SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF NEW HIGH-VALENT INORGANIC FLUORINE COMPOUNDS AND THEIR OXIDIZING PROPERTIES:

VOLUME 1.

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FOREWORD

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Noble gas fluorine oxidizers of Neon, Krypton, Argon, and Xenon have been synthesized and characterized. \( \text{KrF}^+ \) and \( \text{XeF}^+ \) cations have been made with neutral organic bases. \( \text{Kr-N} \) and \( \text{Kr-O} \) bonded molecules are also synthesized and characterized. The hypervalent compounds \( \text{ClF}_6^- \) and \( \text{XeF}_5^- \) are made. The anions \( \text{IF}_6^- \), \( \text{TeF}_6^2^- \), \( \text{TeF}_7^- \) and \( \text{TeF}_8^2^- \) anions are also made. Proof that the \( \text{ClF}_6^- \) anion exists is also presented. The photoelectron spectra of \( \text{XeF}_2 \), \( \text{XeF}_4 \), and \( \text{XeF}_6 \) are obtained using x-ray nonchromatized synchrotron radiation.

The synthesis and characterization of \( \text{Sb(OTeF}_5)_6^- \) \( \text{Et}_4\text{N}^+ \) and \( \text{Bi(OTeF}_5)_6^- \) \( \text{Et}_4\text{N}^+ \) salts is completed. Radiotracer experiments involving \( ^{18}\text{F} \) are also accomplished to show the inability to synthesize \( \text{NF}_5 \) is due to mainly steric reasons.
OVERVIEW OF THE REPORT

The following annual report encompasses eleven areas of research funded by the United States Air Force Astronautics Laboratory, Edwards Air Force Base, California under Contract F49620-87-C-0049. Where possible published or about to be published work is included in this Report under each of the eleven appropriate subheadings. The basic philosophy underpinning this work has been to develop the technology for the synthesis, storage and handling of new high-energy density materials. The importance of performing the "easier" heavy element chemistry as the ground work to synthesizing the more challenging and potentially more useful lighter analogs has been stressed throughout much of this work. The validity of this approach is best illustrated in Part I where the synthesis of HC≡N-XeF+ is described. The synthesis of the xenon compound has made possible the realization of the lighter and more energetic krypton analog, HC≡N-KrF+. The publication of these results in turn precipitated a total of four theoretical papers on HC≡N-Ngl+ (Ng = Ne, Ar, Kr, Xe). While the neon analog is forecast to be unstable, the argon analog, HC≡N-ArF+ is predicted to be stable. The hope of binding ArF+ (also presently unknown), potentially an oxidant of unprecedented strength, to a fuel moiety, HCN, is intriguing and the direct consequence of having done a thorough job delineating the chemistry of the heavier congeners.

Part I is concerned with the syntheses and characterization of noble-gas species in novel bonding situations, more specifically, the investigation of the interactions of the strong oxidant Lewis acid noble-gas cations, KrF+ and XeF+, with neutral organic nitrogen bases. This work has been summarized previously in two Annual Technical Reports: May 1, 1987 - April 30, 1988 and May 1, 1988 - April 30, 1989. These and the present report outline the syntheses and characterization of a large number of new xenon compounds that had been prepared by the interaction of the strong oxidant Lewis acid cation XeF+ with a number of organic nitrogen bases. The majority of the bases that had been selected for study were oxidatively resistant perfluoro-organic nitrogen bases with first ionization potentials exceeding 10-11 eV. These recent findings represent a major extension of Group VIII (18) chemistry in that they (1) significantly extend the range of known Xe-N bonded species, (2) demonstrate that a large range of fluoro-organic ligands are capable of stabilizing Xe(II), (3) produce several examples of the first compounds in which a noble-gas atom serves as an aromatic substituent; (4) provide new series of model compounds which may aid in developing synthetic approaches to the
formation of new xenon-carbon and krypton-oxygen bonds; (5) provide the first examples of Kr-N bonded species, which, in turn provided the impetus for us to successfully attempt the synthesis of the first compound containing a Kr-O bond. Most importantly from the viewpoint of practical impact on the field of propellants and monopropellants, this aspect of our research has demonstrated that under the appropriate conditions, strongly oxidizing Lewis acid cations can be bound to fuel substrates containing a base center. The best illustration of this which we have discovered in the course of this work has been the F-Kr-N≡CH⁺ cation, where KrF⁺ represents the most potent chemical oxidant known.

The syntheses and attempted syntheses of adduct cations with other xenon Lewis acids are also described in Part I, namely XeOTeF₄⁺ and XeF₃⁺. Using the XeOTeF₅⁺ cation as an acceptor, two novel compounds containing the first examples of N-Xe-O linkages were prepared, s-C₃F₇N₂N-XeOTeF₄⁺AsF₆⁻ and s-C₃F₇N₂N-XeOTeF₅⁺Sb(OTeF₅)₆⁻. The novel salt, XeOTeF₅⁺Sb(OTeF₅)₆⁻, was also synthesized in the course of this work, and is the only noble-gas salt known which is soluble at low temperatures in a low polarity solvent and also represents the first ionic fully OTeF₅ substituted derivative. These compounds were characterized by ¹⁹F NMR, ¹²⁹Xe NMR and low-temperature laser Raman spectroscopy.

Part II describes the syntheses and characterization of the first Kr-N bonded species, HC≡N-KrF⁺ and three further examples of Kr-N bonds in which the KrF⁺ cation is bonded to an organic moiety, namely, RₓC≡N-KrF⁺ (Rₓ = CF₃, C₂F₅, n-C₃F₇) and their xenon analogs.

Part III describes our recently published theoretical findings relating to the HC≡N-KrF⁺ and HC≡N-XeF⁺ cations.

Part IV describes the preparation and characterization of Kr(OTeF₅)₂. This compound provides the first example of a species containing a Kr-O bond and has been prepared by the reaction of KrF₂ with natural abundance and ᵁO-enriched B(OTeF₅)₃ at -90 to -112 °C in SO₂ClF solvent. Characterization of thermally unstable Kr(OTeF₅)₂ and its decomposition products has been achieved using ¹⁹F and ᵁO NMR spectroscopy.

In view of the reported Lewis base properties of N≡SF₃ and its resistance to oxidation (first adiabatic ionization potential, 12.50 eV), it was considered likely that N≡SF₃ would form adducts with the noble-gas cations XeF⁺, XeOTeF₅⁺ and XeOSeF₅⁺, which would be stable to redox degradation. No values of electron affinity (EA) other than for XeF⁺ (10.9 ev), KrF⁺ (13.2 eV) and ArF⁺ (13.6
eV) are available. However, the EA values of XeOSeF$_5^+$ and XeOTcF$_5^+$ are predicted to be less than that of XeF$_4^+$. and all xenon(II) cations are below the first ionization potential (IP) of N≡SF$_3$. Consequently, the xenon(II) cations were expected to form cation-stable adduct cations with N≡SF$_3$. In Part V, the ligand, N≡SF$_3$, was also studied in a variety of oxidatively resistant solvents deemed suitable for noble-gas compound syntheses, and adducted with the Lewis acid AsF$_5$ to assess the base character of the ligand. Aspects of this work were reported on in our Annual Technical Report, May 1, 1989 - April 30, 1990. The F$_5$SeO-Xe-N≡SF$_3^+$ and F-Xe-N≡SF$_3^+$ cations have been synthesized in BrF$_5$ solvent and fully characterized by $^{129}$Xe, $^{14}$N and $^{19}$F NMR spectroscopy. The salt, F-Xe-N≡SF$_3^+$AsF$_6^-$, was also synthesized by the direct combination of XeF$_4^+$AsF$_6^-$ and N≡SF$_3$ at -20 °C and the vibrational spectrum was studied using low-temperature Raman spectroscopy. In addition, the solvolysis of F-Xe-N≡SF$_3^+$ has been studied in anhydrous HF and has lead to the novel F$_5$S=N(H)-Xe-1$^+$ cation. The latter cation has been characterized in solution by $^{129}$Xe, $^{14}$N and $^{19}$F NMR spectroscopy. Based on the $^{19}$F and $^{129}$Xe NMR spectroscopic data, further solvolysis of this cation in HF gives rise to the F$_5$S=N(H$_2$)-Xe-F$^+$ cation, the first example of an sp$^3$-nitrogen bonded to a noble gas. Based on our understanding of Lewis acid-base adduct chemistry incorporating the strongly oxidizing noble-gas cations as acceptor centers, it should be possible to extend the range of bases coordinated to noble-gas cations and to other strong oxidizers such as chlorine fluoro-cations to include related bases having heats of formation that are more endothermic such as NH$_2$F ($\Delta H_{\text{f}} = 9.1$ kcal mol$^{-1}$, as a pure compound: NH$_2$F is a violent detonator; cf., gas phase heats of formation for HC≡N, -31.2; NF$_3$, -31.9; NF$_2$H, -15.5; NH$_3$, -11.0 kcal mol$^{-1}$). Although the latter chemistry has not yet been achieved, much of the ground work has been laid by demonstrating that the higher molecular weight analogs exist. In this instance that XeF$_4^+$ can be coordinated to the SF$_3$ analog, F$_5$SNH$_2$, and to F$_5$S=NH in their respective novel cations FXe-N(H$_2$)SF$_5^+$ and FXe-N(H)=SF$_4^+$.

In Parts VI and VII the hypervalent anions ClF$_n^-$ and XeF$_n^-$ were prepared and studied for the first time. Aspects of the work described in Parts VI and VII were carried out in collaboration with Drs. K.O. Christe and W.W. Wilson, Rocketdyne Division, North American Rockwell, Canoga Park, California. This work has previously been summarized in our Annual Technical Report, May 1, 1989 - April 30, 1990. Hypervalent fluoro- and oxofluoro-anions are known to offer the best possibility for stabilizing high oxidation states of the elements. These species are of particular importance as they serve to extend our knowledge of the interrelation of valence electron lone pair
stereochernical activity and coordination number in strong oxidizer fluorides. The CIF₆⁻ anion was determined to possess a stereochemically inactive lone pair while the two valence lone pairs of XeF₅⁻ are active. Since our last Annual Technical Report, the hypervalent, highly coordinated, high-oxidation state anions IF₆O⁻, TeF₆O²⁻, TeF₇⁻, IF₈⁻ and TeF₈²⁻ have been synthesized in anhydrous CH₃C≡N using anhydrous N(CH₃)₄⁺F as the fluoride ion source and are reported on in Part VII.

In Part VI, the low-temperature reaction of either N(CH₃)₄F or CsF with ClF₅ in CH₃C≡N solutions are shown to produce white solids (the N(CH₃)₄⁺ salt is explosive) which, based on material balances and low-temperature Raman spectra, contain the ClF₆⁻ anion. The similarity of the Raman spectrum of ClF₆⁻ to that of the octahedral BrF₆⁻ indicates that ClF₆⁻ is also octahedral and that the free valence electron pair on chlorine is sterically inactive. The existence of the ClF₆⁻ anion was further supported by an ¹⁹F exchange experiment between ClF₅ and ¹³F-labelled NO₃⁻ which showed complete randomization of the ¹⁹F isotope among the two molecules. A high-field ¹⁹F NMR study of neat ClF₅ and ClF₆ in anhydrous HF solution in the presence and absence of excess CsF has provided accurate measurements of the ClF₆ NMR parameters including, for the first time, both ¹⁷/¹³C₁ secondary isotopic ¹⁹F NMR shifts. Moreover, the NMR study also supports the existence of ClF₆⁻; showing that ClF₅ undergoes slow chemical exchange with excess CsF in anhydrous HF at room temperature.

In Part VII, the low-temperature reaction of N(CH₃)₄F with XeF₅ in CH₃C≡N was shown to produce N(CH₃)₄⁺XeF₅⁻, a stable white crystalline solid at room temperature, but shock-sensitive at -196 °C. The structure of the XeF₅⁻ anion was determined by X-ray crystallography and shown to be pentagonal planar, representing the first example of an AX₅E₂ (in VSEPR nomenclature) geometry. The anion was also characterized by vibrational spectroscopy and in solution by ¹⁹F and ¹²⁹Xe NMR spectroscopy. The XeF₅⁻ anion has also been prepared as the N(CH₃)₄⁺ salt and studied in CH₃C≡N solution by ¹²⁹Xe NMR spectroscopy and shown to be fluxional on the NMR time scale.

Our preparation of the XeF₅⁻ anion, the first known example of a pentagonal planar AX₅E₂ (where E stands for a free valence electron pair) species, prompted us to study some closely related iodine and tellurium compounds. Furthermore, there are relatively few examples of main-group species which allow the applicability of the valence shell electron pair repulsion (VSEPR) rules to coordination numbers exceeding six to be tested. In Part VIII the IF₆O⁻, TeF₆O²⁻, TeF₇⁻, IF₈⁻ and TeF₈²⁻ anions have been synthesized in anhydrous CH₃C≡N using anhydrous N(CH₃)₄⁺F as the fluoride ion source and characterized by NMR spectroscopy and vibrational spectroscopy and represent examples
of seven- and eight-coordinate species having symmetries $C_{5\nu}$ ($\text{IF}_6\text{O}^-$ and $\text{TeF}_8\text{O}^-$), $D_{5h}$ ($\text{TeF}_7^-$) and $D_{4d}$ ($\text{IF}_8^-, \text{TeF}_8^-$).

Part IX describes the photoelectron spectra of $\text{XeF}_2$, $\text{XeF}_4$ and $\text{XeF}_6$ obtained using monochromatized synchrotron radiation. We have resolved ligand field splittings by photoelectron spectroscopy in relatively deep core levels ($E_b > 30$ eV) for the first time. To resolve these effects required very high resolution not previously attained. The spectra have been characterized using a simple Hamiltonian involving crystal field splitting and spin-orbit splitting. Of particular interest, we have estimated the gas phase structure of $\text{XeF}_6$ from the $\text{Xe} 4d$ spectra using an additive model similar to that used in Mossbauer spectroscopy. It has been shown that for a $C_3v$ $\text{XeF}_6$ structure, $\Theta_{1,2,3} = 50^\circ$ and $\Theta_{4,5,6} = 76 \pm 4^\circ$. This is perhaps the best experimental evidence for the distortion of gas phase $\text{XeF}_6$, and it is shown to be in excellent agreement with the recent theoretical calculations.

Part X describes the syntheses and characterization of the fully substituted -$\text{OTeF}_5$ derivatives of the powerful Lewis acids $\text{SbF}_5$ and $\text{BiF}_5$, namely $\text{M(OTeF}_5)_6$ ($\text{M} = \text{Sb, Bi}$) and the isolation of $\text{Et}_4\text{N}^+$ salts containing the novel octahedral anions $\text{M(OTeF}_5)_6^\text{.}$ The properties of these interesting species are described together with their characterization by $^{19}\text{F}$ NMR spectroscopy and, in the case of $\text{M(OTeF}_5)_6^\text{.}$, by $^{121}\text{Sb}$ and $^{209}\text{Bi}$ NMR spectroscopy. A previous Annual Report (May 1, 1987 - April 31, 1988) described the syntheses and characterization of the fully substituted -$\text{OTeF}_5$ derivatives of the powerful Lewis acids $\text{SbF}_5$ and $\text{BiF}_5$, namely $\text{M(OTeF}_5)_6$ ($\text{M} = \text{Sb, Bi}$) and the isolation of $\text{Et}_4\text{N}^+$ salts containing the novel octahedral anions $\text{M(OTeF}_5)_6^\text{.}$ The properties of these interesting species were described together with their characterization by $^{19}\text{F}$ NMR spectroscopy and, in the case of $\text{M(OTeF}_5)_6^\text{.}$, by $^{121}\text{Sb}$ and $^{209}\text{Bi}$ NMR spectroscopy. As a continuation of this study, Part X also describes the $[\text{Pb(OTeF}_5)_8]^2^-$ anion, which has been generated in $\text{CH}_3\text{C}_2\text{N}$ by means of the reaction of $(\text{Et}_4\text{N})_2\text{PbCl}_6$ with (i) $\text{AgOTeF}_5$ and (ii) $\text{Xe(OTeF}_5)_2$. This is the first example of a $\text{Pb(IV)}$ compound containing the highly electronegative, monovalent $\text{OTeF}_5$ ligand. The $[\text{Pb(OTeF}_5)_8]^2^-$ anion is a large oxidatively resistant anion which is of great interest for stabilizing strongly oxidizing cations such as the noble-gas cations. The $[\text{Pb(OTeF}_5)_8]^2^-$ anion has thus far been characterized in $\text{CH}_3\text{C}_2\text{N}$ by $^{207}\text{Pb}$ and $^{19}\text{F}$ NMR spectroscopy. The inorganic chemistry of $\text{Pb(IV)}$ has also been extended by synthesizing mixtures of the previously unknown octahedral anions $[\text{PbCl}_6\text{F}_8]^2^-$. All the above anions have been characterized in $\text{CH}_3\text{C}_2\text{N}$ solution by $^{19}\text{F}$ and $^{207}\text{Pb}$ NMR spectroscopy. All of these anions are expected, unlike their fluorine analogs, $\text{AsF}_6^-$, $\text{SbF}_6^-$ and $\text{BiF}_6^-$, to be weakly coordinating anions.
For example, \( \text{XeF}^+\text{SbF}_6^- \) is strongly fluorine-bridged in the solid state, i.e., \( \text{F-Xe}^+-\text{F-SbF}_5^- \), whereas

the cation and anion in the \( \text{OTeF}_5^- \)-analog, \( \text{XeOTeF}_5^+\text{Sb(OTeF)}_5^- \), are only weakly interacting. It is anticipated that these anions hold considerable promise for the preparation of novel and unusual species by virtue of their weakly coordinating natures. For example, one might anticipate being able to protonate xenon if the following reaction were carried out in a solvent having a proton affinity lower than that of Xe:

\[
\text{Xe(OTeF}_5^\text{2} + \text{Sb(OTeF}_5^\text{3} + \text{HOTeF}_5 \quad \longrightarrow \quad \text{HXe}^+\text{Sb(OTeF}_5^- \quad (1)
\]

In this instance, \( \text{Sb(OTeF}_5^- \) could reasonably be expected to have a proton affinity lower than that of Xe; if this were so then so that Xe would be preferentially protonated. These large weakly basic anions may also be useful in stabilizing the methyl analog, \( \text{XeCH}_4^- \). The \( \text{XeH}^+, \text{XeCH}_3^+\) and \( \text{KrCH}_3^+\) cations are spectroscopically well characterized in the gas phase and the other \( \text{NgH}^+\) cations are also stable gas phase species and one might anticipate using these weakly coordinating anions to protonate lighter noble gases. The isolation of the first salts of the heavy and light noble-gas cations, \( \text{NgH}^+\) and \( \text{NgCH}_3^+\), could be of general interest to the development and storage of monopropellants and fuels.

Part XI represents a collaborative effort with Drs. K.O. Christie and W.W. Wilson, Rocketdyne Division, North American Rockwell, Canoga Park, California. The project is concerned with \( ^{18}\text{F} \) radiotracer exchange experiments which confirm that the lack of pentacoordinated nitrogen species, namely \( \text{NF}_5 \), is due mainly to steric reasons.
PART I

LEWIS ACID PROPERTIES OF XeL+ (L = F, OSeF₅, OTeF₅) CATIONS; ADDUCTS WITH ORGANIC AND FLUOROOrganic NITROGEN BASES AND SOLVOLYTIC BEHAVIOR OF HC≡N-XeF⁺ IN ANHYDROUS HF
INTRODUCTION

While many examples of 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 (1), over a decade had elapsed before an example with a ligating atom other than oxygen and fluorine, namely nitrogen, was synthesized (2) 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 (3). Other imidodisulfurylfluoride xenon-nitrogen bonded species have since been definitively characterized using primarily NMR spectroscopy, namely, \( \text{Xe[N(SO}_2\text{F)}_2]_2 } \) (4,5), \( \text{F[XeN(SO}_2\text{F)}_2]_2 } \) (4,5), \( \text{XeN(SO}_2\text{F)}_2 \text{AsF}_6^- \) (6) and \( \text{XeN(SO}_2\text{F)}_2 \text{Sb}_3\text{F}_{16}^- \) (6) and the latter salt has also been characterized by single crystal X-ray diffraction. The compound, \( \text{Xe[N(SO}_2\text{CF}_3)_2]_2 } \) (7), has also been prepared and characterized, and is the most thermally stable of the imido derivatives of xenon.

Recently, a significant extension of noble-gas chemistry, and in particular, noble-gas nitrogen bonds, has been achieved by taking advantage of the Lewis acid properties of noble-gas cations. This has given rise to numerous new examples of xenon-nitrogen and krypton-nitrogen bonds. The
adduct salts, which have stabilities ranging from explosive at -60 °C for F-Kr-N=CH'AsF₆⁻ (8) to stable at room temperature for s-C₃F₇N₃N-XeF'AsF₆⁻ (9), have donor-acceptor bonds which are among the weakest bonds that still deserve to be called bonds. The present Review outlines the syntheses, structural characterization and bonding of noble-gas adduct cations for a variety of organic and inorganic nitrogen base centers.

LEWIS ACID AND OXIDANT PROPERTIES OF NOBLE-GAS CATIONS

In view of the propensity of the XeF⁺ cation to form strong fluorine bridges to counter anions in the solid state (10), the XeF⁺ cation may be regarded as having a significant Lewis acid strength. Based on considerations of the high electron affinities of the cations (ArF⁺, 13.7 eV (11); KrF⁺, 13.2 eV (12); XeF⁺, 10.9 eV (12)) and first adiabatic ionization potentials of selected bases, where the first adiabatic ionization potential, IP₁, determined from photoelectron spectroscopy, is equal to or greater than the estimated electron affinity, EA, of the noble-gas cation; it has been possible to single out specific nitrogen bases and classes of nitrogen bases which offer reasonable promise for preparing noble-gas adduct cations in which the strongly oxidizing noble-gas cations are bound to organic and perfluoro-organic fragments through the nitrogen of the base. A list of some nitrogen bases that have potential or proven compatibility with the estimated electron affinities of the XeF⁺ and/or KrF⁺ cations is given in Table 1 along with their IP₁ values.

In many ways HC≡N, with IP₁ = 13.59 eV (14), is archetypical of the other oxidatively resistant organic and perfluoro-organic nitrogen bases which form adducts with noble-gas Lewis acid centers. For that reason, its interactions
# Table 1: First Adiabatic Ionization Potentials of Some Organic and Inorganic Nitrogen Bases

<table>
<thead>
<tr>
<th>Compound</th>
<th>1st Ionization Potential</th>
<th>References</th>
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<tr>
<td>CF&lt;sub&gt;3&lt;/sub&gt;C≡N</td>
<td>13.90</td>
<td>14</td>
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<tr>
<td>N≡C-C≡N</td>
<td>13.57</td>
<td>15</td>
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<tr>
<td>BC≡N</td>
<td>13.59</td>
<td>13</td>
</tr>
<tr>
<td>trans-N&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;2&lt;/sub&gt;</td>
<td>13.10 ± 0.1</td>
<td>16</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;F≡N</td>
<td>13.00 ± 0.1</td>
<td>17</td>
</tr>
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<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl≡N</td>
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<td>17</td>
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<td>B-B≡F&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10.46</td>
<td>24</td>
</tr>
<tr>
<td>NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>10.34 ± 0.07</td>
<td>28</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;3&lt;/sub&gt;N</td>
<td>10.08</td>
<td>24</td>
</tr>
<tr>
<td>s-C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10.07 ± 0.05</td>
<td>29</td>
</tr>
</tbody>
</table>
with the XeF⁺ and KrF⁺ cations will be discussed in considerable detail.

SYNTHETIC APPROACHES AND CHARACTERIZATION

Multi-nuclear magnetic resonance spectroscopy has played an important role in the characterization of noble-gas species (31-33). A substantial portion of the present Review is concerned with structural characterization and inferences regarding bonding derived from NMR studies. The role of NMR in noble-gas chemistry is exemplified by xenon, although the observation of the \(^{19}F, \ ^{14}N, \ ^{13}C\) and \(^{1}H\) NMR spectra is equally crucial. Xenon is the most favorable noble-gas from an NMR standpoint since it has a spin-1/2 nuclide, \(^{129}Xe\) (26.44% natural abundance), with a receptivity of 31.8 relative to that of natural abundance \(^{13}C\). The high receptivity, non-quadrupolar nature and short spin-lattice relaxation times of \(^{129}Xe\) allow spectral data to be readily acquired using modern FT NMR spectrometers.

The Hydrocyanato Cations, HCN-N邢F⁺ (N邢 = Kr or Xe). Hydrogen cyanide is oxidatively among the most resistant ligands investigated thus far (Table 1), having a first adiabatic ionization potential of 13.59 eV. The estimated electron affinity of XeF⁺ (10.9 eV) (13) suggested that HCN would be resistant to oxidative attack by the XeF⁺ cation and that HCN-XeF⁺ might have sufficient thermal stability to permit its spectroscopic characterization in solution and in the solid state.

The reaction of XeF⁺ with HCN and the subsequent isolation of HCN-XeF⁺AsF₆⁻ and its characterization have indeed been realized. The reactions of
XeF'AsF₆⁻ and Xe₂F₃'AsF₆⁻ with HC≡N have been reported (34, 35) and were carried out according to equations (1) and (2) by combining stoichiometric amounts of the reactants in anhydrous HF (-20 to -10 °C).

\[
\text{XeF'AsF}_6^- + \text{HC≡N} \rightarrow \text{HC≡N-XeF'AsF}_6^- \quad (1)
\]

\[
\text{Xe}_2\text{F}_3'\text{AsF}_6^- + \text{HC≡N} \rightarrow \text{HC≡N-XeF'AsF}_6^- + \text{XeF}_2 \quad (2)
\]

The compound, HC≡N-XeF'AsF₆⁻, has been isolated as a white microcrystalline solid upon removal of the solvent at -30 °C and was stable for up to 4 - 6 hrs. at 0 °C. Solutions of HC≡N-XeF'AsF₆⁻ in HF solution at ambient temperature slowly decompose over a period of 13 hrs.

Every element in the HC≡N-XeF' cation possesses at least one nuclide which is suitable for observation by NMR spectroscopy, namely, the spin-1/2 nuclei \(^1\text{H}, \, ^{13}\text{C}, \, ^{15}\text{N}, \, ^{129}\text{Xe}\) and \(^{19}\text{F}\), and the spin-1 nucleus \(^{14}\text{N}\) (Figure 1). Multinuclear magnetic resonance spectra were recorded for HC≡N-XeF'AsF₆⁻ in HF and BrF₃ solvents for all six spin-1/2 nuclei of the cation using natural abundance and \(^1\text{C}\) and \(^{15}\text{N}\) enriched compounds. All possible nuclear spin-spin couplings have been observed, establishing the solution structure of the HC≡N-XeF' cation (Table 2). Included among these scalar couplings are \(^1\text{J}^{(129}\text{Xe}-^{14}\text{N})\), \(^1\text{J}^{(129}\text{Xe}-^{13}\text{C})\) and \(^3\text{J}^{(129}\text{Xe}-^{1}\text{H})\), representing the first time these scalar couplings have been observed between these nuclides.

An interesting feature of the NMR spectroscopy of the HC≡N-XeF' cation is the ready observation of the directly bonded \(^{129}\text{Xe}-^{14}\text{N}\) and \(^{14}\text{N}-^{13}\text{C}\) scalar couplings. The observation of both couplings and the relative ease of observing \(^1\text{J}^{(129}\text{Xe}-^{14}\text{N})\) in the alkyl nitrile, s-trifluorotriazine and
Figure 1.

$^{129}$Xe NQR spectra (69.563 MHz) recorded in HF solvent at -10 °C for (a) HC$_2$N-XeF$_3$AsF$_3$ for a 99.2% $^{13}$C enriched sample; and CH$_2$C$_2$N-XeF$_3$AsF$_3$ where (b) is the natural spectrum and (c) is 99.7% $^{13}$C enriched at the 2-carbon. (Reprinted with permission from ref. (34)).
perfluoropyridine adducts of XeF$^+$ (see Spectroscopic Findings and Table 3) is attributed to several factors which minimize quadrupole relaxation of the $^{129}$Xe-$^{14}$N and $^{14}$N-$^{13}$C couplings; the low electric field gradient at the $^{14}$N nucleus of the adduct cations, low viscosity of the HF solvent leading to a short molecular correlation time and the small line width factor for $^{14}$N (36). However, in the higher viscosity solvent BrF$_5$ (-58 °C), the $^{129}$Xe-$^{14}$N and $^{14}$N-$^{13}$C couplings are quadrupole collapsed into single lines. Because they are generally obscured owing to quadrupolar relaxation caused by the $^{14}$N nucleus, $^{15}$N enrichment was required for the observation of scalar couplings between nitrogen and non-directly bonded nuclei where the magnitudes of the couplings are small (Table 2).

Prior to the synthesis of the HC=NH$_2$F cation, no examples of krypton compounds had been reported in which krypton is bonded to an element other than fluorine. In view of the previous success in forming the HC=NH$_2$F cation (34,35), the synthesis of the krypton(II) analog was undertaken (8). The estimated electron affinity for KrF$^+$ of 13.2 eV suggested that HC=NH$_2$F might have at least a marginal resistance to oxidative attack by the KrF$^+$ cation and that HC=NH$_2$F might have sufficient thermal stability to permit its spectroscopic characterization.

Unlike the xenon(II) analog, the direct interaction of KrF$^+$AsF$_6^-$ with HC=NH$_2$F solutions in HF and BrF$_5$ solvents was not attempted owing to the strongly oxidizing character of the KrF$^+$ cation towards HC=NH$_2$F and BrF$_5$ as well as its tendency to undergo auto-redox reactions in both solvent media. Rather, the interaction of less reactive KrF$_2$ with HC=NH$_2$F$^+$ in HF was the preferred synthetic route. Reaction of sparingly soluble HC=NH$_2$F$^+$ with KrF$_2$ in HF at -60 °C led to instantaneous deposition of a white solid which, upon warming
Table 2. NMR Chemical Shifts and Spin-Spin Coupling Constants for the HC≡N–XeF⁺ Cation

<table>
<thead>
<tr>
<th>Chemical Shifts (ppm) b</th>
<th>δ(129Xe)</th>
<th>δ(19F)</th>
<th>δ(14N/15N)</th>
<th>δ(13C)</th>
<th>δ(1H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1555</td>
<td>-199.0</td>
<td>-234.5</td>
<td>104.1</td>
<td>4.70</td>
<td></td>
</tr>
<tr>
<td>(-1570)</td>
<td>(-193.1)</td>
<td>(-230.2)</td>
<td></td>
<td>(6.01)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1J(129Xe–19F)</td>
</tr>
<tr>
<td>1J(129Xe–14N)</td>
</tr>
<tr>
<td>1J(14N–13C),</td>
</tr>
<tr>
<td>2J(129Xe–13C),</td>
</tr>
<tr>
<td>2J(15N–19F),</td>
</tr>
<tr>
<td>2J(15N–1H),</td>
</tr>
<tr>
<td>3J(15F–13C),</td>
</tr>
<tr>
<td>4J(19F–1H),</td>
</tr>
</tbody>
</table>

(a) References (34) and (35). Spectra were recorded in anhydrous HF at -10 °C or at -58 °C on BrF₅ solvent (values in parentheses).

