^{203}$ resulting from the reaction of $\text{HOTeF}_5$ and the $\text{OTeF}_5^-$ anion [equation (5.9)] in the $^{19}\text{F}$ NMR spectrum. Dissociation of $\text{F}_5\text{TeNH}_3^+\text{As(OTeF}_3)_6^-$ according to equation (5.10) also does not occur since the

$$\text{As(OTeF}_3)_6^- \rightleftharpoons \text{OTeF}_5^- + \text{As(OTeF}_3)_5$$

(5.8)

$$\text{HOTeF}_5 + \text{OTeF}_5^- \rightleftharpoons [\text{F}_5\text{TeO} \cdots \text{H} \cdots \text{OTeF}_5]^+$$

(5.9)

$$\text{F}_5\text{TeNH}_3^+\text{As(OTeF}_3)_6^- \rightleftharpoons \text{F}_5\text{TeNH}_2 + \text{HOTeF}_5 + \text{As(OTeF}_3)_5$$

(5.10)

free base, $\text{F}_5\text{TeNH}_2$, was not observed in the $^{19}\text{F}$ NMR spectrum (see Chapter 4 for $^{19}\text{F}$ NMR parameters). This is consistent with the stability of $\text{N(CH}_3)_4^+\text{As(OTeF}_3)_6^-$ with respect to
dissociation to give \( \text{N(CH}_2\text{)}_4^+\text{OTeF}_5^- \) and \( \text{As(OTeF}_3\text{)}_5 \) in \( \text{SO}_2\text{ClIF} \) solvent at 30 °C.\(^{110}\) The presence of \( \text{As(OTeF}_3\text{)}_5 \) in the reaction mixture cannot be accounted for with the available data.

The two doublets at -33.67 \( \text{ppm} \left[ ^{2}J(\text{F}_{\text{ax}}\text{-F}_{\text{eq}}) = 178 \text{ Hz} \right] \) and -33.96 ppm \( \text{ppm} \left[ ^{2}J(\text{F}_{\text{ax}}\text{-F}_{\text{eq}}) = 178 \text{ Hz} \right] \) (B) exhibit \(^{125}\text{Te} \) satellites (b) and result from unidentifiable \( \text{F}_5\text{Tc} \) groups. The broad resonance at -24.5 ppm and the doublets centered at -32.86 and -36.18 ppm (C) are not assigned. Broad resonances at -2.8, -11.1, -13.5 and -22.2 ppm are also unidentified.

(D) **CHARACTERIZATION OF \( \text{F}_5\text{TcN(H)}_1\text{-Xe}^+\text{AsF}_6^- \) BY LOW-TEMPERATURE RAMAN SPECTROSCOPY**

The low-temperature Raman spectrum (-165 °C) of the pale orange microcrystalline solid isolated from the reaction of equimolar amounts of natural abundance \( \text{F}_5\text{TcNH}_3^+\text{AsF}_6^- \) with \( \text{XeF}_2 \) in anhydrous HF solvent is shown in Figure 5.8. The observed frequencies along with their assignments are listed in Table 5.2. The 99.5 atom % \(^{15}\text{N} \)-enriched salt was prepared in order to aid in the assignments of modes of vibration that involve the displacement of an \( \text{X-N} \) bond (\( \text{X} = \text{Tc, Xe} \)). The Raman frequencies for 99.5% \(^{15}\text{N} \)-enriched \( \text{F}_5\text{TcN(H)}_1\text{-Xe}^+\text{AsF}_6^- \) are also listed in Table 5.2, and regions of the Raman spectra of natural abundance and 99.5% \(^{15}\text{N} \)-enriched \( \text{F}_5\text{TcN(H)}_1\text{-Xe}^+\text{AsF}_6^- \) that exhibit \(^{14/15}\text{N} \) isotopic shifts are shown in Figure 5.9. The isotopic shifts, \( \Delta \nu(14/15\text{N}) \), are given as \( \nu(15\text{N}) - \nu(14\text{N}) \) where \( \nu \) is the observed Raman frequency.

The Raman spectra are consistent with the formation of \( \text{F}_5\text{TcN(H)}_1\text{-Xe}^+\text{AsF}_6^- \) in the solid state. Impurities present in the solid have been identified from the known Raman spectra as \( \text{F}_5\text{TcNH}_3^+\text{AsF}_6^- \) (see Chapter 4) and \( \text{Xe}_2\text{F}_3^+\text{AsF}_6^- \)\(^{176}\) which have been crystallized from the HF solution of \( \text{F}_5\text{TcN(H)}_1\text{-Xe}^+\text{AsF}_6^- \). Attempts to remove the contaminants by washing with HF or recrystallization resulted in thermal decomposition of the \( \text{F}_5\text{TcN(H)}_1\text{-Xe}^+ \) cation. A peak of low
Figure 5.8  Raman Spectrum of natural abundance F$_2$TeN(H)-Xe$^+$AsF$_6^-$, recorded at -165 °C with use of 514.5-nm excitation. Asterisks (*) denote FEP sample tube lines, a dagger (†) denotes an artifact characteristic of the Raman instrument; (A), Xe$_2$F$_3$+$^+$AsF$_6^-$; (B), F$_2$TeNH$_3$+$^+$AsF$_6^-$; (C), unidentified impurities or decomposition products.
Figure 5.9a

Raman spectra of natural abundance (lower trace) and 99.5% $^{15}$N-enriched (upper trace) $\text{F}_5\text{TeN(H)}$-$\text{Xe}^4\text{AsF}_6^-$ recorded at -165 °C by use of 514.5-nm excitation (200 - 800 cm$^{-1}$ region; asterisks (*) denote FRIP sample tube lines; (A) $\text{Xe}_2\text{F}_3^+\text{AsF}_6^-$, (B) $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$, (C) unidentified impurities or decomposition products.
Figure 5.9b  Raman spectra of natural abundance (lower trace) and 99.5\% {sup}{15}N-enriched (upper trace) \( \text{F}_2\text{TeN(H)-Xe}\text{AsF}_6^– \) recorded at -165 °C with use of 514.5-nm excitation (1200 - 1350 and 3100 - 3200 cm\(^{-1}\) regions); an asterisk (*) denotes an FEP sample tube lines.
intensity centered at 511 cm\(^{-1}\) and two peaks at 656.9 and 661.6 cm\(^{-1}\) (see Figures 5.8 and 5.9) have not been assigned and are attributed to minor impurities or decomposition products. The intensities of the peaks assigned to impurities, including Xe\(_2\)F\(_3\)\(^+\)AsF\(_6\)\(^-\) and F\(_2\)TeNH\(_3\)\(^+\)AsF\(_6\)\(^-\), varied from sample to sample relative to those of F\(_2\)TeN(H)-Xe\(^+\)AsF\(_6\)\(^-\).

The Raman spectrum of the F\(_2\)TeN(H)-Xe\(^+\) cation has been assigned by the assumption of sp\(^3\) hybridization at the nitrogen atom, and a staggered conformation of the N-Xe group with respect to the equatorial fluorine atoms of the F\(_2\)Te\(^-\) group, by analogy with the isoelectronic F\(_2\)TeO-Xe\(^+\) cation.\(^\footnote{54}\) The resulting \(C_1\) point symmetry is expected to give rise to \(3N - 6 = 21\) normal modes belonging to irreducible representations of symmetry species \(A\). All 21 modes are predicted to be infrared and Raman active, and since no modes are degenerate, 21 bands are expected in the Raman spectrum. However, 16 bands have been assigned to the F\(_2\)TeN(H)-Xe\(^+\) cation. In Table 5.2 the modes of the F\(_2\)TeN-Xe group of the F\(_2\)TeN(H)-Xe\(^+\) cation have been assigned with the assumption of \(C_2\) point symmetry, so that a direct comparison could be made with the modes of the F\(_2\)TeO-Xe\(^+\) cation,\(^\footnote{54}\) which are also listed in Table 5.2. The vibrations of the NH group have been assigned by analogy with similar molecules, without consideration of point symmetry.

Assignments for the F\(_2\)TeN(H)-Xe\(^+\) cation have been aided by comparison with the vibrational frequencies of F\(_2\)TeOCl,\(^\footnote{233}\) F\(_2\)TeOF,\(^\footnote{233}\) F\(_2\)TeO-Xe\(^+\)AsF\(_6\)\(^-\),\(^\footnote{54}\) F\(_2\)TeNH\(_3\)\(^+\)AsF\(_6\)\(^-\) (see Chapter 4) F\(_2\)NH\(^\footnote{256}\) and Cl\(_2\)NH.\(^\footnote{257}\) Assignments for the AsF\(_6\)\(^-\) anion have been made by comparison with those of XeF\(^+\)AsF\(_6\)\(^-\),\(^\footnote{73}\) HC\(_{15}\)NXC\(_{15}\)F\(^+\)AsF\(_6\)\(^-\),\(^\footnote{73}\) and O\(_2\)\(^+\)AsF\(_6\)\(^-\).\(^\footnote{159}\)

The band assigned to \(v(\text{NH})\) is observed at 3145.9 cm\(^{-1}\) and exhibits an \(^{14}\text{N}/^{15}\text{N}\) isotopic shift of -7.1 cm\(^{-1}\). The presence of one band in the NH stretching region is consistent with the vibrational spectra of secondary amines, R\(_2\)NH.\(^\footnote{250}\) The NH stretch is comparable to those
observed in the related compounds difluoramine, F$_2$NH (3193 cm$^{-1}$)\textsuperscript{256} and Cl$_2$NH (3279.0 cm$^{-1}$)\textsuperscript{257} although the anomalously high value for Cl$_2$NH likely arises from reduced intermolecular hydrogen bonding in the gas phase.\textsuperscript{258}

Although two NH bending modes are expected, only one is observed at 1270.8 cm$^{-1}$, exhibiting an $^{14}$/\textsuperscript{15}N isotopic frequency dependence [$\Delta \nu (^{14}/^{15}N) = -2.6$ cm$^{-1}$]. By comparison with F$_2$NH ($\delta$(NH) = 1307 (a"'), 1424 cm$^{-1}$ (a"'))\textsuperscript{256} and Cl$_2$NH ($\delta$(NH) = 1002 (a"'), 1295 cm$^{-1}$ (a"')),\textsuperscript{257} it is possible that a band arising from the second NH bending vibration overlaps with one of the relatively intense FEP bands at 1217, 1310, or 1385 cm$^{-1}$. Because of the larger masses of the groups attached to the nitrogen atom in the F$_5$TeN(H)-Xe$^+$ cation, it is also possible that the second NH bend occurs at lower frequency than in F$_2$NH and Cl$_2$NH, but is too low in intensity to be observed.

The band observed at 444.1 cm$^{-1}$ has been assigned to the asymmetric and symmetric (Te-N-Xe) stretching modes, because of the large isotopic shift [$\Delta \nu (^{14}/^{15}N) = -10.9$ cm$^{-1}$] and similar frequency to that observed in the related F$_5$TeO-Xe$^+$ cation (see Table 5.2). Although a band assigned to $\nu$(Te-N) is observed at 566.5 cm$^{-1}$ in the Raman spectrum of F$_5$TeNH$_3^+AsF_6^-$ (see Chapter 4), a shift to lower frequency is expected in F$_5$TeN(H)-Xe$^+$ because of the mass effect of xenon. The only intense band at lower frequency than 566.5 cm$^{-1}$ which has an $^{14}$/\textsuperscript{15}N isotopic dependence is at 444.1 cm$^{-1}$. The observation of only one band in this region indicates that $\nu$(Te-N) and $\nu$(Xe-N) are strongly coupled, as stated above. The bands in the Raman spectrum of F$_5$TeO-Xe$^+$AsF$_6^-$ assigned to $\nu_{\text{sym}}$(Xe-O-Te) [492 (16), 483 (14) cm$^{-1}$] and $\nu_{\text{asy}}$(Xe-O-Te) [476 sh, 470 (18) cm$^{-1}$] were close together in frequency, so it is possible by analogy that bands due to $\nu_{\text{asy}}$(Te-N-Xe) and $\nu_{\text{sym}}$(Xe-N-Te) are not resolved in the Raman spectrum of F$_5$TeN(H)-Xe$^+$AsF$_6^-$.
The known range of Xe-F stretching frequencies for compounds of xenon(II) containing the X-Xe-F linkage (X = F, N, O) is defined by XeF₂ [ν_{sym}(Xe-F) = 496 cm⁻¹],¹⁷⁵b which exhibits the most ionic Xe(II)-F bond, and XeF²⁺Sb₂F₁₁⁻ [ν(Xe-F) = 619 cm⁻¹],⁶⁸ where the terminal Xe-F bond is substantially more covalent, because of the weak basicity of Sb₂F₁₁⁻. Since the Xe-F stretching vibration involves a large polarizability change, the bands are usually the most intense in the Raman spectra. The absence of an intense band between 494 and 619 cm⁻¹ that could be assigned to ν(Xe-F) in the Raman spectrum of F₅TeN(H)-Xe⁺AsF₆⁻ is consistent with the absence of a covalent Xe-F bond.

By analogy with the AsF₆⁻ salts of F₅TeO-Xe⁺,⁵⁴ XeF⁺,⁶⁸ and KrF⁺,⁶⁹ it is possible that a fluorine-bridge interaction between the cation and anion in F₅TeN(H)-Xe⁺AsF₆⁻ exists (e.g., F₅TeN(H)-Xe⁺-F-AsF₅⁻). However, the band attributable to ν(Xe=⁻F) in the Raman spectra of F₅TeO-Xe⁺AsF₆⁻ (365 cm⁻¹),⁵⁴ XeF⁺AsF₆⁻ (339 cm⁻¹),⁶⁸ and α-KrF⁺AsF₆⁻ (328 cm⁻¹),⁶⁹ was usually more intense than the ν₄(AsF₆⁻) and ν₅(AsF₆⁻) modes which occurred in the same region. Such a band is not observed in the Raman spectrum of F₅TeN(H)-Xe⁺AsF₆⁻. Bands observed between 307 and 330 cm⁻¹ in the Raman spectrum of F₅TeN(H)Xe⁺AsF₆⁻ have been tentatively assigned to bending modes of the F₅Te⁻ group, although one of these bands might be assigned to ν(Xe=⁻F). The band assigned to ν(Xe=⁻F) in the Raman spectrum of F₅TeO-Xe⁺AsF₆⁻ is twice as intense as the F₅Te⁻ bending modes, allowing a distinction to be made between them. For F₅TeN(H)-Xe⁺AsF₆⁻, all modes in the F₅Te⁻ bending region are similar in intensity, and given the established regularity of these bending mode frequencies,²³³ none are assigned to ν(Xe=⁻F). The absence of a band in the 300 - 370 cm⁻¹ region which may be attributed to ν(Xe=⁻F), or alternatively, the reduced intensity of this band relative to that observed in the Raman spectrum of F₅TeO-Xe⁺AsF₆⁻, may be explained by comparing the bonding in the F₅TeO-Xe⁺ and
F₂TeN(H)-Xe⁺ cations. The lower electronegativity of F₂TeN(H)- than the F₂TeO- group [see Section (E) of this Chapter] is expected to result in a lower Lewis acidity for F₂TeN(H)-Xe⁺ than for F₂TeO-Xe⁺. As a result, the Xe−···F bridge bond in the former cation may be substantially more ionic than in the latter, if not completely ionic. The small polarizability change associated with the vibration of a predominantly ionic bond is expected to result in a low Raman intensity. Support for this statement was provided by George et al.,²⁵⁹ who calculated the Raman intensity for the first vibrational transition for a purely electrostatic linkage in Ti⁺OH⁻. Comparison with the vibrations of covalent linkages indicated that the Raman intensities from vibrations of purely electrostatic linkages are 10² to 10⁵ lower than those from covalent linkages.

Assignment of the band at 273.8 cm⁻¹ to δ(NTeF₂) was made by comparison to F₂TeNH₃⁺ (Chapter 4). This is confirmed by the ¹⁴/¹⁵N isotopic shift (±0.8 cm⁻¹) of the band. The in-plane (δ) and out-of-plane (τ) Te-N-Xe bends have been assigned to the bands at 201.6 and 186.8 cm⁻¹ by comparison with F₂TeO-Xe⁺AsF₆⁻ (see Table 5.2), but it was not possible to assign each of these bands to a particular mode.

The assignment of the modes of the F₂Te- group for F₂TeN(H)-Xe⁺ have been made by comparison with the Raman spectrum of F₂TeO-Xe⁺AsF₆⁻;²⁵⁴ with the assumption that the stretching and bending force constants of the F₂Te- moieties in F₂TeO-Xe⁺ and F₂TeN(H)-Xe⁺ are not significantly different. This assumption is true for compounds of the form F₂TeX, where X is an electronegative group such as Cl;²³³ F,²³³ OH,²²₀ OXe⁺,²⁵⁴ Comparison with F₂TeO⁻²⁰⁵ and F₂TeNH₂ (Chapter 4) is not possible since electron donation from the lone pairs on the oxygen and nitrogen atoms to the tellurium atom results in a significant decrease in the axial and equatorial Te-F bond force constants. All modes associated with the F₂Te- group have been assigned to bands in the Raman spectrum, except for the asymmetric out-of-plane bend,
\( \delta_{\text{sym}}(\text{TeF}_2) \). This mode correlates with \( \nu_6 \) (b\(_1\)) for compounds of the form \( \text{F}_2\text{TeX} \) (X = Cl,\(^{234}\) OH,\(^{220}\) OF,\(^{233}\) OCl\(^{233}\)) under \( C_{4v} \) point symmetry, and is not observed in the vibrational spectra of these compounds. A value of \( \nu_6 \) for \( \text{F}_2\text{TeCl} \) (199.1 cm\(^{-1}\)) was calculated from the force constants obtained by use of the Wilson F and G matrix method.\(^{234}\)

The bands assigned to the out-of-phase \( \nu_{\text{sym}}(\text{TeF}_2) \) (672.3 cm\(^{-1}\)) and the \( \nu_{\text{sym}}(\text{TeF}_2) \) breathing (653.8 cm\(^{-1}\)) modes exhibit large \(^{14/15}\)N isotopic shifts. This provides evidence for vibrational coupling of these modes and \( \nu(\text{Te-N}) \). This is likely since these vibrational modes all involve displacement of the tellurium atom, and under the true point symmetry of \( \text{F}_2\text{TeN(H)-Xe}^+ \) (\( C_1 \)), all modes belong to the same irreducible representation, \( A \), and all modes could in theory couple.

The octahedral \( \text{AsF}_6^- \) anion is expected to give rise to three Raman active bands under \( O_h \) symmetry, namely, \( \nu_1(a_{1g}) \), \( \nu_2(e_g) \) and \( \nu_5(t_{2g}) \). The presence of \( \text{F}_2\text{TeNH}_3^+\text{AsF}_6^- \) and \( \text{Xe}_2\text{F}_3^+\text{AsF}_6^- \) in the solid prevents a rigorous assignment of the anion bands of \( \text{F}_2\text{TeN(H)-Xe}^+\text{AsF}_6^- \). The amount of \( \text{F}_2\text{TeNH}_3^+\text{AsF}_6^- \) in the natural abundance sample is small, and only the band at 682.1 cm\(^{-1}\) [\( \nu_{\text{sym}}(\text{TeF}_2) \) labelled (B) in Figure 5.8], which is the most intense band in the Raman spectrum of \( \text{F}_2\text{TeNH}_3^+\text{AsF}_6^- \) (see Chapter 4), is assigned to this impurity. This band is also coincident with \( \nu_1(a_{1g}) \) of the \( \text{AsF}_6^- \) anions of all three species. Overlap of the \( \nu_2(e_g) \) and \( \nu_5(t_{2g}) \) \( \text{AsF}_6^- \) bands for \( \text{F}_2\text{TeN(H)-Xe}^+\text{AsF}_6^- \) and \( \text{Xe}_2\text{F}_3^+\text{AsF}_6^- \) is also expected. Bands at 686.6 and 690.8 cm\(^{-1}\) and at 397.3 and 401.5 cm\(^{-1}\) are assigned to the split \( \nu_3(t_{1u}) \) and \( \nu_4(t_{1u}) \) \( \text{AsF}_6^- \) modes. Since these bands are not observed in the Raman spectrum of \( \text{Xe}_2\text{F}_3^+\text{AsF}_6^- \),\(^{176}\) they must arise from \( \text{F}_2\text{TeN(H)-Xe}^+\text{AsF}_6^- \). The observation of \( \nu_3 \) and \( \nu_4 \) in the Raman spectrum indicates an \( \text{AsF}_6^- \) point symmetry which is lower than \( O_h \). A point symmetry of \( C_{4v} \), or lower would account for the Raman activity of the \( \nu_3 \) and \( \nu_4 \) modes, and lowering of the \( \text{AsF}_6^- \) point symmetry may
Table 5.2. Raman Frequencies and Assignments for $[^{14}\text{N}]\text{F}_5\text{TcN(H)}-\text{Xe}^+\text{AsF}_6^-$ and $[^{15}\text{N}]\text{F}_5\text{TcN(H)}-\text{Xe}^+\text{AsF}_6^-$, Compared to Those of $\text{F}_5\text{TcO-Xe}^+\text{AsF}_6^-$.  

<table>
<thead>
<tr>
<th>Frequency, cm$^{-1}$ $^a$</th>
<th>$[^{15}\text{N}]\text{F}_5\text{TcN(H)}-\text{Xe}^+\text{AsF}_6^-$</th>
<th>$[^{14}\text{N}]\text{F}_5\text{TcN(H)}-\text{Xe}^+\text{AsF}_6^-$</th>
<th>$\Delta\nu(^{14/15}\text{N})^c$</th>
<th>Frequency, cm$^{-1}$ $^b$</th>
<th>Assignment and Approx Mode Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3145.9 (6.2)</td>
<td>3138.8 (8.5)</td>
<td>-7.1</td>
<td></td>
<td>739 (6)</td>
<td>$v(\text{NH})$</td>
</tr>
<tr>
<td>1270.8 (4.3)</td>
<td>1268.2 (5.1)</td>
<td>-2.6</td>
<td></td>
<td>775 (20)</td>
<td>$\delta(\text{NH})$</td>
</tr>
<tr>
<td>750.1 (18.6)</td>
<td>751.0 (22.0)</td>
<td></td>
<td></td>
<td></td>
<td>$a''$, $v_{\text{asymp(TeF}_4\text{)}}$, asym to Te-X-Xe plane</td>
</tr>
<tr>
<td>719.6 (24.8)</td>
<td>719.3 (25.8)</td>
<td></td>
<td></td>
<td>713 (34)</td>
<td>$a'$, $v_{\text{sym(TeF}_4\text{)}}$, sym to Te-X-Xe plane</td>
</tr>
<tr>
<td>672.3 (90.1)</td>
<td>666.1 (100.0)</td>
<td>-6.2</td>
<td></td>
<td>663 (58)</td>
<td>$a''$, $v(\text{Te-F}_{\text{ax}})$</td>
</tr>
<tr>
<td>653.8 (100.0)</td>
<td>644.6 (67.2)</td>
<td>-9.2</td>
<td></td>
<td>668 (100)</td>
<td>$a'$, $v_{\text{sym(TeF}_4\text{)}}$ breathing</td>
</tr>
<tr>
<td>444.1 (85.7)</td>
<td>433.2 (76.1)</td>
<td>-10.9</td>
<td></td>
<td>492 (16)</td>
<td>$a'$, $v_{\text{sym(Xe-O-Tc)}}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>483 (14)</td>
<td></td>
</tr>
<tr>
<td>320.6 (9.6)</td>
<td>321.2 (20.1)</td>
<td></td>
<td></td>
<td>365 (15)</td>
<td>$v(\text{Xe}\cdots\text{F})$</td>
</tr>
<tr>
<td>316.7 (13.0)</td>
<td>318.1 (22.2)</td>
<td></td>
<td></td>
<td>333 (2)</td>
<td>$a''$, $\delta(\text{FTeF}_4\text{)}$, out of Te-X-Xe plane</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>320 (7)</td>
<td>$a'$, $\delta(\text{FTeF}_4\text{)}$,</td>
</tr>
<tr>
<td>Frequency (MHz)</td>
<td>Value (MHz)</td>
<td>Description</td>
<td></td>
<td></td>
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<td>----------------</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>329.8</td>
<td>330.4</td>
<td>in Te-X-Xe plane $a'$, $\delta_{sym}(TeF_4)$, out of $TeF_4$ plane $a''$, $\delta_{asym}(TeF_4)$, in Te-X-Xe plane $a''$, $\delta_{asym}(TeF_4)$,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>310.1</td>
<td>310.2</td>
<td>$a'$, $\delta_{sciss}(TeF_4)$, in Te-X-Xe plane $a''$, $\delta_{asym}(TeF_4)$, sym to Te-X-Xe plane $a''$, $\delta_{asym}(TeF_4)$, asym to Te-X-Xe plane $a''$, $\delta(XTeF_4)$, out of Te-X-Xe plane $a''$, $\delta(XTeF_4)$, in Te-X-Xe plane $a''$, $\tau(\text{Te-X-Xe})$ or $a''$, $\delta(\text{Te-X-Xe})$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>306.9</td>
<td>307.4</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>250.3</td>
<td>250.9</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>274.4</td>
<td>273.0</td>
<td>-1.4</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>201.6</td>
<td>202.4</td>
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<td>186.8</td>
<td>186.5</td>
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<tr>
<td>312</td>
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<td>295</td>
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</tr>
<tr>
<td>174</td>
<td>32</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Table 5.2 (continued)

aThe Raman data for F$_2$TeN(H)-Xe$^+$AsF$_6^-$ were obtained at -165 °C in an FEP sample tube by use of 514.5-nm excitation. The estimated precision of each value is ± 0.6 cm$^{-1}$. Although the point symmetry of the F$_2$TeN(H)-Xe$^+$ cation is C$_1$, assignments of modes have been made for the F$_2$Te-N-Xe group under C$_5$ symmetry to allow direct comparison with the modes of the F$_2$TeO-Xe$^+$ cation [see reference (54)]. The modes of the NH group are assigned by analogy with similar molecules, without consideration of molecular point symmetry. bRaman data for F$_2$TeO-Xe$^+$AsF$_6^-$ were recorded at -196 °C in a glass sample tube at -196 °C by use of 514.5-nm excitation [reference (54)]. Low frequency lattice or bending modes reported in reference (54) have been omitted from the present table. cIsotopic shifts $\Delta \nu^{(14/15N)} = \nu^{(15N)} - \nu^{(14N)}$, where the frequencies of the bands $\nu$ are given in cm$^{-1}$. Isotopic shifts less than the estimated error are not considered to be significant.
Table 5.3 Raman Frequencies and Assignments for AsF₆⁻, Compared to Those of XeF⁺AsF₆⁻ and HC≡NXeF⁺AsF₆⁻

<table>
<thead>
<tr>
<th></th>
<th>frequency, cm⁻¹</th>
<th>assignt and approx mode description</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂TeN(H)-Xe⁺AsF₆⁻&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>690.8 (20.3)</td>
<td>735 (20)</td>
<td>t₁ᵤ, v₃</td>
<td>a&quot;</td>
</tr>
<tr>
<td>686.6 (25.0)</td>
<td>730 (5)</td>
<td></td>
<td>a'</td>
</tr>
<tr>
<td></td>
<td>723 (13)</td>
<td></td>
<td>a'</td>
</tr>
<tr>
<td></td>
<td>707 (2)</td>
<td></td>
<td>a'</td>
</tr>
<tr>
<td></td>
<td>693 (11)</td>
<td></td>
<td>a'</td>
</tr>
<tr>
<td>682.1 (68.0)</td>
<td>681 (56)</td>
<td>a₁g, v₁</td>
<td>a'</td>
</tr>
<tr>
<td>573.7 sh</td>
<td>582 (12)</td>
<td>e₉, v₂</td>
<td>a'</td>
</tr>
<tr>
<td>570.6 sh</td>
<td>577 (5)</td>
<td></td>
<td>a'</td>
</tr>
<tr>
<td>543.2 (6.6)</td>
<td>465 (3)</td>
<td>v(As···F)</td>
<td>a'</td>
</tr>
<tr>
<td>401.5 (10.5)</td>
<td>421 (11)</td>
<td>t₁ᵤ, v₄</td>
<td>a'</td>
</tr>
<tr>
<td></td>
<td>419 (&lt;1)</td>
<td></td>
<td>a&quot;</td>
</tr>
<tr>
<td></td>
<td>415 (1)</td>
<td></td>
<td>a&quot;</td>
</tr>
<tr>
<td>397.3 (4.1)</td>
<td>406 (1)</td>
<td></td>
<td>a'</td>
</tr>
<tr>
<td></td>
<td>401 (2)</td>
<td></td>
<td>a&quot;</td>
</tr>
<tr>
<td></td>
<td>386 (14)</td>
<td>t₂g, v₅</td>
<td>a'</td>
</tr>
<tr>
<td>363.2 sh</td>
<td>378 (5)</td>
<td></td>
<td>a&quot;</td>
</tr>
<tr>
<td>366.5 (20.3)</td>
<td>370 (10)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Observation in this work.
<sup>b</sup> From previous work.
369.6 sh

244 (1)

$t_{1u}, v_6$

$a''$

$a'$

$a''$

$a''$

113.9 (6.7)

104.7 (2.8)

83.4 (3.6)

68.9 (3.6)

56.0 (10.3)

41.4 (5.1)

lattice modes and/or
hydrogen bonding modes

$^a$This work; Raman spectrum obtained at -165 °C in an FEP sample tube by use of 514.5-nm excitation. The estimated precision of each value is ± 0.6 cm$^{-1}$. The Raman intensities and multiplicities of $v_1$, $v_2$, and $v_5$ are affected by the presence of Xe$_2$F$_3$ AsF$_6^-$ (reference (176)) and F$_5$TeNH$_3$ AsF$_6^-$ (Chapter 4) and do not reflect those of pure F$_5$TeN(H)-Xe$^+$AsF$_6^-$.

$^b$Raman spectra recorded at -196 °C by use of 514.5-nm excitation [see reference (73)].

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arise from a low crystallographic site symmetry. Confirmation of this statement would require a crystal structure of the pure compound.

Although it is not possible to assess the site symmetry from the Raman data, the bands of the AsF$_6^-$ anion have been assigned to modes under $C_s$ point symmetry by correlating the representations of $O_h$ with $C_s$ (Table 5.10). The assignments for AsF$_6^-$ must remain tentative since the bands assigned to $v_1$ ($a_{1g}$), $v_2$ ($e_g$) and $v_5$ ($e_g$) overlap with those of Xe$_2$F$_3^+$AsF$_6^-$. A similarity of modes is observed upon comparison of F$_5$TeN(H)-Xe$^+$AsF$_6^-$ with XeF$^+$AsF$_6^-$ and HC=NXeF$^+$AsF$_6^-$. Although two bands are reported for $v_2(e_g)$ under $O_h$ symmetry in the Raman spectrum of F$_5$TeN(H)-Xe$^+$AsF$_6^-$, further bands may be obscured by the FEP sample tube band at 579 cm$^{-1}$. A band assignable to a derivative of $v_6(t_{1u})$ under $O_h$ symmetry is not observed.

