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Article

Structure and Heats of Formation of Iodine Fluorides and the Respective Closed-Shell Ions from CCSD(T) Electronic Structure Calculations and Reliable Prediction of the Steric Activity of the Free-Valence Electron Pair in ClF_6^-, BrF_6^-, and IF_6^-

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Atomization energies at 0 K and heats of formation at 0 and 298 K are predicted for IF, IF_2^-, IF_2^+, IF_3, IF_4^-, IF_4^+, IF_5, IF_6^-, IF_6^+, IF_7, IF_8^-, BrF_6^-, and ClF_6^- from coupled cluster theory [CCSD(T)] calculations with effective-core potential correlation-consistent basis sets for I. In order to achieve near chemical accuracy (±1 kcal/mol), three 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, and a correction for first-order atomic spin−orbit effects. Vibrational zero-point energies were computed at the coupled-cluster level of theory except for IF_6^-, IF_7, and IF_8^-. The calculated heats of formation for the neutral and ionic IF_n fluorides were used to predict fluoride affinities. It is shown that high-level calculations are required to predict correctly the steric activity of the free-valence electron pair on the central atoms in IF_6^- (C_{3v}), BrF_6^- (O_h), and ClF_6^- (O_h). The vibrational spectrum of IF_8^- was reanalyzed, and complete mode descriptions for square-antiprismatic XF_8 species of D_{4d} symmetry are given.

Introduction

There is significant interest in the role of stereochemically active lone pairs in main-group compounds.[1] Famous examples of this are XeF_6 and the isoelectronic anion IF_6^-. Xenon fluorides have been known[2,3] since the early 1960s beginning with the work of Bartlett.[4] The gas-phase structure of XeF_6 has been controversial with regards to the stereoactivity of the xenon valence electron lone pair. 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 seventh ligand, with the electron lone pair occupying a triangular face of the octahedron and the resulting structure deviating from O_h symmetry. Experimental evidence based on electron diffraction, vibrational spectroscopy, and photoelectron studies suggests that XeF_6 does not have O_h symmetry.[5–8]

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We recently used CCSD(T) (coupled cluster including single and double excitations with an approximate triples correction)[9] calculations, which were extrapolated to the complete basis set (CBS) limit using the new effective-core potential/correlation-consistent basis sets developed by Peterson and co-workers,[10] to predict the structures and heats of formation of the xenon fluorides.[1h] We showed that predicting the structure of XeF_6 correctly is difficult and requires very large basis sets. At the CCSD(T)/CBS level and using an approximate geometry for the C_{3v} structure, the C_{3v} and O_h structures of XeF_6 have essentially the same energy, with the O_h structure only 0.19 kcal/mol below the C_{3v} one. However, with an optimized C_{3v} geometry, the C_{3v} structure would probably become slightly lower in energy than the O_h one. The results for XeF_6 are consistent with the earlier study of Kutzelnigg and co-workers.[1g]

Thus, an interesting question is, how reliably can theory predict the structure of compounds with stereoactive lone pairs? Because the lighter homologues of IF_6^-, i.e., BrF_6^- and ClF_6^-, are known to be octahedral,[1a,b,d,e] the IF_6^-, BrF_6^-, and ClF_6^- series offers a unique opportunity to test the reliability of different computational methods to predict the steric activity of a free-valence electron pair correctly. A further objective of the present study was to predict heats of formation for all of the known iodine fluoride molecules and ions. We have previously reported the heat of formation of IF using a comparable approach.[11] We obtained $\Delta H_f(0\ K) = -19.4$ kcal/mol as compared to an experimental value of -22.2 ± 0.9 kcal/mol.[12]

Computational Methods

We have developed a composite approach[13] to the prediction of the thermodynamic properties of molecules based on molecular orbital theory using coupled-cluster methods at the CCSD(T) level with correlation-consistent basis sets extrapolated to the CBS limit.[14] The standard aug-cc-pVnZ basis sets were used for F and Cl. A small-core relativistic effective-core potential (RECP) was used for Br and I.[10] We use the shorthand notation of aVnZ to denote the combination of the aug-cc-pVnZ basis set on F/Cl and the aug-cc-pVnZ-PP basis set on Br/I. Due to issues with our normal treatment of core-valence effects for the compounds containing I, calculations that included the core−electrons with the aug-cc-pwCVnZ basis sets for n = D, T, Q were done, and these energies were extrapolated to the CBS limit. For the ClF_x and BrF_x compounds, we included the core-valence correction (ΔE_{CV}) obtained in the normal way. The atomic spin−orbit (SO) corrections are not small for the halogens, $\Delta E_{SO}(F) = 0.39$, $\Delta E_{SO}(Cl) = 0.84$, $\Delta E_{SO}(Br) = 3.90$, and $\Delta E_{SO}(I) = 7.24$ kcal/mol from the tables of Moore[15] and must be included. In addition to the atomic SO correction, a molecular SO correction for the IF_x compounds was calculated using the SO/density functional theory method.[16] ΔE_{SO}(molecule) was calculated at the B3LYP level with the aVTZ-PP SO basis set on I and the aVTZ basis set on F. The computed $\sum D_0$ values are given by the following expressions:

$$\sum D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{SR} + \Delta E_{SO} \qquad (1)$$

for the IF_x compounds where ΔE_{ZPE} is the zero-point energy and ΔE_{SR} is the scalar relativistic correction (for the IF_x compounds, this is for the F atoms only because it is already included in the I pseudopotential) and

$$\sum D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} \qquad (2)$$

for the ClF_x and BrF_x compounds. By combining the $\sum D_0$ with the known[12] heats of formation at 0 K for the elements, $\Delta H_f^0(F) = 18.47 \pm 0.07$ kcal/mol, $\Delta H_f^0(Cl) = 28.59$ kcal/mol, $\Delta H_f^0(Br) = 28.18 \pm 0.01$ kcal/mol, and $\Delta H_f^0(I) = 25.61 \pm 0.01$ kcal/mol, we can derive ΔH_f^0 values for the molecules under study. Heats of formation at 298 K were obtained by following the procedures outlined by Curtiss et al. using a value of 1.58 kcal/mol for the temperature correction of the I atom.[17] Complete details of the calculations are given in the Supporting Information.

