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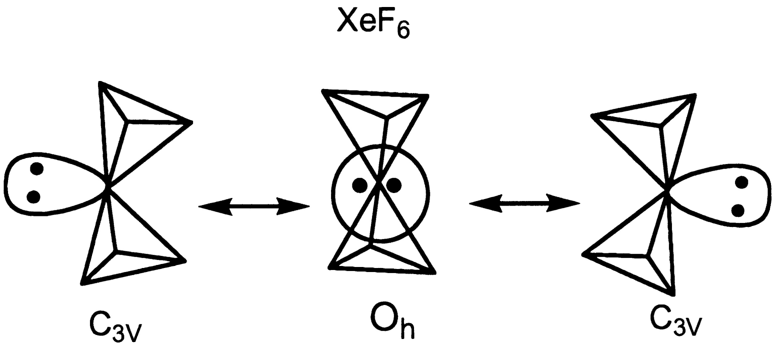

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Heats of Formation of Xenon Fluorides and the Fluxionality of XeF_6 from High Level Electronic Structure Calculations

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Abstract: Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted for XeF^+, XeF^-, XeF_2, XeF_4, XeF_5^-, and XeF_6 from coupled cluster theory (CCSD(T)) calculations with new correlation-consistent basis sets for Xe. To achieve near chemical accuracy (±1 kcal/mol), up to four corrections were added to the complete basis set binding energies based on frozen core coupled cluster theory energies: a correction for core-valence effects, a correction for scalar relativistic effects, a correction for first-order atomic spin−orbit effects, and in some cases, a second-order spin−orbit correction. Vibrational zero-point energies were computed at the coupled cluster level of theory. The structure of XeF_6 is difficult to obtain with the C_{3v} and O_h structures having essentially the same energy. The O_h structure is only 0.19 kcal/mol below the C_{3v} one at the CCSD(T)/CBS level using an approximate geometry for the C_{3v} structure. With an optimized C_{3v} geometry, the C_{3v} structure would probably become slightly lower in energy than the O_h one. The calculated heats of formation for the neutral XeF_n fluorides are less negative than the experimental values from the equilibrium measurements by 2.0, 7.7, and 12.2 kcal/mol for $n = 2$, 4, and 6, respectively. For the experimental values, derived from the photoionization measurements, this discrepancy becomes even larger, suggesting a need for a redetermination of the experimental values. Evidence is presented for the fluxionality of XeF_6 caused by the presence of a sterically active, free valence electron pair on Xe.

Introduction

The first stable noble gas compounds, the xenon fluorides, have been available,[1,2] since the early 1960s beginning with the work of Bartlett[3] who reported the first evidence for a xenon-containing compound, $XePtF_6$, which appears to be comprised of $XeF^+PtF_6^-$, PtF_5, and $XeF^+Pt_2F_{11}^-$. The syntheses of XeF_2, XeF_4, XeF_6, and $XeOF_4$ were described soon thereafter.[4−7] The field of noble gas compounds underwent a renaissance in the 1980s when compounds with numerous other elements bonded to Xe were discovered.[8] For example, adducts between XeF^+ and numerous oxidatively resistant nitrogen bases have been described.[9]

The heats of formation of the xenon fluorides have been the subject of a number of studies and have been obtained from classical thermodynamic equilibrium measurements in combination with predicted entropies.[10] The following equilibria were measured,

$$Xe + F_2 \leftrightarrow XeF_2$$
$$Xe + 2F_2 \leftrightarrow XeF_4$$
$$Xe + 3F_2 \leftrightarrow XeF_6$$

and the free energy changes for the reactions were obtained at

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elevated temperatures. The bond energy of XeF^+ and the heats of formation of XeF_2, XeF_4, and XeF_6 were reported a number of years ago based on photoionization experiments.[11] The heats of formation were based on extrapolated appearance potential measurements for reactions such as

$$XeF_2 + h\nu \rightarrow Xe^+ + F^- + F$$

$$XeF_2 + h\nu \rightarrow XeF^+ + F^-$$

The ability of Xe to bind F^+ was discussed in the construction of an F^+ detachment energy scale to develop a quantitative scale for the oxidizing strength of oxidative fluorinators.[12] The binding energy of $XeF^+ \rightarrow Xe + F^+$ serves as an anchor point within the fluorocation affinity scale. Salts of the XeF_5^- anion have been synthesized, and the anion is the first example of a pentagonal planar AX_5E_2 (A = Xe, X = F, E = valence electron lone pair) species.[13] The fluoride affinities of Xe and XeF_4 have been calculated as part of an extensive study of fluoride affinities for use as a Lewis acidity scale.[14] The binding energy of $XeF^- \rightarrow Xe + F^-$ serves as an anchor point at the low end of the fluoride affinity scale, and the binding energy of $XeF_5^- \rightarrow XeF_4 + F^-$ serves as a midpoint anchor.

The gas-phase structure of XeF_6 has been controversial with regards to the stereoactivity of its valence electron lone pair.[15] A stereoinactive xenon valence electron lone pair is expected to give rise to octahedral (O_h) symmetry, but if the lone pair is stereoactive, it is expected to behave as a seven coordinate structure and to deviate from O_h symmetry. Gillespie has predicted that the geometry of XeF_6 is a distorted octahedron having C_{3v} symmetry in which the electron lone pair occupies a triangular face of the octahedron, splaying open the occupied face and contracting the opposite triangular face.[16] Experimental evidence based on electron diffraction, vibrational spectroscopy, and photoelectron studies[17-20] suggests that XeF_6 does not have O_h symmetry.