(b) Samples were referenced externally at 24 °C with respect to the neat liquid references standards XeOF₄ (129Xe), CFCI₃ (19F), CH₃NO₂ (14N and 15N), (CH₃)₃Si (13C and 1H) where a positive chemical shift denotes a resonance occurring to high frequency of the reference compound.
Table 3. A Comparison of Xenon-Nitrogen Reduced Coupling Constants in F-Xe-L Type Systems

<table>
<thead>
<tr>
<th>Species</th>
<th>Hybridization at Nitrogen</th>
<th>(^1)K(\text{Xe-N}) \times 10^{-2} \text{ NAm}^{-3}</th>
<th>(\delta(^{133}\text{Xe})) ppm</th>
<th>T, °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN-XeF(^+)</td>
<td>sp</td>
<td>1.381(^b)</td>
<td>-1555 (-1570)</td>
<td>-10 (-58)</td>
<td>34, 35</td>
</tr>
<tr>
<td>RCH=O-XeF(^+)</td>
<td>sp</td>
<td>1.297-1.393</td>
<td>-1541 to -1721</td>
<td>-10 to -50</td>
<td>34, 37</td>
</tr>
<tr>
<td>F(_2)S=O-XeF(^+)</td>
<td>sp</td>
<td>1.435</td>
<td>(-1661)</td>
<td>(-60)</td>
<td>38</td>
</tr>
<tr>
<td>s-C(_3)F(_3)N(_2)N-XeF(^+)</td>
<td>sp(^2)</td>
<td>1.013</td>
<td>-1808 (-1863)</td>
<td>-5 (-50)</td>
<td>9</td>
</tr>
<tr>
<td>C(_2)F(_4)N-XeF(^+)</td>
<td>sp(^2)</td>
<td>0.983</td>
<td>-1872 (-1922)</td>
<td>-30 (-30)</td>
<td>39</td>
</tr>
<tr>
<td>4-CF(_3)C(_3)F(_4)N-XeF(^+)</td>
<td>sp(^2)</td>
<td>0.991</td>
<td>-1803 (-1853)</td>
<td>-15 (-50)</td>
<td>39</td>
</tr>
<tr>
<td>(FO(_2)S)(_2)N-XeF</td>
<td>sp(^2)</td>
<td>0.913(^c)</td>
<td>-2009</td>
<td>-40</td>
<td>6</td>
</tr>
<tr>
<td>F(_4)S=N(H)-XeF(^+)</td>
<td>sp(^2)</td>
<td></td>
<td>-2672</td>
<td>-20</td>
<td>38</td>
</tr>
<tr>
<td>F(_3)S-N(H(_2))-XeF(^+)</td>
<td>sp(^3)</td>
<td></td>
<td>-2886</td>
<td>-20</td>
<td>38</td>
</tr>
<tr>
<td>F(_4)Te-N(H(_2))-XeF(^+)</td>
<td>sp(^3)</td>
<td></td>
<td>-2841 (-2903)</td>
<td>-45 (-50)</td>
<td>40</td>
</tr>
</tbody>
</table>

(a) Values, unless otherwise indicated, were determined in HF and in BrF\(_3\), (in parentheses) solvent; \n\(^1\)K(\text{Xe-N}) = \left[\frac{4\pi^2 \cdot 1J(^{129}\text{Xe}-^{19}F)}{\hbar \gamma(14/15)\gamma(129\text{Xe})}\right].

(b) Recorded for the \(^{15}\)N enriched cation. (c) Measured in SO\(_2\)ClF solvent.
above -50 °C, rapidly evolved Kr, NF₃ and CF₄ gases and was usually followed by a violent detonation and accompanying emission of white light. When these reactions were allowed to proceed at approximately -60 °C, the mixtures were periodically quenched to -196 °C in order to study the development of the Raman spectrum of the product (see Bonding Considerations). The interaction of HC≡NH'AsF₆⁻ and KrF₂ in BrF₅ led to a soluble product which was stable to at least -55 °C in BrF₅ with only slight decomposition. The ¹⁹F NMR spectra of these solutions at -58 °C and in HF at -60 °C are consistent with equation (3)

\[
\text{KrF}_2 + \text{HC≡NH'AsF}_6^- \rightarrow \text{HC≡N-KrF}^+ \text{AsF}_6^- + \text{HF}
\] (3)

The structure of the HC≡N-KrF⁺ cation in solution has been confirmed by reaction with 99.5% ¹⁵N enriched HC≡NH'AsF₆⁻ in BrF₅ solvent. The ¹⁹F and ¹H resonances exhibit new doublet splittings attributed to ¹⁵N coupling (Figure 2a). The new splitting (26 Hz) on the ¹⁹F resonance was assigned to the two-bond spin-spin coupling ²J(¹⁹F-¹⁵N) and compares favorably in magnitude with previously reported values for F-Xe-N(SO₂F)₂ (²J(¹⁹F-¹⁵N) = 39.2 Hz) and CH₃C≡N-XeF⁺ (²J(¹⁹F-¹⁵N) = 25 Hz, calculated from ²J(¹⁹F-¹⁴N) = 18 Hz). Krypton isotopic shifts arising from ⁸²Kr (11.56%), ⁸⁴Kr (56.90%) and ⁸⁶Kr (17.37%) were resolved on the ¹⁹F resonance (0.0138 ppm/amu) and served as an added confirmation that the fluorine resonance arose from fluorine directly bonded to krypton. The doublet fine structure (12.2 Hz) on the ¹H resonance of the ¹⁵N enriched cation (Figure 2b) was assigned to ²J(¹⁵N-¹H) (cf. ²J(¹⁵N-¹H) = 19.0 Hz for HC≡NH⁺ in HF solvent). The ¹⁵N NMR spectrum comprised well-resolved doublet of doublets (Figure 2c) arising from ²J(¹⁹F-¹⁵N) and ²J(¹⁵N-¹H) which simplified to a doublet (26 Hz) upon broad band ¹H decoupling, confirming the aforementioned coupling...
Figure 2.

NMR spectra of the BCuN-KrF⁺ cation enriched to 99.5% with ¹⁵N, in BrF₃ as solvent at -57°C. (a) ¹⁹F Spectrum (235.36 MHz) depicting ²J(¹⁹F-¹⁵N) and ⁴J(¹⁹F-¹H) and krypton isotope shifts. Lines assigned to fluorine bonded to ¹⁰Kr (11.56%), ¹²Kr (56.90%), and ¹³Kr (17.37%) are denoted by the krypton mass number. The innermost lines of the ¹⁰Kr and ¹²Kr doublets overlap their corresponding ¹⁰Kr doublets. The isotopic shift arising from ¹³Kr (11.53%) is not resolved; those of ¹⁰Kr (0.35%) and ¹²Kr (2.27%) are too weak to be observed. (b) ¹H Spectrum (80.02 MHz) depicting ²J(¹⁵N-¹H) and ⁴J(¹⁵N-¹H). (c) ¹⁵N Spectrum (50.70 MHz) depicting ²J(¹⁹F-¹⁵N) and ²J(¹⁵N-¹H). (Reprinted with permission from ref. (C)).
constant assignments.

Perfluoroalkyl- and Alkynitrile Adducts of XeF⁺. The measured value of the first adiabatic IP of CF₃C≡N (13.90 eV) (15) suggests that this base should be even more resistant to oxidative attack by KrF⁺ and XeF⁺ than HC≡N. Moreover, CF₃C≡N would be expected to possess a more weakly basic nitrogen that would be conducive to the formation of a correspondingly more ionic Ng−N bond (see section on Theoretical Calculations). The perfluoroalkyl nitrile adduct cations of XeF⁺ have been prepared by the interaction of equimolar amounts of XeF⁺AsF₆⁻ or Xe₂F₃⁺AsF₆⁻ and RₓC≡N (Rₓ = CF₃, C₂F₅, n-C₃F₇) in BrF₅ solvent (9) according to equation (4)

\[
RₓC≡N + XeF⁺AsF₆⁻(Xe₂F₃⁺AsF₆⁻) \rightarrow RₓC≡N-XeF⁺AsF₆⁻ (+ XeF₂) \quad (4)
\]

The syntheses of the krypton(II) analogs have also been reported and were undertaken at low temperatures in BrF₅ solvent using the general synthetic approach given in equation (5)

\[
RₓC≡N-AsF₅⁻ + KrF₂ \rightarrow RₓC≡N-KrF⁺AsF₆⁻ \quad (5)
\]

The RₓC≡N-NgF⁺ cations have been characterized in BrF₅ by low-temperature (-57 to -61 °C) ¹⁹F and ¹²⁹Xe NMR spectroscopy and consisted of two sets of new signals: a singlet in the F-on-Kr(II) and in the F-on-Xe(II) regions, and resonances in the F-on-C region with characteristic ³J(¹⁹F-¹³F) and ¹J(¹⁹F-¹³C) couplings having chemical shifts to high frequency of the parent base molecules (Table 4). In each case, the singlet assigned to F-on-Xe(II) was
Table 4. Correlation of Physical Properties for Representative Ng-F Bonds

<table>
<thead>
<tr>
<th>Species*</th>
<th>(r) (Ng-F)</th>
<th>(v) (Ng-F)</th>
<th>(1^1J)((^{129})Xe-(^{19})F)</th>
<th>(\delta)((^{129})Xe)</th>
<th>(\delta)((^{19})F)</th>
<th>T, °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>KrF'</td>
<td>(1.740)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KrF'SbF'</td>
<td>1.82 (3)</td>
<td>619</td>
<td>7230</td>
<td>-574</td>
<td>-290.20</td>
<td>23</td>
<td>31, 42, 45, 46</td>
</tr>
<tr>
<td>KrF'AsF'</td>
<td>1.873 (6)</td>
<td>610</td>
<td>6892</td>
<td>-869</td>
<td>-47</td>
<td></td>
<td>9, 42, 47, 48</td>
</tr>
<tr>
<td>(FKr)₂F'</td>
<td>1.90 (3)</td>
<td>593</td>
<td>6740</td>
<td>-1051</td>
<td>-252.0</td>
<td>-62</td>
<td>31, 42, 46, 49</td>
</tr>
<tr>
<td>HC≡N-KrF'</td>
<td>(1.748)</td>
<td>560</td>
<td>6181</td>
<td>-1569</td>
<td>-198.4</td>
<td>-58</td>
<td>34</td>
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<tr>
<td>CF₃C≡N-KrF'</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C₂F₃C≡N-KrF'</td>
<td>91.1</td>
<td>-59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>C₂F₅C≡N-KrF'</td>
<td>91.9</td>
<td>-59</td>
<td></td>
<td></td>
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<td></td>
<td>9</td>
</tr>
<tr>
<td>KrF₂</td>
<td>1.875</td>
<td>462</td>
<td></td>
<td>68.0</td>
<td>-56</td>
<td></td>
<td>43, 44</td>
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<tr>
<td>XeF'</td>
<td>(1.886)</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>XeF'SbF'</td>
<td>1.940 (8)</td>
<td>528</td>
<td>5830</td>
<td>-1666</td>
<td>-50</td>
<td>-5</td>
<td>9</td>
</tr>
<tr>
<td>cis/trans-XeF'</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>FO,SO-XeF</td>
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<tr>
<td>F₅O₁₀-XeF</td>
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<td>-1824/</td>
<td>-161.7¹</td>
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<tr>
<td>C₂F₃N-XeF'</td>
<td>5910</td>
<td>-1720</td>
<td>-170.1¹</td>
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<td>0</td>
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<tr>
<td>C₂F₅N-XeF'</td>
<td>5926</td>
<td>-1922</td>
<td>-139.6</td>
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<td>39</td>
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<td></td>
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<tr>
<td>4-CF₃C₂F₅N-XeF'</td>
<td>5963</td>
<td>-1853</td>
<td>-144.6</td>
<td>-50</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F₅TeO-XeF'</td>
<td>520</td>
<td>-2051</td>
<td>-151.08</td>
<td>26</td>
<td>53, 54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(FO,S)₂N-XeF</td>
<td>1.967 (3)</td>
<td>506</td>
<td>5586</td>
<td>-1977</td>
<td>-126.1</td>
<td>-58</td>
<td>34</td>
</tr>
<tr>
<td>F₅S=N(N(H)) -XeF'</td>
<td>5664¹</td>
<td>-2009¹</td>
<td>-126.0</td>
<td>-40</td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>F₅S=N(N(H)) -XeF'</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>F₅TeN(N(H)) -XeF'</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40</td>
</tr>
</tbody>
</table>

Continued...
Table 4 (continued)

(a) Unless otherwise indicated, all cations have AsF$_6^-$ as the counterion.
(b) Values in parentheses are calculated values determined in Ref. (41).
(c) Spectra were obtained in BrF$_3$ solvent unless otherwise indicated.
(d) The NMR parameters of KrF and XeF groups are very sensitive to solvent and temperature conditions; it is therefore important to make comparisons in the same solvent medium at the same or nearly the same temperatures.
(e) Referenced with respect to the neat liquids XeOF$_4$ (129Xe) and CFCl$_3$ (19F) at 24 °C; a positive sign denotes the chemical shift of the resonance in question occurs to higher frequency of (is more deshielded than) the resonance of the reference substance.
(f) Table entries refer to the terminal fluorine on the noble-gas atom.
(g) Recorded in SbF$_5$ solvent.
(h) δ(19F) measured in anhydrous HF solvent at -10 °C.
(i) δ(19F) measured in SO$_2$ClF solvent at -40 °C.
(j) NMR parameters measured in SO$_2$ClF solvent.
(k) NMR parameters measured in SO$_2$ClF solvent at -50 °C.
(l) Not observed; Xe-F is relatively ionic and readily undergoes exchange in HF solvent.
(m) δ(129Xe) measured in HF solvent.
flanked by natural abundance (26.44%) $^{129}$Xe satellites arising from $^1J(^{129}$Xe-$^1$F). The integrated relative intensities of the fluorine-on-noble gas environments and perfluoroalkyl group are consistent with the proposed formulations. Furthermore, the F-on-Kr(II) resonance of CF$_3$C≡N-KrF$^+$ could be resolved to show the $^{82}$Kr, $^{84}$Kr and $^{86}$Kr isotopic shifts (0.0105 ppm/amu), which compare favorably with previously measured values for HC≡N-KrF$^+$ (0.0138 ppm/amu) (7) and KrF$_2$ (0.0104 ppm/amu) (54). In addition, the F-on-Kr(II) resonances occur to high frequency of KrF$_2$ while the F-on-Xe(II) resonances occur to low frequency of XeF$_2$ (Table 4). Similar, but slightly more positive $^1$F chemical shifts have been observed for HC≡N-KrF$^+$ ($\delta(^1$F) 99.4 ppm; -57 °C; BrF$_3$ solvent) with respect to KrF$_2$ ($\delta(^1$F) 68.0 ppm; -56 °C; BrF$_3$ solvent) (8). This is in contrast to the R$_x$C≡N-XeF$^+$ series of cations which display significantly more positive $^1$F (F-on-Xe(II)) and $^{129}$Xe chemical shifts when compared with HC≡N-XeF$^+$ ($\delta(^1$F) -198.4 ppm; $\delta(^{129}$Xe) -1552 ppm; $^1J(^{129}$Xe-$^1$F) 6150 Hz; -10 °C; HF solvent) (34) and XeF$_2$ ($\delta(^1$F) -184.3 ppm; $\delta(^{129}$Xe) -1685.2 ppm; $^1J(^{129}$Xe-$^1$F) 5621 Hz; -52 °C; BrF$_3$). The $^{129}$Xe and $^1$F complexation shifts indicate the Xe-N bonds of the R$_x$C≡N-XeF$^+$ cations are significantly more ionic than in HC≡N-XeF$^+$ or RC≡N-XeF$^+$ (9) and is further supported by significantly larger $^1J(^{129}$Xe-$^1$F) values measured for the R$_x$C≡N-XeF$^+$ cations, which are known to increase with ionic character of the Xe-L bond in F-Xe-L type compounds (see Table 4) (31-33). The R$_x$C≡N-XeF$^+$ cations represent the most ionic Xe-N bonded species presently known. In contrast, the analogous comparison of $^1$F chemical shifts for R$_x$C≡N-KrF$^+$ cations suggests that the Kr-N bonds of these cations may be slightly more covalent than in HC≡N-KrF$^+$.

All three fluoro(perfluoroalkynitrile)krypton(II) cations are thermally less stable with respect to redox decomposition than HC≡N-KrF$^+$ or their
xenon(II) analogs, preventing their isolation and characterization in the solid state. Decompositions monitored by $^{19}$F NMR spectroscopy occurred over periods of approximately 1 to 2 hours at -57 to -61 °C. The major decomposition products consisted of Kr and the fluorinated products ($^{19}$F NMR parameters listed in parentheses): CF$_4$ (-63.1 ppm), C$_2$F$_6$ (-88.6 ppm) and NF$_4^+$ (219.4 ppm, $^1J(^{19}$F-^{15}$N$) 229 Hz) for all three R$_x$C≡N-KrF$^+$ cations studied, and n-C$_3$F$_6$ (-83.8 ppm, F$_3$C-; -132.8 ppm, -CF$_2$-) for C$_2$F$_5$C≡N-KrF$^+$ and n-C$_5$F$_{10}$ (-82.8 ppm, F$_3$C-; -129.2 ppm, -CF$_2$-) for n-C$_3$F$_7$C≡N-KrF$^+$ (9).

Reactions of XeF$^+$AsF$_6^-$ with alkyl nitriles, R=C≡N, and C$_6$F$_3$CN have also been carried out by combining stoichiometric amounts of the reactants in anhydrous HF and warming to -50 to -10 °C to effect reaction and dissolution in the solvent (34,37). The reactions proceed by analogy with equation (1). In the case of the alkyl nitriles and HČ=N, equilibrium (6) is significant so that equilibrium amounts of XeF$_2$, R=C=N and HČ=N are observed in the $^{129}$Xe, $^1$F, $^{14}$N, $^{15}$N and $^1$H NMR spectra but XeF$_2$ frequently is not observed in the $^{19}$F and $^{129}$Xe NMR spectra. The apparent absence of XeF$_2$ in the NMR spectra is attributed to chemical exchange involving free XeF$^+$ arising from equilibrium (7) and Xe$_2$F$_3^+$ as an exchange intermediate (equilibrium (8)).

\[
\text{RC≡N-XeF}^+ + \text{HF} \underset{\text{RC≡NH}^+ + \text{XeF}_2}{=} \quad (6)
\]

\[
\text{RC≡N-XeF}^+ \underset{\text{RC≡NH} + \text{XeF}^+}{=} \quad (7)
\]

\[
\text{XeF}^+ + \text{XeF}_2 \underset{\text{Xe}_2\text{F}_3^+}{=} \quad (8)
\]

Multi-NMR spectra ($^{129}$Xe, $^{19}$F, $^{14}$N, $^{15}$N, $^{13}$C and $^1$H) have provided
unambiguous proof for the structures of the RC=NXeF + cations in HF solution (Table 5). Several alkyl nitrile adducts of the XeF + cation have also been isolated and characterized in the solid state by low-temperature Raman spectroscopy. The Xe-F stretching frequencies are consistent with weak covalent bonding between xenon and nitrogen (see Bonding Considerations): CH3 (560), CH2F (565), CH2Cl (564), C2H5 (541), (CH3)2CH (556), (CH3)3C (560); values in parentheses are the Xe-F stretching frequencies, cm⁻¹.

The decompositions of the nitrile adduct cations CH3(CH2)nC=NXeF + (n = 0 - 3) have been monitored in HF solution by multi-NMR spectroscopy. The rate of fluorination of the alkyl chain increases with increasing chain length with degree of fluorination increasing at the alkyl carbons in the order β < γ < δ, where no fluorination is observed at the α-carbon.

Perfluoropyridine and s-Trifluorotriazine Adducts of XeF +. The fluoro-(perfluoropyridine)xenon(II) cations, 4-RC5F4N-XeF + (R = F or CF3), have been observed in HF and BrF₅ solutions and are stable in both media up to -30 °C. The salts 4-RC5F4N-XeF⁺AsF₆⁻ have been isolated at -30 °C from BrF₅ solutions initially containing equimolar amounts of 4-RC5F4NH⁺AsF₆ and XeF₂. The resulting white solids were stable to -25 °C. Low-temperature Raman and ¹²⁹Xe, ¹⁹F and ¹⁴N NMR spectroscopic results are consistent with planar cations (Structure I) in which the xenon atom is coordinated to the aromatic ring.
Table 5. Selected NMR Chemical Shifts and Coupling Constants for RC=N-XeF’ Cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>δ(^13Xe)</th>
<th>δ(^19F)</th>
<th>δ(^14N)</th>
<th>J(^13Xe-^19F)</th>
<th>J(^13Xe-^14N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3C=N-XeF'</td>
<td>-1707</td>
<td>-185.5</td>
<td>-251.1</td>
<td>6020</td>
<td>313</td>
</tr>
<tr>
<td>CH3FC=N-XeF'</td>
<td>-1541</td>
<td>-198.2 (XeF)</td>
<td>-229.2</td>
<td>6164</td>
<td>333</td>
</tr>
<tr>
<td>CH2ClC=N-XeF'</td>
<td>-1582</td>
<td>-195.5</td>
<td>-236.6</td>
<td>6147</td>
<td>331</td>
</tr>
<tr>
<td>CH3CHClC=N-XeF'</td>
<td>-1717</td>
<td>-184.6</td>
<td>-251.9</td>
<td>6016</td>
<td>312</td>
</tr>
<tr>
<td>CH2FCH2ClC=N-XeF'</td>
<td>-1662</td>
<td>-182.8 (XeF)</td>
<td>-218.8</td>
<td>6063</td>
<td>322</td>
</tr>
<tr>
<td>CH3CH2CH2C=N-XeF'</td>
<td>-1718</td>
<td>-189.1</td>
<td>-249.7</td>
<td>6020</td>
<td>309</td>
</tr>
<tr>
<td>CH2FCH2CH2C=N-XeF'</td>
<td>-1663</td>
<td>-187.7 (XeF)</td>
<td>-222.7</td>
<td>6065</td>
<td>321</td>
</tr>
<tr>
<td>CH3CHFCH2C=N-XeF'</td>
<td>-1700</td>
<td>-186.1 (XeF)</td>
<td>-257.8</td>
<td>6038</td>
<td>315</td>
</tr>
<tr>
<td>CH2FCH2CH2C=N-XeF'</td>
<td>-1720</td>
<td>-183.2</td>
<td>-247.1</td>
<td>6022</td>
<td>309</td>
</tr>
<tr>
<td>CH3CH2CH2CH2C=N-XeF'</td>
<td>-1703</td>
<td>-184.6 (XeF)</td>
<td>-202.7</td>
<td>6027</td>
<td>311</td>
</tr>
<tr>
<td>CH3CHFCCH2CH2C=N-XeF'</td>
<td>-1705</td>
<td>-185.1 (XeF)</td>
<td>-175.9</td>
<td>6015</td>
<td></td>
</tr>
<tr>
<td>(CH3)2CHC=N-XeF'</td>
<td>-1721</td>
<td>-184.5</td>
<td>-251.4</td>
<td>6016</td>
<td>309</td>
</tr>
<tr>
<td>(CH3)2CC=N-XeF'</td>
<td>-1721</td>
<td>-184.3</td>
<td>-251.4</td>
<td>6024</td>
<td>309</td>
</tr>
<tr>
<td>CH2ClC(CH3)HC=N-XeF'</td>
<td>-1703</td>
<td>-184.3</td>
<td>-251.4</td>
<td>6027</td>
<td>314</td>
</tr>
<tr>
<td>CH3FC(CH3)HC=N-XeF'</td>
<td>-1669</td>
<td>-187.9 (XeF)</td>
<td>-243.8</td>
<td>6027</td>
<td>301</td>
</tr>
<tr>
<td>C4F5C=N-XeF'</td>
<td>-1424</td>
<td>-201.8</td>
<td>-235.3</td>
<td>6610</td>
<td></td>
</tr>
</tbody>
</table>

(a) References (34) and (37).
(b) Recorded at -10 to -30 °C and referenced externally at 24 °C with respect to neat liquid references: XeOF4 (^13Xe), CFCl3(^19F), CH3NO2(^14N) and TMS(^13C) and (^1H).
(c) Resonance overlaps with that of CH2FCH2CH2CH2C≡N-XeF'.

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through the lone pair of electrons on the nitrogen (ref. (39) and Tables 3 and 4).

Equimolar amounts of XeF"AsF^− and the perfluoropyridine, 4-RC,F,N (R = F or CF₃), react in anhydrous HF at -30 to -20 °C according to equation (9) and equilibria (10) and (11) to give the novel Xe-N bonded cations, 4-RC,F,N-XeF", as the AsF^− salts in solution.

\[
4-\text{RC,F}_4\text{N} + (1 + x)\text{HF} \rightarrow 4-\text{RC,F}_4\text{NH}^+(\text{HF})\text{xF}^− \quad (9)
\]

\[
4-\text{RC,F}_4\text{NH}^+(\text{HF})\text{xF}^− + \text{XeF}''\text{AsF}^− \rightleftharpoons 4-\text{RC,F}_4\text{NH}''\text{AsF}^− + \text{XeF}_2 + x\text{HF} \quad (10)
\]

\[
\text{XeF}''\text{AsF}^− + 4-\text{RC,F}_4\text{NH}''\text{AsF}^− \rightleftharpoons 4-\text{RC,F}_4\text{N-XeF}''\text{AsF}^− + '\text{HAsF}_6'' \quad (11)
\]

At -30 °C these solutions consisted of equilibrium mixtures of XeF₂, 4-RC,F₄NH''AsF^− and 4-RC,F₄N-XeF''AsF^− as determined by NMR spectroscopy (Table 3). Removal of HF solvent by pumping at -50 °C resulted in white solids which Raman spectroscopy at -196 °C also showed to be mixtures of 4-RC,F₄N-XeF''AsF^−, XeF₂ and 4-RC,F₄NH''AsF^−.

An alternative approach, which led to isolation of the Xe-N bonded cations, allowed stoichiometric amounts of XeF₂ and the perfluoropyridinium cations, as their AsF^− salts, to react in HF and BrF₅ solvents at -30 °C according to equilibrium (12).

\[
\text{XeF}_2 + 4-\text{RC,F}_4\text{NH}''\text{AsF}^− \rightleftharpoons 4-\text{RC,F}_4\text{N-XeF}''\text{AsF}^− + \text{HF} \quad (12)
\]

The equilibria in both solvents were monitored by ¹²⁸Xe, ¹⁹F and ¹⁴N NMR.
spectroscopy. In the case of BrF₅, formation of 4-RC₅F₄N-XeF'AsF₆⁻ was strongly favored over that in HF solvent; the equilibrium ratio [4-RC₅F₄N-XeF]/[4-RC₅F₄NH⁺] being 0.25 and 2.1 in HF and BrF₅ solvents, respectively, at -30 °C for R = F and 3.7 for R = CF₃ in BrF₅ at -50 °C (Kᵥ = 4.5 at -30 °C and Kᵥ = 13.6 at -50 °C in BrF₅ for equilibrium (8)). Consequently, removal of BrF₅ solvent under vacuum at -30 °C yielded white solids corresponding to the salts 4-RC₅F₄N-XeF'AsF₆⁻. The CF₃-derivatives substituted at the 2- and 3-positions have also been synthesized from the their perfluoropyridinium salts in BrF₅ solvent and characterized by NMR spectroscopy (δ(¹²⁹Xe), -1899 and -1877, respectively) (37).

The interaction of liquid s-trifluorotriazine, s-C₃N₃F₃, with XeF'AsF₆⁻ at room temperature for three hours followed by removal of excess s-trifluorotriazine under vacuum resulted in a white powder which is stable indefinitely at room temperature (9). The combining ratio XeF'AsF₆⁻ : s-C₃N₃F₃ = 1.00 : 1.00 is consistent with equation (13)

$$\text{XeF'AsF}_6^- + \text{s-C}_3\text{N}_3\text{F}_3 \rightarrow \text{s-C}_3\text{F}_3\text{N}_2\text{N-XeF'}$$  \hspace{1cm} (13)

Both the ¹⁹F and ¹²⁹Xe NMR findings (Tables 3 and 4) for the salt dissolved in BrF₅ and HF solvents are consistent with the cation formulation given by Structure II. The ¹²⁹Xe NMR spectrum recorded in BrF₅ at -50 °C consists of a
doublet arising from $^1J(^{129}\text{Xe}-^1\text{F}) = 5932$ Hz. The $^{129}\text{Xe}^-\text{N}^1$ coupling is quadrupole collapsed, as has been observed previously for $4\text{-CF}_3\text{C}_5\text{F}_4\text{N}^-\text{XeF}^+\text{AsF}_6^-$ and $\text{C}_5\text{F}_5^-\text{XeF}^+\text{AsF}_6^-$ in BrF$_5$ at low temperatures (39). In HF solvent, however, $^1J(^{129}\text{Xe}^-\text{N}) = 245$ Hz was observed at $-5 \degree\text{C}$ and compares favorably in magnitude with those reported previously for the related perfluoropyridine cations (235 - 238 Hz).

The $^1\text{H}^1\text{F}$ NMR spectrum shows two F-on-C environments in the ratio of 1:2 and a F-on-Xe(II) environment with accompanying $^{129}\text{Xe}$ natural abundance (26.44%) satellites arising from $^1J(^{129}\text{Xe}-^1\text{F})$ and a 1:2:1 triplet arising from $^1J(F_1-F_2)$ = 10.9 Hz. The latter coupling has also been observed for the perfluoropyridine cations $4\text{-CF}_3\text{C}_5\text{F}_4\text{N}^-\text{XeF}^+$ (25.8 Hz) and $\text{C}_5\text{F}_5^-\text{N}^-\text{XeF}^+$ (25.0 Hz) (39).

The reaction of $\text{XeF}_3^-\text{SbF}_4^-$ with $\text{s-C}_3\text{F}_3\text{N}_3$ in BrF$_5$ solvent at 20 °C fails to give $\text{C}_3\text{F}_3\text{N}_2\text{N}^-\text{XeF}_3^+$ (57). Rather, reduction of Xe(IV) to Xe(II) occurs according to equation (14)

$$2\text{XeF}_3^-\text{SbF}_4^- + 3\text{s-C}_3\text{F}_3\text{N}_3 \rightarrow \text{s-C}_3\text{F}_3\text{N}_2\text{N}^-\text{XeF}^+ +$$

![Image](14)

The Lewis Acid Properties of the XeOTeF$_5^+$ and XeOSeF$_5^+$ Cations. More recently, this work has been extended to the Lewis acid properties of the noble-gas cations XeOTeF$_5^+$ and XeOSeF$_5^+$ (38, 57). The XeOSeF$_5^+$ cation, which was previously unknown, was prepared according to equations (15) - (17)
\[
2\text{SeOF}_2 + 3\text{XeF}_2 \rightarrow \text{Xe(SeF}_5)_2 + 2\text{Xe}
\] (15)

\[
\text{Xe(SeF}_5)_2 + \text{XeF}_2 \rightarrow 2\text{FXeOSeF}_5
\] (16)

\[
\text{AsF}_5 + \text{FXeOSeF}_5 \rightarrow \text{XeOSeF}_5^-'\text{AsF}_6^-
\] (17)

While the XeOMF\(^+_5\) cations (M = Se, Te) are expected to be weaker Lewis acids, they are expected to be less strongly oxidizing than NgF\(^+_7\) cations, and have been shown to form stable adducts at low temperature with several organic and inorganic nitrogen bases leading to the first examples of O-Xe-N linkages (Table 6).

