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Bond Dissociation Energy and Lewis Acidity of the Xenon Fluoride Cation

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This study focuses upon the Lewis acid reactivity of XeF^+ with various bases in the gas phase and the determination of the bond dissociation energy of XeF^+. The bond dissociation energy of XeF^+ has been measured by using energy-resolved collision-induced dissociation with neon, argon, and xenon target gases. Experiments with neon target yield a 298 K bond dissociation enthalpy of 2.81 ± 0.09 eV, and those with argon target give a similar value at 2.83 ± 0.12 eV. When using a xenon target, a significantly lower value of 1.95 ± 0.16 eV was observed, which corresponds closely with previous measurements and theoretical predictions. It is proposed that the lighter target gases give inefficient excitation of the XeF^+ vibration leading to dissociation at energies higher than the BDE. Novel xenon-base adducts have been prepared in a flowing afterglow mass spectrometer by termolecular addition to XeF^+ and by reaction of base with $XeF^+(H_2O)$. New species have been characterized qualitatively by CID, and it is found that the products formed reflect the relative ionization energies of the fragments. Among the new xenon-containing species that have been prepared are the first examples of xenon carbonyls.

Introduction

The combination of xenon with other elements through chemical means presents a scientific challenge. In 1962, Bartlett[1] reported the first evidence of a xenon-containing compound, believed to be $XeF^+PtF_6^-$, and shortly after compounds such as XeF_2,[2,3] XeF_4,[4] XeF_6, and $XeOF_4$[5] were described. Until 1980, the only stable xenon-containing compounds generally had xenon bonded to F or O, although the carbon-bonded species CH_3Xe^+ had been detected by ICR mass spectrometry.[6,7] The landscape changed in the early 1980s when several xenon−nitrogen-bonded species were reported.[8−10] Many types of xenon-containing compounds are now fairly common, and some, such as xenon difluoride, are commercially available. Because of their availability, their physical properties and reactivity are becoming better understood.[11−14] For example, xenon difluoride is known to be a strong Lewis acid and acts as such in most applications.[15] Its Lewis acidity has been studied extensively in both the solid and solution phases. Thus, molecules with highly electronegative atoms such as O and N and even activated carbon-based ligands[16] bond readily with XeF_2, with most products involving a XeF^+ moiety. Several of these species and methods of generating them are reviewed by Schrobilgen,[15] who gives a fairly comprehensive list of XeF^+ adducts with hydrocyano, perfluoroalkyl, alkyl nitrile, and perfluoropyridine ligands and inorganic bases, such as $N{\equiv}SF_3$, in the condensed phase. XeF^+-containing compounds have been primarily characterized by means of X-ray crystallography, Raman/IR spectroscopy, ^{19}F and ^{129}Xe NMR, and mass spectrometry.[17−20]

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Although much of the previous work has involved the characterization of XeF^+ reagents in the condensed phase, some gas-phase studies have been performed. Both positive[21,22] and negative[23,24] ion mass spectrometry of XeF_2 has been reported. Positive ion electron ionization (EI) of XeF_2 produces XeF_2^+, XeF^+, and Xe^+, whereas negative EI leads to XeF_2^-, XeF^-, and F^-. There have also been several positively charged xenon cluster ions investigated, such as $XeNO_3^+$,[25] $Xe_2F_3^+$,[26−28] $C_2H_4Xe^+$, and $C_2H_4XeF^+$.[29] A recent mass spectrometric study by Zelenov et al.[30] examined xenon species such as XeF_n ($n = 1-6$), XeO_3, XeO_4, and $XeOF_4$, and the corresponding cations, and reported the determination of various thermochemical parameters such as ionization energies, appearance energies, enthalpies of formation, and binding energies. Christe and Dixon[31] have discussed the oxidizing strength of XeF^+, as measured by the $Xe-F^+$ binding energy.

In conjunction with our recent studies of main group fluorides,[32] we have examined the properties and gas-phase reactivity of xenon containing ions. In this work, we describe the determination of the bond dissociation energy in XeF^+ and an examination of the reactivity of the gaseous ion. We find that XeF^+ is a Lewis acid, in agreement with previous characterization, and show that a wide variety of XeF^+-containing ions can be generated by direct addition of base or by reaction of base with $XeF^+(H_2O)$.