A number of theoretical studies of XeF_6 has been carried out on the energy difference between octahedral and nonoctahedral structures. Schaefer and co-workers[21] calculated the geometry of XeF_6 at the Hartree-Fock level with a large all electron basis set, which can be considered to be of polarized double-ζ plus an *f* function quality. They found a C_{3v} structure with the three longer XeF bonds having $r = 1.927$ Å and an $<$FXeF of 80.8° and three shorter XeF bonds with $r = 1.796$ Å and an $<$FXeF of 115.1°. They also discovered a structure of C_{2v} symmetry that is close in energy to the C_{3v} one. However, the O_h structure was higher in energy than both of these by 46 kcal/mol. Using the HF geometries, they found at the MP2 level that the O_h structure was the most stable by 4.7 kcal/mol, but at the CISD+Q level, the C_{3v} structure became more stable by 22.8 kcal/mol.

In an elegant study,[22] Kutzelnigg and co-workers used both all-electron basis sets and eight-valence electron basis sets with nonrelativistic and quasi-relativistic ECPs to study XeF_6 at the Hartree-Fock, MP2, and DFT levels. At the SCF level, they obtained energetics similar to those of Schaefer and co-workers for the all-electron basis sets and for the nonrelativistic and quasi-relativistic ECPs. However, their C_{3v} geometries were different, with the longer bond distances being associated with the larger FXeF bond angles. At the MP2 level, they were unable to optimize the C_{3v} structure with the ECPs as this converged to the O_h structure. Again, at the MP2 correlated level, the O_h structure was favored. In their best CCSD(T) calculation with an effective triple-ζ basis set, including some accounting for relativistic effects, they find the O_h structure to be more stable than the C_{3v} structure, but only by 1.6 kcal/mol, and concluded that "the structure of XeF_6 is controlled by a very delicate balance of various competing effects".

In view of the general interest in the bonding in noble gas halides and the scarcity of experimental data and their large discrepancies, reliable theoretical calculations are very important. Most of the recent computational studies of the noble gas halides have been made with density functional theory and modest sized basis sets and, therefore, may not provide reliable energetic information for these computationally very challenging systems. We have been developing an approach to the prediction of the thermodynamic properties of molecules based on molecular orbital theory. The calculations start with a systematic sequence of extended basis set, frozen core CCSD(T)(FC) calculations[23] that approach the complete basis set (CBS) limit. The resulting total energies are extrapolated to the CBS limit in an attempt to eliminate the basis set truncation error. They are further adjusted to include core-valence correlation, molecular scalar relativistic corrections, and atomic spin-orbit corrections.[24] Finally, one must include a correction for zero-point vibrational energies, ZPEs, to obtain zero-point inclusive atomization energies, ΣD_0. Given ΣD_0 and the heats of formation of the elements, we can then calculate the heat of formation of a given compound. Our composite, nonparametrized approach implicitly assumes that the effects of the smaller corrections are additive to the extrapolated CBS energies, which only account for valence correlation effects. In general, this composite CCSD(T) approach is capable of achieving near chemical accuracy (i.e., ±1 kcal/mol with respect to experiment) in thermochemical calculations for chemical systems composed of first and second row elements, as documented for nearly 300 compounds in the

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Environmental and Molecular Sciences Laboratory Computational Results Database.[25] Ruden et al.[26] suggest that the reason that the reason that CCSD(T) works so well for atomization energies is due to a cancellation of errors in the approximate treatment of triples and the neglect of connected quadruples. Similar conclusions were reached earlier by Feller and Sordo.[24f] For example, we have recently applied this approach to the prediction of the binding energies and heats of formation of a number of small halogenated compounds including IF and found excellent agreement with reliable experimental values.[27]

In order for this approach to work, one must have a reliable sequence of basis sets that extrapolate to the complete basis set limit. These basis sets were initially only available for first, second, and third row main-group elements.[28] Recently, Peterson and co-workers[29] have developed such basis sets in combination with effective core potentials from the Stuttgart/Köln group for all of the main-group atoms, thereby opening up these compounds to reliable calculations. These basis sets were used for our halogen and interhalogen work.[27] In addition to our approach, other workers have been developing approaches to predict reliable heats of formation including the familiar Gaussian-X (e.g., G3) methods,[30] the W methods (e.g., W3) of Martin and co-workers,[31] and the recently proposed HEAT method,[32] which is fundamentally based on our approach.

We have used this approach to calculate the heats of formation and various binding energies for XeF^+, XeF^-, XeF_2, XeF_4, XeF_5^-, and XeF_6.

Computational Methods

In most CCSD(T) calculations of atomization energies (or heats of formation), the largest source of error typically arises from the finite basis set approximation unless there is significant multireference character to the wave function. Our composite approach for predicting atomization energies makes use of the systematic convergence properties of the valence correlation consistent family of basis sets including additional diffuse functions. These basis sets are conventionally denoted aug-cc-pVnZ, $n = D - 5$ for the atoms for which they are available. For F, the standard aug-cc-pVnZ basis sets were used. For heavier elements, we need to include the effects of relativity in the basis sets. For Xe, a small core relativistic effective core potential (RECP) was used. The RECP subsumes the ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, and $3d^{10}$) orbital space into the 28-electron core set, leaving the ($4s^2$, $4p^6$, $5s^2$, $4d^{10}$, and $5p^6$) space with 26 electrons to be handled explicitly. Of the latter, only the ($5s^2$, $5p^6$) are active in our valence correlation treatment. The polarized relativistic basis sets are labeled as aug-cc-pVnZ-PP. We use the shorthand notation of aVnZ to denote the combination of the aug-cc-pVnZ basis set on F and the aug-cc-pVnZ-PP basis set on Xe. Only the spherical component subset (e.g., five-term *d* functions, seven-term *f* functions, etc.) of the Cartesian polarization functions was used. All CCSD(T) calculations were performed with either the MOLPRO-2000[33] program system on a single processor of an SGI Origin computer or with NWChem[34] and MOLPRO on the massively parallel HP Linux cluster in the Molecular Science Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory.