Although the s-C\(_2\)F\(_3\)N\(_2\)-XeOMF\(^+_5\)'AsF\(_6\)^- salts were successfully prepared near room temperature by reaction of the neat compounds (equation (18)), other potential organic ligands such as nitriles and pyridines are vigorously oxidized by XeOMF\(^+_5\) cations when these reactions are attempted in the absence of a solvent under similar conditions.

\[
\text{XeOMF}_5^-'\text{AsF}_6^- + s-\text{C}_2\text{F}_3\text{N}_3 \rightarrow \text{F}_3\text{MO-Xe-NN}_2\text{C}_3\text{F}_3^-'\text{AsF}_6^-
\] (18)

To partially address this problem, XeOTeF\(_5\)Sb(OTeF\(_5\))\(_6\)^- was synthesized and is the first fully substituted OTef\(_5\) salt prepared to date (57). The salt was prepared in SO\(_2\)ClF using the redox synthesis described by equation (19).

\[
2\text{Xe(OTeF}_5)_2 + \text{Sb(OTeF}_5)_3 \rightarrow \text{XeOTeF}_5^+'\text{Sb(OTeF}_5)_6^- + \text{Xe}
\] (19)

It was shown that the decreased polarity of the Sb(OTeF\(_5\))\(_6\)^- anion relative to
Table 6. Selected NMR Parameters for XeOMF₅⁺ (M = Se or Te) Adducts Cations With Nitrogen Bases

<table>
<thead>
<tr>
<th>Cation</th>
<th>Chemical Shifts, ppm</th>
<th>Coupling Constants, Hz</th>
<th>Solvent (T, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\delta^{129}\text{Xe})</td>
<td>(\delta^{19}\text{F})</td>
<td>(^2J(\text{F}<em>\text{A}-\text{F}</em>\text{B}))</td>
</tr>
<tr>
<td>CH₃C≡N-Xe-OTeF₅⁺ a</td>
<td>-2061</td>
<td>-45.8 Fₐ</td>
<td>181</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-44.0 Fₐ</td>
<td></td>
</tr>
<tr>
<td>C₂F₅N-Xe-OTeF₅⁺ a</td>
<td>-2246</td>
<td>-46.3 Fₐ</td>
<td>-180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-42.8 Fₐ</td>
<td></td>
</tr>
<tr>
<td>s-C₃F₃N₂N-Xe-OTeF₅⁺ a</td>
<td>-2192</td>
<td>-47.1 Fₐ</td>
<td>-187</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-42.3 Fₐ</td>
<td></td>
</tr>
<tr>
<td>F₅S≡N-Xe-OSeF₅⁻ b</td>
<td>-1979</td>
<td>67.9 Fₐ</td>
<td>219</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70.4 Fₐ</td>
<td></td>
</tr>
</tbody>
</table>

(a) Prepared as the Sb(OTeF₅)₆⁻ salt; ref. (57). (b) Prepared as the AsF₆⁻ salt; ref. (38).
AsF₆⁻ anion facilitated solubility in SO₂ClF at low-temperatures and was found to be soluble in high concentrations down to the freezing point of the solvent (-124 °C). This synthetic approach allowed the formation of adduct species with XeOTeF₅⁺ and representative members of the series of nitrogen bases, i.e., acetonitrile and pentafluoropyridine, at low temperatures and under non-solvolytic conditions in a low-polarity solvent (Table 6 and ref. (57)). Low-temperature ¹⁹F NMR studies show that the XeOTeF₅⁺ cation possesses sufficient Lewis acid strength to coordinate to SO₂ClF (57). The only other known examples of adduct formation with the weakly basic SO₂ClF molecule have been reported for SbF₅ and AsF₅ at low temperatures (58), suggesting that the ability of the XeOTeF₅⁺ cation to coordinate with the weak electron donor, SO₂ClF, is a consequence of the weak coordinating ability of the Sb(OTeF₅)₆⁻ anion. Removal of excess SO₂ClF from these solutions under vacuum at 25 °C results in the 1:1 adduct salt, F₅TeOXe-OSOClF-Sb(OTeF₅)₆⁻ which slowly dissociates upon further pumping at room temperature (57). In addition, Bi(OTeF₅)₅ and Et₄N'M'(OTeF₅)₆⁻ (M' = Sb or Bi) were also synthesized and characterized by ¹²¹Sb, ²⁰⁹Bi, ¹⁹F and ¹²⁵Te NMR (57). Prior to these studies only the As(OTeF₅)₅ and As(OTeF₅)₆⁻ had been reported (59).

Noble-Gas Cation Adducts with Inorganic Bases. The synthesis of N≡SF₅ Lewis acid-base adducts with the noble-gas cations XeF⁺, XeOSeF₅⁺, and XeOTeF₅⁺ have also been investigated (38). Several synthetic approaches have been used (equation (19)).

\[ \text{XeL'}\text{AsF}_6^- + \text{N≡SF}_5 \rightarrow \text{L Xe-N≡SF}_5\text{'AsF}_6^- \]

(20)
where \( L = \text{XeF}^+ \), \( \text{OSeF}_3^+ \) and the solvent was \( \text{BrF}_5 \) at -50 °C. In addition, solid \( \text{F}^-\text{Xe-N=S}^\cdot\text{F}_2\text{AsF}_6^- \) has been synthesized by the direct interaction of liquid \( \text{N}=\text{SF}_3 \) with solid \( \text{XeF}^+\text{AsF}_6^- \). Structures have been characterized using primarily \( ^{19}\text{F} \) and \( ^{129}\text{Xe} \) NMR spectroscopy (Tables 3, 4 and 6) in solution and by low-temperature Raman spectroscopy in the solid state (Table 4).

The solvolytic behavior of the \( \text{F}_3\text{S-N=XeF}^+ \) cation has been monitored in anhydrous HF (38). Two successive additions of HF occur across the sulfur-nitrogen bond to give the \( \text{F}_4\text{S-N(H)-XeF}^+ \) (Structure III) and \( \text{F}_5\text{S-N(H)\_XeF}^+ \) (Structure IV) cations. The \( ^{129}\text{Xe} \) NMR spectrum of the \( \text{SF}_3 \) derivative shows that this xenon is the most shielded \( ^{129}\text{Xe} \) environment (most covalent \( \text{Xe-N} \) bond) observed for a xenon-nitrogen bonded species (Tables 3 and 4). Moreover, the \( \text{F}_5\text{S-N(H)}\_\text{XeF}^+ \) cation represents the first example of a bond between xenon and an \( \text{sp}^3 \)-hybridized nitrogen. More recently, the tellurium analog has been prepared in HF and \( \text{BrF}_5 \) solvent at -45 and -50 °C, respectively, (40) according to equation (21).

\[
\text{F}_5\text{TeNH}_3^+\text{AsF}_6^- + \text{XeF}_2 \rightarrow \text{F}_5\text{Te-N(H)}\_\text{XeF}^+\text{AsF}_6^- \quad (21)
\]

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BONDING CONSIDERATIONS

The Ng-N bonds described in this Review may be thought of as classical Lewis acid-base donor acceptor bonds. Implicit in this description is a considerable degree of ionic character for these weak covalent bonds, which is a dominant feature of their stability. This premise has been supported and further illuminated by several theoretical calculations on HC≡N-Ngf⁺ cations (Ng = Ne, Ar, Kr, Xe) and spectroscopic measurements on a wide range of XeF⁺, KrF⁺ and XeOMF₃⁺ adducts of nitrogen bases in which the formal hybridization of nitrogen ranges from sp, sp² to sp³.

Spectroscopic Findings. The reaction of the gas phase NgF⁺ ions with F⁻ to yield the difluorides results in increases in the calculated Ng-F bond lengths of 0.1 Å, while their reaction with HC≡N causes the same bond lengths (calculated) to increase on average by only 0.016 Å (41). There is a correlation of Ng-F bond length and the Ng-F vibrational frequency with the base strength of the ligand attached to NgF⁺. This is illustrated by the examples shown in Table 4. The NgF⁺ species are only weakly coordinated by a fluorine bridge to the Sb₂F₁₁⁻ anion, providing the highest Ng-F stretching frequencies (Xe, 619; Kr, 624 cm⁻¹) while the interaction of XeF⁺ with N(SO₂F)₂⁻ is representative of a much stronger covalent interaction and provides the lowest Xe-F stretching frequency observed to date for a covalent derivative of XeF₂ (506 cm⁻¹) (3). The C-N bond of HC≡N is calculated to shorten by -0.05 Å on forming the adduct, while the C-H bond is calculated to lengthen by 0.008 Å (41). These predicted changes in bond length also correlate with the
shielding (more negative chemical shift) with a transfer of negative charge to Xe and, hence, with increased covalent character of the Ng-L interaction (increased ionic character of the Ng-F bond) (31-33). The \( \text{F}_5\text{S=N(H)-XeF}^+ \), \( \text{F}_5\text{S-N(H}_2\text{)-XeF}^+ \) and \( \text{F}_5\text{Te-N(H}_2\text{)-XeF}^+ \) cations are characterized by the high shieldings of their \( ^{129}\text{Xe} \) nuclei and the absence of \( ^1J(^{129}\text{Xe}-^{19}\text{F}) \) arising from fluorine exchange with the solvent (Tables 3 and 4). The NMR findings are consistent with a strong covalent bonding interaction between xenon and nitrogen with a commensurate increase in Xe-F bond lability and ionic character and may be conveniently represented by an increased contribution from valence bond Structure VIII and/or by deprotonation upon adduct formation to give the neutral derivatives \( \text{F}_4\text{S=N-XeF} \), \( \text{F}_5\text{S-N(H)-XeF} \) and \( \text{F}_5\text{Te-N(H)-XeF} \), which may be in equilibrium with the cations in HF and BrF\(_5\) solvents. Whatever the precise nature of the nitrogen bonded ligand may be in solution, these Xe–N bonded derivatives represent the most covalent Xe–N bonds synthesized to date.

Quadrupolar nuclei in noncubic environments generally yield poorly resolved one-bond coupling patterns in their NMR spectra due to quadrupolar relaxation effects (36). In spite of the low symmetries about the nitrogen atoms in the cations investigated to date, the \( ^{14}\text{N} \) NMR spectra frequently show well resolved and only partially quadrupole collapsed scalar couplings, \( ^1J(^{129}\text{Xe}-^{14}\text{N}) \) (and \( ^1J(^{14}\text{N}-^{13}\text{C}) \) in the case of HC=N-XeF\(^+\); Tables 2, 3 and 5). In prior studies of the imidodisulfurylfluoride derivatives of xenon(II) (3,4,6), the lack of cubic symmetry and the small electric field gradient at \( ^{14}\text{N} \) in the trigonal planar \(-\text{N(SO}_2\text{F})_2\) group necessitated \( ^{15}\text{N} \) enrichment in order to observe xenon–nitrogen scalar couplings and nitrogen chemical shifts in \( \text{F,XeN(SO}_2\text{F})_2 \) (3), \( \text{XeN(SO}_2\text{F})_2^+ \) (6), \( \text{Xe[N(SO}_2\text{F})_2]_2 \) (4) and \( \text{F[XeN(SO}_2\text{F})_2]_2^+ \) (4) cations in SbF\(_5\), BrF\(_5\) and \( \text{SO}_2\text{ClF} \) solvents. The extent of minimal quadrupolar
relaxation via a reduced electric field gradient has been examined theoretically for HC≡N-NgF⁺ (Ng = Kr, Xe) by calculating the field gradient at the nitrogen nucleus and comparing it to that in isolated HC≡N (41). Relative to free HC≡N, the principal component of the electric field gradient tensor in the H → N direction, is halved upon formation of both HC≡N-XeF⁺ and HC≡N-KrF⁺ and is in agreement with the fact that ¹J(¹²⁹Xe-¹⁵N) can be readily observed under conditions favoring low molecular correlation times. The electric field gradients at the Xe nucleus in XeF⁺ and HC≡N-XeF⁺ have also been calculated (41), and differ by less than 7%, a result in agreement with the experimental observation that the quadrupolar splitting observed in the ¹²⁹Xe Mössbauer spectrum of HC≡N-XeF⁺ (40.2 ± 0.3 mm/s) is, within experimental error, the same as that obtained for the salt XeF⁺AsF₆⁻ (40.5 ± 0.1 mm/s) (60).

The difference in the magnitudes of ¹J(¹²⁹Xe-¹⁵N) in HC≡N-XeF⁺ (471 Hz) (34) and FXeN(SO₂F)₂ (307 Hz) (3) may be discussed using a previous assessment of the nature of bonding to xenon in solution for FXeN(SO₂F)₂, where the Xe-N bond of FXeN(SO₂F)₂ is regarded as a σ-bond having sp² hybrid character (3,4,6). In high-resolution NMR spectroscopy spin-spin coupling involving heavy nuclides is, with few exceptions, dominated by the Fermi contact mechanism (61). For Xe-N spin-spin couplings dominated by the Fermi contact mechanism, one-bond coupling constants can be discussed on the basis of the formalism developed by Pople and Santry (62). In discussions of xenon-nitrogen scalar couplings in xenon(II) imidodisulfurylfluoride compounds (6), the s-electron density at the xenon nucleus was assumed constant and a change in the hybridization at nitrogen accounted for changes in xenon-nitrogen spin-spin coupling. Even though the Xe-N bond is markedly less covalent in the hydrocyano cation than in FXeN(SO₂F)₂, the ¹J(¹²⁹Xe-¹⁵N) values observed for
HC≡N-XeF⁺ are substantially larger than for xenon bonded to the trigonal planar nitrogen in FXeN(SO₂F)₂ (Table 3). The dependence of xenon-nitrogen spin–spin coupling on nitrogen s-character in the xenon-nitrogen bonds may also be invoked to account for the relative magnitudes of the scalar couplings. A comparison of ¹J(^₁²⁹Xe-¹⁵N) for HC≡N-XeF⁺ with that of the trigonal planar sp² hybridized nitrogen atom in FXeN(SO₂F)₂ illustrates this point and allows assessment of the relative degrees of hybridization of the nitrogen orbitals used in σ-bonding to xenon. The ratio, [¹J(^₁²⁹Xe-¹⁵N)ₚ₂]/[¹J(^₁²⁹Xe-¹⁵N)ₚ₃], = 1.53, for the HC≡N-XeF⁺ cation and FXeN(SO₂F)₂ is in excellent agreement with the theoretical ratio, 1.50, calculated from the predicted fractional s-characters of the nitrogen orbitals used in bonding to xenon in both compounds.

The formal s-character in the Xe-N bond of other adduct cations, for which either ¹J(^₁²⁹Xe-¹⁴N) or ¹J(^₁²⁹Xe-¹⁵N) are known, can be related to the reduced coupling constant, ¹K(Xe-N), thus eliminating the effect of the different gyromagnetic ratios of ¹⁴N and ¹⁵N on the magnitude of the scalar coupling (6,62). A comparison of ¹K(Xe-N) of XeF⁺ adduct cations with nitrogen bases and of xenon(II) derivatives containing the N(SO₂F)₂ group is given in Table 3. In general, ¹K(Xe-N) values occur in two discreet ranges corresponding to the formal hybridization of nitrogen, sp or sp². There are presently no measured values for xenon coordinated to an sp³ example, even though the F₅S-N(H₂)-XeF⁺ and F₅Te-N(H₂)-XeF⁺ cations are known (see Structure IV), owing to quadrupole relaxation of their ¹J(^₁²⁹Xe-¹⁴N) scalar couplings.

**Theoretical Calculations.** In order to better characterize the nature of the Ng-N bonds in HC≡N-KrF⁺ and HC≡N-XeF⁺, their syntheses and spectroscopic
measurements have been complemented by several theoretical calculations on
the HC=NgF' (Ng = Ne, Ar, Kr or Xe) cations (41, 63-66).

Theoretical investigation of HC=Ng-KrF' and HC=Ng-KrF' at the SCF level
using the theory of atoms in molecules (41) has shown that the ability of KrF'
and XeF' cations to act as Lewis acids is related to the presence of holes in
the valence shell of the concentrations of the noble-gas atoms that expose
their core. The mechanism of formation of the Ng-N bonds in the adducts of
KrF' and XeF' with HC=N is similar to the formation of a hydrogen bond, i.e.,
the mutual penetration of the outer diffuse non-bonded densities of the Ng
and N atoms is facilitated by their dipolar and quadrupolar polarizations,
which remove density along their axis of approach, to yield a final density
in the interatomic surface that is only slightly greater than the sum of the
unperturbed densities (Figures 3 and 4). Thus, not surprisingly, the KrF' and
XeF' cations are best described as hard acids. The energies of formation of
these adducts are dominated by the large stabilizations of the Ng atoms that
result from the increase in the concentration of charge in their inner
quantum shells. The Ng-N bonds that result from the interaction of the
closed-shell reactants KrF'/XeF' and HC=N lie closer to the closed shell limit
than do bonds formed in the reaction of KrF'/XeF' with F-. The calculated gas
phase energies of the reaction between the closed-shell species are -136.0
and -144.3 kJ mol⁻¹ for Ng = Kr and Xe, respectively, for

\[
\text{NgF'} + \text{HC=N} \rightarrow \text{HC=N-NgF'} \quad (22)
\]
Figure 3.

(a) Contour map of the charge density in the adduct HC=\(\text{N}\)-Kr\(^{6+}\) showing the bond paths and the intersection of the interatomic surfaces. Bond critical points are denoted by black circles. Note the near planarity of the Kr-N interatomic surface, which is also a characteristic of a hydrogen bond. The outer contour value is 0.001 au. The remaining contours increase in value in the order 2 \(\times\) 10\(^{-5}\), 4 \(\times\) 10\(^{-5}\), 8 \(\times\) 10\(^{-5}\) with \(n\) starting at -3 and increasing in steps of 1 to give a maximum contour value of 20. (b) Contour map of the Laplacian distribution for HC=\(\text{N}\)-Kr\(^{6+}\). The positions of the nuclei are the same as in part (a). Solid contours denote positive and dashed lines denote negative values of \(\nabla^{2}\rho\). The magnitudes of the contour values are as in part (a), without the initial value of 0.001 au. (c) A relief map of \(-\nabla^{2}\rho\). A maximum in the relief map is a maximum in charge concentration. If the inner spikelike feature at its nucleus is counted, the Kr atom exhibits four alternating regions of charge concentration and charge depletion corresponding to the presence of four quantum shells. Note the absence of a lip on the N side of the Kr VSCC demonstrating the presence of a hole in its outer sphere of charge concentration. Contrast the localized, atomic-like nature of the Laplacian distribution for the F and Kr atoms with the continuous valence shell of charge concentration enveloping all three of the nuclei in HC=\(\text{N}\). (Reprinted with permission from ref. [41]).
Figure 4.

Zero envelopes of the Laplacian distributions ($\nabla^2 \rho = 0$ for all points on the surface) for isolated KrF$^*$ and HCN shown aligned for adduct formation and shown to the same scale. The separation between the Kr and H nuclei is 5.0 Å. All that remains of the VSOC of the Kr atom is a belt of charge concentration, and the diagram clearly illustrates the exposure of its penultimate spherical shell of charge concentration—the core of the krypton atom. The diagram also contrasts the interatomic nature of the charge concentration in HCN with its pronounced intraatomic form in KrF$^*$. (Reprinted with permission from ref. (41)).
and -874.5 and -886.6 kJ mol\(^{-1}\) for

\[
\text{NgF}^+ + F^- \longrightarrow \text{F-Ng-F} \tag{23}
\]

The molecular structure and force field of HC≡N-KrF\(^+\) have also been calculated at higher levels of theory (Tables 7 and 8 and ref. (63-66)). The incorporation of electron correlation is necessary to describe satisfactorily the structures, stabilities and vibrational frequencies. The force field has been calculated, and the cation is predicted to be linear. Reasonable agreement with the two observed vibrational Raman bands in the solid has been found in all four sets of calculations. The stretching mode leading to dissociation into KrF\(^+\) and HC≡N was calculated to be near 200 cm\(^{-1}\) (66). The KrF and HC≡N fragments in the complex have geometries similar to those for the isolated molecules (Table 8): the Kr-N bond distance is predicted to be relatively long, 2.18 - 2.32 Å (cf. sum of Kr and N van der Waals radii; 3.4 Å), the Kr-F distance in the adduct is predicted to increase by only 0.0 - 0.13 Å relative to that of KrF\(^+\). The HC≡N-KrF\(^+\) cation is predicted to be bound by 130.1 - 176.1 kJ mol\(^{-1}\) with respect to KrF\(^+\) and HC≡N at higher levels of theory (cf. 126.4 - 136.0 kJ mol\(^{-1}\) at SCF level) with zero-point energy corrections (63-66).

All four of the calculated results are consistent with an ionic and a covalent component in the bonding of KrF\(^+\) with HC≡N, i.e., the fragments are \(\sigma\)-bonded with a high degree of ionic character. The Kr-N bond is the result of a donor-acceptor interaction between the sp-lone pair on N and the empty \(\sigma^*\) orbital on KrF\(^+\). In the study by Dixon and Arduengo (66), the molecular orbitals and bonding are analyzed in terms of hypervalent bonds. Their
Table 7. Bond Distances (Å) for Optimized Geometries for KrF⁺, HC≡N and HC≡N-KrF⁺

<table>
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<tr>
<th>Species</th>
<th>r(C-H)</th>
<th>r(C≡N)</th>
<th>r(Kr-F)</th>
<th>r(Kr-N)</th>
<th>Ref.</th>
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<tr>
<td>KrF⁺</td>
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<td>1.752</td>
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<td></td>
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<td></td>
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<tr>
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<td>1.126</td>
<td></td>
<td></td>
<td>66</td>
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<td>1.064</td>
<td>1.156</td>
<td></td>
<td></td>
<td>73</td>
</tr>
<tr>
<td>HC≡N-KrF⁺</td>
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<td>1.122</td>
<td>1.709</td>
<td>2.320</td>
<td>66</td>
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<tr>
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<td>1.772</td>
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<td>64</td>
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<tr>
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<td>1.175</td>
<td>1.83</td>
<td>2.281</td>
<td>63</td>
</tr>
</tbody>
</table>
Table 8. Calculated Vibrational Frequencies (cm$^{-1}$) and Infrared Intensities (km/mol) for HC$\equiv$N-Kr$^+$

| Vibrational Assignment | $v$(calc) | $v$(scaled) | $v$(calc) | $v$(calc) | $v$(calc) | $v$(expt)$^d$ | $I$(calc)$^e$
|------------------------|-----------|-------------|-----------|-----------|-----------|--------------|-------------
| C-H str.               | 3556      | 3253        | 3588      | 3467      | 3446      | 133          |
| C≡N str.               | 2446      | 2128        | 2461      | 2130      | 2100      | 2158         | 221         |
| H-C≡N bend             | 935       | 760         | 940       | 762       | 752       | 43           |
| Kr-F str.              | 782       | 620         | 782       | 644       | 562       | 560          | 66          |
| F-Kr-N≡C bend          | 253       | 228         | 256       | 271       | 244       | 63           |
| Kr-N str.              | 217       | 195         | 222       | 287       | 267       | 72           |
| F-Kr-N≡C bend          | 115       | 104         | 120       | 116       | 117       | 28           |

(a) Reference (66), (b) Reference (64), (c) Reference (63), (d) Reference (8).
results indicate that the bonding between Kr and N is not a simple covalent σ-bond but is best described in terms of three-center and four-center hypervalent bonds, where both types of hypervalent bonds are needed to describe the covalent σ-bonding in HC=N-KrF'. The charge distribution for HC=N-KrF' shows some transfer of electronic charge from the carbon to the KrF' region, consistent with a contribution from the resonance structure H-C=N-Kr-F.

High-level ab initio calculations (65) also predict that the HC=N-ArF' cation is a stable argon-nitrogen bonded species with a heat of association, -160 kJ mol⁻¹, corresponding to equation (22), which is comparable to that of the observed krypton analog (-157 kJ mol⁻¹). These results, together with another recent high-level theoretical calculation which estimates the electron affinity for ArF' to be 13.66 eV (11) suggest that HC≡N, with its high first ionization potential (13.59 eV) (13), may be oxidatively resistant enough to withstand the formidable electron affinity of the ArF' cation. The synthesis of the HC≡N-ArF' cation is likely to require the ArF' cation, which is expected to be an oxidizer of unprecedented strength, if and when it is synthesized. Reactions analogous to those given in equations (3) and (5) involving ArF₂ are not feasible, as ArF₂ is predicted to be unbound (11). The synthesis of ArF' is in itself, formidable and will entail the use of a counter anion which is capable of withstanding its high electron affinity (11).

At the correlated level, the HC≡N-NeF' cation (65) is found to be an unstable species, dissociating spontaneously to HC≡N-Ne' + F, where the HC≡N-Ne' fragment is itself a weakly bound species having a binding energy of only 6 kJ mol⁻¹.
EPILOGUE

The gap resulting from the syntheses of the first examples of Kr-N bonds (8,9) and the previous existence of several examples of Kr-F bonds (KrF₂), KrF' and F(KrF)₂⁺ (42) has prompted the reinvestigation of the possibility of forming the first Kr-O bonded species (67). Using $^{19}F$ and $^{17}O$ NMR spectroscopy of $^{17}O$ enriched samples, it has been possible to document the formation of the first Kr-O bonds by the synthesis and decomposition of thermally unstable Kr(OTeF₅)₂ according to equations (24) and (25).

$$3\text{KrF}_2 + 2\text{B(OTeF}_5)_3 \longrightarrow 3\text{Kr(OTeF}_5)_2 + 2\text{BF}_3$$

(24)

$$\text{Kr(OTeF}_5)_2 \longrightarrow \text{Kr} + \text{F}_5\text{TeOCTeF}_5$$

(25)

The syntheses of the first examples of xenon bonded to aromatic rings; n-CF₃C₅F₄N-XeF⁺ (n = 2, 3, 4) (37,39), C₅F₅N-XeF⁺ (39), C₅F₅N-Xe-OTeF₅⁺ (57), s-C₃F₁₃N₂N-XeF⁺ (9) and s-C₃F₁₃N₂N-Xe-OTeF₅⁺ (57) have recently been complemented by the first documented case of xenon bonded to an aromatic ring through carbon, namely, the C₅F₅Xe⁺ cation (70-72). While the aryl group of the C₅F₅Xe⁺ cation serves to reduce the electron density at Xe(II), as evidenced from the extreme low-frequency position of the $^{129}\text{Xe}$ chemical shift (-3769 ppm relative to XeOF₄ in CH₃C≡N solvent), the $^{129}\text{Xe}$ shieldings in the s-trifluorotriazine and perfluoropyridine derivatives are less than in the carbon analog and may in large part be associated with the electron-withdrawing character of the fluorine on xenon. The electron donating character of the nitrogen heterocycles relative to HC≡N and RC≡N in the XeOTeF₅⁺ and XeF⁺ adducts is,
however, apparent from the higher $^{129}$Xe shieldings in the former (Tables 3 and 4). The crystal structure of the $C_2F_5Xe^+$ ($C_6F_5)_2BF_4^-$ shows the Xe-C distance (2.092(8) Å) (72) is comparable to the I-C distance in $C_6F_5I(O_2CC_6F_5)_2$ (2.072(4) Å) (73). Coordination of CH$_3$C≡N with the C$_2F_5Xe^+$ cation serves to lower the effective positive charge at xenon by coordination to the nitrogen of CH$_3$C≡N, to give an Xe···N contact of 2.681 Å, that is significantly shorter than the sum of the van der Waals radii for Xe and N (3.6 Å) and substantially longer than in the Xe-N(SO$_2$F)$_2^+$ (2.02(1) Å) (6) and FXe-N(SO$_2$F)$_2$ (2.200(3) Å) (3). The Xe-N bond in C$_5$F$_5Xe$-N=CCH$_3^+$ is clearly weakly covalent and can be described in terms very similar to those used to describe the XeL$^+$ adducts considered in this Review.

Acknowledgments—The United States Air Force Astronautics Laboratory, Edwards Air Force Base, California (Contract F49620-87-C-0049) and the Natural Sciences and Engineering Research Council of Canada (NSERC) are gratefully acknowledged for their financial support.
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12. \[ \text{EA(KrF}^+) = \text{IP(Kr)} + \text{BE(KrF}^{-}) - \text{BE(KrF}^+) = 14.0 + 0.8 - 1.6 = 13.2 \text{ eV.} \]
13. \[ \text{EA(XeF}^+) = \text{IP(Xe)} + \text{BE(XeF}^{-}) - \text{BE(XeF}^+) = 12.1 + 0.86 - 2.1 = 10.9 \text{ eV.} \]
p. 113.


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47. G.J. Schrobilgen, unpublished work.


54. J.C.P. Sanders and G.J. Schrobilgen, unpublished work.


Fluoro\(\text{nitrile}\)xenon(\(\alpha\)) Cations, \(\text{RC} \equiv \text{N} - \text{XeF}^+ \text{AsF}_6^-\) (\(R = \text{H}, \text{CH}_3, \text{CH}_2\text{F}, \text{C}_2\text{H}_5, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7,\) or \(\text{C}_6\text{F}_{13}\)); Novel Examples of Xenon–Nitrogen Bonds and \(^{129}\text{Xe} - ^{13}\text{C}, ^{129}\text{Xe} - ^1\text{H},\) and \(^{129}\text{Xe} - ^{14}\text{N}\) Nuclear Spin–Spin Couplings

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A new class of Xe–N bonded compound results from the interaction of the electron lone pair of a nitrile with the Lewis and, XeF; the cationic adducts, \(\text{RC} \equiv \text{N} - \text{XeF}^+\), have been derived from the interaction of the appropriate nitrile with either \(\text{XeF} - \text{AsF}_6^-\) or \(\text{XeF}_2 - \text{AsF}_5^-\) in anhydrous HF at low temperature and characterized in the solid state by Raman spectroscopy (for \(R = \text{H}\) and Me) and in HF solution by \(^{129}\text{Xe}, ^{19}\text{F}, ^{13}\text{C}, ^{14}\text{N}, ^{1}\text{H}\) n.m.r. spectroscopy. Herein we report a new ligand group for xenon which is bonded to the noble gas atom through nitrogen. In choosing a likely ligand precursor for a Xe-C or Xe-N bond, the very weak protonic acid HCN was considered and initially found to be unreactive towards XeF\(_2\) in SO\(_2\)Cl\(_2\) at room temperature by the usual HF displacement to give the Xe-C and Xe-N bonded compounds, Xe(CN) and Xe(CN). Although the conventional HF displacement is not a viable route to xenon(\(\alpha\)) cyanides and isocyanides, we have found that HCN, and nitriles in general, behave as nitrogen bases towards the XeF\(^+\) cation. The reactions of XeF\(^+\)AsF\(_6^-\) and XeF\(_3\)AsF\(_6^-\) with HCN, CH\(_3\)CN, CH\(_2\)F CN, C\(_2\)H\(_5\)CN, C\(_2\)F\(_5\)CN, C\(_3\)F\(_7\)CN, and C\(_6\)F\(_{13}\)CN were carried out by combining stoichiometric amounts of the reactants in anhydrous HF and warming to \(-20\) to \(-10^\circ\text{C}\) to effect reaction and dissolution in the solvent (HCN reactions were also conducted in SO\(_2\)Cl\(_2\) solvent). The reactions proceed according to equations (1) and (2).

\[
\text{XeF}^+\text{AsF}_6^- + \text{RC} \equiv \text{N} \rightarrow \text{RC} \equiv \text{N} - \text{XeF}^+\text{AsF}_6^- \quad (1)
\]

\[
\text{XeF}_3\text{AsF}_6^- + \text{H} \rightarrow (2) + \text{XeF}_2 \quad (2)
\]

Multinuclear magnetic resonance spectra were recorded for the nitride cations in \(^{1}\text{H}\) solvent, and in the case of the \(^{129}\text{Xe}\) n.m.r. spectra of the \(\text{HC} \equiv \text{N} - \text{XeF}^+\) cation, in BrF\(_3\) solvent. As every element in the \(\text{RC} \equiv \text{N} - \text{XeF}^+\) cations studied be: unreactive toward,; XeF, in SO\(_2\)Cl\(_2\) it room temperature possesses at least one n'icidlewhich is suitable for observation by the usual HF displacement to give the Xe-C and Xe-N by n.m.r. spectroscopy. n.m.r. studies using both natural and enriched compounds were undertaken and have provided unambiguous proof for the structures of a majority of the cations in solution (Table 1). In the case of \(\text{HC} \equiv \text{N} - \text{XeF}^+\), the chemical shifts of all five nuclei and eight of the ten possible spin–spin couplings that have been observed are listed in Table 1. The \(^{129}\text{Xe}, ^{14}\text{N}, ^{1}\text{H}\) spectra are illustrated in Figures 1 and 2. The couplings, \(\mathcal{J}(^{129}\text{Xe} - ^{1}\text{H}), \mathcal{J}(^{129}\text{Xe} - ^{14}\text{N}), \mathcal{J}(^{129}\text{Xe} - ^{14}\text{N})\), and \(\mathcal{J}(^{129}\text{Xe} - ^{14}\text{N})\), represent the first examples of nuclear spin–spin couplings observed between these nuclei. Owing to the cylindrical symmetry of the \(\text{HC} \equiv \text{N} - \text{Xe}- \text{F} \) moiety in the new cation series, low viscosity of the HF solvent medium, and the small quadrupole moment of \(^{14}\text{N}\), quadrupole relaxation c. the \(^{129}\text{Xe} - ^{14}\text{N}\) coupling is found to be minimal giving rise to slightly quadrupole collapsed 1:1:1 triplets in the \(^{129}\text{Xe}\) spectra and \(^{129}\text{Xe}\) satellites in the \(^{14}\text{N}\) spectra (Figures 1 and 2). The similarities of \(\mathcal{J}(^{129}\text{Xe} - ^{14}\text{N})\) and \(\mathcal{J}(^{129}\text{Xe} - ^{14}\text{N})\) values to those of the \(\text{HC} \equiv \text{N} - \text{Xe}- \text{F} \) cation

Herein we report a new ligand group for xenon which is bonded to the noble gas atom through nitrogen. In choosing a likely ligand precursor for a Xe-C or Xe-N bond, the very weak protonic acid HCN was considered and initially found to be unreactive towards XeF\(_2\) in SO\(_2\)Cl\(_2\) at room temperature by the usual HF displacement to give the Xe-C and Xe-N bonded compounds, Xe(CN) and Xe(CN). Although the conventional HF displacement is not a viable route to xenon(\(\alpha\)) cyanides and isocyanides, we have found that HCN, and nitriles in general, behave as nitrogen bases towards the XeF\(^+\) cation. The reactions of XeF\(^+\)AsF\(_6^-\) and XeF\(_3\)AsF\(_6^-\) with HCN, CH\(_3\)CN, CH\(_2\)F CN, C\(_2\)H\(_5\)CN, C\(_2\)F\(_5\)CN, C\(_3\)F\(_7\)CN, and C\(_6\)F\(_{13}\)CN were carried out by combining stoichiometric amounts of the reactants in anhydrous HF and warming to \(-20\) to \(-10^\circ\text{C}\) to effect reaction and dissolution in the solvent (HCN reactions were also conducted in SO\(_2\)Cl\(_2\) solvent). The reactions proceed according to equations (1) and (2).

\[
\text{XeF}^+\text{AsF}_6^- + \text{RC} \equiv \text{N} \rightarrow \text{RC} \equiv \text{N} - \text{XeF}^+\text{AsF}_6^- \quad (1)
\]

\[
\text{XeF}_3\text{AsF}_6^- + \text{H} \rightarrow (2) + \text{XeF}_2 \quad (2)
\]
Figure 1. N.m.r. spectra of HCN-N-XeF-AsF₅⁺: (a) $^{129}$Xe spectrum for a 99.2% $^{13}$C enriched sample recorded in HF solvent at -10°C; (b) $^1$H spectrum for a natural abundance sample recorded in BrF₅ solvent at -58°C at 1.879 T; (c) $^{13}$C spectrum for a 99.2% $^{13}$C enriched sample recorded in HF at -10°C. Asterisks (*) denote $^{129}$Xe satellites.