Results and Discussion

Geometries. Geometries for the polyatomics were optimized with the aVDZ and aVTZ basis sets. In addition, the geometry for IF_2^- was optimized with the aVQZ basis set. For IF_2^-, the CCSD(T)/aVQZ I−F bond distance of 2.0830 Å is closer to the experimental average from the crystal structure[18] of 2.078 (5) Å than the CCSD(T)/aVTZ distance. The I−F bond distance at the aVTZ level is only 0.010 Å longer than the aVQZ value. For IF at the CCSD(T)/aVTZ

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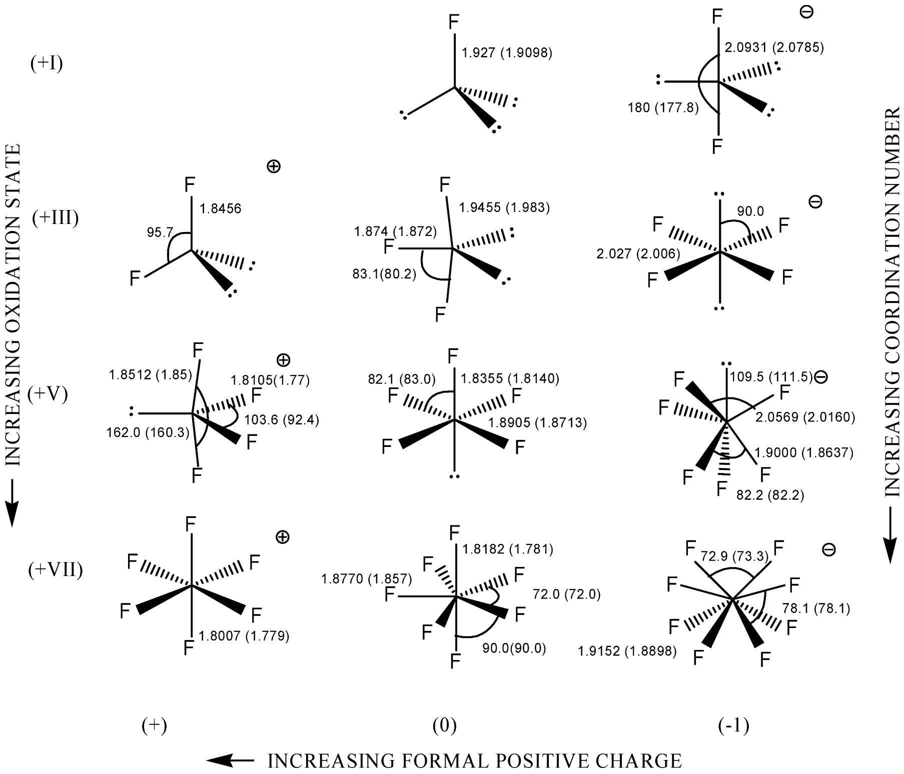

Figure 1. Calculated CCSD(T)/aVTZ and experimental geometries in parentheses of the iodine fluoride molecules and their ions (bond lengths in angstroms and bond angles in degrees).

level, we obtain a value of 1.9270 Å in comparison to our previously calculated value[11] of 1.9110 Å at the aug-cc-pV5Z-PP level (a corrected value of 1.8991 Å) as compared to the experimental value of 1.9098 Å.[19]

The experimentally observed and calculated CCSD(T)/aVTZ geometries are summarized in Figure 1. The CCSD(T)/aVTZ geometries are in excellent agreement with the experimental ones,[18,20–26] particularly if one keeps in mind that, on the basis of the IF_2^- calculations, the aVTZ basis set is expected to result in bond lengths that are too long by about 0.01 Å. In accordance with these expectations, the average observed deviations for most I−F bond lengths are 0.014 ± 0.012 Å. The exceptions are IF_3, IF_4^+, IF_7, and IF_6^-. In the crystal structure of solid IF_3, the axial I−F bonds are lengthened by about 0.05 Å because of strong association.[20] In the crystal structure of $IF_4^+SbF_6^-$, the compression of the equatorial F−I−F bond angle is caused by fluorine bridges from the anions.[26] The experimental values[22] for IF_6^- also come from a crystal structure with significant fluorine bridging and variations in the individual bond lengths, which might account for the somewhat larger deviations (about 0.04 Å) from the predicted values. The deviation of 0.037 Å for the axial bonds in IF_7 could be attributed to the fluxional character[23,27] of this molecule.

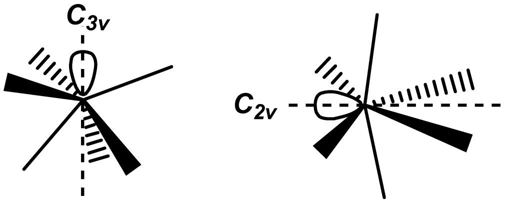

Figure 2. Minimum and low-energy structure of the MF_6^- anions with a sterically active free-valence electron pair of M.

For IF_6^-, three different structures are possible that are very close in energy. If the free-valence electron pair of iodine is sterically inactive, the structure is octahedral with O_h symmetry. If the free pair is sterically active, two possibilities must be considered. The first has C_{3v} symmetry and is derived from a monocapped octahedron in which the free pair occupies the cap. Because of the repulsion from the free pair, the angle between the three adjoining fluorines is enlarged and that between the three opposite fluorines is compressed (see Figure 2). The second has C_{2v} symmetry and is derived from a pentagonal bipyramid in which the free pair occupies one of the equatorial positions. Because of the repulsion from the free pair, the angle between the neighboring equatorial fluorines is spread, whereas that

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Table 1. Relative Energies of IF_6^- in kcal/mol at the CCSD(T) Level as a Function of the Basis Set

basis set	C_{3v}	C_{2v}	O_h
aVDZ	3.98	4.24	0.0
aVTZ//scaled	0.0	0.91	1.39
aVTZ//opt	0.0	0.76	3.01
aVQZ//scaled	0.0	1.08	3.45
aVQZ//aVTZ opt	0.0	0.96	4.41
CBS	0.0	1.06	5.25

between the two remote fluorines is compressed. Furthermore, the two axial fluorine ligands are bent away from the free pair. If the ligands are placed on the surface of a sphere, the C_{3v} structure corresponds to a 1:3:3 arrangement, while that of the C_{2v} structure can be considered as a 1:2:2:2 configuration with respect to the 2-fold rotation axis.