Of the three reported coupled cluster approaches to handling open shell systems, we have chosen to use the restricted method for the starting Hartree−Fock wave function and then relaxing the spin restriction in the coupled cluster portion of the calculation. This method is conventionally labeled R/UCCSD(T) and is relevant to the atomic energies for F, F^+, and Xe^+.

The slow convergence of one-electron functions (basis set) to the CBS limit means that the remaining basis set truncation error remains unacceptably large if accuracy on the order of ±1 kcal/mol is desired. By exploiting the systematic convergence properties of the correlation consistent basis sets, it is possible to obtain reasonably accurate estimates of the CBS limit without having to resort to such extremely large basis sets that would unavoidably limit the use of our composite approach to small diatomic molecules. In previous work, we based our CBS estimates on one or more of the following formulas: a mixed exponential/Gaussian function of the form[35]

$$E(n) = E_{CBS} + b \exp[-(n-1)] + c \exp[-(n-1)^2] \qquad (1)$$

where $n = 2$(aVDZ), 3(aVTZ), 4(aVQZ); a simple exponential function[36]

$$E(n) = E_{CBS} + b \exp(-cx) \qquad (2)$$

or a formula that involves the reciprocal of ℓ_{max}[37]

$$E(\ell_{max}) = E_{CBS} + B/\ell_{max}^{3} \qquad (3)$$

The latter formula is formally to be applied to the correlation component of the total energy only, with the HF component extrapolated separately or taken from the largest basis set value. In practice, the effect on the energy differences of treating the HF component separately or extrapolating the total energy is small. Experience has shown that the best extrapolation formula varies with the level of the basis set and molecular system and that there is no universally agreed upon definition of the best extrapolation approach. Eqs 1 and 2 are based on the observed convergence pattern displayed by the double through quadruple-ζ correlation consistent basis sets. In a large number of comparisons of computed and experimental atomization energies (∼150 comparisons), eq 1 was statistically slightly superior to eq 3 when the largest basis sets were of quadruple-ζ quality.[24b] Both of these expressions, in turn, were better than eq 2, the simple exponential fit. Eq 3 and similar expressions involving $1/\ell_{max}$ are best suited for basis sets beyond quadruple-ζ because they are motivated by the $1/Z$ perturbation theory work of Schwartz,[38] who dealt with two-electron systems in the case where each angular momentum space was saturated. The spread in CBS estimates can serve as a crude measure of the

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uncertainty in the CBS extrapolation. We have used eq 3 to obtain CBS estimates of the total energy for the molecules where calculations with the 5-ζ level were computationally feasible and eq 1 for molecules where the largest basis set was aug-cc-pVQZ.

Most electronic structure calculations invoke the frozen core approximation in which the energetically lower lying orbitals (e.g., the 1s in fluorine) are excluded from the correlation treatment. To achieve thermochemical values within ± 1 kcal/mol of experiment, it is necessary to account for core-valence (e.g., intershell $1s^2 - 2s^2 2p^5$ in F) correlation energy effects. Core-valence (CV) calculations were carried out with new weighted core-valence basis sets (i.e., cc-pwCVnZ) or their diffuse function augmented counterparts, aug-cc-pwCVnZ.[39] The CV calculations utilized a triple-ζ level basis set in some cases augmented with diffuse functions. For Xe, the cc-pwCVTZ basis set contains up through *g* functions to provide a consistent degree of angular correlation for the active 4d electrons. The cc-pwCVTZ (or aug-cc-pwCVTZ) basis set for Xe is based on the cc-pVTZ-PP (aug-cc-pVTZ-PP) basis set and accompanying small core RECP. Core/valence calculations for Xe involve all 26 electrons outside the RECP core (i.e., $4s^2$, $4p^6$, $5s^2$, $4d^{10}$, and $5p^6$).

Up to three adjustments to ΣD_0 are necessary to account for relativistic effects in atoms and molecules. The first correction lowers the sum of the atomic energies (decreasing ΣD_0) by replacing energies that correspond to an average over the available spin multiplets with energies for the lowest multiplets as most electronic structure codes are only capable of producing spin multiplet averaged wave functions. The atomic spin−orbit correction, ΔE_{SO}, for F is 0.39 kcal/mol and is from the tables of Moore.[40] The atomic spin−orbit correction for Xe^+ is 10.04 kcal/mol. Obviously, such corrections are not negligible in considering accuracies of ± 1 kcal/mol.

A second relativistic correction to the atomization energy accounts for molecular scalar relativistic effects, ΔE_{SR}. We evaluated ΔE_{SR} by using expectation values for the two dominant terms in the Breit−Pauli Hamiltonian, the so-called mass velocity and one-electron Darwin (MVD) corrections from configuration interaction singles and doubles (CISD) calculations. The quantity ΔE_{SR} was obtained from CISD wave functions with an aVTZ basis set at the CCSD(T)/aVTZ geometry. The CISD(MVD) approach generally yields ΔE_{SR} values in good agreement (± 0.3 kcal/ mol) with more accurate values from, for example, Douglass−Kroll−Hess calculations, for most molecules. A potential problem arises in computing the scalar relativistic correction for the molecules in this study as there is the possibility of double counting the relativistic effect on Xe when applying a MVD correction to an energy that already includes some relativistic effects via the RECP. Because the MVD operators mainly sample the core region where the pseudo-orbitals are small, we assume any double counting to be small.