Also allow analogous structures to be assigned to the alkyl-, fluoroalkyl- and perfluorobenzonitrile cations.

The observation of $^1J(^{129}$Xe-$^1$N) in both the $^{13}$N and $^{129}$Xe spectra is particularly noteworthy and provides conclusive proof that in each case the nitrogen atom is directly bonded to xenon. This is confirmed by comparing their respective reduced coupling constants, $^1K(^{129}$Xe-$^1$N) (calculated using the expression given in refs. 1-3; see Table 1), with that of $^{129}$XeN(SO₂F)₂ $^1J(^{129}$Xe-$^1$N) 307 Hz; $^1K(^{129}$Xe-$^1$N) 0.913 x $10^{-22}$ NA⁻² nm²⁻¹. In addition, the small value of the J-coupling, $^{129}$Xe-$^{13}$C, observed for the $^{13}$C enriched sample of H-C≡N-XeF⁺, and a one-bond $^1$C-$^1$H coupling, also confirm that the xenon atom is not bonded to carbon in this species.

Assuming that the Xe-N spin-spin couplings in xenon-nitrogen compounds are dominated by the Fermi contact term, a comparison of $^1K(Xe-N)$ values for R-C≡N-XeF⁺ with that of the trigonal planar sp²-hybridised nitrogen atom in F-XeN(SO₂F)₂ allows assessment of the relative degrees of hybridisation of the nitrogen orbitals used in bonding to xenon. The ratios of $^1K(Xe-N)_{p^+}$ to $^1K(Xe-N)_{p^2}$ are 1.42-1.53 for the cations listed in Table 1, in excellent agreement with the theoretical ratio, 1.50, calculated from the predicted fractional s-characters of the nitrogen orbitals used in bonding to xenon.

In the case of the perfluoroalkyl derivatives (R = C₂F₅ and C₃F₇), the Xe-N bonds are found to be labile on the n.m.r. time scale in HF solvent at temperatures down to -30°C as a result of a decrease in base strength for R-C≡N: with increasing fluorine substitution at C-2.

The salts HCN-N-XeF⁺AsF₅⁻ and CH₃CN-N-XeF⁺AsF₅⁻ were isolated from HF solvent by pumping the solutions under vacuum at -50 to -30°C to give white solids whose Raman spectra were recorded at -196°C (514.5 nm excitation). The Raman spectrum of HCN-N-XeF⁺AsF₅⁻ was assigned in detail, while only key frequencies of CH₃CN-N-XeF⁺AsF₅⁻ have presently been assigned. In addition to the three Raman active...
Table 1. N.m.r. parameters for RC=NXeF \textsuperscript{-} cations

<table>
<thead>
<tr>
<th>Chemical shifts</th>
<th>R</th>
<th>( \delta)\textsuperscript{(125}Xe)</th>
<th>( \delta)\textsuperscript{(19}F)</th>
<th>( \delta)\textsuperscript{(1}N)</th>
<th>( \delta)\textsuperscript{(1}C)</th>
<th>( \delta)\textsuperscript{(1}H)</th>
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<td>-235.4</td>
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<td>5.44</td>
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<tr>
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<td>-235.4</td>
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<td>CH\textsubscript{3}F</td>
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<td>-251.1</td>
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<td>0.6(CH\textsubscript{3})</td>
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<th>Coupling Constants</th>
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<th>( \text{CH}=\text{C}=\text{N}=\text{Xe}=\text{F} \textsuperscript{-} \text{f} )</th>
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<th>( \text{C}=\text{F}=\text{C}=\text{N}=\text{Xe}=\text{F} )</th>
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<td>333</td>
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<tr>
<td>( J(\text{1}Xe,\text{N}) )</td>
<td>1.293 \times 10\textsuperscript{22}</td>
<td>1.389 \times 10\textsuperscript{22}</td>
<td>1.305 \times 10\textsuperscript{22}</td>
<td>1.297 \times 10\textsuperscript{22}</td>
<td></td>
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</tbody>
</table>

\* Spectra were recorded in anhydrous HF at \(-10^\circ\) C using 9 mm o.d. FEP sample tubes at 5.8719 T, and spectrometer frequencies (MHz): \( \text{125}Xe \) 69.563, \( \text{19}F \) 235.261, \( \text{1}N \) 18.075, \( \text{1}C \) 62.915, \( \text{1}H \) 251.132. \* Samples were referenced externally at \( 24^\circ\) C with respect to the neat liquid references: \( \text{XeOF}_{2} \) (\( \text{125}Xe \)), CFCI (\( \text{19}F \)), CH\textsubscript{3}NO (\( \text{1}N \)), SiMe\textsubscript{4} (\( \text{1}C \) and \( \text{1}H \)). A positive chemical shift denotes a resonance occurring to high frequency of the reference compound. \* All \( \text{19}F \) spectra displayed a broad saddle-shaped feature at \( ca. -68\) ppm, arising from the partially quadrupole collapsed \( \text{A}_{\text{e}}\text{m}^{\text{F}} \) coupling of the octahedral \( \text{AsF}_{6}^{-} \) anion. \* Sample prepared from \( 99.2\% \) \( \text{1}C \) enriched \( \text{H}_{\text{2}}\text{CN} \). Measured in BrF\textsubscript{5} solvent at \(-58^\circ\) C; the \( J(\text{125}Xe,\text{19}F) \) coupling was found to be completely quadrupole collapsed under these conditions. The sample was prepared by redissolving solid \( \text{H}=\text{C}=\text{N}\text{Xe}=\text{F}\text{AsF}_{6}^{-} \), prepared in HF solvent, in BrF\textsubscript{5} at \(-50^\circ\) C. \* Measured in a 5 mm o.d. precision glass tube in BrF\textsubscript{5} solvent at \(-58^\circ\) C, at 80.022 MHz (1.8790 T) for \( \text{H} \). The sample was prepared by redissolving solid \( \text{H}=\text{C}=\text{N}\text{Xe}=\text{F}\text{AsF}_{6}^{-} \), prepared in HF solvent, in BrF\textsubscript{5} at \(-50^\circ\) C. \* Sample prepared from \( 99\% \) \( \text{1}C \) enriched \( \text{H}=\text{C}=\text{N}\text{CN} \). \* Sample prepared from \( 99.7\% \) \( \text{1}C \) enriched \( \text{CH}\text{CN} \). \* Deomposition occurred at \(-10 \) to \(-20\) C, preventing further characterisation. \* \( J \) values in Hz; \( K \) values in NA\textsuperscript{-1}m\textsuperscript{3}.

Additional examples of nitriles and other inorganic and organic nitrogen bases are under active investigation as potential electron-pair donors towards noble gas cations, as well as representative X-ray crystal structures containing the RC=NXeF\textsuperscript{-} cations.

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References
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The Fluoro(hydrocyano)xenon(II) Cation: Preparation of HC≡N-XeF⁺AsF₆⁻; a Multinuclear Magnetic Resonance and Raman Spectroscopic Study

Adel A.A. Emara and Gary J. Schrobilgen

Abstract

The XeF⁺ or Xe₂F⁺ cations react with HC≡N in anhydrous HF solvent to give the Lewis acid-base adduct cation, HC≡N-XeF⁺. The HC≡N-XeF⁺ cation has been characterized in HF and BrF₅ solvents by ¹²⁹Xe, ¹⁹F, ¹⁴,¹⁵N, ¹³C and ¹H NMR spectroscopy and has been characterized as its AsF₆⁻ salt in the solid state by low-temperature Raman spectroscopy. The scalar couplings, ¹J(¹²⁹Xe-¹⁴N), ²J(¹²⁹Xe-¹³C) and ³J(¹²⁹Xe-¹H), represent the first examples of couplings observed between these nuclides. The vibrational assignments of the ν(Xe-N) stretching and δ(XeNC) δ(FXeN) bending modes have been aided by obtaining Raman spectra for natural abundance ¹⁵N- and ¹³C-enriched HC≡N-XeF⁺AsF₆⁻. The solution NMR and low-temperature Raman spectroscopic studies are consistent with a linear Cᵥ structure for the HC≡N-XeF⁺ cation. The vibrational data together with the NMR chemical shifts indicate that the Xe-N bond is weakly covalent and are in agreement with recent theoretical calculations. NMR spectroscopic studies also show that solutions of HC≡N-XeF⁺AsF₆⁻ in HF are extensively solvolyzed to give equilibrium concentrations of the HC≡NH⁺ cation and XeF₂.
INTRODUCTION

While many examples of 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,¹ over a decade had elapsed before an example with a ligating atom other than oxygen and fluorine, namely nitrogen, was synthesized² and two decades before the Xe-N bond in FXeN(SO₂F)₂ was definitively characterized in the solid state by X-ray crystallography and in solution by multinuclear magnetic resonance spectroscopy.¹ Other imidodisulfurylfluoride xenon-nitrogen bonded species have since been definitively characterized using primarily NMR spectroscopy, namely, Xe[N(SO₂F)₂]₂,⁴⁻⁵ F[XeN(SO₂F)₂]₂,⁴⁻⁵ XeN(SO₂F)₂⁺AsF₆⁻⁶ and XeN(SO₂F)₂⁺Sb₅F₁₆⁻⁶ and the latter salt has also been characterized by single crystal X-ray diffraction. The compound, Xe[N(SO₂CF₃)₂]₂,⁷ has also been prepared and characterized, and is the most thermally stable of the imido derivatives of xenon.

Recently, a significant extension of noble-gas chemistry, and in particular compounds containing noble-gas nitrogen bonds, has been achieved by taking advantage of the Lewis acid properties of noble-gas cations.⁸ In view of the propensity of the XeF⁺ cation to form strong fluorine bridges to counter anions in the solid state,⁹ the XeF⁺ cation may be regarded as having a significant Lewis acid strength. Based on photoionization studies, HCN is one of the most oxidatively resistant ligands among the perfluoropyridines and nitriles we have investigated thus far (first adiabatic ionization potential, 13.59 eV¹⁰). The estimated electron affinity of XeF⁺ (10.9 eV)¹¹ suggested that HCN would be resistant to oxidative attack by the XeF⁺ cation and that the HCN-XeF⁺ cation might have sufficient thermal stability to permit its spectroscopic
characterization in solution and in the solid state. The reaction of XeF+ with HC≡N and the subsequent isolation and characterization of HC≡N-XeF+AsF6+ have been reported in our previous communication.12 We subsequently reported that a large number of oxidatively resistant Lewis nitrogen bases can interact with XeF+ to form Lewis acid-base cations with XeF+. Included among these bases are alkyl nitriles and pentfluorophenyl nitrile,12 perfluoroalkyl nitriles,13 perfluoropyridines14 and s-trifluorotriazine.13 The present paper provides a detailed account of the synthesis and structural characterization of the HC≡N-XeF+ cation by low-temperature Raman spectroscopy in the solid state and in solution by 1H, 13C, 14N, 19F and 129Xe NMR spectroscopy. More recently the krypton(II) analog, HC≡N-KrF+ 15 and RfC≡N-KrF+ (Rf = CF3, C2F5, n-C3F713 have also been synthesized and characterized in this laboratory, representing the first examples of krypton-nitrogen bonds.

The present paper and previous communications outlining the syntheses of HC≡N-XeF+AsF6+ 12 and HC≡N-KrF+AsF6+ 15 have been complemented by a recent theoretical investigation of HC≡N-NgF+ (Ng = Kr, Xe) at the SCF level by determination of the properties of the atoms and bonds in these molecules using the theory of atoms in molecules.16

RESULTS AND DISCUSSION

The reactions of XeF+AsF6+ and Xe2F3+AsF6+ with HC≡N were carried out according to equations (1) and (2) by combining stoichiometric amounts of the reactants in anhydrous HF and warming to -20 to -10 °C to effect reaction and dissolution.
The compound, HC≡N-XeF⁺AsF₆⁻, was isolated as a colorless microcrystalline solid upon removal of HF solvent under vacuum at -30 °C and was stable for up to 6 hrs. at 0 °C. After HF removal at -30 °C following reaction (2), XeF₂ was observed in the Raman spectrum of the solid sample prior to pumping off XeF₂ at 0 °C (ν₁(Σ⁺), 495 cm⁻¹). Solutions of HC≡N-XeF⁺AsF₆⁻ in HF at ambient temperature slowly decompose over a period of 14 hrs. The solvolytic behavior of HC≡N-XeF⁺AsF₆⁻ in anhydrous HF at room temperature has been compared with that of HC≡N in the accompanying paper. The reactions were also conducted in SO₂Cl₂ solvent at 0 °C, but owing to the low solubility of the reactants and product in this solvent, the reactions did not go to completion.

**NMR Spectroscopy**

**Structure of the HC≡N-XeF⁺ Cation in Solution.** Every element in the HC≡N-XeF⁺ cation possesses at least one nuclide which is suitable for observation by NMR spectroscopy, namely, the spin-½ nuclei ¹H, ¹³C, ¹⁵N, ¹²⁹Xe and ¹⁹F, and the spin-1 nucleus ¹⁴N. Multinuclear magnetic resonance spectra were recorded for HC≡N-XeF⁺AsF₆⁻ in HF and BrF₅ solvents for all six nuclei using natural abundance and ¹³C and ¹⁵N enriched compounds. All possible nuclear spin-spin couplings have been observed (Structure I and Table 1), establishing the solution structure of the
HC≡N-XeF⁺ cation. In the course of the present NMR study, the couplings, \( ^1J(\text{Xe}^\text{14N}) \), \( ^2J(\text{Xe}^\text{13C}) \) and \( ^3J(\text{Xe}^\text{1H}) \) were observed, representing the first examples of scalar couplings between these nuclides.

In prior studies of the imidodisulfurylfluoride derivatives of xenon(II), the low symmetry and resulting large electric field gradient (efg) at the \( ^14\text{N} \) nucleus in the trigonal planar \( -\text{N}(\text{SO}_2\text{F})_2 \) group necessitated \( ^{15}\text{N} \) enrichment in order to observe xenon-nitrogen scalar couplings and nitrogen chemical shifts in \( \text{FXeN}(\text{SO}_2\text{F})_2, \text{XeN}(\text{SO}_2\text{F})_2^+, \text{Xe}[\text{N}(\text{SO}_2\text{F})_2]_2^- \) and \( \text{F}[\text{XeN}(\text{SO}_2\text{F})_2]_2^+ \) cations in \( \text{SbF}_5, \text{BrF}_5 \) and \( \text{SO}_2\text{ClF} \) solvents. In contrast, the axial symmetry of the HC≡N-XeF⁺ cation and resulting low efg at the \( ^{14}\text{N} \) nucleus, low viscosity of the HF solvent at -10 °C and small quadrupole moment of \( ^{14}\text{N} \) serve to minimize quadrupole relaxation of the \( ^{129}\text{Xe}^\text{14N} \) and \( ^{14}\text{N}^\text{13C} \) couplings (see Nature of Bonding in HC≡N-XeF⁺), allowing ready observation of the directly bonded \( ^{129}\text{Xe}^\text{14N} \) and \( ^{14}\text{N}^\text{13C} \) scalar couplings. However, in the higher viscosity solvent, \( \text{BrF}_5 (-58 °C) \), the \( ^{129}\text{Xe}^\text{14N} \) and \( ^{14}\text{N}^\text{13C} \) couplings are quadrupole collapsed into single lines. Because they are generally obscured owing to quadrupolar relaxation caused by the \( ^{11}\text{N} \) nucleus,
$^{15}\text{N}$ enrichment was required for the observation of scalar couplings between nitrogen and non-directly bonded nuclei when the magnitudes of the couplings were small.

The $^{129}\text{Xe}$ NMR spectrum of natural abundance HC≡N-XeF$^+$ consists of a doublet arising from $^1J(^{129}\text{Xe}^-\text{F})$ in the Xe(II) region of the spectrum and is centered at -1570 ppm in BrF$_3$ solvent at -50 °C; $^1J(^{129}\text{Xe}^-\text{F})$, 6176 Hz. The doublet ($^1J(^{129}\text{Xe}^-\text{F})$, 6161 Hz) is centered at -1552 ppm in HF at -10 °C and each doublet branch is further split into partially quadrupole collapsed 1:1:1 triplets arising from the one-bond scalar coupling $^1J(^{129}\text{Xe}^-\text{N})$, 332 Hz. The magnitude of $^1J(^{129}\text{Xe}^-\text{F})$ is comparable to directly bonded $^{129}\text{Xe}^-\text{F}$ couplings of other xenon(II) compounds. Failure to observe $^1J(^{129}\text{Xe}^-\text{N})$ in BrF$_3$ at -50 °C is attributed to the increased viscosity of BrF$_3$ relative to HF, leading to a longer molecular correlation time in the former solvent and quadrupole collapse of the $^{129}\text{Xe}^-\text{N}$ scalar coupling. Carbon-13 enrichment (99.2%) led to further splitting into a doublet (84 Hz) on each peak in the $^{129}\text{Xe}$ NMR spectrum, and is assigned to $^2J(^{129}\text{Xe}^-\text{C})$, representing the first reported example of a scalar coupling between $^{13}\text{C}$ and $^{129}\text{Xe}$ (Figure 1a).

Nitrogen-15 enrichment (99.5%) of the HC≡N-XeF$^+$ cation was necessary because $^2J(^{15}\text{N}^-\text{H})$ and $^2J(^{15}\text{F}^-\text{N})$ could not be observed in natural abundance HC≡N-XeF$^+$AsF$_3$. In addition to observing $^2J(^{15}\text{N}^-\text{H})$ and $^2J(^{15}\text{F}^-\text{N})$ in their respective $^{15}\text{F}$, $^{15}\text{N}$ and $^1\text{H}$ NMR spectra (vide infra), a well resolved doublet of doublets on each doublet ($^1J(^{129}\text{Xe}^-\text{F})$) branch in the $^{129}\text{Xe}$ NMR spectrum of the $^{15}\text{N}$-enriched cation was observed in both HF (-10 °C) and BrF$_3$ (-50 °C) solvents (Figure 1b). The fine structure is assigned to $^1J(^{129}\text{Xe}^-\text{N})$ (471 Hz in HF; 483 Hz in BrF$_3$) and $^1J(^{129}\text{Xe}^-\text{H})$ (4.7 Hz in HF; 26.8 Hz in BrF$_3$); the $^{129}\text{Xe}^-\text{H}$ coupling was confirmed by a $^1\text{H}$ broad band decoupling experiment in the $^{129}\text{Xe}$ spectrum. Because of the smaller size of $^3J(^{129}\text{Xe}^-\text{N})$...
'H), quadrupolar line broadening by 14N precludes observation of the latter coupling in the 129Xe
NMR spectrum of the natural abundance cation. The magnitudes of \( J(129\text{Xe}-14\text{N}) \) in the absence
of quadrupole relaxation have been calculated for comparison with their observed values in HF
solvent from the measured values of \( J(129\text{Xe}-15\text{N}) \) using equation (3): 334 Hz (BrF\(_5\) solvent at -50
°C) and 336 Hz (HF solvent at -10 °C; cf., 332 Hz, measured value) and show the effect of
residual quadrupolar relaxation on the measurement of \( J(129\text{Xe}-14\text{N}) \) is negligible.

\[
J_{129\text{Xe}-14\text{N}} = J_{129\text{Xe}-15\text{N}} \left( \frac{\gamma_{14\text{N}}}{\gamma_{15\text{N}}} \right)
\]  

(3)

The \(^1\text{H}\) NMR spectra for natural abundance and 99.2% \(^1^3\text{C}-\text{enriched \text{HCO-}\text{XeF}^+\text{AsF}_6^-} \) in HF solvent at -10 °C and for 99.5% \(^1^5\text{N}-\text{enriched \text{HCO-}\text{XeF}^+\text{AsF}_6^-} \) in BrF\(_5\) solvent at -50 °C
(Figure 2) consist of single \(^1\text{H}\) environments with accompanying satellites that are attributed to
\( J(129\text{Xe}-^1\text{H}) \). Under high resolution and in the absence of quadrupolar line broadening arising
from \(^1\text{H}, J(1^9\text{F}-^1\text{H}), 2.6 \) (HF), 2.7 (BrF\(_5\)); \( J(1^9\text{F}-^1^3\text{C}), 24.7 \) (HF), 26.8 (BrF\(_5\)) and \( J(1^9\text{F}-^1^5\text{N}), 23.9 \)
Hz were observed in the \(^1^5\text{N} \) enriched compounds (Table 1). A broad, saddle-shaped feature
(3150 Hz linewidth) also occurs at -68 ppm in these spectra and arises from the partially
quadrupole collapsed \( J(^{75}\text{As}^+\text{F}^-) \) coupling in the \text{AsF}_6^- anion.

The \(^1\text{N} \) and \(^1\text{^1}\text{N} \) NMR spectra have been recorded for natural abundance and 99.5% \(^1\text{^1}\text{N}-\text{enriched \text{HCO-}\text{XeF}^+\text{AsF}_6^-} \), respectively. The \(^1\text{N} \) NMR spectrum recorded in HF solvent at -10
°C consisted of a single line at -235.1 ppm with \( J(129\text{Xe}-^1\text{N}) \). The \(^1\text{N} \) NMR spectrum of a 99.5% enriched sample was also recorded under the same conditions in HF at -10
°C (-234.5 ppm) and in BrF\(_5\) at -50 °C (-230.2 ppm) (Figure 3). The splitting pattern in the \(^1\text{N} \)

The $^1$H NMR resonance of natural abundance HC≡N-XeF$^+$AsF$_6^-$ in BrF$_3$ solvent at -58 °C occurred at 6.01 ppm and consisted of a doublet with $^{129}$Xe satellites, $^3J(^{129}$Xe-$^1$H), 2.7 Hz. The doublet is assigned to $^4J(^{19}$F-$^1$H), but the two-bond $^{14}$N-$^1$H coupling was not observed due to quadrupole relaxation by $^{14}$N. However, $^4J(^{19}$F-$^1$H) and $^2J(^{15}$N-$^1$H) were both observed in the $^1$H NMR spectrum for a 99.5% $^{15}$N enriched sample in BrF$_3$ solvent at -50 °C (Figure 4). The $^1$H resonance in HF at -10 °C has also been observed for a natural abundance sample and consisted of a single line at 4.70 ppm with $^{129}$Xe satellites ($^1J(^{129}$Xe-$^1$H)).

The $^{13}$C NMR resonance of HC≡N-XeF$^+$ (Figure 5) for a 99.2% $^{13}$C enriched sample in HF solvent at -10 °C occurred at 104.1 ppm and consisted of a doublet ($^1J(^{13}$C-$^1$H)) of partially quadrupole collapsed 1:1:1 triplets ($^1J(^{14}$N,$^{13}$C), 22 Hz) with $^{129}$Xe satellites ($^1J(^{129}$Xe-$^{13}$C)) on each doublet branch.

Intense signals assigned to the HC≡NH$^+$ cation were also observed in the $^1$H and $^{13}$C NMR spectra and are attributed to equilibrium (4). The relative concentrations [HC≡NH$^+$]/[HC≡N-XeF$^+$] measured in the $^1$H NMR spectrum of an HF solution having an initial [HC≡N-XeF$^+$AsF$_6^-$] of 2.18 M at -10 °C was 4 : 1. The proton chemical shift, $\delta(^1$H), 7.43 ppm and $^2J(^{14}$N-$^1$H), 18.6 Hz for the proton on carbon of a $^{15}$N-enriched sample are in excellent agreement with the previously reported values for HC≡NH$^+$ in the FSO$_3$H-SbF$_5$-SO$_2$ solvent system.\footnote{In contrast to the previous work in FSO$_3$H-SbF$_5$-SO$_2$, the proton on nitrogen environment and $^1J(^{14,15}$N-$^1$H) were not observed, and is presumably the result of proton exchange}
with HF solvent. Additional NMR parameters for the HC≡NH' cation are reported here for the first time: \( \delta(^{13}\text{C}) \), 97.1 ppm; \( ^1J(^{13}\text{C}-^1\text{H}) \), 324.6; \( ^1J(^{13}\text{C}-^{14}\text{N}) \), 40.7 and \( ^1J(^{13}\text{C}-^{15}\text{N}) \), 59.5 Hz. However, neither the \(^{14}\text{N}\) nor \(^{15}\text{N}\) spectra of the HC≡NH' cation could be observed, even after a relaxation delay of 30 s was applied in the \(^{15}\text{N}\) spectrum. A previous determination of \( \delta(^{15}\text{N}) \) in \( \text{FSO}_3\text{H-SbF}_5\text{-SO}_2 \) solvent by the INDO method gave a value of 119.4 ppm relative to external aqueous \( \text{NH}_4^+ \) (chemical shift relative to neat external \( \text{CH}_3\text{NO}_2 \) is -240.3 ppm calculated from a \( \delta(^{14}\text{N}) \) value of -359.7 ppm for aqueous \( \text{NH}_4^+\text{Cl}^- \) relative to \( \text{CH}_3\text{NO}_2^- \)).

Although significant equilibrium amounts of HC≡NH' are observed in the \(^{13}\text{C}\) and \(^1\text{H}\) NMR spectra, XeF\(_2\) is not observed in the \(^{19}\text{F}\) and \(^{129}\text{Xe}\) NMR spectra even in the presence of an equimolar amount of XeF\(_2\) as in reaction (2). The apparent absence of XeF\(_2\) in the NMR spectra is presumed to result from chemical exchange involving trace amounts of XeF\(^+\) and Xe\(_2\)F\(_3^+\) as exchange intermediates arising from equilibria (4) - (7) and XeF\(_2\).

\[
\text{HC≡N-XeF}^+ + \text{HF} \rightleftharpoons \text{HC≡NH}^+ + \text{XeF}_2 \quad (4)
\]

\[
\text{HC≡N-XeF}^+ \rightleftharpoons \text{HC≡N} + \text{XeF}^+ \quad (5)
\]

\[
\text{XeF}^+ + 2\text{HF} \rightleftharpoons \text{XeF}_2 + \text{H}_2\text{F}^+ \quad (6)
\]

\[
\text{XeF}^+ + \text{XeF}_2 \rightleftharpoons \text{Xe}_2\text{F}_3^+ \quad (7)
\]

The \(^{129}\text{Xe}\) NMR spectra of HC≡N-XeF\(^+\)AsF\(_6^-\) and CH\(_3\)C≡N-XeF\(^+\)AsF\(_6^-\) in HF at -10 °C have been
reported previously\textsuperscript{12} and clearly show that the \textsuperscript{129}Xe linewidth of HC≡\textsuperscript{1}XeF\textsuperscript{2}AsF\textsubscript{6} (84 Hz, center line of the triplet) compared to that of CH\textsubscript{3}C≡\textsuperscript{N}XeF\textsuperscript{2}AsF\textsubscript{6} (40 Hz, center line of the triplet) is significantly larger. This observation is consistent with the anticipated lower base strength of HC≡\textsuperscript{N} towards XeF\textsuperscript{2} relative to that of CH\textsubscript{3}C≡\textsuperscript{N}, resulting in a greater degree of dissociation for HC≡\textsuperscript{N}XeF\textsuperscript{2} (equilibrium (5)) and ensuing chemical exchange by means of equilibria (4), (6) and (7).