The relative energies of the different structures for IF_6^- are given in Table 1, and there is a significant dependence on the basis set for the relative stability of the three structures. (The total energies are given in Tables SM-2 and SM-3 in the Supporting Information.) At the CCSD(T)/aVDZ level, the O_h structure is predicted to have the lowest energy, with the C_{3v} structure lying 3.98 kcal/mol higher in energy. The C_{2v} structure is 4.24 kcal/mol higher in energy than the O_h structure and is slightly higher than the C_{3v} structure by 0.26 kcal/mol. Improving the basis set quality to aVTZ leads to a reordering in the relative energies, with the C_{3v} structure now predicted to be the lowest-energy structure. At this level, the C_{2v} structure is higher than the C_{3v} structure by 0.76 kcal/mol, and the O_h structure is now the least stable, 3.01 kcal/mol above the C_{3v} structure. Single-point CCSD(T)/aVQZ calculations at the CCSD(T)/aVTZ-optimized geometries predict the same ordering in the relative energies. The C_{3v} structure has the lowest energy, followed by the C_{2v} structure, 0.96 kcal/mol higher in energy, and the O_h structure, 4.41 kcal/mol higher in energy. At the CCSD(T)/CBS level, the C_{3v} structure is predicted to have the lowest energy, with the C_{2v} and O_h structures being higher in energy by 1.06 and 5.25 kcal/mol, respectively. Thus, the stereoactive lone pair of IF_6^- distorts the octahedron, forming a more stable structure of C_{3v} symmetry. In a comparable study of the xenon fluorides,[1h] the C_{3v} structure of XeF_6 was predicted to lie 0.19 kcal/mol above the O_h structure at the CCSD(T)/CBS level. However, the O_h geometry had been estimated more precisely than the C_{3v} one, and it was concluded that upon complete CCSD(T) optimizations the C_{3v} structure of XeF_6 would likely be of equal or lower energy than the O_h structure and that XeF_6 would exhibit fluxional behavior involving both the O_h and C_{3v} structures.

The I−F bond distance in $IF_6^-(O_h)$ is calculated to be 1.998 Å at the CCSD(T)/aVTZ level. The I−F bond distance of the splayed triangular face of the C_{3v} structure is 2.057 Å, 0.059 Å longer than the I−F bond distance in the octahedral structure. The I−F bond distance of the contracted triangular face is 1.900 Å, and it is smaller by 0.098 Å compared to the I−F bond in $IF_6^-(O_h)$. The C_{2v} structure of IF_6^- has three pairs of equivalent I−F bonds, two equatorial and one axial. The axial I−F bond distance is 1.959 Å shorter by 0.039 Å than the I−F bond in $IF_6^-(O_h)$. Of the equatorial bonds, one pair is contracted with an I−F bond distance of 1.899 Å, the same as the I−F bond distance found in the contracted triangular face of the C_{3v} structure and 0.039 Å shorter than the I−F bond length in the O_h structure. The expanded I−F bond distance is 2.087, 0.089, and 0.03 Å longer than the I−F bond distances in the O_h structure and the splayed triangular face of the C_{3v} structure, respectively.

The structures of ClF_6^- and BrF_6^- in O_h symmetry were also optimized with the aVDZ and aVTZ basis sets. The optimized C_{3v} structure for IF_6^- at the CCSD(T)/aVTZ level was then taken, and the bond distances were scaled by the ratio of r(Cl−F)/r(I−F) and r(Br−F)/r(I−F) from the O_h geometries at this level to obtain a starting structure for ClF_6^- and BrF_6^- in C_{3v} symmetry. These ions optimized to the O_h structure, showing that the halogen lone pair is not stereoactive. The crystal structure of BrF_6^- has been determined to be almost perfectly octahedral with a Br−F bond distance of 1.854(1) Å.[28]

Vibrational Frequencies. The harmonic frequencies calculated at the CCSD(T)/aVTZ level are given in Table 2 and are compared with the available experimental values. The corresponding calculated MP2/aVTZ frequencies and HF/aVTZ frequencies are given as Supporting Information (Tables SM-4 and SM-5, respectively). The MP2 frequencies are higher than and within ~10 cm^{-1} of the calculated CCSD(T) frequencies at the aVTZ level.

The general agreement between calculated and experimental[1a,b,29–38] frequencies is very good, except for IF_3, IF_4^+, and IF_6^-, which are strongly affected by fluorine bridging in the solid state.[20,22,26] The frequency deviations for ClF_6^- and BrF_5 are all in the same direction and could be alleviated by applying different scaling factors to the calculated frequencies.

It was not possible to obtain harmonic frequencies for $IF_6^-(C_{3v})$ at the MP2 or CCSD(T) levels because the calculations at the CCSD(T)/aVTZ level are too expensive and the O_h structure is the minimum at the MP2/aVTZ level. At the Hartree−Fock (HF) level with the aVTZ basis set, the C_{3v} structure is the minimum energy structure, and we thus calculated harmonic frequencies at the HF/aVTZ level. These HF frequencies were scaled by a factor of 0.891 derived from ΔE_{ZPE}(MP2)/ΔE_{ZPE}(HF) for $IF_6^-(O_h)$ with the aVTZ basis set and are the ones reported in Table 2. This

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Table 2. Observed and Calculated Frequencies (cm^{-1})[a]