(E) Nature of the Bonding in the F$_5$TeN(H)-Xe$^+$ Cation

Previous NMR studies of xenon(II) derivatives containing Xe-F groups bonded to oxygen or fluorine atoms have shown that the NMR parameters measured in $^{19}$F and $^{129}$Xe spectra could be used to assess the relative covalent characters of the Xe-O, Xe-···F bridge, and Xe-F terminal bonds.$^{103,104,108}$ Schrobilgen$^{26}$ recently extended this work to include derivatives with xenon(II)-nitrogen bonds. In general, as the covalent character of the Xe-L (L = ligand atom) bond increases, the terminal Xe-F bond becomes more ionic, decreasing the formal charge on xenon. These trends are paralleled by increased shielding of the $^{129}$Xe resonance, a decrease in the magnitude of $J(^{129}$Xe-$^{19}$F), and increased $^{19}$F chemical shifts for the terminal Xe-F group. The $^{129}$Xe chemical shift is therefore a powerful tool for estimating the relative covalent characters of the Xe-L bond for a series of xenon(II) compounds, and is used to assess qualitatively the bonding in F$_5$TeN(H)-Xe$^+$ in the following discussion. Table 5.3 lists the $^{129}$Xe chemical shifts and
reduced scalar couplings $^1K({\text{Xe-N}})$ for a number of compounds containing xenon(II)-nitrogen bonds. NMR data for the XeF$_3^+$ cation in SbF$_5$ solvent are included for comparison since the $^{129}$Xe chemical shift and $^1J(^{129}$Xe-$^{19}$F) are representative of uncoordinated XeF$_3^+$, because of the very weak basicity of SbF$_5$ solvent and the polymeric Sb$_n$F$_{5n+1}^-$ anion in solution. The compounds are listed approximately in order of increasing Xe-N bond covalent character. The HCN$\equiv$N-XeF$_3^+$ and F$_3$S$\equiv$N-XeF$_3^+$ cations have the most ionic Xe-N bonds in Table 5.3. This is apparent from the $^{129}$Xe NMR resonances, which are deshielded relative to the other compounds containing Xe(II)-N bonds. As also shown in Table 5.3, the $^{129}$Xe resonances become increasingly shielded as the s-character of the nitrogen valence hybrid orbitals decreases. This is consistent with decreasing electronegativity of the ligand group,$^{105}$ resulting in a more covalent Xe-N bond. Thus the highly shielded $^{129}$Xe NMR resonance indicates that the F$_3$TeN(H)-Xe$^+$ cation, with formal $sp^3$ hybridization at the nitrogen atom, has one of the most covalent Xe-N bonds known and that the Xe-N bond covalent characters of the F$_3$TeN(H)-Xe$^+$ and F$_3$SN(H)-Xe$^+$ cations are similar. Examination of Table 5.3 reveals that the magnitude of $^1K({\text{Xe-N}})$ decreases as the % s-character of the nitrogen valence orbitals decreases. This is predicted by the Fermi contact mechanism which is usually the dominant mechanism for scalar couplings that involve heavy nuclei.$^{260}$ In a formalism developed by Pople and Santry,$^{242}$ the Fermi contact mechanism is proportional to the product of the valence s-electron densities at the coupled nuclei, so that decreased s-character in the nitrogen valence hybrid orbitals on moving down Table 5.3 predicts a decrease in the magnitude of $^1K({\text{Xe-N}})$. A scalar coupling model which assumes dominance of the Fermi contact term for Xe(II)-N bonds has been used to assess the hybridization at nitrogen in the HCN$\equiv$N-XeF$_3^+$ cation. This was achieved by comparing the magnitude of the Xe-N scalar coupling with that in (PO$_2$S)$_2$N-XeF, which was shown to contain a formally $sp^2$-hybridized nitrogen center from the
short S-N bond lengths [1.628(3) and 1.623(3) Å] and trigonal planar geometry at nitrogen by X-ray crystallography.\textsuperscript{57} The use of the xenon-nitrogen scalar coupling to determine the hybridization at the nitrogen atom assumes that the s-electron density at the xenon atom is approximately the same in HCN=\text{XeF}^+ and (FO\textsubscript{2}S)\textsubscript{2}=N-XeF. The successful prediction of sp hybridization at the nitrogen atom in HCN=\text{XeF}^+ indicated that this assumption was valid. In attempting to evaluate the hybridization at the nitrogen atom in F\textsubscript{3}TeN(H)-Xe\textsuperscript{+} cation, a species which could be assumed to have a similar s-electron density at xenon is the (FO\textsubscript{2}S)\textsubscript{2}=N-Xe\textsuperscript{+} cation. The crystallographically determined trigonal planar geometry and short S-N bond lengths [1.68(1) and 1.70(1) Å] for the (FO\textsubscript{2}S)\textsubscript{2}=N-Xe\textsuperscript{+} cation indicated formal sp\textsuperscript{2} hybridization at the nitrogen atom.\textsuperscript{60} Thus, with the assumption that the Xe-N scalar coupling is dominated by the Fermi contact term, it should be possible to estimate the hybridization at the nitrogen atom in F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} with use of the values of \textsuperscript{1}K(Xe-N), but problems arise in this treatment. If the hybridization of the nitrogen atom is sp\textsuperscript{3} in F\textsubscript{5}TeN(H)-Xe\textsuperscript{+}, one would expect a lower value of \textsuperscript{1}K(Xe-N) than in (FO\textsubscript{2}S)\textsubscript{2}=N-Xe\textsuperscript{+}, which is opposite to the observed values. Resonance Structures 5.4 and 5.5 indicate the potential for N \rightarrow Te \pi-donation in F\textsubscript{5}TeN(H)-Xe\textsuperscript{+}, which was established for F\textsubscript{5}TeNH\textsubscript{2} in Chapter 4, and may increase the nitrogen valence s-character in the Xe-N bond. However, it is unlikely that the nitrogen atom is formally sp\textsuperscript{2}-hybridized, since a normal coordinate analysis of the related OTeF\textsubscript{5} anion\textsuperscript{206} indicated that the Te-O bond is intermediate between a single and a double bond. Therefore a formal nitrogen atom hybridization which is intermediate between sp\textsuperscript{2} and sp\textsuperscript{3} may be closer to reality. It is likely that S-N \pi-bonding in (FO\textsubscript{2}S)\textsubscript{2}=N-Xe\textsuperscript{+} surpasses the degree of Te-N \pi-bonding in F\textsubscript{3}TeN(H)-Xe\textsuperscript{+}, given the planarity of the nitrogen center in the former cation, and the short S-N bond lengths (see above). Thus it is not possible to use X-N \pi-bonding (X = S, Te) to rationalize the magnitudes of \textsuperscript{1}K(Xe-N). An alternative approach, which
also assumes dominance of the Fermi contact term, is derived from a study of $^1J(^{15}\text{N},^1\text{H})$ in nitrogen-15 enriched main group compounds of the form $\text{XNH}_2$ and $\text{X}_2\text{NH}$, by Cowley and Schweiger, which relied on the so-called isovalent hybridization hypothesis. This hypothesis, applied to nitrogen, states that the nitrogen atom valence $s$-character concentrates in the bonds directed toward electropositive substituents. It was observed that in most cases $^1J(^{15}\text{N},^1\text{H})$ increases as the electronegativity of X increases for $\text{XNH}_2$ and $\text{X}_2\text{NH}$ compounds. Since it is clear from the $^{129}\text{Xe}$ chemical shifts of $(\text{FO}_2\text{S})_2\text{N-Xe}^+$ and $\text{F}_5\text{TeN(H)}\cdot\text{Xe}^+$ that the $(\text{FO}_2\text{S})_2\text{N}$-group is more electronegative than the $\text{F}_5\text{TeN(H)}$-group, the isovalent hypothesis predicts greater valence $s$-character in the Xe-N bond of $(\text{FO}_2\text{S})_2\text{N-Xe}^+$. It follows that this model also incorrectly predicts a greater value of $^1K\text{(Xe-N)}$ in $(\text{FO}_2\text{S})_2\text{N-Xe}^+$. The failure to predict the relative magnitudes of $^1K\text{(Xe-N)}$, by solely considering the contribution of the Fermi contact term to the scalar coupling, indicates that the dipolar or orbital contributions to the xenon-nitrogen scalar coupling may be important. Although the Fermi contact term is expected to be the largest contributor to the Xe-N scalar coupling, it may be similar for the $\text{F}_5\text{TeN(H)}\cdot\text{Xe}^+$ and $(\text{FO}_2\text{S})_2\text{N-Xe}^+$ cations. The presence of Xe-N $\pi$ bonding in the $\text{F}_5\text{TeN(H)}\cdot\text{Xe}^+$ and $(\text{FO}_2\text{S})_2\text{N-Xe}^+$ cations, which is represented by resonance Structures (5.3) and (8.11), respectively, may give rise to a significant orbital contribution, $K_{AB}^2$. Factors contributing to the magnitude of $K_{AB}^2$ are described in equation (5.11), which uses an average energy approximation in an LCAO

$$K_{AB}^2 = \mu_o(\mu_B)^2<\mathbf{r}_A^{-3}>_p<\mathbf{r}_B^{-3}>_p(\Delta \mathcal{E})^{-1}$$

$$x \left[ 2(P_\sigma^2 + P_\pi^2 + P_\pi^2) + 3(P_\sigma P_\pi + P_\sigma P_\pi + P_\pi P_\pi) \right]$$  \hspace{1cm} (5.11)
framework. The terms $\mu_\sigma$ and $\mu_\pi$ are the permittivity of a vacuum and the Bohr magneton, respectively, $<r^{-3}_A>\_p$ and $<r^{-3}_B>\_p$ are the inverse cube radial distributions of the valence $p$ orbitals for the coupled nuclei, $\Delta E$ is the average excitation energy, and $P_\sigma$, $P_\pi$ and $P_\pi'$ are the $\sigma$ and $\pi$ bond orders for the bonding between nuclei A and B. In comparing $F_2TeN(H)$-$Xe^+$ and $(FO_2S)_2N$-$Xe^+$, an argument for a greater $Xe-N$ $\pi$-bonding contribution in the former could be made, which in turn rationalizes the relative magnitudes of $^1\chi(Xe-N)$. The greater electronegativity of $(FO_2S)_2N$- than $F_2TeN(H)$- is expected to result in a greater $Xe-N$ $\pi$-bonding contribution in the $F_2TeN(H)$-$Xe^+$ cation. A larger $Xe-N$ $\pi$-bonding contribution in $F_2TeN(H)$-$Xe^+$ is expected to result in larger values of $P_\pi$ and $P_\pi'$ in equation (5.11), thus increasing $^1\chi(Xe-N)$ relative to $(FO_2S)_2N$-$Xe^+$. The possibility of $Xe(II)$-$N$ $\pi$-bonding is proposed by analogy with the xenon(II)-carbon bonded cations $R$-$Xe^+$ ($R = fluorophenyl$).

The absence of detectable amounts of the neutral compound $F_2TeN(H)$-$XeF$ in BrF$_5$, SO$_2$ClF and HF solvents is consistent with the NMR parameters for the series of compounds, shown in Table 5.3. As mentioned at the beginning of this Section, increasing covalent character of the $Xe-L$ bond ($L = N, F, O$ ligand atom) results in increasing $Xe-F$ bond ionic character. This is seen in the magnitude of $^1\chi(^{129}Xe-^{19}F)$, which decreases as the $Xe-F$ bond ionic character increases on moving down Table 5.3, towards increasing $Xe-L$ bond covalent character. The cations $F_2TeN(H)$-$Xe^+$, $F_2SN(H)$-$Xe^+$, $FO_2SN(H)$-$Xe^+$ and $F_2S=N$-$Xe^+$ form a series whose $^{129}Xe$ resonances are significantly shielded relative to all other known compounds containing $Xe(II)$-$N$ bonds. This shielding indicates that these $Xe(II)$-$N$ bonds are highly covalent. In agreement with the $^{129}Xe$ and $^{19}F$ NMR trends discussed at the beginning of this section, the $Xe-F$ bonds are completely ionized in solution as a result of the covalent character of the $Xe-N$ bonds.

The relationship of $Xe-F$ bond ionization in compounds of the form $L$-$Xe-F$ and
electronegativity of the ligand L is made explicit by a comparison of \( \text{F}_5\text{TeO-Xe-F} \) and the \( \text{F}_5\text{TeN(H)-Xe}^+ \) cation, since \( \text{F}_5\text{TeO-} \) and \( \text{F}_5\text{TeN(H)-} \) are isoelectronic. Structures 5.6 and 5.7 are the canonical forms that describe the relative ionic characters of the Xe-O and Xe-F bonds in the known compound, \( \text{F}_5\text{TeO-XeF} \), and the analogous canonical forms of the hypothetical neutral compound, \( \text{F}_5\text{TeN(H)-Xe-F} \), are shown in Structures 5.8 and 5.9. The significant Xe-F bond

\[
\text{F}_5\text{TeO-Xe}^+ \text{ F} \quad \longleftrightarrow \quad \text{F}_5\text{TeO}^- \text{ Xe-F}^+
\]

5.6

5.7

\[
\text{F}_5\text{TeN(H)-Xe}^+ \text{ F} \quad \longleftrightarrow \quad \text{F}_5\text{TeN(H)}^- \text{ Xe-F}^+
\]

5.8

5.9

covalent character in \( \text{F}_5\text{TeO-Xe-F} \) is reflected in the \(^{129}\text{Xe} \) NMR chemical shift, -2051 ppm, which is similar to that for XeF\(_2\) -1913 ppm in the same solvent and at the same temperature (SO\(_2\)ClF, 26 °C).\(^{181}\) The scalar coupling \( J(^{129}\text{Xe}-^{19}\text{F}) \) for \( \text{F}_5\text{TeO-XeF} \) is 5743 Hz, which is 122 Hz larger than the corresponding value for XeF\(_2\) (5621 Hz).\(^{181}\) The NMR data are consistent with a greater weighting of Structure of 5.7 over 5.6, and reflects the greater electronegativity of F than F\(_5\)TeO-.\(^{181}\) However, the F\(_5\)TeO- group is sufficiently electronegative that the F\(_5\)TeO-Xe\(^+\) cation has significant Lewis acid character. This is reflected in the fact that ionization of the Xe-F bond of F\(_5\)TeO-XeF required the use of the strong Lewis acids AsF\(_5\) or SbF\(_5\) to form F\(_5\)TeO-Xe\(^+\)AsF\(_6^-\)\(^{54}\) and F\(_5\)TeO-Xe\(^+\)Sb\(_2\)F\(^{11-}\).\(^{54}\) The significant Lewis acid strength of the F\(_5\)TeO-Xe\(^+\) cation was also evident from the presence of a band that was attributed to a covalent fluorine bridge interaction
between the cation and anion in the Raman spectrum of solid $\text{F}_5\text{TeO-Xe}^+\text{AsF}_6^-$.

The Lewis acid strength of the $\text{F}_5\text{TeO-Xe}^+$ cation is also reflected in the formation of the Lewis acid-base adducts $\text{B-Xe-OTeF}_5$ ($\text{B} = \text{C}_3\text{F}_3\text{N}_2$, $\text{C}_3\text{F}_3\text{N}_2\text{N}$, $\text{CH}_3\text{C}=\text{N}$) upon reaction of $\text{F}_5\text{TeO-Xe}^+\text{As(OTeF}_3)_6^-$ with the appropriate nitrogen base in $\text{SO}_2\text{ClIF}$ solvent.

The ionization of the Xe-F bond of the hypothetical neutral compound $\text{F}_5\text{TeN(H)-XeF}$ in HF, $\text{BrF}_3$ and $\text{SO}_2\text{ClIF}$ solution indicates that resonance Structure 5.8 contributes essentially 100% to the bonding. The Lewis acidity of $\text{F}_5\text{TeN(H)-Xe}^+$ is expected to be low relative to $\text{F}_5\text{TeO-Xe}^+$, resulting from the lower electronegativity of $\text{F}_5\text{TeN(H)-}$ than $\text{F}_5\text{TeO-}$. The relative electronegativities of these ligands is reflected in the acid characters of $\text{F}_5\text{TeNH}_2$ and $\text{F}_5\text{TeOH}$. The former is basic, being quantitatively protonated in HF (see Chapter 4). The latter, $\text{F}_5\text{TeOH}$, is a strong acid, having an acidity lying between those of $\text{HNO}_3$ and $\text{HCl}$, and there is no evidence of protonation of $\text{F}_5\text{TeOH}$ in HF acidified with $\text{AsF}_5$. Further evidence for the low Lewis acid strength of $\text{F}_5\text{TeN(H)-Xe}^+$ is indicated by the absence of a band that could be attributed to the Xe—F bridge stretch in the Raman spectrum of solid $\text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^-$.

The instability of $\text{F}_5\text{TeN(H)-XeF}$ relative to $\text{F}_5\text{TeN(H)-Xe}^+$ is evident from unsuccessful attempts to isolate the neutral compound $\text{F}_5\text{TeN(H)-XeF}$ from the reaction of $\text{F}_5\text{TeNH}_2$ or $\text{F}_5\text{TeN(H)-Si(CH}_3)_3$ with $\text{XeF}_2$ in $\text{SO}_2\text{ClIF}$ solvent according to equation (5.12). No reaction was observed on warming the samples to 0 °C ($\text{R} = \text{H}$) and -12 °C ($\text{R} = \text{Si(CH}_3)_3$), well above the temperature at which $\text{F}_5\text{TeNH}_3^+\text{AsF}_6^-$ and $\text{XeF}_2$ reacted to give the $\text{F}_5\text{TeN(H)-Xe}^+$ cation.

$$\text{F}_5\text{TeN(H)-R + XeF}_2 \rightarrow \text{F}_5\text{TeN(H)-XeF} + \text{RF} \quad (5.12)$$

$[\text{R} = \text{H, (CH}_3)_3\text{Si}]$
Table 5.4 Comparison of $^{129}\text{Xe}$ NMR Chemical Shifts, $^{1}K(\text{Xe-N})$ and $^{1}J(^{129}\text{Xe}-^{19}\text{F})$ for Some Xenon(II) Compounds.$^a$

<table>
<thead>
<tr>
<th>Species</th>
<th>$\delta(^{129}\text{Xe})$, (ppm)</th>
<th>Hybridization at Nitrogen</th>
<th>$^{1}J(^{129}\text{Xe}-^{19}\text{F})$, Hz</th>
<th>$^{1}K(\text{Xe-N})$, (10$^{22}$ NA$^{-2}$m$^{-3}$)</th>
<th>T (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF$^+\cdots$FSb$<em>2$F$</em>{10}^-$</td>
<td>-574</td>
<td></td>
<td>7594</td>
<td></td>
<td>25</td>
<td>108</td>
</tr>
<tr>
<td>HC$_2$N-XeF$^+$AsF$_6^-$</td>
<td>-1555 (-1570)</td>
<td>$sp$</td>
<td>6181</td>
<td>1.381$^b$</td>
<td>-10 (-58)</td>
<td>73</td>
</tr>
<tr>
<td>F$_3$S=NC-N-XeF$^+$AsF$_6^-$</td>
<td>-1661</td>
<td>$sp$</td>
<td>6248</td>
<td>1.435</td>
<td>-60</td>
<td>26</td>
</tr>
<tr>
<td>s-C$_3$F$_3$N$_2$N-XeF$^+$AsF$_6^-$</td>
<td>-1808 (-1863)</td>
<td>$sp^2$</td>
<td>5932</td>
<td>1.013</td>
<td>-5 (-50)</td>
<td>71</td>
</tr>
<tr>
<td>C$_3$F$_3$N-XeF$^+$AsF$_6^-$</td>
<td>-1872 (-1922)</td>
<td>$sp^2$</td>
<td>5926</td>
<td>0.983</td>
<td>-30 (-30)</td>
<td>75</td>
</tr>
<tr>
<td>(FO$_2$S)$_2$N-XeF$^+$</td>
<td>-2009</td>
<td>$sp^2$</td>
<td>5586</td>
<td>0.913$^b$</td>
<td>-40</td>
<td>59</td>
</tr>
<tr>
<td>XeF$_2$</td>
<td>-1685</td>
<td></td>
<td>5621</td>
<td></td>
<td>-52</td>
<td>71</td>
</tr>
<tr>
<td>(FO$_2$S)$_2$N-Xe$^+$Sb$<em>n$F$</em>{5n+1}^+$</td>
<td>-1943</td>
<td>$sp^2$</td>
<td></td>
<td>0.272$^b$</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>FO$_2$SN(H)-Xe$^+$AsF$_6^-$</td>
<td>-2616 (-2660)</td>
<td>$sp^2$ or $sp^3$</td>
<td></td>
<td>0.322$^b$</td>
<td>-61</td>
<td>e</td>
</tr>
<tr>
<td>F$_4$S=N-Xe$^+$AsF$_6^-$</td>
<td>-2672</td>
<td>$sp^2$</td>
<td></td>
<td></td>
<td>-20</td>
<td>26</td>
</tr>
<tr>
<td>F$_5$TeN(H)-Xe$^+$AsF$_6^-$</td>
<td>-2840 (-2902)</td>
<td>$sp^3$</td>
<td></td>
<td>0.401$^b$</td>
<td>-45</td>
<td>This work</td>
</tr>
<tr>
<td>F$_5$SN(H)-Xe$^+$AsF$_6^-$</td>
<td>-2886</td>
<td>$sp^3$</td>
<td></td>
<td></td>
<td>-20</td>
<td>26</td>
</tr>
</tbody>
</table>

$^a$ Referenced work.
$^{129}$Xe NMR parameters, unless otherwise indicated, were determined in HF and in BrF$_5$ (in parentheses) solvent. $^b$ Recorded for the $^{15}$N enriched cation. $^c$ Measured in SO$_2$ClIF solvent. $^d$ Measured in SbF$_5$ solvent. $^e$ Chapter 8 of this work.
CHAPTER 6

STUDY OF THE DECOMPOSITION OF \( \text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^- \)

AND

CHARACTERIZATION AND DECOMPOSITION OF \( \text{F}_5\text{TeNF}_2 \) IN SOLUTION

INTRODUCTION

As discussed in Chapter 5, the \( \text{F}_5\text{TeN(H)-Xe}^+\) cation was generated as the \( \text{AsF}_6^- \) salt from the reaction of \( \text{XeF}^+\text{AsF}_6^- \) and \( \text{F}_5\text{TeNH}_2 \) in HF solvent or from the reaction of \( \text{XeF}_2 \) and \( \text{F}_5\text{TeNH}_3^+\text{AsF}_6^- \) in HF or \( \text{BrF}_5 \) solvents. The salt, \( \text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^- \), was isolated from HF solvent at -40 °C, and the Raman spectrum at -165 °C indicated the presence of \( \text{F}_5\text{TeNH}_3^+\text{AsF}_6^- \) and \( \text{Xe}_2\text{F}_3^+\text{AsF}_6^- \). It was not possible to isolate \( \text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^- \) as a pure material for two reasons: (1) \( \text{F}_5\text{TeN(H)-Xe}^+ \) is in equilibrium with \( \text{XeF}_2 \) and \( \text{F}_5\text{TeNH}_3^+ \) in HF solvent [see equation (5.4)], and small amounts of \( \text{F}_5\text{TeNH}_3^+\text{AsF}_6^- \) crystallized with \( \text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^- \); (2) \( \text{F}_5\text{TeN(H)-Xe}^+ \) decomposes slowly at the temperatures which also maximized the yield of \( \text{F}_5\text{TeN(H)-Xe}^+ \) in solution. The presence of \( \text{Xe}_2\text{F}_3^+\text{AsF}_6^- \) can be traced to the decomposition of \( \text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^- \) in HF solvent. In the present Chapter, the composition of the HF solution from which \( \text{F}_5\text{TeN(H)-Xe}^+\text{AsF}_6^- \) was isolated and the decomposition of \( \text{F}_5\text{TeN(H)-Xe}^+ \) in HF solvent were primarily investigated by \( ^{19}\text{F} \) NMR spectroscopy.

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RESULTS AND DISCUSSION

(A) ¹⁹F NMR SPECTROSCOPIC STUDY OF THE DECOMPOSITION OF F₅TeN(H)-Xe⁺AsF₆⁻ IN HF SOLVENT

The formation and decomposition of F₅TeN(H)-Xe⁺AsF₆⁻ in HF solvent which resulted from the reaction of equimolar amounts of XeF⁺AsF₆⁻ and F₅TeNH₂ was followed by ¹⁹F NMR spectroscopy in the range of -40.9 to -1.2 °C.

Figure 6.1 shows the ¹⁹F NMR spectrum at -40.9 °C of an equimolar mixture of XeF⁺AsF₆⁻ and F₅TeNH₂ in HF solvent, which was previously warmed to -35 °C for five minutes, which resulted a pale yellow solution, before it was placed in the NMR probe. Integration of the NMR resonances indicated that the ratio F₅TeNH₃⁺ : F₅TeN(H)-Xe⁺ : TeF₆ was 1.00 : 0.03 : 0.06. A trace of the primary decomposition product, F₅TeNF₂, prepared for the first time, was also observed. A singlet assigned to HF solvent was observed at δ(¹⁹F) = -195.0 ppm (Δν₁/₂ = 47 Hz). A singlet at δ(¹⁹F) = -199.8 ppm assigned to XeF₂ was also observed (Δν₁/₂ = 386 Hz) on the low frequency shoulder of the solvent resonance; the high-frequency ¹²⁹Xe satellite was not observed because of overlap with the HF resonance. Although the initial reactants were XeF⁺AsF₆⁻ and F₅TeNH₂, the absence of a pale yellow precipitate indicative of XeF⁺AsF₆⁻ or Xe₂F₃⁺AsF₆⁻, which are both sparingly soluble in HF at low temperature, and the presence of a resonance assigned to XeF₂ indicated that solvolysis of XeF⁺AsF₆⁻ occurred according to equation (5.2). This was also confirmed by the absence of a ¹⁹F NMR resonance attributable to F₅TeNH₂ (see Figure 4.11).

The sample was then warmed to -33.3 °C, and after ca. one hour, an intense yellow solution and a pale yellow precipitate resulted. As shown in Figure 6.2, the amount of F₅TeN(H)-Xe⁺ increased relative to F₅TeNH₃⁺. The formation of F₅TeN(H)-Xe⁺ was accompanied by
Figure 6.1: ¹⁹F NMR spectrum (499.599 MHz) of the fluorine-on-tellurium(VI) region of an equimolar mixture of natural abundance F₅TeNH₂ and XeF⁺AsF₆⁻ in HF solvent, warmed to -35 °C for 5 minutes before accumulating at -40.9 °C; (A) equatorial fluorine resonance of F₅TeNH₃⁺, (a) and (a') ¹²⁵Te and ¹²³Te satellites, respectively, (B) overlapping resonances of TeF₆ and axial fluorine of F₅TeNH₃⁺, (b) ¹²⁵Te satellites, (C) equatorial fluorine resonance of F₅TeN(H)-Xe⁺, (D) axial fluorine resonance of F₅TeN(H)-Xe⁺, (E) equatorial fluorine-on-tellurium resonance of F₅TeNF₂. The broad saddle-shaped resonance at ca. -68 ppm results from AsF₆⁻.
Figure 6.2  $^{19}$F NMR spectrum (499.599 MHz) of the fluorine-on-tellurium region of an equimolar mixture of natural abundance $F_5TeNH_2$ and XeF$^+$AsF$_6^-$ in HF solvent, after 1 hour at -33.3 °C before accumulating the spectrum at the same temperature; (A) equatorial fluorine resonance of $F_5TeNH_3^+$, (a) and (a') $^{125}$Te and $^{123}$Te satellites, respectively, (B) axial fluorine resonance of $F_5TeNH_3^+$, (C) equatorial fluorine resonance of $F_5TeN(H)-Xe^+$, (c) and (c') $^{125}$Te and $^{123}$Te satellites, respectively, (D) axial fluorine resonance of $F_5TeN(H)-Xe^+$, (E) equatorial fluorine-on-tellurium resonance of $F_5TeNF_2$, (F) TeF$_6$, (f) $^{125}$Te satellites. The broad saddle-shaped resonance at ca. -68 ppm arises from AsF$_6^-$.
decomposition, as evidenced by the increased amounts of \( \text{F}_2\text{TeNF}_2 \) and \( \text{TeF}_6 \). From integration of the \(^{19}\text{F} \) NMR resonances, the ratio \( \text{F}_2\text{TeNH}_3^+ : \text{F}_2\text{TeN(H)}-\text{Xe}^+ : \text{F}_2\text{TeNF}_2 : \text{TeF}_6 \) was found to be 1.00 : 0.26 : 0.02 : 0.28.

The decomposition of \( \text{F}_2\text{TeN(H)}-\text{Xe}^+\text{AsF}_6^- \) to give \( \text{F}_2\text{TeNF}_2 \) is consistent with nucleophilic fluorination of \( \text{F}_2\text{TeN(H)}-\text{Xe}^+ \) with liberation of xenon gas, which was observed in the \(^{129}\text{Xe} \) NMR spectrum at \( \delta(^{129}\text{Xe}) = -5306 \) ppm (HF solvent; -37.0 °C). Atomic xenon can be envisaged as a very good leaving group, producing a transient divalent nitrenium ion [equation (6.1)]. Nucleophilic attack of the nitrenium ion by a fluoride ion donor, \( \text{M}^-\text{F}^- \), is expected to result in the monofluoramine, \( \text{F}_2\text{TeN(H)}-\text{F} \) [equation (6.2)]. Likely fluoride ion donors are HF solvent

\[
\text{F}_2\text{TeN(H)}-\text{Xe}^+\text{M}^-\text{F}^- \longrightarrow \text{F}_2\text{TeN(H)}^+\text{M}^-\text{F}^- + \text{Xe} \tag{6.1}
\]

\[
(\text{M} = \text{H}^+, \text{AsF}_5^-)
\]

\[
\text{F}_2\text{TeN(H)}^+\text{M}^-\text{F}^- \longrightarrow \text{F}_2\text{TeN(H)}^-\text{F}^- + \text{M} \tag{6.2}
\]

\[
(\text{M} = \text{H}^+, \text{AsF}_5^-)
\]

or \( \text{AsF}_6^- \). The mode of decomposition of \( \text{F}_2\text{TeN(H)}-\text{Xe}^+\text{AsF}_6^- \) is similar to that observed for salts of the phenylxenon(II) cations, \( \text{R-Xe}^+ \) (\( \text{R} = \text{C}_6\text{F}_5^-, \text{C}_6\text{F}_4\text{CF}_3 \), \( m-\text{CF}_3\text{C}_6\text{H}_{11} \), and \( p-\text{CF}_3\text{C}_6\text{H}_{11} \)) which contain xenon(II) bonded to a carbon of the aromatic ring. The reaction of \( \text{[C}_6\text{F}_5^-\text{Xe}]^+[(\text{C}_6\text{F}_5)_2\text{BF}_2]^+ \) with the nucleophiles \( \text{X}^- \) (\( \text{X} = \text{Br}, \text{I} \)) lead to the formation of halogenopentafluorobenzenes, \( \text{C}_6\text{F}_5\text{X} \), and interaction of \( \text{[C}_6\text{F}_5^-\text{Xe}]^+[(\text{C}_6\text{F}_5\text{BF}_3)]^- \) with \( \text{C}_6\text{F}_5\text{X} \) and \( (p-\text{CF}_3\text{C}_6\text{H}_4)_3\text{P} \) resulted in the formation of \( \text{[(C}_6\text{F}_5)_2\text{X}]^+[(\text{C}_6\text{F}_5\text{BF}_3)]^- \) and \( \text{C}_6\text{F}_5(p-\text{CF}_3\text{C}_6\text{H}_4)_3\text{P}^+[(\text{C}_6\text{F}_5\text{BF}_3)]^- \), respectively. Reaction of \( \text{[C}_6\text{F}_5^-\text{Xe}]^+[(\text{C}_6\text{F}_5)_2\text{BF}_2]^+ \) with species
containing acidic C-H protons, such as (C₆H₅)CH₂CN, (C₆H₅)₃CH and C₆H₅CF₃ resulted in replacement of an acid proton by the C₆F₅ group.²⁶³ Naumann and Tyrrell²⁶⁵ also prepared [(C₆F₅)₃Te]⁺[B(C₆F₅)₃F]⁻ and [(C₆F₅)₂I]⁺[B(C₆F₅)₃F]⁻ from the reaction of Te(C₆F₅)₂ and C₆F₅I with [C₆F₅Xe⁺][B(C₆F₅)₃F]⁻. All of these reactions are consistent with the generation of electrophilic "C₆F₅⁺⁺" and atomic xenon, and nucleophiles present in the system react with the aryl cation.