In the course of this study it has also been shown that XeF\textsubscript{2} displaces HF in its reaction with HC≡\textsuperscript{N}AsF\textsubscript{6} in HF or BrF\textsubscript{3} solvents according to the reverse of equilibrium (4). The \textsuperscript{129}Xe NMR spectrum was recorded for the molar ratio XeF\textsubscript{2}/HC≡\textsuperscript{N}AsF\textsubscript{6} = 2.47 at -15 °C in HF solvent (initial [XeF\textsubscript{2}] = 0.230 M), and gave the relative equilibrium concentrations [XeF\textsubscript{2}]/[HC≡\textsuperscript{N}XeF\textsuperscript{2}] = 0.81. While the XeF\textsubscript{2} 1:2:1 triplet (-1555 ppm; \textsuperscript{1}J(\textsuperscript{129}Xe-\textsuperscript{19}F), 5530 Hz) could be observed under these conditions, it was significantly exchange broadened (linewidth, 2590 Hz) relative to that of HC≡\textsuperscript{N}XeF\textsuperscript{2} (-1555 ppm; \textsuperscript{1}J(\textsuperscript{129}Xe-\textsuperscript{19}F), 6156 Hz; \textsuperscript{1}J(\textsuperscript{129}Xe-\textsuperscript{14}N), 330 Hz; linewidth, 110 Hz), indicating that XeF\textsubscript{2} was undergoing slow chemical exchange, presumably via equilibria (5) - (7). Because HC≡\textsuperscript{N}XeF\textsuperscript{2}AsF\textsubscript{6} has a low solubility in HF at temperatures approaching -30 °C, an equilibrium mixture of HC≡\textsuperscript{N}AsF\textsubscript{6} and XeF\textsubscript{2} was also studied in BrF\textsubscript{3} solvent at -50 °C for the molar ratio XeF\textsubscript{2}/HC≡\textsuperscript{N}AsF\textsubscript{6} = 2.17, giving [XeF\textsubscript{2}]/[HC≡\textsuperscript{N}XeF\textsuperscript{2}] = 0.72 at equilibrium (initial [XeF\textsubscript{2}] = 0.314 M). In contrast, the XeF\textsubscript{2} triplet (-1666 ppm; \textsuperscript{1}J(\textsuperscript{129}Xe-\textsuperscript{19}F), 5629 Hz) was significantly sharper (linewidth, 250 Hz), which is consistent with a lower degree of dissociation of HC≡\textsuperscript{N}XeF\textsuperscript{2} according to equilibrium (5) (-1573 ppm; \textsuperscript{1}J(\textsuperscript{129}Xe-\textsuperscript{14}N) was quadrupole collapsed at low temperatures in BrF\textsubscript{3}; linewidth, 470 Hz).
Raman Spectroscopy. The low-temperature (-14.5 °C) Raman spectra of the crystalline product, isolated from the reaction of natural abundance, $^{15}$N- and $^{13}$C-enriched HC≡N with XeF$^+$AsF$_6^-$ in anhydrous HF solvent are shown in Figures 6 and 7 and the observed frequencies, along with their assignments, are listed in Table 2. The $^{13}$C (99.2%) and $^{15}$N (99.5%) enriched salts were prepared in order to aid in the assignments of the ν(XeN) stretching and δ(HC≡N), δ(CNxe) and δ(NXeF) bending frequencies. The isotopic shifts are given by the ratios $\Delta\nu(\nu^{14}N)/\nu^{(14}N)$ and $\Delta\nu(\nu^{12}C)/\nu^{(12}C)$, as described in reference (24) and are defined and listed in Table 2.

The Raman spectra are consistent with the formation of HC≡N-XeF$^+$AsF$_6^-$ in the solid state. The linear HC≡N-XeF$^+$ cation is expected to give rise to 3N - 5 = 10 normal modes belonging to the irreducible representations $4\Sigma^+ + 3\Pi$ under the point symmetry $C_{\infty v}$. All ten modes are predicted to be Raman and infrared active, and consist of four stretching modes, ν$_1$($\Sigma^+$), ν(H-C); ν$_2$($\Sigma^+$), ν(C-N); ν$_3$($\Sigma^+$), ν(Xe-F) and ν$_4$($\Sigma^+$), ν(Xe-N) and three doubly degenerate bending modes ν$_5$(Π), δ(HCN); ν$_6$(Π), δ(CNxe) and ν$_7$(Π), δ(NXeF). Therefore, seven bands are expected in the Raman and infrared spectra of the HC≡N-XeF$^+$ cation. In addition, the octahedral AsF$_6^-$ anion is expected to give rise to three Raman-active vibrational bands under $O_h$ symmetry, ν$_1$(a$_{1g}$), ν$_2$(e$_g$) and ν$_3$(t$_{2g}$). However, 28 bands as opposed to the predicted 13 from a consideration of free ion symmetries are observed in the Raman spectrum of HC≡N-XeF$^+$AsF$_6^-$ (Table 2). The disparity between the number of observed bands and the number predicted from a consideration of the free species is attributed to vibrational coupling within the unit cell and/or reduction of the free ion symmetries due to site symmetry effects. The removal of all degeneracies by lowering of the cation and anion site symmetries to $C_2v$ or lower would result in 25 Raman-active bands, however, in the absence of a crystallographic space group for HC≡N-XeF$^+$AsF$_6^-$, it has not been
possible in the ensuing discussion to determine their site symmetries and thereby account for the additional splittings and assign their symmetry species in a rigorous manner.

Vibrational assignments were aided by comparison with the vibrational frequencies of HC≡N, \(^\text{22}\) FXe-N(SO\(_2\)F)\(_2\), \(^\text{1}\) XeF'AsF\(_6\); \(^\text{24}\) Xe\(_2\)F\(_3\)AsF\(_6\); \(^\text{26}\) and M'AsF\(_6\); \(^\text{23}\) where M is an alkali metal and by recent theoretical calculations of the harmonic frequencies of the HC≡N-KrF\(_2\) cation. \(^\text{27-30}\)

The three fundamental stretching modes ν(Xe-F), ν(C-N) and ν(C-H) are readily assigned by comparison with the Raman spectra of HC≡N in the gas phase and XeF'AsF\(_6\); which are also listed in Table 2. As the Xe-F and C-N stretching modes belong to the totally symmetric representation, Σ\(^t\), their splittings can only be attributed to coupling of vibrational modes within the unit cell. The C-H stretching mode is also presumed to be factor-group split, but owing to its broadness, the anticipated splitting could not be resolved.

The most intense bands at 561(100) and 569(93) cm\(^{-1}\) are assigned to the Xe-F stretching frequency of the HC≡N-XeF\(^t\) cation and is characteristic of the terminal Xe-F bond in xenon(III) species of the type L-Xe-F (see Table 3). The Xe-F stretching frequency can be used to assess the covalent nature of the Xe-F bond. The XeF\(^t\) cation has been shown to be weakly coordinated to the anion by means of a fluorine bridge, and the Xe-F stretch has been shown to correlate with the degree of covalent character in the Xe---F bridge bond, decreasing with increasing base strength of the anion. \(^\text{8}\) Consequently, the Xe-F stretching frequency is expected to increase as the xenon-nitrogen bond becomes more ionic and the terminal XeF bond becomes more covalent. A comparison of the Xe-F stretching frequency of HC≡N-XeF\(^t\) with other Xe-N bonded species, XeF\(^t\) and Xe\(_2\)F\(_3\)\(^t\), allows one to assess the relative covalency of the Xe-N bond in the HC≡N-XeF\(^t\) cation. The stretching frequencies of the terminal XeF bond for F-Xe-L type derivatives are listed...
in Table 3 along with their Xe-F and Xe-L bond lengths when known. The HC≡N-XeF⁺ cation has the most ionic xenon-nitrogen bond when compared to previously reported Xe-N bonded compounds for which vibrational data are available and is also in accord with our NMR findings (see above and Table 3) and theoretical calculations at the SCF level (see Nature of the Bonding in HC≡N-XeF⁺). The latter calculations show that the reaction of the gas phase XeF⁺ ion with F⁻ to yield the difluoride results in an increase in the calculated Xe-F bond length of 0.1 Å, while the reaction of XeF⁺ with HC≡N causes the same bond length (calculated) to increase on average by only 0.016 Å.¹⁶ Similar conclusions have been reached based on the high-frequency position of the Kr-F stretching frequency of HC≡N-KrF⁺AsF₆⁻¹⁵ and theoretical calculations for the HC≡N-KrF⁺ cation.¹⁶,²⁷,³⁰

The ν₁(Σ⁺) C-H stretching vibration is assigned to a broad, weak band at 3142(2) cm⁻¹ and occurs at a significantly lower frequency than in gaseous HC≡N, i.e., 3311 cm⁻¹,²² and is consistent with coordination of the nitrogen lone pair to an electron pair acceptor. Two sharp lines at 2160(41) and 2162(18) cm⁻¹ are assigned to the factor-group split ν₂(Σ⁺) C≡N stretching mode and occur 63 cm⁻¹ to higher frequency than the C≡N stretch of gaseous HC≡N. The shift to higher frequency upon coordination to XeF⁺ is consistent with cation formation and with HC≡N acting as a σ-electron pair donor to XeF⁺. The C-H and C≡N stretching frequencies also exhibit the expected sensitivities to¹⁷⁻¹⁷ and¹⁵⁻¹⁵ substitution (Table 2). The calculated changes in C-H and C≡N bond lengths parallel the observed shifts in the stretching frequencies in the HC≡N-XeF⁺AsF₆⁻ salt (see Nature of the Bonding in HC≡N-XeF⁺).¹⁶

The assignments of the low-frequency cation bands arising from ν(Xe-N), δ(CN-Xe) and δ(FXeN) were aided by¹⁵⁻¹⁵ and¹³⁻¹³ isotopic enrichment. The relative order of the corresponding
calculated frequencies for HC≡N-KrF⁺, which are uniformly lower than in the xenon analog, are consistent with the order arrived at for HC≡N-KrF⁺, i.e., ν(Xe-N) > δ(CNXe) > δ(FXeN).

The ν₁(Σ⁺) Xe-N stretching vibration of the HC≡N-XeF⁺ cation is assigned to the weak, low-frequency lines 328(4) and 335(2) cm⁻¹ where the splitting is again attributed to vibrational coupling within the crystallographic unit cell. The assignment of the Xe-N stretch has been confirmed using ¹⁵N and ¹³C enrichment and results in relative shifts Δλ(¹⁴¹⁴N)/λ(¹⁵N), -0.027 and -0.024, for the two bands in the spectrum of ¹⁴N‖HC≡N-XeF⁺AsF₆⁻, and Δλ(¹²¹⁴C)/λ(¹²C), -0.030 and -0.024 for ¹⁴C‖HC≡N-XeF⁺AsF₆⁻ (Figure 7). The similarity between the ¹⁴N/¹⁵N and ¹³C/¹²C isotopic shifts is expected from a consideration of the form of the normal coordinate corresponding to ν₁(Σ⁺). In the case of a heavy atom like Xe, the N and C displacements are expected to essentially equal one another and in the same but opposite sense to the small Xe displacement (cf. the actual form of the dis, lacement in the normal coordinate corresponding to ν₁(Σ⁺), the C-X stretch in XC≡N, where X = Cl, Br or I). The Xe-N frequency of the HC≡N-XeF⁺AsF₆⁻ salt occurs at lower frequency than those of ¹XeN(SO₂F)₂ (422 cm⁻¹) and Xe[N(SO₂F)]₂ (386 - 413 cm⁻¹). This is attributed to the greater covalent character of the Xe-N bonds in the imidodisulfurylfluoride derivatives, whereas the Xe-N bond of the HC≡N-XeF⁺ cation is among the most ionic Xe-N bonded species presently known (the Xe-N bonds in n-C₃F₇C≡N-XeF⁺, C₃F₇C≡N-XeF⁺ and CF₃C≡N-XeF⁺ appear to be weaker based on a comparison of their ¹²⁶Xe and ¹⁹F chemical shifts, however, the vibrational spectra of these cations have not been recorded¹). This is corroborated by the high-frequency position of the Xe F stretch, which is among the highest of any F-Xe-L type species known where L is not bonded to the XeF⁺ group through fluorine.
The formally doubly degenerate bending mode $\nu_3(\Pi)$, $\delta$(HCN) was not observed; this band is very weak in the Raman spectrum of gaseous HC≡N.\textsuperscript{22} Although the frequency of the weak band at 707(2) is similar to $\delta$(HCN) of gaseous HC≡N (712 cm\textsuperscript{-1}), it was found to be insensitive to either $^{12}$C or $^{15}$N isotopic substitution and was accordingly assigned to an anion mode (vide infra). The assignments of the remaining doubly degenerate bending modes have been made with the aid of their relative $^{12}$C/$^{13}$C and $^{14}$N/$^{15}$N isotopic shift data. The presence of more than a single band for the $\delta$(CNXe) and $\delta$(FXeN) bending modes is ascribed to factor-group splitting and/or removal of the degeneracy by a cation site symmetry lower than $C_{av}$.

The bending mode $\nu_4(\Pi)$, $\delta$(CNXe) is assigned to lines at 271(6), and 281(14) cm\textsuperscript{-1} and exhibits the anticipated low-frequency shifts in the Raman spectra of $[^{13}]$HC≡N-XeF\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} and $[^{15}]$HC≡N-XeF\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}, i.e., $\Delta \lambda(^{14/15}N)/\lambda(^{15}N)$, -0.038 and -0.032 and $\Delta \lambda(^{12/13}C)/\lambda(^{13}C)$, -0.005 and -0.008 (Figure 7). The $^{14}$N/$^{15}$N dependence is large, and is in fact similar to $\nu_1(\Sigma^+)$, the Xe-N stretching mode. The displacement of nitrogen from the molecular axis is expected to be large when bonded to a heavy atom while that of carbon is expected to be considerably less than the nitrogen displacement and in the opposite sense (cf. displacements for the normal modes in XC≡N\textsuperscript{42}). The relatively small $^{12}$C/$^{13}$C isotopic dependence for this mode is also supported by this qualitative description and is consistent with a smaller carbon displacement.

The bending mode $\nu_7(\Pi)$, $\delta$(FXeN) is expected at lower frequencies than $\delta$(CNXe), and is assigned to the moderately intense bands at 118(20) and 135(10), 158(6) and 181(3) cm\textsuperscript{-1} by comparison with XeF\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}\textsuperscript{25} and Xe\textsubscript{2}F\textsubscript{5}AsF\textsubscript{6}\textsuperscript{-}\textsuperscript{26} where $\delta$(FXe---F) are 155 (average) and 161 cm\textsuperscript{-1} (average), respectively, and FXe-N(SO\textsubscript{2}F)\textsubscript{2}\textsuperscript{1}, where $\delta$(FXeN) is 200 cm\textsuperscript{-1} (average). The FXeN bend of HC≡N-XeF\textsuperscript{+} is expected to be significantly lower than that of FXe-N(SO\textsubscript{2}F)\textsubscript{2}.
These modes also exhibit $^{14}\text{N}/^{14}\text{N}$ and $^{12}\text{C}/^{13}\text{C}$ isotopic dependences (Table 2 and Figure 7); however, no simple explanation for the relative magnitudes of each shift for each component of this doubly degenerate bend is presently available.

Although the AsF$_6^-$ anion is not expected to be fluorine bridged to the HC≡N-XeF$^+$ cation, the AsF$_6^-$ anion exhibits 14 bands compared to the three Raman-active bands that are expected under O$_h$ symmetry. Because the totally symmetric mode of AsF$_6^-$, $v_1(a_{1g})$, is not split, additional Raman-active bands are largely attributed to site symmetry lowering (15 Raman-active bands are expected for a site symmetry of C$_2v$ or lower), although vibrational coupling in the unit cell may also contribute to the number of observed bands. The modes have been assigned under C$_s$ symmetry by analogy with XeF$^+$AsF$_6^-$ (Table 2) in which the O$_h$ symmetry of the anion is reduced to C$_s$ or lower symmetry by formation of a fluorine bridge to the anion. The vibrational frequencies for AsF$_6^-$ under O$_h$ symmetry have also been listed for comparison.

Lines occurring below 112 cm$^{-1}$ exhibit no measurable shifts upon $^{13}\text{C}$ or $^{15}\text{N}$ substitution and have been assigned to lattice modes.

**Nature of the Bonding in HC≡N-XeF$^+$.** 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 $^{129}\text{Xe}$ spectra can generally be used to assess relative covalent characters of the Xe-O, Xe---F bridge and Xe-F terminal bonds.$^{18,20}$ In general, as the ionic character of the Xe-L (L = ligand atom) bond increases, the covalent character of the terminal Xe-F bond increases, increasing the formal charge on xenon. These trends are paralleled by decreases in $\delta(^{129}\text{Xe})$ and increases in
both $^{1}J(^{129}\text{Xe}-^{19}\text{F})$ and $\delta(^{19}\text{F})$ for the terminal XeF group. Table 3 provides the $\delta(^{129}\text{Xe})$ and $\delta(^{19}\text{F})$ chemical shifts and $^{1}J(^{129}\text{Xe}-^{19}\text{F})$ for a number of xenon(II) compounds containing terminal Xe-F bonds for comparison with HC≡N-XeF$, showing that the Xe-F bond of HC≡N-XeF$ is second only to $\text{R}_\text{C}=\text{N}-\text{XeF}^+$ ($\text{R}_\text{C} = \text{CF}_3, \text{C}_2\text{F}_6, \text{n-C}_3\text{F}_7$, $\text{Xe}_2\text{F}_3^+$ and $\text{XeF}^+$) in covalent character. Excluding fluorine bridging to xenon and the $\text{R}_\text{C}=\text{N}-\text{XeF}^+$ cations,$^{11}$ the Xe-N bond of HC≡N-XeF$^+$ is then among the weakest xenon-ligand bonds observed thus far. The XeF$^+$ character of the XeF group in HC≡N-XeF$^+$ is supported by theoretical calculations of the efgs at the Xe nuclei in XeF$^+$ and HC≡N-XeF$^+$, which are found to differ by only 7%, in agreement with the experimental observation that the quadrupolar splitting in the $^{129}\text{Xe}$ Mössbauer spectra of HC≡N-XeF$^+$ (40.2 ± 0.3 mm s$^{-1}$) is the same, within experimental error, as that obtained for the salt XeF$^+$AsF$_6$ (40.5 ± 0.1 mm s$^{-1}$).$^{41}$

The observation of a well resolved $^{129}\text{Xe}^{-14}\text{N}$ coupling in HF is the combined result of the low viscosity of HF, the axial symmetry and accompanying low efg at the $^{14}\text{N}$ nucleus.$^{44}$ The axial symmetry of the cation results in an asymmetry parameter $\eta = 0$ so that the efg at the $^{14}\text{N}$ nucleus is dominated by $q_{xz}$, the efg component along the $C_\text{m}$ axis of the cation. Consequently, the effect of the efg on quadrupolar relaxation of $^{14}\text{N}$ will only depend on $q_{xz}$ and the molecular correlation time, $\tau_\text{c}$. Coordination of XeF$^+$ to the nitrogen sp lone pair of HC≡N is expected to reduce $q_{xz}$ significantly in the adduct cation, leading to a longer spin lattice relaxation time relative to the free base, further enhancing the possibility of observing $^{1}J(^{129}\text{Xe}^{-14}\text{N})$ in the low viscosity solvent, HF. The principal components of the efg tensor (+z is in the direction $\text{H} \rightarrow \text{N}$) at the nitrogen nuclei in HC≡N and HC≡N-XeF$^+$ have been calculated and the corresponding reduction in efg in going from HC≡N to HC≡N-XeF$^+$ is 48%, in accord with our observation of
$^1J(^{129}\text{Xe},^1\text{N})$ and $^1J(^{14}\text{N},^1\text{C})$ for $\text{HC}≡\text{N-Xe}^+$ in HF solvent. The axial component of the efg tensor at the nitrogen nucleus is also halved upon the formation of $\text{HC}≡\text{N-Kr}^+$. The difference in the magnitudes of the reduced coupling constants $^1K(\text{Xe-N})$ in $\text{HC}≡\text{N-Xe}^+$ (1.389 x $10^{22}$ NA$^2$m$^{-1}$) and $\text{FXeN(SO}_2\text{F)}_2$ (0.949 x $10^{22}$ NA$^2$m$^{-1}$)$^{1,46}$ may be discussed using a previous assessment of the nature of bonding to xenon in solution for $\text{FXeN(SO}_2\text{F)}_2$. The Xe-N bond of $\text{FXeN(SO}_2\text{F)}_2$ is regarded as a σ-bond having sp$^2$ hybrid character. In high-resolution NMR spectroscopy spin-spin coupling involving heavy nuclides is generally dominated by the Fermi contact mechanism.$^6$ For Xe-N spin-spin couplings dominated by the Fermi contact mechanism, one-bond coupling constants can be discussed on the basis of the formalism developed by Pople and Santry.$^4$ In discussions of xenon-nitrogen scalar couplings in xenon(II) imidodisulfurylfluoride compounds,$^46$ the s-electron density at the xenon nucleus was assumed constant and a change in the hybridization at nitrogen accounted for changes in xenon-nitrogen spin-spin coupling. The dependence of xenon-nitrogen spin-spin coupling on nitrogen s-character in the xenon-nitrogen bond may also be invoked to account for the substantially larger $^1K(\text{Xe-N})$ value observed for $\text{HC}≡\text{N-Xe}^+$ than for xenon bonded to the trigonal planar nitrogen in $\text{FXeN(SO}_2\text{F)}_2$. A comparison of $^1K(\text{Xe-N})$ for $\text{HC}≡\text{N-Xe}^+$ with that of the trigonal planar sp$^2$ hybridized nitrogen atom in $\text{FXeN(SO}_2\text{F)}_2$ allows assessment of the relative degrees of hybridization of the nitrogen orbitals used in σ-bonding to xenon. The ratio, $[^1K(\text{Xe-N})]_{sp}/[^1K(\text{Xe-N})]_{sp^2} = 1.46$, for the $\text{HC}≡\text{N-Xe}^+$ cation and $\text{FXeN(SO}_2\text{F)}_2$ is in excellent agreement with the theoretical ratio, 1.50, calculated from the predicted fractional s-characters of the formally sp- and sp$^2$-hybridized nitrogen orbitals used in bonding to xenon in these compounds.

The Xe-N bond of the $\text{HC}≡\text{N-Xe}^+$ cation may be thought of as a classical Lewis acid-
base donor acceptor bond. Implicit in this description of the Xe-N bond is a considerable degree of ionic character, which appears to be a dominant feature of the stability of the HC≡N-XeF⁺ cation. This premise has been supported and further illuminated by theoretical calculations on the HC≡N-NgF⁺ cations.¹⁶,²⁷,³⁰ The ability of NgF⁺ (Ng = Kr, Xe) cations to act as Lewis acids was shown to be related to the presence of holes in the valence shell charge concentrations of the Ng atoms that expose their cores.¹⁶ The mechanism of formation of the Ng-N bonds in the adducts of NgF⁺ with HC≡N is similar to the formation of a hydrogen bond, i.e., the mutual penetration of the outer diffuse nonbonded densities of the Ng and N atoms is facilitated by their dipolar and quadrupolar polarizations, which remove density along their axis of approach, to yield a final density in the interatomic surface that is only slightly greater than the sum of the unperturbed densities. Thus, not surprisingly, the KrF⁺ and XeF⁺ cations are best described as hard acids, which form weak covalent Ng-N adduct bonds as already noted in the context of the present NMR and Raman spectroscopic studies. The energies of formation of these adducts are dominated by the large stabilizations of the Ng atoms that result from the increase in the concentration of charge in their inner quantum shells. The Ng-N bonds that result from the interaction of the closed-shell reactants NgF⁺ and HC≡N actually lie closer to the closed shell limit than do bonds formed in the reaction of NgF⁺ with F. The calculated gas phase energies of the reactions between the closed-shell species are -32.5 and -34.5 kcal mol⁻¹ for Ng = Kr and Xe,¹⁶ respectively, for

\[ \text{NgF}^⁺ + \text{HC≡N} \rightarrow \text{HC≡N-NgF}^⁺ \] (8)
and -209.0 and -211.9 kcal mol\(^{-1}\) for

\[
\text{NgF}^+ + \text{F} \rightarrow \text{F-Ng-F}
\]

(9)

The reaction of the gas phase NgF\(^+\) ions with \text{F} to yield the difluorides results in increases in the calculated Ng-F bond lengths of 0.1 \(\text{Å}\), while their reaction with HC≡\text{N} causes the same bond lengths (calculated) to increase on average by only 0.016 \(\text{Å}\).\textsuperscript{10} The C-N bond of HC≡\text{N} is calculated to shorten by -0.005 \(\text{Å}\) on forming the adduct, while the C-H bond is calculated to lengthen by 0.008 \(\text{Å}\).\textsuperscript{10} These predicted changes in bond length also correlate with the observed shifts in their corresponding stretching frequencies, \(\nu(\text{C≡N})\), increasing by 63 cm\(^{-1}\) and \(\nu(\text{C-H})\) decreasing by 169 cm\(^{-1}\) for HC≡\text{N-XeF}\(^+\).

A simple valence bond description may also be used to satisfactorily account for qualitative trends in bond lengths and associated spectroscopic parameters. The bonding in XeF\(_2\) and HC≡\text{N-XeF}\(^+\) may be represented by valence bond Structures II-VII, where Structures IV and VII are the least important contributing structures. The XeF\(_2\) molecule has a formal bond order of \(\frac{1}{2}\) and the Xe-F bond of HC≡\text{N-XeF}\(^+\) has a formal bond order of \(\frac{1}{2} \leq \text{b.o.} < 1\); b.o. \(= 1\) is approached only in the most weakly coordinated case of FXe\(^+\)--F-Sb\(_2\)F\(_6\).

\[
\text{F-Xe}^+ \text{F} \leftrightarrow \text{F}^+ \text{Xe-F} \leftrightarrow \text{F}^- \text{Xe}^{2+} \text{F}
\]

\hspace{2cm} II III IV

\[
\text{HC≡N-Xe}^{2+} \text{F} \leftrightarrow \text{HC≡N}^+ \text{Xe-F} \leftrightarrow \text{HC≡N} \text{Xe}^{2+} \text{F}
\]

\hspace{2cm} V VI VII
Unlike valence bond Structures II and III of XeF₂, the analogous structures for HC≡N-XeF⁺, namely, Structures V and VI, do not have equal weighting owing to the large build up of formal positive charge on the Xe atom of Structure V, consequently, Structure VI dominates, resulting in an Xe-F bond having considerable covalent (XeF⁺) character and a weak covalent Xe-N bond.

EXPERIMENTAL SECTION

Apparatus and Materials. All manipulations involving air-sensitive materials were carried out under anhydrous conditions on vacuum lines or in a dry box. Bromine pentafluoride and hydrogen fluoride were transferred on vacuum lines constructed largely from 316 stainless steel and nickel. Glass vacuum lines equipped with glass/Teflon grease-free stopcocks (J. Young) were used for the transfer of dry HC≡N and H¹³C≡N.

Air-sensitive substances of low volatility and/or low thermal stability were transferred in a dry box equipped with cryogenic wells. Dry box moisture levels were routinely maintained at <0.1 ppm in a Vacuum Atmospheres Model DLX dry box.

Bromine pentafluoride (Ozark Mahoning Co.) was distilled into a ½" Kel-F tube fitted with a Kel-F valve containing dry KF and purified by maintaining F₂ (2 atm.) above the liquid for 5 to 7 days or until all the Br₂ and BrF₃ had reacted. The solvent was stored at room temperature under 1 atm. of F₂ until used.
Anhydrous hydrogen fluoride (Harshaw Chemical Co.) was purified by treatment with 5 atm. of F₂ gas in a nickel can for a period of at least 1 month, converting residual water to HF and O₂ gas. After the specified time period, anhydrous HF was vacuum distilled into a dry Kel-F storage vessel equipped with a Kel-F valve and stored at room temperature until used.

Hydrogen cyanide, HC≡N and H²¹³C≡N, was prepared by dropwise addition of H₂O to an equimolar mixture of KC≡N (British Drug Houses) or K²¹³C≡N (Merck) and P₂O₅ (British Drug Houses). The HC≡N/H²¹³C≡N gas evolved was condensed into a glass U-tube at -196 °C, and finally vacuum distilled into a glass vessel for drying over P₂O₅. In a typical reaction, 10.00 g, 154 mmol, of KC≡N (1.0098 g, 15.27 mmol, of K²¹³C≡N) was allowed to react to give 4.15 g of HC≡N and 0.428 g of H²¹³CN. The purities of the products were checked by recording the ¹H and ¹³C NMR spectra of the neat liquids.

The salts, XeF²⁺AsF₆⁻, and Xe₂F⁺AsF₆⁻ were prepared as previously described. The salt, HC≡N-XeF²⁺AsF₆⁻, was prepared according to equations (1) and (2). In typical preparations, two equal portions totalling 0.452 mmol of anhydrous HC≡N gas were condensed from a 54.41 mL bulb onto 0.1176 g (0.347 mmol) of XeF²⁺AsF₆⁻ in 1.0 - 1.5 mL of HF solvent in a ¼" o.d. FEP tube outfitted with a Kel-F valve and previously cooled to -196 °C. The ambient pressure of anhydrous HC≡N gas that was condensed was 100 - 200 Torr to minimize dimer formation. After the additions were complete, the mixture was warmed to -20 °C to effect dissolution and complete reaction. The product, HC≡N-XeF²⁺AsF₆⁻, was only sparingly soluble in HF at -30 °C and by increasing the
temperature gradually to -10 °C, the product dissolved. Slow cooling of the solution to -35 °C resulted in colorless needle-shaped crystals. The product was isolated by removal of HF solvent and excess HC≡N under vacuum at -30 °C. In the case of Xe$_2$F$_3^+$AsF$_6^-$, two equal portions of anhydrous HC≡N totaling 1.365 mmol were condensed onto 0.4722 g (0.9285 mmol) of Xe$_2$F$_3^+$AsF$_6^-$ in ca. 1.0 - 1.5 mL of anhydrous HF at -196 °C. The remainder of the procedure was identical to that used in the XeF$_2$AsF$_6$/HC≡N reaction except the product was pumped on for 6 hrs. at 0 °C to remove XeF$_2$.

Nitrogen-15 (99.5%) and carbon-13 enriched (99.2%) HC≡N-XeF$_2$AsF$_6^-$ were prepared according to the equation (1). In typical preparations, anhydrous hydrogen fluoride (1 mL) was condensed at -196 °C onto 0.1124 g (1.700 mmol) of [¹⁵N]KC≡N in a 9 mm FEP tube fitted with a Kel-F valve. The sample was agitated until all the [¹⁵N]KC≡N had dissolved. The resulting [¹⁵N]HC≡N was vacuum distilled, along with the HF solvent, onto 0.4631 g (1.365 mmol) of XeF$_2$AsF$_6^-$ in an ¼" o.d. FEP reaction tube/Kel-F valve assembly, followed by warming to -10 °C. A colorless solution resulted, which was rapidly cooled to -40 °C, whereupon HF and excess [¹⁵N]HC≡N were removed under vacuum. In a typical preparation of [¹³C]HC≡N-XeF$_2$AsF$_6^-$, 0.1498 g (2.266 mmol) of [¹³C]KC≡N and 0.5480 g (1.630 mmol) of XeF$_2$AsF$_6^-$ were used. The procedure was then the same as for the preparation of [¹⁵N]HC≡N[XeF$_2$AsF$_6^-$].

After HF removal, Raman spectra were obtained by running the spectra directly on the ¼" FEP reaction tube under 2 atm. (ambient temperature) of dry N$_2$ gas. The [¹⁵N]- and [¹³C]-enriched samples were subsequently divided and transferred into 4 mm, 9 mm (FEP) and/or 5 mm glass sample tubes for NMR spectroscopy. During transfers, samples were maintained at low temperature by placing the sample tubes inside drilled copper blocks previously cooled to -196
"C in a cryogenic well inside the dry box. Natural abundance samples for NMR spectroscopy were prepared by condensing a 30 - 35% molar excess of HCN onto the appropriate amount of XeF₄AsF₆ or Xe₂F₆AsF₆ in HF contained in the FEP NMR sample tube. In cases where the exact stoichiometry was desired, the sample was isolated as described above and redissolved in the appropriate solvent. All samples were dissolved at low temperature in either HF (-20 to -10 °C) or BrF₅ (-60 to -50 °C) and heat sealed off from their Kel-F valves and stored at -196 °C until their NMR spectra could be recorded.

**Nuclear Magnetic Resonance Spectroscopy**

All NMR spectra were recorded unlocked (field drift < 0.1 Hz h⁻¹) with the use of Bruker AC-200 (4.6975 T) and WM-250 (5.8719 T) spectrometers.

Spectra were recorded on natural abundance, 99.2% ¹³C and 99.5% ¹⁵N enriched samples in heat sealed 9 mm o.d. or 4 mm o.d. FEP NMR tubes (HF and BrF₅ solvents) or in 5 mm precision Pyrex tubes (BrF₅ solvent; Wilmad Glass Co.) as described below. The FEP sample tubes were placed inside precision 10 mm o.d. or 5 mm o.d. glass NMR tubes before being placed in the probe.

