The Xenon–Oxygen-Bonded Cation $CF_3C(OXeF)NH_2^+$ and Related $CF_3C(OH)NH_2^+AsF_6^-$ and $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$ Salts. Their Syntheses and Characterization by Multi-NMR and Raman Spectroscopy

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The salt $CF_3C(OH)NH_2^+AsF_6^-$ reacts with XeF_2 in BrF_5 solvent by means of an HF elimination reaction to give the novel xenon–oxygen-bonded $CF_3C(OXeF)NH_2^+$ cation. Both $CF_3C(OH)NH_2^+$ and $CF_3C(OXeF)NH_2^+$ have been characterized in BrF_5 solvent using ^{129}Xe, ^{19}F, ^{13}C, and ^1H NMR spectroscopy. Hindered rotation about the C–N bonds in both cations results in chemical inequivalence of the amido protons in the ^1H NMR spectra. Assignment of the amido proton resonances was made using the two-dimensional heteronuclear ($^1H-^{19}F$) NOESY technique. The $CF_3C(OXeF)NH_2^+$ cation is not observed in anhydrous HF solution, but complete removal of the HF solvent *in vacuo* results in the isolation of $CF_3C(OXeF)NH_2^+AsF_6^-$ as a white powder which has been characterized by Raman spectroscopy. The Xe–O bond of the $CF_3C(OXeF)NH_2^+$ cation is interpreted as having substantial covalent character on the basis of trends among ^{129}Xe and ^{19}F NMR chemical shifts, $^1J(^{19}F-^{129}Xe)$, and Xe–F stretching frequencies for related xenon(II) species. The substantial covalent character of the Xe–O bond is attributed, in great measure, to π-bonding between carbon and nitrogen. An intermediate HF solvate, $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$, has also been isolated from anhydrous HF at low temperature. Raman spectroscopy indicates that the XeF_2 molecule is weakly coordinated to the $CF_3C(OH)NH_2^+$ cation, possibly through hydrogen-bonding interactions with the protonated carbonyl and/or amino groups. This solvate represents the first example of an isolated intermediate in an HF elimination reaction involving XeF_2.

Introduction

The noble-gas cations NgF^+ (Ng = Xe, Kr) have long been known to exhibit Lewis acid character in their salts with weakly fluorobasic anions such as AsF_6^-, SbF_6^-, and $Sb_2F_{11}^-$, where the NgF^+ cation interacts with the fluoroanion in the solid state by means of a fluorine bridge.[1] Recently, the Lewis acidities of NgF^+ (Ng = Kr, Xe) cations have been exploited to synthesize novel adduct cations containing Xe–N and Kr–N bonds.[2–7] A variety of oxidatively resistant organic nitrogen bases have now been shown to form adducts with XeF^+, including hydrogen cyanide,[2,6] alkanenitriles,[2] perfluorobenzenenitrile,[2] perfluoroalkanenitriles,[2,3] perfluoropyridines[4] and *s*-trifluorotriazine.[3] Adducts of the strong oxidant cation KrF^+ with hydrogen cyanide[5] and perfluoroalkanenitriles[3] have also been stabilized at low temperatures to give the $R_FC{\equiv}N{-}KrF^+$ (R_F = CF_3, C_2F_5, *n*-C_3F_7) and $HC{\equiv}N{-}KrF^+$ cations and provide the only examples of Kr–N bonds presently known. The Ng–N bonds in the cations have been shown by ^{19}F and ^{129}Xe NMR spectroscopy to have high degrees of ionic character.[6,7] The ability of a base to resist oxidation by the strongly oxidizing NgF^+ cations correlates well with the first adiabatic ionization potential (IP_1) of the nitrogen base. It has been shown that a base having an IP_1 value that is similar to or greater than the estimated electron affinities of XeF^+ (10.9 eV) and KrF^+ (13.2 eV) may be sufficiently resistant to oxidation by NgF^+ to form kinetically stable Ng–N bonds at low temperatures.[7]

Where possible, the general preparative strategy has been straight forward and has entailed the interaction of the appropriate base with an NgF^+ salt in HF solvent. In instances where the protonated form of the base predominates in HF solvent, or when the base is readily oxidized by the noble-gas cation, NgF_2 is allowed to react with the oxidatively more resistant protonated nitrogen base cation in the strongly oxidizing solvent BrF_5. Equilibrium displacement of HF from the protonated base by the difluoride occurs to a significant extent in BrF_5 solvent at the low temperatures usually required to stabilize the adduct cations. These synthetic approaches are illustrated by the NgF^+ adducts of $HC{\equiv}N$. Hydrogen cyanide (IP_1 = 13.80 eV)[8] forms the adduct cation $HC{\equiv}N{-}XeF^+$ upon reaction of $HC{\equiv}N$ with $XeF^+AsF_6^-$ or $Xe_2F_3^+AsF_6^-$ in HF solution at −20 to −10 °C,[2,6] whereas the powerful oxidizing ability of KrF^+ requires the reaction of $HC{\equiv}NH^+AsF_6^-$ with KrF_2 in BrF_5 solvent near the melting point of the solvent to prepare the krypton analog, $HC{\equiv}N{-}KrF^+AsF_6^-$.[5] A third synthetic approach, which also avoids the use of the strong oxidant NgF^+ cations, is exemplified by the perfluoroalkanenitriles $R_FC{\equiv}N$ (R_F = CF_3, C_2F_5, *n*-C_3F_7) and relies upon the reaction of the adducts $R_FC{\equiv}N{-}AsF_5$ and KrF_2 to form the $R_FC{\equiv}N{-}NgF^+$ (Ng = Kr, Xe) adduct cations at low temperatures in BrF_5 solvent.[3]

Oxygen electron-pair donors have not been investigated to any significant extent as bases toward NgF^+ cations. Only one example of a cation containing the O–Xe–F linkage, namely $(CF_3)_2S{=}O{-}XeF^+$, has been reported.[9] This cation was prepared by reaction of the sulfurane, $(CF_3)_2S{=}O$, with

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$XeF^+SbF_6^-$ in HF at −65 °C over a 12 h period; the solid decomposes explosively above −78 °C if mechanically shocked. The present work describes the second example of an adduct cation containing the O—Xe—F linkage, namely $CF_3C(OXeF)NH_2^+$, and its characterization in the solid state by low-temperature Raman spectroscopy and in solution by ^{19}F, ^1H, ^{13}C, and ^{129}Xe NMR spectroscopy.

Results and Discussion

Syntheses of $CF_3C(OH)NH_2^+AsF_6^-$, $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}xHF$, and $CF_3C(OXeF)NH_2^+AsF_6^-$. The first adiabatic ionization potential of 2,2,2-trifluoroacetamide (10.77 eV)[13] is similar to the estimated electron affinity of the XeF^+ cation (10.9 eV),[6] suggesting that it is potentially resistant to oxidation by XeF^+ under suitable solvent conditions and at low temperature, enabling an Xe−O-bonded adduct cation to be formed.

The $CF_3C(OXeF)NH_2^+$ cation results from the HF elimination reaction of the conjugate acid of $CF_3C(O)NH_2$, namely $CF_3C(OH)NH_2^+$, with XeF_2. The strong electrophilic characters of XeF^+ and BrF_5 solvent and nucleophilicities of the oxygen and nitrogen base sites are mitigated by protonation of $CF_3C(O)NH_2$ under superacid conditions by reaction of the amide with excess AsF_5 in HF solvent. Upon removal of the solvent, $CF_3C(OH)NH_2^+AsF_6^-$ was isolated as a white microcrystalline powder in quantitative yield according to eq 1 and underwent

$$CF_3C(O)NH_2 + AsF_5 \xrightarrow[-50\ °C]{HF} CF_3C(OH)NH_2^+AsF_6^- \qquad (1)$$

$$CF_3C(OH)NH_2^+AsF_6^- + XeF_2 \xrightleftharpoons[-62\ to\ -55\ °C]{BrF_5} CF_3C(OXeF)NH_2^+AsF_6^- + HF \qquad (2)$$

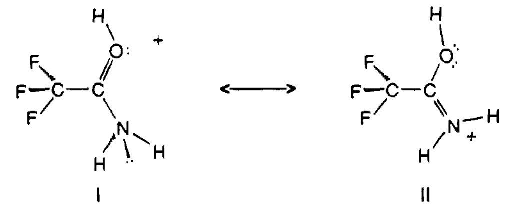
$$CF_3C(O)NH_2 + XeF^+AsF_6^- \xrightleftharpoons[-50\ °C]{HF} CF_3C(OH)NH_2^+AsF_6^- + XeF_2 \qquad (3)$$

slow decomposition at room temperature. The salt $CF_3C(OH)NH_2^+AsF_6^-$ was characterized in solution by multi-NMR using BrF_5 as the solvent at low temperature. The slow reaction of the $CF_3C(OH)NH_2^+$ cation with BrF_5 solvent at −55 °C is indicated by the presence of broad resonances at $\delta(^1H)$ = 5.2, 3.3, and 2.6 ppm in the ^1H NMR spectrum, which likely result from the rapidly exchanging H-on-N environments of NH_4^+, N_2H_4, and HN_3. A doublet at $\delta(^1H)$ = 5.1 ppm [$^1J(^1H-^{19}F)$ = 535 Hz] indicates the presence of HF. Combining stoichiometric amounts of $CF_3C(OH)NH_2^+AsF_6^-$ with XeF_2 in BrF_5 solvent at −62 to −55 °C (eq 2) resulted in the formation of the xenon cation $CF_3C(OXeF)NH_2^+$. The HF elimination reaction represented by eq 2 is directly analogous to the reaction of $CF_3C(O)OH$ and XeF_2 to give the neutral species $CF_3C(O)OXeF$.[10-12] The ^{19}F and ^{129}Xe NMR spectra show that the reaction between $CF_3C(O)NH_2$ and $XeF^+AsF_6^-$ does not proceed to any measurable extent in anhydrous HF solvent owing to solvolysis reactions; i.e., the XeF^+ cation is a fluoride ion acceptor in HF solvent and $CF_3C(O)NH_2$ is protonated according to eq 3. However, slow removal of HF solvent at −50 °C under dynamic vacuum displaces eq 3 toward the right, yielding a pale yellow viscous solution which, after continued pumping, yielded $CF_3C(OXeF)NH_2^+AsF_6^-$ as a white microcrystalline solid. The ^{129}Xe and ^{19}F NMR spectra of solutions of this material in BrF_5 solvent (-60 °C) confirm the presence of the $CF_3C(OXeF)NH_2^+$ cation. In the solid state, $CF_3C(OXeF)NH_2^+AsF_6^-$ decomposes rapidly with gas evolution and liquefaction at temperatures approaching 0 °C. In contrast, rapid removal of HF solvent from a solution of $XeF^+AsF_6^-$ and $CF_3C(O)NH_2$ under dynamic vacuum at −50 °C results in immediate precipitation of the solvated adduct, $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}xHF$, as a white powder (eq 4); no $CF_3C(OXeF)NH_2^+AsF_6^-$ salt was observed in the solid by Raman spectroscopy.

$$CF_3C(OH)NH_2^+AsF_6^-(HF) + XeF_2(HF) \xrightarrow[-50\ °C]{-HF} CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}xHF(s) \qquad (4)$$

Elimination of HF from $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}xHF$ did not occur after pumping under dynamic vacuum for 28 h at −50 °C; however, redissolution of the adduct in HF at −50 °C followed by slow removal of the solvent under vacuum resulted in the isolation of pure $CF_3C(OXeF)NH_2^+AsF_6^-$ (see Raman Spectroscopy). The adduct, $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}xHF$, is considered to be an intermediate in the HF elimination reaction of $CF_3C(OH)NH_2^+$ and XeF_2. Although several examples of HF elimination reactions involving XeF_2 and acids, HL, are known (L = FO_2SO-,[14-16] CF_3O_2SO-,[15] CH_3O_2SO-,[15] F_5TeO-,[17-21] F_5SeO-,[22] ClO_3O-,[15] $CF_3C(O)O$-,[10,11] and $(FSO_2)_2N$-[23-27]), $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}xHF$ represents the first reported instance of the isolation of an intermediate in an HF elimination reaction involving XeF_2.