Although F₅TeN(H)-F is expected to be the primary product resulting from the nucleophilic fluorination of F₅TeN(H)-Xe⁺, the observed product is F₅TeNF₂. This may be explained by considering the effect of the decomposition of F₅TeN(H)-Xe⁺ on the fluoroacidity of the medium. It is clearly seen that fluoride donation from AsF₆⁻ will increase the fluoroacidity of the solution by generating AsF₅. If the HF solvent is the primary fluoride donor towards F₅TeN(H)-Xe⁺, H₂F⁺ is formally generated, which will also increase the fluoroacidity of the medium through equilibrium (6.3). Increased fluoroacidity of the medium generates cationic xenon(II) species [equations (6.4) and (6.5)], which are substantially stronger oxidative fluorinators

\[
H₂F⁺ + AsF₆⁻ \rightleftharpoons 2 HF + AsF₅ \tag{6.3}
\]

\[
AsF₅ + XeF₂ \rightleftharpoons XeF⁺AsF₆⁻ \tag{6.4}
\]

\[
XeF⁺AsF₆⁻ + XeF₂ \rightleftharpoons Xe₂F₅⁺AsF₆⁻ \tag{6.5}
\]

than XeF₂,⁷⁹ which is present in the system according to equilibrium (5.1). The generation of cationic xenon(II) species was indicated by the precipitation of pale yellow crystals, which were
shown to be $\text{XeF}_2^+\text{AsF}_6^-$ by comparing the crystallographically determined unit cell parameters of a single crystal with the previously published data.$^{265}$ The salt $\text{XeF}_2^+\text{AsF}_6^-$ was also observed as an impurity in the Raman spectrum of solid $\text{F}_5\text{TeN(H)}\cdot\text{Xe}^+\text{AsF}_6^+$ (Chapter 5). The cationic xenon(II) species present in solution are assumed to rapidly oxidize $\text{F}_5\text{TeN(H)}\cdot\text{F}$ to $\text{F}_5\text{TeN(H)}\text{F}_2^+$ [equation (6.6)], and the electron withdrawing effect of the three highly electronegative ligands is expected to result in deprotonation of $\text{F}_5\text{TeN(H)}\text{F}_2^+$ [equation (6.7)], by analogy with $\text{NF}_3$.\textsuperscript{173}

$\text{F}_5\text{TeN(H)}\cdot\text{F} + \text{XeF}^+\text{AsF}_6^- \rightarrow \text{F}_5\text{TeN(H)}\text{F}_2^+\text{AsF}_6^- + \text{Xe}$ \hspace{1cm} (6.6)

$\text{F}_5\text{TeN(H)}\text{F}_2^+\text{AsF}_6^- + \text{HF} \rightarrow \text{F}_5\text{TeNF}_2 + \text{H}_2\text{F}^+\text{AsF}_6^-$ \hspace{1cm} (6.7)

which is too weakly basic to be protonated in HF / SbF$_5$ solution. In Equation (6.4), the XeF$^+$ cation is formally behaving as an "F$^+$" donor. Similar behavior has been observed in the reaction of XeF$^+\text{MF}_6$ (M = As, Sb) with the sulfur (IV) species CF$_3$S(O)F, which results in the formation of CF$_3$S(O)F$_2^+\text{MF}_6$.\textsuperscript{85} Sulfur (II) species such as the disulfane CF$_3$SSCF$_3$\textsuperscript{80} are also oxidized by XeF$^+\text{MF}_6^-$ to give CF$_3$SS(F)CF$_3^+\text{MF}_6^-$.\textsuperscript{80}

The possibility that $\text{F}_5\text{TeNF}_2$ might arise from the reaction of HF with $\text{F}_5\text{TeNH}_2$ was investigated by observing the $^{19}$F and $^1$H NMR spectra of $\text{F}_5\text{TeNH}_2$ in HF solvent at -33.3 °C. The $^{19}$F NMR spectrum indicated the presence of $\text{F}_5\text{TeNH}_3^+$ and TeF$_6$; integration of the $^{19}$F NMR resonances indicated that the ratio $\text{F}_5\text{TeNH}_3^+$ : TeF$_6$ was 1.00 : 0.08. In the $^1$H NMR spectrum, a 1 : 1 : 1 triplet at $\delta$(H) = 5.67 ppm\textsuperscript{173} [$^1J(^1H-^{14}N) = 54 \text{ Hz}$\textsuperscript{244}] indicated the presence of NH$_4^+$. These observations are consistent with the slow displacement of NH$_4^+$ from $\text{F}_5\text{TeNH}_3^+$ by HF solvent at -33.3 °C [equation (6.8)], and that $\text{F}_5\text{TeNF}_2$ arises solely from the
oxidative fluorination of $\text{F}_5\text{TeN(H)}$-$\text{Xe}^+$-$\text{AsF}_6^-$.

$$\text{F}_5\text{TeN}_2^+\text{AsF}_6^- + \text{HF} \longrightarrow \text{TeF}_6 + \text{NH}_2^+\text{AsF}_6^- \quad (6.8)$$

(B) **RELATIONSHIP OF THE BONDING AND THE MODE OF DECOMPOSITION OF $\text{F}_5\text{TeN(H)}$-$\text{Xe}^+$ IN SOLUTION**

The similar decomposition modes of $\text{F}_5\text{TeN(H)}$-$\text{Xe}^+$ and the phenylxenon(II) cations, $\text{R}$-$\text{Xe}^+$ ($\text{R} =$ fluorinated phenyl group), are unique for compounds of xenon(II). Previous studies on compounds containing $\text{Xe(II)}$-$\text{N}$ and $\text{Xe(II)}$-$\text{O}$ bonds have indicated radical decomposition mechanisms as shown in equations (6.9) and (6.10). The radicals $\text{L}^-$ may dimerize or undergo further reactions. Detailed studies have indicated radical mechanisms for the decompositions of

$$\text{XeL}_2 \longrightarrow \text{Xe} + 2 \text{L}^- \quad (6.9)$$

$$\text{F-Xe-L} \longrightarrow \text{XeF}_2 + \text{Xe} + 2 \text{L}^- \quad (6.10)$$

$\text{Xe[NS}_2\text{CF}_3\text{]}_2$, $\text{Xe[NS}_2\text{F}_2\text{]}_2$, F$\text{Xe(NS}_2\text{F)}_2$, $\text{Xe[OP(O)]F}_2$,$^\text{43}$ $\text{FxeOP(O)F}_2$,$^\text{43}$ $\text{Xe[OS}_2\text{F}_2\text{]}_2$, $^{28}$ F$\text{XeOSO}_2\text{F}$,$^\text{28}$ $\text{Xe[OTeF}_3\text{]}_2$, $^{142}$ $\text{Xe[OScF}_5\text{]}_2$, $^{142}$ F$\text{XeOTeF}_5$, $^{41}$ F$\text{XeOC(O)CF}_3$,$^{39,41}$ and $\text{Xe[OC(O)CF}_3\text{]}_2$. $^{28,39,41}$ The radical decomposition of the neutral xenon(II) derivatives $\text{XeL}_2$ and F$\text{Xe-L}$ mentioned above are analogous to the radical decomposition of $\text{XeF}_2$, to give fluorine radicals and xenon at temperatures above 500 $^\circ\text{C}$,$^{20}$ [equation (6.11)]. The similarity of the

$$\text{XeF}_2 \longrightarrow \text{Xe} + 2 \text{F}^- \quad (6.11)$$
decomposition of XeF₂, FXeL and XeL₂ is related to the fact that the electronegativities of the ligands L approach that of fluorine, so that the ionic characters of the Xe-F and Xe-L bonds are similar, resulting in homolytic cleavage of the Xe-F and Xe-L bonds upon decomposition. For F₅TeN(H)-Xe⁺ and the phenylxenon(III) cations such as C₆F₅-Xe⁺, the Xe-N and Xe-C bonds are much more covalent than in the class of compounds FXeL and XeL₂ mentioned above, which results from the lower electronegativities of the F₅TeN(H)- and C₆F₅⁻ ligands. The lower electronegativities of these ligands are reflected in the ¹²⁹Xe NMR resonances for F₅TeN(H)-Xe⁺ (-2902 ppm; Chapter 5) and C₆F₅-Xe⁺ (-3763 ppm),⁵⁵,⁵⁶ which are significantly more shielded relative to the values observed for the neutral Xe(II) derivatives. The relationship of ligand electronegativity and ¹²⁹Xe chemical shift is discussed in Chapter 5. Representative ¹²⁹Xe NMR chemical shifts for the class of neutral xenon(II) derivatives are XeF₂⁺, ¹⁰⁸-1708 ppm (BrF₅ solvent; -40 °C), FXeOSO₂F, ¹⁰⁸ -1613 ppm (BrF₅ solvent; -40 °C), FXeN(SO₂F)₂, ⁵⁹ -2099 ppm (SO₂ClF solvent; -40 °C), and Xe[N(SO₂F)₂]₂, ⁵⁹ -2257 ppm, (SO₂ClF solvent; -40 °C).

Owing to the covalent character of the Xe-N and Xe-C bonds in the F₅TeN(H)-Xe⁺ and R-Xe⁺ cations (R = fluorophenyl group), the most favorable decomposition pathway involves complete transfer of the Xe-N or Xe-C bond electron pair to xenon, giving xenon gas and a transient, highly electrophilic cation, such as F₅TeN(H)⁺ or C₆F₅⁺, which is immediately attacked by a nucleophile in solution.

(C) CHARACTERIZATION OF F₅TeNF₂ BY ¹⁵N AND ¹⁹F NMR SPECTROSCOPY

Difluoraminotellurium(VI) pentafluoride, F₅TeNF₂, is the primary decomposition product resulting from the nucleophilic fluorination of F₅TeN(H)-Xe⁺ in HF and BrF₅ solvents [see Section (A) of this Chapter]. The structure of F₅TeNF₂ in solution was determined from the ¹⁹F
and $^{15}\text{N}$ NMR spectra of the natural abundance and 99.5% $^{15}\text{N}$-enriched compounds in HF and BrF$_5$ solvents and were consistent with Structure 6.1. The best NMR spectra of F$_5$TeNF$_2$ were obtained in BrF$_5$ solvent, and these spectra are discussed below.

The fluorine-on-nitrogen resonance in the $^{19}\text{F}$ NMR spectrum of natural abundance F$_5$TeNF$_2$ in BrF$_5$ solvent (-60.1 °C) consists of a singlet at 64.2 ppm ($\Delta v_{1/2} = 209$ Hz) which results from quadrupole collapse of the one-bond scalar coupling to $^{15}\text{N}$ ($I = 1$). The chemical shift is comparable to that observed for other difluoramo compounds such as F$_2$SNF$_2$ (68.2 ppm) and F$_2$N-NF$_2$ (60.4 ppm). The fluorine-on-nitrogen region of the $^{19}\text{F}$ NMR spectrum of 99.5% $^{15}\text{N}$-enriched F$_5$TeNF$_2$ consisted of a broad doublet centered at 64.2 ppm (Figure 6.3; BrF$_5$ solvent, -44.4 °C). The doublet arises from the one-bond scalar coupling $^1J(^{19}\text{F}_N, ^{15}\text{N}) = 165$ Hz, and is flanked by satellite doublets attributed to the two-bond scalar coupling $^2J(^{19}\text{F}_N, ^{125}\text{Te}) = 1025$ Hz. Gaussian multiplication of the free induction decay before Fourier transformation resulted in the resolution of quintet structure arising from the scalar coupling of the fluorine-on-nitrogen environment with the four chemically equivalent fluorines directly bonded to tellurium [$^3J(^{19}\text{F}_N, ^{19}\text{F}_{eq}) = 15$ Hz]. The scalar coupling of the fluorine-on-nitrogen environment with the axial fluorine is not resolved. In general, three-bond couplings with the axial fluorine-on-tellurium in F$_2$TeO- and F$_2$TeN- derivatives are not resolved. Examples include the inability to resolve the three-bond scalar couplings $^3J(^{129}\text{Xe}, ^{19}\text{F}_{ax})$ in XeOTeF$_5$; $^{54}$ Xe(OTeF$_5$)$_2$, $^{141}$ FXeOTeF$_5$, and F$_5$TeN(H)-Xe$^+$ (see Chapter 5).

The fluorine-on-tellurium(VI) region of the $^{19}\text{F}$ NMR spectrum (470.599 MHz) of 99.5% $^{15}\text{N}$-enriched F$_5$TeNF$_2$ (BrF$_5$ solvent; -44.4 °C) consists of a typical AB$_4$ pattern (Figure 6.4).
Figure 6.3  \(^{19}\text{F NMR spectrum (470.599 MHz)}\) of the fluorine-on-nitrogen environment (\(F_N\)) of 99.5% \(^{15}\text{N-enriched F}_2\text{TeNF}_2\) in BrF\(_5\) solvent at -44.4 °C: Asterisks (*) denote \(^{125}\text{Te satellites arising from the scalar coupling }^{2}J(^{19}\text{F}_N,^{125}\text{Te}) = 1025 \text{ Hz};\) (A) resolution of central doublet enhanced by Gaussian multiplication of the free induction decay before Fourier transformation.
$^{19}F$ NMR spectrum (470.599 MHz) of the fluorine-on-tellurium environment of 99.5% $^{15}$N-enriched F$_2$TeNF$_2$ in BrF$_5$ solvent at -44.4 °C, the asterisk (*) and dagger (†) denote a $^{125}$Te and a $^{123}$Te satellite, respectively, that arise from the scalar couplings $J(^{19}F$-$^{125}$Te) and $J(^{19}F$-$^{123}$Te) of TeF$_6$ present in the sample.
From the ratio $2J(^{19}F_{ax} - ^{19}F_{eq})/\nu_0 \delta(^{19}F_{ax} - ^{19}F_{eq}) = 0.125$, resolution of the individual transitions in the $B_4$ portion of the spectrum of the $F_5Te$- should be possible. This was shown in the $^{19}F$ NMR spectrum of XeOTeF$_5$*, where $2J(^{19}F_{ax} - ^{19}F_{eq})/\nu_0 \delta(^{19}F_{ax} - ^{19}F_{eq}) = 0.1497$, and the individual transitions of the AB$_4$ pattern were well resolved. This comparison is based on the fact that the appearance of the AB$_4$ spin system depends solely on this ratio.$^{268}$ However, in the AB$_4$ spectrum of $F_5TeNF_2$, the individual transitions of the $B_4$ portion (centered at ca. -59.5 ppm) were not resolved because of the scalar couplings $2J(^{19}F_{eq} - ^{15}N) = 11$ Hz (obtained from the $^{15}N$ NMR spectrum, see below) and $3J(^{19}N-^{19}F_{eq}) = 15$ Hz, which further split each transition of the $B_4$ subspectrum into a triplet of doublets, resulting in two broad envelopes. The NMR parameters of the AB$_4$ spin system of natural abundance $F_5TeNF_2$ were obtained using the method of Harris and Packer$^{268}$ and the LAOCOON simulation program. The $^{19}F$ chemical shifts for the axial and equatorial fluorine resonances were determined to be -57.0 and -59.5 ppm, respectively, and the two-bond scalar coupling, $2J(^{19}F_{ax} - ^{19}F_{eq})$, was determined to be 148 Hz.

The $^{15}N$ NMR spectrum of 99.5% $^{15}N$-enriched $F_5TeNF_2$ in BrF$_5$ solvent at -57.3 °C (Figure 6.5) consists of a triplet of quintets centered at $\delta(^{15}N) = -11.1$ ppm. The quintet structure arises from the scalar coupling of $^{15}N$ with the four chemically equivalent fluorine atoms bonded to tellurium(VI), $2J(^{15}N^{19}F_{eq}) = 11$ Hz. The unresolved scalar coupling, $2J(^{15}N^{19}F_{ax})$, of $^{15}N$ and the axial fluorine on tellurium is consistent with the inability to resolve two- and three-bond couplings with the axial fluorine in NMR studies of compounds containing $F_5TeN$- or $F_5TeO$- groups$^{54,141}$ (see also Chapters 4 and 5). The triplet splitting arises from the one-bond scalar coupling of $^{15}N$ with the fluorines on nitrogen, $1J(^{15}N^{19}F_{N}) = 165$ Hz, confirming the coupling observed in the $^{19}F$ NMR spectrum (Figure 6.3). The $^{15}N$ NMR chemical shift of $F_5TeNF_2$ is deshielded relative to 99.5% $^{15}N$-enriched $F_5TeNH_5^{+}$ (-317.9 ppm) and $F_5TeN(H)\cdot Xe^+AsF_6^-$. 
Figure 6.5

$\delta^{15}N$ (ppm from CH$_3$NO$_2$) of 99.5% $^{15}N$-enriched F$_5$TeNF$_2$ in BrF$_5$ solvent (57.3 °C).
(-266.1 ppm), which were present in the solution. The deshielding can be rationalized from a consideration of the factors contributing to an approximate version of the local paramagnetic shielding term for nitrogen, \( \sigma_P^N \) [equation (6.12)]. A negative value for the local paramagnetic contribution to the shielding of nitrogen, \( \sigma_P^N \), deshields the nitrogen nucleus; \( \mu_0 \) and \( \mu_B \) are the permittivity of a vacuum and the Bohr magneton, respectively, and \( <r^3>_{2p} \) is the inverse cube of the average radius of the valence \( p \) electrons on nitrogen. The \( \Sigma Q \) term expresses the imbalance of electronic charge that allows the paramagnetic circulation in the magnetic field. The \( Q_{NN} \) part of this term depends on the \( 2p \) orbital populations on nitrogen, whereas \( \Sigma Q_{NX} \) is a multiple bond term. The term \( \Delta E \) refers to the average energy for promotion of electrons to excited states that result in paramagnetic circulations. For molecules where the lone-pairs are strongly linked to the \( \sigma \) framework, such as the molecules discussed in the present Chapter, the electronic circulations deshielding nitrogen are all of \( \sigma \rightarrow \sigma^* \) and \( n_N \rightarrow \sigma^* \) type, where \( n_N \) represents a nitrogen lone-pair. The greater deshielding of \( ^{15}\text{N} \) in \( \text{F}_5\text{TeNF}_2 \) relative to \( \text{F}_5\text{TeN(H)}-\text{Xe}^+ \) and \( \text{F}_5\text{TeNH}_3^+ \) results mainly from \( \sigma \) fluoro effects. The replacement of hydrogen by fluorine is expected to remove electron density from nitrogen, increasing the radial term \( <r^3>_{2p} \) and thus deshielding \( ^{15}\text{N} \) by increasing \( \sigma_P^N \). This argument qualitatively explains the deshielding of nitrogen in \( \text{NF}_3 \) relative to \( \text{NH}_3 \) \( [\Delta \delta(^{15}\text{N}) = 370 \text{ ppm}] \) and \( \text{NF}_4^+ \) relative to \( \text{NH}_4^+ \) \( [\Delta \delta(^{15}\text{N}) = 280 \text{ ppm}] \), since for these two pairs \( <r^3>_{2p} \) decreases by 17 and 20%, respectively. It is noteworthy that the \( ^{15}\text{N} \) chemical shifts of \( \text{NF}_3 \) \( [\delta(^{15}\text{N}) = -14 \text{ ppm}] \) and \( \text{F}_5\text{TeNF}_2 \) are similar, which reflects, in part, the high electronegativity of the \( \text{F}_5\text{Te}^- \) group.
A resonance assignable to $F_5TeNF_2$ was not observed in the $^{125}$Te NMR spectrum of the mixture resulting from the reaction of $F_5TeNH_2$ and $XeF^+AsF_6^-$ in HF solvent. This was attributed to the low concentration of $F_5TeNF_2$ in the decomposition of $F_5TeN(\text{H})$-$Xe^+$ in HF solvent, as shown in the $^{19}$F NMR spectrum at -33.3 °C (Figure 6.2).

(D) $^{19}$F NMR SPECTROSCOPIC STUDY OF THE DECOMPOSITION OF $F_5TeNF_2$ IN HF SOLVENT ACIDIFIED WITH $AsF_5$

The sample of an equimolar mixture of $F_5TeNH_2$ and $XeF^+AsF_6^-$ in HF solvent studied in Section (A) of this Chapter was warmed to -20 °C for 5 minutes, and the resulting $^{19}$F NMR spectrum of the fluorine-on-tellurium(VI) region is shown in Figure 6.6 (-36.4 °C). Resonances assignable to $F_5TeNH_3^+$, $F_5TeN(\text{H})$-$Xe^+$ and $TeF_6$ were observed. A $1:1:1$ triplet centered at 96.8 ppm ($^1J(^{19}F-^{15}N) = 335$ Hz) is assigned to $FN\equiv N^+$ by comparison with the published $^{19}$F NMR data for $FN\equiv N^+AsF_6^-$ in HF solvent at room temperature ($\delta(^{19}F) = 103$ ppm; $^1J(^{19}F-^{14}N) = 328$ Hz).$^{272a}$ Resonances assignable to $AsF_6^-$ and $F_5TeNF_2$ were not observed (see below).

It should be noted that careful sample warming was required in order to observe $FN\equiv N^+$ by $^{19}$F NMR spectroscopy. This is expected since $FN\equiv N^+$ is a powerful oxidative fluorinator,$^{272b}$ capable of fluorinating xenon gas in HF solvent at 25 °C according to equation (6.13).$^{273}$ It is likely that $FN\equiv N^+$ is capable of oxidatively fluorinating several species present in the system,

$$FN\equiv N^+AsF_6^- + Xe \longrightarrow Xe-F^+AsF_6^- + N\equiv N$$  \hspace{1cm} (6.13)

including xenon gas formed in the decomposition of $F_5TeN(\text{H})$-$Xe^+$. Taking care not to warm samples above the temperatures at which the $^{19}$F NMR spectra were recorded sufficiently slowed
Figure 6.6  $^{19}$F NMR spectrum (499.599 MHz) of the fluorine-on-tellurium(VI) region of an equimolar mixture of natural abundance $^{125}$TeNH$_2$ and XeF$^+$AsF$_6^-$ in HF solvent, warmed for 5 minutes at -20 °C before accumulating the spectrum at -36.4 °C; (A) equatorial fluorine resonance of $F_5$TeNH$_3^+$, (a) and (a') $^{125}$Te and $^{123}$Te satellites, respectively, (B) axial fluorine resonance of $F_5$TeNH$_3^+$, (C) equatorial fluorine resonance of $F_5$TeN(H)-Xe$^+$, (c) $^{125}$Te satellites; (D) unassigned resonance, (E) axial fluorine resonance of $F_5$TeN(H)-Xe$^+$, (F) TeF$_6$, (f) $^{125}$Te satellites.
the oxidative fluorination reactions so that FN=N⁺ could be observed in the ¹⁹F NMR spectra. Evidence for the reaction of FN=N⁺ was provided by the observation of a peak [δ(¹⁵N) = -73.0 ppm] in the ¹⁵N NMR spectra of the 99.5% ¹⁵N-enriched system which is assignable to nitrogen gas²⁷⁴ dissolved in HF solvent.

From the integrations of the ¹⁹F NMR resonances (Figure 6.6), the ratio F₅TeNH₃⁺ : F₅TeN(H)-Xe⁺ : TeF₆ : FN=N⁺ was found to be 1.00 : 0.03 : 0.44 : 0.03, and resonances due to AsF₆⁻ and F₅TeNF₂ were not observed (see below). The presence of FN=N⁺ and the increased amount of TeF₆ relative to F₅TeNH₃⁺ when compared to the observed ratio prior to warming to -20 °C [see Section (A) of this Chapter] is consistent with the decomposition of F₅TeNF₂ to TeF₆ and FN=N⁺. The HF resonance [δ(¹⁹F) = -191.4 ppm] is shifted to high frequency by 3.7 ppm relative to that observed before warming of the sample to -20 °C. The HF resonance was also significantly broadened [Δν₁/₂ = 3450 Hz] and the XeF₂ resonance was no longer observed. The absence of a resonance assignable to AsF₆⁻ and the high frequency shift of the HF resonance is consistent with AsF₅ formation and the resulting exchange equilibrium (6.3) with HF. Since a large amount of F₅TeNH₃⁺ is still present in solution, the XeF₂ has not completely reacted and is believed to undergo exchange with AsF₅ generated in the decomposition of F₅TeN(H)-Xe⁺ according to equilibria (6.4) and (6.5).

The decomposition of F₅TeNF₂ in AsF₅-acidified HF solution to give TeF₆ and FN=N⁺ appeared to indicate that a Lewis acid induced intramolecular redox decomposition of F₅TeNF₂ had occurred. A detailed study of this process was published by Christe et al. for the difluoramino compounds R-NF₂ (R = Cl, F₃C, F₅S, F₃CO, F₅SO).²⁷⁵ Difluoramino compounds are in general thermodynamically unstable, and their stability results from a kinetic barrier to decomposition. Suitable catalysts such as the strong Lewis acids, SbF₅ and AsF₅, lower the energy barrier to
decomposition, resulting in multiply bonded nitrogen species such as F-N≡N-F and N≡N, and more highly fluorinated byproducts. Christe et al.\textsuperscript{275} showed by Raman spectroscopy that CINF\textsubscript{2} forms an adduct with AsF\textsubscript{5} at -78 °C which is best interpreted as a fluorine-bridged adduct, CIN(F)\textsuperscript{--}F-AsF\textsubscript{5}, which decomposed on warming via the Lewis acid induced intramolecular redox decomposition process mentioned above. This indicated that the initial step in the decomposition of difluoramine compounds, RNF\textsubscript{2}, involved fluoride abstraction from nitrogen by the Lewis acid, MF\textsubscript{5} (M = As, Sb). It has been proposed that the fluorine-bridged adduct decomposes according to equation (6.14), producing fluoronitrene, F-N, which dimerizes to give

\[
\begin{align*}
\text{cis- and trans- isomers of F-N≡N-F. The cis-isomer of N}_2\text{F}_2 & \text{ behaves as a fluoride ion donor towards the strong Lewis acid, MF}_5 \text{ (M = As, Sb), forming F-N≡N}^+\text{MF}_6^-; \text{ but the trans-isomer of N}_2\text{F}_2 & \text{ is not a fluoride ion donor.}\textsuperscript{276} \text{ The decomposition of F}_5\text{TeNF}_2 \text{ in the present system may, in fact, be catalyzed by AsF}_5, \text{ which is produced in the nucleophilic fluorination of F}_5\text{TeN(H)-Xe}^+ \text{ [see Section (A)]. It is, however, unlikely that the source of F-N≡N}^+ \text{ results from the dimerization of fluoronitrene radicals as in the study of Christe et al.}\textsuperscript{275} \text{ since no trans-N}_2\text{F}_2 \text{ was observed in the reaction mixture after complete decomposition of F}_5\text{TeNF}_2; \text{ dimerization of fluoronitrene is expected to give a mixture of cis- and trans-isomers.}\textsuperscript{275,277} \text{ It was postulated that the absence of trans-N}_2\text{F}_2 \text{ in the present system might result from the isomerization of the cis- and trans-isomers,}
\end{align*}
\]
with cis-N$_2$F$_2$ acting as a sink for FN≡N$^+$ formation in the presence of AsF$_5$ [equation (6.15)]. However, isomerization of trans-N$_2$F$_2$ is very slow, and attempts to increase the rate at elevated temperatures result in low yields due to decomposition of N$_2$F$_2$ to N$_2$ and F$_2$. Christe et al. were able to obtain an 80% yield of FN≡N$^+$AsF$_6^-$ by combining trans-N$_2$F$_2$ with an excess of AsF$_5$ at 70 °C, however, the process was slow, requiring three days. The possibility of HF

\[
\text{trans-N}_2\text{F}_2 \rightleftharpoons \text{cis-N}_2\text{F}_2 + \text{AsF}_5 \rightarrow \text{FN≡N}^+\text{AsF}_6^-
\]

(6.15)

solvent acting as a catalyst for trans/cis isomerization at -20 °C was investigated in the present study by combining equimolar amounts of trans-N$_2$F$_2$ and AsF$_5$ in HF at -196 °C. The sample was warmed to -20 °C for five minutes, similar to the conditions under which FN≡N$^+$ was formed in the reaction of F$_5$TeNH$_2$ and XeF$^+$AsF$_6^-$ in HF solvent, and the $^{19}$F NMR spectrum was observed at -37 °C. Only trans-N$_2$F$_2$ was observed ($\delta^{(19)}F = 89.01$ ppm), which indicated that isomerization of trans-N$_2$F$_2$ did not occur. The second reason to discount fluoronitrene dimerization as the major source of FN≡N$^+$ is apparent when one considers the low concentration of F$_5$TeNF$_2$ relative to the F$_5$TeNH$_3^+$ cation in HF solvent before warming the sample to -20 °C [see Section (A) and Figure 6.2], and there is precedent in the literature for the reaction of fluoronitrene with primary amines. It is very unlikely that fluoronitrene is sufficiently unreactive towards F$_5$TeNH$_2$ to react solely by dimerization, given the slow fluoronitrene dimerization kinetics expected from the low concentration of fluoronitrene in solution. In considering this, it is important to realize that nitrenes are highly reactive species, usually requiring trapping agents to infer their existence. Primary amines undergo deamination reactions with difluoramine, HF$_2$N, or isopropyl N,N-difluorocarbamate, which behaves as a source of
HNF$_2$$^{121}$ as shown in equation (6.16)$^{279,280}$ It was postulated that the initial step involved

$$3 \text{RNH}_2 + \text{HNF}_2 \rightarrow 2 \text{RNH}_3^+ \text{F}^- + \text{N}_2 + \text{R-H} \quad (6.16)$$

the reaction of the primary amine with fluoronitrene to give RNH$_2$\textsuperscript{NF} [equation (6.17)], followed by rearrangement to give a substituted hydrazine, from which elimination of HF resulted in the

$$\text{RNH}_2 + \text{NF} \rightarrow \text{RNH}_2\text{NF}^- \rightarrow$$

$$\text{RN(H)}\text{N(H)}\text{F} \rightarrow \text{RN=NH} \rightarrow \text{R-H} \quad (6.17)$$

unstable diazene, RN=NH, which eliminated N$_2$ to give R-H. Bumgardner and Liebman$^{282}$ have proposed an alternative mechanism for the reaction of primary amines with HNF$_2$, in which the first step is the bimolecular displacement of fluoride from HNF$_2$ by RNH$_2$, without inference of fluoronitrene formation [equation (6.18)]

$$\text{RNH}_2 + \text{HNF}_2 \rightarrow \text{R-NH}_2\text{-N(H)}\text{F}^+ + \text{F}^- \quad (6.18)$$