The ¹²⁹Xe, ¹⁴N, ¹⁵N, and ¹³C spectra were recorded at 5.8719 T in 9 mm FEP sample tubes (HF and BrF₅ solvent) on the same 10 mm probe (broad-banded over the frequency range 23 - 103 MHz) tuned to 69.563 (¹²⁹Xe), 18.075 (¹⁴N), 25.347 (¹⁵N) or 62.915 (¹³C) MHz, respectively. Fluorine-19 spectra (23.5361 MHz) were obtained on a 5 mm dual ¹H/¹⁹F probe. Proton spectra (200.133 MHz) were recorded at 4.6975 T in HF solvent in 4 mm FEP sample tubes and in BrF₅ solvent in medium or thin wall 5 mm o.d. precision glass sample tubes.
Xenon-129 NMR spectra of natural abundance HC≡N-XeF'AsF₆⁻ samples were recorded for spectral widths of 25 and 100 kHz with acquisition times of 0.164 and 0.082 s (17,000 and 150,000 scans), respectively, and a data point resolution of 6.10 Hz/pt. The ¹²⁹Xe NMR spectra of ¹³C- and ¹⁵N-enriched samples were recorded for spectral widths of 50 and 25 kHz (50,000 and 1200 - 2500 scans), respectively, with acquisition times of 0.328 and 0.655 s and data point resolutions of 3.05 and 1.53 Hz/pt., respectively. Fluorine-19 NMR spectra were recorded for spectral widths of 50 and 100 kHz with acquisition times of 0.082 and 0.164 s and data point resolutions of 3.05 and 6.10 Hz/pt. (4500 and 7500 scans), respectively. Nitrogen-15 and -14 NMR spectra were recorded for spectral widths of 25 and 10 kHz with acquisition times of 0.655 and 0.410 s and data point resolutions of 1.53 and 2.44 Hz/pt. (1400 and 26,000 scans), respectively. Carbon-13 NMR spectra were recorded for a spectral width of 15 kHz with an acquisition time of 0.541 s and data point resolution of 1.85 Hz/pt. (3000 scans). Proton spectra were recorded for spectral widths of 800 Hz and 3 kHz with acquisition times of 5.12 and 2.80 s and data point resolutions of 0.098 and 0.357 Hz/pt. (64 and 172 scans), respectively.

Pulse widths corresponding to bulk magnetization tip angles of −90° were 22 (¹²⁹Xe), 2 (¹⁹F), 49 (¹⁴N), 35 (¹⁵N), 7 (¹³C) and 0.5 μs (¹H). No relaxation delays were applied except in the case of ¹⁵N, where a relaxation delay of 10 s was applied. Line broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data point resolutions. All line shape functions were Lorentzian with the exception of the ¹H spectra and the ¹²⁹Xe NMR spectrum of [¹³C]HC≡N-XeF'AsF₆⁻, in these cases Gaussian line shapes were applied for resolution enhancement.

The respective nuclei were referenced externally to neat samples of XeOF₄ (¹²⁹Xe), CFCl₃,
(19F), CH₃NO₂ (¹⁴N and ¹⁵N) and (CH₃)₂Si (¹⁴C and ¹H) at 24 °C. Positive chemical shifts were assigned to resonances occurring to high frequency of the reference substance.⁴⁸

For variable temperature measurements, samples were kept cold (-196 or -78 °C) until immediately prior to their placement in the 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.

**Raman Spectroscopy.** A Coherent Model Innova 90 argon ion laser giving up to 3.5 W of power at 5145 Å was used to excite the Raman spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with 1800 grooves/mm holographic gratings. Slit widths depended on the scattering efficiency of the sample, laser power, etc., and were set at 100 - 150 μm. An RCA C31034 phototube detector in conjunction with a pulse count system consisting of pulse amplifier, analyzer and rate meter (Hamner NA-11, NC-11, and N-780 A, respectively) and a Texas Instruments Model FSOZWBA strip-chart recorder were used to record the spectra. The scanning rates used were 0.2 and 0.5 cm⁻¹ s⁻¹. The typical power range used was between 0.7 and 1 W. The spectrometer was periodically calibrated by recording the discharge lines from an argon lamp over the spectral range of interest; all the Raman shifts quoted are estimated to be accurate to at least ±2 cm⁻¹ while the precision of each Raman shift measurement is estimated to be ±0.2 cm⁻¹.
Cylindrical ¼" FEP sample tubes were mounted vertically. The angle between the incident laser beam and sample tube was 45°, and Raman scattered radiation was observed at 45° to the laser beam (90° to the sample tube axis). Low-temperature spectra were recorded at -196 °C by mounting the sample vertically in an unsilvered Pyrex glass dewar filled with liquid nitrogen. All spectra were obtained directly in ¼" FEP reaction vessels. The spectrum of the FEP sample tube was nearly always observed, however, their prominence in the overall spectrum depended on the efficiency of the sample as a Raman scatterer, and could be minimized by focusing the laser beam on the sample surface. Lines arising from FEP have been subtracted out of the spectra reported in the Tables but not in the Figures.

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FIGURE CAPTIONS

Figure 1. $^{129}$Xe NMR spectra (69.563 MHz) of HC≡N-XeF$^\ast$AsF$_6$ recorded in HF solvent at -10 °C (a) 99.2% $^{13}$C enriched sample. (b) 99.5% $^{15}$N enriched sample; expansion (A) with proton coupling and expansion (B) [$^1$H]-decoupled.

Figure 2. $^{19}$F NMR spectrum (235.361 MHz) of 99.5% $^{15}$N-enriched HC≡N-XeF$^\ast$AsF$_6$ recorded in BrF$_3$ solvent at -50 °C. Asterisks (*) denote $^{129}$Xe satellites.

Figure 3. $^{15}$N NMR spectrum (25.347 MHz) of HC≡N-XeF$^\ast$AsF$_6$ for a 99.5% $^{15}$N-enriched sample recorded in BrF$_3$ solvent at -50 °C. Asterisks (*) denote $^{129}$Xe satellites.

Figure 4. $^1$H NMR spectrum (200.133 MHz) of 99.5% $^{15}$N-enriched HC≡N-XeF$^\ast$AsF$_6$ recorded in BrF$_3$ solvent at -50 °C. Asterisks (*) denote $^{129}$Xe satellites.

Figure 5. $^{1}$C NMR spectrum (62.915 MHz) of HC≡N-XeF$^\ast$AsF$_6$ for a 99.2% $^{13}$C-enriched sample recorded in HF solvent at -10 °C. Asterisks (*) denote $^{129}$Xe satellites.

Figure 6. Raman spectrum of natural abundance HC≡N-XeF$^\ast$AsF$_6$ recorded at -196 °C. Asterisks (*) denote FEP sample tube lines.
Figure 7. Raman spectra of natural abundance, 99.2% $^{13}$C-enriched and 99.5% $^{15}$N-enriched HC≡N-XeF$_2$AsF$_5^-$, recorded at -196 °C; (a) 3200 - 2100 cm$^{-1}$ region and (b) 400 - 100 cm$^{-1}$ region. Asterisks (*) denote FEP sample tube lines.
Table 1. NMR Chemical Shifts and Spin-Spin Coupling Constants for the HCN=NXeF⁻ Cation

<table>
<thead>
<tr>
<th>Chemical Shifts</th>
<th>Coupling Constants, Hz</th>
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</thead>
<tbody>
<tr>
<td>$\delta(^{127}\text{Xe})$</td>
<td>-1552 (-1570)</td>
</tr>
<tr>
<td>$\delta(^{19}\text{F})^b$</td>
<td>-198.7 (-193.1)</td>
</tr>
<tr>
<td>$\delta(^{14}\text{N})$</td>
<td>-235.1</td>
</tr>
<tr>
<td>$\delta(^{1}\text{H})$</td>
<td>104.1</td>
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<tr>
<td>$\delta(^{1}\text{C})$</td>
<td>4.70 (6.01)$^b$</td>
</tr>
</tbody>
</table>

$^b$ Mean deviation from the weighted mean.

$^a$ Mean deviation from the weighted mean.
a Samples were referenced externally at 24 °C with respect to the neat liquid references; $\text{XeOF}_4$ ($^{129}\text{Xe}$), $\text{CFCl}_3$ ($^{19}\text{F}$), $\text{CH}_3\text{NO}_2$ ($^{14}\text{N}$ and $^{15}\text{N}$), (CH$_3$)$_3\text{Si}$ ($^{13}\text{C}$ and $^1\text{H}$). A positive chemical shift denotes a resonance occurring to high frequency of the reference compound. The values in parentheses have been measured in BrF$_5$ solvent.

b All $^{19}\text{F}$ spectra displayed a broad saddle-shaped feature at ca. -68 ppm. arising from the partially quadrupole collapsed $^1J(^{75}\text{As}^\sim-^{19}\text{F})$ of the octahedral AsF$_6$ anion.

c Obtained from a 99.5%/ $^{15}\text{N}$ enriched sample of HC≡N-XeF$^\ast$AsF$_6$.

d The sample was prepared and run at -50 °C in BrF$_5$ solvent by redissolving a solid sample of 99.5% $^{15}\text{N}$-enriched HC≡N-XeF$^\ast$AsF$_6$, that had been prepared in HF solvent.

e Obtained from a 99.2% $^{13}\text{C}$ enriched sample of HC≡N-XeF$^\ast$AsF$_6$.

f The sample was prepared and run at -50 °C in BrF$_5$ solvent by redissolving a solid sample of natural abundance HC≡N-XeF$^\ast$AsF$_6$, that had been prepared in HF solvent.
Table 2. Raman Frequencies and Assignments for HCN=\text{XeF}_4\text{AsF}_6, [^{15}\text{N}]\text{HCN}=\text{XeF}_4\text{AsF}_6, and [^{13}\text{C}]\text{HCN}=\text{XeF}_4\text{AsF}_6, and Related Compounds

<table>
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<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>HCN</th>
<th>XeF$^+$AsF$_6$</th>
<th>[^{15}\text{N}]\text{HCN}=\text{XeF}_4\text{AsF}_6</th>
<th>[^{13}\text{C}]\text{HCN}=\text{XeF}_4\text{AsF}_6</th>
<th>$\Delta \nu (^{15}\text{N})$</th>
<th>$\Delta \nu (^{13}\text{C})$</th>
<th>$\lambda (^{15}\text{N})$</th>
<th>$\lambda (^{13}\text{C})$</th>
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<td>3139.3(3)</td>
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<tr>
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<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
<th>O₆ (AsF₆⁻)</th>
<th>C₄ (AsF₆⁻)</th>
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<td>700</td>
<td>v₉(AsF)</td>
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<td>693(1)</td>
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<td>v₆(AsF)</td>
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<td>v₄(AsF)</td>
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<td>665(3)</td>
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<td>573</td>
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<td>577(5)</td>
<td>v₂(AsF)</td>
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<td>552(3)</td>
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<td>465(3)</td>
<td>v₃(AsF)</td>
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<td>421(11)</td>
<td>v₄(AsF)</td>
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<td>406(1)</td>
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<td>v₉(AsF)</td>
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<td>244(1)</td>
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<td>73(9)</td>
<td>v₁₀(AsF)</td>
<td>A&quot;</td>
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<td>71(1), 66(6), 62(8), 54(5), 44(2), 43(3)</td>
<td>Lattice modes</td>
<td></td>
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</table>
Raman spectra of all of the HC≡N-XeF₄AsF₆ salts were recorded with FEP sample tubes at -196 °C using 514.5 nm excitation. Lines due to FEP have been deleted from the spectra. Values in parentheses denote intensities; sh denotes a shoulder. Data given are for the spectra depicted in Figures 6 and 7.

Reference (22).

Recorded at -196 °C; this work.

Δν(¹⁵N) = ν(¹⁵N) - ν(¹⁴N); Δν(¹²¹C) = ν(¹²¹C) - ν(¹²C).

The estimated precision of each value is ±0.4 cm⁻¹.

Δλ(¹⁵N) = λ(¹⁵N) - λ(¹⁴N); Δλ(¹²¹C) = λ(¹²¹C) - λ(¹²C) : where λ = 4π²c²ν².

c is the velocity of light and ν the observed frequency (in cm⁻¹).

Reference (23).
# Table 3. Comparison of Xe-F Stretching Frequencies, Chemical Shifts and Coupling Constants in F-Xe-L Derivatives

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond Lengths (Å)</th>
<th>ν(Xe-F) (cm⁻¹)</th>
<th>NMR Parameters&lt;sup&gt;c&lt;/sup&gt;</th>
<th>T. °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>J&lt;sup&gt;129&lt;/sup&gt;Xe-1&lt;sup&gt;19&lt;/sup&gt;F&lt;sup&gt;a&lt;/sup&gt;</td>
<td>δ&lt;sup&gt;129&lt;/sup&gt;Xe&lt;sup&gt;c&lt;/sup&gt;</td>
<td>δ&lt;sup&gt;19&lt;/sup&gt;F&lt;sup&gt;ab&lt;/sup&gt;</td>
</tr>
<tr>
<td>XeF&lt;sub&gt;2&lt;/sub&gt;...FSbF&lt;sub&gt;10&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.82(3)/2.34(3)</td>
<td>619</td>
<td>7230</td>
<td>-574</td>
<td>-290.2</td>
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<tr>
<td>XeF&lt;sub&gt;2&lt;/sub&gt;...FAsF&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.873(6)/2.212(5)</td>
<td>610</td>
<td>6892</td>
<td>-869</td>
<td>-252.0</td>
</tr>
<tr>
<td>(FXe)&lt;sub&gt;2&lt;/sub&gt;F&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.90(3)/2.14(3)</td>
<td>593</td>
<td>6740</td>
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</tr>
<tr>
<td>CF,&lt;sub&gt;2&lt;/sub&gt;C=N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>564</td>
<td>6181</td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;F,&lt;sub&gt;2&lt;/sub&gt;C=N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>560</td>
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<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;2&lt;/sub&gt;C=N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>548</td>
<td>5932</td>
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<tr>
<td>HC=NC=N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5909</td>
<td>5926</td>
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<td>CH,C=N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>528</td>
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<tr>
<td>s-C&lt;sub&gt;2&lt;/sub&gt;F,N,N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>524</td>
<td>5963</td>
<td>-1853</td>
<td>-144.6</td>
<td>-50</td>
</tr>
<tr>
<td>FO&lt;sub&gt;3&lt;/sub&gt;S=O-XeF</td>
<td>1.940(8)/2.155(8)</td>
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<td>5903/</td>
<td>-1824/</td>
<td>-161.7</td>
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<td>cis/trans-</td>
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<td>FO&lt;sub&gt;3&lt;/sub&gt;O-XeF</td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;F&lt;sub&gt;3&lt;/sub&gt;N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>528</td>
<td>5926</td>
<td>-1922</td>
<td>-139.6</td>
<td>-30</td>
</tr>
<tr>
<td>4-CF&lt;sub&gt;2&lt;/sub&gt;C,F,N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>524</td>
<td>5963</td>
<td>-1853</td>
<td>-144.6</td>
<td>-50</td>
</tr>
<tr>
<td>F&lt;sub&gt;2&lt;/sub&gt;TeO-XeF&lt;sup&gt;b&lt;/sup&gt;</td>
<td>520</td>
<td>5963</td>
<td>-1853</td>
<td>-144.6</td>
<td>-50</td>
</tr>
<tr>
<td>(FO&lt;sub&gt;3&lt;/sub&gt;S)N-XeF&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.967(3)/2.200(3)</td>
<td>500</td>
<td>5586</td>
<td>-1977</td>
<td>-126.1</td>
</tr>
<tr>
<td>XeF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>496</td>
<td>5621</td>
<td>-1685</td>
<td>-184.3</td>
<td>-52</td>
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</table>

<sup>a</sup>Ref. 12
<sup>b</sup>Ref. 13
<sup>c</sup>Ref. 14
<sup>d</sup>Ref. 15
<sup>e</sup>Ref. 16
<sup>f</sup>Ref. 17
<sup>g</sup>Ref. 18
<sup>h</sup>Ref. 19
Unless otherwise indicated, all cations have AsF₆⁻ as the counterion.

Bond lengths obtained from theoretical calculations are indicated in parentheses.

Spectra were obtained in BrF₅ solvent unless otherwise indicated.

The NMR parameters of XeF group, in particular δ(¹²⁷Xe), are very sensitive to solvent and temperature conditions; it is therefore important to make comparisons in the same solvent medium at the same or nearly the same temperature.

Referenced with respect to the neat liquids XeOF₄ (¹²⁷Xe) and CFCl₃ (¹⁹F) at 24 °C; a positive sign denotes the chemical shift of the resonance in question occurs to higher frequency of (is more deshielded than) the resonance of the reference substance.

Table entries refer to the terminal fluorine on the xenon atom.

Recorded in SbF₅ solvent.

δ¹⁹F) measured in anhydrous HF solvent at -10 °C.

NMR parameters measured in HF solvent.

δ¹⁹F) measured in SO₂ClF solvent at -40 °C.

NMR parameters measured in SO₂ClF solvent.

NMR parameters measured in SO₂ClF solvent at -50 °C.
REFERENCES


11. \( E(A(XeF^+)) = IP(Xe) + BE(XeF) - BE(XeF^+) = 12.1 + 0.86 - 2.1 = 10.9 \) eV.


25. This work.
34. Schrobilgen, G.J., unpublished work.


40. Sanders, J.C.P.; Schrobilgen, G.J. unpublished work.


43. Schrobilgen, G.J.; Valsdóttir, N., unpublished work.


The Fluoro(perfluoropyridine)xenon(ii) Cations, \( \text{C}_5\text{F}_5\text{N}^-\text{XeF}^+ \) and \( \text{4-CF}_3\text{C}_5\text{F}_4\text{N}^-\text{XeF}^+ \); Novel Examples of Xenon as an Aromatic Substituent and of Xenon–Nitrogen Bonding

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Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M7, Canada

The fluoro(perfluoropyridine)xenon(ii) cations, \( \text{4-RC}_5\text{F}_4\text{N}^-\text{XeF}^+ \) \((\text{R} = \text{F} \text{or} \text{CF}_3) \), have been observed in HF and BrF\(_5\) solutions (stable up to \(-30^\circ\text{C}\)) and their AsF\(_6^-\) salts have been isolated from BrF\(_5\) solutions; low temperature Raman and \( ^{129}\text{Xe}, ^{19}\text{F}, \text{and} ^{14}\text{N} \) n.m.r. spectroscopic results are consistent with planar cations in which the xenon atom is co-ordinated to the aromatic ring through the lone pair of electrons on the nitrogen.

Compounds containing xenon–nitrogen bonds have only been characterized relatively recently and include the neutral species \( \text{FXeN(SO}_2\text{F})_n \) \((\text{n} = 1, 2) \), \( \text{Xe}[\text{N(SO}_2\text{F})_2]_n \) \((\text{n} = 2, 3) \), and \( \text{Xe}[\text{N(SO}_2\text{CF}_3)_2]_n \) \((\text{n} = 2, 4) \); and the cations \( \text{XeN(SO}_2\text{F})_2^+ \), \( \text{F}[\text{XeN(SO}_2\text{F})_2]^+ \), \( \text{XeN(SO}_2\text{F})_2]_n^+ \), \( \text{XeN(SO}_2\text{CF}_3)_2]_n^+ \) \((\text{n} = 2, 3) \) and the recently reported series of nitrile cations \( \text{R'}\text{C}^-\text{N}^-\text{XeF}^+ \) \((\text{R'} = \text{H}, \text{CH}_3, \text{CH}_2\text{F}, \text{C}_3\text{H}_5, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7) \). In this communication we report the synthesis and characterization of two novel xenon–nitrogen bonded cations which, thus far, represent unique examples of noble gas atoms functioning as aromatic ring substituents.

Equimolar amounts of \( \text{XeF}^+\text{AsF}_6^- \) and the perfluoropyridine 4-\( \text{RC}_5\text{F}_4\text{N} (\text{R} = \text{F} \text{or} \text{CF}_3) \) react in anhydrous HF at \(-30^\circ\text{C}\) to generate the cations \( \text{R'}\text{C}^-\text{N}^-\text{XeF}^+ \) \((\text{R'} = \text{H}, \text{CH}_3, \text{CH}_2\text{F}, \text{C}_3\text{H}_5, \text{C}_2\text{F}_5, \text{C}_3\text{F}_7) \).
Table 1. N.m.r. parameters for the 4-RC₃F₇-N-XeF⁺ (R = F or CF₃) cations.

<table>
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<tr>
<th>Chemical shifts/ p p.m.</th>
<th>Coupling constants/Hz</th>
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</thead>
<tbody>
<tr>
<td>δ(1⁴Xe)</td>
<td>δ(1₄N)</td>
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<tr>
<td>C₅F₇-N-XeF⁺ (HF, -30°C)</td>
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<tr>
<td>C₅F₇-N-XeF⁺ (BrF₃, -30°C)</td>
<td>-1922.5</td>
</tr>
<tr>
<td>4-CF₃C₇F₇-N-XeF⁺ (HF, -30°C)</td>
<td>-1902.6</td>
</tr>
<tr>
<td>4-CF₃C₇F₇-N-XeF⁺ (BrF₃, -50°C)</td>
<td>-1853.4</td>
</tr>
</tbody>
</table>

* Spectra recorded without an external lock (field drift < 1 Hz h⁻¹) at an external field strength B₀ = 5.8719 T using 9 mm o.d. FEP sample tubes. The corresponding spectrometer frequencies were 89.63 MHz (1F-Xe), 18.073 MHz (1⁴N), and 235.361 MHz (1₁F). * Spectra were referenced with respect to neat liquid external standards at 24°C. XeOF₃ (1F-Xe), CHNO₃ (1⁴N), and CF₃Cl (1₁F). A positive chemical shift denotes a resonance occurring to high frequency of the reference compound. * For equilibrium reaction mixtures of XeF₂ and 4-RC₃F₇-NH⁺·AsF₆⁻, the following ¹⁹F environments were also observed: (i) R = F, -30°C, HF solvent: HF (196.0 p.p.m.), XeF₂ [-200 p.p.m., w₁₁ = 435 Hz, J(1⁻¹⁹Xe-¹⁹F) 5600 Hz], AsF₆⁻ [-64.9 p.p.m., broad saddle-shaped resonance arising from partial quadrupole collapse of J(¹⁴As-¹⁹F)], and 4-CF₃C₇F₇-NH⁺·AsF₆⁻ [F(1) -100.2 p.p.m., F(3) -158.6 p.p.m., F(4) -108.0 p.p.m.]; (ii) R = F, -30°C, BrF₃ solvent: HF (-194.4 p.p.m., w₂ = 240 Hz), BrF₃ (quartet, 273.7 p.p.m., doublet, 135.5 p.p.m.; J(F-F) 76.5 Hz), XeF₂ [δ (¹⁻F) -187.4 p.p.m., δ(¹⁴Xe) -162.9 Hz, AsF₆⁻ (-64.0 p.p.m., w₁₁ = 1780 Hz), CF₃NH⁺·F(2) -196.8 p.p.m., F(3) -154.5 p.p.m., F(4) -103.2 p.p.m.]; (iii) R = CF₃, -20°C, HF solvent: HF (-196.6 p.p.m.), AsF₆⁻ [-68.9 p.p.m., broad saddle-shaped resonance arising from partial quadrupole collapse of J(¹⁴As-¹⁹F)], 4-CF₃C₇F₇-NH⁺·AsF₆⁻ [F(1) -198.5 p.p.m., F(3) -136.1 p.p.m., CF₃ -61.7 p.p.m.]; (iv) R = CF₃, -50°C, BrF₃ solvent: HF (-193.1 p.p.m., w₂ = 150 Hz), BrF₃ (quartet, 273.2 p.p.m., doublet, 135.8 p.p.m.; J(F-F) 76.4 Hz], XeF₂ [δ(¹⁹F) -188.2 p.p.m., o(¹⁴Xe) -1585.4 p.p.m.; J(¹⁴Xe-¹⁹F) 5645 Hz], AsF₆⁻ (-63.7 p.p.m., w₁₁ = 980 Hz), 4-CF₃C₇F₇-NH⁺·F(2) -196.2 p.p.m., F(3) -131.8 p.p.m., CF₃ -59.5 p.p.m. |

Although observed, intra-ring F-F couplings are not reported. * The spin-spin coupling J(¹⁴Xe-¹¹N) is quadrupole collapsed in BrF₃ solvent at -30 and -50°C.

\[ \text{NF} \cdot \text{AsF}_{6}^{-} \text{ and } 4-\text{RC}_3\text{F}_7\text{N}-\text{XeF}^+ \cdot \text{AsF}_{6}^{-} \text{ (determined by n.m.r. spectroscopy) (Table 1). Removal of HF solvent by pumping at -50°C resulted in white solids which Raman spectroscopy at -196°C also showed to be mixtures of 4-RC₃F₇-N-XeF⁺·AsF₆⁻, XeCF₃, and 4-RC₃F₇-NH⁺·AsF₆⁻.} \]

An alternative approach which lead to isolation of the Xe-N bonded cations allowed stoichiometric amounts of XeF₂ and the perfluoropyridinium cations, as their AsF₆⁻ salts, to react in HF and BrF₃ solvents at -30°C according to equilibrium (3). The equilibria in both solvents were again monitored by ¹⁹Xe, ¹⁴F, and ¹¹N n.m.r. spectroscopy. In BrF₃, formation of 4-RC₃F₇-N-XeF⁺·AsF₆⁻ was more strongly favoured than in HF solvent; the equilibrium ratio [4-RC₃F₇NXeF⁺]/[4-RC₃F₇N⁺HF⁻] being 0.25 and 2.1 in HF and BrF₃ solvents, respectively, at -30°C for R = F and 3.7 for R = CF₃ in BrF₃ at -50°C [Kₑ = 4.5 at -30°C and Kₑ = 13.6 at -50°C in BrF₃, for equilibrium (3)]. Consequently, removal of BrF₃ solvent under vacuum at -30°C yielded white solids corresponding to 4-RC₃F₇-N-XeF⁺·AsF₆⁻ salts.

The Raman and n.m.r. spectroscopic findings confirm the formulations of the compounds isolated from BrF₃ solution as AsF₆⁻ salts possessing cation structures in which a xenon atom is co-ordinated to the aromatic perfluoropyridine ring (6), thus providing the first examples of compounds in which the...
noble gas atoms serve as aromatic substituents. In addition to lines arising from the AsF3 anions \( v_1(a_{1g}) 677, 680 \text{ cm}^{-1}; v_2(e_g) 577 \text{ cm}^{-1}; v_3(t_{2g}) 375 \text{ cm}^{-1} \), several key frequencies have been assigned. The Xe-N stretching frequencies can only be tentatively assigned to weak bands at 367(2) (R = F) and 367(12) (R = CF3) cm\(^{-1}\) [cf. 422 cm\(^{-1}\) in FXeN(SO2F)2] while the F-Xe-N bands are assigned to moderately strong bands at 158(13) (R = F) and 162(13) (R = CF3) cm\(^{-1}\). The intense bands in the Raman spectra of the salts occur at 524(100) cm\(^{-1}\) (R = F) and 524(100) cm\(^{-1}\) (R = CF3) and are assigned to Xe-F stretching frequencies. These frequencies are higher than that of FXeN(SO2F)2 (506 cm\(^{-1}\)) and lower than in the recently reported nitrile cations, R'CeN-XeF+ (564 and 565 cm\(^{-1}\) for \( R' = H \) and Me, respectively), reflecting the intermediate base strengths of 4-RCxF3N: with respect to the Lewis acid XeF+.

The latter point is corroborated by comparison of the 129Xe and 19F chemical shifts of the Xe-F groups within a well-established trend in which \( \delta(19F) \) increases in frequency with increasing covalency of the Xe-ligand bond, while \( \delta(129Xe) \) is observed to decrease. The nuclear spin-spin couplings \( J(129Xe-19F) \) (doublet), \( J(129Xe-14N) \) (partial quadrupole collapsed 1:1 triplet), \( J(F1-F2) \) (1:2:1 triplet) also support the proposed cation structures in solution (Figure 1). Owing to the higher viscosity of BrF3, \( J(129Xe-14N) \) is quadrupole collapsed at -50 and -30°C but is observed at HF at -15 and -30°C. The magnitude of \( J(129Xe-14N) \) is consistent with a one-bond \( ^{129}Xe-14N \) coupling. On the assumption that the Fermi contact contribution to the \( ^{129}Xe-14N \) spin-spin coupling is dominant, a comparison of the reduced coupling constants, \( K(Xe-N)_{BrF3} = 0.983 \times 10^{-2} \) and \( K(Xe-N)_{HF} = 0.991 \times 10^{-2} \text{ N A}^{-2} \text{ m}^{-1} \), with those in which the nitrogen atom \( \alpha \)-bonded to xenon is sp hybridized (R'CeN-XeF+ 1.297-1.393 \times 10^{-2} \text{ N A}^{-2} \text{ m}^{-1})^6 and sp\(^2\) hybridized [FXe-N(SO2F)2 0.913 \times 10^{-2}]^7 is also consistent with bonding between the sp\(^2\) hybridized nitrogens of the perfluoropyridines and xenon.

Other pyridine derivatives and nitrogen bases are currently being investigated as potential electron-pair donors towards noble gas cations. X-ray crystallographic studies of the fluoro(perfluoropyridine)xenon(II) cations are also underway in this laboratory.

This research was sponsored by the United States Air Force Astronautics Laboratory, Edwards Air Force Base, California (Contract F49620-87-C-0049) and by a Natural Sciences and Engineering Research Council of Canada (NSERC) operating grant.

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References

SECTION I. Trifluoro-s-triazine Adducts of XeF³ AND XeOTeF₅⁺; Novel Xe-N Bonding

INTRODUCTION

General Criteria Required for Ligands to Bond to Xenon

Numerous attempted preparations and successful syntheses of Xe-O compounds have provided sufficient data for the formulation of several general guidelines for selecting a ligand that may be suitable for bonding to xenon. Ligands exhibiting the following criteria generally satisfy the condition that the ligand must be capable of withstanding the high electron affinity of xenon in its positive formal oxidation states:

1. the ligand should form a moderate to strong monoprotic acid,

2. each ligand has a high effective group electronegativity,

3. each ligand exists as a stable anion in alkali metal salts,

4. each group forms a positive chlorine derivative.

For example, FXeOTeF₅ and Xe(OOTeF₅)₂ and the precursor acid, HOTeF₅, and its alkali metal salts M⁺OTeF₅ and the chlorine derivative ClOTeF₅ are known.

Xenon Nitrogen Chemistry

It was not until 1974, that the first xenon-nitrogen compound was prepared.¹ The general approach was to use a ligand satisfying the criteria listed above. To this end, a nitrogen ligand made highly
Electronegative by substitution with electron withdrawing SO₂F groups was selected. The reaction was shown to proceed according to equation (1).

\[
{\text{CF}_3\text{Cl}_2} \\
\text{XeF}_2 + \text{HN(SO}_2\text{F})_2 \rightarrow \text{F-Xe-N(SO}_2\text{F})_2 + \text{HF} \quad (1)
\]

\[0^\circ\text{C, 4 days}\]

Owing to the instability of the product, the imidodisulfuryl derivative was not fully characterized until 1982 when definitive evidence for Xe-N bonding was obtained in the form of the low-temperature crystal structure" (Figure 1). Several other compounds containing Xe-N-(SO₂X)₂ (X = F, CF₃) were also prepared (Table 1), however, the aforementioned method was limited by the number of suitable electron withdrawing groups which could be attached to nitrogen to provide a sufficiently electronegative nitrogen ligand.