NMR Spectroscopy. The $CF_3C(OH)NH_2^+$ Cation. Since the $CF_3C(OXeF)NH_2^+$ cation is in equilibrium with $CF_3C(OH)NH_2^+$ in BrF_5 solvent (equilibrium 2), unambiguous NMR characterization of the $CF_3C(OXeF)NH_2^+$ cation required a detailed NMR study of $CF_3C(OH)NH_2^+AsF_6^-$ in BrF_5 solution. Although $CF_3C(O)NH_2$ is potentially an ambident base, the ^1H NMR spectrum of $CF_3C(OH)NH_2^+AsF_6^-$ in BrF_5 solvent at −55.4 °C (Figure 1a) confirms that protonation occurs exclusively at the oxygen and that the oxygen site is more basic (cf. resonance structures **I** and **II**). Previous work has shown that amides are protonated at oxygen in strong acid and superacid



I

II

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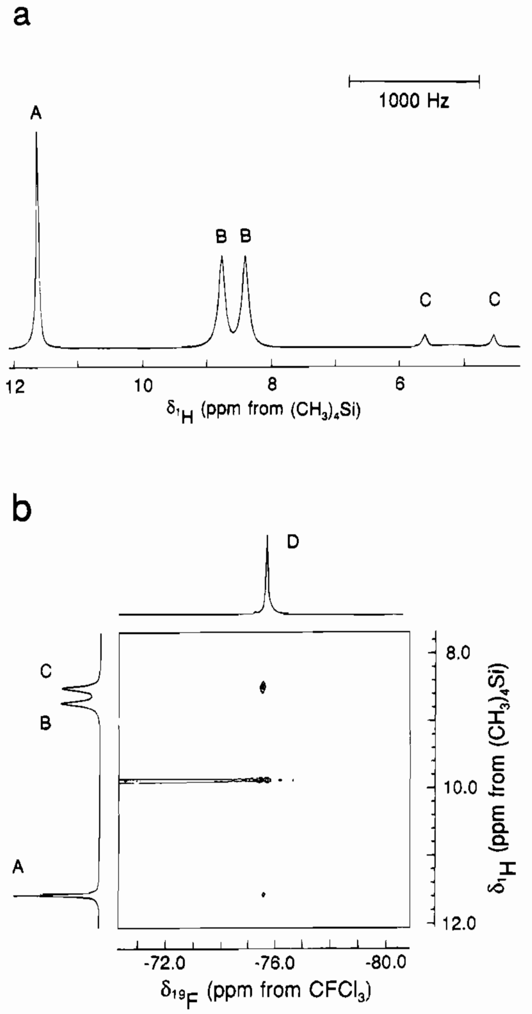

Figure 1. (a) ^1H NMR spectrum (500.138 MHz) at −55.4 °C of $CF_3C(OH)NH_2^+AsF_6^-$ (0.25 M) in BrF_5 solvent: (A) proton on oxygen of the protonated carbonyl group; (B) two singlets of equal intensity arising from the chemically inequivalent amido protons; (C) HF. (b) Heteronuclear [^1H(500.138 MHz)−^{19}F(470.599 MHz)] NOESY spectrum at −58.9 °C of $CF_3C(OH)NH_2^+AsF_6^-$ (0.48 M) in BrF_5 solvent, with one-dimensional ^1H and ^{19}F NMR spectra displayed along the vertical and horizontal axes, respectively: (A) proton on oxygen environment of the protonated carbonyl group; (B) amido proton trans to the CF_3 group; (C) amido proton cis to the CF_3 group; (D) fluorine on carbon environment of the $CF_3C(OH)NH_2^+$ cation. The continuous horizontal line of peaks running through the two-dimensional plot is an axial peak artifact along F1 = 0.[78]

media.[28−34] The ^1H NMR resonance of the protonated carbonyl group of the $CF_3C(OH)NH_2^+$ cation is a singlet at $\delta(^1H) = 11.61$ ppm, $\Delta\nu_{1/2} = 20$ Hz, in agreement with the value reported for the protonated carbonyl group of the $FC(OH)NH_2^+$ cation ($\delta(^1H) = 11.07$ ppm, HSO_3F/SO_2 solution at −80 °C).[34] Similar ^1H chemical shifts have been reported for O-protonated acetamide ($\delta(^1H) = 10.72$ ppm, −80 °C),[30] formamide ($\delta(^1H) = 10.81$ ppm, −85 °C),[30] and benzamide ($\delta(^1H) = 10.14$ ppm, −85 °C)[29] in HSO_3F solvent. The NH protons of the $CF_3C(OH)NH_2^+$ cation are inequivalent on the NMR time scale (Figure 1a), giving two broad singlets ($\Delta\nu_{1/2} = 61$ Hz) of equal intensity at 8.75 and 8.38 ppm. The large line widths are primarily attributed to residual one-bond scalar coupling between the protons and ^{14}N ($I = 1$). The chemical inequivalence of the NH protons is attributed to hindered rotation about the C−N bond and is consistent with the large barriers to C−N bond rotation found for neutral $[^{15}N]CF_3C(O)NH_2$ in dioxane ($E^{\ddagger} = 76.5 \pm 2.9$ kJ mol^{-1}) and methyl propyl ketone ($E^{\ddagger} = 77.8 \pm 2.5$ kJ mol^{-1}) solvents.[35] Oxygen coordination of amides has been shown to substantially increase the barrier to rotation about the C−N bond by increasing the C−N double bond character relative to that of the free amide.[28] Examples of increases in C−N bond rotational barriers resulting from O-coordination have been extensively studied by NMR spectroscopy and include O-protonation of dimethylformamide, *N*-methylformamide and *N*-methylacetamide in 100% H_2SO_4[31] and O-coordination of BF_3 in *sym*- and *unsym*-dimethylureas[36] and of BX_3 in tetramethylurea (X = Br, Cl, F).[37] In all cases, resonance structures can be drawn representing "amide-like" linkages containing C−N double bonds which dominate the bonding when oxygen is coordinated to a Lewis acid. Resonance structure **II** represents π-donation from nitrogen to carbon and is expected to be the dominant contributing structure for the $CF_3C(OH)NH_2^+$ cation. (see Raman Spectroscopy.) Hindered rotation in protonated primary amides in acidic solution has been observed in a variety of acidic media and at different temperatures by ^1H NMR spectroscopy. The relative shieldings of the amido proton resonances in the $CF_3C(OH)NH_2^+$ cation cannot be unambiguously assigned by comparison with previously reported examples.[38] However, definitive assignments of the amido protons in the $CF_3C(OH)NH_2^+$ cation were obtained from a two-dimensional heteronuclear ($^1H-^{19}F$) NOESY experiment performed on a sample of $CF_3C(OH)NH_2^+AsF_6^-$ dissolved in BrF_5 solvent at −58.9 °C (Figure 1b). A correlation was observed between the ^{19}F NMR resonance of the CF_3 group and both the low-frequency proton-on-nitrogen resonance and the proton-on-oxygen resonance. This experiment utilizes the nuclear Overhauser effect (nOe), which results from a through-space dipolar interaction between nuclei.[39] This effect rapidly diminishes with internuclear distance, so that correlations are only observed for nuclei which are close to one another. The presence of a correlation between the CF_3 group and the low-frequency proton-on-nitrogen resonance indicates that this ^1H resonance arises from the proton cis to the CF_3 group (cf. resonance structures **I** and **II**). A correlation is also observed between the proton-on-oxygen resonance and the fluorine resonance of the CF_3 group, indicating that intermolecular exchange involving the proton on oxygen is slow relative to dipolar relaxation induced by the fluorine atoms of the CF_3 group. The ^{19}F NMR spectrum of the $CF_3C(OH)NH_2^+$ cation in BrF_5 solvent at −55.4 °C consisted of a singlet at −75.6 ppm assigned to the CF_3 resonance. A value of $^4J(^{19}F-^1H) =$

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(38) Hindered rotation was observed in the ^1H NMR spectra of O-protonated carbamyl fluoride, $FC(OH)NH_2^+$, in HSO_3F/SO_2 solution, resulting in two unassigned resonances for the chemically inequivalent NH protons at $\delta(^1H) \approx 8.5$ ppm.[34] The ^1H NMR spectrum of ^{15}N-enriched O-protonated benzamide in HSO_3F or 100% H_2SO_4 solvent shows two peaks of equal intensity at 8.36 and 7.94 ppm, at temperatures below 65 °C. The high-frequency peak was assigned to the proton trans to the protonated carbonyl group.[33] Birchall and Gillespie[30] reported proton-on-nitrogen resonances at 8.36 and 8.24 ppm for O-protonated acetamide in HSO_3F solvent at −80 °C; the high-frequency resonance was assigned to the proton cis to the protonated carbonyl group. Using the nOe difference technique, the proton cis to the carbonyl group was assigned to the high-frequency ^1H NMR resonance in the structurally related protonated trichloroacetimidate cation, $CCl_3C(OCH_3)NH_2^+$, in 95% H_2SO_4 solution.[32]
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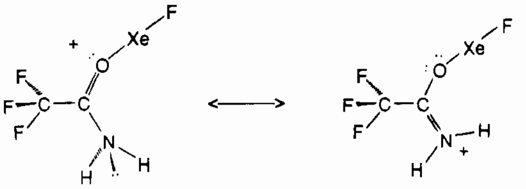
1.8 Hz was observed by Akiyama *et al.*[40] for the scalar coupling between the NH proton trans to the carbonyl group and the fluorines of the CF_3 group in $CF_3C(O)NH_2$ at −40 °C in tetrahydrofuran, using ^{19}F NMR spectroscopy. The large line width ($\Delta\nu_{1/2}$ = 32 Hz) observed in the ^{19}F NMR spectrum of the $CF_3C(OH)NH_2^+$ cation precluded resolution of the $^4J(^{19}F-{}^1H)$ scalar coupling. The quadrupole-collapsed ^{19}F NMR resonance of the AsF_6^- anion occurs at −60.7 ppm ($\Delta\nu_{1/2}$ = 284 Hz), as previously observed for AsF_6^- in BrF_5 solvent at low temperature.[6]

The carbon-13 spectrum of $CF_3C(OH)NH_2^+AsF_6^-$ (−56.2 °C) in BrF_5 solvent consists of two binomial quartets at $\delta(^{13}C)$ = 166.2 [$^2J(^{13}C-{}^{19}F)$ = 46 Hz] and at 114.0 ppm [$^1J(^{13}C-{}^{19}F)$ = −284 Hz], which are assigned to the COH and CF_3 resonances, respectively, and are similar to those reported for related compounds containing the $CF_3C(O)$- moiety.[41]

The $CF_3C(OXeF)NH_2^+$ Cation. The structure of the $CF_3C(OXeF)NH_2^+$ cation was established in solution by ^1H, ^{13}C, ^{19}F, and ^{129}Xe NMR spectroscopy and is consistent with resonance structures **III** and **IV**.