A third relativistic correction can be applied to molecules containing heavy atoms such as Xe. For these molecules, second-order spin−orbit corrections may not be small when compared with chemical accuracy. The lowest spin−orbit coupled eigenstates were obtained by diagonalizing relatively small spin−orbit matrixes in a basis of pure spin ($\Lambda-S$) eigenstates. In each case, the identity of the electronic states used as an expansion basis was restricted to all states (singlets and triplets) that correlated in the dissociation limit to ground-state atomic products. For XeF^+, this corresponded to 12 states (six singlets and six triplets), and for XeF_2, 18 states (nine singlets and nine triplets) correlating to ground-state products were used.[41] The electronic states and SO matrix elements were obtained in singles-only multireference configuration interaction calculations with a full valence complete active space (CAS) reference function with the aug-cc-pVTZ-PP basis set.

To verify that our ECP approach properly accounts for relativistic corrections, fully relativistic Dirac−Hartree−Fock CCSD(T) benchmark calculations were performed on the dissociation energy of XeF_2. These calculations were performed using the parallel MOLFDIR program package.[42,43] In the CCSD(T) calculation, the valence orbitals, $5s^2$ and $5p^6$ for Xe and $2s^2$ and $2p^5$ for F, were correlated. The aug-cc-pVTZ basis set for Xe was generated using the exponents from Dyall[44] and the contraction pattern used for the RECP basis sets, while the F basis was taken from earlier studies on interhalogens.[45]

Optimized bond lengths and harmonic frequencies for the diatomic molecular ions XeF^+ and XeF^- were obtained from a sixth degree Dunham fit of the potential energy surface.[46] For the polyatomic molecules XeF_2, XeF_4, XeF_5^-, and XeF_6 (O_h), geometry optimizations were performed with a convergence threshold on the gradient of approximately 10^{-4} E_h/b or smaller. Geometries were optimized at the aug-cc-pVDZ, aug-cc-pVTZ, and aug-cc-pVQZ levels for XeF^+, XeF^-, and XeF_2, and the first two basis sets were used in the XeF_4, XeF_5^-, and XeF_6 (O_h) optimizations. The geometry obtained with the aug-cc-pVTZ basis set was then used for the aug-cc-pVQZ calculations for the latter two molecules. The geometry of XeF_6 (C_{3v}) was optimized at the Hartree−Fock (HF) level with the aug-cc-pVDZ and aug-cc-pVTZ basis sets as all correlated geometry optimizations beginning with this structure optimized to the octahedral structure. To estimate the geometry for the correlated calculations, we took the ratio of r(XeF-(CCSD(T)))/rXeF(HF) for the O_h structure with the two basis sets and multiplied the bond distances at the HF level by these values to get estimated bond distances. The bond angles obtained at the HF level were used in the correlated calculations.

To convert vibrationless atomization energies, ΣD_e, to $\Sigma D_0{}^0$, and ultimately to $\Delta H_f{}^0$, we require as accurate vibrational frequencies as possible to calculate molecular zero-point vibrational energy corrections, ΔE_{ZPE} (and the temperature dependence of ΔE and ΔH for these quantities at 298 K). For the diatomics, we calculated anharmonic zero-point energies at the CCSD(T)/aug-cc-pVQZ level. For the polyatomic molecules, we calculated the frequencies at the CCSD(T) or MP2 level with the aug-cc-pVDZ basis set and averaged these values with the experimental ones to estimate the anharmonic zero-point energy following the suggestion of Grev et al.[47]

By combining our computed ΣD_0 values with the known[1] heats of formation at 0 K for the elements: $\Delta H_f{}^0(\mathrm{Xe}) = 0$ kcal/mol and $\Delta H_f{}^0(\mathrm{F}) = 18.47 \pm 0.07$ kcal/mol, we can derive $\Delta H_f{}^0$ values for the molecules under study. We can obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[48]

Results and Discussion

The total energies used in this study are given as Supporting Information. The geometries are given in Table 1, where they are compared with the available experimental values. The calculated harmonic frequencies are given in Table 2 and are compared with the available experimental values.

The calculated bond distance in XeF_2 is within 0.004−0.005 Å of the best experimental values.[49,50] The size of this difference

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Table 1. Calculated Geometry Parameters[a]

molecule	method /basis set	R_e (Å)	<FXeF (deg)
XeF^+	CCSD(T)/aVdZ	1.9193	
	CCSD(T)/aVTZ	1.8830	
	CCSD(T)/aVQZ	1.8721	
XeF^-	CCSD(T)/aVDZ	3.0882	
	CCSD(T)/aVTZ	2.9830	
	CCSD(T)/aVQZ	2.9679	
XeF_2	CCSD(T)/aVDZ	2.0226	180.0
	CCSD(T)/aVTZ	1.9909	180.0
	CCSD(T)/aVQZ	1.9816	180.0
	expt.[49]	1.977	180.0
	expt.[50]	1.9744	180.0
XeF_4	CCSD(T)/aVDZ	1.9847	90.0
	CCSD(T)/aVTZ	1.9515	90.0
	expt[51]	1.94 ± 0.01	90.0
	expt[52]	1.953	90.0
	expt[53]	1.93487	90.0
XeF_5^-	CCSD(T)/aVDZ	2.0605	72.0
	CCSD(T)/aVTZ	2.0342	72.0
	expt[13]	2.012	72.0
XeF_6 (O_h)	CCSD(T)/aVDZ	1.9740	90.0
	CCSD(T)/aVTZ	1.9420	90.0
	HF/aVDZ	1.9156	90.0
	HF/aVTZ	1.8908	90.0
XeF_6 (C_{3v})	HF/aVDZ	1.9616[b]	112.01
		1.8340[b]	81.86
	HF/aVTZ	1.9341[c]	113.16
		1.7953[c]	81.64
	expt[19]	1.941	
		1.850	

[a] Bond distances in Å and bond angles in degrees. [b] Scaled distances used in the CCSD(T)/aug-cc-pVDZ calculations are 2.0215 and 1.890 Å. [c] Scaled distances used in the CCSD(T)/aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ calculations are 1.9865 and 1.8439 Å.