molecule	symmetry	aVTZ	expt
$\mathrm{IF_2^+}(C_{2v})$	a_1	710.5	
		223.0	
	b_2	711.9	
$\mathrm{IF_2^-}(D_{\infty h})$	σ_g^+	445.4	446^{b}
	σ_u^+	416.9	*397*^{b}
	π_u	191.6	*206*^{c}
$\mathrm{IF_3}(C_{2v})$	a_1	667.9	*640*^{d}
		569.8	*[550]*^{d}
		202.4	*228*^{d}
	b_2	202.6	*240*^{d}
	b_1	597.9	*535*^{e}
		306.2	*331*^{d}
$\mathrm{IF_4^+}(C_{2v})$	a_1	745.5	729^{f}
		671.8	625, 614^{f}
		308.7	316, *311*^{f}
		117.9	151^{f}
	b_1	760.7	720^{f}
		221.4	
	b_2	732.9	729^{f}
		349.7	385, *388*^{f}
	a_{2g}	337.9	341, *345*^{f}
$\mathrm{IF_4^-}(D_{4h})$	a_{1g}	517.1	522^{g}
	b_{1g}	459.3	455^{g}
	b_{2g}	195.9	195^{g}
	a_{2u}	281.0	*271*^{g}
	e_u	474.4	*448*^{g}
		125.8	
$\mathrm{IF_5}(C_{4v})$	a_1	712.0	698, *710*^{h}
		618.7	593^{h}
		321.4	315, *318*^{h}
	b_1	601.1	575^{h}
		206.0	
	b_2	264.7	273^{h}
	e	653.6	*640*^{h}
		362.7	374, *372*^{h}
		186.6	189^{h}
$\mathrm{IF_6^+}(O_h)^r$	a_{1g}	724.3	708^{i}
	e_g	738.8	732^{i}
	t_{2g}	330.4	340^{i}
	t_{1u}	817.9	*797*, *790*^{i}
		343.7	*343*^{i}
	t_{2u}	213.5	
$\mathrm{IF_6^-}(C_{3v})^j$	a_1	662	620^{k}
		448	451^{k}
		355	347^{k}
		206	199^{k}
	a_2	244	275^{k}
	e	603	527, *500−570*, *599*^{k}
		371	391, *390*^{k}
		352	347, *335*^{k}
		231	*260*^{k}
		58	
$\mathrm{IF_7}(D_{5h})^r$	a_1'	694.5	676^{l}
		643.5	635^{l}
	a_2''	774.5	*746*^{l}
		352.0	*365*^{l}
	e_1'	682.7	*670*^{l}
		425.5	425^{l}
		250.7	257^{l}
	e_1''	310.2	*319*^{l}
	e_2'	598.7	*596*^{l}
		518.6	510^{l}
	e_2''	31.8	[68]^{l}
$\mathrm{IF_8^-}(D_{4d})^r$	a_1	590.3	595, 588^{m}
		412.8	410^{m}
	b_1	217.5	
	b_2	597.2	*590*^{m}
		404.2	*410*^{m}
	e_1	603.9	*590*^{m}
		418.9	*410*^{m}
		346.3	*314*^{m}
	e_2	513.4	530^{m}
		464.9	463^{m}
		114.4	119^{m}
	e_3	539.9	550^{m}
		410.4	419^{m}
$\mathrm{ClF_5}(C_{4v})^r$	a_1	750.5	709,^{h} *722*^{n}
		551.6	538, *541*,^{h} *539*^{n}
		487.7	480, *486*,^{h} *493*^{n}
	b_1	379.2	375^{h}
	b_2	490.7	480^{h}
		282.8	
	e	746.9	*732*, ^{h} *726*^{n}
		505.4	*482*^{h}
		302.6	296, *302*,^{h} *299*^{n}
$\mathrm{ClF_6^-}(O_h)^r$	a_{1g}	504.2	525^{o}
	e_g	347.7	384^{o}
	t_{2g}	258.9	289^{o}
	t_{1u}	727.1	
		310.3	
	t_{2u}	194.8	
$\mathrm{BrF_5}(C_{4v})^r$	a_1	708.6	682, *683*^{h}
		590.2	570, *587*^{h}
		374.9	365, *369*^{h}
	b_1	318.1	312^{h}
	b_2	555.2	535^{h}
		236.5	237^{h}
	e	656.6	*644*^{h}
		425.9	414, *415*^{h}
		242.6	237^{h}
$\mathrm{BrF_6^-}(O_h)^r$	a_{1g}	561.0	565,^{p} 561^{q}
	e_g	439.4	450,^{p} 445^{q}
	t_{2g}	236.5	240,^{p} 241^{q}
	t_{1u}	572.8	
		208.8	
	t_{2u}	167.0	

[a] Calculated at the CCSD(T) level unless noted. Where applicable, Raman vibrational frequencies are given first, followed by IR frequencies given in italics. [b] Reference 29a. [c] Reference 29b. [d] Reference 30a. [e] Reference 30b. [f] Reference 31. [g] Reference 32. [h] Reference 33. [i] Reference 34. [j] For $\mathrm{IF_6^-}$, the frequency calculations at the CCSD(T) level for the C_{3v} structure are too computationally expensive. The MP2 method predicts an O_h structure so the C_{3v} frequencies were obtained at the HF/aVTZ level and scaled by 0.891. [k] Reference 35. [l] Reference 27. [m] Frequencies from ref 36. Assignments from Table 3. [n] Reference 37. [o] Reference 1b. [p] Reference 1a. [q] Reference 38. [r] Frequencies calculated at the MP2/aVTZ level.

could introduce an error of ±1 kcal/mol into our calculation of the heat of formation of $\mathrm{IF_6^-}$.

A comparison of the calculated $\mathrm{IF_8^-}$ frequencies with the literature data revealed that the previously proposed assignments,[36] which were made without the aid of theoretical calculations, needed a thorough revision. Our corrected assignments for $\mathrm{IF_8^-}$, together with a complete mode description,[39] are given in Table 3 and result in an excellent agreement between the observed and calculated spectra. They represent the first reliable assignments for a D_{4d} XY_8 species.

Heats of Formation and Reaction Enthalpies. The total energies used in this study are given as Supporting Information (Tables SM-2 and SM-3). The energetic components for predicting the total molecular dissociation energies are given for IF_x in Table 4 and for $\mathrm{ClF_5}$, $\mathrm{ClF_6^-}$, $\mathrm{BrF_5}$, and $\mathrm{BrF_6^-}$ in Table 5. An estimate of the potential for significant multireference character in the wavefunction can be obtained

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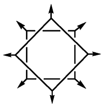
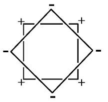
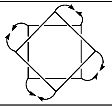
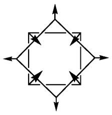
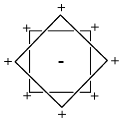
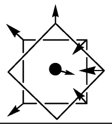
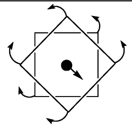
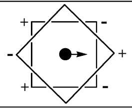
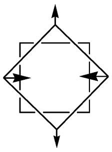
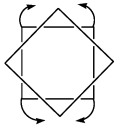
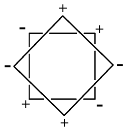
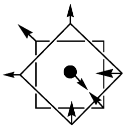
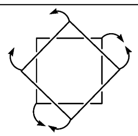
(39) The mode description is derived from the F and G matrix elements previously published by: Schlaefer, H. L.; Wasgestian, H. F. *Theor. Chim. Acta (Berlin)* **1963**, *1*, 369.