Experimental Section

Instrumental/Data Analysis. All experiments were carried out using a flowing afterglow-triple quadrupole mass spectrometer that has been described previously.[33,34] XeF^+ is prepared by 70 eV EI of XeF_2 and carried by helium buffer gas (ca. 0.400 Torr, flow(He) = 190 STP cm^3/s) through the flow tube, where it is allowed to react with neutral reagents added through micrometering valves. Other ions observed from the EI of xenon difluoride include Xe^+ and $Xe_2F_3^+$ under normal operating conditions, in agreement with what has been reported previously.[26] Addition of air near the ionization source or water downstream readily yields $XeF^+(H_2O)$. Ions generated in the flow tube are sampled through a 1 mm nose cone orifice into a differentially pumped region, where they are analyzed with a triple quadrupole mass filter. Collision-induced dissociation (CID) is carried out by mass selecting specific reactant ions with the first quadrupole and injecting the ion into the second quadrupole, which serves as a gastight collision cell containing the target gases neon (BOC Gases), argon (Airco), or xenon (Spectra Gases). The CID collision energy is controlled by the pole offset voltage, and the absolute energy origin is established by using retarding potential analysis. The uncertainty in the absolute energy scale is estimated to be ±0.15 eV in the laboratory frame. Product ions are mass analyzed with the third quadrupole and detected with a channeltron particle detector operated in pulsed-counting mode.

Cross sections for CID, σ, are calculated using $I/I_o = \sigma N l$, where I and I_o are the intensities of the product and reactant ions, respectively, N is the number density of the target, and l is the effective collision path length. The path length is calibrated to be 24 ± 4 cm[34] by using the reaction of $Ar^+ + D_2$.[35] Cross sections are measured as a function of target pressure and extrapolated to zero pressure, single-collision conditions.

Cross sections are modeled with the exponential expression shown in eq 1,[36,37] where E is the center-of-mass collision energy of the parent ion, g_i is the fraction of the ions with internal energy E_i, E_0 is the dissociation energy, n is a parameter that reflects the energy deposition in the collision,[38] and σ_0 is a scaling factor. The data are modeled by adjusting the parameters to correspond with the steeply rising portion of the appearance curve directly above the onset. Also convoluted into the fit are the ion kinetic energy distributions,[35] approximated as a Gaussian with a 1.5 eV (laboratory frame) full width at half-maximum and a Doppler broadening function to account for motion of the target. Data analysis and modeling of the cross sections were carried out using the CRUNCH 4D program.[35−37]

$$\sigma(E) = \sigma_0 \sum_i g_i (E + E_i - E_0)^n / E \qquad (1)$$

Experimentally determined dissociation energies, E_0, correspond to 0 K ΔE values and are converted to 298 K bond dissociation enthalpies by using the integrated heat capacities of reactants and products, calculated from theoretical frequencies. Uncertainties in enthalpy values are calculated by statistical combination of the uncertainty in the absolute energy scale for the experiment (±0.15 eV laboratory frame) and the standard deviation of values obtained from replicate experimental trials.

Materials. Reagents were used as received without further purification. XeF_2 was purchased from SynQuest Laboratories (Alachua, FL). All other reagents were purchased from commercial sources.

Computational Details. Geometries, energies, and vibrational frequencies for $^{132}XeF^+$ have been calculated at various levels of

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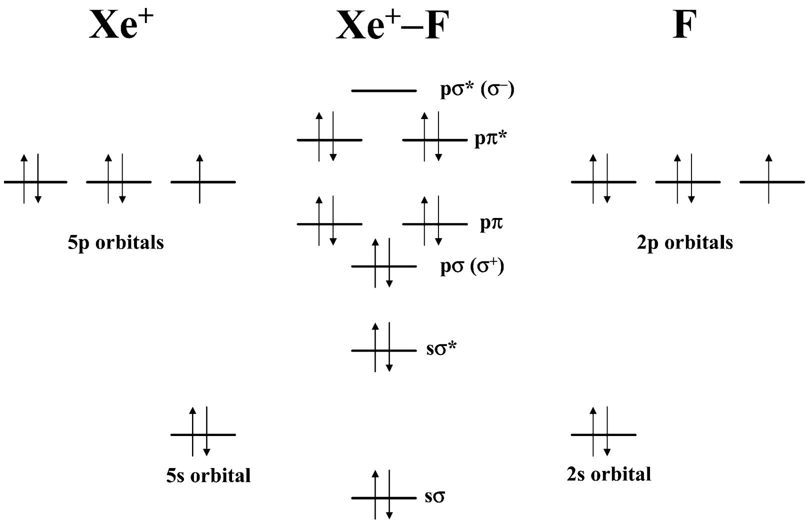