**Lewis Acid Behavior of XeF⁺ and KrF⁺**

In 1987, the discovery that XeF⁺ had Lewis acid properties, and, as such, "would undergo reactions with nitrogen bases to form adducts," significantly broadened the scope of xenon-nitrogen chemistry, and noble-gas chemistry in general (Annual Report, May 1, 1987 - April 30, 1988 and references therein). In these acid-base reactions, XeF⁺ functions as an electron-pair acceptor towards the lone pair on the nitrogen base of specific ligands, provided the ligand can withstand oxidation by XeF⁺. The electron affinity of XeF⁺ is
Figure 1. Crystal structure of F-Xe-N(SO₂F)₂.
Table 1.
Xe-N Derivatives of the N(SO₂X)₂ Group (X = F, CF₃)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FXeN(SO₂F)₂</td>
<td>2</td>
</tr>
<tr>
<td>[XeN(SO₂F)₂]⁺AsF₆⁻</td>
<td>3</td>
</tr>
<tr>
<td>[XeN(SO₂F)₂]⁺SbF₆⁻</td>
<td>3</td>
</tr>
<tr>
<td>F[XeN(SO₂F)₂]₂⁺AsF₆⁻</td>
<td>3, 4</td>
</tr>
<tr>
<td>Xe[N(SO₂F)₂]₂</td>
<td>5</td>
</tr>
<tr>
<td>Xe[N(SO₂CF₃)₂]₂</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2.
Ionization Potentials of Some Nitrogen Containing Ligands

<table>
<thead>
<tr>
<th>Compound</th>
<th>Potential (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃C≡N</td>
<td>13.90</td>
<td>9</td>
</tr>
<tr>
<td>HCN</td>
<td>13.59</td>
<td>10</td>
</tr>
<tr>
<td>CH₂F=C≡N</td>
<td>13.00 ± 0.1</td>
<td>11</td>
</tr>
<tr>
<td>CF₃CEN</td>
<td>12.60</td>
<td>9</td>
</tr>
<tr>
<td>CHF₂C≡N</td>
<td>12.40</td>
<td>12</td>
</tr>
<tr>
<td>CH₃C≡N</td>
<td>12.19 ± 0.005</td>
<td>13</td>
</tr>
<tr>
<td>s-C₅F₅N₃</td>
<td>11.50</td>
<td>14</td>
</tr>
<tr>
<td>CH₃NEC</td>
<td>11.32</td>
<td>15</td>
</tr>
<tr>
<td>C₅F₅N</td>
<td>10.08</td>
<td>16</td>
</tr>
</tbody>
</table>
estimated to be 10.9 eV,8 accordingly ligands are required to have first ionization potentials exceeding 11 eV if they are to be capable of forming stable adducts. Examination of the known first adiabatic ionization potentials of several nitrogen containing ligands provides insight into which ligands are likely to be suitable candidates for adduct formation (Table 2).

The method of adduct preparation is generally straightforward and involves the interaction of stoichiometric amounts of XeF\(^+\)AsF\(_6^-\) and a suitable organic nitrogen base in anhydrous HF solvent or the interaction of a stoichiometric amount of a protonated base salt with XeF\(_2\) in HF or BrF\(_5\) solvents. Brief warming to -30 to -20°C is generally sufficient to effect reaction and dissolution in the solvent without significant decomposition. Vacuum pumping at -50 to -30°C, resulted in the isolation of white solids, many of which are not stable above -10°C. Using this approach a large number of new xenon-nitrogen compounds were recently prepared, including adducts with perfluoroalkyl-nitrile cations7 (Figure 2) and perfluoropyridine cations17 (Figure 3). Solid samples of a large number of these compounds have been characterized by low-temperature laser Raman spectroscopy and solutions of the adducts in HF and/or BrF\(_5\) have been examined by \(^{19}\)F, \(^{129}\)Xe, and \(^{14}\)N NMR spectroscopy.

Another cationic noble-gas species which was believed to exhibit Lewis acid properties was KrF\(^+\) which has an estimated electron affinity of 13.2 eV.32 Consequently, it was desirable to test the hypothesis by allowing KrF\(^+\) to react with a suitable oxidatively resistant ligand using the synthetic methods outlined above. Unfortunately, KrF\(^+\) proved to be more difficult to work with owing to the fact that its salts are unstable near room temperature. In
\[
\left[ \text{H-C} = \text{N} - \text{Xe} - \text{F} \right]^+ \text{AsF}_6^-
\]

\[
\left[ \text{R-C} = \text{N} - \text{Xe} - \text{F} \right]^+ \text{AsF}_6^-
\]

Figure 2. Hydrogen cyanide, alkylnitrile and perfluoroalkynitrile adducts of XeF\(^+\)AsF\(_6^-\).

[Diagram]

\( R_F = \text{CF}_3, \text{F} \)

Figure 3. Perfluoropyridine adducts of XeF\(^+\)AsF\(_6^-\).
addition, KrF\(^{+}\) undergoes autocatalytic redox reactions in HF solvent. In view of these properties, the interaction of neutral KrF\(_2\) with HCNH\(^{--}\)AsF\(_6\)\(^{-}\) (1st IP of HCN, 13.59 eV) in BrF\(_5\) was attempted. The reaction proceeded according to equation (2) resulting in the formation of HCN\(-\)KrF\(^{+}\)AsF\(_6\)\(^{-}\), the first species containing a krypton-nitrogen bond.\(^{18}\)

\[
\text{KrF}_2 + \text{HCN} + \text{AsF}_6^{-} \rightarrow \text{HCN-Kr-F}^{+}\text{AsF}_6^{-} + \text{HF} \quad (2)
\]

The Trifluoro-s-Triazine Adduct of XeF\(^{+}\)

The first ionization potential of trifluoro-s-triazine, s-C\(_3\)F\(_3\)N\(_3\), (11.50 eV) indicated that it should resist oxidation by XeF\(^{+}\) and form a stable Xe-N adduct (Table 2). The synthesis of the trifluoro-s-triazine adduct of XeF\(^{+}\) was consequently attempted using HF as the solvent at -10\(^\circ\)C. The presence of fluorinated ring byproducts from this reaction demonstrated that trifluoro-s-triazine is subject to solvolysis in HF, and attempts to prepare the compound in other solvents also proved unsuccessful. Accordingly, the direct reaction of solid XeF\(^{+}\)AsF\(_6\)\(^{-}\) with liquid trifluoro-s-triazine in absence of solvent was attempted. The synthesis of s-C\(_3\)F\(_3\)N\(_2\)N-XeF\(^{+}\) has recently been reported,\(^{19}\) (see Section II) and is formed in the reaction of s-C\(_3\)F\(_3\)N\(_3\) with XeF\(^{+}\)AsF\(_6\)\(^{-}\) according to equation (3)

\[
\text{F} - \text{N} - \text{N} - \text{F} + \text{XeF}^{+}\text{AsF}_6^{-} \rightarrow \text{F} - \text{N} - \text{N} - \text{XeF}^{+}\text{AsF}_6^{-} \quad (3)
\]
The compound was characterized by low-temperature laser Raman spectroscopy, $^{19}$F and $^{129}$Xe NMR spectroscopy.

Unlike other Xe-N compounds, the trifluoro-s-triazine adduct exhibited remarkable stability at room temperature. In addition, the solid XeF$^+$ appeared to react with a second mole of trifluoro-s-triazine during the reaction, a feature unique to this system and the subject of a portion of the present report.

Purpose and Scope of Present Work

In the present work we have undertaken to prepare noble-gas compounds containing novel Xe-N bonds. In general electronegative nitrogen organic bases with first ionization potentials greater than the electron affinity of XeF$^+$ (10.9 eV) \(^{19}\) have proved to be suitable ligands for adduct formation. Trifluoro-s-triazine fulfills this criterion and exhibits resistance to oxidation. Moreover, the XeF$^+$ adduct of s-C$_3$F$_3$N$_3$ has demonstrated remarkable stability at room temperature. For these reasons s-C$_3$F$_3$N$_3$ was selected as the ligand to test the possibility of forming new Xe-N compounds from other suspected xenon Lewis acids, namely XeF$_5^+$ and XeOTeF$_5^+$.

In addition, the potential binding of a second mole of trifluoro-s-triazine to the xenon Lewis acid, XeF$^+$, was examined using low-temperature laser Raman spectroscopy.
EXPERIMENTAL

Apparatus and Materials

The majority of compounds prepared and used in this work are air and moisture sensitive, accordingly manipulations were carried out under anhydrous conditions. Non-volatile air-sensitive solids, XeF\(^+\)AsF\(_5\)\(^-\), XeOTeF\(_5\)\(^+\)AsF\(_5\)\(^-\), XeF\(_3\)\(^+\)SbF\(_5\)\(^-\), Xe(OTeF\(_5\))\(_2\), Sb(OTeF\(_5\))\(_3\), XeOTeF\(_5\)\(^+\)Sb(OTeF\(_5\))\(_6\)\(^-\) were weighed and transferred to reaction vessels in a dry box (Vacuum Atmospheres Model DLX; <0.01 ppm H\(_2\)O and <0.1 ppm O\(_2\)). Volatile reactants and solvents were transferred using glass or metal vacuum lines.

Preparation and Purification of Starting Materials

Solvents. All solvents were transferred on a metal vacuum line through all fluoroplastic connections. The former was constructed of 316 stainless steel, nickel, Teflon and Kel-F.

Sulfurylchlorofluoride, SO\(_2\)ClF (Columbia Organic Chemicals), was purified by distillation onto F\(_2\)S to remove SO\(_2\) contaminate, as previously described\(^2\). Subsequently the solvent was distilled (from SbF\(_5\)), into a glass storage bulb, equipped with a Rota-Flo valve, containing dry KF to remove residual SbF\(_5\) and HF. The purified solvent was used directly from this vessel.

Bromine pentafluoride, BrF\(_5\), (Ozark Mahoning) was purified as described earlier\(^2\) and stored over dry KF in a 3/4" Kel-F storage vessel equipped with a Kel-F valve.

Anhydrous hydrogen fluoride, HF, (Harshaw Chemical Co.) was
purified by treatment with 5 atmospheres of F₂ gas in a nickel can for a period of 1 month, converting residual water to HF and O₂ gas. After the specified time period, the excess F₂ gas was removed under vacuum at -196°C. The anhydrous HF was subsequently warmed to room temperature and vacuum distilled into a dry Kel-F storage vessel equipped with a Kel-F valve and stored at room temperature until used.

**Trifluoro-s-Triazine.** Trifluoro-s-triazine, s-C₃F₃N₃ (Armageddon Chemicals, Durham, N.C.) was treated prior to use, by transferring it to a glass bulb containing anhydrous CaH₂ powder (British Drug Houses) in a fume hood. Trifluoro-s-triazine was transferred on a glass vacuum line equipped with J. Young 6mm glass/FEP valves (Figure 4) using a glass vacuum distillation apparatus equipped with J. Young 4mm glass/FEP valves (Figure 5). To avoid contamination of samples with CaH₂, trifluoro-s-triazine was always transferred to an intermediate preweighed evacuated glass bulb prior use in syntheses.

**Xenon Cations Salts, Xe(OTeF₅)₂ and Sb(OTeF₅)₃.** Preparations of Xe⁺AsF₆⁻,²² XeF₃⁺SbF₆⁻,²³ XeOTeF⁺AsF₆⁻,²⁴ Xe(OTeF₅)₂²⁵ and Sb(OTeF₅)₃²⁶ are described elsewhere.
Figure 5. Glass grease-free vacuum line; (A) manometer, (B) dry nitrogen inlet, (C) liquid nitrogen trap.
Preparation of Xe-N Compounds

$s\text{-}C_3F_3N_2N\text{-}XeF^+\text{AsF}_6^-$. In a typical preparation 0.850 g (6.294 mmol) of $s\text{-}C_3F_3N_3$ was transferred to an evacuated glass bulb using a glass vacuum distillation apparatus (Figure 6a) attached to a glass vacuum line. $XeF^+\text{AsF}_6^-$, (0.281 g, 1.852 mmol), was weighed into a 1/4" o.d FEP reaction vessel equipped with a Kel-F valve in a dry box. Trifluoro-s-triazine was vacuum distilled onto the solid at -196°C (Figure 6b). The sample was allowed to warm to room temperature and left to react for 2 hrs. with periodic agitation to effect even distribution of the liquid throughout the solid. Reaction was generally apparent within 20 min. of mixing at room temperature, resulting in the formation of a fine white solid suspended in excess trifluoro-s-triazine. Upon completion of the reaction, the sample was pumped under vacuum at room temperature for 40 min. to remove excess $s\text{-}C_3F_3N_3$. The yield was 0.8489 g (96.7%) and the product was stable indefinitely at room temperature. A Raman sample was prepared according to the methods described later in this section, as were solutions of the product in HF and BrF₅ for examination by $^{19}F$ NMR and $^{129}Xe$ NMR spectroscopy.

Preparation of the Higher Adducts $x\text{-}s\text{-}C_3F_3N_3\text{-}XeF^+\text{AsF}_6^-$ ($x > 1$). In typical preparations of the title compounds, the weight of $s\text{-}C_3F_3N_3$ required for the desired stoichiometry was vacuum distilled into an evacuated glass bulb. The required amount of $XeF^+\text{AsF}_6^-$ was
Figure 6a. Vacuum distillation apparatus for purification of \( s-C_2F_3N_3 \).
Figure 6b. Glass vacuum distillation apparatus for the preparation of trifluoro-s-triazine adducts of XeF and XeOTeF$_5^+$. 

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ubsequently weighed into a 1/4" o.d. FEP tube in a dry box. Tri-
fluoro-s-triazine was distilled onto the solid and the reaction was
allowed to proceed for 2 hrs. The amounts of XeF\(^{+}\)AsF\(_6\)\(^{-}\) and s-C\(_3\)F\(_3\)N\(_3\) used in each reaction as well as the appearance of the mixture after 2 hrs. are listed in Table 3.

Upon completion of the reaction, the reaction tube was heat sealed
under vacuum at -196°C and subsequently examined by low-temperature Raman spectroscopy.

Preparation of s-C\(_3\)F\(_3\)N\(_2\)N-XeOTeF\(_5\)\(^+\)AsF\(_6\)\(^-\). The title compound was prepared from XeOTeF\(_5\)\(^+\)AsF\(_6\)\(^-\) according to equation (4).

\[
\text{XeOTeF}_5^{+}\text{AsF}_6^{-} + \text{s-C}_3\text{F}_3\text{N}_3 \rightarrow \text{s-C}_3\text{F}_3\text{N}_2\text{N-XeOTeF}_5^{+}\text{AsF}_6^{-} \quad (4)
\]

Solid XeOTeF\(_5\)\(^+\)AsF\(_6\)\(^-\) (0.3379 g, 0.6047 mmol) was weighed into a 1/4" FEP o.d. tube in a dry box and excess s-C\(_3\)F\(_3\)N\(_3\) (0.5686 g, 4.212 mmol) was distilled into an evacuated glass bulb on a glass vacuum line. Trifluoro-s-triazine was distilled onto solid XeOTeF\(_5\)\(^+\)AsF\(_6\)\(^-\) and the mixture was warmed to -10°C. A color change from yellow to off-white was immediate and the reaction was allowed to proceed for an additional 10 min. at -10°C and 5 min. at 0°C. The mixture was subsequently pumped under vacuum at room temperature for 20 min. to remove excess s-C\(_3\)F\(_3\)N\(_3\). The product was an extremely fine white solid which was stable at room temperature. The yield was 98.7% based on a 1:1 combining for XeOTeF\(_5\)\(^+\)AsF\(_6\) and s-C\(_3\)F\(_3\)N\(_3\). Solid samples for Raman
Table 3. Preparation of the adducts, $x \text{s-C}_2\text{F}_3\text{N}_3 : \text{XeF}^+\text{AsF}_6^-$; amounts of reagents and appearance of products.

<table>
<thead>
<tr>
<th>$x$</th>
<th>s-C$_2$F$_3$N$_3$</th>
<th>XeF$^+$AsF$_6^-$</th>
<th>Appearance of Products</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g)</td>
<td>(mmol)</td>
<td>(g)</td>
</tr>
<tr>
<td>1.243</td>
<td>0.2834</td>
<td>2.097</td>
<td>0.5724</td>
</tr>
<tr>
<td>1.497</td>
<td>0.3374</td>
<td>2.498</td>
<td>0.5649</td>
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<tr>
<td>2.317</td>
<td>0.4460</td>
<td>3.303</td>
<td>0.4833</td>
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<tr>
<td>3.007</td>
<td>0.3669</td>
<td>2.717</td>
<td>0.3052</td>
</tr>
<tr>
<td>4.951</td>
<td>0.6662</td>
<td>4.933</td>
<td>0.3880</td>
</tr>
</tbody>
</table>
spectroscopy, and $^{19}$F NMR and $^{129}$Xe NMR samples in BrF₅ solvent were prepared as described later in this section.

Preparation of XeOTeF₅−Sb(OTeF₅)₆−. The title compound was prepared by the following series of reactions:

$$\text{SbF}_3 + \text{B(OTeF}_5\text{)}_3 \rightarrow \text{Sb(OTeF}_5\text{)}_3 + \text{BF}_3 \quad (5)$$

$$3\text{XeF}_2 + 2\text{B(OTeF}_5\text{)}_3 \rightarrow 3\text{Xe(OTeF}_5\text{)}_2 + 2\text{BF}_3 \quad (6)$$

$$2\text{Xe(OTeF}_5\text{)}_2 + \text{Sb(OTeF}_5\text{)}_3 \rightarrow \text{Xe(OTeF}_5\text{)}_2 (\text{SbOTeF}_5)_6^- + \text{Xe} \quad (7)$$

Xe(OTeF₅)₂ (3.408 g, 5.601 mmol) and Sb(OTeF₅)₃ (2.315 g, 2.763 mmol) were weighed in a dry box, then combined in a 1/2" o.d. FEP tube equipped with a Kel-F valve and maintained at -196°C. The tube was transferred to a metal vacuum line where SO₂ClF was distilled onto the cold solids. The mixture was slowly warmed from -40°C to -10°C. However, the reaction was slow, consequently the temperature was raised to 0°C resulting in the generation of a bright orange solution and steady evolution of xenon gas. The evolved xenon gas was bled off periodically, and the reaction deemed to be complete when xenon evolution had ceased. Upon completion of the reaction, the mixture was pumped under vacuum at 0°C until a pale orange powder was obtained, then further pumped at room temperature for an additional hr. The yield of the product was 96.3%. A solid Raman sample, and solutions of the product dissolved in SO₂ClF for examination by $^{19}$F NMR, were prepared by methods described later in this section.
Preparation of \(\text{s-C}_3\text{F}_3\text{N}_3\text{-N-XeOTeF}_5\text{Sb(OTeF}_3\text{)}\text{)}\). The title compound was prepared from \(\text{XeOTeF}_3\text{Sb(OTeF}_3\text{)}\text{)}\) in a manner analogous to the synthesis of \(\text{s-C}_3\text{F}_3\text{N}_3\text{N-XeOTeF}_5\text{Sb(OTeF}_3\text{)}\text{)}\). \(\text{XeOTeF}_3\text{Sb(OTeF}_3\text{)}\text{)}\) (0.5197 g, 0.2702 mmol) and excess \(\text{s-C}_3\text{F}_3\text{N}_3\) were combined in a 1/4" o.d. FEP tube equipped with a Kel-F valve and warmed to \(-20^\circ\text{C}\) at which point an immediate color change from orange/yellow to off-white occurred. The reaction was allowed to proceed for 5 min. and was then pumped under vacuum at 0°C for 20 min. to remove excess trifluoro-s-triazine. The product was an extremely fine off-white grey solid, yield 98.6%. The solid Raman sample as well as a sample dissolved in \(\text{SO}_2\text{ClF}\) for \(\text{^19F NMR spectroscopy}\) were subsequently prepared from this material.

Reaction of \(\text{XeF}_3\text{SbF}_5\) with Trifluoro-s-Triazine. In a typical reaction solid \(\text{XeF}_3\text{SbF}_5\), (0.3183 g, 0.7490 mmol) was transferred to a 1/4" o.d. FEP reaction vessel equipped with a 316 stainless steel metal valve (Figure 7) and attached to a glass vacuum distillation apparatus by means of Air Drome AN fittings. It was necessary to use a metal valve and fittings as solid \(\text{XeF}_3\text{SbF}_5\) is a potent oxidant which is known to attack and rupture Kel-F. Excess trifluoro-s-triazine (0.5276 g, 3.907 mmol) was vacuum distilled onto solid \(\text{XeF}_3\text{SbF}_5\) using a glass vacuum line,
Figure 7. Metal valve assembly used for reactions involving XeF$_3$+SbF$_5$. 

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and the samples were warmed to -30°C at which point a color change from yellow to white occurred within 5 min. The sample was warmed further to 0°C, and allowed to react for a further 30 min. Upon completion of the reaction, the samples were pumped at 0°C for 20 min. to remove excess s-C₃F₇N₃. The product was stable at room temperature. Samples for ²⁹F NMR, ¹²⁹Xe NMR and Raman spectroscopy were prepared according to the methods described later in this section.

**Nuclear Magnetic Resonance Spectroscopy**

Several different containers were used for NMR samples depending on the nucleus under investigation and the solvent used:

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Solvent</th>
<th>Sample Tube Materials and Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>³²⁶Sb</td>
<td>SO₂ClF</td>
<td>9 mm o.d. FEP tube for insertion into Wilmad thin wall 10 mm o.d. precision glass tube</td>
</tr>
<tr>
<td>¹²⁹Xe</td>
<td>BrF₅</td>
<td>9 mm o.d. FEP tube for insertion into Wilmad thin wall 10 mm o.d. precision glass tube</td>
</tr>
<tr>
<td></td>
<td>SO₂ClF</td>
<td></td>
</tr>
<tr>
<td>¹⁹F</td>
<td>HF</td>
<td>4 mm o.d. FEP tube for insertion into Wilmad thin wall 5 mm o.d. precision glass tube</td>
</tr>
<tr>
<td>¹⁹F</td>
<td>BrF₅</td>
<td>Wilmad precision 5 mm o.d. medium wall glass tube</td>
</tr>
<tr>
<td></td>
<td>SO₂ClF</td>
<td></td>
</tr>
</tbody>
</table>

Solid samples were transferred to NMR tubes in a dry box and sufficient solvent was distilled onto the solid to effect dissolution. The tubes were subsequently heat sealed under vacuum between -195°C, and stored
in liquid nitrogen. All spectra were recorded on a Bruker WM-250 pulse spectrometer at an external applied field strength of 5.8719 Telsa. The observed frequencies for $^{19}$F, $^{129}$Xe and $^{121}$Sb were 235.36, 69.50 and 59.86 MHz, respectively. NMR spectra were referenced externally at 24°C using the following reference substances: CFCl₃ (neat $^{19}$F), XeOF₄ (neat, $^{129}$Xe), Et₄N*SbF₆⁻ (0.1 M in CH₃CN). Free induction decays were accumulated in a 16K or 32K memory with spectral width settings between 10 and 25 KHz yielding data point resolutions of 1.6 to 6.0 Hz. The number of scans obtained varied with each sample, with $^{19}$F spectra generally requiring 500-2000 scans, and $^{121}$Sb and $^{129}$Xe spectra requiring between 1000 and 10000 scans for sufficient signal to noise.

Laser Raman Spectroscopy

Excluding reaction mixtures $x$-C₃F₃NₓC3F3N₃ : XeF⁺ where $x > 1$, all Raman spectra were obtained from solid samples in sealed precision medium wall glass NMR tubes (Wilmad 5 mm o.d.) A Coherent Nova 90-5 argon ion laser, providing up to 5 W at 514.5 nm was used as the excitation source in conjunction with a Spex Industries Model 14018 double monochromator equipped with 1800-grooves/mm holographic grating. The spectra were accumulated using a RCA C 31034 phototube detector combined with a pulse count system (Hamner NA11) consisting of a pulse amplifier analyzer (Hamner NC-11), and a rate meter (Hamner N-708 A). Spectra were recorded using a Texas Instruments Model FSOZWBA strip chart recorder. The spectrometer was periodically calibrated by recording the discharge lines from an argon lamp over the spectral range of interest, and the Raman shifts quoted are estimated to be
accurate to ±1 cm⁻¹. Slit widths were set to 150, 200, 200, 150 μm and all spectra were recorded at a chart speed of 0.5 cm⁻²/s with gains between 10K and 100K, and time constants between 0.25 and 1.0 s. The approximate power of the beam at the sample ranged from 0.60 to 0.93 w.

Sample tubes were mounted vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen such that the angle between the incident beam and the sample was 45° (Figure 8). In cases where immersion in liquid nitrogen was insufficient to prevent decomposition at the site of excitation the sample was rotated to effect increased cooling.
Figure 8. Sample holder for recording laser Raman spectra at -196 °C.
RESULTS AND DISCUSSION

INVESTIGATION OF \((\text{C}_3\text{F}_3\text{N}_2\text{N})_2\text{-XeF}^-\text{AsF}_6^-\)

As noted in the introduction, the reaction of trifluoro-s-triazine with \(\text{XeF}^+\) resulted in solid white products, even when a significant excess of liquid \(\text{s-C}_3\text{F}_3\text{N}_3\) was employed. It was speculated that at least two moles of \(\text{s-C}_3\text{F}_3\text{N}_3\) may be coordinated to \(\text{Xe(II)}\). To investigate this possibility further, a series of \(\text{s-C}_3\text{F}_3\text{N}_3: \text{XeF}^-\text{AsF}_6^-\) reaction mixtures was prepared. Since removal of excess \(\text{s-C}_3\text{F}_3\text{N}_3\) from the products by pumping under vacuum at room temperature invariably resulted in the formation of the thermally stable 1:1 adduct, \(\text{s-C}_3\text{F}_3\text{N}_3\text{-XeF}^-\text{AsF}_6^-\), the reaction mixtures were heat sealed under vacuum in FEP tubes at \(-196\,^\circ\text{C}\), and subsequently examined by low-temperature Raman spectroscopy.

Raman Spectra

A comparison of the Raman spectra for the reaction mixtures (Table 4) with the spectrum for \(\text{s-C}_3\text{F}_3\text{N}_2\text{N}-\text{XeF}^-\text{AsF}_6^-\) (Section II) indicated that there was a definite change in the most intense band, characteristic of the \(\text{Xe-F}\) stretch from 544 in \(\text{s-C}_3\text{F}_3\text{N}_2\text{N}-\text{XeF}^-\text{AsF}_6^-\) to 560 cm\(^{-1}\) upon addition of excess \(\text{s-C}_3\text{F}_3\text{N}_3\) (Figure 9). This high-frequency shift of the \(\text{Xe-F}\) stretch is indicative of strengthening in the \(\text{Xe-F}\) bond, resulting from increased \(\text{Xe-F}\) character in the resonance structure of the adduct

\[
\text{F-Xe-L} \rightleftharpoons \text{F-Xe}^+ \text{L}^-
\]
Table 4. Some key Raman frequencies $\text{XeF}^+\text{AsF}_6^-$ and $\text{s-C}_3\text{F}_3\text{N}_2\text{N-XeF}^+\text{AsF}_6^-$ \(\cdot\) s-C\(_3\)F\(_3\)N\(_3\)

<table>
<thead>
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<th>Frequency, cm(^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1504(10)</td>
<td>(a_1), sym breathing</td>
</tr>
<tr>
<td>648(20)</td>
<td>(a_1), ring breathing, all atoms in phase</td>
</tr>
<tr>
<td>553(53)</td>
<td>(a_1), Xe-F</td>
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<tr>
<td>544(100)</td>
<td>(a_1), Xe-F</td>
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<tr>
<td>156(23)</td>
<td>(b_1, b_2, \delta(C-N-Xe))</td>
</tr>
<tr>
<td>110(15)</td>
<td>(b_1, b_2, \delta(N-Xe-F))</td>
</tr>
</tbody>
</table>

* Peak positions invariant for $\text{s-C}_3\text{F}_3\text{N}_2\text{N-XeF}^+\text{AsF}_6^-$ \(\cdot\) s-C\(_3\)F\(_3\)N\(_3\) adducts, but the intensity varied.
RAMAN SPECTRA OF $3\cdot\text{C}_3\text{F}_3\text{N}_3$ + XeF$^+$ AsF$_6^-$ SYSTEM

Figure 9. Raman Xe-F stretch of $\sigma$-CsF$_2$Na$_2$N-XeF$^+$ and $\sigma$-CsF$_2$Na$_2$N-XeF$^+$, x-s-
Other vibrational frequencies associated with the \(s\text{-}C_3F_3N_2NXeF^+\) cation were also found to be shifted.

In general, the spectra obtained for the different \(x:1\) ratios were very similar, the major difference being relative peak intensities, with little apparent change in peak positions. Unfortunately, the peak intensities were shown to vary while scanning the spectra, preventing a rigorous analysis of the effect of increasing the ratio of trifluoro-s-triazine \(XeF^+\). The variation of peak intensities is thought to arise from dissociation of the more weakly bonded excess \(s\text{-}C_3F_3N_3\) adducts in the laser beam. No such intensity variation was observed in the spectrum of the \(1:1\) adduct \(s\text{-}C_3F_3N_2N\text{-}XeF^+\text{AsF}_6^-\).

One prominent spectral feature which deserves special mention is the fact that even as \(x\) approached 1, the most intense peak, corresponding to the Xe-F, stretch occurred at 560 cm\(^{-1}\), and was invariant. However, below the \(1:1\) ratio, only one Xe-F stretch at 544 cm\(^{-1}\) was present, corresponding to that of \(XeF^+\text{AsF}_6^-\). These results are significant in that they indicate a product with a different Xe-F bond was formed even when little excess trifluoro-s-triazine was present. Consequently, the formation of a simple \((C_3F_3N_2N)_2\text{-}XeF^+\) monomer is unlikely, since it does not account for the change in bonding at \(x:1\) ratios less than 2. To explain these results it is necessary to postulate the formation of a polymer in which each XeF\(^+\) is bonded to two trifluoro-s-triazine rings and which immediately converts, under vacuum, to the monomeric \(1:1\) adduct \(s\text{-}C_3F_3N_2N\text{-}XeF^+\text{AsF}_6^-\) upon removal of excess trifluoro-s-triazine. One possible structure
for such a polymer is suggested below [Structure (I)]. Branching in the polymer is unlikely because it could only occur where XeF$^+$ was bonded to three s-C$_3$F$_3$N$_3$ molecules, consequently one can only account for the higher adducts by postulating the formation of cyclic s-C$_3$F$_3$N$_2$NXeF$^+$AsF$_6^-$-x s-C$_3$F$_3$N$_3$ polymers.

If polymeric s-C$_3$F$_3$N$_2$NXeF$^+$AsF$_6^-$-x s-C$_3$F$_3$N$_3$ structures do exist, they might be expected to have the novel AX$_3$E$_3$ VSEPR arrangement of lone pairs and bond pairs about the central xenon atom. Two representations of this geometry are given by Structures (II) and (III). Of the two possibilities, Structure (II) is more likely because it minimizes the lone pair - lone pair repulsions relative to the only other alternative, the facial isomer represented by Structure (III). In either case, the binding of the second mole of trifluoro-s-triazine to Xe should result in a lowering of the electric field gradient at the xenon nucleus sufficient to significantly decrease the quadrupole splitting in the $^{129}$Xe Mössbauer spectrum. Presently, $^{129}$Xe Mössbauer studies are pending; it is expected that they may provide further
insight into the local environment of xenon in the \( s\text{-C}_3\text{F}_3\text{N}_2\text{N}\text{-XeF}^+\text{AsF}_6^- \) \(-x\) \( s\text{-C}_3\text{F}_3\text{N}_3\) systems.

\[ \text{F} \]
\[ \begin{array}{c}
\text{Xe} \\
\text{N}
\end{array} \]

II

\[ \text{F} \]
\[ \begin{array}{c}
\text{Xe} \\
\text{N}
\end{array} \]

III

**REACTION OF XeF\(_3^+\)SbF\(_6^-\) WITH TRIFLUORO-\(s\)-TRIAZINE**

In light of the resistance to oxidation exhibited by the trifluoro-\(s\)-triazine ligand, the direct reaction of the ligand with a salt of the Xe(IV) cation, XeF\(_3^-\), was attempted. The salt, XeF\(_3^+\)SbF\(_6^-\), was selected in the hope that it, like XeF\(_3^+\)AsF\(_6^-\), would exhibit Lewis acid characteristics, providing a means of preparing the first example of Xe(IV) bonded to nitrogen. The XeF\(_3^+\) cation is, however, a more potent oxidant than XeF\(^+\) and could possibly oxidize the base upon adduct formation.

\[ ^{19}\text{F} \text{ and } ^{129}\text{Xe NMR Spectroscopy} \]

The \(^{19}\text{F} \) and \(^{129}\text{Xe} \) chemical shifts and coupling constants of
the products in BrF₅ (Table 5) gave no evidence for the formation of the desired compound, s-C₃F₅N₂N-XeF⁺SbF₆⁻. In fact, the ¹²⁹Xe spectrum shows no peaks in the Xe(IV) region (-663 to +595 ppm), and a doublet in the Xe(II) region with a chemical shift similar to that of s-C₃F₅N₂N-XeF⁺AsF₆⁻ (Figure 10). Furthermore, the chemical shifts and splittings in the F-on-C region of the ¹⁹F spectrum (one triplet (1F), one doublet of doublets (2F), Figures 11 and 12), and the F-on-Xe region (triplet with ¹²⁹Xe satellites, Figure 13) correspond to those obtained for s-C₃F₅N₂N-XeF⁻ (Figures 14 and 15), indicating Xe(IV) has undergone a two electron reduction to Xe(II) to form of s-C₃F₅N₂N-XeF⁺SbF₆⁻ (Table 5). It should be noted that the ¹²⁹Xe is an NMR-active nucleus having 26.44% natural abundance. Consequently, 26.44% of the fluorines bonded to Xe couple with ¹²⁹Xe to produce satellites which, owing to shielding anisotropy, do not exhibit the fine structure of the central multiplet (Figures 13 and 15).