III IV

The ^{129}Xe NMR spectrum of the $CF_3C(OXeF)NH_2^+$ cation consists of a doublet centered at −1578 ppm (−53.0 °C, BrF_5 solvent) arising from $^1J(^{129}Xe-{}^{19}F)$ = 5991 Hz, in the region expected for xenon(II) covalently bonded to fluorine (Figure 2a). The magnitude of $^1J(^{129}Xe-{}^{19}F)$ is comparable to other directly bonded $^{129}Xe-{}^{19}F$ couplings.[42-44] The XeF_2 triplet is also present [$\delta(^{129}Xe)$ = −1572 ppm; $^1J(^{129}Xe-{}^{19}F)$ = 5651 Hz] and is consistent with equilibrium 2. In the ^{19}F NMR spectrum, a singlet at $\delta(^{19}F)$ = −183.1 ppm with a satellite doublet [$^1J(^{19}F-{}^{129}Xe)$ = 6012 Hz] is assigned to the F-on-Xe(II) of the $CF_3C(OXeF)NH_2^+$ cation (Figure 2b). The ^{19}F resonance centered at −187.5 ppm with accompanying ^{129}Xe satellites [$^1J(^{129}Xe-{}^{19}F)$ = 5650 Hz] is assigned to XeF_2. A doublet centered at −193.1 ppm [$^1J(^{19}F-{}^1H)$ = 534 Hz] is assigned to HF formed according to equilibrium 2. The ^{19}F NMR resonance of the CF_3 group of the $CF_3C(OXeF)NH_2^+$ cation consists of a singlet at $\delta(^{19}F)$ = −74.4 ppm (−54.0 °C, BrF_5 solvent). The CF_3 group of the $CF_3C(OH)NH_2^+$ cation occurs at $\delta(^{19}F)$ = −75.6 ppm. Integration of the ^{129}Xe NMR spectrum and F-on-Xe(II) region of the ^{19}F NMR spectrum gave values of 0.29 and 0.30[45] for the ratio $[CF_3C(OXeF)NH_2^+]/[XeF_2]$ (initial molar ratios were $CF_3C(OH)NH_2^+AsF_6^-/XeF_2$ = 0.892 and 0.946; initial $[XeF_2]$ = 0.29 and 0.20 M), respectively. Integration of the CF_3 group resonances gave a value of 0.32[45] for the ratio $[CF_3C(OXeF)NH_2^+]/[CF_3C(OH)NH_2^+]$ (initial molar ratio $CF_3C(OH)NH_2^+AsF_6^-/XeF_2$ = 0.946; initial $[XeF_2]$ = 0.20 M), in good agreement with values obtained from the ^{129}Xe NMR spectrum and from the ^{19}F NMR spectrum of the F-on-Xe(II) region.

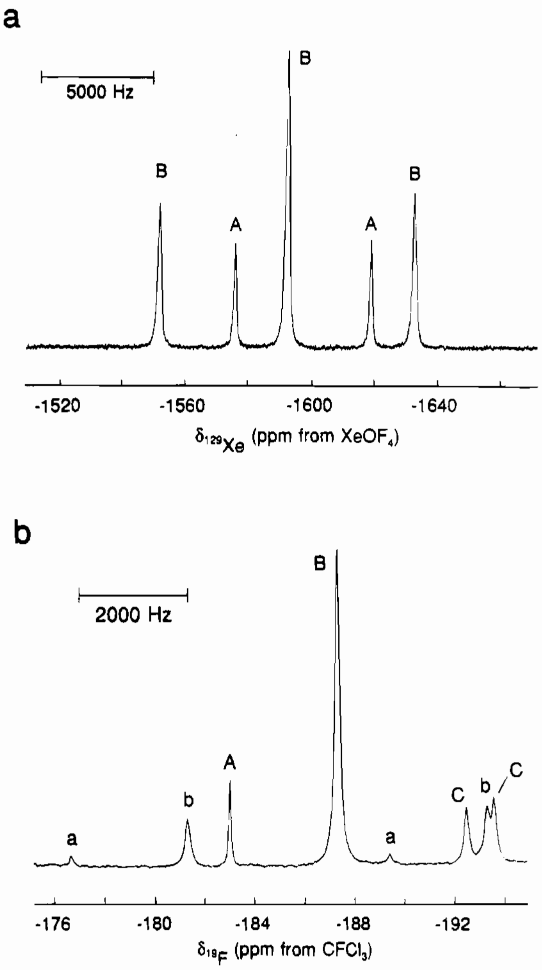


Figure 2. (a) ^{129}Xe NMR spectrum (139.051 MHz) at −53.0 °C of $CF_3C(OXeF)NH_2^+AsF_6^-$ (0.26 M) and XeF_2 (0.29 M) dissolved in BrF_5 solvent: (A) doublet arising from the one-bond coupling $^1J(^{129}Xe-{}^{19}F)$ in the $CF_3C(OXeF)NH_2^+$ cation; (B) triplet arising from the one-bond coupling $^1J(^{129}Xe-{}^{19}F)$ in XeF_2. (b) ^{19}F NMR spectrum (470.599 MHz) at −54.0 °C of $CF_3C(OXeF)NH_2^+AsF_6^-$ (0.18 M) and XeF_2 (0.19 M) dissolved in BrF_5 solvent, where only the F-on-Xe(II) region is shown: (A) $CF_3C(OXeF)NH_2^+$ cation; (B) singlet arising from the fluorine environment of XeF_2; (C) HF. Lower case letters denote ^{129}Xe satellites.

The ^{13}C NMR spectrum of the $CF_3C(OXeF)NH_2^+$ cation (−59.4 °C, BrF_5 solvent) consists of two binomial quartets at −165.7 ppm [$^2J(^{13}C-{}^{19}F)$ = 42 Hz] and at −113.7 ppm [$^1J(^{13}C-{}^{19}F)$ = 285 Hz], which are assigned to the CO and CF_3 carbons, respectively. Satellites arising from $^2J(^{13}C-{}^{129}Xe)$ were not observed in the ^{13}C NMR spectrum due to a low signal-to-noise ratio. The ^1H NMR spectrum of an equimolar mixture of $CF_3C(OXeF)NH_2^+AsF_6^-$ and XeF_2 in BrF_5 solvent at −55.0 °C (Figure 3a) is consistent with equilibrium 2. The two broad peaks of equal intensity at 7.88 and 7.71 ppm are assigned to the chemically inequivalent proton-on-nitrogen resonances of the $CF_3C(OXeF)NH_2^+$ cation arising from hindered rotation about the C−N bond (*vide supra*). This is consistent with an O−Xe−F linkage, since an N−Xe−F linkage would result in free rotation about the C−N bond and the observation of only one proton-on-nitrogen resonance in the ^1H NMR spectrum. The proton-on-oxygen resonance of the $CF_3C(OH)NH_2^+$ cation is observed at 12.04 ppm and is deshielded by 0.41 ppm relative to that of $CF_3C(OH)NH_2^+AsF_6^-$ in BrF_5 solvent at the same temperature (Figure 1a). The two equal-intensity singlets at 8.48 and 8.39 ppm are assigned to the amido protons of the $CF_3C(OH)NH_2^+$ cation (Figure 3a); the separation of the peaks

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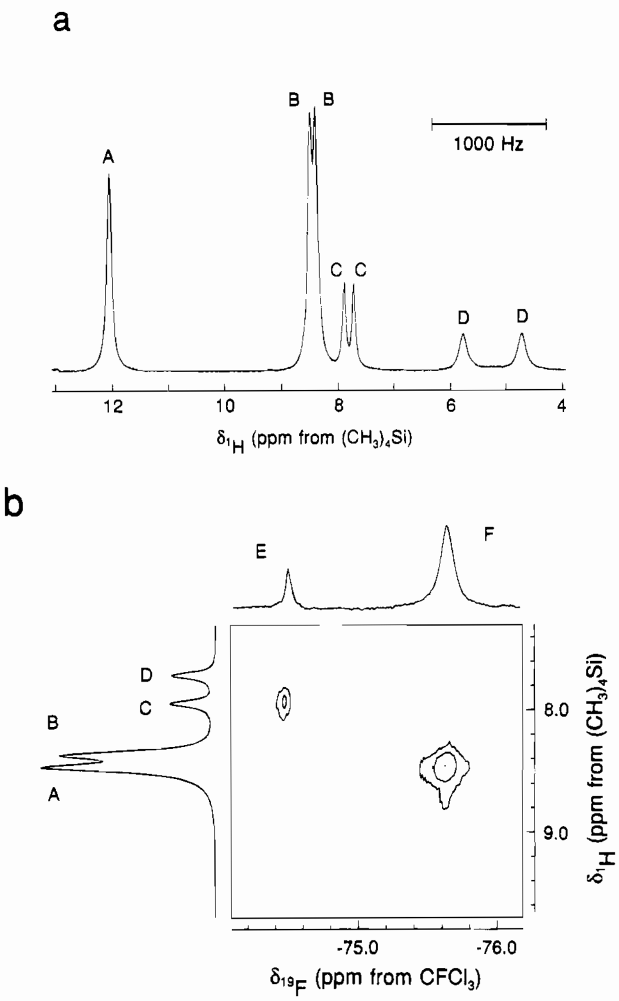

Figure 3. (a) ^1H NMR spectrum (500.138 MHz) at −55.0 °C of $CF_3C(OH)NH_2^+AsF_6^-$ (0.18 M) and XeF_2 (0.19 M) dissolved in BrF_5 solvent: (A) proton on oxygen of $CF_3C(OH)NH_2^+$; (B) protons on nitrogen of $CF_3C(OH)NH_2^+$; (C) protons on nitrogen of $CF_3C(OXeF)NH_2^+$; (D) HF. (b) Heteronuclear [^1H(500.138 MHz)−^{19}F(470.599) MHz)] NOESY spectrum at −57.6 °C of $CF_3C(OH)NH_2^+AsF_6^-$ (0.35 M) and XeF_2 (0.38 M) dissolved in BrF_5 solvent, where portions of the one-dimensional ^1H and ^{19}F NMR spectra are displayed along the vertical and horizontal axes, respectively: (A, B) protons on nitrogen resonances of $CF_3C(OH)NH_2^+$; (C, D) protons on nitrogen which are cis and trans to the CF_3 group, respectively, in $CF_3C(OXeF)NH_2^+$; (E) CF_3 group resonance of $CF_3C(OXeF)NH_2^+$; (F) CF_3 group resonance of $CF_3C(OH)NH_2^+$.