A mechanism for the formation of TeF$_6$ and FN=NT from the Lewis acid-catalyzed reaction F$_5$TeNF$_2$ and F$_5$TeNH$_3^+$ in HF solvent is proposed and supported by literature analogies in the following discussion. The generation of fluoronitrene as an intermediate in the reaction of F$_5$TeNH$_2$ and F$_5$TeNF$_2$ in the present study cannot be addressed; however, by analogy with the
AsF$_5$-catalyzed decomposition of CINF$_2$, it is likely that the interaction of AsF$_5$ with a fluorine atom on nitrogen in F$_5$TeNF$_2$ facilitates the reaction [equation (6.19)]. This process is analogous to the bimolecular addition depicted in equation (6.18). Equilibria (6.3) and (6.20) are expected to facilitate the reaction of F$_5$TeNH$_2$ and F$_5$TeNF$_2$ to give the protonated hydrazine. The presence of AsF$_5$ also results from the nucleophilic fluorination of F$_5$Te(NH)Xe$^+$ in the same system [see equation (6.2)]. The cationic xenon(II) species, XeF$^+$ and Xe$_2$F$_3^+$, are present from the increased fluoroacidity of the solution as discussed in Section (A) of this Chapter. The deprotonation equilibrium (6.21) to give $\underline{2}$ is expected to precede oxidative fluorination by XeF$^+$,
resulting in 3 [equation (6.22)]. Evidence for the oxidative fluorinating ability of the

\[
\begin{align*}
F_5\text{Te} & \quad \text{N} \quad \text{N} \quad \text{TeF}_5 & \quad \text{AsF}_6^- & + \quad \text{HF} & \quad \Rightarrow \\
& \quad \text{H} & & \quad \text{F} \quad \text{H} & \quad \text{F} \\
1
\end{align*}
\]

\[
\begin{align*}
F_5\text{Te} & \quad \text{N} \quad \text{N} \quad \text{TeF}_5 & + & \quad \text{H}_2\text{F}^+\text{AsF}_6^- \\
& \quad \text{H} & & \quad \text{F} & \quad \text{F} \\
2
\end{align*}
\]

\[
\begin{align*}
F_5\text{Te} & \quad \text{N} \quad \text{N} \quad \text{TeF}_5 & + & \quad \text{XeF}^+\text{AsF}_6^- & \quad \Rightarrow \\
& \quad \text{H} & & \quad \text{F} & \quad \text{F} & \quad \text{H} \\
2
\end{align*}
\]

\[
\begin{align*}
F_5\text{Te} & \quad \text{N} \quad \text{N} \quad \text{TeF}_5 & \quad \text{AsF}_6^- & + & \quad \text{Xe} \\
& \quad \text{F} & & \quad \text{F} & \quad \text{F} \\
3
\end{align*}
\]

solution is provided by the fact that the monofluoramine, $F_5\text{TeN(H)}-\text{F}$, was not observed as the
initial product of the nucleophilic fluorination of \( \text{F}_5\text{TeN(H)-Xe}^+ \) [Section (A) of this Chapter]. This has been attributed to the immediate oxidative fluorination of the monofluoramine to the difluoramine, \( \text{F}_5\text{TeNF}_2 \), by \( \text{XeF}^+ \). By analogy with the weak basicity of \( \text{N(CF}_3)_3 \) and the inability to protonate \( \text{NF}_3 \) in superacid (HF / SbF\(_5\)) solution, species 3 is expected to be deprotonated, giving 4 in the \( \text{AsF}_5 \)-acidified HF solution [equation (6.23)]. In the presence of \( \text{AsF}_5 \), 4 may undergo Lewis acid induced intramolecular redox decomposition by analogy with difluoramino compounds [equation (6.24)]. The short-lived nitrene, 5, is expected to have some 1,1-diazene character (6) due to \( \pi \)-donation from the tricoordinate nitrogen. Resonance contributor 6 is electronically similar to \( \text{F}_2\text{N}=\text{N} \), which has been proposed by Christe et al. as the intermediate in the formation of \( \text{cis-N}_2\text{F}_2 \) from the reaction of \( \text{FN}=\text{N}^+ \) and the fluoride ion donor, FNO [equation (6.25)]. Although \( \text{F}_2\text{N}=\text{N} \) rearranges by \( \alpha \)-migration of fluorine to give \( \text{cis-} \)

\[
\text{F}_5\text{Te}\begin{array}{c}
\text{N} \\
\text{F}
\end{array}\begin{array}{c}
\text{N} \\
\text{F}
\end{array}\text{TeF}_5 \quad \text{AsF}_6^- + \text{HF} \quad \rightarrow \\
\text{F}_5\text{Te}\begin{array}{c}
\text{N} \\
\text{F}
\end{array}\begin{array}{c}
\text{N} \\
\text{F}
\end{array}\text{TeF}_5 \quad \text{H}_2\text{F}^+\text{AsF}_6^- \\
\text{F} \quad \text{F} \\
\text{F} \quad \text{F}
\]

\text{3}

\text{4}
\[ \text{FNO} + \text{FN=N}^+ \rightarrow \text{NO}^+ + [\text{F}_2\text{N=N}] \rightarrow \text{cis-} \text{N}_2\text{F}_2 \]  
(6.25)

\[ \text{F}_2\text{Te-N=N} \rightarrow \text{F}_2\text{Te-N-N} \rightarrow \text{F}_2\text{Te-N=N} \]  
(6.24)

N\textsubscript{2}F\textsubscript{2}, the more favorable process in the case of the transient species 6 may involve elimination of "TeF\textsubscript{5}" in the presence of XeF\textsuperscript{+} to give the stable species TeF\textsubscript{6}, xenon, and FN=N\textsuperscript{+} according to equation (6.26). It is also possible that a second decomposition process occurs. By analogy with F\textsubscript{2}N=N, 6 may rearrange by α-migration of fluorine to give the diazene, F\textsubscript{5}Te-N=N-F, which then
eliminates the stable species N\textsubscript{2} and TeF\textsubscript{6} (equation (6.27)). This is analogous to the formation

\[
F_5\text{Te}(F)N=NF + XeF^+AsF_6^- \rightarrow TeF_6 + FN=N^+AsF_6^- + Xe
\]  \hspace{1cm} (6.26)

\[
F_5\text{Te}(F)N=NF \rightarrow F_5\text{Te-N=N-F} \rightarrow TeF_6 + N=N
\]  \hspace{1cm} (6.27)

of RH, N\textsubscript{2} and HF in the reductive deamination of primary amines by HNF\textsubscript{2}, which is believed to involve a similar short-lived diazene, R-N=N-H\textsuperscript{279} (equation (6.17)). Evidence for N\textsubscript{2} formation is provided by the observation of a resonance attributable to molecular nitrogen dissolved in HF [\delta\textsuperscript{15}N = -73.0 ppm; -45 °C]\textsuperscript{274} in the \textsuperscript{15}N NMR spectrum of the analogous 99.5\% \textsuperscript{15}N enriched materials.

It is noteworthy that, although the F\textsubscript{5}TeNF\textsubscript{2} is completely reacted after warming to -20 °C for five minutes, a small amount of F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} is still present in solution. This may result from the increased fluoroacidity of the HF solution, which decreases the nucleophilicity of the solvent medium, thus decreasing the rate of nucleophilic fluorination of F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} according to equation (6.1). On warming the sample to -1.2 °C, \textsuperscript{19}F NMR indicated that all but a trace of F\textsubscript{5}TeN(H)-Xe\textsuperscript{+} was decomposed. Also, a resonance assignable to FN=N\textsuperscript{+} was not observed. The only F-on-Te(VI) environments observed were those of F\textsubscript{5}TeNH\textsubscript{3}\textsuperscript{+} and TeF\textsubscript{6} (relative integrated ratio = 1.00 : 0.50). The broad saddle-shaped resonance for AsF\textsubscript{6}\textsuperscript{3-} (ca. -68 ppm) was also not observed. Separate resonances for AsF\textsubscript{6}\textsuperscript{3-}, HF and XeF\textsubscript{2} were coalesced to a broad peak (\Delta\nu\textsubscript{1/2} = 386 Hz) at -188.9 ppm, which indicated exchange of these three species according to equilibria (6.3) to (6.5) in the AsF\textsubscript{5}-acidified HF solution.
CHAPTER 7

CHARACTERIZATION OF FO₂SNH₂ AND FO₂SNH₃⁺AsF₆⁻ USING ¹⁹F AND ¹H NMR AND RAMAN SPECTROSCOPY

AND

COMPARISON OF THE BONDING IN FO₂SNH₂ AND THE FO₂SNH₃⁺ CATION

INTRODUCTION

The synthesis of fluorosulfuryl amide, FO₂SNH₂, was first reported in 1958 by two different routes, namely, fluorination of ClO₂SNH₂ with KF in boiling acetonitrile[133] [equation (7.1)] and fluorination of chlorosulfuryl isocyanate with NaF followed by careful hydrolysis[134]

\[ \text{ClO}_2\text{SNH}_2 + \text{KF} \rightarrow \text{KCl} + \text{FO}_2\text{SNH}_2 \] (7.1)

[equations (7.2) and (7.3)]. The preparation of FO₂SNH₂ from the reaction of disulfuryl fluoride,

\[ \text{ClO}_2\text{SNCO} + \text{NaF} \rightarrow \text{NaCl} + \text{FO}_2\text{SNCO} \] (7.2)

\[ \text{FO}_2\text{SNCO} + \text{H}_2\text{O} \rightarrow \text{FO}_2\text{SNH}_2 + \text{CO}_2 \] (7.3)
\[ S_2O_5F_2 + 2 \text{NH}_3 \rightarrow FO_2SNH_2 + NH_4^+SO_2F^- \] (7.4)

S\textsubscript{2}O\textsubscript{5}F\textsubscript{2}, and NH\textsubscript{3} at low temperature was reported in 1961\textsuperscript{129} [equation (7.4)] Fluorosulfuryl amide is a colorless liquid at room temperature (m.p. 8 °C) and is soluble in organic solvents such as acetonitrile, ether and chloroform. Unlike ClO\textsubscript{2}SNH\textsubscript{2}, which reacts explosively with water to give sulfamic acid and HCl,\textsuperscript{284} FO\textsubscript{2}SNH\textsubscript{2} is soluble in water and hydrolyzes slowly, producing sulfamic acid and HF [equation (7.5)]. The compound, FO\textsubscript{2}SNH\textsubscript{2}, is isoelectronic with O\textsubscript{3}SNH\textsubscript{2}\textsuperscript{\textminus}

\[ FO_2SNH_2 + H_2O \rightarrow O_3SNH_3 + HF \] (7.5)

and has similar bonding properties. For instance, the similar SN bond lengths in K\textsuperscript{+}O\textsubscript{3}SNH\textsubscript{2}\textsuperscript{\textminus} [1.60(1) Å]\textsuperscript{285} and FO\textsubscript{2}SNH\textsubscript{2} [1.61(3) Å],\textsuperscript{286} that were determined by X-ray crystallography and electron diffraction, respectively, are significantly shorter than a typical S-N single bond, such as that in O\textsubscript{3}SNH\textsubscript{3} [1.7714(3) Å],\textsuperscript{287} indicating the presence of S-N π bonding in FO\textsubscript{2}SNH\textsubscript{2} and O\textsubscript{3}SNH\textsubscript{2}\textsuperscript{\textminus}.\textsuperscript{130,288} Sulfur-nitrogen π-bonding in O\textsubscript{3}SNH\textsubscript{3} is not possible since the lone pair on nitrogen is not available for π-donation to the acceptor orbitals on sulfur. Recent ab initio SCF calculations utilizing natural population analysis\textsuperscript{217} for the related molecules SO\textsubscript{2}Cl\textsubscript{2}, SO\textsubscript{2}(CH\textsubscript{3})Cl and SO\textsubscript{2}(CH\textsubscript{3})\textsubscript{2} indicate that the hybrid acceptor orbitals on sulfur, that are predominantly 3p in character, arise from π(O) → σ\textsuperscript{\textast} SX) negative hyperconjugation with a minor contribution (19 - 27%) from sulfur 3d orbitals. It seemed reasonable therefore to stress the importance of π(N) → σ\textsuperscript{\textast} SX) negative hyperconjugation (X = F, O) over pure [N(2p) → S(3d)]π donation as a mechanism for S-N π bonding in FO\textsubscript{2}SNH\textsubscript{2} and O\textsubscript{3}SNH\textsubscript{2}\textsuperscript{\textminus}.
Semmoud and Vast\textsuperscript{130} have used infrared spectroscopy to investigate the effect of deprotonation on the S-O, S-N and S-F symmetric stretching frequencies (and hence the bond orders) for the acid/base pairs FO\textsubscript{2}SNH\textsubscript{2}/FO\textsubscript{2}SNH\textsubscript{g} and AgO\textsubscript{2}SNH\textsubscript{2}/Ag\textsubscript{3}O\textsubscript{3}SN. They have shown that the S-N bonds are strengthened through increased S-N π-bonding at the expense of the S-O and S-F bonds when lone pairs on nitrogen become available for S-N π-bonding upon deprotonation of FO\textsubscript{2}SNH\textsubscript{2} and O\textsubscript{2}SNH\textsubscript{2}\textsuperscript{2-}.

The present work involved a more detailed vibrational study of FO\textsubscript{2}SNH\textsubscript{2} with use of \textsuperscript{14/15}N isotopic shift information obtained from the Raman spectra of the natural abundance and 99.5% \textsuperscript{15}N-enriched compounds. As well, the FO\textsubscript{2}SNH\textsubscript{2}\textsuperscript{2+} cation was prepared for the first time as the AsF\textsubscript{6}\textsuperscript{-} salt. Assignments of the Raman spectra of natural abundance and 99.5% \textsuperscript{15}N-enriched FO\textsubscript{2}SNH\textsubscript{2}\textsuperscript{2+}AsF\textsubscript{6}\textsuperscript{-} completed the study of Semmoud and Vast\textsuperscript{130} by allowing a comparison of the S-O, S-F, and S-N symmetric stretching frequencies for the series FO\textsubscript{2}SNH\textsubscript{g}, FO\textsubscript{2}SNH\textsubscript{2} and FO\textsubscript{2}SNH\textsubscript{2}\textsuperscript{2+} with the isoelectronic sulfonamide series O\textsubscript{3}SNA\textsubscript{g}, O\textsubscript{3}SNH\textsubscript{2}Ag, and O\textsubscript{3}SNH\textsubscript{3}.

\textbf{RESULTS AND DISCUSSION}

(A) \textbf{PREPARATION AND ISOLATION OF NATURAL ABUNDANCE FO\textsubscript{2}SNH\textsubscript{2} AND FO\textsubscript{2}SNH\textsubscript{2}\textsuperscript{2+}AsF\textsubscript{6}\textsuperscript{-} AND THE 99.5% \textsuperscript{15}N-ENRICHED ANALOGUES}

Natural abundance FO\textsubscript{2}SNH\textsubscript{2} was prepared by the fluorination of ClO\textsubscript{2}SNCO with NaF [equation (7.6)] followed by reaction with a stoichiometric amount of H\textsubscript{2}O in acetonitrile solution [equation (7.7)] by modifying the literature procedure.\textsuperscript{134} The unstable carbamic acid,

\[
\text{ClO}_2\text{SNCO} + \text{NaF} \rightarrow \text{NaCl} + \text{FO}_2\text{SNCO}
\]  
(7.6)
\[ \text{FO}_2\text{SNCO} + \text{H}_2\text{O} \rightarrow [\text{FO}_2\text{SN(H)C(O)OH}] \]
\[ \rightarrow \text{FO}_2\text{SNH}_2 + \text{CO}_2 \] (7.7)

\( \text{FO}_2\text{SN(H)C(O)OH} \), is believed to be an intermediate in the hydrolysis of \( \text{FO}_2\text{SNCO} \). The 99.5% \(^{15}\text{N}\)-enriched compound \( \text{FO}_2\text{SNH}_2 \) was prepared from the stoichiometric reaction of \( \text{S}_2\text{O}_3\text{F}_2 \) and 99.5% \(^{15}\text{N}\)-enriched \( \text{NH}_3 \) in diethyl ether solution at -45 °C by following the literature method\(^{129}\) [equation (7.8)]

\[ \text{S}_2\text{O}_3\text{F}_2 + [^{15}\text{N}]\text{NH}_3 \rightarrow [^{15}\text{N}]\text{FO}_2\text{SNH}_2 + [^{15}\text{N}]\text{NH}_4\text{SO}_3\text{F} \] (7.8)

The natural abundance and \(^{15}\text{N}\)-enriched salts \( \text{FO}_2\text{SNH}_3^+\text{AsF}_6^- \) are finely divided white powders that were prepared from the reaction of \( \text{AsF}_5 \) with \( \text{FO}_2\text{SNH}_2 \) or \( [^{15}\text{N}]\text{FO}_2\text{SNH}_2 \) in HF solvent at -40 °C according to equation (7.9) followed by vacuum removal of the HF solvent at the same temperature. The white powder is indefinitely stable at room temperature under anhydrous conditions, but hydrolyses rapidly with fuming and liquefaction in the presence of moist air.
CHARACTERIZATION OF NATURAL ABUNDANCE AND 99.5% $^{15}$N
ENRICHED $\text{FO}_2\text{SNH}_2$ AND $\text{FO}_2\text{SNH}_2^+\text{AsF}_5^-$ BY $^1\text{H}$ AND $^{19}\text{F}$ NMR SPECTROSCOPY

The $^{19}\text{F}$ and $^1\text{H}$ NMR spectra of neat liquid $\text{FO}_2\text{SNH}_2$ at ambient temperature consist of broad singlets at $\delta(^{19}\text{F}) = 56.51$ and $\delta(^1\text{H}) = 5.41$ ppm. The $^{19}\text{F}$ NMR resonance was consistent with the $\text{FO}_2\text{SN}$- group. The scalar couplings are not resolved because of quadrupolar broadening from the presence of natural abundance nitrogen ($I = 1$). The $^1\text{H}$ and $^{19}\text{F}$ NMR spectra in BrF$_5$ solvent at $-61.4\, ^\circ\text{C}$ do not indicate any reaction of $\text{FO}_2\text{SNH}_2$ with the solvent and consisted of a broad doublet [$\delta(^1\text{H}) = 4.68$ ppm; Figure 7.1a] and a triplet [$\delta(^{19}\text{F}) = 56.91$ ppm; Figure 7.1b]. The multiplet structures arise from $^3J(^1\text{H}-^{19}\text{F}) = 6.3$ Hz. The collapse of the scalar coupling, $^1J(^1\text{H}-^{14}\text{N})$, which is estimated to be 61.8 Hz from equation (7.10) (see below), results from scalar relaxation of the second kind, when the tranverse relaxation rate of the quadrupolar

$$^1J(^1\text{H}-^{14}\text{N}) = [\gamma(^{14}\text{N})/\gamma(^{15}\text{N})] \times ^1J(^1\text{H}-^{15}\text{N})$$  \hspace{1cm} (7.10)

$^{14}\text{N}$, $1/T_2(^{14}\text{N})$, is much greater than the magnitude of the scalar coupling to the proton. The coupling $^1J(^1\text{H}-^{14}\text{N})$ is completely quadrupole collapsed, but is sufficiently narrow to allow resolution of $^3J(^1\text{H}-^{19}\text{F})$.

All possible scalar couplings between spin-$1/2$ nuclei are observed in the $^1\text{H}$ and $^{19}\text{F}$ NMR spectra of 99.5% $^{15}$N-enriched $\text{FO}_2\text{SNH}_2$ in acetonitrile solution (30 $^\circ\text{C}$). The $^1\text{H}$ NMR spectrum consists of a doublet of doublets [$\delta(^1\text{H}) = 6.79$ ppm; Figure 7.2a] arising from $^3J(^1\text{H}-^{19}\text{F}) = 6.1$ and $^1J(^1\text{H}-^{15}\text{N}) = 86.7$ Hz, and the $^{19}\text{F}$ NMR spectrum consists of a triplet of doublets [$\delta(^{19}\text{F}) = 56.78$ ppm; Figure 7.2b] arising from $^2J(^{19}\text{F}-^{15}\text{N}) = 2.7$ and $^3J(^{19}\text{F}-^1\text{H}) = 6.3$ Hz.
Figure 7.1  (a) \(^1\)H NMR (500.138 MHz) and (b) \(^{19}\)F (470.599 MHz) NMR spectra of natural abundance FO\(_2\)SNH\(_2\) in BrF\(_5\) solvent recorded at -61.4 °C. Daggers (†) denote F-on \(^{34}\)S(VI) environment.
\( \delta_{19F} \) (ppm from CFC\(_4\))

\( \delta_{1H} \) (ppm from \((\text{CH}_3)_2\text{Si})\)

Figure 7.2

(a) \( \text{H} \) NMR (500.138 MHz) and (b) \( ^{19F} \) (470.599 MHz) NMR spectra of 99.5\% \( ^{15N} \)-enriched \( \text{FO}_2\text{NH}_2 \) in acetonitrile recorded at 30 °C. Asterisks (*) denote impurities.
The $^1$H NMR resonance of natural abundance $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ in BrF$_5$ solvent at
-57.0 °C is a broad quadrupole collapsed singlet at $\delta(^1\text{H}) = 7.26$ ppm. The $^1$H chemical shift is
deshielded by 2.58 ppm relative to $\text{FO}_2\text{SNH}_2$, as expected upon protonation [cf., $\text{F}_2\text{NH}^-$: $^1\delta(^1\text{H})$
= 7.2 ppm; $\text{F}_2\text{NH}_2^+$: $^1\delta(^1\text{H}) = 14.2$ ppm]. The $^1$H NMR spectrum of 99.5% $^{15}\text{N}$-enriched
$\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ in BrF$_5$ at -57.0 °C [$\delta(^1\text{H}) = 7.30$ ppm] consists of a doublet arising from the
scalar coupling $^1J(^1\text{H},^{15}\text{N}) = 72$ Hz. The magnitude of $^1J(^1\text{H},^{15}\text{N})$ is comparable to that observed
in other inorganic amine derivatives, and indicates protonation of $\text{FO}_2\text{SNH}_2$ at nitrogen but not
at oxygen, since the magnitude of the resulting three-bond $^{15}\text{N}-^1\text{H}$ coupling would be significantly
smaller. The long-range coupling, $^3J(^1\text{H},^{19}\text{F})$, was not resolved. The $^{19}\text{F}$ NMR resonances in BrF$_5$
solvent (-57.0 °C) of natural abundance and 99.5% $^{15}\text{N}$ enriched $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ are singlets at
$\delta(^{19}\text{F}) = 56.47$ and 56.25 ppm, respectively, with no resolution of the scalar couplings $^2J(^{19}\text{F},^{15}\text{N})$
and $^3J(^{19}\text{F},^1\text{H})$.

Significant decomposition of the salt $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ was observed in BrF$_5$ solvent at
-57.0 °C. Singlets observed in the $^{19}\text{F}$ NMR spectra at $\delta(^{19}\text{F}) = 32.08$ and 70.47 ppm are
attributed to decomposition products containing $\text{FO}_2\text{S}$- groups. The former singlet is assignable
to $\text{SO}_2\text{F}_2$, and the latter has not been identified. Integration of the $^{19}\text{F}$ NMR resonances at -57.0
°C indicates that the ratio $\text{FO}_2\text{SNH}_3^+\text{SO}_2\text{F}_2\text{X}$ (X = unidentified product) is 1.00:0.63:0.73. The
decomposition is believed to involve radical formation since a purple color was initially formed,
which faded on mixing to give a clear colorless solution. The NMR resonances were not observed
until the unidentified purple material was quenched. The AX$_4$ pattern of BrF$_5$ solvent is not
exchange broadened. The $^1$H NMR spectrum at -57.0 °C in BrF$_5$ solvent indicates the presence
of several additional exchange broadened lines at $\delta(^1\text{H}) = 5.6, 5.2, 3.4, 2.9$ and 2.3 ppm. The
broad resonance at 5.6 ppm is attributed to HF, and the peak at 5.2 ppm is assigned to $\text{FO}_2\text{SNH}_2$. 


indicating deprotonation of \( \text{FO}_2\text{SNH}_3^+ \). The resonances at 3.4, 2.9 and 2.3 ppm are assigned to H-on-N environments of oxidation products of the \( \text{FO}_2\text{SNH}_3^+ \) cation, where \( \text{BrF}_5 \) is the oxidizing agent. It is not possible to identify the nitrogen-containing oxidation products from the \( ^1\text{H} \) NMR resonances since no couplings are observed and exchange may affect the \( ^1\text{H} \) chemical shifts. By analogy with the decomposition of \( \text{F}_5\text{TeNH}_3^+ \) in \( \text{BrF}_5 \) (Chapter 6), likely nitrogen-containing decomposition products include \( \text{NH}_4^+ \), \( \text{N}_2 \), \( \text{HN}_3 \), \( \text{N}_2\text{H}_4 \), and \( \text{N}_2\text{H}_2 \). Deprotonation of the \( \text{FO}_2\text{SNH}_3^+ \) cation may involve proton exchange equilibria with the nitrogen-containing decomposition products [equation (7.11)]

\[
\text{FO}_2\text{SNH}_3^+ + \text{N}_y\text{H}_y \rightleftharpoons \text{FO}_2\text{SNH}_2 + \text{N}_y\text{H}_{y+1}^+ \quad (7.11)
\]

(C) **RAMAN SPECTROSCOPIC STUDY OF NATURAL ABUNDANCE AND 99.5\% \( ^{15}\text{N} \)-ENRICHED FO\(_2\)SNH\(_2\)**

The Raman spectra of liquid natural abundance and 99.5\% \( ^{15}\text{N} \)-enriched \( \text{FO}_2\text{SNH}_2 \) were obtained at room temperature. Figure 7.3 depicts the Raman spectrum of \( \text{FO}_2\text{SNH}_2 \), and the frequencies are listed in Table 7.1. A total of \( 3N - 6 = 15 \) modes are expected for \( \text{FO}_2\text{SNH}_2 \). Without making assumptions about the orbitals involved in the S-N bond, the mutual orientation of the \( \text{FO}_2\text{S}- \) and \( -\text{NH}_2 \) groups could not be predicted. Therefore, in Table 7.1 the bands were assigned by treating the \( \text{FO}_2\text{SN}^- \) and \( -\text{SNH}_2 \) groups as separate entities of \( C_2 \) point symmetry, each having 9 and 6 vibrational modes, respectively, and by analogy with a previous infrared study of \( \text{FO}_2\text{SNH}_2 \) by Semmoud and Vast.\(^{130}\) Since the highest symmetry for \( \text{FO}_2\text{SNH}_2 \) is \( C_2^* \), all modes are infrared and Raman active.

The nine vibrational modes of the \( \text{FO}_2\text{SN}^- \) group belong to the irreducible representations
Figure 7.3  Raman spectrum of neat liquid natural abundance \( \text{FO}_2\text{SNaN}_2 \) recorded at 25 °C by use of 514.5-nm excitation.
Figure 7.4  Raman spectrum (300 - 1000 cm⁻¹ region) of neat liquid 99.5% ¹⁵N-enriched (upper trace) and natural abundance (lower trace) FO₂SNH₂ recorded at 25 °C by use of 514.5-nm excitation.
6 A' + 3 A'' and were assigned to bands observed in the Raman spectrum of \( \text{FO}_2\text{SNH}_2 \) (Table 7.1); however, all of the bands in the Raman spectrum of \( [^{15}\text{N}]\text{FO}_2\text{SNH}_2 \), except those assigned to the symmetric S-O (\( v_1 \)) and asymmetric S-O (\( v_2 \)) stretching modes (1205.5 and 1417.1 cm\(^{-1} \), respectively) are shifted to lower frequency relative to those in the Raman spectrum of natural abundance \( \text{FO}_2\text{SNH}_2 \) (see Figure 7.4 and Table 7.1). The \( ^{14}/^{15}\text{N} \) isotopic shifts of these bands indicate vibrational coupling of modes that was not implied in the assignments of Semmoud and Vast.\(^{130} \) This justified a revision of their assignments. Firstly, the bands at 964.5 and 797.2 cm\(^{-1} \) were assigned to symmetric S-N and S-F stretching modes in the infrared spectrum of \( \text{FO}_2\text{SNH}_2 \),\(^{130} \) but because both Raman bands exhibit large \( ^{14}/^{15}\text{N} \) isotopic shifts, it is clear that both bands have contributions from the S-N stretching mode. Thus, the bands at 964.5 and 797.2 cm\(^{-1} \) were assigned to asymmetric and symmetric combinations of the S-N and S-F stretching modes. Crow and Lagemann\(^{292} \) reported a similar coupling of \( \nu(\text{S-Br}) \) and \( \nu(\text{S-F}) \) in the infrared spectrum of \( \text{FO}_2\text{SBrF} \), referring to asymmetric and symmetric Br-S-F stretches. Gillespie and Robinson\(^{128} \) chose to treat the S-F and S-Br bonds separately in their assignment of the vibrational spectrum of \( \text{SO}_2\text{BrF} \).

The low frequency bands (360 - 560 cm\(^{-1} \)) have also been reassigned in light of the observed \( ^{14}/^{15}\text{N} \) isotopic shifts. The Raman band at 361.0 cm\(^{-1} \) [\( \Delta \nu(^{14}/^{15}\text{N}) = -4.3 \text{ cm}^{-1} \)] is attributed to the A'' torsional mode, which involves torsional motion of the entire FSO\(_2\text{N}^-\) group and is therefore expected to have an \( ^{14}/^{15}\text{N} \) isotopic dependence. Similar frequencies have been assigned for \( \text{SO}_2\text{F}_2 \)\(^{128} \) (360 cm\(^{-1} \)) and \( \text{SO}_2\text{Cl}_2 \) (388 cm\(^{-1} \))\(^{128} \). The Raman band at 560.0 cm\(^{-1} \) [\( \Delta \nu(^{14}/^{15}\text{N}) = -3.1 \text{ cm}^{-1} \)] was assigned to the in-plane F-S-N bend by analogy with \( \text{SO}_2\text{F}_2 \)\(^{128} \) (\( \delta(\text{SF}_2) = 545 \text{ cm}^{-1} \)). The bands at 501.4 [\( \Delta \nu(^{14}/^{15}\text{N}) = -1.2 \)] and 534.5 [\( \Delta \nu(^{14}/^{15}\text{N}) = -1.7 \)] cm\(^{-1} \) are attributed to bending and rocking modes of the FSO\(_2\text{N}^-\) group by analogy with \( \text{SO}_2\text{F}_2 \) (545
$cm^{-1}$\textsuperscript{128} and \textit{SO}_2\textit{BrF} (497 - 608 $cm^{-1}$).\textsuperscript{128,292} Of these two bands, the band at 534.5 $cm^{-1}$ has the greater $^{14/15}N$ isotopic shift and is, therefore, tentatively assigned to the $A'$ rocking mode [$\rho_c(\textit{FO}_2\textit{SN}^-)$] since this mode involves motion of the entire $\textit{FO}_2\textit{SN}^-$ group. The $v_2$ [$\delta_{\text{sym}}(\textit{SO}_2)$] and $v_8$ [$\rho_r(\textit{SO}_2)$] modes are tentatively assigned to the band at 501.4 $cm^{-1}$.