Table 2. Comparison of Calculated and Experimental Frequencies (cm^{-1})

molecule	basis set	ω_e (cm^{-1})	expt $\nu_e(\omega_e)$	other calcd values[a]
XeF^+	aug-cc-pVQZ	645.6		
		($\omega_e x_e = 4.2$)		
XeF^-	aug-cc-pVQZ	122.9		
		($\omega_e x_e = 2.0$)		
XeF_2	aug-cc-pVTZ	567.4 (Σ_u^+)	560.2(566.1)[50]	583.1[50]
		522.8 (Σ_g^+)	519.2(526.0)	515.1
		215.3 (Π_u)	212.5(214.2)	218.4
XeF_4	aug-cc-pVDZ	596.5 (e_u)	584.0[53]	603(608)[53]
		542.7 (a_{1g})	554.3	557(563)
		518.2 (b_{2g})	524	521(527)
		278.8 (a_{2u})	290.6	307(310)
		205.1 (b_{1g})	218	219(225)
		164.6 (b_{1u})	216	176(178)
		156.4 (e_u)	123 or 161	168(167)
XeF_5^-	aug-cc-pVDZ	499 (e_1')	400−550[13]	502[b]
		489 (a_1')	502	496
		433 (e_2')	423	428
		360 (e_2')	377	379
		282 (a_2'')	274	294
		267 (e_1')	290	284
		84 (e_2'')		86
XeF_6	aug-cc-pVDZ	597.6 (t_{1u})	619[18]	
		569.1 (a_{1g})	613	
		506.5 (e_g)	507	
		198.6 (t_{1u})	252	
		151.4 (t_{2g})	156[19]	
		131 (t_{2u})	69	

[a] At the CCSD(T) level except for XeF_5^-, which is MP2/aug-cc-pVTZ. Values of ω_e in parentheses. [b] This paper.

Table 3. Energy Differences between O_h and C_{3v} Structures for XeF_6

basis set	ΔE ($O_h - C_{3v}$) (kcal/mol)
aVDZ	9.16
aVTZ	2.44
aVQZ	0.96
CBS (eq 1)	0.19

is that expected without the inclusion of additional core-valence correlation in the calculations. The calculated bond distance in XeF_4 is in good agreement with the older experimental data from electron diffraction[51] and an X-ray structure[52] and is just over 0.015 Å longer than the most recent value[53] of 1.935 Å. Comparison with the XeF_2 values shows that the bond distance for XeF_4 should shorten on improvement of the basis set to aug-cc-pVQZ by about 0.01 Å. For XeF_5^-(D_{5h}), the calculated bond distance at the aug-cc-pVTZ level is 0.02 Å longer than the average value from the crystal structure of 2.012 Å; the Xe−F bond distances in the crystal range from 1.979 to 2.034 Å.[13]

The ground-state geometry of XeF_6 has not been firmly established. The optimized CCSD(T) geometry for the O_h structure of XeF_6 has bond distances that are slightly longer than those for XeF_4, consistent with more steric repulsion between the fluorine atoms in the O_h structure. The HF optimized bond distances for $XeF_6(O_h)$ are shorter than the CCSD(T) values as expected. The CCSD(T) values are 1.0305 and 1.027 times the HF bond distances with the aug-cc-pVDZ and aug-cc-pVTZ basis sets, respectively. The geometry of XeF_6 in C_{3v} symmetry optimized at the HF level shows that the open face (larger FXeF bond angle) has the longer bonds and that the face with the smaller FXeF angle has the shorter XeF bonds. This is consistent with the bonding model that would place the lone pair in the open face and that this lone pair has significant steric repulsions with the three Xe−F bonds in this face. We also calculated the energy of the geometry that has the long bonds with the small angle and the short bonds with the large angle, which would be expected from simple models of the interactions of the Xe−F bonds excluding the role of the lone pair. This structure is 20.1 and 21.7 kcal/mol higher in energy at the CCSD(T)/aug-cc-pVDZ and CCSD(T)/aug-cc-pVTZ levels, respectively. We were unable to optimize a geometry with C_{3v} symmetry based on a correlated wave function because of the high level of basis set required for the nonoctahedral geometry to be of lower energy. To estimate the energy difference between the O_h and the C_{3v} geometries, we used estimated geometries for the C_{3v} structure as described previously based on the optimized HF structure for $XeF_6(C_{3v})$. The HF optimized angles were used, and the ratio r(XeF(CCSD(T)))/rXeF(HF) obtained for the O_h structure with the aug-cc-pVDZ and -pVTZ basis sets was used to scale the HF bond distances for the C_{3v} structure for each basis set; the aug-cc-pVTZ geometry was used for the aug-cc-pVQZ calculation. The scaled bond distances are given in Table 1. As shown in Table 3, the energy difference between C_{3v} and O_h structures is very basis set dependent. (The total energies used to obtain the energy differences in Table 3 are given as Supporting Information.) At the CCSD(T)/aug-cc-pVDZ level, the C_{3v} structure is 9.16

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kcal/mol higher in energy, whereas at the CCSD(T)/CBS level, the energy difference is only 0.19 kcal/mol. This result suggests that, with an optimized C_{3v} geometry, the C_{3v} structure would probably be slightly lower in energy than the O_h structure. An important result of this comparison is that the energies of the C_{3v} and O_h structures are very similar. This means that XeF_6 will exhibit fluxional behavior with the O_h and C_{3v} structures rapidly interconverting. Because the two structures possess different properties, the fluxionality will exhibit a temperature dependence that is influenced by both the energy difference between the two structures and the vibrational effects.