is 135 Hz less than that observed for pure $CF_3C(OH)NH_2^+AsF_6^-$ in BrF_5 solvent (Figure 1a) and is consistent with partial coalescence of the amido protons of the $CF_3C(OH)NH_2^+$ cation arising from proton exchange between the $CF_3C(OH)NH_2^+$ cation and HF according to equilibrium 2. Exchange was confirmed by recording the ^1H NMR spectrum of $CF_3C(OH)NH_2^+AsF_6^-$ in the presence of HF (1.83 molar equiv of anhydrous HF in BrF_5 solvent at −57.6 °C). Complete collapse of the proton-on-nitrogen resonance to a broadened singlet resulted [$\delta(^1H) = 8.59$ ppm, $\Delta\nu_{1/2} = 88$ Hz] with retention of the proton-on-oxygen resonance [$\delta(^1H) = 11.68$ ppm]. Coalescence of the amido proton peaks can arise from two possible mechanisms: deprotonation to give the amidic acid $CF_3C(OH){=}NH$ (eq 5) and N-protonation to give the $CF_3C(OH)-NH_3^{2+}$ dication (eq 6). Both equilibria would account for retention of the proton-on-oxygen resonance. Equilibrium 5 can be discounted since the amidic acid mechanism has been shown to be inhibited by strong acid (H_2SO_4) and contributes to proton exchange only in dilute aqueous acid.[32] The transient diprotonated cation, $CF_3C(OH)-NH_3^{2+}$ (equilibrium 6) could undergo free rotation about the C−N bond, resulting in partial collapse of the amido proton doublet with retention of the proton on oxygen resonance.

$$CF_3C(OH){=}NH_2^+ + HF \rightleftharpoons CF_3C(OH){=}NH + H_2F^+ \quad (5)$$

$$CF_3C(OH){=}NH_2^+ + 2HF \rightleftharpoons CF_3C(OH)-NH_3^{2+} + HF_2^- \quad (6)$$

The protons on nitrogen were assigned by performing a two-dimensional heteronuclear ($^1H-^{19}F$) NOESY experiment in BrF_5 solvent at −57.6 °C (Figure 3b). A correlation was observed between the ^{19}F NMR resonance of the CF_3 group and the high-frequency [$\delta(^1H) = 7.88$ ppm] proton on nitrogen resonance of the $CF_3C(OXeF)NH_2^+$ cation, implying that the high-frequency ^1H NMR resonance arises from the proton cis to the CF_3 group (trans to the OXeF group). It is interesting that the relative shieldings of the proton-on-nitrogen resonances for the $CF_3C(OXeF)NH_2^+$ cation are opposite to those observed for the $CF_3C(OH)NH_2^+$ cation. The change in relative shieldings may result from differences in electronic anisotropy resulting from the different moieties bonded to oxygen in the $CF_3C(OXeF)NH_2^+$ and $CF_3C(OH)NH_2^+$ cations. The CF_3 group in the $CF_3C(OH)NH_2^+$ cation correlates with both the cis and trans protons of the amido group (Figure 3b). This is attributed to insufficient resolution of the partially coalesced proton on nitrogen resonances for the $CF_3C(OH)NH_2^+$ cation resulting from exchange with HF (*vide supra*).

Raman Spectroscopy. $CF_3C(OXeF)NH_2^+AsF_6^-$. Assignments for the $CF_3C(OXeF)NH_2^+$ cation (Table 1 and Figure 4a) were based on the Raman spectra of $CF_3C(O)NH_2$[51] and related compounds containing the O−Xe−F linkage.[15,46,47] Assignments for the AsF_6^- anion were made by comparison with those of $XeF^+AsF_6^-$,[46] $HC{\equiv}NXeF^+AsF_6^-$,[6] and $O_2^+AsF_6^-$.[48]

Evidence for the O−Xe−F linkage is provided by the characteristic bands arising from O−Xe−F stretching and bending fundamentals. Five bands are observed in the ν(Xe−O) and ν(Xe−F) regions. The intense bands at 543 and 530 cm^{-1} are assigned to ν(Xe−F) by comparison with the assigned Xe−F stretches in related xenon(II) compounds: FO_2SOXeF (539, 532, 527, 521 cm^{-1}),[46] *cis*- and *trans*-$F_4OIOXeF$ (527 cm^{-1}),[47] $F_5TeOXeF$ (520 cm^{-1}),[11] CF_3O_2SOXeF (534 cm^{-1}),[15] and $(CF_3)_2S{=}OXeF^+SbF_6^-$ (552 cm^{-1}).[9] The bands at 508, 502, and 476 cm^{-1} are assigned to ν(Xe−O) by comparison with the assigned Xe−O stretches in FO_2SOXeF (434 cm^{-1}),[46] *cis*- and *trans*-$F_4OIOXeF$ (488, 438 cm^{-1}),[47] $F_5TeOXeF$ (457 cm^{-1}),[11] CF_3O_2SOXeF (369 cm^{-1}),[15] and $(CF_3)_2S{=}OXeF^+SbF_6^-$ (494 cm^{-1}).[9] The splitting of the ν(Xe−F) and ν(Xe−O) bands may result from vibrational coupling of two or more cations in the unit cell (factor-group splitting) but cannot be confirmed without knowledge of the crystal structure of $CF_3C(OXeF)NH_2^+AsF_6^-$. Site-symmetry effects can be eliminated as the source of the splitting since the highest possible point-group symmetry for the $CF_3C(OXeF)NH_2^+$ cation is C_s, which does not possess any degenerate irreducible representations. Similar band splittings for modes assigned to ν(Xe−F) are observed in the Raman spectra of $HC{\equiv}N-XeF^+AsF_6^-$,[6] FO_2SOXeF,[46] and $XeF^+MF_6^-$ salts (M = Ru, Pt, Ir).[49] It is interesting to compare the ν(Xe−O) and ν(Xe−F) stretching modes of the $CF_3C(OXeF)NH_2^+$ cation with those of the $(CF_3)_2S{=}O-XeF^+$ cation, since these are the only reported examples of cations containing the O−Xe−F linkage. The ν(Xe−F) and ν(Xe−O) Raman

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Table 1. Raman Frequencies[a] and Assignments for $CF_3C(O)NH_2$, $CF_3C(OH)NH_2^+AsF_6^-$, $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$, and $CF_3C(OXeF)NH_2^+AsF_6^-$

$CF_3C(O)$-NH_2[b]	$CF_3C(OH)$-$NH_2^+AsF_6^-$[c]	$CF_3C(OH)$-$NH_2^+AsF_6^-\cdot$ $XeF_2\cdot xHF$[c]	$CF_3C(OXeF)$-$NH_2^+AsF_6^-$[c]	assgnts
3337 (7)		3336 (0.2)[e]		$\nu_{asym}(NH_2)$
	3227 (3)[d]		3355 (1)[d]	
	3211 (3)[d]			
3174 (11)		3205 (0.9)[e]		$\nu_{sym}(NH_2)$
		3090 (1.5)		$\nu_{sym}(HF)$
1706 (40)	1519 (3)	1549 (2)	1562 (1)	$\nu(CO)$
			1543 (1)	
1629 (5)	*f*	1631 (0.4)	1623 (0.5)	$\delta(NH_2)$
1460 (31)	1767 (5)	1750 (1.5)	1745 (2)	$\nu(CN)$
	1276 (5)	1262 (3)		$\delta(OH)$
		1232 (4)		
1199 (4)	1197 (3)	1202 (1)	*f*	$\gamma(NH_2)$
		1182 (2)		
f	1314 (11) or 1384 (19)[g]	1308 (0.5) or 1385 (1)[g]	1304 (1) or 1384 (4)[g]	$\nu_{sym}(CF_3)$
1135 (100)	1218 (7)[g]	1064 (6)	1073 (3)	$\nu_{asym}(CF_3)$
796 (45)	806 (3)	827 (0.6)	810 (8)	$\tau(NH_2)$
		806 (7)		
f	734 (8)[g]	742 (0.7)	747 (5)	$\delta_{sym}(CF_3)$
	720 (23)	719 (2)	724 (sh)	$\nu_3(AsF_6)$[h]
		714 (sh)	702 (3)	
		703 (0.7)	693 (2)	
	691 (100)	688 (13)	683 (19)	$\nu_1(AsF_6^-)$[h]
		680 (2)		
		646 (2)	647 (6)	
666 (11)	670 (15)	674 (6)	672 (1)	$\omega(NH_2)$
		669 (2)		
591 (10)	600 (23)	610 (1)	596 (5)	$\delta(OCN) + \pi(OCN)$
		605 (1)		
		600 (3)		
	578 (15)	589 (2)	589 (2)	$\nu_2(AsF_6^-)$[h]
		583 (5)	577 (2)[g]	
		578 (1)		
		571 (0.8)		
		560 (3)		
			543 (29)	$\nu_{asym}(OXeF)$
			530 (100)	
			508 (18)	$\nu_{sym}(OXeF)$
			502 (34)	
			476 (23)	
513 (2)	547 (13)	*f*	523 (4)	$\delta_{asym}(CF_3)$
	513 (8)			
		515 (100)		$\nu_{sym}(FXeF)$
		511 (79)		
430 (30)	434 (13)	436 (2)	432 (8)	$\gamma(CF_3)$
415 (39)	412 (13)	409 (2)	419 (3)	
	389 (25)[g]	*f*	409 (0.3)	$\nu_4(AsF_6^-)$[h]
		f	405 (0.3)	
	372 (18)	398 (0.8)	398 (3)	$\nu_5(AsF_6^-)$[h]
	363 (15)	394 (0.8)	393 (8)	
		363 (0.4)	390 (6)	
		343 (0.4)	385 (14)[g]	
			379 (14)[g]	
			371 (9)	
			366 (12)	
			363 (12)	
			292 (12)[i]	$\delta(COXe)$
291 (8)	273 (6)	274 (0.8)	255 (10)	$\gamma(C{-}C)$
266 (23)		261 (1)		
	251 (9)	248 (0.1)	277 (1)	$\nu_6(AsF_6^-)$[h]
		242 (0.3)	265 (3)	
			247 (2)	
			239 (2)	
168 (9)	167 (1)	*f*	*f*	$\tau(C{-}C)$
			141 (9)	$\delta(OXeF)$
	139 (50)	157 (3)		H-bonding and lattice modes
	100 (3)	152 (5)		
	78 (4)	141 (2)		
		119 (6)		
		112 (6)		
		97 (2)		
		81 (7)		
		70 (4)		
		58 (3)		

[a] Values in parentheses denote relative intensities; sh denotes a shoulder. [b] Recorded at room temperature in a glass sample tube; this work. Assignments have been taken from ref 51. [c] Raman spectra were recorded in FEP sample tubes at −165 °C. Raman lines due to the FEP sample tube have been omitted from the table unless overlap with a sample tube band is likely. Data are given for the spectra depicted in Figure 4a−c. [d] The symmetries of the N−H stretches cannot be assigned from the available data. [e] The broadness of the $\nu_{asym}(NH_2)$ and $\nu_{sym}(NH_2)$ bands is attributed, in part, to hydrogen bonding involving solvated HF. [f] Bands not observed in the Raman spectrum. [g] Band may overlap with an FEP sample tube band. [h] Notation provided for the fundamental modes of the AsF_6^- anion is that for O_h symmetry. The splitting of degenerate modes may be attributable to low site symmetry in the solid state or vibrational coupling within the unit cell. [i] The band assigned to the δ(C−O−Xe) bend in the $CF_3C(OXeF)NH_2^+$ cation is coincident with an FEP band at 292 cm^{-1}. This is indicated by the increased intensity of this band relative to the most intense FEP band at 734 cm^{-1}.