The six modes of the $\textit{-SNH}_2$ group of $\textit{FO}_2\textit{SNH}_2$ belong to the irreducible representations $4 A' + 2 A''$ and all but one are assignable to bands in the Raman spectrum (Figure 7.3 and Table 7.1), by analogy with the vibrational assignments for \textit{FNH}_2\textsuperscript{239}, \textit{ClNH}_2\textsuperscript{257} and aniline \textit{C}_6\textit{H}_5\textit{NH}_2.\textsuperscript{232} The S-N stretch is identical with $v_3$ of the $\textit{FO}_2\textit{SN}$- group and is not repeated. The symmetric ($v_{10}$) and asymmetric ($v_{13}$) stretches of the NH$_2$ group are assigned to the broad bands at 3422 and 3298 $cm^{-1}$, which are characteristic for primary amines.\textsuperscript{250} The symmetric NH$_2$ bend ($v_{12}$) and the symmetric S-N-H bend ($v_{11}$) are observed at 1553.6 and 1088.1 $cm^{-1}$, respectively. An $^{14/15}N$ isotopic shift is not observed for $v_{11}$ because of the presence of bands from organic impurities in this region of the Raman spectrum of 99.5\% $^{15}N$-enriched $\textit{FO}_2\textit{SNH}_2$ (see Chapter 2). A band attributable to the NH$_2$ wag, $v_{14}$ [$\delta_{\text{asym}}(\textit{SNH})$] was not observed although it is expected at ca. 1200 $cm^{-1}$ by analogy with \textit{FNH}_2 (1233 $cm^{-1}$).\textsuperscript{239} A band attributable to this mode is not observed in the infrared spectrum of \textit{ClNH}_2.$^{257}$
Table 7.1. Raman Spectra and Assignments for $[^{14}\text{N}]\text{FO}_2\text{SNH}_2$ and $[^{15}\text{N}]\text{FO}_2\text{SNH}_2$.

<table>
<thead>
<tr>
<th>Frequency, cm$^{-1}$</th>
<th>$[^{14}\text{N}]\text{FO}_2\text{SNH}_2$</th>
<th>$[^{15}\text{N}]\text{FO}_2\text{SNH}_2$</th>
<th>$\Delta \nu (^{14/15}\text{N})$</th>
<th>Molecular Group</th>
<th>Point Group</th>
<th>Assgn and Approx Mode Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1417.1 (5.7)</td>
<td>1419.4 (6.3)</td>
<td>2.3</td>
<td>FO$_2$S$^-$</td>
<td>$C_s$</td>
<td>$A^n$ $\nu_7$, $\nu_{\text{asym(SO}}_2$)</td>
<td></td>
</tr>
<tr>
<td>1205.5 (100.0)</td>
<td>1206.1 (100.0)</td>
<td>0.6</td>
<td></td>
<td></td>
<td>$A'$ $\nu_1$, $\nu_{\text{sym(SO}}_2$)</td>
<td></td>
</tr>
<tr>
<td>964.5 (26.9)</td>
<td>947.6 (24.0)</td>
<td>-16.9</td>
<td></td>
<td></td>
<td>$A'$ $\nu_{\text{asym [\nu}_3$, $\nu($SN$) + \nu_4$, $\nu($SF$)]}$</td>
<td></td>
</tr>
<tr>
<td>797.2 (25.6)</td>
<td>786.9 (36.2)</td>
<td>-10.3</td>
<td></td>
<td></td>
<td>$A'$ $\nu_{\text{sym [\nu}_3$, $\nu($SN$) + \nu_4$, $\nu($SF$)]}$</td>
<td></td>
</tr>
<tr>
<td>560.0 (19.3)</td>
<td>556.9 (22.8)</td>
<td>-3.1</td>
<td></td>
<td></td>
<td>$A'$ $\nu_6$, $\delta($FSN$)$</td>
<td></td>
</tr>
<tr>
<td>534.5 (22.1)</td>
<td>532.8 (26.1)</td>
<td>-1.7</td>
<td></td>
<td></td>
<td>$A'$ $\nu_5$, $p_x($FO$_2$SN$)$</td>
<td></td>
</tr>
<tr>
<td>501.4 (10.1)</td>
<td>500.2 (13.9)</td>
<td>-1.2</td>
<td></td>
<td></td>
<td>$A'$ $\nu_2$, $\delta_{\text{sym(SO}}_2$)</td>
<td></td>
</tr>
<tr>
<td>361.0 (14.9)</td>
<td>356.7 (18.8)</td>
<td>-4.3</td>
<td></td>
<td></td>
<td>$A^n$ $\nu_8$, $p_x($SO$_2$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$A^n$ $\nu_9$, FO$_2$SN$^-$ torsion</td>
<td></td>
</tr>
<tr>
<td>3422 (5.8)$^c$</td>
<td>3404 (2.4)$^c$</td>
<td>-18</td>
<td>-SNH$_2$</td>
<td>$C_s$</td>
<td>$A'$ $\nu_{10}$, $\nu_{\text{sym(NH}}_2$)</td>
<td></td>
</tr>
<tr>
<td>3298 (26.6)$^c$</td>
<td>3295 (10.3)$^c$</td>
<td>-3</td>
<td></td>
<td></td>
<td>$A^n$ $\nu_{13}$, $\nu_{\text{sym(NH}}_2$)</td>
<td></td>
</tr>
<tr>
<td>1533.3 (3.9)</td>
<td>1551.5 (4.0)</td>
<td>-1.8</td>
<td></td>
<td></td>
<td>$A'$ $\nu_{12}$, $\delta($NH$_2$)</td>
<td></td>
</tr>
<tr>
<td>1088.1 (4.7)</td>
<td>n.o.$^d$</td>
<td></td>
<td></td>
<td></td>
<td>$A'$ $\nu_{11}$, $\delta_{\text{sym(SNH)}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>n.o.</td>
<td></td>
<td></td>
<td></td>
<td>$A^n$ $\nu_{14}$, $\delta_{\text{asym(SNH)}}$</td>
<td></td>
</tr>
</tbody>
</table>

\( ^c \) from Ref. 7, \( ^d \) n.o. = not observed.
Table 7.1 (continued)

*A Assignments for the modes of the FO₂SN- group have been made assuming C₃ symmetry with use of the mode descriptions from reference (292). The assignments for the modes of the -SNH₂ group have been made by assuming C₂ symmetry and with use of the mode descriptions from reference (293). Only five of the six normal modes have been tabulated for the SNH₂ group since the sixth, v(SN) is the same as v₃ for the FO₂SN- group. *b Raman spectra obtained at room temperature with use of 514.5-nm excitation. *c Because of the broadness of the bands attributed to asymmetric and symmetric NH₂ stretching modes, the accuracy of the reported frequencies is estimated to be ± 1 cm⁻¹. *d Peaks caused by organic impurities are observed in this region.
CHARACTERIZATION OF NATURAL ABUNDANCE AND 99.5 % $^{15}$N-
ENRICHED FO$_2$SNH$_3^+$AsF$_6^-$ BY RAMAN SPECTROSCOPY

The Raman spectra of natural abundance and 99.5 % $^{15}$N enriched FO$_2$SNH$_3^+$AsF$_6^-$ were obtained at room temperature. Figure 7.5 depicts the Raman spectrum of FO$_2$SNH$_3^+$AsF$_6^-$, and the frequencies are listed in Table 7.2. A total of 3N - 6 = 18 modes are expected for the FO$_2$SNH$_3^+$ cation; the highest possible point symmetry is $C_3$, so that all modes are both infrared and Raman active. Assignments for the FO$_2$SNH$_3^+$ cation have been aided by observing the $^{14/15}$N isotopic shifts in the Raman spectrum of 99.5% $^{15}$N-enriched FO$_2$SNH$_3^+$AsF$_6^-$ (Table 7.2 and Figure 7.6). Following the procedure for FO$_2$SNH$_2$, assignments for the FO$_2$SNH$_3^+$ cation have been made by treating the FO$_2$SN- ($C_3$) and the -SNH$_3^+$ ($C_3v$) groups separately.

The nine modes of the FO$_2$SN- group have been assigned following the method used for FO$_2$SNH$_2$ (see above). The band at 1503.4 cm$^{-1}$ has been assigned to $\nu_7$, $\nu_{asym}(SO_2)$ by analogy with SO$_2$F$_2$ (1502 cm$^{-1}$)$^{128}$ and SO$_2$BrF (1460 cm$^{-1}$).$^{128,292}$ Similarly, comparison with these compounds allows the assignments of the bands at 1270.3, 1259.1 and 1254.8 cm$^{-1}$ to $\nu_{sym}(SO_2)$ (cf., SO$_2$F$_2$: 1269 cm$^{-1}$,$^{128}$ SO$_2$BrF: 1228 cm$^{-1}$ $^{128,292}$). The presence of three bands assigned to $\nu_{sym}(SO_2)$ may arise from factor group splitting. The only band assigned to the SO$_2$ stretching modes which exhibits a measurable $^{14/15}$N isotopic shift is the most intense band attributed to $\nu_{sym}(SO_2)$ at 1259.1 cm$^{-1}$. The value of the shift (-0.6 cm$^{-1}$) is at the detection limit for the $^{14/15}$N frequency shifts. Therefore these bands do not contain significant contributions from modes that involve the motion of the nitrogen center.

The S-F stretch has been assigned to the band at 862.3 cm$^{-1}$ [cf., SO$_2$F$_2$:128 885 cm$^{-1}$ ], which does not have an $^{14/15}$N isotopic shift. The bands at 709.9 and 677.2 cm$^{-1}$ exhibit large $^{14/15}$N isotopic shifts (-5.1 and -2.1 cm$^{-1}$, respectively) and are similar to $\nu$(SN) for FO$_2$SNH$_2$ and
Figure 7.5  Raman spectrum of solid natural abundance FO$_2$SNH$_3^+$AsF$_6^-$ recorded at 25 °C by use of 514.5-nm excitation.
Figure 7.6  Raman spectrum (300 - 750 cm$^{-1}$ region) of solid 99.5\% $^{15}$N-enriched (upper trace) and natural abundance (lower trace) FO$_2$SNH$_3^+$AsF$_6^-$ recorded at 25 °C by use of 514.5-nm excitation.
thus are both assigned to $\nu_3$ [v(S-N)]. The presence of two bands is attributed to solid state
effects.

The band at 521.4 cm$^{-1}$ has the largest $^{14/15}\text{N}$ isotopic shift (-5.69 cm$^{-1}$) of the bands
attributable to the bending modes; by analogy with FO$_2$SNH$_2$ it is assigned to $\nu_6$, the in-plane F-S-N bend.

The bands at 479.7 and 496.9 cm$^{-1}$ are assigned to the bending modes of the FSO$_2$N-
group, namely $\nu_2$ [$\delta_{\text{sym}}$(SO$_2$)], $\nu_5$ [$\rho_t$(FO$_2$SN-); in-plane FSN rock] and $\nu_8$ [SO$_2$ asymmetric rock].
The rocking motion of the FO$_2$SN- group is assigned to the band at 496.9 cm$^{-1}$ which has the
larger $^{14/15}\text{N}$ isotopic shift [-1.1 cm$^{-1}$] since this mode involves motion of the nitrogen atom. The
SO$_2$ rocking modes, $\nu_8$ [$\delta_{\text{asy}}$(SO$_2$)] and $\nu_2$ [$\delta_{\text{sym}}$(SO$_2$)] are assigned to the band at 479.7 cm$^{-1}$
although these modes may also contribute to the band at 496.9 cm$^{-1}$. The $^{14/15}\text{N}$ isotopic shifts
of the bands at 479.7 and 496.9 cm$^{-1}$ imply some vibrational coupling of the SO$_2$ asymmetric rock
and symmetric bending modes with the FO$_2$SN- rocking and F-S-N bending modes. An exact
description of the vibrational coupling would require a normal coordinate analysis, which is not
necessary for the assignment of the Raman spectra in the present study.

The band at 334.6 cm$^{-1}$ is assigned to the torsional mode of the FO$_2$SN- group, which is
similar to that observed in FO$_2$SNH$_2$ (361.0 cm$^{-1}$) and SO$_2$F$_2$ (388 cm$^{-1}$).$^{128}$

The nine modes of the -SNH$_3$ group belong to the irreducible representations 3 A$_1$ + 3
E ($C_{3v}$ point symmetry), all of which are infrared and Raman active. All nine modes have been
assigned to bands in the Raman spectrum of FO$_2$SNH$_3^+$AsF$_6^-$ (Figure 7.5) and are listed in Table
7.2. The S-N stretching mode is identical to $\nu_3$ of the FO$_2$SN- group and is not repeated.
Fluorescence prevented the observation of the low-intensity bands associated with the -SNH$_3$
group in the Raman spectrum of 99.5% $^{15}\text{N}$-enriched FO$_2$SNH$_3^+$AsF$_6^-$, so that $^{14/15}\text{N}$ isotopic
shift data are not available to confirm the bands in the Raman spectrum of the natural abundance FO₂SNH₃⁺AsF₆⁻. However, assignments other than those given are unlikely.

The asymmetric stretching modes are assigned to the peaks at 3168, 3100 and 3024 cm⁻¹, by analogy with FNH₃⁺SO₃F⁻ ²⁹⁴,²⁹⁵ [v₅ asym(NH₃) = 3000 cm⁻¹, v₅ sym(NH₂) = 2735 cm⁻¹]. Since three peaks are observed, it is not possible to assign the peaks rigorously to the asymmetric and symmetric stretching modes, although v₅ asym(NH₃) is usually greater than v₅ sym(NH₂).

The bending modes δ sym(NH₃) [v₁₁] and δ asym(NH₂) [v₁₃] are assigned to the bands at 1438.6 and 1503.4 cm⁻¹, respectively, by analogy with FCH₃ ²⁹⁶ [δ sym(CH₃) = 1460 cm⁻¹; δ asym(CH₃) = 1468 cm⁻¹] and the FNH₃⁺ cation in FNH₃⁺CF₃SO₃⁻ ²⁹⁵ [δ sym(NH₃) = 1523 cm⁻¹; δ asym(NH₂) = 1585 cm⁻¹]. The roểnmg mode p₁₄ (p₁(SNH)) is assigned to the band at 1040.5 cm⁻¹ by analogy with FCH₃ (1183 cm⁻¹) ²⁹⁶ and the FNH₃⁺ cation (1262 cm⁻¹).²⁹⁵ The somewhat lower value of p₁(SNH) in the FO₂SNH₃⁺ cation is expected since the mass of the FO₂S⁻ group is much greater than F in FCH₃ and FNH₃⁺.

A total of six bands can be attributed to the AsF₆⁻ anion (Figure 7.5 and Table 7.2). These bands are best assigned modes which belong to the irreducible representations A₁g + E₈ + T₂₈ + 3 T₁u under O₉ point symmetry by comparison with M⁺AsF₆⁻ salts. (M = O₂,²⁹⁷ Cs,²⁹⁷ and OH₃.¹⁷¹ Bands in the Raman spectrum of FO₂SNH₃⁺AsF₆⁻ are attributable to all modes of AsF₆⁻ except v₆ (T₁u), which is often not observed¹⁵⁹,¹⁷¹ although it is expected at ca. 252 cm⁻¹. The totally symmetric v₁ (A₁g) mode, which usually gives rise to the most intense AsF₆⁻ band in the Raman spectra of AsF₆⁻ salts, is believed to overlap with v(S-N) of the FO₂SNH₃⁺ cation at 709.9 cm⁻¹. From the number of bands observed, it is clear that the symmetry of the AsF₆⁻ anion in FO₂SNH₃⁺AsF₆⁻ is lower than O₉, since under O₉ symmetry only v₁, v₂ and v₅ are Raman active. However, lowering of the AsF₆⁻ site symmetry to C₂ᵥ or lower would result in the observation of
bands attributable to all modes. The lowering of the AsF$_6^-$ symmetry in the solid may result from interactions with the cation through fluorine bridging or from a low site symmetry for AsF$_6^-$ within the unit cell. Of the doubly or triply degenerate modes, $v_5$ ($T_{2g}$) is split with unequal intensities and $v_2$ ($E_g$) is broad, indicating that the degeneracy has been removed but the peak separation has not been resolved. Qureshi and Aubke$^{298}$ reported a similar splitting of $v_5$ in the hexafluoroarsenate salts of several nitrogen cations (ONF$_2^+$, N$_2$F$_3^+$, NO$^+$, NO$_2^+$) and noted that this mode appeared to be particularly sensitive to site symmetry lowering effects.

The low intensity peak at 83.8 cm$^{-1}$ is attributed to a lattice mode vibration.
<table>
<thead>
<tr>
<th>frequency, cm⁻¹</th>
<th>$[^{14}\text{N}]\text{F}O_2\text{S}N\text{H}_3^+$</th>
<th>$[^{15}\text{N}]\text{F}O_2\text{S}N\text{H}_3^+$</th>
<th>Δν(¹⁴/¹⁵N)</th>
<th>Molecular Group</th>
<th>Point Group</th>
<th>Assign and approx mode description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1503.4 (3.8)</td>
<td>1270.3 (sh)</td>
<td>n.o.</td>
<td></td>
<td></td>
<td></td>
<td>FO₂S⁻</td>
</tr>
<tr>
<td>1259.1 (48.1)</td>
<td>1258.5 (40.0)</td>
<td>-0.6</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1254.8 (sh)</td>
<td>n.o.</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>862.3 (16.5)</td>
<td>862.1 (17.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>709.9 (100.0)</td>
<td>704.8 (100.0)</td>
<td>-5.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>677.2 (23.1)</td>
<td>675.1 (19.5)</td>
<td>-2.1</td>
<td></td>
<td></td>
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<tr>
<td>521.4 (35.5)</td>
<td>515.7 (29.9)</td>
<td>-5.7</td>
<td></td>
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</tr>
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<td>496.9 (17.9)</td>
<td>495.8 (15.6)</td>
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<td></td>
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<td>479.7 (14.4)</td>
<td>479.1 (12.6)</td>
<td>-0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>334.6 (21.0)</td>
<td>332.2 (19.1)</td>
<td>-2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-SNH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C₃v</td>
<td></td>
</tr>
<tr>
<td>3167.9 (2.3)</td>
<td>3100.4 (6.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3024.4 (0.9)</td>
<td>1503.4 (3.8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1438.6 (1.8)</td>
<td>1040.5 (3.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>738.6 (5.6)</td>
<td>709.9 (100.0)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>565.6 (13.7)</td>
<td>410.3 (4.2)</td>
<td></td>
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</tr>
<tr>
<td>410.3 (4.2)</td>
<td></td>
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</tr>
</tbody>
</table>

Table 7.2. Raman Spectra and Assignments for $[^{14}\text{N}]\text{F}O_2\text{S}N\text{H}_3^+\text{AsF}_6^-$ and $[^{15}\text{N}]\text{F}O_2\text{S}N\text{H}_3^+\text{AsF}_6^-$.
\[ T_{2g} \quad \nu_5 \]
\[ T_{1u} \quad \nu_6 \]

* Assignments for the modes of the FO\(_2\)SN\(_-\) group have been made by assuming \( C_2 \) symmetry and with use of the mode descriptions from references (130), (292), and (299). Assignments for the -SNH\(_3\) group have been made by assuming \( C_{3v} \) symmetry, and with use of the mode description of reference (300). Only five of the six normal modes of the -SNH\(_3\) group have been tabulated; the sixth is identical to \( \nu_3 \) for the FO\(_2\)SN- group \([\nu(\text{SN})]\). * Raman spectra obtained at room temperature by use of 514.5-nm excitation. * The totally symmetric \( \nu_1 \) (\( A_{1g} \)) mode is presumed to overlap with the intense band at 709.9 cm\(^{-1}\) assigned to \( \nu_3 \) \([\nu(\text{SN})]\) of the FO\(_2\)SNH\(_3\)\(^+\) cation. * Because of broadness, the errors associated with the bands assigned to \( \nu_{10} \) \([\nu_{\text{sym}}(\text{NH}_3)]\) and \( \nu_{12} \) \([\nu_{\text{sym}}(\text{NH}_2)]\) are estimated to be \( \pm 1 \) cm\(^{-1}\).
COMPARISON OF THE BONDING IN $\text{FO}_2\text{SNH}_2$ AND THE $\text{FO}_2\text{SNH}_3^+$ CATION BY RAMAN SPECTROSCOPY

The bonding in $\text{FO}_2\text{SNH}_2$ and the mercury salt $\text{HgNSO}_2\text{F}$ was investigated using infrared spectroscopy by Semmoud and Vast.\textsuperscript{130} Differences in the S-O, S-F, and S-N bond orders of $\text{FO}_2\text{SNH}_2$ and $\text{FO}_2\text{SNHg}$, as reflected in the corresponding symmetric infrared stretching frequencies, was investigated and compared with several sulfur(VI) oxyacid derivatives. The present Raman spectroscopic study of $\text{FO}_2\text{SNH}_2$ and the $\text{FO}_2\text{SNH}_3^+$ cation provides information that allows the bonding changes resulting from protonation of $\text{FO}_2\text{SNH}_2$ to be assessed and related to the work of Semmoud and Vast.\textsuperscript{130}

Semmoud and Vast\textsuperscript{130} have shown that deprotonation of $\text{FO}_2\text{SNH}_2$ to give $\text{FO}_2\text{SNHg}$ results in decreases in $\nu_{\text{sym}}$(S-O) and $\nu$(S-F) by 46 and 37 cm\textsuperscript{-1}, respectively and an increase in $\nu$(S-N) by 70 cm\textsuperscript{-1}, as shown in Table 7.3. This has been explained by invoking $(p-d)\pi$ bonding involving vacant 3$d$ orbitals on sulfur and filled 2$p$ orbitals on oxygen and nitrogen.\textsuperscript{130} The S-N bond length in $\text{FO}_2\text{SNH}_2$, as determined by electron diffraction\textsuperscript{286}, was 1.60(1) Å, which is significantly shorter than the single bond in $\text{H}_2\text{NSO}_3$ [1.7714(3) Å].\textsuperscript{287} and has been interpreted as evidence for S-N $\pi$ bonding.\textsuperscript{286} Deprotonation of $\text{FO}_2\text{SNH}_2$ increases the availability of 2$p$ orbitals on the nitrogen atom for $\pi$-bonding to the sulfur atom, resulting in an increase in the S-N bond order, which is reflected in the increase in $\nu$(S-N). The S-O bonds are weakened since the same 3$d$ orbitals on sulfur ($d^2$-$\gamma^2$ and $d^2$) are used to form S-O $\pi$-bonds.\textsuperscript{288} The decrease in $\nu$(S-F) may result from an increase in the S-F bond ionic character or a decrease in the S-F $\pi$-bonding.

As noted by Semmoud and Vast,\textsuperscript{130} similar effects are observed for the isoelectronic compounds $\text{AgO}_2\text{SNH}_2$ and $\text{Ag}_2\text{O}_3\text{SN}$. The existence of S-N $\pi$-bonding in $\text{O}_2\text{SNH}_2^+$ is evidenced by the S-N bond length [1.60(1) Å],\textsuperscript{285} which is substantially shorter than the S-N single bond in $\text{H}_2\text{NSO}_3$.\textsuperscript{287}
(see above). As shown in Table 7.3, deprotonation of the $\text{H}_2\text{NSO}_3^-$ anion to give $\text{NSO}_3^2$ results in a decrease in $\nu_{\text{sym}}(\text{S-O})$ by 38 cm$^{-1}$ and an increase in $\nu_{\text{sym}}(\text{S-N})$ by 134 cm$^{-1}$, again a result of increased S-N π-bonding.

The higher $\nu_{\text{sym}}(\text{S-O})$ frequencies for the $\text{H}_x\text{NSO}_2\text{F}$ derivatives relative to the analogous $\text{H}_x\text{NSO}_3$ ($x = 0, 2, 3$) species in Table 7.3 may be explained by use of the resonance structures proposed by Gillespie and Robinson$^{301}$ to describe the covalent and ionic contributions to the bonding of sulfuryl compounds (resonance Structures 7.1 and 7.2). The covalent resonance

\[ \begin{array}{c}
\text{L} \equiv \text{S} \equiv \text{NH}_x \\
\text{:O:} \\
\text{L} \equiv \text{S} \equiv \text{NH}_x \\
\text{:O:} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{L} \equiv \text{S} \equiv \text{NH}_x \\
\text{O}^\equiv \text{S} \equiv \text{NH}_x \\
\text{:O:} \\
\text{L} \equiv \text{S} \equiv \text{NH}_x \\
\text{:O:} \\
\end{array} \]

Structure 7.1 predominates in the presence of a highly electronegative ligand (L) which increases the electronegativity of sulfur. The greater electronegativity of F compared to O$^-$ therefore results in increased S-O bond orders and correspondingly higher $\nu_{\text{sym}}(\text{S-O})$ frequencies. In accordance with this, the values of $\nu_{\text{sym}}(\text{S-O})$ for $\text{SO}_2\text{F}_2$ (1269 cm$^{-1}$)$^{128}$ and $\text{F}_2\text{NSO}_2\text{F}$ (1250 cm$^{-1}$)$^{130}$ are among the highest values known.$^{301}$

The Raman data for $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ extends the comparison of the sulfuryl amides $\text{H}_x\text{NSO}_3$ and the fluorosulfuryl amides $\text{H}_x\text{NSO}_2\text{F}$ ($x = 0, 2, 3$) of Semmoud and Vast.$^{130}$ The
similarity of $\nu_{\text{sym}}(\text{S-N})$ for $\text{H}_3\text{NSO}_3$ (680 cm$^{-1}$) and the $\text{FO}_2\text{SNH}_3^+$ (709.9 cm$^{-1}$) indicate similar S-N bond orders (i.e., SN single bonds). The larger value of $\nu_{\text{sym}}(\text{SO})$ for $\text{FO}_2\text{SNH}_3^+$ than for $\text{H}_3\text{NSO}_3$ is predicted by the dominance of resonance Structure 7.1 over 7.2 (see above).$^{301}$ As shown in Table 7.3, protonation of $\text{FO}_2\text{SNH}_2$ to give the $\text{FO}_2\text{SNH}_3^+$ cation lowers $\nu(\text{S-N})$ by 254.6 cm$^{-1}$, while $\nu(\text{S-F})$ and $\nu_{\text{sym}}(\text{S-O})$ are increased by 65.1 and 53.6 cm$^{-1}$, respectively. The changes in the stretching frequencies are consistent with weakening of the S-N bond and strengthening of the S-O and S-F bonds and are expected since the nitrogen atom lone pair is no longer available for S-N $\pi$-bonding upon protonation. Reduction of the S-N $\pi$ bond order is accompanied by an increase in the S-O $\pi$ bond order. Fluorine is not expected to be a good $\pi$ donor to sulfur, thus S-F $\pi$ bonding is not an appropriate explanation for the increase in $\nu(\text{S-F})$. However, protonation of nitrogen is expected to increase the electronegativity of the sulfur center, thus reducing the ionic character and strengthening the S-F bond. The trends observed in $\nu_{\text{sym}}(\text{S-O})$ and $\nu_{\text{sym}}(\text{S-N})$ for the $\text{FO}_2\text{SNH}_2 / \text{FO}_2\text{SNH}_3^+$ pair parallel those observed for $\text{H}_2\text{NSO}_3^- / \text{H}_3\text{NSO}_3$, indicating that similar bonding changes occur upon protonation of $\text{FO}_2\text{SNH}_2$ and $\text{H}_2\text{NSO}_3^-$. 
Table 7.3. Selected Vibrational Frequencies and Bond Lengths of Some Sulfur(VI) Oxyacid Derivatives.

<table>
<thead>
<tr>
<th></th>
<th>Vibrational Frequencies, cm$^{-1}$</th>
<th>Bond Lengths, Å</th>
<th>refs</th>
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</thead>
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<tr>
<td></td>
<td>$v_{\text{sym(SO)}}$</td>
<td>$v_{\text{sym(SN)}}$</td>
<td>$v_{\text{sym(SF)}}$</td>
</tr>
<tr>
<td>$\text{H}_3\text{NSO}_3$</td>
<td>1065</td>
<td>680</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{NSO}_3^{-}$</td>
<td>1038</td>
<td>796</td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}_3\text{NSO}_3$</td>
<td>1000</td>
<td>930</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_3\text{NSO}_2\text{F}^{+}$</td>
<td>1259.1</td>
<td>709.9</td>
<td>862.3</td>
</tr>
<tr>
<td>$\text{H}_2\text{NSO}_2\text{F}^{d,e}$</td>
<td>1205.5</td>
<td>964.5</td>
<td>797.2</td>
</tr>
<tr>
<td>$\text{HgNSO}_2\text{F}$</td>
<td>1160</td>
<td>1035</td>
<td>760</td>
</tr>
<tr>
<td>$\text{SO}_2\text{F}_2$</td>
<td>1269</td>
<td>848</td>
<td></td>
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<tr>
<td>$\text{F}_2\text{NSO}_2\text{F}$</td>
<td>1250</td>
<td>715</td>
<td>850</td>
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</tbody>
</table>
Table 7.3 (continued)

- Vibrational data obtained from infrared spectra unless otherwise specified.  
- Bond lengths obtained from single crystal X-ray diffraction unless otherwise specified.  
- Vibrational data obtained from infrared spectra of AgH$_2$NSO$_3$, ref (130). Bond lengths obtained from single crystal X-ray analysis of KH$_2$NSO$_3$, ref (285).  
- Vibrational frequencies obtained from Raman spectra; this work.  
- Bond lengths obtained from electron diffraction [ref (286)].  
- Bond lengths obtained from microwave data [ref (302)].
CHAPTER 8

[FLUOROSULFURYLAMIDO]XENONIUM(II) HEXAFLUOROARSENATE

$\text{FO}_2\text{SN(H)-Xe}^+\text{AsF}_6^-$

INTRODUCTION

While many examples of compounds containing xenon bonded to oxygen or fluorine and of xenon bonded to other highly electronegative inorganic ligands through oxygen were synthesized immediately following the discovery of noble-gas reactivity, over a decade had elapsed before an example with a ligating atom other than oxygen or fluorine, namely nitrogen, was synthesized and two decades before the Xe-N bond in $\text{FXeN(SO}_2\text{F})_2$ was definitively characterized in the solid state by X-ray crystallography and in solution by multinuclear magnetic resonance spectroscopy. Other imidosulfurylfluoride xenon-nitrogen bonded species have since been synthesized and characterized primarily by use of NMR spectroscopy, namely $\text{Xe}[\text{N(SO}_2\text{F})_2]_2$, $\text{F}[\text{XeN(SO}_2\text{F})_2]_2^+$, $\text{XeN(SO}_2\text{F})_2^+\text{AsF}_6^-$, and $\text{XeN(SO}_2\text{F})_2^+\text{Sb}_3\text{F}_{16}^-$. The last salt has also been characterized by single-crystal X-ray diffraction. The compound, $\text{Xe}[\text{N(SO}_2\text{CF})_2]_2$, has also been prepared and characterized and is the most stable imido derivative of xenon presently known. Recently the scope of xenon-nitrogen chemistry has been dramatically expanded by taking advantage of the Lewis acid properties of noble-gas cations. A significant number of oxidatively resistant nitrogen bases (D) have been shown to form xenon-nitrogen bonded Lewis acid-base adduct cations with XeF$^+$ of the form D-XeF$^+$, such as HC≡N, alkynitriles and perfluoroalkynitriles, trihalogen triazines, pentafluorobenzenenitrile, and perfluoropyridines. The krypton(II) adduct cations, HC≡N-
KrF$^{+}$ and R$_2$C=CN-KrF$^+$ (R$_F$ = CF$_3$, C$_2$F$_5$, n-C$_3$F$_7$) have also been synthesized and characterized in this laboratory and provide the first examples of krypton bonded to an element other than fluorine.