An estimate of the potential for significant multireference character in the wave function can be obtained from the T_1 diagnostic[54] for the CCSD calculation. The value for the T_1 diagnostics for the O_h and C_{3v} geometries of XeF_6 are in the range of 0.019−0.021 depending on the basis set (decreasing with increasing basis set), showing that the wave function is dominated by a single configuration.

The calculated frequencies for XeF_2, XeF_4, and XeF_5^- can be compared with the experimental values. The calculated harmonic frequencies for XeF_2 at the CCSD(T)/aug-cc-pVTZ level are in excellent agreement with the experimental harmonic values within 5 cm^{-1}. They are also in good agreement with previous CCSD(T) calculations done with an ECP and a polarized double-ζ basis set.[50] The calculated frequencies for XeF_4 are lower than the experimental values for the a_{1g}, b_{2g}, and b_{1g} modes by <15 cm^{-1}.[53,55] The e_u stretch is higher in frequency than the experimental value by comparable amounts. Improvement of the basis set at the CCSD(T) level to an effective polarized triple-ζ with f polarization functions leads to increases in the calculated frequencies.[53] The calculated values show that the assigned value based on weak overtones at 220 cm^{-1} for the silent b_{1u} mode is too high and should be closer to 165 cm^{-1}. The calculated e_u bend is consistent with the calculated values of Burger et al.,[53] suggesting that the assigned value at 161 cm^{-1} is correct in contrast with the value at 123 cm^{-1}. Ruden et al.[56] for first row diatomics have shown that one can obtain improved frequencies to within a few cm^{-1} by using higher order coupled cluster methods and again suggest that cancellation of errors that occurs at the CCSD(T) level provides the agreement with experiment.

The vibrational spectrum for XeF_5^- was calculated at the CCSD(T)/aug-cc-pVDZ and MP2/aug-cc-pVTZ levels. The agreement between the two calculations is excellent with the largest differences being only 20 cm^{-1}. The calculated results are in good agreement with the experimental values.[13] We predict that the $e_{1'}$ Xe−F stretch is above the $a_{1'}$ stretch by 10 cm^{-1} at the CCSD(T) level, and this can be used to narrow substantially the range predicted from experiment for the $e_{1'}$ stretching mode from 400 to 550 to 480−520 cm^{-1}. The calculated values are within 25 cm^{-1} of the experimental values. The only real difference between the observed and the experimental values is for the ordering of the $a_{2''}$ and $e_{1'}$ bends, which are the out-of-plane and in-plane bending modes. The calculations predict the $a_{2''}$ (out-of-plane) mode to be higher than the $e_{1'}$ (in-plane) mode by 15 cm^{-1}, whereas the experimental difference is the opposite by the same amount. This difference between theory and experiment was also found at the local DFT level.[13] The asymmetric out-of plane $e_{2''}$ bend is predicted to be 84 cm^{-1} at the CCSD(T) level. For XeF_5^-, the zero-point energy, calculated as the average of the experimental data (using the calculated values for the $e_{1'}$ stretch and the $e_{2''}$ bend), gives 5.84 kcal/mol. Using the calculated values for the $e_{1'}$ stretch and the $e_{2''}$ bend with the remaining frequencies taken from experiment gives ZPE = 5.89 kcal/mol, whereas the pure calculated ZPE is 5.80 kcal/mol.

The interpretation of the vibrational spectrum for XeF_6 is complicated by the lack of knowledge of the actual gas-phase structure of the isolated molecule. However, there is reasonable agreement between the available data[18,19] and the frequencies computed for the O_h structure. The largest differences between theory and the experiment occur for the a_{1g} stretching mode that the calculations predict to be low by about 45 cm^{-1} and the t_{1u} bend calculated at 198.6 cm^{-1}, which is about 50 cm^{-1} lower than the experimental value. The calculated frequency of the lowest t_{2u} mode is almost double the experimentally assigned mode, but this quantity is hard to measure. The zero-point energy calculated from experimental frequencies is 7.02 kcal/mol based on the observed and estimated frequencies and the zero-point energy from the CCSD(T) calculations is 6.88 kcal/mol, a difference of only 0.14 kcal/mol.

The various energy quantities in Table 4 are summed to obtain the total molecular dissociation energies. The differences in the valence electronic dissociation energies between eqs 1 and 3 for those molecules where calculations at the aug-cc-pV5Z level were done are small with the largest difference (0.7 kcal/mol) arising for the $XeF^+ \rightarrow Xe + F^+$ channel. The core valence correction for all of the molecules except XeF^- is negative, lowering the total bond dissociation energies. The use of only the cc-pVTZ basis set when compared with the aug-cc-pVTZ basis set gives a larger core-valence correction, suggesting that the cc-pVTZ core-valence corrections may be slightly too large for XeF_4, XeF_5^-, and XeF_6. The scalar relativistic corrections are also negative and can be as high as 1 kcal/mol. The second-order spin−orbit correction for XeF^+ is large, 2.1 kcal/mol, and even for XeF_2, it is close to 1 kcal/mol.

For XeF_2, fully relativistic all-electron four-component CCSD(T) calculations were performed using a basis set comparable to aug-cc-pVTZ. Only the valence electrons (i.e., $2s^2$ and $2p^5$ for F and $5s^2$ and $5p^6$ for Xe) were correlated, and the calculated equilibrium geometry from the CCSD(T)/aug-cc-pVTZ-PP calculation was used. Our fully relativistic calculation gives a dissociation energy of 59.55 kcal/mol. At the CCSD(T)/aug-cc-pVTZ-PP level, we obtained a total electronic dissociation energy of 59.67 kcal/mol, based on a valence dissociation energy of 59.80 kcal/mol and including all relativistic corrections (−0.13 kcal/mol). The close agreement between our approximate additive relativistic approach using an ECP and the fully relativistic all-electron approach shows that the relativistic effects have been properly accounted for in our calculation.