bands in the structurally related $(CF_3)_2S{=}O{-}XeF^+$ cation were observed at 552 and 494 cm^{-1}, respectively.[9] The average of the bands assigned to ν(Xe−O) for the $CF_3C(OXeF)NH_2^+$ cation, 495 cm^{-1}, is very similar to ν(Xe−O) in the $(CF_3)_2S{=}O{-}XeF^+$ cation, and the average of the bands assigned to ν(Xe−F) for the $CF_3C(OXeF)NH_2^+$ cation, 536 cm^{-1}, is 16 cm^{-1} lower than ν(Xe−F) for the $(CF_3)_2S{=}O{-}XeF^+$ cation. Raman spectroscopic trends in the terminal Xe−F stretches of xenon(II) compounds indicate a more ionic Xe−F bond in the $CF_3C(OXeF)NH_2^+$ cation than in the $(CF_3)_2S{=}O{-}XeF^+$ cation (see Nature of the Bonding in $CF_3C(OXeF)NH_2^+$). The bands at 141 and 292 cm^{-1} are assigned to the O−Xe−F and C−O−Xe bending modes, respectively. Comparable values for δ(O−Xe−F) and δ(X−O−Xe) are observed in structurally related xenon(II) compounds containing the O−Xe−F linkage.[9,11,15,46,47]

The band at 3335 cm^{-1} in the Raman spectrum of $CF_3C(OXeF)NH_2^+AsF_6^-$ is assigned to an NH stretching mode. Two bands are usually observed in the vibrational spectra of primary amides arising from the symmetric and asymmetric NH_2 stretches.[50] Although peaks observed at 3174 and 3337 cm^{-1} can be assigned to $\nu_{sym}(NH_2)$ and $\nu_{asym}(NH_2)$, respectively, in the Raman spectrum of solid trifluoroacetamide,[51] it is not possible to assign the NH stretch of $CF_3C(OXeF)NH_2^+AsF_6^-$ to a particular symmetry species since the bands observed in this region for O-complexed amides are often not directly comparable to the bands of the free amide.[52,53] The out-of-plane wag of the NH_2 group, $\omega(NH_2)$, is assigned to the band at 672 cm^{-1} by comparison with $CF_3C(O)NH_2$ (666 cm^{-1}),[51] and the frequency increase (6 cm^{-1}) is attributed to O-coordination of $CF_3C(O)NH_2$ to the XeF^+ cation and an attendant increase in C−N double bond character. This mode is observed at 639 cm^{-1} in matrix isolated $CF_3C(O)NH_2$, and complexation with HF by bridging of the HF molecule between oxygen and an NH proton results in an increase of 17 cm^{-1}.[54] The fundamental arising from the torsional motion of the NH_2

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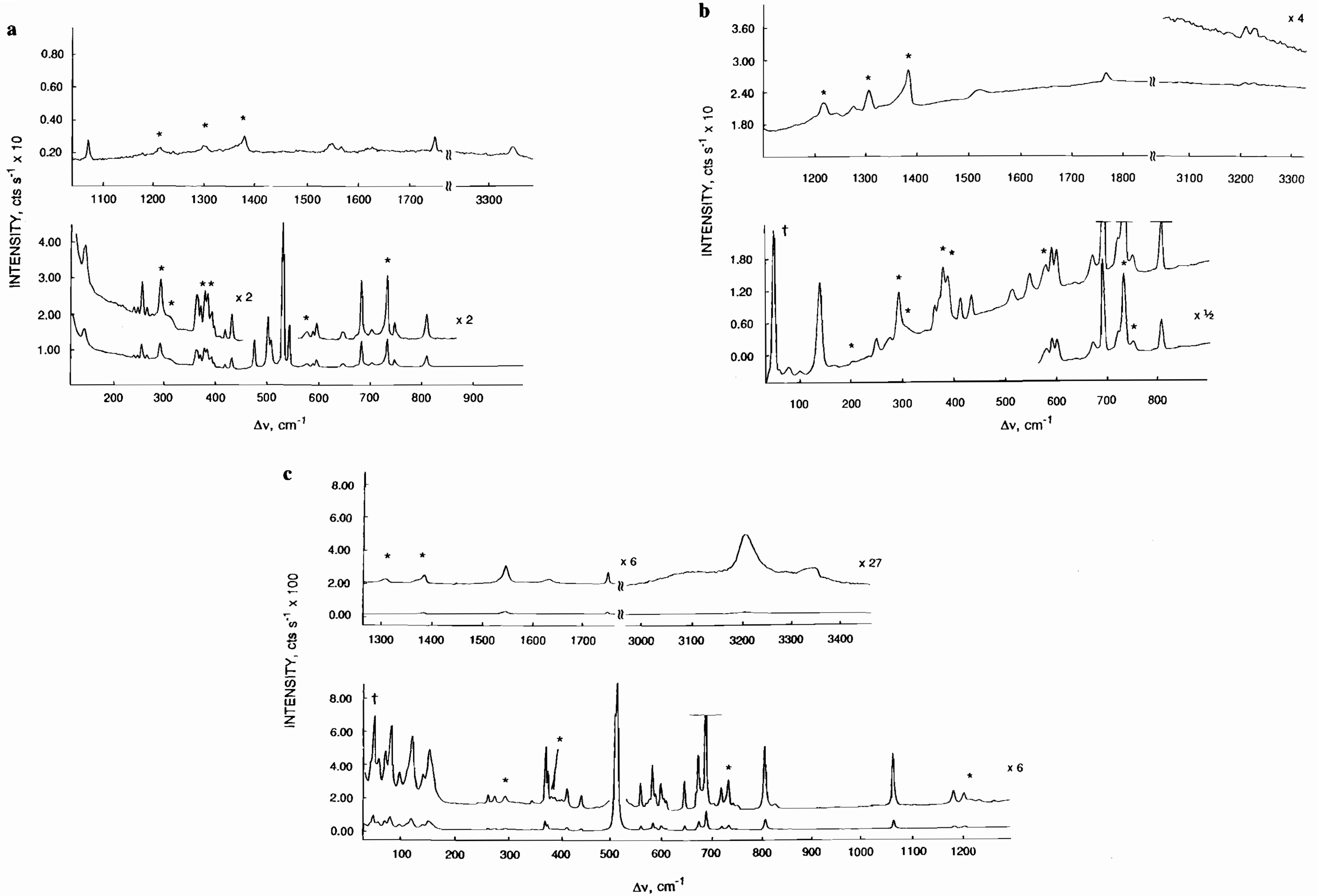

Figure 4. Raman spectra of microcrystalline (a) CF$_3$C(OXeF)NH$_2$$^+AsF_6$$^-$, (b) CF$_3$C(OH)NH$_2$$^+AsF_6$$^-$, and (c) CF$_3$C(OH)NH$_2$$^+AsF_6$$^-$·XeF$_2$·$x$HF recorded in FEP sample tubes at −165 °C using 514.5-nm excitation. Asterisks (*) denote FEP sample tube lines. Daggers (†) denote an artifact characteristic of the instrument.

group, $\tau(NH_2)$, is tentatively assigned to the band at 810 cm^{-1} by analogy with solid $CF_3C(O)NH_2$ (796 cm^{-1}).[51] The increase in $\tau(NH_2)$ (14 cm^{-1}) is attributed to an increase in C−N double bond character resulting from O-coordination. The rocking motion fundamental, $\gamma(NH_2)$, is not observed in the Raman spectrum of $CF_3C(OXeF)NH_2^+AsF_6^-$ but is observed as a weak band at 1199 cm^{-1} in the Raman spectrum of solid $CF_3C(O)NH_2$.[51] The band at 1623 cm^{-1} has been assigned primarily to the in-plane bending mode, $\delta(NH_2)$, which is 6 cm^{-1} lower than that observed for $CF_3C(O)NH_2$. This mode is relatively insensitive to complexation, as observed for several primary amides and their HF complexes.[54]

The bands at 1543, 1562, and 1745 cm^{-1} result from the ν(CO) and ν(CN) stretching modes. Although vibrational coupling of these modes is likely, ν(CO) is formally assigned to the bands at 1543 and 1562 cm^{-1} (Table 1) following the method of assignment for amidium salts,[55] which are electronically similar to the $CF_3C(OXeF)NH_2^+$ cation. The CO stretching frequency is expected to be lower than that of uncomplexed $CF_3C(O)NH_2$ because the double-bond character of the C−O linkage is significantly reduced upon O-coordination. This implies dominance of resonance structure **IV** in the bonding of the $CF_3C(OXeF)NH_2^+$ cation. Correspondingly, the C−N stretch is expected to increase significantly and is assigned to the band at 1745 cm^{-1}, which is close to the observed range for ν(CN) in the infrared spectra of O-protonated and O-alkylated amides[56] (ca. 1600−1730 cm^{-1}). Unambiguous evidence for the reversal of ν(CO) and ν(CN) frequencies upon O-protonation of amides has been provided by Cook,[57] who compared the infrared spectra of *N*-acyltrialkylammonium halides and O-protonated *N,N*-dicyclohexylacetamide hydrohalide salts. Since the former are isoelectronic with the hypothetical N-protonated amides, a direct comparison of the infrared spectra of these salts with those of the neutral compounds aided in the assignment of the ν(CO) and ν(CN) bands. Following previously published assignments,[51] the bands at 1706 and 1460 cm^{-1} in the Raman spectrum of $CF_3C(O)NH_2$ are assigned to ν(CO) and ν(CN), respectively. When compared to $CF_3C(OXeF)NH_2^+AsF_6^-$, these values show a decrease in ν(CO) of 154 cm^{-1} and an increase in ν(CN) of 285 cm^{-1} in the xenon cation. Similar values of ν(CO) and ν(CN) have been reported from the infrared spectra of protonated amides; for example, ν(CO) for the O-protonated salt of *N,N*-dimethylacetamide, $CH_3C(OH)N(CH_3)_2^+SbCl_6^-$,[55] is observed at 1401 cm^{-1} and that of *N,N*-dimethylacetamide vapor is observed at 1651 cm^{-1} ($\Delta\nu$(CO) = 250 cm^{-1}),[58] whereas the value of ν(CN) increases to 1680 cm^{-1} (average of three bands) upon O-protonation of *N,N*-dimethylacetamide,[55] compared to 1492 cm^{-1} for the amide vapor ($\Delta\nu$(CO) = 188 cm^{-1}).[58] An incomplete report of the infrared spectrum of $CF_3(O)NH_2{\cdot}BF_3$ provides a value of 1760 cm^{-1} for ν(CO).[59] If $CF_3(O)NH_2{\cdot}BF_3$ is indeed O-bonded, it is likely that ν(CO) has been misassigned in light of the well-established trends noted above for ν(CO) and ν(CN).

The in-plane (δ) and out-of-plane (π) OCN bends are tentatively assigned to the peak at 596 cm^{-1} by analogy with $CF_3C(O)NH_2$,[51] assuming that they are similar in the $CF_3C(OXeF)NH_2^+$ cation.

The CF_3 group modes of $CF_3C(OXeF)NH_2^+$ are assigned by analogy with those in the Raman spectrum of solid $CF_3C(O)NH_2$: 1073 [$\nu_{asym}(CF_3)$], 747 [$\delta_{sym}(CF_3)$], 523 [$\delta_{asym}(CF_3)$], and 432, 419 cm^{-1} [$\gamma(CF_3)$]. The symmetric stretch, $\nu_{sym}(CF_3)$, is not observed in the Raman spectra of $CF_3C(O)NH_2$ and $CF_3C(OXeF)NH_2^+$ but is observed at 1340 cm^{-1} in the infrared spectrum of $CF_3C(O)NH_2$.[51] The symmetric stretch of the CF_3 group is not observed in the Raman spectrum of the $CF_3C(OXeF)NH_2^+$ cation, because it is too weak and/or because it coincides with an FEP sample tube band at 1384 cm^{-1}.