The present Chapter describes the synthesis and characterization of the [fluorosulfurylamido] xenonium(II) cation, FO$_2$SN(H)-Xe$^+$, at low temperature in BrF$_5$ and HF solvents. The natural abundance and 99.5% $^{15}$N-enriched salts, FO$_2$SN(H)-Xe$^+$AsF$_6^-$, have been synthesized in BrF$_5$ and HF solvents and characterized by $^{19}$F, $^1$H, and $^{129}$Xe NMR spectroscopy.

RESULTS AND DISCUSSION

(A) PREPARATION OF FO$_2$SN(H)-Xe$^+$AsF$_6^-$ IN HF AND BrF$_5$ SOLVENTS

The reaction of FO$_2$SNH$_3^+$AsF$_6^-$ with XeF$_2$ was carried out according to equation (8.1) by combining stoichiometric amounts of the reactants in BrF$_5$ solvent and warming to -62 to -58 °C to effect reaction and dissolution, and gave a pale yellow solution. The FO$_2$SN(H)-Xe$^+$ cation was significantly decomposed at this temperature. Alternately, FO$_2$SN(H)-Xe$^+$AsF$_6^-$ was generated according to equation (8.2) by combining stoichiometric amounts of FO$_2$SNH$_2$ and

\[
\text{FO}_2\text{SNH}_3^+\text{AsF}_6^- + \text{XeF}_2 \rightleftharpoons \text{FO}_2\text{SN(H)-Xe}^+\text{AsF}_6^- + 2 \text{HF} \quad (8.1)
\]

cation in HF solvent and warming to -50 °C to effect reaction. A pale yellow solution above
white and yellow solids was present at this temperature; complete decomposition of the FO₂S₅(H)-Xe⁺ cation occurred after ca. 1 hour. Warming of reaction mixtures to -35 °C resulted in complete decomposition within ca. 30 seconds. Decomposed samples invariably consisted of a colorless supernatant and a white precipitate. As a result of the instability and relatively low concentration of FO₂S₅(H)-Xe⁺AsF₆⁻ in BrF₅ and HF solvents, no attempt was made to isolate the salt.

(B) CHARACTERIZATION OF FO₂S₅(H)-Xe⁺AsF₆⁻ BY ^{129}Xe, ^{1}H AND ^{19}F NMR SPECTROSCOPY

The ^{129}Xe, ^{1}H and ^{19}F NMR spectra of the natural abundance and 99.5% ^{15}N-enriched FO₂S₅(H)-Xe⁺ cation in solution are consistent with the xenon-nitrogen bonded structure illustrated in Structure 8.1.

The ^{129}Xe NMR spectrum of the FO₂S₅(H)-Xe⁺ cation in BrF₅ solvent (-57.7 °C) consists of a singlet at -2663 ppm (Δν₁/₂ = 222 Hz) as shown in Figure 8.1a. The ^{129}Xe resonance was observed at δ(^{129}Xe) = -2616 ppm (Δν₁/₂ = 183 Hz) in HF solvent at -48.9 °C, but the presence of undissolved material in the HF sample resulted in an irregular line shape. Attempts to dissolve the solid material by warming the HF sample to -35 °C resulted in rapid (ca. 30 seconds) decomposition of the FO₂S₅(H)-Xe⁺ cation, as shown by the disappearance of the ^{129}Xe resonance. As a result, all further work was performed in BrF₅ solvent, in which the reagents were soluble at lower temperatures. The absence of any resolved couplings in the ^{129}Xe NMR spectra is consistent with the absence of an Xe-F bond, since the range of the one-bond scalar couplings, \( {^1J(^{129}Xe, ^{19}F)} \), for xenon(II) is 7594 (XeF⁺ in SbF₅ solvent, 25 °C)⁷⁸ to 5621 Hz (XeF₂ in BrF₅ solvent, -52 °C),⁷¹ which is much greater than the line widths of the ^{129}Xe resonances for the
8.1
Figure 8.1  $^{129}$Xe NMR spectra (139.051 MHz) of (a) natural abundance FO$_2$SN(H)-Xe$^+$ AsF$_6^-$ recorded at -57.7 °C and (b) 99.5% $^{15}$N-enriched FO$_2$SN(H)-Xe$^+$AsF$_6^-$ recorded at -61.0 °C in BrF$_5$ solvent.
FO₂SN(H)-Xe⁺ cation. The $^{129}$Xe NMR chemical shift is similar to that observed for xenon(II)-nitrogen bonded cations in which the group electronegativity of the ligand is relatively low [see Section (C) of this Chapter]. Examples include F₅TeN(H)-Xe⁺ [δ($^{129}$Xe) = -2902 ppm; see Chapter 5], F₅SN(H)-Xe⁺ [δ($^{129}$Xe) = -2886 ppm],²⁶,¹⁸⁰ and F₄S≡N-Xe⁺ [δ($^{129}$Xe) = -2672 ppm].²⁶,¹⁸⁰ The Xe-F bonds for all of these species are ionized in solution.

The one-bond Xe-N scalar coupling is not observed in the $^{129}$Xe NMR spectra of natural abundance FO₂SN(H)-Xe⁺AsF₆⁻ in HF and BrF₅ solvents because of quadrupolar collapse of the Xe-N scalar coupling caused by the rapid relaxation of the directly bonded $^{14}$N nucleus ($I = 1$) in an asymmetric electric field. The geometry at nitrogen in FO₂SN(H)-Xe⁺ may be pyramidal or planar depending on the relative contributions of resonance Structures 8.2 - 8.4. Resonance Structure 8.2 represents a pure σ contribution to Xe-N and S-N bonding. Dominance of this resonance structure implies formal sp³-hybridization with a pyramidal nitrogen geometry. The presence of a lone pair of electrons is expected to result in a significant σfg at the nitrogen nucleus. Resonance Structures 8.3 and 8.4 represent Xe-N and S-N π bonding contributions, which imply a trigonal planar, formally sp²-hybridized nitrogen center. Evidence in favor of xenon(II)-ligand π-bonding is provided in the $^{19}$F and $^{13}$C NMR spectra of the xenon-carbon bonded cations R-Xe⁺ (R = C₆F₅-Xe⁺,⁹⁵,⁹⁹ 2,4,6-F₃C₆H₂-Xe⁺,⁹⁸ 2,6-F₂C₆H₃-Xe⁺,²⁵³ 2-FC₆H₄-Xe⁺ and 4-FC₆H₄-Xe⁺,²⁵³), where the deshieldings of the aryl fluorine $^{19}$F and aryl carbon $^{13}$C NMR resonances in the 2, 4 and 6 positions on the aryl ring are consistent with xenon-carbon π-bonding.⁹⁸,²⁵³ Resonance Structure 8.4 represents the contribution of sulfur-nitrogen π-bonding, which may be significant by analogy with the (FO₂S)$_2$NXe⁺Sb₃F₁₆⁻ cation,⁶⁰ in which the trigonal planar nitrogen geometry and the S-N bond lengths [1.68(1) - 1.70(1) Å] that are significantly less than S-N single bonds [cf., O₃SNH₃; S-N = 1.771±(3) Å]²⁸⁷ indicate substantial S-N π-bonding.
8.2

8.3

8.4

etc.
and formal $sp^2$-hybridization at the nitrogen atom. The trigonal planar nitrogen geometries in the related imidofluorosulfanyl xenon(II) compounds $\text{FXeN(SO}_2\text{F})_2$, $\text{XeN(SO}_2\text{F})_2^+$ and $\text{Xe}[\text{N(SO}_2\text{F})_2]_2$ all have significant electric field gradients at nitrogen, resulting in rapid relaxation of the $^{14}\text{N}$ nuclei so that the $^{14}\text{N}$ NMR chemical shifts and the xenon-nitrogen scalar couplings were not observed. Nitrogen-15 enrichment was necessary to observe the xenon-nitrogen scalar couplings in these compounds. In the present study $^{15}\text{N}$-enrichment of the $\text{FO}_2\text{SN(H)}$-$\text{Xe}^+$ cation was also required to observe the xenon-nitrogen scalar coupling. The $^{129}\text{Xe}$ NMR spectrum of 99.5% $^{15}\text{N}$-enriched $\text{FO}_2\text{SN(H)}$-$\text{Xe}^+$AsF$_6^-$ in BrF$_5$ solvent at -61.0 °C (Figure 8.1b) consists of a doublet arising from $^1J(^{129}\text{Xe},^{15}\text{N}) = 109$ Hz [$^1K(\text{Xe-N}) = 0.322 \times 10^{22}$ NA$^{-2}$m$^{-3}$] centered at $\delta(^{129}\text{Xe}) = -2660$ ppm [$\Delta\nu_{1/2} = 63$ Hz]. As shown in Table 8.1, the value of the reduced coupling constant, $^1K(\text{Xe-N})$, for $\text{FO}_2\text{SN(H)}$-$\text{Xe}^+$ is similar in magnitude to those observed in related cations containing xenon-nitrogen bonds [cf., $\text{F}_2\text{TeN(H)}$-$\text{Xe}^+$ (see Chapter 5): $0.401 \times 10^{22}$ NA$^{-2}$m$^{-3}$; (FO$_2$S)$_2$N-$\text{Xe}^+$, $0.272 \times 10^{22}$ NA$^{-2}$m$^{-3}$]. The alternative xenon-oxygen bonded structure for the cation, namely $\text{FO(NH)SO}_2$-$\text{Xe}^+$, is shown in Structure 8.5, and may be discarded because the magnitude of the xenon-nitrogen scalar coupling is similar to known values of $^1K(\text{Xe-N})$. The magnitude of $^2K(\text{Xe-N})$ in the hypothetical xenon-oxygen bonded cation is expected to be less than that observed. Although no two bond xenon-nitrogen coupling constants are known for comparison, the one- and two-bond xenon-carbon coupling constants observed for (CH$_3$)$_3$CC=C-$\text{Xe}^+$ are 120 and 79 Hz, respectively, illustrating the expected decrease in magnitude. The hypothetical xenon-oxygen bonded cation is also unlikely since all xenon(II) derivatives of $\text{HN(SO}_2\text{F})_2$ contain exclusively xenon-nitrogen bonds in solution [cf., $\text{FXeN(SO}_2\text{F})_2$, $\text{Xe}[\text{N(SO}_2\text{F})_2]_2$ and $\text{XeN(SO}_2\text{F})_2^+$]. The line width of the $^{129}\text{Xe}$
Table 8.1. Comparison of $^{129}$Xe NMR Chemical Shifts and One-Bond Xenon-Nitrogen Reduced Coupling Constants of Some Compounds Containing Xenon(II)-Nitrogen Bonds.\(^1\)

<table>
<thead>
<tr>
<th>Species</th>
<th>$\delta^{129}$Xe, (ppm)</th>
<th>Hybridization at Nitrogen</th>
<th>$^{1}K$(Xe-N) ($10^{22}$ N A$^{-2}$ m$^{-3}$)</th>
<th>T (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC≡N-XeF$^+$</td>
<td>-1555 (-1570)</td>
<td>$sp$</td>
<td>1.381$^b$</td>
<td>-10 (-58)</td>
<td>72,73</td>
</tr>
<tr>
<td>s-C$_3$F$_3$N$_2$N-XeF$^+$</td>
<td>-1808 (-1863)</td>
<td>$sp^2$</td>
<td>1.013</td>
<td>-5 (-50)</td>
<td>71</td>
</tr>
<tr>
<td>C$_3$F$_5$N-XeF$^+$</td>
<td>-1872 (-1922)</td>
<td>$sp^2$</td>
<td>0.983</td>
<td>-30 (-30)</td>
<td>75</td>
</tr>
<tr>
<td>(FO$_2$S)$_2$N-XeF$^c$</td>
<td>-2009</td>
<td>$sp^2$</td>
<td>0.913$^b$</td>
<td>-40</td>
<td>59</td>
</tr>
<tr>
<td>(FO$_2$S)$_2$N-XeF$^d$</td>
<td>-1943</td>
<td>$sp^2$</td>
<td>0.272$^b$</td>
<td>25</td>
<td>60</td>
</tr>
<tr>
<td>FO$_2$SN(H)-Xe$^+$</td>
<td>-2616 (-2660)</td>
<td>$sp^2$ or $sp^3$</td>
<td>0.322$^b$</td>
<td>-61</td>
<td>This work</td>
</tr>
<tr>
<td>F$_4$S=N-Xe$^+$</td>
<td>-2672</td>
<td>$sp^2$</td>
<td></td>
<td>-20</td>
<td>26,180</td>
</tr>
<tr>
<td>F$_5$TeN(H)-Xe$^+$</td>
<td>-2840 (-2902)</td>
<td>$sp^3$</td>
<td>0.401$^b$</td>
<td>-45</td>
<td>c</td>
</tr>
<tr>
<td>F$_5$SN(II)-Xe$^+$</td>
<td>-2886</td>
<td>$sp^3$</td>
<td></td>
<td>-20</td>
<td>26,180</td>
</tr>
</tbody>
</table>

\(^1\) $^{129}$Xe NMR parameters, unless otherwise indicated, were determined in HIF and in BrF$_5$ (in parentheses) solvent. \(^b\) Recorded for the $^{15}$N enriched cation. \(^c\) Measured in SO$_2$ClF solvent. \(^d\) Measured in SbF$_5$ solvent. \(^e\) Chapter 5 of this work.
resonance is larger than previously known examples of the long range couplings $^2J(^{129}\text{Xe}^{-1}\text{H})$ [cf., $\text{F}_2\text{TeN(H)}\text{-Xe}^+$ (Chapter 5), 24 Hz] and $^3J(^{129}\text{Xe}^{-16}\text{F})$ [cf., $\text{FXeN(SO}_2\text{F})_2$,$^{58}$ 18 Hz], so that they are not resolved.

The large line width of the $^{129}\text{Xe}$ NMR resonance for the $\text{FO}_2\text{SN(H)}\text{-Xe}^+$ cation results primarily from SA induced relaxation of $^{129}\text{Xe}$, and is analogous to the $(\text{FO}_2\text{S})_2\text{N-Xe}^+$ cation in SbF$_5$ solvent.$^{60}$ The SA broadening is proportional to $B_o^2$, where $B_o$ is the strength of the external magnetic field used in the NMR experiment. Since the present $^{129}\text{Xe}$ NMR experiments were conducted with use of an 11.7440 T magnet, the SA broadening is significant. This is exemplified by the magnetic field dependence of the $^{129}\text{Xe}$ NMR line width for 30% $^{15}\text{N}$-enriched $(\text{FO}_2\text{S})_2\text{NXe}^+$ in SbF$_5$ solvent.$^{6}$ At an external field strength of 5.8719 T, the linewidth of the $^{129}\text{Xe}$ resonance was 139 Hz, and the $^{129}\text{Xe}^{-15}\text{N}$ scalar coupling was not resolved. At 2.3488 T, the linewidth was significantly reduced and the $^{129}\text{Xe}^{-15}\text{N}$ scalar coupling was resolved. Resolution of $^2J(^{129}\text{Xe}^{-1}\text{H})$ and $^3J(^{129}\text{Xe}^{-16}\text{F})$ in the $^{129}\text{Xe}$ NMR spectrum of 99.5% $^{15}\text{N}$-enriched $\text{FO}_2\text{SN(H)}\text{-Xe}^+$ may be attained by use of a lower field strength. The field dependence of the $^{129}\text{Xe}$ NMR line width for the related $\text{F}_2\text{TeN(H)}\text{-Xe}^+$ cation is discussed in Chapter 5.

The $^1\text{H}$ NMR spectrum of the equilibrium mixture resulting from the reaction of equimolar amounts of natural abundance $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ and $\text{XeF}_2$ in BrF$_5$ solvent at -57.8 °C is shown in Figure 8.2. The initial concentrations of $\text{XeF}_2$ and $\text{FO}_2\text{SNH}_3^+$ were 1.12 and 0.974 M, respectively. The $\text{FO}_2\text{SN(H)}\text{-Xe}^+$ cation is assigned to the quadrupole collapsed singlet at $\delta(^1\text{H}) = 7.95$ ppm. It is deshielded by 0.58 ppm relative to the $\text{FO}_2\text{SNH}_3^+$ cation, which is also a quadrupole collapsed singlet, observed at $\delta(^1\text{H}) = 7.37$ ppm. The presence of both $\text{FO}_2\text{SNH}_3^+$ and $\text{FO}_2\text{SN(H)}\text{-Xe}^+$ is consistent with equilibrium (8.1). Integration of the $^1\text{H}$ NMR resonances indicates that the ratio $[\text{FO}_2\text{SNH}_3^+] : [\text{FO}_2\text{SN(H)}\text{Xe}^+]$ is 8 : 1. The singlets observed at 9.35 and
$^1$H NMR spectrum (500.138 MHz) of the equilibrium mixture arising from the reaction of natural abundance FO$_2$SNH$_3^+$AsF$_5^-$ and XeF$_2$ in BrF$_5$ solvent recorded at -57.8 °C; (A) unidentified singlets, possibly divalent nitrenium ions, RR'N:+, (B) FO$_2$SN(H)-Xe+, (C) FO$_2$SNH$_3^+$, (D) HF.
8.77 ppm cannot be definitely assigned but may arise from small amounts of divalent nitrenium ions\(^{304}\) such as FO\(_2\)SN(H):\(^+\), which are likely decomposition products in the elimination of xenon gas from the FO\(_2\)SN(H)-Xe\(^+\) cation (see decomposition of F\(_3\)TeN(H)-Xe\(^+\) in Chapter 6). No NMR data has been obtained for nitrenium ions in solution, but one would expect that the \(^1\)H NMR resonance for FO\(_2\)SN(H):\(^+\) would be highly deshielded. Other resonances observed in the \(^1\)H NMR spectrum include a broad singlet attributed to exchanging HF at 6.03 ppm \(\Delta \nu_{1/2} = 146\) Hz, and broad resonances without fine structure at 4.94, 3.31 and 2.58 ppm, which are attributed to rapidly exchanging H-on-N environments resulting from oxidative attack on the FO\(_2\)SNH\(_3\):\(^+\) cation by BrF\(_5\) solvent (see Chapter 7).

The \(^1\)H NMR spectrum of 99.5\% \(^{15}\)N-enriched FO\(_2\)SN(H)-Xe\(^+\)AsF\(_6\) in BrF\(_5\) at -59.9 °C consists of a doublet arising from \(J(^1\)H-\(^{15}\)N\) = 72 Hz centered at \(\delta(^1\)H\) = 7.48 ppm (Figure 8.3). The magnitude of \(J(^1\)H-\(^{15}\)N\) for the \(^{15}\)N-enriched FO\(_2\)SN(H)-Xe\(^+\) cation is comparable to other \(^{15}\)N-enriched inorganic amines, such as \([(\text{CH}_3)_2\text{Si}]_2^{15}\text{NH}\) (66.5 Hz)\(^{124}\) and \([\text{CF}_3\text{S}]_2^{15}\text{NH}\) (99.1 Hz).\(^{124}\) A value of \(J(^1\)H-\(^{15}\)N\) = 62 Hz is also observed in the related F\(_3\)Te\(^{15}\)N(H)-Xe\(^+\) cation (Chapter 5). Satellite peaks arising from \(J(^1\)H-\(^{129}\)Xe\) = 16 Hz were also observed in the \(^1\)H NMR spectrum of the FO\(_2\)S\(^{15}\)N(H)-Xe\(^+\) cation, as seen in Figure 8.3 [cf., F\(_3\)Te\(^{15}\)N(H)-Xe\(^+\) (Chapter 5): \(J(^{129}\)Xe-\(^1\)H\) = 24 Hz].

The \(^19\)F NMR spectrum of the identical sample used to obtain the \(^1\)H NMR spectrum of natural abundance FO\(_2\)SN(H)-Xe\(^+\) in BrF\(_5\) solvent at -57.8 °C is shown in Figure 8.4. The singlets at 57.45 and 56.25 ppm are attributed to the fluorine-on-sulfur(VI) resonances of FO\(_2\)SN(H)-Xe\(^+\) and FO\(_2\)SNH\(_3\):\(^+\), respectively. Integration of these resonances indicates a ratio [FO\(_2\)SNH\(_3\):\(^+\)] : [FO\(_2\)SN(H)-Xe\(^+\)] of 8 : 1. The \(^19\)F integrations are in agreement with those from the \(^1\)H NMR spectrum (see above), so that the number of hydrogens and fluorines is consistent with the
Figure 8.3 $^1$H NMR spectrum (300.144 MHz) of 99.5% $^{15}$N-enriched FO$_2$SN(H)-Xe$^+$ recorded at -59.9 °C in BrF$_5$ solvent.

Asterisks (*) denote $^{129}$Xe satellites.
Figure 8.4  $^{19}$F NMR spectrum (470.599 MHz) of the equilibrium mixture arising from the reaction of $\text{FO}_2\text{SNH}_3^+\text{AsF}_6^-$ and $\text{XeF}_2$ in $\text{BrF}_5$ solvent recorded at -57.8 °C; (A) $\text{FO}_2\text{SN(H)-Xe}$, (B) $\text{FO}_2\text{SNH}_3^+$. 
assignment of the resonances to the \( \text{FO}_2\text{SN(}H\text{)}\text{-Xe}^+ \) and \( \text{FO}_2\text{SNH}_3^+ \) cations. The \( ^{19}\text{F} \) NMR spectra of the 99.5% \( ^{15}\text{N} \)-enriched \( \text{FO}_2\text{SNH}_3^+ \) and \( \text{FO}_2\text{SN(}H\text{)}\text{-Xe}^+ \) cations consists of singlets without resolution of the long range couplings \( ^2J(^{19}\text{F}^-^{15}\text{N}) \) and \( ^3J(^{19}\text{F}^-^{1}\text{H}) \). A broad singlet at \( \delta(^{19}\text{F}) = -61.5 \text{ ppm} \) (\( \Delta\nu_{1/2} = 858 \text{ Hz} \)) is attributed to the partially quadrupole collapsed \( \text{AsF}_6^- \) anion. Peaks from \( \text{XeF}_2 \) are observed in the \( ^{19}\text{F} \) and \( ^{129}\text{Xe} \) NMR spectra in \( \text{BrF}_5 \) solvent, consistent with equilibrium (8.1). The \( \text{XeF}_2 \) triplet in the \( ^{129}\text{Xe} \) NMR spectrum is observed at \( \delta(^{129}\text{Xe}) = -1623 \text{ ppm} \), and is exchange broadened (\( \Delta\nu_{1/2} = 1604 \text{ Hz} \)). The \( ^{19}\text{F} \) NMR resonance of \( \text{XeF}_2 \) is centered at \( \delta(^{19}\text{F}) = -186.5 \text{ ppm} \), \( ^1J(^{19}\text{F}^-^{129}\text{Xe}) = 5670 \text{ Hz} \), and is also exchange broadened (\( \Delta\nu_{1/2} = 392 \text{ Hz} \)). The \( ^{19}\text{F} \) NMR resonance for \( \text{XeF}_2 \) is shielded by ca. 2 ppm relative to pure \( \text{XeF}_2 \) in \( \text{BrF}_5 \) at -52 °C\(^7\) (\( \delta(^{19}\text{F}) = -184.3 \text{ ppm} \)), indicating exchange with HF at \( \delta(^{19}\text{F}) = -192.5 \text{ ppm} \). The HF resonance is a singlet, \( \Delta\nu_{1/2} = 301 \text{ Hz} \), and the absence of doublet structure arising from \( ^1J(^{19}\text{F}^-^{1}\text{H}) \) confirms intermolecular exchange. The broadening of the \( \text{XeF}_2 \) resonances in the \( ^{129}\text{Xe} \) and \( ^{19}\text{F} \) NMR spectra may also be attributable to exchange of \( \text{XeF}_2 \) with \( \text{H}_2\text{F}^+ \) and \( \text{AsF}_5 \), producing trace amounts of \( \text{XeF}^+ \) and \( \text{Xe}_2\text{F}_3^+ \) according to equations (8.3) to (8.6). The presence of \( \text{AsF}_5 \)

\[
\text{2 HF} + \text{AsF}_5 \rightleftharpoons \text{H}_2\text{F}^+ + \text{AsF}_6^-
\]

(8.3)

\[
\text{XeF}_2 + \text{AsF}_5 \rightleftharpoons \text{XeF}^+ + \text{AsF}_6^-
\]

(8.4)

\[
\text{XeF}_2 + \text{H}_2\text{F}^+ \rightleftharpoons \text{XeF}^+ + 2 \text{HF}
\]

(8.5)

\[
\text{XeF}_2 + \text{XeF}^+ \rightleftharpoons \text{Xe}_2\text{F}_3^+
\]

(8.6)
is expected from the decomposition of \( \text{FO}_2\text{SN(H)}-\text{Xe}^+\text{AsF}_6^- \) by analogy with the decomposition of \( \text{F}_5\text{TeN(H)}-\text{Xe}^+\text{AsF}_6^- \) (Chapter 6), with HF arising from equilibrium (8.1) and from the oxidation of \( \text{FO}_2\text{SNH}_3^+ \) by \( \text{BrF}_3 \) solvent (see Chapter 7).

(C) **NATURE OF THE BONDING IN THE FO\(_{2}\)SN(H)-Xe\(^+\) CATION**

Previous NMR studies of xenon(II) derivatives containing XeF groups bonded to oxygen or fluorine have shown that the NMR parameters measured in the \(^{19}\text{F}\) and \(^{129}\text{Xe}\) NMR spectra can generally be used to assess the relative covalent characters of the Xe-O, Xe-F bridge and Xe-F terminal bonds.\(^{103,104,108}\) In general, as the covalent character of the Xe-L (L = ligand atom) bond increases, the terminal Xe-F bond becomes more ionic, decreasing the formal charge on xenon. These trends are paralleled by increased shielding of the \(^{129}\text{Xe}\) resonance and decreases in both \( J(^{129}\text{Xe},^{19}\text{F}) \) and \( \delta(^{19}\text{F}) \) for the terminal Xe-F group. Recently, Schrobilgen\(^{26}\) extended the trend to include neutral and cationic species containing xenon(II)-nitrogen bonds. Table 8.1 lists the \(^{129}\text{Xe}\) NMR chemical shifts and reduced coupling constants \( ^1K(\text{Xe-N}) \) for a number of representative xenon(II)-nitrogen bonded compounds for comparison with \( \text{FO}_2\text{SN(H)}-\text{Xe}^+ \). The \( \text{FO}_2\text{SN(H)}-\text{Xe}^+ \) cation has one of the most shielded \(^{129}\text{Xe}\) NMR resonances for a compound containing a xenon-nitrogen bond. Compounds whose \(^{129}\text{Xe}\) resonances are similar to that of the \( \text{FO}_2\text{SN(H)}-\text{Xe}^+ \) cation are \( \text{F}_4\text{S=NXe}^+ \) (-2672 ppm),\(^{26,180}\) \( \text{F}_5\text{TeN(H)}-\text{Xe}^+ \) (-2841 ppm; Chapter 5) and \( \text{F}_5\text{SN(H)}-\text{Xe}^+ \) (-2886 ppm).\(^{26,180}\) Assuming the validity of the NMR spectroscopic trends mentioned above, the highly shielded \(^{129}\text{Xe}\) NMR resonance of \( \text{FO}_2\text{SN(H)}-\text{Xe}^+ \) indicates a very covalent Xe-N bond, which arises from the relatively low electronegativity of the \( \text{FO}_2\text{SN(H)} \)-ligand. From the highly shielded \(^{129}\text{Xe}\) NMR resonance for the \( \text{FO}_2\text{SN(H)}-\text{Xe}^+ \) cation, a high degree of Xe-F bond ionic character is expected, and this is manifested in the absence of a xenon-
fluorine scalar coupling in the $^{129}$Xe NMR spectra, indicating complete Xe-F bond ionization in solution. The same argument can be applied to $F_4S=N-Xe^+$, $F_5TeN(H)-Xe^+$ and $F_5SN(H)-Xe^+$, since the Xe-F bonds are also ionized in solution. The remaining xenon-nitrogen bonded compounds in Table 8.1 involve ligands of higher electronegativity, resulting in Xe-F bonds with considerable covalent character. In agreement with the above trends, the $^{129}$Xe resonances of these compounds are between 600 and 1100 ppm more deshielded than those observed for $FO_2SN(H)$-Xe$, F_5XeN(H)-Xe^+$ (X = S, Te), and $F_4S=N-Xe^+$. An apparent anomaly in Table 8.1 is the ($FO_2S$)$_2N$-Xe$^+$ cation, for which $\delta(^{129}$Xe$) = -1943$ ppm, since according to the above trends, the $^{129}$Xe resonance is expected to be much more shielded as a result of the ionized Xe-F bond. However, the high electronegativity of the ($FO_2S$)$_2N$- ligand results in substantial Xe-F bond covalent character in ($FO_2S$)$_2NXeF$. The crystallographically determined Xe-F and Xe-N bond lengths are similar [1.967(3) and 2.200(3) Å, respectively],$^{57}$ and a determination of the Xe-F and Xe-N bond orders using the bond order-bond length relationship of Pauling$^{305}$ indicates that the valence bond formulation ($FO_2S$)$_2N$-Xe-F$^+$ dominates over the formulation ($FO_2S$)$_2N$-Xe$^+$ F$^-$ by 59:41.$^{57}$ As expected, the Xe-F bond is not ionized in $BrF_5$ solvent.$^{56-58}$ Ionization of the Xe-F bond in solution to give ($FO_2S$)$_2N$-Xe$^+$ requires the use of the strong fluoride acceptor $SbF_5$ as solvent.$^{60}$

The effect of ligand electronegativity on the $^{129}$Xe chemical shift and Xe-F bond ionization is further illustrated by comparing resonance structures for the hypothetical compound, $FO_2SN(H)$-Xe-F, with those for the neutral fluorosulfate derivative, $FO_2SO$-Xe-F, since $FO_2SO$- and $FO_2SN(H)$- are isoelectronic. The electronegativity of $FO_2SO$- is undoubtedly greater than that of $FO_2SN(H)$-, since $FO_2SOH$ is a strong acid ($H_o = -15.1$)$^{306}$ and $FO_2SNH_2$ is a nitrogen base.
\[ \text{ FO}_2\text{SN(H)}^+\text{Xe}^+ \text{F}^- \longleftrightarrow \text{ FO}_2\text{SN(H)}^-\text{Xe-F}^+ \]

8.6

8.7

\[ \text{ FO}_2\text{SO}^-\text{XeF}^+ \longleftrightarrow \text{ FO}_2\text{SO-}^+\text{Xe-F}^- \]

8.8

8.9

which can be protonated in HF solvent acidified with AsF$_5$ (see Chapter 7). The ionization of the Xe-F bond for FO$_2$SN(H)-Xe-F in solution is represented by dominance of resonance Structure 8.6 to the exclusion of Structure 8.7. The Xe-F bond in FO$_2$SO-Xe-F is not ionized in solution, since $^1J(^{129}\text{Xe}^-^1\text{F}) = 5830 \text{ Hz}$ is observed in the $^{129}\text{Xe}$ NMR spectrum in BrF$_5$ solvent.\textsuperscript{108} This indicates substantial Xe-F bond covalent character in FO$_2$SOXeF. The crystallographically determined Xe-F [1.940(8) Å] and Xe-O [2.155(8) Å] bond lengths for FO$_2$SOXeF have been used to assess relative covalent characters of the Xe-F and Xe-O bonds using the bond order-bond length relationship of Pauling.\textsuperscript{38} This relationship indicates that the canonic form FO$_2$SO$^-\text{Xe-F}^+$ (Structure 8.8) has a 63:37 dominance over the canonical form FO$_2$SO$-\text{Xe}^+\text{F}^-$ (Structure 8.9). As expected from the substantial Xe-F bond covalent character, the $^{129}\text{Xe}$ NMR resonance of FO$_2$SOXeF [$\delta(^{129}\text{Xe}) = -1666 \text{ ppm}$]\textsuperscript{108} is much more deshielded than the FO$_2$SN(H)-Xe$^+$ cation.