The oxidized product of two trifluoro-s-triazine molecules coupled through nitrogen [Structure (IV)] accounts for the remaining multiplets in the ¹⁹F spectrum (Table 5), and the reaction was determined to proceed according to equation (8).

\[
XeF_3^+ + SbF_6^- + 3 s-C_3F_5N_3 \xrightleftharpoons{20^\circ C} \quad s-C_3F_5N_2N-XeF^+SbF_6^- + F \quad \text{[Structure (IV)]}
\]
Figure 10. $^{129}$Xe spectrum (69.563 MHz) of $s$-$C_3F_3N_2N$-$XeF^+$AsF$_6^-$ in (a) BrF$_5$ at -50°C illustrating quadrupole collapse of the $^{129}$Xe-$^{14}$N coupling and a doublet arising from $^1J[^{129}$Xe-$^{14}$N], and (b) HF at -5°C showing $^1J[^{129}$Xe-$^{19}$F] and the partially quadrupole collapsed 1:1:1 multiplet arising from $^1J[^{129}$Xe-$^{14}$N] coupling.
Figure 11. $^{19}$F NMR spectrum (235.361 MHz) of $s$-$C_3F_8N_2N$-XeF$^+$AsF$_6^-$ in BrF$_5$ at -36°C, F-on-C region.
Figure 12: $^{19}$F NMR spectrum (235.361 MHz) of $s$-$C_3F_3N_2N$-$XeF^+$AsF$_6^-$ in BrF$_6$ at -36°C, F-on-Xe region. Asterisks (*) denote $^{129}$Xe satellites.
Table 5. NMR parameters for \( s-C_3F_3N_2N-XeF^+AsF_6^- \) and products resulting from the reaction of \( XeF_3^+SbF_6^- \) with trifluoro-\( s \)-triazine. *

<table>
<thead>
<tr>
<th>Sample</th>
<th>Species</th>
<th>( \delta^{19}F ) ppm</th>
<th>( \delta^{129}Xe ) ppm</th>
<th>Coupling Cons. Hz</th>
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<tbody>
<tr>
<td>( s-C_3F_3N_2N-Xe^+AsF_6^- )</td>
<td>( s-C_3F_3N_2N-Xe^+ )</td>
<td>( F(1), -145.6 )</td>
<td>( -1862 )</td>
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<td></td>
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<td>( [D, 1F] )</td>
<td>( [D] )</td>
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<td></td>
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<td>( F(2), -26.2 )</td>
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<td>( ^4J[F(2)-F(3)], 13.3 )</td>
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<td></td>
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<td>( [T, 2F] )</td>
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<tr>
<td></td>
<td></td>
<td>( F(3), -8.7 )</td>
<td></td>
<td>( ^2J[^{19}F-^{129}Xe], 5932 )</td>
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<tr>
<td></td>
<td></td>
<td>( [T, 1F] )</td>
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<td></td>
</tr>
<tr>
<td>( s-C_3F_3N_3 ) + ( s-C_3F_3N_2N-XeF_3^+SbF_6^- )</td>
<td>( s-C_3F_3N_3-XeF_3^+ )</td>
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<td>( -1858 )</td>
<td>( ^4J[F(1)-F(2)], 11.6 )</td>
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<td>( [D, 1F] )</td>
<td>( [D] )</td>
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<td>( F(2), -25.4 )</td>
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<td>( ^4J[F(2)-F(3)], 14.6 )</td>
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<td>( [d.d., 2F] )</td>
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<td>( ^2J[^{19}F-^{129}Xe], 5917 )</td>
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<td>( [T, 1F] )</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( (C_3F_4N_2N^-)^2 )</td>
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<tr>
<td></td>
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<td>( F(1'), -36.9 )</td>
<td></td>
<td>( ^4J[F(1')-F(2')], 17.4 )</td>
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<td>( F(2'), -19.6 )</td>
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<td>( ^4J[F(1')-F(3')], 16.4 )</td>
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<td></td>
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<td>( F(3'), +5.7 )</td>
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<td></td>
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<td>( [d.o.t., 2F] )</td>
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</table>

* Recorded in BrF$_5$ solvent at -50°C.
Figure 13. $^{19}$F NMR spectrum (235.361 MHz) of products resulting from the reaction of XeF$_3$·SbF$_6$ with trifluoro-s-triazine in BrF$_5$ at -50°C, F-on-C region.
Figure 14. $^{19}F$ NMR spectrum (235.361 MHz) of products resulting from the reaction of XeF$_3$-SbF$_6^-$ with trifluoro-s-triazine in BrF$_3$ at $-50^\circ$C. F-on-C region expansion.
Figure 15. $^{19}$F NMR spectrum (235.361 MHz) of products resulting from the reaction of XeF$_3$+SbF$_6^-$ with trifluoro-s-triazine in BrF$_3$ at -50°C, F-on-Xe region. Asterisks (*) denote $^{129}$Xe satellites.
Energy calculations performed on the coupled ring product using the computer program MODEL indicate the minimum energy conformation is one with two fused boat forms of the coupled six-membered rings depicted by Structure (IV). This geometry accounts for the presence of three multiplets in the $^{19}F$ NMR spectrum arising from three non-equivalent fluorines and their accompanying spin-spin couplings (Figures 11 and, Figure 12).

[Diagram of Structure (IV)]

**Compounds Containing Novel N-Xe-O Linkages**

In addition to XeF$^+$, XeOTeF$_5^+$ has been known for some time and is expected to exhibit Lewis acid properties. The salt, XeOTeF$_5$-AsF$_6^-$, can be prepared in good yield according to the following series of reactions:

\[ \text{XeF}_2 + \text{B(OTeF}_5)\_3 \rightarrow \text{Xe(OTeF}_5)\_2 + \text{BF}_3 \] (9)

\[ \text{Xe(OTeF}_5)\_2 + \text{XeF}_2 \rightarrow 2\text{FXeOTeF}_5 \] (10)

\[ 2\text{FXeOTeF}_5 + \text{AsF}_6 \rightarrow \text{XeOTeF}_5^+\text{AsF}_6^- \] (11)
Because the XeOTeF$_5^+$ cation readily undergoes solvolysis in HF and BrF$_5$, the only solvents suitable for the preparation of the previous series of Xe-N adducts, its potential use as a Lewis acid has never been investigated.$^{24}$ Fortunately, the direct interaction of XeOTeF$^+$AsF$_6^-$ with trifluoro-s-triazine requires no solvent, and XeOTeF$_5^+$AsF$_6^-$ has been used to prepare s-C$_3$F$_3$N$_2$N-XeOTeF$_5^+$AsF$_6^-$, the first compound with an N-Xe-O linkage, according to equation (12).

$$\text{XeOTeF}_5^{+}\text{AsF}_6^{-} + s\text{-C}_3\text{F}_3\text{N}_2\text{N} \rightarrow s\text{-C}_3\text{F}_3\text{N}_2\text{N}\text{-XeOTeF}_5^{+}\text{AsF}_6^{-} \quad (12)$$

$^{19}$F and $^{129}$Xe NMR Spectroscopy

The product, s-C$_3$F$_3$N$_2$N-XeOTeF$_5^+$AsF$_6^-$, proved to be insoluble in SO$_2$ClF and was subject to solvolysis in HF. Accordingly, it was necessary to use BrF$_5$ solvent for NMR sample preparation, though the XeOTeF$_5^+$ group undergoes solvolysis with BrF$_5$, resulting in the production of TeF$_6$ and bromine oxofluorides, equation (13).

$$\text{XeOTeF}_5^{+}\text{AsF}_6^{-} + \text{BrF}_5 \rightarrow \text{XeF}_2 + \text{BrOF}_2^{+}\text{AsF}_6^{-} + \text{TeF}_6 \quad (13)$$

Fortunately, reaction of s-C$_3$F$_3$N$_2$N-XeOTeF$_5^+$AsF$_6^-$ with the solvent was slow and incomplete at -50°C, and peaks indicative of the novel cation could be identified in the $^{19}$F spectrum (Table 6).

The $^{19}$F NMR spectrum of the compound was quite complex owing to the fact that the equatorial and axial fluorines of the -OTeF$_5$
<table>
<thead>
<tr>
<th>Compound</th>
<th>Species</th>
<th>$\delta^{19}F$ (ppm)</th>
<th>$\delta^{125}Xe$ (ppm)</th>
<th>Coupling Consts. (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-C$_3$F$_3$N$_2$N$-$XeOTeF$_5$'AsF$_6^-$</td>
<td>s-C$_3$F$_3$N$_2$N$-$XeOTeF$_5$'AsF$_6^-$</td>
<td>F(2), -26.8$^a$ [D,2F]</td>
<td>-2250$^b$ [S]</td>
<td>$^4J(F(2)-F(3))$, 14.4</td>
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<td>$^1J[F_{eq}-1^{125}Te]$, 3723</td>
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<td>F$_{eq}$, -43.1</td>
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<td>s-C$_3$F$_3$N$_2$N$-$XeF$^+$AsF$_6^-$</td>
<td>s-C$_3$F$_3$N$_2$N$-$XeF$^+$AsF$_6^-$</td>
<td>F(1'), -145.0 [T,1F]</td>
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<td>Sb(OTeF$_5$)$_2^-$</td>
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<td>s-C$_3$F$_3$N$_2$N$-$XeOTeF$_5^+$</td>
<td>F(2), -25.6$^a$ [D,2F]</td>
<td>$^1J[^{19}F-^{125}Xe]$, 24.78</td>
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<td>$^1J[^{19}F-^{125}Te]$, 2951</td>
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</table>

* BrF$_5^-$, -55°C.  b BrF$_5^-$, -51°C.  c SO$_2$ClF, -51°C.  a SO$_2$ClF, 25°C.  ** 1$^{211}$Sb spectrum obtained in SO$_2$ClF at 25°C.  $^{121}$Sb, -13.21 ppm, broad singlet.  * spectrum obtained in SO$_2$ClF at -51°C after warming to room temperature.
Figure 16. $^{19}F$ NMR spectrum (235.361 MHz) of $s$-C$_3$F$_3$N$_2$N-XeOTeF$_5$$^+$/AsF$_6^-$ and byproducts of solvolysis in BrF$_3$ -55°C, AB$_4$ region. Plus signs (+) denote $^{128}$Te satellites of TeF$_6$. Asterisks (*) denote $^{123}$Te satellite of TeF$_6$. 

\[ \delta_{19F} \text{(ppm from CFCl}_3) \]
Figure 17. $^{19}$F NMR spectrum (235.361 MHz) of $s$-$C_3F_3N_2N-XeOTeF_6$-$AsF_6^-$ and byproducts of solvolysis in BrF_3 $-55^\circ$C. F-on-C region expansions. Asterisks (*) denote $^{129}$Xe satellites.
Figure 18. $^{19}$F NMR spectrum (235.361 MHz) of $s$-CaF$_3$Na$_2$N-XeOTeF$_6$-AsF$_6^-$ and byproducts of solvolysis in BrF$_5$ -55°C, F-on-Xe region. Asterisks (*) denote $^{129}$Xe satellites.
group give rise to an AB spin system consisting of 25 transitions (Figure 16). It is interesting to note that line 1 of the AB pattern, which denotes the chemical shift for the lone axial fluorine, is sharper than the rest of the peaks, as is predicted by theory. In addition to the AB pattern, the spectrum of s-C₃F₅N₂N-XeOTeF₅⁺AsF₆⁻ gave rise to two multiplets in the F-on-C region; a doublet with ¹²⁵Xe satellites, and a triplet (Figure 17).

Additional multiplets arising from TeF₆³⁺, s-C₃F₅N₂N-XeOTeF₅⁺AsF₆⁻ (Figures 17 and 18 and Table 9) and a broad peak attributed to BrF₃ were also present (Figure 16). Satellites arising from coupling of ¹⁹F with ¹²⁵Te and ¹²³Te (Table 5) are evident for the strong TeF₆ peak.

XeOTeF₅⁻Sb(OTeF₅)₂⁻

Although s-C₃F₅N₂N-XeOTeF₅⁺AsF₆⁻ was successfully prepared, the XeOTeF₅⁺AsF₆⁻ Lewis acid could not be used in other Xe-N adduct preparations for lack of a suitable solvent. Other potential ligands such as nitriles and pyridines could not be allowed to react as neat compounds owing to their previously demonstrated thermal instabilities at or near room temperature. To address this problem XeOTeF₅⁻Sb(OTeF₅)₂⁻ was prepared in the hope that the decreased polarity of the Sb(OTeF₅)₂⁻ anion relative to AsF₆⁻ anion would facilitate its low-temperature dissolution in SO₂ClF (m.p., -124°C), an inert, low-polarity solvent. It was hoped this synthetic approach would allow the formation of adduct species with XeOTeF₅⁺ and other more reducing nitrogen bases at low temperatures.

XeOTeF₅⁺Sb(OTeF₅)₂⁻, the first fully substituted OTeF₅ salt
prepared to date, was prepared using the redox synthesis described by equation (14).

\[
2\text{Xe(OTeF}_5\text{)}_2 + \text{Sb(OTeF}_5\text{)}_3 \rightarrow \text{XeOTeF}_6^{\text{+}}\text{Sb(OTeF}_5\text{)}_6^{-} + \text{Xe} \quad (14)
\]

Dissolution of the product in \(\text{SO}_2\text{ClF}\) at \(-50^\circ\text{C}\) resulted in the formation of a bright orange solution and demonstrated the high solubility of \(\text{XeOTeF}_6^{\text{+}}\text{Sb(OTeF}_5\text{)}_6^{-}\) in \(\text{SO}_2\text{ClF}\) at low temperatures. Chemical shifts and coupling constants obtained using \(^{19}\text{F}, ^{129}\text{Xe}\) and \(^{121}\text{Sb}\) NMR confirm the presence of \(\text{XeOTeF}_6^{\text{+}}\text{Sb(OTeF}_5\text{)}_6^{-}\) (Table 6). The \(^{19}\text{F}\) NMR of the product was very complex, owing to the presence of two \(\text{AB}_4\) patterns arising from the -OTeF\(_5\) groups on Xe and Sb (Figure 19). Although the \(\text{AB}_4\) spin system for the OTeF\(_5\) group on \(\text{XeOTeF}_6^{\text{+}}\) was better resolved than that for the anion, owing to incomplete resolution of the individual transitions in the \(\text{B}_4\) region of the cation spectrum, only approximate chemical shifts and coupling constants for the axial and equatorial fluorines of the cation could be obtained (Table 6). The \(\text{AB}_4\) pattern arising from the \(\text{Sb(OTeF}_5\text{)}_6^{-}\) anion was very severe, and only one approximate chemical shift for the two fluorine environments could be obtained (Table 6). Owing to the severity of the latter \(\text{AB}_4\) pattern, a high-field NMR instrument will likely have no significant effect on the observed resolution, and it is expected that computer simulation will be necessary to obtain even approximate chemical shifts and coupling constants. Tellurium-125 satellites for the \(\text{AB}_4\) pattern of the anion were also observed (Figure 19).

The \(^{129}\text{Xe}\) spectrum of the \(\text{XeOTeF}_6^{\text{+}}\text{Sb(OTeF}_5\text{)}_6^{-}\) consisted of a
XeOTeF₅⁻Sb(OTeF₅)₆⁻

A: F(A) of XeOTeF₅⁺
B: F(B₄) of XeOTeF₅⁺
C: Sb(OTeF₅)₆⁻

Figure 20. ¹⁹F NMR spectrum (235.361 MHz) of XeOTeF₅⁺Sb(OTeF₅)₆⁻ in SO₂ClF at 25°C, AB₄ region. Lower case letters denote ¹²⁷Te satellites of Sb(OTeF₅)₆⁻ anion.
broad quadrupole collapsed peak at -1457 ppm, which is within the expected range for Xe(II). The $^{121}$Sb NMR spectrum was also a broad singlet, (-13.21 ppm, $\omega_w = 1650$ Hz) resulting from partial relaxation of $^{121}$Sb in a near-octahedral environment of six OTeF$_5$ groups.

$\text{S-C}_3\text{F}_3\text{N}_2\text{N-XeOTeF}_5^+\text{Sb(OTeF}_5)_6^-$

The Lewis acid properties of XeOTeF$_5^-$Sb(OTeF$_5$)$_6^-$ were studied by allowing the solid to react with trifluoro-s-triazine at 0°C. The reaction was immediate, and proceeded according to equation (14)

$$\text{XeOTeF}_5^+\text{Sb(OTeF}_5)_6^- + \text{S-C}_3\text{F}_3\text{N}_3^+ \rightarrow \text{S-C}_3\text{F}_3\text{N}_2\text{N-XeOTeF}_5^+\text{Sb(OTeF}_5)_6^- (14)$$

The product proved to be soluble in SO$_2$ClF at low temperatures, and the $^{19}$F NMR confirmed the presence of $\text{S-C}_3\text{F}_3\text{N}_2\text{N-XeOTeF}_5^+\text{Sb(OTeF}_5)_6^- (\text{Table 6})$. Owing to the presence of the two AB$_4$ spin systems, the $^{19}$F NMR spectrum was again very complex (Figure 20). The AB$_4$ pattern for the Sb(OTeF$_5$)$_6^-$ anion was severe, and only one $^{19}$F chemical shift could be obtained in addition to the tellurium satellite couplings $^1J[^{19}\text{F-}^{125}\text{Te}]$ and $^1J[^{19}\text{F-}^{125}\text{Te}]$ (Table 6). The AB$_4$ pattern corresponding to XeOTeF$_5^+$ was better resolved, and it was possible to determine chemical shifts for the axial and equatorial fluorine environments in addition to approximate values for $^3J[^{19}\text{F-}^{125}\text{Te}]$ (Table 6). Fortunately, the multiplets arising from fluorines bonded to carbon (Figure 21) were well resolved, occurring at significantly higher frequencies than the
Figure 20. $^{19}$F NMR spectrum (235.361 MHz) of XeOTeF$_5$-Sb(OTeF$_5$)$_6^-$ in SO$_2$ClF at 25°C. AB$_4$ region. Lower case letters denote $^{125}$Te satellites of Sb(OTeF$_5$)$_6^-$ anion.
Figure 21. $^19$F NMR spectrum (235.361 MHz) of $\varepsilon$-C$_3$F$_3$N$_2$N-XeOTeF$_6$Sb(OTeF$_6$)$_6^-$ in SDCl$_3$ at 25°C, F-on-C region. Asterisks (*) denote $^{129}$Xe satellites.
complex AB₄ patterns, thus affording ready measurement of the coupling constants and chemical shifts (Table 6). Xenon-129 NMR spectroscopy studies are presently pending.

It should be noted that some evidence for the presence of byproducts was obtained, however, it is believed that decomposition occurred when the sample was warmed to 25°C prior to obtaining the spectrum at -50°C. Future work will consequently entail ¹⁹F NMR characterization of s-C₃F₃N₂N-XeOTeF₅⁺Sb(OTeF₅)₆⁻ at temperatures not exceeding -30°C.

Raman Spectroscopy

The Raman spectrum for s-C₃F₃N₂N-XeF⁺AsF₆⁻ was assigned on the basis of the vibrational assignments for of s-C₃F₃N₃ under D₃h symmetry, 3A₁' + 4A₂' + 5E' + 2A₂" + 2E"⁻²⁷ Formation of the XeF⁺ adducts of trifluoro-s-triazine lowers the ring symmetry from D₃h to C₂v, accordingly, 21 bands (3N - 6, N = 9) for the triazine moiety of s-C₃F₃N₂N-XeF⁺AsF₆⁻ are expected, 8A₁ + 4B₁ + 7B₂ + 2A₂. In addition, the XeF⁺ moiety gives rise to 6 bands, [Xe-F stretch, A₁; Xe-N stretch, A₁; δ(N-Xe-F), B₁; δ(N-Xe-F), B₂; δ(C-N-Xe), B₁; δ(C-N-Xe), B₂] resulting in a total of 27 bands for s-C₃F₃N₂N-XeF⁺ (10A₁ + 6B₁ + 9B₂ + 2A₂) (Table 7). The octahedral AsF₆⁻ anion is expected to give rise to three additional bands in the Raman spectrum, namely, v₁(a₁g), v₂(e₂g), and v₃(t₂g) (Table 7).

The vibrational Raman assignments for the XeOTeF₅⁺ group in s-C₃F₃N₂N-XeOTeF₅⁺Sb(OTeF₅)₆⁻ and s-C₃F₃N₂N-XeOTeF₅⁺AsF₆⁻ are by analogy with XeOTeF₅⁺AsF₆⁻ (Table 7). In both cases the symmetries
Table 7

Raman Frequencies and Assignments for \( \text{e-C}_4\text{Fe}_2\text{N}_2\text{N}-\text{XeF}_4\text{AsF}_6^- \), \( \text{e-C}_3\text{Fe}_3\text{N}_2\text{N}-\text{XeOTeF}_5\text{AsF}_6^- \), \( \text{e-C}_4\text{Fe}_2\text{N}_2\text{N}-\text{XeOTeF}_5\text{AsF}_6^- \), \( \text{e-C}_3\text{Fe}_3\text{N}_2\text{N}-\text{XeOTeF}_5\text{Sb(OTeF}_5\text{)AsF}_6^- \) and \( \text{XeOTeF}_5\text{Sb(OTeF}_5\text{)AsF}_6^- \)

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<td>ring mode, ( \text{e}_2 ), symmetric breathing</td>
</tr>
<tr>
<td>1293(11)</td>
<td>ring mode, ( \text{e}_3 ), C atom twist against N</td>
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<tr>
<td>1015(9)</td>
<td>ring mode, ( \text{e}_2, \text{bs} ) C-F stretching</td>
</tr>
<tr>
<td>803(1)</td>
<td>ring mode, ( \text{e}_3 ), ( \text{bs} ) out of plane</td>
</tr>
<tr>
<td>700(1)</td>
<td>ring mode, ( \text{e}_2, \text{bs} ) C-F wagging</td>
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<td>533(3)</td>
<td>ring mode, ( \text{a}' ), ( \text{v}_{\text{sym}} )(TeF(_5)), symmetric to plane of sym</td>
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<td>30(33)</td>
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<td>ring mode, ( \text{e}_1, \text{bs} ) ring stretching</td>
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<td>ring mode, ( \text{e}_2, \text{bs} ) C-F stretching</td>
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<td>ring mode, ( \text{a}' ), ( \text{v}_{\text{sym}} )(TeF(_5)), symmetric to plane of sym</td>
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<tr>
<td>ring mode, ( \text{a}_1 ), ( \text{v}\text{(TeF}_5\text{)} ) out of plane</td>
</tr>
</tbody>
</table>

\( a \) \( \text{AsF}_6^- \) modes. \( b \) External modes and/or low-frequency bending and torsional modes. \( c \) Non-assigned modes arising from \( \text{OTeF}_5 \) group.
Figure 22. Raman Spectrum of $C_3F_3N_2N\text{-}Xe\text{-}OTeF_5^+\text{AsF}_6^-$
of the cations are assumed to be low (C\textsubscript{m} or C\textsubscript{1}); for the purposes of this discussion and labelling, C\textsubscript{m} symmetry is assumed. In either case, all the modes associated with the XeOTeF\textsubscript{5}\textsuperscript{+} group are expected to be Raman active (11A' + 7A" under C\textsubscript{m} and 18A under C\textsubscript{1}).

The modes associated with the OTeF\textsubscript{5} group of the anion Sb(OTeF\textsubscript{3})\textsubscript{6} were very difficult to assign owing to their proximity to the OTeF\textsubscript{5} bands of XeOTeF\textsubscript{5}\textsuperscript{+}. The only Sb(OTeF\textsubscript{3})\textsubscript{6} band assigned is that corresponding to the intense and strongly coupled Sb-O-Te stretches.

In general, one would expect the less electronegative OTeF\textsubscript{5} group (3.38 relative to 4.10 for F on the Allred-Rochow/Pauling scale\textsuperscript{29}) to give rise to a more covalent Xe-N adduct than in the XeF\textsuperscript{+} analogue. Accordingly, the increased electron donating ability of the XeOTeF\textsubscript{5}\textsuperscript{+} group relative to XeF\textsuperscript{+} should result in overall shifts of bands to lower frequencies. However, many other factors, such as the site symmetry and the symmetry of the crystal environment also play a role in activities and, to a lesser extent, peak positions. Thus, comparison of the spectra of the XeOTeF\textsubscript{5} and s-C\textsubscript{3}F\textsubscript{3}N\textsubscript{2}N- moieties as well as the As\textsubscript{3} anion in s-C\textsubscript{3}F\textsubscript{3}N\textsubscript{2}N-XeF\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-}, s-C\textsubscript{3}F\textsubscript{3}N\textsubscript{2}N-XeOTeF\textsubscript{5}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} and s-C\textsubscript{3}F\textsubscript{3}N\textsubscript{2}N-Xe-OTeF\textsubscript{5}Sb(OTeF\textsubscript{3})\textsubscript{6} show little variation enabling one to "transfer" the modes from XeOTeF\textsubscript{5}\textsuperscript{+}AsF\textsubscript{6}\textsuperscript{-} and s-C\textsubscript{3}F\textsubscript{3}N\textsubscript{2}N- for the purpose of assignment of these compounds.

Among the major difficulties encountered when analyzing the Raman spectra for the three adducts was the fact that the low frequency Xe-N stretch is generally weak and therefore hard to assign. Consequently, the vibrational mode is expected to vary the most among the
three compounds, the Xe-N stretch, could not be definitively assigned. Although the Xe-O, Te-O and Sb-O stretches associated with these compounds was generally very intense, it is not possible to assign discrete stretching modes to the bands owing to strong coupling of stretching vibrations arising from atoms of nearly identical masses, i.e., Xe-O-Te and Sb-O-Te.

The spectrum for XeOTeF₅⁺Sb(OTeF₅)₆⁻ was poorly resolved by virtue of the nature of the compound itself, i.e., poor crystallinity. It was, however, possible to assign a number of modes including OTeF₅ modes and the intense and strongly coupled Xe-O-Te stretching modes all correlating well with those observed in the spectra of s-C₃F₃N₂N-XeOTeF₅⁺AsF₆⁻ and s-C₃F₃N₂N-XeOTeF₅⁺Sb(OTeF₅)₁⁶⁻.
We have recently added $^{129}$Xe Mössbauer spectroscopy to our in-house arsenal of structural characterization techniques. In conjunction with establishing the capability in our laboratory, we have prepared a high quality sealed source, namely, Na$_5^{129}$IO$_6$. To date, we have remeasured a number of previously determined compounds as well as a number of new xenon(II) cations described in our previous Annual Technical Report (see Table 8).

In $^{129}$Xe Mössbauer spectroscopy, only the quadrupole splitting is sufficiently sensitive to provide information relating to xenon-ligand atom bond covalency, and is therefore the parameter we are primarily concerned with. In general, the quadrupole splitting in xenon(II) species is seen to decrease with increasing covalency as determined from the $^{129}$Xe NMR chemical shift and the Xe-F stretching frequency.

We have reported the reaction of XeF$^+$/AsF$_6^-$ with trifluoro-s-triazine, s-C$_3$F$_3$N$_3$, leading to the formation of a new class of Xe-N bonded cation, s-C$_3$F$_3$N$_2$N-XeF$^+$/AsF$_6^-$ in Section II. We propose to investigate the 2:1 cation described earlier in this report by Mössbauer spectroscopy. The Mössbauer spectrum of s-C$_3$F$_3$N$_2$N-XeF$^+$/AsF$_6^-$ has been measured. The quadrupole splitting in [s-C$_3$F$_3$N$_2$N-]$_2$XeF$^+$/AsF$_6^-$ ought to be significantly smaller than in the 1:1 cation or any other xenon(II) derivative presently known if the second nitrogen is coordinated to the xenon. If our speculations are confirmed, the
addition of this technique will prove invaluable in establishing the existence of the first compound known to possess an AX₃E₃ arrangement of bond pairs and lone pairs. The isolation of examples of solid fluoro(alkynitrile) and fluoro(pyridine) xenon(II) cations in the course of these investigations have also provided us with further opportunities to measure their Mössbauer spectra (Table 8).
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<th>Compound</th>
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<th>$\Gamma_q$ mm/s</th>
<th>$\chi^2$ c</th>
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<td>$\text{XeF}_2$</td>
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<td>-0.4(10)</td>
<td>0</td>
<td>11.5(4)</td>
<td>0.82</td>
</tr>
</tbody>
</table>

a The compounds being reported for the first time are denoted by an asterisk (*).
b Relative to hydroquinone clathrate.
c Full width at half height.
d Per degree of freedom.
Conclusions and Directions for Further Research

1. XeF₂AsF₆⁻ may react with excess trifluoro-s-triazine to form polymeric s-C₆F₃N₂N-XeF₂-x s-C₆F₃Nₓ, x > 1. ³²⁹Xe Mössbauer studies may provide evidence for this novel bonding situation;

2. XeF₆⁻SbF₆⁻ is too potent an oxidizing agent to form a stable Xe(IV)-N adduct with trifluoro-s-triazine;

3. XeOTeF₅⁻AsF₆⁻ has Lewis acid properties and, as such, can be used to prepare s-C₆F₃N₂N-Xe-OTeF₅⁻AsF₆⁻, the first compound containing an N-Xe-O linkage;

4. The preparation and characterization of XeOTeF₅⁻Sb(OTeF₅)₆⁻ and s-C₆F₃N₂N-XeOTeF₅⁻Sb(OTeF₅)₆⁻ represents an important new development in noble-gas chemistry. The high solubility of XeOTeF₅⁻Sb(OTeF₅)₆⁻ and its trifluoro-s-triazine adduct in SO₂CLF are significant in that they indicate a means to prepare and characterize novel Xe-N compounds in an inert, low-polarity solvent. The use of the Lewis acid XeOTeF₅⁻Sb(OTeF₅)₆⁻, as in the preparation of s-C₆F₃N₂N-XeOTeF₅⁻Sb(OTeF₅)₆⁻, may extend to the syntheses of numerous novel noble-gas compounds which would be protonated and/or fluorinated in BrF₇ and HF.

5. To a certain extent follow-up work stemming from this work has served to illustrate point (4) above. Cation adducts of the more easily oxidized nitrogen CH₃CN and C₆F₅N (perfluoropyridine) have been stabilized at low temperatures in SO₂CLF solvents as the salts CH₃CN-XeOTeF₅⁻Sb(OTeF₅)₆⁻ and C₆F₅N-XeOTeF₅⁻Sb(OTeF₅)₆⁻. **
REFERENCES