Table 3. Observed[a] and Calculated (MP2/aVTZ) Vibrational Frequencies (cm^{-1}) of IF_8^- and Their Assignments in Point Group D_{4d}

assignment IR, RA activ	approx mode descript[b]	obsd freq, rel intens RA (-142 °C)	IR	calcd freq, intens[c] (IR)[RA]
A_1 (- , RA) ν_1	 $\nu_{\text{sym in phase}}$	595 [10] 588 [6.5]		590 (--)[68]
ν_2	 $\delta_{\text{sym in phase}}$	410 [1.4]		413 (--)[3.4]
B_1 (- , -) ν_3	 τ_{torsion}			218 (--)[--]
B_2 (IR, -) ν_4	 $\nu_{\text{sym out of phase}}$		590 vs,br	597 (167)[--]
ν_5	 $\delta_{\text{sym out of phase}}$		410 s	404 (92)[--]
E_1 (IR, -) ν_6	 $\nu_{\text{asym in plane}}$		590 vs,br	604 (337)[--]
ν_7	 $\delta_{\text{asym in plane}}$		410 s	419 (213)[--]
ν_8	 δ_{wag}		314 m	346 (3)[--]
E_2 (- , RA) ν_9	 $\nu_{\text{sym out of phase}}$	530 sh[0+]		513 (--)[2.7]
ν_{10}	 $\delta_{\text{sym in plane}}$	463 [1.9]		465 (--)[7.3]
ν_{11}	 $\delta_{\text{sym out of plane}}$	119 [0.2]		114 (--)[0.6]
E_3 (- , RA) ν_{12}	 $\nu_{\text{asym in plane}}$	550 [0.5]		540 (--)[10]
ν_{13}	 $\delta_{\text{asym in plane}}$	419 [0.9]		410 (--)[5.7]

[a] Data from ref 36. [b] The normal modes were derived from the symmetry coordinates previously reported for D_{4d} $[Mo(CN)_8]^{4-}$ in ref 39. [c] IR intensities are in km/mol; Raman intensities are in Å^4/amu.

Table 4. CCSD(T) Atomization and Reaction Energies for IF_x in kcal/mol[a]

molecule	CBS			ΔE_{ZPE}[d]	ΔE_{SR}[e]	ΔE_{SO}		$\Sigma D_0(0\ K)$[g]		
	DTQ[b]	Q5[c]	DTQ_{CV}[b]			molecule	atom[f]	DTQ	Q5	DTQ_{CV}
$IF \rightarrow I + F$	70.31	70.07	70.32	0.91	−0.18	1.7	−7.63	63.28	63.05	63.30
$IF_2^+ + e^- \rightarrow I + 2F$	−106.65	−107.04	−107.62	2.35	−0.35	2.8	−8.02	−114.57	−114.96	−115.53
$IF_2^- \rightarrow I + 2F + e^-$	214.85	214.56	214.36	1.78	−0.42	1.0	−8.02	205.62	205.34	205.13
$IF_3 \rightarrow I + 3F$	194.71	194.14	193.34	3.64	−0.65	2.2	−8.41	184.21	183.64	182.84
$IF_4^+ + e^- \rightarrow I + 4F$	21.80	20.78	19.74	6.07	−0.82	2.1	−8.80	8.22	7.20	6.16
$IF_4^- \rightarrow I + 4F + e^-$	349.65	348.83	348.53	3.79	−0.93	2.0	−8.80	338.12	337.30	337.00
$IF_5 \rightarrow I + 5F$	336.38	335.12	334.03	7.33	−1.20	2.3	−9.19	320.97	319.70	318.61
$IF_6^+ + e^- \rightarrow I + 6F$	128.22		122.92	9.81	−1.30	3.8	−9.58	111.33		106.07
$IF_6^-(C_{3v}) \rightarrow I + 6F + e^-$	478.26		475.44	7.35	−1.52	1.8	−9.58	461.60		458.78
$IF_7 \rightarrow I + 7F$	406.21		400.66	11.58	−1.73	3.6	−9.97	386.53		380.97
$IF_8^- \rightarrow I + 8F + e^-$	555.70		549.43	12.93	−2.17	3.0	−10.36	533.23		526.97

[a] The atomic asymptotes were calculated with R/UCCSD(T). [b] Extrapolated by using eq 1 with aVDZ, aVTZ, and aVQZ (frozen core) or aCDZ, aCTZ, and aCQZ (CV calculations). [c] Extrapolated by using eq 2 with aVQZ and aV5Z. [d] The zero-point energies for the polyatomics were taken as 0.5 of the sum of the CCSD(T) harmonic frequencies, except for IF_6^-, where the harmonic frequencies for the C_{3v} structure were calculated at the HF/aVTZ level including a scaling factor of 0.891, and IF_7 and IF_8^-, which were calculated at the MP2/aVTZ level. [e] The scalar relativistic correction is based on a CISD(FC)/VTZ 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 RECP. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on Moore's tables.[15] [g] The theoretical value of $\Delta D_0(0\ K)$ was computed with the CBS estimates.

Table 5. CCSD(T) Atomization Energies for ClF_5, ClF_6^-, BrF_5, and BrF_6^- in kcal/mol[a]

molecule	CBS		ΔE_{CV}[d]	ΔE_{ZPE}[e]	ΔE_{SR}[f]	ΔE_{SO}[g]	$\Sigma D_0(0\ K)$[h]	
	DTQ[b]	Q5[c]					DTQ	Q5
$ClF_5 \rightarrow Cl + 5F$	186.01	186.39	0.09	8.65	−0.70	−2.79	173.96	174.34
$ClF_6^-(O_h) \rightarrow Cl + 6F + e^-$	311.66	310.94	0.47	8.11	1.19	−3.18	302.03	301.32
$BrF_5 \rightarrow Br + 5F$	239.99	238.94	−2.89	7.77	0.15	−5.45	224.03	222.98
$BrF_6^-(O_h) \rightarrow Br + 6F + e^-$	383.05	380.86	−0.49	7.14	−0.45	−5.84	369.12	366.94

[a] The atomic asymptotes were calculated with R/UCCSD(T). [b] Extrapolated by using eq 1 with aVDZ, aVTZ, and aVQZ. [c] Extrapolated by using eq 2 with aVQZ and aV5Z. [d] Core-valence correction calculated as the difference in energy between the valence electron correlation calculation and that with the appropriate core electrons included at the CCSD(T)/wCVTZ-PP level. [e] The zero-point energies for the polyatomics were taken as 0.5 of the sum of the MP2/aVTZ harmonic frequencies. [f] The scalar relativistic correction is based on a CISD(FC)/VTZ 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 RECP. [g] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on Moore's tables.[15] [h] The theoretical value of $\Delta D_0(0\ K)$ was computed with the CBS estimates.

from the T_1 diagnostic[40] for the CCSD calculation. The values for the T_1 diagnostics are all about 0.014−0.018, showing that the wavefunction is dominated by a single configuration. The scalar relativistic corrections (for the F atom substituents) are all negative and not large, ranging in size from −0.42 kcal/mol for IF_2^- to −2.17 kcal/mol for IF_8^-.