We estimate that the error bars for the calculated heats of formation for XeF^+, XeF^-, and XeF_2 are ±0.3 kcal/mol considering errors in the energy extrapolation, frequencies, and other electronic energy components. The errors for XeF_4 and XeF_5^- are estimated as ±1.0 kcal/mol. Because of the difficulty

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Table 4. CCSD(T) and Experimental Atomization Energies in Kcal/Mol[a]

molecule	eq 1[b]	eq 3[c]	ΔE_{ZPE}[d]	ΔE_{CV}[e]	ΔE_{SR}[f]	ΔE_{SO}[g]	ΔE_{SO}[h]	ΣD_0 (0 K)[i]	ΣD_0 (0 K) exptl
$XeF^+ \rightarrow Xe + F^+$	164.49	165.22	−0.92	−1.04	−0.30	−0.26	2.09	164.79 164.06	
$XeF^+ \rightarrow Xe^+ + F$	50.94	50.99	−0.92	−0.02	−0.07	−10.43	2.09	41.64 41.59	
$XeF^+ + e^- \rightarrow Xe + F$	−236.76	−236.52	−0.92	−1.33	−0.07	−0.39	2.09	−237.38 −237.14	
$XeF^- \rightarrow Xe + F^-$	6.40	6.48	−0.18	0.03	−0.03	0.0		6.22 6.30	
$XeF^- \rightarrow Xe + F + e^-$	85.33	85.38	−0.18	0.12	−0.19	−0.39		84.74 84.69	
$XeF_2 \rightarrow Xe + 2F$	63.65	63.69	−2.16	−1.15	−0.32	−0.78	0.97	60.26	62.24,[10] 63.42[11]
$XeF_4 \rightarrow Xe + 4F$	125.08		−4.59	−1.88	−0.63	−1.56		116.42	124.1,[10] 131.5[11]
$XeF_5^- \rightarrow Xe + 5F + e^-$	264.64		−5.84	−2.84	−1.01	−1.95		253.00	
$XeF_5^- \rightarrow XeF_4 + F^-$	60.63		−1.23	−0.88	−0.27	0		58.25	
XeF_6 (O_h) $\rightarrow Xe + 6F$	179.21		−6.88	−2.22	−1.02	−2.34		166.75	178.9,[10] 200.8[11]

[a] The atomic asymptotes were calculated with the R/UCCSD(T) method. [b] Extrapolated by using eq 1 with aD, aT, and aQ. [c] Extrapolated by using eq 3 with aQ and a5. [d] The zero-point energies were obtained as follows: (1) for diatomics, the anharmonic ZPE values were computed as $0.5\omega_e - 0.25\omega_e x_e$; (2) for XeF_2, the ZPE was taken as 0.5 the sum of the average of the anharmonic and harmonic experimental frequencies; (3) for XeF_4, XeF_5^-, and XeF_6, the anharmonic ZPE values were taken as the average of the zero-point energies based on the experimental fundamentals and the CCSD(T) harmonic frequencies. [e] Core/valence corrections were obtained with the cc-pWCVTZ (F) and cc-pwCVTZ (for Xe) basis sets or with the augmented sets at the optimized CCSD(T)/aug-cc-pVTZ geometries. [f] The scalar relativistic correction is based on a CISD(FC)/cc-pVTZ-PP MVD calculation and is expressed relative to the CISD result without the MVD correction (i.e., including the existing relativistic effects resulting from the use of a relativistic effective core potential). [g] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on Moore's tables, ref 40. [h] Second-order molecular spin−orbit effects obtained with an aug-cc-pVTZ-PP basis set and a relativistic ECP. [i] The theoretical value of ΔD_0 (0 K) was computed with the CBS estimates. If two values are given, the top value is from CBS (eq 3) and the lower value is from CBS (eq 1).

Table 5. Calculated and Experimental Heats of Formation (kcal/mol)

molecule	theory (0 K)	theory (298 K)	expt equilibrium (0 K)[10]	expt PI (0 K)[11]
XeF^+	255.8 ± 0.3	255.4 ± 0.3		
XeF^-	−66.3 ± 0.3	−66.8 ± 0.3		
XeF_2	−23.3 ± 0.3	−23.9 ± 0.3	−25.3	−28.0 ± 0.5
XeF_4	−42.5 ± 1.0	−43.5 ± 1.0	−50.2	−57.7 ± 2
XeF_5^-	−160.6 ± 1.0	−162.9 ± 1.0		
XeF_6	−55.9 ± 2.0	−58.3 ± 2.0	−68.1	$-(90_{-3}^{+8})$

in obtaining the structure for XeF_6, we estimate that the errors in the heat of formation are ±2.0 kcal/mol.

The calculated total dissociation energies for XeF_2 and XeF_4 are smaller than the experimental values[10,11] derived from the experimental heats of formation leading to calculated heats of formation that are less negative than the experimental values (Table 5). The calculated total dissociation energy for XeF_2 is smaller than the experimental value from equilibrium measurements[10] by 2.0 kcal/mol and smaller than the photoionization value[11] by 5.3 kcal/mol. The calculated total bond dissociation energy for XeF_4 is 7.7 kcal/mol lower than the experimental equilibrium value[10] and 15.1 kcal/mol lower than the photoionization value.[11] We do not expect such large differences at this level of theory and suggest that the photoionization values[11] are far too large. Our calculated values also suggest that there are issues with the equilibrium thermodynamic values,[10] noting that it is difficult to obtain data of high accuracy for such highly reactive species.