Figure 1. Simple molecular orbital description of XeF^+.

theory using Gaussian 98.[39] The LANL2DZ[40−44] and SDD[40] basis sets were used for the calculations. Levels of theory included HF,[45] MP2,[46,47] two-configurational SCF (MCSCF(2,2)), QCISD(T),[48] BLYP,[49−51] and B3LYP.[52] In addition, with the LANL2DZ basis set, dynamic correlation was included by using an MP2 calculation with the MCSCF(2,2) orbitals as implemented in Gaussian 98. This calculation is designated in this work as MCSCF(2,2)-MP2. Default SCF and geometry convergence criteria were used in all calculations. The optimized geometry reported for the MCSCF(2,2)-MP2 calculation was obtained manually.

Table 1. Fitting Parameters for the Modeling of XeF^+ CID Cross Sections[a]

target gas	E_0 (eV)[b]	n[c]	ΔH_{298} (eV)[b]
neon	2.75 ± 0.09	1.4 ± 0.1	2.81 ± 0.09
argon	2.76 ± 0.12	1.7 ± 0.3	2.83 ± 0.12
xenon	1.88 ± 0.16	1.8 ± 0.2	1.95 ± 0.16

[a] Parameters used for the model function in eq 1. [b] See text for discussion of uncertainties. [c] Uncertainty is one standard deviation.

Results and Discussion

Molecular Orbital Picture. Before reporting the experimental results, we provide a brief overview of the electronic structure of XeF^+. The ion is a simple diatomic, isoelectronic with IF, and a molecular orbital diagram is given in Figure 1. The key orbitals in the wave function are the σ^+ (pσ) and σ^- (pσ*) orbitals. From the MO diagram it appears that the ground state of XeF^+ has a doubly occupied σ^+ orbital. However, two-configuration SCF (MCSCF(2,2)) calculations show that a single configuration is not sufficient and that proper description of the wave function requires a mixture of $(\sigma^+)^2$ and $(\sigma^-)^2$ configurations, creating a $^1\Sigma^+$ wave function. At the MCSCF(2,2)/LANL2DZ level of theory, the CI coefficients, c_+ and c_-, on the $(\sigma^+)^2$ and $(\sigma^-)^2$ configurations at the optimized geometry are 0.938 and −0.347, respectively ($c_+^2 + c_-^2 = 1$), such that the $(\sigma^-)^2$ configuration makes up ∼12% of the wave function ($100c_-^2$). A similar calculation with IF finds that c_+ and c_- are 0.975 and −0.223, respectively, such that the $(\sigma^-)^2$ configuration makes up less than 5% of the wave function. Although the optimized lengths suggest that contributions from the antibonding configuration are likely overstated at the MCSCF(2,2) level of theory, the results indicate that electronic correlation is required for a proper description of the electronic structure.

Bond Dissociation Energy. The bond dissociation energy (BDE) in XeF^+ has been measured by using energy-resolved CID. Cross sections for $^{132}Xe^+$ formation upon CID of $^{132}XeF^+$ with neon, argon, and xenon target are shown in Figure 2, along with modeled fits to the data. Parameters used to calculate the fits shown in the Figure 2 are listed in Table 1. Two different values for the $\Delta H_{298}(Xe^+{-}F)$ are obtained from the data. Values obtained when using neon (2.81 ± 0.09 eV) and argon (2.83 ± 0.12 eV) targets are in agreement with each other, whereas a lower value of 1.95 ± 0.16 eV is obtained with xenon as the target. The xenon value is in good agreement with the value of 2.03 eV (technically a lower limit) reported by Berkowitz and co-