The calculated value for $\Delta H_f^{298}(ClF_5)$ of −55.2 kcal/mol is in good agreement with the experimental values of −59.9 ± 3.9,[41] −57.2 ± 4.2,[42] −57.7,[43] and −56 ± 4.5 kcal/mol.[44] The calculated value for $\Delta H_f^{298}(BrF_5)$ of −106.4 kcal/mol is about 4 kcal/mol more negative as compared to the experimental value of −102.5 ± 0.5 kcal/mol.[45]

There was a significant issue in predicting the heats of formation of the IF_x compounds when our usual approach to the core-valence correction was taken.[13] Use of the difference between the valence and core-included calculations with the same core-valence basis set led to corrections as high as 12 kcal/mol for IF_7, which is not consistent with expectations and leads to serious discrepancies with experiment. This most likely arises from the need to include additional tight f-type functions at the HF level of theory.[46] In order to eliminate this effect, we extrapolated core-valence calculations with the aCnZ basis set for n = D, T, and Q to the CBS limit. Inclusion of core-valence effects in this approach leads to a decrease in the total atomization energy (TAE) for all molecules except for IF, where there is essentially no effect. We also examined the effect of extrapolating the aVQZ and aV5Z valence electron correlation calculations using eq 2. This led to a decrease in the TAE as compared to the CBS extrapolations with eq 1 for n = D, T, and Q. The effect increases with an increase in the size of the molecule with a difference between the two extrapolated values of 1.27 kcal/mol for IF_5. We note that the effect of including the core-valence effect is to decrease the TAE, and for IF_5, this would lower the TAE by 2.36 kcal/mol.

Our electronic contribution to the bond dissociation energy (BDE) of IF is 70.3 kcal/mol using eq 1 and 70.1 kcal/mol using eq 2. These results are comparable to our previously reported values of 70.4 and 70.2 kcal/mol,[11] calculated at the same levels but using a slightly different basis set. There is a second-order spin−orbit correction of +1.7 kcal/mol, which increases the bond energy of IF. This led to a BDE of 63.3 kcal/mol using the DTQ extrapolation from eq 1 and 63.0 kcal/mol using the extrapolation from eq 2, both with

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(40) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

(41) Bisbee, W. R.; Hamilton, J. V.; Gerhauser, J. M.; Rushworth, R. *J. Chem. Eng. Data* **1968**, *13*, 382.

(42) Barberi, P.; Caton, J.; Guillin, J.; Hartmanshenn, O. *Rapp. CEA-R—Fr., Commis. Energ. At.* **1969**, 3761.

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(44) Caton, J. Barberi, P. Note Interne, CEA/ESU no 1061. *Commis. Energ. At. [Fr.]* **1966.**

(45) Stein, L. *J. Phys. Chem.* **1962**, *66*, 2236.

(46) Weigand, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

no core-valence correction. If the core-valence correction is included in the DTQ extrapolation using eq 1, we obtain a value of 63.2 kcal/mol. The calculated BDEs can be compared to the experimental value of 66.3 ± 0.3 kcal/mol (23 220 ± 120 cm^{-1}) from Birks et al.'s and Coxon's spectroscopic dissociation limit.[47] Thus, the calculated heat of formation using the DTQ-extrapolated value including core-valence corrections in the extrapolation is 3.0 kcal/mol higher than the experimental heat of formation of −22.2 ± 0.9 kcal/mol at 0 K.[12] We[11] and others[48] have suggested that the experimental BDE may be in error and that the error bars on the experimental dissociation energy may be larger than those given. This is consistent with the results given below, which show better agreement between theory and experiment for IF_5 and IF_7.

The experimental heats of formation of IF_5 and IF_7 are well-established as −198.8 ± 0.4 kcal/mol at 0 K and −200.8 ± 0.4 at 298 K for the former and −226.4 ± 0.6 kcal/mol at 0 K and −229.7 ± 0.6 kcal/mol at 298 K for the latter.[12] These values serve as benchmarks for the calculations. For IF_5, good agreement is found for the extrapolated core-valence CBS value, with the spin−orbit correction giving −202.6 kcal/mol at 298 K. The valence only value for the Q5 extrapolation for IF_5 is also in reasonable agreement with experiment, but the extrapolated DTQ valence value is too negative. Thus, improvement of the basis set should bring the calculated value into even better agreement with experiment. At the same extrapolated DTQ core-valence level, excellent agreement is also found for IF_7 with a calculated value of −229.0 kcal/mol at 298 K. For IF_7, the extrapolated DTQ valence value is too negative by ~5 kcal/mol.

The calculated atomization energies (see Table 4) at 0 K allow us to calculate the average I−F bond dissociation energies for the neutral iodine fluorides IF, IF_3, IF_5, and IF_7 as 63, 61, 64, and 55 kcal/mol, respectively, using the extrapolated $\mathrm{DTQ_{CV}}$ values. For the iodine fluoride anions, IF_2^-, IF_4^-, IF_6^-, and IF_8^-, the average I−F bond dissociation energies for dissociation to $I^- + nF$ are 67, 67, 65, and 57 kcal/mol given an electron affinity for I of 3.059 038 ± 0.000 010 eV.[49] For the IF_2^+, IF_4^+, and IF_6^+ cations, the average I−F bond energies are 63, 62, and 58 kcal/mol, respectively, assuming dissociation to nF atoms and I^+ using an ionization energy for I of 10.451 26 eV.[50] At first sight, the result for the anions is surprising because, on the basis of our general knowledge of the bond strengths in cations and anions, the bonds in the anions are more polar and, therefore, are weaker and easier to break than those in the cations. However, our model is that the iodine fluoride anions would dissociate to F atoms and an I^- ion instead of an I atom, F atoms, and one F^- ion. If one were to use the latter dissociation model and correct the BDE values of the anions for the 7.9 kcal/mol difference between the electron affinities of I and F, the BDEs of the anions would be 1−4 kcal/mol smaller than those in the cations.