The magnitude of the reduced coupling constant $^1K(\text{Xe-N})$ for the FO$_2$SN(H)-Xe$^+$ cation (0.322 x 10$^{22}$ NA$^{-2}$m$^{-3}$) may be used to gain insight into the bonding by comparison with other xenon(II)-nitrogen bonded compounds (see Table 8.1). In a previous study,\textsuperscript{73} the hybridization at
nitrigen in the H\textsubscript{2}C≡N-XeF\textsuperscript{+} cation was determined to be \textit{sp} by comparing the magnitude of $^1\text{K}(\text{Xe-N})$ (1.389 $\times$ 10\textsuperscript{22} \text{NA}^{-2}\text{m}^{-3})$ for the H\textsubscript{2}C≡N-XeF\textsuperscript{+} cation with that of (\text{FO}_2\text{S})\textsubscript{2}N-XeF (0.949 $\times$ 10\textsuperscript{22} \text{NA}^{-2}\text{m}^{-3}).\textsuperscript{57} The use of $^1\text{K}(\text{Xe-N})$ to assess the hybridization at nitrogen assumes that the Fermi contact term is the dominant mechanism for the xenon-nitrogen nuclear spin-spin coupling, which is generally true for spin-spin coupling involving heavy nuclides.\textsuperscript{260} Assessment of the hybridization at nitrogen in Xe-N bonded compounds uses a formalism developed by Pople and Santry.\textsuperscript{242} for Fermi contact-dominated scalar couplings, which states that the magnitude of the scalar coupling between two nuclei is proportional to the product of the valence \textit{s}-electron densities at the coupled nuclei. The use of the magnitude of $^1\text{K}(\text{Xe-N})$ to assess the hybridization at nitrogen in H\textsubscript{2}C≡N-XeF\textsuperscript{+} depended on the assumption that the \textit{s}-electron density at xenon in H\textsubscript{2}C≡N-XeF\textsuperscript{+} was essentially the same as in (\text{FO}_2\text{S})\textsubscript{2}N-XeF, and the difference in the nitrogen hybridization in the two compounds accounted for the different magnitudes of $^1\text{K}(\text{Xe-N}).$\textsuperscript{73} Thus the hybridization at nitrogen in the H\textsubscript{2}C≡N-XeF\textsuperscript{+} cation could be determined, since the formal hybridization at nitrogen in (\text{FO}_2\text{S})\textsubscript{2}N-XeF is considered to be \textit{sp}\textsuperscript{2}, as evidenced by the short S-N bond lengths [1.628(3) and 1.623(3) Å], indicating S-N \pi-bonding, and the trigonal planar nitrogen geometry.\textsuperscript{57} The same treatment cannot be used to assess the nitrogen hybridization in the FO\textsubscript{2}SN(H)-Xe\textsuperscript{+} cation since the Xe-F bond is ionized in solution, and therefore the \textit{s}-electron density at xenon cannot be assumed to be the same as in H\textsubscript{2}C≡N-XeF\textsuperscript{+} or (\text{FO}_2\text{S})\textsubscript{2}N-XeF. A comparison of the reduced coupling constants of FO\textsubscript{2}SN(H)-Xe\textsuperscript{+} and (\text{FO}_2\text{S})\textsubscript{2}N-Xe\textsuperscript{+} would seem reasonable for assessing the nitrogen atom hybridization of the FO\textsubscript{2}SN(H)-Xe\textsuperscript{+} cation, but the magnitudes of $^1\text{K}(\text{Xe-N})$ are opposite to what is expected. The single crystal X-ray structure of (\text{FO}_2\text{S})\textsubscript{2}N-Xe\textsuperscript{+}Sb\textsubscript{2}F\textsubscript{16}.\textsuperscript{60} shows that the nitrogen center is trigonal planar in the (\text{FO}_2\text{S})\textsubscript{2}N-Xe\textsuperscript{+} cation, and the S-N bond lengths [1.68(1) to 1.70(1) Å] are significantly shorter than S-N single
bonds [cf., O₂SNH₂; S-N = 1.7714(3) Å], indicating substantial S-N π bonding and formal sp²-hybridization at nitrogen. The FO₂SN(H)-Xe⁺ cation is related to (FO₂S)₂N-Xe⁺ by replacement of one FO₂S- group with a hydrogen atom, so that the degree of S-N π bonding in the former can be assumed to be reduced relative to the latter since only half the number of resonance structures involving S-N π bonding can be drawn [compare resonance Structures 8.10 - 8.13 with Structures 8.2 - 8.4]. As a result, the s-character of the nitrogen valence orbitals is expected to be lower (i.e., greater p character) in the FO₂SN(H)-Xe⁺ cation. Assuming dominance of the Fermi contact mechanism for the Xe-N bond, a greater magnitude of ¹K(Xe-N) is expected, opposite to the measured values of ¹K(Xe-N). An alternative analysis of ¹K(Xe-N) in the FO₂SN(H)-Xe⁺ and (FO₂S)₂N-Xe⁺ cations, which also assumes dominance of the Fermi contact term, is derived from a study of the magnitudes of ¹J(¹⁵N-¹H) in main group compounds of the form X¹⁵NH₂ and X₂¹⁵NH by Cowley and Schweiger, which relied on the so-called isovalent hybridization hypothesis. This hypothesis states that s-character concentrates in the bonds which are directed toward electropositive substituents. It was observed that increasing electronegativity of X resulted in increasing magnitudes of ¹J(¹⁵N-¹H), which implied that nitrogen 2s character was progressively diverted into the NH bonds with increased electronegativity of X. As expected from the Fermi contact term, in most cases the value of ¹J(¹⁵N-¹H) increased in proceeding from the XNH₂ to the X₂NH compound. Once again, the opposite trend is observed in the FO₂SN(H)-Xe⁺ and (FO₂S)₂N-Xe⁺ cations since the (FO₂S)₂N- group is expected to be more electronegative than the FO₂SN(H)- group. The failure to qualitatively predict the relative magnitudes of ¹K(Xe-N) by only considering the Fermi contact term may indicate that the dipolar and orbital contributions to the xenon-nitrogen scalar coupling may be important. Although the Fermi contact term is expected to be the largest contributor to the Xe-N scalar coupling, it may be similar for the
FO$_2$SN(H)-Xe$^+$ and (FO$_2$S)$_2$N-Xe$^+$ cations. The presence of Xe-N $\pi$-bonding in the FO$_2$SN(H)-Xe$^+$ and (FO$_2$S)$_2$N-Xe$^+$ cations, which is represented by resonance Structures 8.3 and 8.11, respectively, may give rise to a significant orbital contribution, $K^2_{AB}$ to the scalar Xe-N coupling. Factors contributing to the magnitude of $K^2_{AB}$ are described in equation (8.7) using an average

$$K^2_{AB} = \mu_o(\mu_B)^2<r_A^{-3}>_p<r_B^{-3}>_p(3\Delta E)^{-1}$$

$$\times [2(P_{\sigma^2} + P_{\pi^2} + P_{\pi'}^2) + 3(P_{\sigma\pi} + P_{\sigma\pi'} + P_{\pi\pi'})]$$

(8.7)

energy approximation in a LCAO framework. The terms $\mu_o$ and $\mu_B$ are the permittivity of a vacuum and the Bohr magneton, respectively. $<r_A^{-3}>_p$ and $<r_B^{-3}>_p$ are the inverse cube radial distributions of the valence $p$ orbitals for the coupled nuclei, ($\Delta E$) is the average excitation energy and $P_{\sigma}$, $P_{\pi}$ and $P_{\pi'}$ are the $\sigma$ and $\pi$ bond orders for the bonding between the coupled nuclei, A and B. In comparing FO$_2$SN(H)-Xe$^+$ and (FO$_2$S)$_2$N-Xe$^+$, an argument for a greater Xe-N $\pi$-bonding contribution in the former can be made by examining resonance Structures 8.2 to 8.4 and 8.10 to 8.13, which in turn rationalizes the relative magnitudes of $^1K$(Xe-N). The greater electronegativity of (FO$_2$S)$_2$N- than FO$_2$SN(H)- and the greater proportion of resonance contributors involving S-N $\pi$-bonding in the (FO$_2$S)$_2$N-Xe$^+$ cation both contribute to a smaller degree of Xe-N $\pi$-bonding in the (FO$_2$S)$_2$N-Xe$^+$ cation than in the FO$_2$SN(H)-Xe$^+$ cation. A larger Xe-N $\pi$-bonding contribution in FO$_2$SN(H)-Xe$^+$ is expected to result in larger values of $P_{\pi}$ and $P_{\pi'}$ in the orbital contribution to the Xe-N scalar coupling, thus increasing $^1K$(Xe-N) relative to (FO$_2$S)$_2$N-Xe$^+$. 
CHAPTER 9

SUMMARY, CONCLUSIONS AND DIRECTIONS FOR FURTHER RESEARCH

(A) SUMMARY

The present work represents a significant extension of noble-gas chemistry, in particular, the synthesis of several compounds containing xenon-nitrogen and xenon-oxygen bonds. This has been achieved by HF elimination reactions of the salts, CF₂C(OH)NH₂⁺AsF₆⁻, F₅TeNH₂⁺AsF₆⁻ and FO₂SNH₂⁺AsF₆⁻ with XeF₂ in HF and BrF₅ solvents, resulting in the preparation of AsF₆⁻ salts of the novel cations, CF₂C(OXeF)NH₂⁺, F₅TeN(H)-Xe⁺ and FO₂SN(H)-Xe⁺. The HF elimination reactions are analogous to the reaction of the strong oxoacids CF₂C(O)OH, F₅TeOH and FO₂SOH with XeF₂, which result in the neutral xenon(II) derivatives, CF₂C(O)-XeF, F₅TeO-XeF and FO₂SO-XeF which were prepared in the decade which followed the discovery of noble-gas reactivity (see Chapter 1). The ligands used in the present studies are among the least electronegative ligands known to form isolable xenon(II) derivatives. Since high ligand electronegativity is central to the stabilization of xenon(II) derivatives (see Chapter 1), the low stability of these compounds is to be expected. The salts CF₂C(OXeF)NH₂⁺AsF₆⁻ and F₅TeN(H)-Xe⁺AsF₆⁻ isolated from solution decompose rapidly at 0 and -30 °C, respectively, whereas FO₂SN(H)-Xe⁺AsF₆⁻ could not be isolated from solution owing to decomposition above ca. -40 °C. Prior to this work, only one example of xenon(II) bonded to an sp³-hybridized nitrogen center was known, namely F₅SN(H)-Xe⁺AsF₆⁻.26 In the F₅TeN(H)-Xe⁺ and FO₂SN(H)-Xe⁺ cations,
xenon(II) is bonded to nitrogen centers which are formally \( sp^3 \)-hybridized, providing two new examples of a rare class of compounds.

The salts, \( \text{CF}_3\text{C}({\text{OH}})\text{NH}_2^+\text{AsF}_6^- \), \( \text{F}_5\text{TeNH}_2^+\text{AsF}_6^- \) and \( \text{FO}_2\text{SNH}_2^+\text{AsF}_6^- \), which are starting materials for the preparation of the xenon cations, represent the first reported examples of the protonated forms of \( \text{CF}_3\text{C}({\text{O}})\text{NH}_2 \), \( \text{F}_5\text{TeNH}_2 \) and \( \text{FO}_2\text{SNH}_2 \). The natural abundance salts and \( 99.5\% \) \( ^{15}\text{N} \)-enriched \( \text{F}_5\text{TeNH}_2^+\text{AsF}_6^- \) and \( \text{FO}_2\text{SNH}_2^+\text{AsF}_6^- \) have been fully characterized by \( ^{19}\text{F}, ^{13}\text{C}, ^{1}\text{H}, ^{15}\text{N} \) and \( ^{125}\text{Te} \) NMR spectroscopy in HF and/or \( \text{BrF}_5 \) solvents. They have also been characterized in the solid state by Raman spectroscopy, and the assignments for the Raman spectra of \( \text{F}_5\text{TeNH}_2^+\text{AsF}_6^- \) and \( \text{FO}_2\text{SNH}_2^+\text{AsF}_6^- \) were aided by obtaining the Raman spectra of the \( 99.5\% \) \( ^{15}\text{N} \)-enriched salts and observing the \( ^{14/15}\text{N} \) isotopic shifts of bands associated with the vibrational motions of the nitrogen atom. The NMR and Raman spectral data for the unprotonated compounds, \( \text{CF}_3\text{C}({\text{O}})\text{NH}_2 \), \( \text{F}_5\text{TeNH}_2 \), and \( \text{FO}_2\text{SNH}_2 \) were compared with the data for the salts of the protonated compounds, and the effect of protonation on the bonding in these ligands was assessed.

(i) **Preparation and Characterization of \( \text{CF}_3\text{C}({\text{OH}})\text{NH}_2^+\text{AsF}_6^- \)**

The \( \text{CF}_3\text{C}({\text{O}})\text{XeF})\text{NH}_2^+ \) cation was best prepared in \( \text{BrF}_5 \) solvent from the HF elimination reaction of the conjugate acid, \( \text{CF}_3\text{C}({\text{OH}})\text{NH}_2^+ \), with \( \text{XeF}_2 \) (equation (3.2)). As well as facilitating the HF elimination reaction, protonation of \( \text{CF}_3\text{C}({\text{O}})\text{NH}_2 \) made the ligand more resistant to electrophilic attack by \( \text{BrF}_5 \) solvent. Xenon difluoride is also a weaker oxidative fluorinator than \( \text{XeF}^+ \), which reduced the rate of ligand oxidation. Attempting the reaction of \( \text{XeF}^+\text{AsF}_6^- \) and \( \text{CF}_3\text{C}({\text{O}})\text{NH}_2 \) in \( \text{BrF}_5 \) solvent resulted in extensive oxidative decomposition of \( \text{CF}_3\text{C}({\text{O}})\text{NH}_2 \).

The salt, \( \text{CF}_3\text{C}({\text{OH}})\text{NH}_2^+\text{AsF}_6^- \), was prepared by reacting \( \text{CF}_3\text{C}({\text{O}})\text{NH}_2 \) with an excess
of AsF₅ in anhydrous HF solvent at -50 °C. The resulting white powder decomposed slowly (ca. one month) with liquefaction at room temperature under anhydrous conditions, but was indefinitely stable at -78 °C. The solution structure of CF₃C(OH)NH₂⁺ was determined by obtaining the ¹⁹F, ¹H and ¹³C NMR spectra of CF₃C(OH)NH₂⁺AsF₆⁻ in BrF₅ solvent. The ¹H NMR spectrum indicated chemical inequivalence of the amido protons resulting from hindered rotation of the C-N bond which possesses considerable double bond character, a proton resonance attributable to the protonated carbonyl group was also observed. The NMR data were consistent with resonance Structures 3.1 and 3.2. The assignment of the chemically inequivalent amido protons in the ¹H NMR spectrum was facilitated by use of a two-dimensional heteronuclear (¹H-¹⁹F) NOESY experiment.

The Raman spectrum (-165 °C) of CF₃C(OH)NH₂⁺AsF₆⁻ was consistent with resonance Structures 3.1 and 3.2. O-protonation was evident from the increase and decrease, respectively, of the bands assigned to v(C-N) and v(C-O), relative to those for CF₃C(O)NH₂, since O-protonation is expected to increase and decrease, respectively, the C-N and C-O double bond characters. A band attributable to δ(OH) was observed but bands attributable to γ(OH) and ν(OH) were not observed. The characteristic low intensity of the vibrations of small atoms was assumed to be responsible for the unobserved γ(OH) and ν(OH) bands. Bands attributable to AsF₆⁻ were also observed.

(ii) Preparation and Characterization of CF₃C(OXeF)NH₂⁺AsF₆⁻ and

CF₃C(OH)NH₂⁺AsF₆⁻XeFₓ×HF

The first adiabatic ionization potential (IP₁) of CF₃C(O)NH₂ (10.77 eV)¹⁰⁶ is similar to the observed electron affinity of XeF⁺ (10.77 eV),²⁵ suggesting that it may be resistant to oxidation by XeF⁺ at low temperature. The reaction of equimolar amounts of CF₃C(O)NH₂ and
XeF⁺AsF₆⁻ in HF solvent did not result in measurable amounts of CF₃C(OXeF)NH₂⁺AsF₆⁻ (monitored by ¹⁹F and ¹²⁹Xe NMR spectroscopy), owing to protonation of CF₃C(O)NH₂ to give CF₃C(OH)NH₂⁺ in the XeF⁺-acidified HF solvent [equation (3.3)]. However, slow removal of HF solvent under vacuum at -50 °C resulted in a white powder. The Raman spectrum (-165 °C) was consistent with the formulation CF₃C(OXeF)NH₂⁺ AsF₆⁻. The solid decomposed with gas evolution and liquefaction at temperatures approaching 0 °C. The ¹²⁹Xe and ¹⁹F NMR spectra of the undecomposed white powder dissolved in BrF₅ solvent at -60 °C confirmed that the material was CF₃C(OXeF)NH₂⁺ AsF₆⁻. The solution structure of CF₃C(OXeF)NH₂⁺ AsF₆⁻ was determined by dissolving equimolar amounts of CF₃C(OH)NH₂⁺ AsF₆⁻ and XeF₂ in BrF₅ solvent at -60 °C and obtaining the ¹²⁹Xe, ¹⁹F, ¹H and ¹³C NMR spectra. The NMR spectra indicated an HF elimination equilibrium, resulting in the formation of CF₃C(OXeF)NH₂⁺ AsF₆⁻ [equation (3.2)]; the ratio [CF₃C(OH)NH₂⁺] : [CF₃C(OXeF)NH₂⁺] was determined to be 3 : 1 from integration of the NMR resonances. The CF₃C(OXeF)NH₂⁺ cation can be thought of as an adduct cation, where CF₃C(O)NH₂ behaves as an oxygen-donor towards the Lewis acid cation, XeF⁺; the synthesis of CF₃C(OXeF)NH₂⁺ represents the second reported example of an adduct of XeF⁺ with an oxygen donor ligand; the first to be reported was the thermally unstable SbF₆⁻ salt of the sulfurane adduct, (CF₃)₂S=O-XeF⁺SbF₆⁻.⁸⁵ The ¹H NMR spectrum of CF₃C(OXeF)NH₂⁺ in BrF₅ solvent indicated chemical inequivalence of the amido protons, resulting from hindered rotation about the C-N bond. The hindered rotation results from substantial C-N double bond character, as depicted in resonance Structures 3.3 and 3.4. Assignment of the chemically inequivalent amido protons in the ¹H NMR spectrum was facilitated by use of a two-dimensional heteronuclear (¹⁹F-¹H) NOESY experiment. The NOESY technique is well established as a very important tool for determining the spatial orientation of organic molecules in solution. This work represented the first use of a NOESY experiment to facilitate the NMR assignments of a thermally unstable noble-gas compound in
solution.

Combining stoichiometric amounts of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ and XeF$_2$ in HF solvent at -50 °C resulted in pale yellow solutions. As described above, slow removal of HF under vacuum over four hours resulted in completion of the HF elimination reaction depicted in equation (3.2), resulting in the isolation of essentially pure CF$_3$C(OXeF)NH$_2^+$AsF$_6^-$. If the HF solvent was removed rapidly under vacuum at -50 °C, a white solid precipitated after removal of approximately half of the solvent. After complete removal of the solvent, the Raman spectrum (-165 °C) of the resulting white powder was consistent with a hydrogen-bonded solvate, which was formulated as CF$_3$C(OH)NH$_2^+$AsF$_6^-$·XeF$_2$·HF. This indicated that the faster rate of HF removal resulted in the precipitation of a hydrogen-bonded solvate [see equation (3.4)] The Raman spectrum (Figure 3.9) exhibits two intense peaks at 515 and 511 cm$^{-1}$, which are best described as the factor group split symmetric F-Xe-F stretch of hydrogen-bonded XeF$_2$. The absence of a band assignable to the asymmetric F-Xe-F stretch indicates that the local $D_{\infty h}$ symmetry of XeF$_2$ in the solvate is preserved, since the asymmetric F-Xe-F stretch ($\Sigma^+_u$ symmetry) is Raman forbidden for $D_{\infty h}$ symmetry. Bands were observed which were consistent with the presence of CF$_3$C(OH)NH$_2^+$ and AsF$_6^-$. It is likely that XeF$_2$ is hydrogen-bonded to the protons of CF$_3$C(OH)Na$_2^+$ in a fashion that conserves the local $D_{\infty h}$ symmetry of XeF$_2$. Possible arrangements of XeF$_2$ in the solid are shown in Structures 3.5 - 3.7.

The variation in products which resulted from the reaction of CF$_3$C(OH)NH$_2^+$AsF$_6^-$ and XeF$_2$ in HF solvent depended on the rate of HF removal. This illustrates the need to closely monitor the reaction conditions used for the preparations of xenon compounds. This is a reiteration of the same statement made by Bartlett et al.,$^{28}$ concerning the carefully controlled conditions required to properly conduct HF elimination reactions of strong oxoacids such as HSO$_3$F, CF$_3$C(O)OH and HClO$_4$ with XeF$_2$. 
(iii) **Preparation and Characterization of F₅TeNH₂ and F₅TeNH₃⁺AsF₆⁻**

The importance of F₅TeNH₃⁺AsF₆⁻ in this work lies primarily in its use as a precursor for the preparation of F₅TeN(H)-Xe⁺AsF₆⁻ in BrF₅ and HF solvents. This Thesis also reports the first isolation of the protonated form of F₅TeNH₂. The salt, F₅TeNH₃⁺AsF₆⁻, was prepared by reaction of F₅TeNH₂ and excess AsF₅ in HF solvent at -55 °C, which resulted in a white powder that was indefinitely stable at room temperature in the absence of moisture. The solution structures of natural abundance and 99.5% ¹⁵N-enriched F₅TeNH₃⁺AsF₆⁻ were determined by ¹⁹F, ₁H, ¹⁵N and ¹²⁵Te NMR spectroscopy in HF and/or BrF₅ solvents. The Raman spectra at ambient temperature of natural abundance and 99.5% ¹⁵N-enriched samples were obtained, and with the aid of ¹⁴/¹⁵N isotopic shifts of bands associated with the vibrations of the nitrogen center, detailed assignments of all vibrational modes were made.

The vibrational assignments for F₅TeNH₂, although previously published, were reassigned using additional information provided from the ¹⁴/¹⁵N isotopic shifts in the Raman spectra of the natural abundance and 99.5% ¹⁵N-enriched samples. A comparison of the Raman and ¹⁹F NMR spectra of natural abundance and 99.5% ¹⁵N-enriched F₅TeNH₃⁺AsF₆⁻ with those of natural abundance and 99.5% ¹⁵N-enriched F₅TeNH₂ indicated that the Te-N bond order decreases on protonation of F₅TeNH₂. This implied some degree of Te-N π-bonding in F₅TeNH₂, which decreased upon incorporation of the nitrogen lone pair in an electron-pair bond with H⁺ in F₅TeNH₃⁺. The Raman spectra and ¹⁹F NMR spectra also indicated that protonation increases the Te-F bond orders, particularly the axial Te-F bond.

The trends observed on protonation of F₅TeNH₂ to give F₅TeNH₃⁺ are consistent with a reduction in Te-N π-bonding, and are directly analogous to the changes in the bonding of F₅XO⁻ upon protonation to give F₅XOH (X = S, Se, Te).
(iv) [Pentafluorotellurium(V)amido]xenonium(II) hexafluoroarsenate:

\[ \text{F}_5\text{TeN(H)}-\text{Xe}^+\text{AsF}_6^- \]

The amine, \( \text{F}_5\text{TeNH}_2 \), is valence isoelectronic with \( \text{F}_5\text{TeOH} \), which is known to undergo HF elimination reactions with \( \text{XeF}_2 \) to give \( \text{FXeOTeF}_5 \) and \( \text{Xe(OTeF}_2\text{)}_2 \). Although the resistance of \( \text{F}_5\text{TeNH}_2 \) to oxidation by \( \text{XeF}^+ \) could not be estimated in the absence of photoionization studies for this compound, it is reasonable to assume that the inductive effect of five fluorines on tellurium, by analogy with \( \text{F}_5\text{TeOH} \), might result in considerable oxidative resistance. The basicity of \( \text{F}_5\text{TeNH}_2 \) was confirmed by the stability of the \( \text{F}_5\text{TeNH}_2\cdot\text{AsF}_5 \) adduct at room temperature. Prior to this study, a considerable number of cations with \( \text{Xe-N} \) bonds were prepared from the reaction of the Lewis acid \( \text{XeF}^+ \) with oxidatively resistant nitrogen bases, \( \text{D} \), such as the nitriles, \( \text{RC}=-\text{N} \) (\( \text{R} = \text{alkyl}, \text{C}_6\text{F}_5, \text{fluoroalkyl}, \text{H} \)) the pyridines \( \text{C}_2\text{F}_3\text{N} \) and \( 4\text{-CF}_3\text{C}_2\text{F}_4\text{N} \) and \( \text{s-C}_3\text{F}_3\text{N}_3 \) [equation (9.1)].

\[ \text{D} + \text{XeF}^+\text{AsF}_6^- \rightarrow \text{D-XeF}^+\text{AsF}_6^- \]  \hspace{1cm} (9.1)

All of the ligands mentioned above contain \( sp^2 \)- or \( sp^3 \)-hybridized nitrogen centers, and prior to this work, no attempt was made to react an oxidatively resistant amine (\( sp^3 \)-hybridized nitrogen center) with \( \text{XeF}^+ \) with the aim of preparing a cation of the form \( \text{R-NH}_2\cdot\text{XeF}^+ \). It was shown in Chapter 5 that the reaction of \( \text{F}_5\text{TeNH}_2 \) and \( \text{XeF}^+\text{AsF}_6^- \) in HF solvent or the reaction of \( \text{F}_5\text{TeNH}_2^+\text{AsF}_6^- \) and \( \text{XeF}_2 \) in \( \text{BrF}_5 \) solvent resulted in the formation of \( \text{F}_5\text{TeN(H)}-\text{Xe}^+\text{AsF}_6^- \). The \( \text{F}_5\text{TeN(H)}-\text{Xe}^+ \) cation was not the expected product but the simple adduct formation of the base \( \text{F}_5\text{TeNH}_2 \) and the Lewis acid, \( \text{XeF}^+ \). The anticipated cation, \( \text{F}_5\text{TeNH}_2\cdot\text{XeF}^+ \), was not observed and it was postulated that \( \text{F}_5\text{TeNH}_2\cdot\text{XeF}^+ \) eliminated HF according to equation (9.2). The \( \text{F}_5\text{TeN(H)}-\text{Xe}^+ \) cation was characterized in solution by \( ^{19}\text{F}, ^1\text{H}, ^{129}\text{Xe} \) and \( ^{125}\text{Te} \) NMR.
\[ \text{F}_5\text{TeNH}_2\text{-XeF}^+ \longrightarrow \text{F}_5\text{TeN(H)-Xe}^+ + \text{HF} \]  \hspace{1cm} (9.2)

spectroscopy in BrF$_5$ and HF solvents. Quadrupolar collapse of the $^{129}\text{Xe}$-$^{14}\text{N}$ scalar coupling prevented the use of NMR to definitively characterize the Xe-N bond in solution. It was possible to observe the $^{129}\text{Xe}$-$^{15}\text{N}$ scalar coupling, however, by preparing the 99.5\% $^{15}\text{N}$-enriched F$_5$TeN(H)-Xe$^+$ cation. This also facilitated the observation of the $^{15}\text{N}$ NMR spectrum of F$_5$TeN(H)-Xe$^+$.

A dominant relaxation mechanism for $^{129}\text{Xe}$ is shielding anisotropy, which results in significant line broadening at high field strengths. This was demonstrated in the $^{129}\text{Xe}$ NMR spectrum of 99.5\% $^{15}\text{N}$-enriched F$_5$TeN(H)-Xe$^+$ with an external magnetic field strength of 11.7440 T; only the one-bond scalar coupling $^1J(^{129}\text{Xe},^{15}\text{N})$ was resolved. However, all possible spin-spin couplings were observed in the $^{129}\text{Xe}$ NMR spectrum at 7.4630 T, except the three-bond scalar coupling of $^{129}\text{Xe}$ with the axial fluorine-on-tellurium(VI). This posed the possibility of a misassignment in the $^{129}\text{Xe}$ NMR spectrum, since $^2J(^{129}\text{Xe},^{1}\text{H})$ might have been the unresolved coupling, as opposed to $^3J(^{129}\text{Xe},^{19}\text{F}_{\text{ax}})$. The unresolved coupling was confirmed to be $^3J(^{129}\text{Xe},^{19}\text{F}_{\text{ax}})$ by performing a $(^{1}\text{H}-^{129}\text{Xe})$ INEPT experiment; this was the first example of the use of the well-established INEPT pulse sequence for the characterization of a noble-gas compound.

The salt F$_5$TeN(H)-Xe$^+$AsF$_6^-$ was isolated as an orange microcrystalline powder by precipitation from HF solvent at -40 °C. The salt decomposed rapidly in the solid state at -30 °C. Natural abundance and 99.5\% $^{15}\text{N}$-enriched samples of F$_5$TeN(H)-Xe$^+$AsF$_6^-$ were characterized by Raman spectroscopy at -165 °C. The $^{14}/^{15}\text{N}$ isotopic shifts associated with the vibrations of the nitrogen atom allowed for the assignments of bands attributable to the asymmetric and symmetric stretches of the Xe-N-Te linkage, the NH stretches and bends, and vibrations of the F$_5$TeN- group. Minor amounts of the salts, Xe$_2$F$_3^+$AsF$_6^-$ and F$_5$TeNH$_3^+$AsF$_6^-$, were also detected.
in the Raman spectra, and arise from decomposition reactions (Chapter 6) and equilibrium (5.4), respectively.