A total of 21 bands are assigned to the AsF_6^- anion and are derived from the six normal modes for AsF_6^- under O_h point symmetry.[60] Since only three bands [$\nu_1(A_{1g})$, $\nu_2(E_g)$, and $\nu_5(F_{2g})$] are Raman active for O_h symmetry, a reduction of anion symmetry is apparent. A symmetry of C_{2v} or C_s would account for the observation of 15 normal modes, since all mode degeneracies would then be removed. The number of bands may result from a low site symmetry for the AsF_6^- anion in the unit cell or from a true distortion of the molecular geometry of the anion due to hydrogen-bonding interactions with the protons of the cation, as observed in the SbF_6^- and AsF_6^- salts of OH_3^+,[61] SH_3^+,[62] and $NF_2H_2^+$.[63] The observation of more than 15 bands is attributed to intermolecular vibrational coupling within the crystallographic unit cell. This is likely since low site symmetry alone cannot account for the splitting of the nondegenerate $\nu_1(A_{1g})$ mode for AsF_6^- (647, 683 cm^{-1}). A crystal structure is required, however, to confirm these assignments.

$CF_3C(OH)NH_2^+AsF_6^-$. The assignments for the Raman spectrum of $CF_3C(OH)NH_2^+AsF_6^-$ were made by analogy with those of $CF_3C(O)NH_2$[51] and $CF_3C(OXeF)NH_2^+AsF_6^-$ (Table 1 and Figure 4b). The ν(CO) and ν(CN) modes are assigned to the bands at 1519 and 1767 cm^{-1}, indicating greater double-bond character for the C−N bond than for the C−O bond and are similar to those of the $CF_3C(OXeF)NH_2^+$ cation. The bands attributed to $\omega(NH_2)$ (670 cm^{-1}), $\tau(NH_2)$ (806 cm^{-1}), and $\gamma(NH_2)$ (1197 cm^{-1}) are also similar to those observed in the Raman spectra of $CF_3C(O)NH_2$ and $CF_3C(OXeF)NH_2^+AsF_6^-$. A band attributable to $\delta(NH_2)$ was not observed and is likely the result of the inherent low Raman intensity of this band.[64]

The band at 1276 cm^{-1} has been tentatively assigned to δ(OH) of the protonated carbonyl group. Infrared spectra of the related salts $CH_3C(OH)NH_2^+X^-$ (X = $SbCl_6$, NO_3, Cl),[52] $[CH_3C(OH)NH_2^+]_2X^{2-}$ (X = $SnCl_6$, $PtCl_6$),[52] and $CH_3C(OH)N(CH_3)_2^+X^-$ (X = Cl, Br, I, $SbCl_6$)[55] exhibit bands at 1333−1368 and 1040−1192 cm^{-1}, respectively, which are assigned to δ(OH). Bands attributable to γ(OH) and ν(OH), which, like $\delta(NH_2)$, usually have very low Raman intensities,[64] were too weak to be observed.

Seven bands have been assigned to the AsF_6^- anion, as opposed to three bands expected for AsF_6^- with O_h symmetry. Again, hydrogen bonding between cation and anion, as in the salt, $CF_3C(OXeF)NH_2^+AsF_6^-$, may contribute to symmetry lowering of the anion. Low site symmetry in the solid may also give rise to the splitting of the ν_5 band and observation of ν_3 (720 cm^{-1}) and ν_6 (251 cm^{-1}), both of which are formally Raman forbidden for octahedral XY_6 species.[60] All bands are assigned except ν_4 (ca. 420 cm^{-1}). This can be accounted for by considering the low intensity of this band in the Raman spectrum of $HC{\equiv}NXeF^+AsF_6^-$,[6] combined with the presence of bands in this region due to the FEP sample tube.

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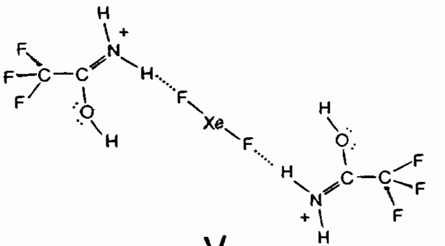
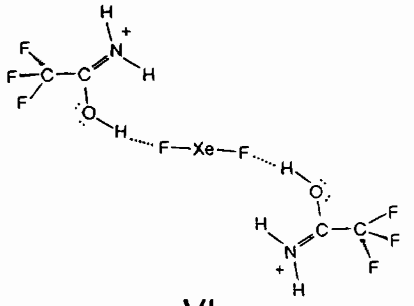
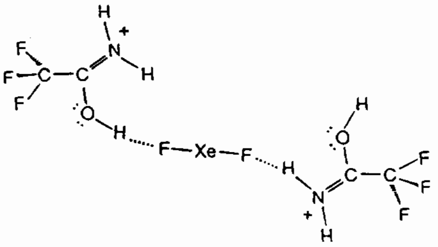
$CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$. A white microcrystalline powder precipitates upon rapid removal of the HF solvent under vacuum from a solution containing stoichiometric amounts of $CF_3C(O)NH_2$ and $XeF^+AsF_6^-$ or $CF_3C(OH)NH_2^+AsF_6^-$ and XeF_2. The Raman spectroscopic results (Table 1 and Figure 4c) are consistent with the formulation $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$. The Raman spectrum resembles that expected for a mixture of polycrystalline XeF_2 and $CF_3C(OH)NH_2^+AsF_6^-$. However, the average of the very intense peaks at 511 and 515 cm^{-1}, assigned to ν_{sym}(Xe−F) of XeF_2 incorporated in the adduct, is 17 cm^{-1} higher in frequency than the symmetric Xe−F stretch for polycrystalline XeF_2 (495 cm^{-1}).[65a] The interaction of XeF_2 with fluoroacids as in $XeF^+AsF_6^-$,[66] $XeF^+Sb_2F_{11}^-$,[67] and $XeF_2\cdot XeF_5^+AsF_6^-$ [68] results in elongation of one Xe—F bond (the Xe---F bridge bond) in complexed XeF_2, accompanied by a shortening of the remaining (terminal) Xe−F bond. This results in bands which are assignable to a bridging Xe•••F stretch and a terminal Xe—F stretch, that are lower and higher in frequency, respectively, than ν_{sym}(Xe—F) [496 cm^{-1}][65b] and ν_{asym}(Xe—F) [547 cm^{-1}][65c] in uncoordinated XeF_2, from which they are formally derived. The latter mode is Raman forbidden for XeF_2 under $D_{\infty h}$ point symmetry. The absence of a relatively intense band assignable to ν_{asym}(Xe−F) at approximately 550 cm^{-1} in the Raman spectrum of $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$ indicates that the Xe−F bonds in coordinated XeF_2 are essentially symmetric. The frequency of ν_{sym}(Xe−F) is also inconsistent with an XeF_2 molecule containing significantly different Xe−F bond lengths (*vide supra*). The observation of two peaks for ν_{sym}(Xe−F) is attributed to vibrational coupling of XeF_2 molecules within the unit cell of $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$. By analogy with known adducts containing symmetric XeF_2,[69] it is probable that the fluorine ligands of XeF_2 interact with the positive centers of the $CF_3C(OH)NH_2^+$ cation in the adduct $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$, namely the hydroxyl and amido protons, through hydrogen bonding. Structures **V−VII** illustrate possible hydrogen bonding interactions of XeF_2 and $CF_3C(OH)NH_2^+$ in which the local molecular point symmetry of XeF_2 does not deviate significantly from $D_{\infty h}$.


V


VI


VII

Further evidence for the assigned structure of the solvate $CF_3C(OH)NH_2^+AsF_6^-\cdot XeF_2\cdot xHF$ was obtained by comparing bands in the amide region of the Raman spectrum with those of $CF_3C(O)NH_2$ and $CF_3C(OH)NH_2^+AsF_6^-$. The bands at 1767 and 1549 cm^{-1} are assigned to ν(CN) and ν(CO), respectively. This is consistent with an increase of 262 cm^{-1} for ν(CN) and a decrease of 157 cm^{-1} for ν(CO) relative to $CF_3C(O)NH_2$ and with the changes in C−N and C−O bond order anticipated upon O-protonation of amides. The bands at 1262 and 1232 cm^{-1} are assigned to the bending mode, δ(OH), and are similar to the value assigned for $CF_3C(OH)NH_2^+AsF_6^-$ (1276 cm^{-1}). As in the Raman spectrum of $CF_3C(OH)NH_2^+AsF_6^-$, modes arising from ν(OH) and γ(OH) are presumably too weak to be observed. Evidence for solvation by HF is provided by the presence of a broad band at 3090 cm^{-1}, which is assigned to ν_{sym}(HF) and is similar to that observed in the infrared spectra of hydrogen-bonded complexes of HF with $CF_3C(O)NH_2$.[54]

A total of 17 bands are attributed to the AsF_6^- anion and have been assigned using arguments similar to those already presented for $CF_3C(OH)NH_2^+AsF_6^-$ and $CF_3C(OXeF)NH_2^+AsF_6^-$.

Nature of the Bonding in $CF_3C(OXeF)NH_2^+$. The bonding in the $CF_3C(OXeF)NH_2^+$ cation can be assessed using trends for xenon(II) compounds that are well established from Raman and NMR spectroscopy. Previous NMR studies of xenon(II) derivatives containing XeF groups bonded to oxygen or fluorine have shown that the ^{19}F and ^{129}Xe NMR parameters can be used to assess the relative covalent characters of the Xe−O, Xe---F bridge, and terminal Xe−F bonds in compounds of the type

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(65) (a) ν_{sym}(Xe−F) = 495 cm^{-1} in the Raman spectrum measured at −165 °C; this work. (b) Smith, D. F. In *Noble Gas Compounds*; Hyman, H. H., Ed.; University of Chicago Press: Chicago and London, 1963; p 295. (c) Turner, J. J.; Pimentel, G. C. In ref 65b, p 101.

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(69) Examples of molecular adducts containing symmetric XeF_2 ($D_{\infty h}$ point symmetry) include $XeF_2\cdot IF_5$ (Jones, G. R.; *et al. Inorg. Chem.* **1970**, *9*, 2264), $XeF_2\cdot XeOF_4$ (Bartlett, N.; Wechsberg, M. *Z. Anorg. Allg. Chem.* **1971**, *385*, 5), $XeF_2\cdot 2XeF_6\cdot 2AsF_5$,[68] $XeF_2\cdot XeF_4$ (Burns, J. H.; *et al. Acta Crystallogr.* **1965**, *18*, 11) and $Ag(XeF_2)_2AsF_6$ (Hagiwara, R.; *et al. Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 855). The Raman spectra of these adducts are essentially reproduced by summing the spectra of the starting materials and are consistent with negligible changes in the bonding of the constituent molecules in the adducts. The adducts $XeF_2\cdot 2XeF_6\cdot 2AsF_5$ and $Ag(XeF_2)_2AsF_6$ are the only previously reported examples of symmetrical XeF_2 coordinated to cations. The Raman spectrum of the former shows a prominent peak at 498 cm^{-1} that is assigned to ν_{sym}(Xe−F) for XeF_2 in the adduct, which is not significantly different from that observed for crystalline XeF_2, at 496 cm^{-1}.[65b] The bands attributed to ν_{sym}(Xe−F) in $Ag(XeF_2)_2AsF_6$ occur at 501 and 508 cm^{-1}, indicating an average increase of 8 cm^{-1} relative to crystalline XeF_2. The crystal structures of $XeF_2\cdot 2XeF_6\cdot 2AsF_5$ and $Ag(XeF_2)_2AsF_6$ indicate that the fluorine ligands of XeF_2 are weakly coordinated to the cations (central Xe atom of XeF_5^+ and Ag^+, respectively) and the Xe−F bond lengths of 2.01(2) and 1.979(3) Å are not significantly different from the Xe−F bond length in crystalline XeF_2 (2.00(1) Å) (Levy, H. A.; Agron, P. A. *J. Am. Chem. Soc.* **1963**, *85*, 241). This is consistent with little alteration of the bonding of XeF_2 in these adducts; the intermolecular bonding in these adducts may be attributed primarily to the electrostatic interaction of the cation and the fluorine atoms of XeF_2, which contain partial negative charge due to a high degree of Xe−F bond polarity (also see ref 70, p 259).