For both the neutral molecules and their ions, the average I−F BDEs are essentially independent of the oxidation state of the iodine up to I^{V+}. For I^{VII+}, their values decrease by 4−10 kcal/mol, with the larger decreases occurring in the heptacoordinated neutral molecule and octacoordinated anion, presumably because of steric crowding. The trend in BDEs noted for the xenon fluorides[1h] is somewhat similar, with the average Xe−F BDEs in XeF_2, XeF_4, and XeF_6 slightly decreasing from 30 to 29 to 28 kcal/mol with increasing n. The trend is slightly more pronounced in the krypton fluorides[51] with the average Kr−F BDEs in KrF_2, KrF_4, and KrF_6 also decreasing from 11 to 8 to 6 kcal/mol.

The calculated heats of formation at 0 K can also be used to calculate the dissociation energies for the stepwise loss of a fluorine molecule for both the neutral and ionic iodine fluorides.

$$IF_7 \rightarrow IF_5 + F_2 \quad \Delta H = 25.4\ \mathrm{kcal/mol} \tag{4}$$

$$IF_5 \rightarrow IF_3 + F_2 \quad \Delta H = 98.8\ \mathrm{kcal/mol} \tag{5}$$

$$IF_3 \rightarrow IF + F_2 \quad \Delta H = 82.6\ \mathrm{kcal/mol} \tag{6}$$

$$IF_8^- \rightarrow IF_6^- + F_2 \quad \Delta H = 31.2\ \mathrm{kcal/mol} \tag{7}$$

$$IF_6^- \rightarrow IF_4^- + F_2 \quad \Delta H = 84.8\ \mathrm{kcal/mol} \tag{8}$$

$$IF_4^- \rightarrow IF_2^- + F_2 \quad \Delta H = 94.9\ \mathrm{kcal/mol} \tag{9}$$

$$IF_2^- \rightarrow I^- + F_2 \quad \Delta H = 97.7\ \mathrm{kcal/mol} \tag{10}$$

$$IF_6^+ \rightarrow IF_4^+ + F_2 \quad \Delta H = 63.0\ \mathrm{kcal/mol} \tag{11}$$

$$IF_4^+ \rightarrow IF_2^+ + F_2 \quad \Delta H = 84.8\ \mathrm{kcal/mol} \tag{12}$$

$$IF_2^+ \rightarrow I^+ + F_2 \quad \Delta H = 88.5\ \mathrm{kcal/mol} \tag{13}$$

The enthalpies of reaction for the neutral and ionic fluorides are endothermic, showing that these species are thermodynamically stable with respect to loss of F_2. Thus, the addition of F_2 to the IF_{n-2} compounds to form IF_n is thermodynamically favorable, which is similar to what occurs in the xenon fluorides[1h] but in contrast to that of the krypton fluorides.[51] IF_7 and IF_8^- are predicted to lose F_2 most readily. It is also apparent that IF_3 should readily add F_2 to form the more stable IF_5.

The calculated heats of formation allow us to predict the fluoride ion (F^-) affinities (FAs) of the neutral IF_x molecules ($x = 1$, 3, 5, and 7) to give the corresponding IF_{x+1}^- anions. The FA is defined as $-\Delta H$ for the reaction $A + F^- \rightarrow AF^-$, and the values are given in Table 8. IF_3 has the highest FA, which is 6−7 kcal/mol above that of IF_7 and about 13−14 kcal/mol above that of IF and IF_5. Thus, these compounds have FAs in the middle-to-low range of the values for FAs.[52] We previously predicted[52] the FA of ClF_5 at a lower level

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Table 6. Calculated Heats of Formation (kcal/mol) for IF_x

	DTQ		Q5		DTQ_{CV}	
molecule	0 K	298 K	0 K	298 K	0 K	298 K
$IF(C_{\infty v})$	−19.2	−19.7	−19.0	−19.4	−19.2	−19.7
$IF_2^+(C_{2v})$	177.1	176.3	177.5	176.7	178.1	177.2
$IF_2^-(D_{\infty h})$	−143.1	−143.6	−142.8	−143.3	−142.6	−143.1
$IF_3(C_{2v})$	−103.2	−104.3	−102.6	−103.7	−101.8	−102.9
$IF_4^+(C_{2v})$	91.3	89.6	92.3	90.6	93.3	91.7
$IF_4^-(D_{4h})$	−238.6	−239.6	−237.8	−238.8	−237.5	−238.5
$IF_5(C_{4v})$	−203.0	−205.0	−201.7	−203.7	−200.6	−202.6
$IF_6^+(O_h)$	25.1	22.5			30.4	27.8
$IF_6^-(C_{3v})$	−325.2	−326.1			−322.3	−323.3
$IF_7(D_{5h})$	−231.6	−234.6			−226.1	−229.0
$IF_8^-(D_{4d})$	−359.9	−363.4			−353.6	−357.2

Table 7. Calculated Heats of Formation (kcal/mol) for ClF_5, ClF_6^-, BrF_5, and BrF_6^-

	DTQ		Q5	
molecule	0 K	298 K	0 K	298 K
$ClF_5(C_{4v})$	−53.0	−54.8	−53.4	−55.2
$BrF_5(C_{4v})$	−103.5	−107.4	−102.5	−106.4
$ClF_6^-(O_h)$	−162.6	−164.1	−161.9	−163.4
$BrF_6^-(O_h)$	−230.1	−233.1	−227.9	−230.9

Table 8. Calculated FAs (kcal/mol)[a]

molecule	0 K	298 K
IF	63.4	64.0
IF_3	75.7	76.1
IF_5	61.7	61.2
IF_7	67.6	68.7
ClF_5	48.6	48.8
BrF_5	65.5	65.0

[a] IF_x calculations from DTQ_{CV}-extrapolated results and ClF_5 and BrF_5 from Q5 extrapolations. Heats of formation of $F^- = -59.96$ kcal/mol at 0 K and −59.46 kcal/mol at 298 K.

to be 74.7 kcal/mol. This value is substantially higher than our currently more reliable value, and much of the difference is due to basis set effects and higher level correlation effects.

The FAs of the cations (heterolytic cleavage of an I−F bond) also exhibit interesting trends, as shown by the following reactions.

$$I^+ + F^- \rightarrow IF \quad \Delta H = 226.7\ \text{kcal/mol} \tag{14}$$

$$IF_2^+ + F^- \rightarrow IF_3 \quad \Delta H = 220.6\ \text{kcal/mol} \tag{15}$$

$$IF_4^+ + F^- \rightarrow IF_5 \quad \Delta H = 234.8\ \text{kcal/mol} \tag{16}$$

$$IF_6^+ + F^- \rightarrow IF_7 \quad \Delta H = 197.3\ \text{kcal/mol} \tag{17}$$

The value for the latter reaction has been estimated to be 208 ± 6 kcal/mol from a set of experimental observations on displacement reactions and lattice enthalpy calculations.[53] The estimated value is in good agreement with our calculated value.