The calculated value for the total bond dissociation energy of XeF_6 differs by 12.2 kcal/mol from the experimental value based on equilibrium measurements[10] and by 34.1 kcal/mol from the value determined in the photoionization experiments.[11] Even if there is a lower energy structure at the C_{3v} level, it is unlikely to be 12 kcal/mol lower than the O_h structure. It is also unlikely that the values of the other corrections to the dissociation energy will change by more than 1−2 kcal/mol when the geometry changes. Thus, based on our results, it is unlikely that the calculated total bond dissociation energy for XeF_6 is in error by more than 2 kcal/mol. Thus, we again suggest that the total bond dissociation energy of XeF_6 as determined by experiment is significantly in error and needs to be remeasured. The differences between the calculated and the equilibrium experimental values[10] for the total bond dissociation energies for XeF_2 and XeF_4 of 2.0 and 7.7 kcal/mol are consistent with the difference of 12.2 kcal/mol found for XeF_6 between the calculated and the equilibrium values.

The bond energy for $XeF^+ \rightarrow Xe + F^+$ has been measured by collision induced dissociation.[57] The calculated ionization potential for Xe is 12.09 eV as compared to an experimental value of 12.13 eV, an error of only 0.9 kcal/mol.[58] The calculated dissociation energy for XeF^+ for the lower energy channel is 41.64 kcal/mol (1.81 eV) as compared to the experimental value of 1.95 ± 0.16 eV obtained from collision induced dissociation (CID) studies with Xe as the collision gas.[57] The CID experiments with Ne and Ar give higher dissociation energies of 2.81 ± 0.09 and 2.83 ± 0.12 eV, respectively. Our value is in agreement with the Xe CID value considering the error limits of the experiment. It is important to note that there is an error of 10.03 kcal/mol if the spin−orbit correction for Xe^+ is not included. A value of 1.06 ± 0.05 eV derived from ion appearance energies is too low.[59] The calculated value for the dissociation energy of the higher energy channel is 164.8 kcal/mol (7.15 eV), in excellent agreement with the value of 164.8 obtained at the lower local density functional theory level by us in our work on fluorocation detachment energies.[12]

The fluoride ion affinity of Xe at 0 K is small, 6.2 kcal/mol, as expected, as this represents the binding of a closed shell anion with a closed shell rare gas. The fluoride affinity of XeF_4 at 0 K is a moderate value of 58.2 kcal/mol.[14]

In Table 5, the calculated heats of formation at 0 K, ΔH_f^0, are compared with the available experimentally derived values.

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(57) Krouse, I. H.; Wenthold, P. G. *Inorg. Chem.* **2003**, *42*, 4293.
(58) NIST Chemistry Webbook, http://webbook.nist.gov/.
(59) Zelenov, V. V.; Aparina, E. V.; Loboda, A. V.; Kukui, A. S.; Dodonov, A. F.; Kashtanov, S. A.; Aleinikov, N. N. *Eur. J. Mass Spectrom.* **2002**, *8*, 233.

Consistent with the previous discussion of the bond dissociation energies, we suggest that there are significant errors in the experimental values. These values can be used to calculate the dissociation energies of the xenon fluorides into Xe and F_2 as follows at 0 K:

$$XeF_2 \rightarrow Xe + F_2 \quad \Delta H = 23.3 \text{ kcal/mol}$$

$$XeF_4 \rightarrow XeF_2 + F_2 \quad \Delta H = 19.2 \text{ kcal/mol}$$

$$XeF_4 \rightarrow Xe + 2F_2 \quad \Delta H = 42.5 \text{ kcal/mol}$$

$$XeF_6 \rightarrow XeF_4 + F_2 \quad \Delta H = 13.4 \text{ kcal/mol}$$

$$XeF_6 \rightarrow XeF_2 + 2F_2 \quad \Delta H = 32.6 \text{ kcal/mol}$$

$$XeF_6 \rightarrow Xe + 3F_2 \quad \Delta H = 55.9 \text{ kcal/mol}$$

As expected, the loss of F_2 from XeF_2 is slightly larger than the loss of F_2 from XeF_4, and the loss of F_2 from XeF_4 is significantly larger than the loss of F_2 from XeF_6. This is consistent with increased steric crowding as more fluorines are added to the central Xe.

Conclusion

A composite CCSD(T)-based approach with extrapolation to the complete basis set limit was used to compute geometries, normal-mode frequencies, atomization energies, and heats of formation for XeF^+, XeF^-, XeF_2, XeF_4, XeF_5^-, and XeF_6. The calculated heats of formation for the neutral XeF_n fluorides are less negative (less stable) than the experimental values from equilibrium measurements by 2.0, 7.7, and 12.2 kcal/mol for $n = 2$, 4, and 6, respectively. The calculated values are even higher as compared to the heats of formation from photoionization measurements. The bond dissociation energy for XeF^+ is in good agreement with the experimental values. The fluoride affinities of Xe and XeF_4 are consistent with lower level estimates of these quantities. The total bond dissociation energy of XeF_2 was checked by a full relativistic calculation, and the result is in excellent agreement with that obtained from our additive approach using an ECP. The calculations strongly suggest that the experimental heats of formation of XeF_2, XeF_4, and XeF_6 need to be remeasured. The geometry of XeF_6 was also studied in detail. Our best estimates place the C_{3v} structure above the O_h structure by 0.19 kcal/mol. Because the O_h geometry was estimated more precisely than the C_{3v} one, the C_{3v} structure is likely to be of equal or lower energy than that for the O_h structure. The fact that the energies of the different structures of XeF_6 are so close in energy suggests that this molecule is highly fluxional. More importantly, the results suggest that the energetics governing the stereoactivity of the lone pair is extremely subtle and that the lone pair has a highly fluxional character.

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Supporting Information Available: Complete refs 24l, 33, and 34 including full author listings as well as total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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