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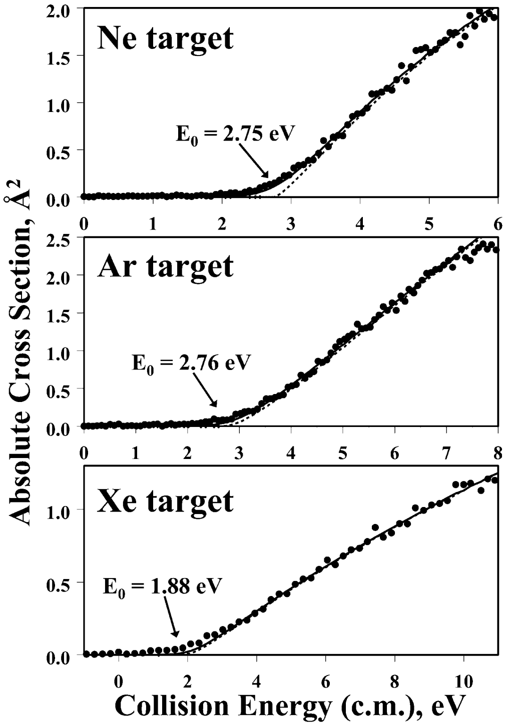

Figure 2. Absolute cross sections for formation of Xe^+ upon CID of XeF^+ with neon, argon, and xenon target gases. The solid line is the modeled fit of the data as described in the Instrumental/Data Analysis section. Dashed lines are the nonconvoluted fits of the data. Dissociation energies at 0 K are indicated with arrows.

workers,[22] measured by using threshold photoionization spectroscopy, and agrees with previously reported theoretical predictions.[53] The values obtained with neon and argon targets are likely too high and are believed to result from impulsive dissociations due to electronic excitation of the diatomic ion due to inefficient vibrational excitation with small target molecules, a phenomenon that has been observed previously in the CID of VO^+.[54] Although low-energy CID generally occurs through vibrational excitation, it has been proposed[54] that collisions can lead to efficient electronic excitation, even at low collision energies. This is more likely to occur when the system has many closely spaced energy levels, such as those created by different configurations of nonbonding electrons, or when the target atoms are small, such that vertical excitation is more likely. Collisions with a larger target, such as xenon, are more likely to excite vibrational levels in the ground electronic state. It is also suggested that the polarizability of xenon may affect the potential energy surfaces for the excited states, such that the dissociation occurs at the adiabatic threshold.[54] The agreement between the values obtained with neon and argon is consistent with the electronic excitation explanation and suggests the existence of an excited state (or states) of XeF^+ with a term energy of ca. 2.8 eV. Our value for the bond dissociation energy of XeF^+, 1.95 ± 0.16 eV, is significantly larger than a recently reported value of 1.06 ± 0.05 eV, derived from ion appearance energies.[30] The BDE for the alternate dissociation process, $Xe + F^+$, is higher by approximately the difference in the ionization energies of Xe and F, 5.29 eV.[31,55]

For comparison, the 298 K BDE in XeF^+ was calculated by utilizing the reaction in eq 2, which minimizes potential systematic errors resulting from uneven treatment of correlation. The BDE in XeF^+ can be calculated from the enthalpy change for the reaction in eq 2, ΔH_{298}(eq 2), by using eq 3, where the 298 K BDE(IF) = 2.91 eV, as determined from the 298 K heats of formation for IF, I, and F.[56]

$$XeF^+ + I \rightarrow IF + Xe^+ \tag{2}$$

$$\mathrm{BDE}(Xe^+{-}F) = \Delta H_{298}(\text{eq } 2) + \mathrm{BDE}(IF) \tag{3}$$

Calculated bond dissociation energy values for XeF^+ are listed in Table 2. Also included in Table 2 are the optimized bond lengths and calculated harmonic frequencies for XeF^+ and IF. Absolute energies are available in the Supporting Information. Whereas the bond lengths for XeF^+ calculated with the SDD basis set are shorter than those obtained when using the LANL2DZ basis set, the bond lengths for IF are similar, regardless of basis set, and are ca. 0.1 Å longer than the experimental value.[57] The best agreement with the experimental BDE is obtained by using the highly correlated (QCISD(T),MCSCF(2,2)-MP2) and density functional methods with the LANL2DZ basis set. Bond dissociation energies obtained with the SDD basis set are much larger than the experimentally determined value.