(v) **Decomposition of F$_2$TeN(H)-Xe$^+$ in Solution and Characterization and Decomposition of F$_2$TeNF$_2$**

Chapter 6 describes the decomposition of F$_2$TeN(H)-Xe$^+$ in HF and BrF$_5$ solvents, using primarily $^{19}$F NMR spectroscopy. Slow decomposition of F$_2$TeN(H)-Xe$^+$AsF$_6^-$ in BrF$_5$ (-40 °C) and HF (-33 °C) solvents resulted in the formation of the difluoramo compound, F$_2$TeNF$_2$. This species was unknown prior to this study. Natural abundance and 99.5% $^{15}$N-enriched F$_2$TeNF$_2$ have been characterized in HF and BrF$_5$ solvents by $^{19}$F and $^{15}$N NMR spectroscopy. The decomposition of F$_2$TeN(H)-Xe$^+$AsF$_6^-$ was postulated to involve nucleophilic fluorination of nitrogen with elimination of xenon gas and AsF$_5$ [equations (6.1) and (6.2)]. This mode of decomposition is similar to that observed for the phenylxenonium(II) cations, R-Xe$^+$ (R = C$_6$F$_5$, m-CF$_3$C$_6$H$_4$, p-FC$_6$H$_4$), as discussed in Chapter 6. The nucleophilic fluorination of F$_2$TeN(H)-Xe$^+$ represents the first complete study of a non-radical decomposition mechanism for a compound containing a xenon(II)-nitrogen bond.

The complete decomposition of F$_2$TeNF$_2$ to FN=N$^+$ and TeF$_6$ in HF solvent at -20 °C was observed by $^{19}$F NMR spectroscopy; some F$_2$TeN(H)-Xe$^+$ was still observed. The decomposition of difluoramo compounds, RNF$_2$ (R = F$_5$S, Cl, F$_3$C, F$_3$CO, F$_5$SO)$^{275}$ in the presence of Lewis acids such as SbF$_5$ and AsF$_5$ indicates that transient fluoronitrenes, NF, may be produced. In the present system, an alternative mechanism for the formation of the decomposition products was proposed [see equations (6.16) to (6.27)]. It was postulated that F$_3$TeNH$_3^+$, which was present in HF solution according to equilibrium (5.4), reacted with F$_2$TeNF$_2$. The strong Lewis fluoroacid, AsF$_5$, which was generated from the decomposition of
F\textsubscript{5}TeN(H)-Xe\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} (see above), likely catalyzed the reaction by abstraction of fluoride from F\textsubscript{5}TeNF\textsubscript{2} [equation (6.19)]. The reaction of F\textsubscript{5}TeNH\textsubscript{3}\textsuperscript{+} and F\textsubscript{5}TeNF\textsubscript{2} is directly analogous to the well-established reactions of primary amines with difluoramine, HNF\textsubscript{2}.\textsuperscript{282} One result of the decomposition of F\textsubscript{5}TeNF\textsubscript{2} was the increased fluoroacidity of the HF solution. Evidence for this was provided by the coalescence of the AsF\textsubscript{6}\textsuperscript{6-}, HF and XeF\textsubscript{2}\textsuperscript{19F NMR resonances, which resulted from exchange of these species with AsF\textsubscript{5} according to equations (6.3) to (6.5).

(vi) Preparation and Characterization of FO\textsubscript{2}SNH\textsubscript{3} and FO\textsubscript{2}SNH\textsubscript{3}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}

The amides, FO\textsubscript{2}SNH\textsubscript{2} and FO\textsubscript{2}SNH\textsubscript{3}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}, were prepared primarily for their use as ligands for the preparation of FO\textsubscript{2}SN(H)-Xe\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}. The salt, FO\textsubscript{2}SNH\textsubscript{3}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}, was prepared by reaction of FO\textsubscript{2}SNH\textsubscript{2} and excess AsF\textsubscript{5} in anhydrous HF solvent at -40 °C. Although preparations of FO\textsubscript{2}SNH\textsubscript{2} were previously reported (see Chapter 7) no attempts to protonate FO\textsubscript{2}SNH\textsubscript{2} have been published. Therefore a detailed Raman and NMR (\textsuperscript{1}H and \textsuperscript{19}F) spectroscopic study of natural abundance and 99.5\% \textsuperscript{15}N-enriched FO\textsubscript{2}SNH\textsubscript{2} and FO\textsubscript{2}SNH\textsubscript{3}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} was performed. The vibrational spectrum of FO\textsubscript{2}SNH\textsubscript{2} was reported by Semmoud and Vast;\textsuperscript{130} however, the assignments were improved in the present Raman spectroscopic study with the aid of \textsuperscript{14/15}N isotopic shifts of bands associated with vibrations of the nitrogen center. In general, the assignments of Semmoud and Vast underestimate the degree of vibrational coupling of modes in FO\textsubscript{2}SNH\textsubscript{2}. This was evidenced by the fact that all bands in the Raman spectrum of FO\textsubscript{2}SNH\textsubscript{2}, except for those assigned to the symmetric and asymmetric S-O stretching modes, had an \textsuperscript{14/15}N isotopic dependence. Assignments for the bands observed in the Raman spectra of FO\textsubscript{2}SNH\textsubscript{3}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} were also aided by the measurement of \textsuperscript{14/15}N isotopic shifts. Comparing the Raman spectra of FO\textsubscript{2}SNH\textsubscript{2} and FO\textsubscript{2}SNH\textsubscript{3}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} indicated changes in the bonding of the FO\textsubscript{2}SN-group on protonation of FO\textsubscript{2}SNH\textsubscript{2} to give FO\textsubscript{2}SNH\textsubscript{3}\textsuperscript{+}. Protonation of FO\textsubscript{2}SNH\textsubscript{2} resulted in
increased values for the S-F and S-O stretches, and a decrease in the S-N stretch. This was consistent with S-N π-bonding in FO2SNH2, which is reduced upon protonation of the nitrogen center by making the nitrogen lone pair of electrons unavailable for S-N π-donation. In a previous vibrational study, a similar reduction in S-N π-bonding was noted on protonation of NSO2F2- to give H2NSO2F. A similar reduction in S-N π-bonding was also reflected in the vibrational spectra and crystallographically determined bond lengths for the series, NSO32-, H2NSO5- and H3SO3, and the analogous behavior in NSO2F2- and H2NSO2F was noted. The present work completes the comparison of the sulfurylamides and the fluorosulfurylamides by providing detailed vibrational assignments for FO2SNH2 and FO2SNH3+, which are isoelectronic with H2NSO3- and H3NSO3.

(vii) Preparation of [Fluorosulfurylamido]xenonium(II) Hexafluoroarsenate;

\[ \text{FO}_2\text{SN(H)}^-\text{Xe}^+\text{AsF}_6^- \]

Fluorosulfuryl amide, FO2SNH2, is isoelectronic with fluorosulfuric acid, FO2SOH. Since the latter is known to undergo HF elimination reactions with XeF2 to give FXeOSO2F and Xe(OSO2F)2, it was postulated that FO2SNH2 might be sufficiently electronegative to form a compound containing a xenon(II)-nitrogen bond. Although no ionization potential data allowing an estimate of the oxidative resistance of FO2SNH2 was available, the success in the use of F2TeNH2 as a ligand for xenon(II) by analogy with F2TeOH provided the incentive to attempt the analogous reactions with FO2SNH2. It was found that the reaction of equimolar amounts of FO2SNH2 and XeF2AsF6 in HF at -50 °C resulted in a yellow solution above white and yellow precipitates. The 129Xe NMR spectrum was consistent with the preparation of FO2SN(H)-Xe+, however, the resonance was broadened, and had an irregular shape (non-Lorentzian) due to the large amount of solid present in the sample. Complete decomposition of FO2SN(H)-Xe+ had
occurred within one hour. Warming of a similar sample to -35 °C in an attempt to dissolve the solids resulted in complete decomposition of FO₂SN(H)-Xe⁺ within 30 seconds.

Protonation of FO₂SNH₂ in HF solvent in the presence of an excess amount of AsF₅ resulted in the N-protonated salt, FO₂SNH₃⁺AsF₆⁻. Reaction of FO₂SNH₃⁺AsF₆⁻ with XeF₂ at -58 °C in BrF₅ solvent resulted in an HF elimination reaction to give FO₂SN(H)-Xe⁺ [equation (8.1)]. The 129Xe NMR resonance (-2663 ppm) was a singlet; the failure to observe the one-bond 129Xe-¹⁴N coupling was attributed to quadrupolar collapse resulting from the rapid relaxation of the quadrupolar ¹⁴N (I = 1) nucleus. This was confirmed by preparing 99.5% ¹⁵N-enriched FO₂SN(H)-Xe⁺; the 129Xe NMR spectrum consisted of a doublet arising from the one-bond scalar coupling, ¹J(¹²⁹Xe-¹⁵N) = 109 Hz. The scalar couplings ²J(¹²⁹Xe-¹H) and ³J(¹²⁹Xe-¹⁹F) were not resolved. This was assumed to result from SA broadening of the 129Xe NMR resonance, since broadening of this nature is proportional to the square of the external magnetic field strength, and the 129Xe NMR spectrum was recorded using a very strong magnetic field (11.7440 T). A broad 129Xe NMR resonance was also observed for ¹⁵N-enriched F₂TeN(H)-Xe⁺ at 11.7440 T; a significant reduction in the 129Xe linewidth was observed at lower field. Natural abundance and 99.5% ¹⁵N-enriched samples of FO₂SN(H)-Xe⁺ cation were also characterized by ¹⁹F and ¹H NMR spectroscopy. The ¹H NMR spectrum of 99.5% ¹⁵N-enriched FO₂SN(H)-Xe⁺ consisted of a doublet arising from the one-bond scalar coupling, ¹J(¹H-¹⁵N). The ¹⁹F NMR spectrum consisted of a singlet, and the scalar couplings ²J(¹⁹F-¹⁵N) and ³J(¹⁹F-¹H) were not resolved. Xenon-129 satellite peaks arising from ³J(¹⁹F-¹²⁹Xe) and ²J(¹H-¹²⁹Xe) were not observed in the ¹⁹F and ¹H NMR spectra, respectively. This was rationalized by considering the low concentration of FO₂SN(H)-Xe⁺ in BrF₅ solvent; integration of the ¹⁹F and ¹H NMR
resonances indicated that the ratio [FO₂SNH₂⁺] : [FO₂SN(H)-Xe⁺] was 8 : 1. The low equilibrium concentration of FO₂SN(H)-Xe⁺AsF₆⁻ in BrF₅ solvent and its thermal instability indicated that it was not feasible to attempt to isolate FO₂SN(H)-Xe⁺AsF₆⁻ in the solid state. The FO₂SN(H)-Xe⁺ cation is certainly the most unstable xenon(II)-nitrogen bonded species to have been characterized in solution.

(viii) **Nature of the Bonding in CF₃C(OXeF)NH₂⁺, F₅TeN(H)-Xe⁺ and FO₂SN(H)-Xe⁺, and the Relative Electronegativities of the F₅TeN(H)- and FO₂SN(H)-Ligand Groups**

Previous NMR studies of xenon(II) derivatives containing Xe-F groups bonded to oxygen or fluorine have shown that the ¹⁹F and ¹²⁹Xe NMR parameters can be used to assess the relative covalent characters of the Xe-O, Xe···F bridge and terminal Xe-F bonds. In general, as the ionic character of the Xe-F bond increases, the ¹²⁹Xe NMR resonance becomes more shielded. This accompanied by decreasing magnitudes of ¹J(¹²⁹Xe-¹⁹F) and deshielded ¹⁹F NMR resonances. In compounds of the form R-Xe-F, increased Xe-F bond ionic character results from decreased electronegativity of the ligand, R. Therefore it is possible to qualitatively rank compounds of the form R-Xe-F according to the relative ionic characters of the Xe-R and Xe-F bonds based on the ¹⁹F and ¹²⁹Xe NMR parameters. The Raman data for compounds of the form R-Xe-F complements the bonding information obtained from the NMR parameters. In general, increased ionic character of the terminal Xe-F bond results in a decrease in the Xe-F stretching frequency.

Table 3.2 was used to assess the relative ionic characters of the Xe-O and Xe-F
bonds in CF₂C(OXeF)NH₂⁺ by comparing the ¹⁹F and ¹²⁹Xe NMR chemical shifts, 
¹J(¹²⁹Xe-¹⁹F) and ν(Xe-F) for a series of compounds of the form R-Xe-F. The compounds have been ranked in order of increasing Xe-F bond ionic character; the magnitude of ¹J(¹²⁹Xe-¹⁹F) has been used to rank the species since the ¹⁹F and ¹²⁹Xe chemical shifts for xenon(II) compounds often vary depending on the temperature and solvent, and ν(Xe-F) is often determined from the average of several peaks. The magnitude of ¹J(¹²⁹Xe-¹⁹F) indicates that the Xe-F bond in CF₂C(OXeF)NH₂⁺ is more ionic than those in the recently characterized xenon-nitrogen bonded adduct cations, 
F₃S≡N-XeF⁺ and HC≡N-XeF⁺. It follows that the Xe-O bond is more covalent than the xenon-nitrogen bonds of those cations. It is interesting to compare the spectroscopic parameters of CF₂C(OXeF)NH₂⁺ and (CF₃)₂S=O-XeF⁺, since these are the only known examples of adduct cations containing xenon-oxygen bonds. Using similar arguments, it is clear that the Xe-O bond in CF₂C(OXeF)NH₂⁺ is more covalent. This is reasonable when one considers that π-donation from nitrogen to carbon in CF₂C(OXeF)NH₂⁺ (see resonance Structures 3.3 and 3.4) may result in a formal oxygen hybridization that is intermediate between sp² and sp³. No such resonance contributors can be drawn for (CF₃)₂S=O-XeF⁺, and the formal oxygen hybridization is sp², which is expected to contribute to a higher ligand electronegativity due to the higher valence s-character of the oxygen hybrid orbitals.

The ¹²⁹Xe NMR chemical shifts of F₂TeN(H)-Xe⁺ and FO₂SN(H)-Xe⁺ are among the most shielded ¹²⁹Xe NMR resonances for xenon(II) compounds containing xenon-nitrogen bonds (see Table 5.3). Only two other cations containing xenon(II)-
nitrogen bonds have similar $^{129}$Xe NMR chemical shifts, namely, $F_4S=N-Xe^+$ and $F_5SN(H)-Xe^+$. The $^{129}$Xe NMR chemical shifts of all other compounds containing xenon(II)-nitrogen bonds are deshielded by 600 to 1000 ppm relative to the xenon(II)-nitrogen bonded cations mentioned above. The absence of Xe-F bonds in these cations is consistent with the highly shielded $^{129}$Xe NMR resonances. As mentioned above, increasing Xe-F bond ionic character in R-Xe-F compounds is accompanied by increased shielding of the $^{129}$Xe NMR resonances. The cations $F_5TeN(H)-Xe^+$, $FO_2SN(H)-Xe^+$, $F_4S=N-Xe^+$ and $F_5SN(H)-Xe^+$ may be considered as compounds of the form R-Xe-F, where the Xe-F bond is completely ionic. Ionization of the Xe-F bonds therefore results from the relatively low electronegativity of the nitrogen ligands and largely accounts for the highly shielded $^{129}$Xe NMR resonances.

Since the $^{129}$Xe NMR chemical shifts for xenon(II) compounds are directly related to the covalent character of the xenon-ligand bonds, it is possible to qualitatively estimate the relative electronegativities of the $F_5TeN(H)$- and $FO_2SN(H)$- ligands. The $^{129}$Xe NMR chemical shifts of $F_5TeN(H)-Xe^+$ (-2902 ppm) and $FO_2SN(H)-Xe^+$ (-2660 ppm) indicate that $FO_2SN(H)$- is more electronegative than $F_5TeN(H)$-. This is in accordance with the greater electronegativity of $FO_2SO^-$ than $F_5TeO^-$, as indicated in a $^{129}$Xe NMR study of the mixed derivatives $XeL_2$ and $FXeL$ ($L = cis-OIOF_4$, $trans-OIOF_4$, -OTeF$_5$, -OSO$_2$F).$^{42}$

(B) CONCLUSIONS

Significant progress has been made in noble-gas chemistry by preparing and
investigating the spectroscopic properties of xenon(II) compounds containing novel xenon-nitrogen and xenon-oxygen bonds. The first ionization potential of CF$_3$C(O)NH$_2$ has been used as a measure of its resistance to oxidation by the XeF$^+$ cation. Bases whose first adiabatic ionization potentials are equal to or greater than the estimated electron affinity of XeF$^+$ are potentially resistant to oxidation by XeF$^+$. The successful preparation of CF$_3$C(OXeF)NH$_2$AsF$_6^-$ at low temperature further illustrates the utility of this method of selecting appropriate bases for preparing adduct cations of XeF$^+$ which are stable at low temperatures.

The overall significance and impact of this work is summarized below:

1. The preparation of CF$_3$C(OXeF)NH$_2$AsF$_6^-$ represents the second example of an adduct cation containing the O-Xe-F linkage, thus contributing to a rare class of compounds.

2. The use of the two-dimensional heteronuclear ($^1$H-$^{19}$F) NOESY technique to determine the assignments for the amido protons in the $^1$H NMR spectrum of CF$_3$C(OXeF)NH$_2$AsF$_6^-$ represents the first use of this well-established technique to facilitate the characterization of a thermally unstable noble-gas compound.

3. The preparation of F$_5$TeNH$_3$AsF$_6^-$ and FO$_2$SNH$_3$AsF$_6^-$ represents the first attempts to protonate the electronegative amines, F$_5$TeNH$_2$ and FO$_2$SNH$_2$, and the Raman spectroscopic study of these amines and their ammonium salts has improved the vibrational characterization of the previously reported amines, and has probed the effect of protonation on the bonding in the F$_5$TeN- and FO$_2$SN- groups.
(4) The preparation of $F_5TeN(H)$-Xe$^+$AsF$_6^-$ and FO$_2$SN(H)-Xe$^+$AsF$_6^-$ has provided two new examples of xenon(II)-nitrogen compounds in which the nitrogen center is $sp^3$-hybridized. Previous to this work, only one example of this class of compounds was known, namely, $F_5SN(H)$-Xe$^+$AsF$_6^-$.

(5) The nucleophilic fluorination of $F_5TeN(H)$-Xe$^+$ to give $F_5TeNF_2$ represents a mode of decomposition not previously observed for compounds containing xenon(II)-nitrogen bonds.

(6) The preparation of $F_5TeNF_2$ from the decomposition of $F_5TeN(H)$-Xe$^+$AsF$_6^-$ is significant in that it represents the first report of this difluoroamino compound, although the sulfur analog, $F_5SNF_2$, has been known since 1963.$^{307}$ The decomposition of $F_5TeNF_2$ in AsF$_5$-acidified HF solvent indicates that the chemical behavior of this compound is similar to other known difluoroamino compounds.

(C) DIRECTIONS FOR FURTHER RESEARCH

(i) Preparation of New Amines from the Reaction of $F_5TeN(H)$-Xe$^+$AsF$_6^-$ with Nucleophiles

The decomposition of $F_5TeN(H)$-Xe$^+$AsF$_6^-$ resulted in the formation of $F_5TeNF_2$ in HF and BrF$_5$ solvents. The decomposition of $F_5TeN(H)$-Xe$^+$AsF$_6^-$ necessarily increases the AsF$_5$ concentration in solution, which probably catalyzes the decomposition of $F_5TeNF_2$ (see Chapter 6). Isolation of the novel monofluoramine, $F_5TeN(H)F$, may be
possible by preparing $F_5TeN(H)$-$Xe^+AsF_6^-$ in a non-acidic solvent such as $CH_3CN$ or $CH_2Cl_2$. Addition of an excess of a fluoride source such as $N(CH_3)_4^+F^-$ may facilitate the nucleophilic fluorination of $F_5TeN(H)$-$Xe^+AsF_6^-$ without generation of $AsF_5$ [equation (9.3)]. In the absence of $AsF_5$, the ionization of $XeF_2$ to give the powerful oxidative

$$F_5TeN(H)$-$Xe^+AsF_6^-$ + $N(CH_3)_4^+X^-$ $\rightarrow$

$$F_5TeN(H)X + Xe + N(CH_3)_4^+AsF_6^-$

(X = F, Br, I)

fluorinator $XeF^+$ will not occur, and $F_5TeN(H)F$, which was assumed to be oxidatively fluorinated by $XeF^+$ in Chapter 6, may be observable by $^{19}F$ and $^1H$ NMR spectroscopy. Addition of $(CH_3)_4N^+I^-$ or $(CH_3)_4N^+Br^-$ may also result in nucleophilic attack on the nitrogen center, by analogy with the analogous reactions of these halide sources with $[C_6F_5Xe^+]$[$C_6F_5BF_3^-$] to give $C_6F_5X$ (X = Br, I) and xenon gas.$^{95}$ In this way it may be possible to prepare the hitherto unknown compounds, $F_5TeN(H)Br$ and $F_5TeN(H)I$.

(ii) **Preparation of Substituted Hydrazines and/or Diazenes**

The decomposition of $F_5TeNF_2$ in the presence of an excess of $F_5TeNH_3^+$-$AsF_6^-$ in $AsF_5$-acidified HF solvent (Chapter 6) is postulated to involve the nucleophilic attack of $F_5TeNF_2$ by $F_5TeNH_3^+$, with $AsF_5$ acting as a catalyst. While the decomposition of the difluoramino compounds, $RNF_2$ (R = CF$_3$, F$_5$S, Cl, F$_5$SO, CF$_3$O), in $AsF_5$-acidified HF has been investigated,$^{275}$ the reaction of these difluoramines with primary amines has
not been investigated. As discussed in Chapter 6, reductive deamination of primary and secondary amines results upon reaction with HNF₂ [equations (6.16) and 6.17]]. It would be interesting to attempt the same reactions with the series of difluoramo compounds mentioned above [equation (9.4)]. In the absence of an oxidative fluorinating agent (e.g., XeF₄), [R-NH₂-N(F)-R']⁺AsF₆⁻ may be isolable. Elimination of HF [equations (9.5) and (9.6)] may result in the diazenes, R-N=N-R'. Although the compounds, R-N=N-H (R =

$$R\cdot NH₂ + R'\cdot NF₂ + AsF₅ \rightarrow [R\cdot NH₂\cdot N(F)\cdot R']⁺AsF₆⁻ \quad (9.4)$$

(R = alkyl, fluoroalkyl; R' = CF₃, F₅S, Cl, etc.)

$$[R\cdot NH₂\cdot N(F)\cdot R']⁺AsF₆⁻ \rightleftharpoons R\cdot N(H)\cdot N(F)\cdot R' + H⁺AsF₆⁻ \quad (9.5)$$

$$R\cdot N(H)\cdot N(F)\cdot R' \rightarrow R\cdot N=N-R' + HF \quad (9.6)$$

alkyl), are not stable, decomposing to give R-H and N₂, the electronegative substituents in R-N=N-R' above may stabilize the diazene in the same way that fluorine stabilizes F=N=N-F, whereas H-N=N-H is not an isolable species.

(iii) **Further Characterization of FO₂SN(H)⁻Xe⁺AsF₆⁻ by ¹²⁹Xe and ¹⁵N NMR**

The ¹²⁹Xe, ¹H and ¹⁹F NMR parameters for natural abundance and 99.5% ¹⁵N-enriched FO₂SN(H)⁻Xe⁺ have been obtained at low temperatures (see Chapter 8). Only the one-bond scalar coupling ¹J(¹²⁹Xe⁻¹⁵N) was observed in the ¹²⁹Xe NMR spectrum


using an external magnetic field strength of 11.7440 T. Similarly, only $^{1}J(^{129}\text{Xe}-^{15}\text{N})$ was observed in the $^{129}\text{Xe}$ NMR spectrum of $\text{F}_3\text{TeN(H)-Xe}^+$ at 11.7440 T. Obtaining the $^{129}\text{Xe}$ NMR spectrum at 7.4630 T significantly reduced the linewidths of $\text{F}_3\text{TeN(H)-Xe}^+$ resulting from SA broadening (see Chapter 5), and all possible scalar couplings were observed except $^{3}J(^{129}\text{Xe}-^{19}\text{F}_{ax})$, the scalar coupling of $^{129}\text{Xe}$ with the axial fluorine bonded to tellurium(VI). By analogy it may be possible to reduce the line width of the $^{129}\text{Xe}$ NMR resonance for $\text{FO}_2\text{SN(H)-Xe}^+$ by performing the NMR experiment at 7.4630 T, enabling the scalar couplings, $^{2}J(^{129}\text{Xe}-^{1}\text{H})$ and $^{3}J(^{129}\text{Xe}-^{19}\text{F})$ to be resolved.

Conditions must be optimized so that the $^{15}\text{N}$ NMR spectrum of $\text{FO}_2\text{SN(H)-Xe}^+$ can be obtained. Due to the low concentration of this species in BrF$_5$ solvent at ca. -60 °C and the thermal instability of $\text{FO}_2\text{SN(H)-Xe}^+$ upon warming samples above this temperature, it was not possible to obtain a satisfactory $^{15}\text{N}$ NMR spectrum. Since the magnitude of the one-bond coupling, $^{1}J(^{1}\text{H}-^{15}\text{N})$, is known from the $^{1}\text{H}$ NMR spectrum, it should be possible to perform an INEPT experiment with $^{15}\text{N}$ as the observed nucleus; polarization transfer from $^{1}\text{H}$ to $^{15}\text{N}$ will significantly improve the signal-to-noise and the rate of acquisition of the $^{15}\text{N}$ NMR spectrum, thus enabling the $^{15}\text{N}$ NMR spectrum of 99.5% $^{15}\text{N}$-enriched $\text{FO}_2\text{SN(H)-Xe}^+$ to be obtained.

(iv) Proposed Preparation of $\text{F}_2\text{P(O)N(H)-Xe}^+\text{AsF}_6^-$

The ligand $\text{F}_2\text{P(O)}$- was shown to stabilize xenon(II) in the compounds $\text{FXeOP(O)F}_2$ and $\text{Xe[OP(O)F}_2]_2$ from the reaction of $\mu$-oxo-bis(phosphoryl difluoride), $\text{P}_2\text{O}_3\text{F}_4$, and $\text{XeF}_2$ at 22 °C in CFCl$_3$ solution. By analogy with $\text{FO}_2\text{SNH}_2$ and
F₂TeNH₂, the amine, F₂P(O)NH₂, may also stabilize xenon(II) in the form of a cation at low temperature [equation (9.7)] in BrF₅ or HF solvents. The compound, F₂P(O)NH₂, has

\[ F₂P(O)NH₃⁺AsF₆⁻ + XeF₂ → F₂P(O)N(H)-Xe⁺AsF₆⁻ + 2 HF \]  (9.7)

been prepared from the reaction of NH₃ with F₂P(O)-O-P(O)F₂ [equation (9.8)], and it may be possible to protonate F₂P(O)NH₂ as well [equation (9.9)] in AsF₅-acidified HF.

\[ F₂P(O)-O-P(O)F₂ + 2 NH₃ → NH₄⁺PO₂F₂⁻ + F₂P(O)NH₂ \]  (9.6)

\[ F₂P(O)NH₂ + HF + AsF₅ → F₂P(O)NH₃⁺AsF₆⁻ \]  (9.7)

The method of synthesis of F₂P(O)NH₂ will allow for a relatively simple synthesis of the ¹⁵N-enriched analog, which will probably be required to observe the scalar Xe-N coupling in the ¹²⁹Xe NMR spectrum.
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153. Hindered rotation was observed in the $^1$H NMR spectra of O-protonated carbamyl fluoride, FC(OH)NH$_2^+$, in HSO$_3$F/SO$_2$ solution, resulting in two unassigned resonances for the chemically inequivalent NH protons at $\delta(^1H) = 8.5$ ppm [reference (149)]. The $^1$H NMR spectrum of $^{15}$N-enriched O-protonated benzamide in HSO$_3$F or 100% H$_2$SO$_4$ solvent shows two peaks of equal intensity at 8.36 and 7.94 ppm, at temperatures below 65 °C. The high-frequency peak was assigned to the proton trans to the protonated carbonyl group [reference (148)]. Birchall and Gillespie [reference (145)] reported proton-on-nitrogen resonances at 8.36 and 8.24 ppm for O-protonated acetamide in HSO$_3$F solvent at -80 °C; the high-frequency resonance was assigned to the proton cis to the protonated carbonyl group. Using the NOE difference technique, the proton cis to the carbonyl group was assigned to the high-frequency $^1$H NMR resonance in the structurally related protonated trichloroacetimidate cation, CCl$_3$C(OCH$_3$)NH$_2^+$, in 95% H$_2$SO$_4$ solution [reference (147)].


157. The errors associated with integration of NMR resonances are estimated to be ± 10%.


175. (a) \( \nu_{\text{sym}}(\text{Xe-F}) = 495 \text{ cm}^{-1} \) in the Raman spectrum measured at -165 °C; this work. (b) D.F. Smith, In "Noble Gas Compounds"; H.H. Hyman, Ed.; University of Chicago Press: Chicago and London, 1963; p. 295. (c) Ibid., J.J. Turner and G.C. Pimentel, p. 101.


The Raman spectra of these adducts are essentially reproduced by summing the spectra of the starting materials and are consistent with negligible changes in the bonding of the constituent molecules in the adducts. The adducts XeF$_2$·2XeF$_5$·2AsF$_5$ and Ag(XeF$_2$)$_2$AsF$_6$ are the only previously reported examples of symmetrical XeF$_2$ coordinated to cations. The Raman spectrum of the former shows a prominent peak at 498 cm$^{-1}$ that is assigned to $\nu_{\text{sym}}$(Xe-F) for XeF$_2$ in the adduct, which is not significantly different from that observed for crystalline XeF$_2$, at 496 cm$^{-1}$ (reference (175b)). The bands attributed to $\nu_{\text{sym}}$(Xe-F) in Ag(XeF$_2$)$_2$AsF$_6$ occur at 501 and 508 cm$^{-1}$, indicating an average increase of 8 cm$^{-1}$ relative to crystalline XeF$_2$. The crystal structures of XeF$_2$·2XeF$_5$·2AsF$_5$ and Ag(XeF$_2$)$_2$AsF$_6$ indicate that the fluorine ligands of XeF$_2$ are weakly coordinated to the cations (central Xe atom of XeF$_5^+$ and Ag$^+$, respectively), and the Xe-F bond lengths are 2.01(2) and 1.979(3) Å that are not significantly different from the Xe-F bond length in crystalline XeF$_2$ (2.00(1) Å) [H.A. Levy and P.A. Agron, J. Am. Chem. Soc., 85, 241 (1963)]. This is consistent with little alteration of the bonding of XeF$_2$ in these adducts; the intermolecular bonding in these adducts may be attributed primarily to the electrostatic interaction of the cation and the fluorine atoms of XeF$_2$, which contain partial negative charge due to a high degree of Xe-F bond polarity [also see reference (25), p. 259].

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