Table 2. Comparison of Chemical Shifts, One-Bond Xe−F Coupling Constants, and ν(Xe−F) of L−Xe−F Derivatives

		NMR parameters[a]				
species	ν(Xe−F),[b] cm^{-1}	$^1J(^{129}Xe-^{19}F)$, Hz	$\delta(^{129}Xe)$,[c] ppm	$\delta(^{19}F)$,[d] ppm	*T*, °C	ref
$F_{10}Sb_2F^- - - -XeF^+$ [e]	619	7230	−574	−290.2	23	42, 67, 73, 75
$F-Xe- - -F- - -Xe-F^+$	593	6740	−1051	−252.0	−62	42, 67, 73
$(CF_3)_2S{=}OXeF^+SbF_6^-$	552	6343	−1679		−70	9
$F_3S{\equiv}NXeF^+AsF_6^-$	554	6248	−1661	−180.5	−60	76
$HC{\equiv}NXeF^+AsF_6^-$	564	6181	−1569	−198.4[f]	−58	2, 6
$CH_3C{\equiv}NXeF^+AsF_6^-$ [g]	560	6020	−1708	−185.5	−10	2
$CF_3C(OXeF)NH_2^+AsF_6^-$	536	5991	−1578	−183.1	−54	*h*
4-$(CF_3)C_5F_4NXeF^+AsF_6^-$	524	5963	−1853	−144.6	−50	4
$C_5F_5NXeF^+AsF_6^-$	528	5926	−1922	−139.6	−30	4
s-$C_3F_3N_2NXeF^+AsF_6^-$	548	5932	−1862	−145.6	−50	3
cis-$F_4OIOXeF$	527	5803	−1824	−161.7[i]	0	47
trans-$F_4OIOXeF$	527	5910	−1720	−170.1[i]	0	47
FO_2SOXeF	528	5830	−1666		−40	15, 42, 46, 73
$F_5TeOXeF$[j]	520	5670	−2051	−151.0[k]	26	76, 77
$(FO_2S)_2NXeF$	506	5586	−1977	−126.1	−58	24, 27
$CF_3C(O)OXeF$[l]	510	5550	−2176		−30	10, 12
XeF_2	495	5621	−1685	−184.3	−52	3, 65a

[a] Spectra were recorded in BrF_5 solvent unless otherwise indicated. The NMR parameters of the XeF group, in particular $\delta(^{129}Xe)$, are very sensitive to solvent and temperature conditions; it is therefore important to make comparisons in the same solvent medium and at the same or nearly the same temperature. Table entries refer to the terminal fluorine on the xenon atom. [b] Vibrational data refer to terminal Xe−F stretches. [c] Referenced with respect to the neat liquid $XeOF_4$ at 30 °C. [d] Referenced with respect to the neat liquid $CFCl_3$ at 30 °C. [e] NMR parameters recorded in SbF_5 solvent. [f] $\delta(^{19}F)$ measured in anhydrous HF solvent at −10 °C. [g] NMR parameters measured in HF solvent. [h] This work. [i] $\delta(^{19}F)$ measured in SO_2ClF solvent at −40 °C. [j] NMR parameters measured in SO_2ClF solvent. [k] NMR parameters measured in SO_2ClF solvent at −50 °C. [l] Vibrational spectrum obtained using infrared spectroscopy in acetonitrile solvent at ambient temperature. NMR parameters obtained in $CD_3C{\equiv}N$ solvent at −30 °C.

F−Xe−L (L = ligand atom).[7,42−44] In general, as the ionic character of the Xe−L bond increases, the covalent character of the terminal Xe−F bond increases, increasing the formal charge on xenon. This trend is paralleled by increasing values of $\delta(^{129}Xe)$ and $^1J(^{129}Xe-^{19}F)$, and decreasing values of $\delta(^{19}F)$ for the terminal Xe−F group. The pattern observed in the ^{19}F and ^{129}Xe NMR spectra is complemented by measurements of ν(Xe−F) provided by Raman spectroscopy, which signify increased covalent character of the Xe−F bond with shifts to higher frequency, and *vice versa*.[7]

Table 2 lists the relevant NMR and Raman spectroscopic data for the $CF_3C(OXeF)NH_2^+$ cation and some related Xe−O, Xe−N, and Xe---F bonded compounds of Xe(II) arranged in approximate order of increasing ionic character of the Xe−F bond. Xenon difluoride and $XeF^+Sb_2F_{11}^-$, in which the XeF^+ cation is fluorine bridged to the weakly fluorobasic $Sb_2F_{11}^-$ anion,[67] provide the upper and lower limits, respectively, of the terminal Xe−F bond ionic character. The charge distribution for XeF_2 may be represented as $F^{-1/2}Xe^+F^{-1/2}$, indicating a high degree of Xe−F bond ionic character.[70] The low basicity of the $Sb_2F_{11}^-$ anion provides the closest approximation to a free XeF^+ cation in $XeF^+Sb_2F_{11}^-$ where the Xe−F bond order approaches one. Consistent with the valence bond structures **VIII** and **IX**, the degree of Xe−F bond ionic character in

$$\underset{\textbf{VIII}}{L-Xe^+\ F^-} \leftrightarrow \underset{\textbf{IX}}{L^-\ Xe-F^+} \leftrightarrow \underset{\textbf{X}}{L^-\ Xe^{2+}\ F^-}$$

$$\underset{\textbf{XI}}{L-Xe^{2+}\ F^-} \leftrightarrow \underset{\textbf{XII}}{L\ Xe-F^+} \leftrightarrow \underset{\textbf{XIII}}{L\ Xe^{2+}\ F^-}$$

L−Xe−F depends upon the basicity of the ligand L.[7] As can be inferred from ^{19}F and ^{129}Xe NMR shielding trends, the magnitude of $^1J(^{19}F-^{129}Xe)$, and terminal Xe−F stretching frequencies (Table 2), the Xe−O bond in the $CF_3C(OXeF)NH_2^+$ cation is significantly more covalent than those of the Xe−N-bonded cations $F_3S{\equiv}N-XeF^+$, $HC{\equiv}N-XeF^+$, and $CH_3C{\equiv}N-XeF^+$, which have been shown to have highly ionic Xe−N bonds.[7] On the basis of $^1J(^{129}Xe-^{19}F)$ and ν(XeF), the Xe−F bond in the $CF_3C(OXeF)NH_2^+$ cation is more ionic than the Xe−F bond in $(CF_3)_2S{=}O-XeF^+$, implying a more covalent Xe−O bond in the former cation. The $\delta(^{129}Xe)$ values are, however, opposite in direction to the trend established above, but the difference in the solvents and temperatures used, and the large influence that these factors are known to have on the ^{129}Xe NMR chemical shifts of Xe(II) compounds,[42,43] renders this parameter unreliable for assessing Xe−F bond ionicity in the present case. One possible factor contributing to the ionic character of the Xe−O bonds in the $(CF_3)_2S{=}O-XeF^+$ and $CF_3C(OXeF)NH_2^+$ cations is the formal hybridization on oxygen. In general, a greater s-contribution to the hybridization of the ligand donor atom is expected to increase its effective electronegativity,[71] resulting in a more ionic Xe−L bond. This is illustrated in the series of cations containing Xe−N bonds, where the Xe−N bonds of the cations containing formally sp-hybridized nitrogen (e.g., $F_3S{\equiv}N-XeF^+$, $RC{\equiv}N-XeF^+$) are consistently more ionic than the Xe−N bonds in cations containing formally sp^2-hybridized nitrogen (e.g., 4-$CF_3C_5F_4N-XeF^+$, $C_5F_5N-XeF^+$, *s*-$C_3F_3N_2N-XeF^+$). The oxygen of the $(CF_3)_2S{=}OXeF^+$ cation is formally sp^2-hybridized, whereas resonance structure **IV** for the $CF_3C(OXeF)NH_2^+$ cation indicates π-donation from nitrogen to carbon, which effectively lowers the s-contribution to hybridization on oxygen so that it is intermediate between sp^2 and sp^3, resulting in a more covalent Xe−O bond in the $CF_3C(OXeF)NH_2^+$ cation. It is also apparent from Table 2 that cationic $L-Xe-F^+$ compounds exhibit spectroscopic properties which are consistent with more ionic Xe−L bonds than the structurally analogous neutral compounds. This can be rationalized using a simple valence bond description. Resonance structures **VIII**−**X** represent the bonding in the neutral molecules L−Xe−F, whereas **XI**−**XIII** represent the corresponding cationic species $L-Xe-F^+$. For the neutral species L−Xe−F, resonance structure **X** contributes least to the bonding as a result of the dipositive charge on xenon. The

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relative weights of **VIII** and **IX** depend on the group electronegativity of the ligand L, with a greater contribution from structure **VIII** for lower electronegativity of L. For the L−Xe−F^+ cations, resonance structures **XI** and **XIII** have reduced weights relative to **XII** as a result of the high charge localization. Thus, resonance structure **XII**, which represents a purely ionic interaction of the ligand L and XeF^+, is expected to dominate the bonding in $CF_3C(OXeF)NH_2^+$ and related O- and N-bonded xenon(II) cations.

Experimental Section

Apparatus and Materials. All manipulations were performed under strictly anhydrous conditions in a nitrogen-filled drybox (Vacuum Atmospheres Model DLX) or on a vacuum line constructed from 316 stainless steel, nickel, Teflon, and FEP.

Preparative work involving anhydrous HF and BrF_5 solvents was carried out in lengths of FEP tubing which were heat-sealed at one end and connected through 45° SAE flares to Kel-F valves, dried under vacuum, and passivated with F_2 prior to use.

Literature methods were used to prepare AsF_5,[72] XeF_2,[72] and $XeF^+AsF_6^-$ [73] and to purify HF[6] (Harshaw Chemical Co.) and BrF_5 [6] (Ozark Mahoning Co.).

Chloroform (Caledon) was dried for 3 days over Davison Type 3A molecular sieves (Fisher Scientific) that had been previously dried under vacuum for 24 h at 120 °C, followed by vacuum distillation into a dry glass bulb equipped with a grease-free glass/Teflon stopcock (J. A. Young).

The compound 2,2,2-trifluoroacetamide (Aldrich) was purified by recrystallization from anhydrous $CHCl_3$ followed by pumping under dynamic vacuum for 12 h at room temperature.