Lewis Acidity and Reactivity of XeF^+. Schrobilgen and co-workers have shown that XeF^+ reacts as a Lewis acid in solution and can form complexes with many Lewis bases.[58] Consequently, Cacace and co-workers have shown that XeF^+ also forms gas-phase complexes with Lewis bases such as ethylene,[29] methanol,[59] and acetonitrile.[60] We have examined the reactivity of XeF^+ with a series of Lewis bases and found that formation of complexes can occur by termolecular addition in the flow reactor and by ligand exchange. Thus, $XeF^+(H_2O)$, which can be formed by the ionization of XeF_2 in the presence of a small amount of air or water vapor, undergoes ligand exchange with a wide variety of bases. The

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Table 2. Calculated Bond Lengths and Vibrational Frequencies for XeF^+ and IF and Bond Dissociation Energy of XeF^+

	XeF^+		IF		
theoretical method	bond length[a]	vibration[b]	bond length[a]	vibration[b]	XeF^+ BDE[c]
LANL2DZ basis					
HF	1.939	643	1.949	629	1.51
MCSCF(2,2)	2.144	339	2.047	459	2.20
MP2	2.012	545	2.015	542	1.68
QCISD(T)	2.061	446	2.021	525	1.84
MCSCF(2,2)-MP2[d]	2.101		2.034		1.96[e]
B3LYP	2.007	556	2.009	546	1.86
BLYP	2.042	577	2.041	509	1.97
SDD basis					
HF	1.856	704	1.965	636	2.31
MCSCF(2,2)	1.998	431	2.065	457	2.65
MP2	1.924	602	2.030	546	2.30
QCISD(T)	1.943	544	2.037	528	2.53
B3LYP	1.912	623	2.022	553	2.61
BLYP	1.941	586	2.037	514	2.77
exptl			1.910[f]	610[f]	≥2.03[g]
					1.06 ± 0.05[h]
					1.95 ± 0.16[i]

[a] Optimized bond length in Å. [b] Calculated harmonic frequency at optimized geometry, in cm^{-1}. [c] The bond dissociation energy at 298 K; derived from the calculated ΔH_{298} for the reaction in eq 2 and 298 K BDE(IF) = 2.91 eV (calculated from 298 K heats of formation of IF, I, and F listed in ref 56) using eq 3; value in eV. [d] An MCSCF(2,2) calculation with MP2 correlation; the optimal bond length is found by manual search. [e] UMP2 energies used for I and Xe^+. ZPE and thermal corrections calculated from QCISD(T) vibrational frequencies. [f] Reference 57. [g] Reference 22. [h] Reference 30. [i] This work.

Table 3. Gas Phase Reactivity of XeF^+ with Various Bases

base	PA (kcal/mol)[a]	IE (eV)[b]	CID products[c]
		Formed by Reaction with $FXe(H_2O)^+$	
pyridine	222.3	9.26 ± 0.01	$\mathbf{(C_6H_5N)}^+$
ethyl acetate	199.7	10.01 ± 0.05	$\mathbf{(CH_3CO_2C_2H_5)}^+$, XeF^+
diethyl ether	198.0	9.51 ± 0.03	$(C_2H_5OCH_2)^+$, $\mathbf{(C_2H_5OC_2H_5)}^+$
cyclopentanone	196.9	9.26 ± 0.01	$(C_4H_8)^+$, $\mathbf{(C_5H_8O)}^+$
THF	196.5	9.40 ± 0.02	$\mathbf{(C_4H_8O)}^+$
ethylene glycol	195.0	10.16	$\mathbf{(HOCH_2CH_2OH)}^+$, XeF^+
2-butanol	194.8	9.88 ± 0.03	$(C_4H_8)^+$, $(C_4H_{10}O)^+$, XeF^+, $\mathbf{XeF^+(H_2O)}$
acetone	194.1	9.703 ± 0.006	$\mathbf{(C_3H_6O)}^+$, $(C_3H_6OF)^+$, XeF^+
propanoic acid	190.5	10.44 ± 0.06	$\mathbf{(C_3H_4O)}^+$, $(C_3H_6O_2)^+$, XeF^+
toluene	187.4	8.828 ± 0.001	$\mathbf{(CH_3C_6H_5)}^+$
fluorobenzene	180.7	9.20 ± 0.01	$\mathbf{(FC_6H_5)}^+$
methanol	180.3	10.84 ± 0.01	$\mathbf{XeF^+}$
benzene	179.3	9.24378 ± 0.00007	$\mathbf{(C_6H_6)}^+$, $(FC_6H_6)^+$
$CH_2(CN)_2$	172.8	12.8 ± 0.1	$\mathbf{XeF^+}$
H_2S	168.5	10.457 ± 0.012	$\mathbf{XeF^+}$, $Xe^+(H_2S)$
		Formed Only by Direct Addition to XeF^+	
CF_3COOH	170.1	11.5	Xe^+, $\mathbf{XeF^+}$
CF_3CH_2OH	167.4	11.49	XeF^+
H_2O	165.2	12.621 ± 0.002	XeF^+
CO	142.0	14.014 ± 0.0003	$\mathbf{XeF^+}$, $Xe^+(CO)$
N_2O	131.4	12.889 ± 0.004	$\mathbf{XeF^+}$, $Xe^+(N_2O)$
CH_4	129.9	12.61 ± 0.01	XeF^+
CO_2	129.2	13.777 ± 0.001	$\mathbf{XeF^+}$, $Xe^+(CO_2)$
		No XeF^+ Adduct Formed	
aniline	210.9	7.720 ± 0.002	N/A[d]
phenol	195.3	8.49 ± 0.02	N/A[d]