General Trends. A summary of the calculated and experimentally observed structures as a function of the iodine oxidation state, coordination number (CN), and formal ionic charge is given in graphical form in Figure 1. As can be seen, the iodine fluorides display the full range of structures ranging from tetrahedra (CN 4), through trigonal bipyramids (CN 5), octahedra (CN 6), and pentagonal bipyramids and monocapped octahedra (CN 7) to a square Archimedian antiprism (CN 8). The species with identical CN can be found on the diagonals from the upper right to the lower left, and the iodine CNs and formal oxidation states increase from the top row to the bottom row. In accordance with our expectations for these hypervalent main-group compounds, some of the bonds within a given species are longer and more ionic than others due to significant contributions from semi-ionic three-center four-electron bonding.[54] Furthermore, the bonds tend to become shorter and more covalent with increasing oxidation state and the formal positive charge of iodine, which enhances the effective electronegativity of iodine and makes it more similar to that of fluorine. As a result, IF_2^- possesses the longest and weakest and IF_6^+ the shortest and strongest I−F bonds in terms of bond lengths.

The steric activity of the lone pair on the central atom is clearly different for I as compared to Cl and Br. When the F ligands are closer to each other as they are in ClF_6^- and BrF_6^-, there is insufficient space for a sterically active lone pair so the lone pair is found in the symmetric A_{1g} orbital. When the F atoms are farther apart as found in IF_6^-, the lone pair can become sterically active as we predict consistent with experiment. XeF_6 presents an interesting case because it most likely has a C_{3v} structure with a sterically active lone pair but is expected to be highly fluxional with the O_h and C_{3v} structures of comparable energy.[1h] The Xe−F bond distances in XeF_6 are predicted to be shorter than the I−F bond distances in IF_6^- with a predicted value for $r(\text{Xe}-\text{F}) = 1.942$ Å in the O_h structure as compared to $r(\text{I}-\text{F}) = 1.998$ Å predicted for octahedral IF_6^-. The best estimated C_{3v} geometry parameters for XeF_6 are $r(\text{Xe}-\text{F}) = 1.844$ and 1.986 Å as compared to the IF_6^- values of $r(\text{I}-\text{F}) = 1.900$ and 2.057 Å. The shorter Xe−F bond lengths mean that there is less space for a sterically active lone pair than in IF_6^- (but more space than that in BrF_6^-) so that the C_{3v} and O_h structures in XeF_6 become essentially degenerate in energy.

Figure 3 depicts a summary of the calculated heats of formation, the energy differences between the different species, and the reaction enthalpies for either the addition or the abstraction of a F^- ion from the neutral parent molecules and for the oxidative addition of F_2. The heterolytic dissociation of an IF bond in IF_x to form an IF_{x-1}^+ species plus F^- range from ∼200 to ∼240 kcal/mol, with IF_7 being the least stable in terms of heterolytic bond cleavage. The fact that the lowest energy for heterolytic bond cleavage is for IF_7 is consistent with the additional steric crowding in this compound. The reaction enthalpies for the oxidative addition of F_2 are additive but not in a linear fashion. As expected, the addition of the last two fluorines in the cation, neutral, and anion series becomes more difficult and the corresponding enthalpies become smaller.

A comparison of the FAs of IF_5, BrF_5, and ClF_5 (see Table 8) does not show the expected periodicity with Lewis acidity increasing as one descends the Periodic Table. As expected, ClF_5 is a considerably weaker Lewis acid than BrF_5 and IF_5. Somewhat surprisingly, BrF_5 is predicted to be the strongest

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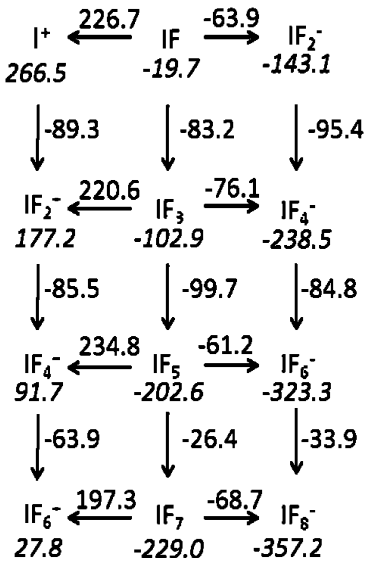

Figure 3. Heats of formation and reaction enthalpies for the addition or loss of a F^- ion and for the addition of F_2 at 298 K. All values are given in kcal/mol. Values in italics are heats of formation at 298 K. Vertical arrows correspond to the addition of F_2 to IF_x to form IF_{x+2} in terms of the cation, neutral, and anion. Horizontal arrows to the left correspond to heterolytic dissociation of an IF bond in IF_x to form an IF_{x-1}^+ species plus F^-. Horizontal arrows to the right correspond to the FA. The heat of formation of F^- is −59.5 kcal/mol using the electron affinity of F given in the text.[12] For all species, the DTQ_{CV} values of Table 6 were used (see text).

Lewis acid in terms of its FA. The unusual behavior of bromine is also reflected by the Brønsted acidity of $HBrO_4$, which is a 6 times stronger acid than $HClO_4$.[55]

Conclusions

The present study provides, for the first time, a self-consistent complete set of thermodynamic data for the iodine fluoride molecules and their ions using high-level theoretical calculations. It is also shown that the steric activity of a free-valence electron pair can be predicted reliably but requires high-level calculations. Furthermore, the vibrational spectra of the square-antiprismatic IF_8^- anion have been thoroughly reanalyzed. The calculations also show that one has to be careful in applying the usual additivity approximation for the core-valence effects when there is a large change in the oxidation state of the central atom in these types of main-group compounds. In addition, molecular spin−orbit effects are clearly not negligible for iodine molecules and need to be considered.

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Supporting Information Available: Details of the calculations, calculated CCSD(T) geometry parameters, total CCSD(T)/aug-cc-pVnZ energies as a function of the basis set for all species, total CCSD(T)/aug-cc-pwCVnZ energies as a function of the basis set for IF_x species, additional MP2/aVTZ calculated frequencies, HF/aVTZ calculated frequencies for IF_6^- in C_{3v} and O_h symmetries, and CCSD(T) atomization and reaction energies including core-valence corrections at the CCSD(T)/wCVTZ-PP level for IF_x. This material is available free of charge via the Internet at http://pubs.acs.org.

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