Preparation of $CF_3C(OH)NH_2^+AsF_6^-$. In a drybox, $CF_3C(O)NH_2$ (1.2708 g, 11.242 mmol) was loaded into a $^1/_2$-in. o.d. FEP tube and dissolved in 4 mL of anhydrous HF at −78 °C, giving a yellow solution. Arsenic pentafluoride was metered from a nickel storage can into a dry 0.4005 L preweighed glass bulb. The AsF_5 was condensed onto the $CF_3C(O)NH_2$ solution at −196 °C. Weighing of the glass bulb before and after the transfer indicated that 2.5086 g (14.764 mmol) of AsF_5 was condensed onto the frozen solution. Warming to −78 °C resulted in a dark orange precipitate and a yellow supernatant. The precipitate dissolved on warming to −50 °C, resulting in a colorless solution. The solvent was removed *in vacuo* at −42 °C leaving a white microcrystalline material. After pumping for 0.5 h at −42 °C and 3.5 h at −10 °C, 3.3820 g of $CF_3C(OH)NH_2^+AsF_6^-$ (99.3% yield) was recovered. Decomposition with liquefaction was observed after 1 month at room temperature; however, indefinite storage without decomposition was possible at −78 °C.

Fluorescence prevented the acquisition of a suitable Raman spectrum for $CF_3C(OH)NH_2^+AsF_6^-$. The fluorescence was largely eliminated by treatment of a solution of $CF_3C(OH)NH_2^+AsF_6^-$ with XeF_2 in anhydrous HF solvent. The salt $CF_3C(OH)NH_2^+AsF_6^-$ (0.1886 g, 0.6225 mmol) was loaded into a $^1/_4$-in. o.d. FEP tube. After cooling of the solid to −196 °C, 0.0068 g (0.040 mmol) of XeF_2 (ca. 5 mol %) was added. Anhydrous HF (ca. 0.5 mL) was distilled onto the solids at −196 °C. Upon warming to −50 °C, the solids dissolved. The HF was pumped off under vacuum at −50 °C for 14 h through a copper U-trap cooled to −196 °C, to give a white polycrystalline material which exhibited little fluorescence. Bands attributable to the $CF_3C(OXeF)NH_2^+$ cation and XeF_2 were not observed in the low-temperature Raman spectrum of $CF_3C(OH)NH_2^+AsF_6^-$.

NMR Samples of $CF_3C(OH)NH_2^+AsF_6^-$. The salt $CF_3C(OH)NH_2^+AsF_6^-$ was characterized in BrF_5 solution by ^{19}F, ^{13}C, and ^1H NMR spectroscopy. Typically, the salt (0.016 67 g, 0.055 02 mmol) was loaded into a 4-mm o.d. FEP tube. Bromine pentafluoride was condensed into the tube at −196 °C. The sample was warmed slowly to −60 °C, resulting in a pale yellow solution (0.25 M).

NMR Samples of $CF_3C(OXeF)NH_2^+AsF_6^-$. The $CF_3C(OXeF)NH_2^+$ cation was characterized in BrF_5 solution by ^1H, ^{13}C, ^{19}F, and ^{129}Xe NMR spectroscopy. The salt, $CF_3C(OH)NH_2^+AsF_6^-$ (0.016 68 g, 0.055 04 mmol), was transferred into a 4-mm o.d. FEP tube; the tube was cooled to −196 °C, and XeF_2 (0.0985 g, 0.058 18 mmol) was added. Bromine pentafluoride (0.3 mL) was condensed onto the walls of the tube above the reagents at −196 °C. The BrF_5 slowly melted upon warming the tube to −60 °C. After agitation for approximately 10 min. at −55 °C, a pale yellow solution resulted. A similar procedure was followed using a 9-mm o.d. FEP tube. The amounts of reagents were 0.134 05 g (0.442 50 mmol) of $CF_3C(OH)NH_2^+AsF_6^-$, 0.0840 g (0.496 mmol) of XeF_2, and 1.7 mL of BrF_5. The tubes were heat-sealed *in vacuo* at −196 °C and stored at this temperature prior to recording their NMR spectra.

Isolation of $CF_3C(OXeF)NH_2^+AsF_6^-$. Solid samples of $CF_3C(OXeF)NH_2^+AsF_6^-$ were prepared and characterized by low-temperature Raman spectroscopy. In a typical preparation, 0.1987 g (1.758 mmol) of $CF_3C(O)NH_2$ was dissolved in ca. 1 mL of anhydrous HF at −50 °C in a $^1/_4$-in. o.d. FEP tube. The tube was cooled to −196 °C, and 0.5970 g (1.760 mmol) of $XeF^+AsF_6^-$ was added. The sample was warmed to −50 °C with agitation, whereupon approximately 95% of the white solid material dissolved; the supernatant was pale yellow. It was necessary to remove the HF solvent under vacuum very slowly to prevent precipitation of $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}x$HF (*vide infra*). Upon reduction of the solvent volume by ca. 75% after 3 h, all of the solid had dissolved, and the solution was pale yellow. A further 3 h of pumping under dynamic vacuum resulted in a free-flowing white powder. The Raman spectrum indicated the presence of solvated HF from the presence of broad peaks at 3150, 3175, and 3299 cm^{-1}, assignable to extensively hydrogen-bonded HF and the amido group. The HF was removed by pumping at −50 °C for 14.5 h using a glass vacuum line and an intermediate copper U-trap (−196 °C) for HF trapping, and its removal was confirmed by the absence of the above peaks in the low-temperature Raman spectrum.

Preparation of $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}x$HF. In a typical preparation, $CF_3C(OH)NH_2^+AsF_6^-$ (0.0919 g, 0.303 mmol) and XeF_2 (0.0516 g, 0.305 mmol) were combined in a 4-mm o.d. FEP tube at −196 °C and dissolved in ca. 0.4 mL of anhydrous HF at −50 °C, following the same procedure as was used in the preparation of $CF_3C(OXeF)NH_2^+AsF_6^-$ (*vide supra*). Alternatively, the reaction of equimolar amounts of $CF_3C(O)NH_2$ and $XeF^+AsF_6^-$ resulted in the isolation of the same product. The solvent was rapidly pumped off at −50 °C, resulting in the isolation of a free-flowing white powder after 1 h. The Raman spectrum (−160 °C) was consistent with the formulation $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}x$HF. The sample was further pumped for 28 h at −50 °C using a glass vacuum line with an intermediate copper U-trap (−196 °C). The Raman spectrum (−160 °C) was still consistent with the formulation, $CF_3C(OH)NH_2^+AsF_6^-{\cdot}XeF_2{\cdot}x$HF. Anhydrous HF was then condensed onto the white solid at −196 °C, giving a pale yellow solution (0.55 M) after periodic agitation for 15 min at −50 °C. After slow removal of the solvent under dynamic vacuum for 4 h, a white free-flowing powder was isolated. The low-temperature Raman spectrum was consistent with the formulation $CF_3(OXeF)NH_2^+AsF_6^-$.

Nuclear Magnetic Resonance Spectroscopy. All NMR spectra were recorded unlocked (field drift < 0.1 Hz h^{-1}) with the use of a Bruker AM-500 (11.745 T) spectrometer.

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

The ^{129}Xe spectra were recorded in 9-mm o.d. FEP sample tubes using a 10-mm probe (broad-banded over the frequency range 23−202 MHz) tuned to 139.051 MHz. Fluorine-19 (470.599 MHz) and proton (500.138 MHz) spectra were obtained using a 5-mm dual ^1H/^{19}F probe. Xenon-129 spectra were typically recorded in 2000 scans in a 16 K memory using a spectral width of 50 kHz, acquisition time of 0.164 s, and data point resolution of 6.1 Hz/pt. Fluorine-19 NMR spectra were recorded in 3900 scans in a 64 K memory using a spectral width setting of 125 kHz, acquisition time of 0.262 s, and a data point resolution of 3.8 Hz/pt. Carbon-13 NMR spectra were recorded in 57 000 scans in a 32 K data memory using a spectral width of 50 kHz, acquisition time of 0.328 s, and data point resolution of 3.05 Hz/pt. Proton spectra were recorded in 243 scans in a 32 K memory using a

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spectral width of 10 kHz, acquisition time of 1.638 s, and data point resolution of 0.61 Hz/pt.

Pulse widths corresponding to bulk magnetization tip angles of ~90° were 18 (^{129}Xe), 1 (^{19}F), 6 (^{13}C), and 5 μs (^{1}H). Line-broadening parameters used in exponential multiplication of the free induction decays were set equal to or less than their respective data point resolutions or the natural line widths of the resonances.

Proton–fluorine heteronuclear 2D spectra were recorded in the absolute value mode using the pulse sequence reported by Yu and Levy.[74] Spectra were acquired in 16 scans for each of the 128 free induction decays that contained 2 K data points in F2 (^{19}F dimension) over a 5 kHz spectral width. The ^{19}F 90° pulse width was 14.3 μs while the ^{1}H 90° pulse width through the decoupler channel was 9.0 μs. A 1.0 s relaxation delay was employed between aquisitions. A mixing time of 0.25 s was used. Zero-filling in the F1 (^{1}H) dimension produced a 1 K × 2 K data matrix with a digital resolution of 7.1 Hz/pt in F2 and 3.5 Hz/pt in F1. During 2D Fourier transformation, a sine-bell squared window function shifted by $\pi/2$ was applied to both dimensions. The transformed data were not symmetrized.

The respective nuclei were referenced externally to neat samples of $XeOF_4$ (^{129}Xe), $CFCl_3$ (^{19}F), and $(CH_3)_4Si$ (^{13}C and ^{1}H) at 30 °C. Positive chemical shifts were assigned to resonances occurring to high frequency of the reference substance and *vice versa*.

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 and were considered to be accurate to within ±1 °C.

Raman Spectroscopy. Raman spectra were recorded on a Jobin-Yvon Mole S-3000 triple spectrograph system equipped with a 0.32-m prefilter, adjustable 25-mm entrance slit, and 1.00-m monochromator. Holographic gratings were used for the prefilter (600 grooves mm^{-1}, blazed at 500 nm) and monochromator (1800 grooves mm^{-1}, blazed at 550 nm) stages. The 514.5-nm line of an Ar^+ ion laser was used for excitation of the samples. The spectrum of microcrystalline $CF_3C(O)NH_2$, which was sealed in a baked-out Pyrex melting point capillary, was recorded at ambient temperature. The Raman spectra of the microcrystalline salts $CF_3C(OH)NH_2{}^+AsF_6{}^-$, $CF_3C(OXeF)NH_2{}^+AsF_6{}^-$, and $CF_3C(OH)NH_2{}^+AsF_6{}^-\cdot XeF_2\cdot xHF$ contained in 9-mm or $^1/_4$-in. o.d. FEP tubes were recorded at −165 °C in the macro-sample chamber of the instrument. The low temperatures were achieved by flowing dry nitrogen gas, chilled by passing through a 50 L tank of liquid nitrogen, along the outside of the sample tube contained in an open-ended unsilvered glass Dewar jacket. The temperature was measured using a copper–constantan thermocouple (error ±0.8 °C). The spectra were recorded by signal averaging using a Spectraview-2D CCD detector equipped with a 25-mm chip (1152 × 298 pixels). The laser powers measured at the samples were 90 ($CF_3C(OXeF)NH_2{}^+AsF_6{}^-$ and $CF_3C(O)NH_2$), 190 ($CF_3C(OH)NH_2{}^+AsF_6{}^-$), and 120 mW ($CF_3C(OH)NH_2{}^+AsF_6{}^-\cdot XeF_2\cdot xHF$). Slit settings corresponded to a resolution of 1 cm^{-1}. A total of 20–30 reads having 10–40 s integration times were summed for each of the Raman spectra. Raman frequencies are estimated to be accurate to ±1 cm^{-1}.

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