[a] Proton affinities from ref 61. [b] Ionization energies from ref 55. [c] Bold fragments represent the major product from 25 eV (laboratory frame) CID with Ar target. [d] Aniline and phenol form clusters with $XeF^+(H_2O)$ as described in the text.

bases that have been found to displace water in $XeF^+(H_2O)$ are listed in the top part of Table 3 and include ethers, alcohols, carbonyls, aromatic compounds, nitriles, and sulfur-containing species. The proton affinities (PA's) of the bases are included in Table 3 for reference.[61] All of the bases that displace water in $XeF^+(H_2O)$ have higher proton affinities than water.

Bases with proton affinities below ~165 kcal/mol do not appear to react with $XeF^+(H_2O)$. However, in those cases the acid–base complexes can be formed by termolecular addition of base to XeF^+. Thus, the bases that were examined and found to form complexes with XeF^+ by direct addition are listed in the middle section of Table 3, along with their proton affinities. The bases listed in the top part of the table will also form complexes by termolecular addition, but reaction with $XeF^+(H_2O)$ is more efficient. Remarkably, XeF^+ complexes can be made with even very weak bases

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(61) Hunter, E. P.; Lias, S. G. Proton Affinity Evaluation. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Linstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD 20899, Mar 2003 (http://webbook.nist.gov).

such as N_2O (PA = 131.4 kcal/mol), CH_4 (PA = 129.9 kcal/mol), and CO_2 (PA = 129.2 kcal/mol).[61] Two species, aniline and phenol, were found to not form adducts with XeF^+ under any conditions, and reaction with these bases leads instead to low yields of clusters with $XeF^+(H_2O)$.

CID has been carried out with all of the XeF^+ complexes that have been formed, and the CID products are listed in the far-right column in Table 3. The major fragments obtained at 25 eV (laboratory frame) with argon target are shown in bold. In general, the observed products can be understood in light of the ionization energies of the fragments. For bases with ionization energies greater than that of XeF (10.3 eV),[55] XeF^+ is the major CID fragment. If the ionization energy of the base is less than that of XeF, then ionized base is the major product observed. However, there are other fragmentation pathways observed. Fragmentation of the base radical cation or XeF^+ is observed for some systems. Additionally, with 2-butanol, the $XeF^+(H_2O)$ product is formed. In the cases of acetone and benzene, loss of a labile xenon atom is seen, leaving a fluorinated base. Also seen with small bases with lower PA's (<165 kcal/mol) is the loss of $F^\bullet$ leaving $Xe(\text{base})^+$. This fragmentation is seen with H_2S (~20%), CO (~5%), and to a minor extent (<2%) N_2O and CO_2.

In terms of novel xenon-containing species, many new adducts have been prepared. Of particular interest is $XeF^+(CO)$, which loses F upon CID to form a xenon carbonyl complex, $Xe^+(CO)$. These ions are the first reported examples of xenon carbonyls. The H_2S and H_2O adducts of XeF^+ can be considered as protonated fluoroxenol[62] and fluorothioxenol,[63] respectively. Further characterization of these complexes is in progress.

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Supporting Information Available: Calculated bond lengths, frequencies, and absolute energies for XeF^+ and IF given at several levels of theory with calculated absolute energies of Xe^+ and I included. This material is available free of charge via the Internet at http://pubs.acs.org.

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(62) Pettersson, M.; Khriachtchev, L.; Lundell, J.; Räsänen, M. *J. Am. Chem. Soc.* **1999**, *121*, 11904−11905.

(63) Pettersson, M.; Lundell, J.; Khriachtchev, L.; Isoniemi, E.; Räsänen, M. *J. Am. Chem. Soc.* **1998**, *120*, 7979−7980.