Inorganic Chemistry
Article
pubs.acs.org/IC

Structural and Energetic Properties of Closed Shell XF_n (X = Cl, Br, and I; n = 1−7) and XO_nF_m (X = Cl, Br, and I; n = 1−3; m = 0−6) Molecules and Ions Leading to Stability Predictions for Yet Unknown Compounds

K. Sahan Thanthiriwatte, Monica Vasiliu, and David A. Dixon*

Department of Chemistry, The University of Alabama, Shelby Hall, Box 870336, Tuscaloosa, Alabama 35487-0336, United States

Karl O. Christe

Loker Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, United States

Ⓢ *Supporting Information*

ABSTRACT: Atomization energies at 0 K and heats of formation at 0 and 298 K were predicted for the closed shell compounds XF, XF_2^-, XF_2^+, XF_3, XF_4^-, XF_4^+, XF_5, XF_6^-, XF_6^+ (X = Cl and Br) and XO^+, XOF, XOF_2^-, XOF_2^+, XOF_3, XOF_4^-, XOF_4^+, XOF_5, XOF_6^-, XO_2^+, XO_2F, $XO_2F_2^-$, $XO_2F_2^+$, XO_2F_3, $XO_2F_4^-$, XO_3^+, XO_3F, $XO_3F_2^-$ (X = Cl, Br, and I) using a composite electronic structure approach based on coupled cluster CCSD(T) calculations extrapolated to the complete basis set limit with additional corrections. The calculated heats of formation are in good agreement with the available experimental data. The calculated heats of formation were used to predict fluoride affinities, fluorine cation affinities, and F_2 binding energies. On the basis of our results, $BrOF_5$ and BrO_2F_3 are predicted to be stable against spontaneous loss of F_2 and should be able to be synthesized, whereas BrF_7, ClF_7, $BrOF_6^-$, and $ClOF_6^-$ are unstable by a very wide margin. The stability of $ClOF_5$ is a borderline case. Although its F_2 loss is predicted to be exothermic by 4.4 kcal/mol, it may have a sufficiently large barrier toward decomposition and be preparable. This situation would resemble ClO_2F_3 which was successfully synthesized in spite of being unstable toward F_2 loss by 3.3 kcal/mol. On the other hand, the $ClOF_4^+$ and $BrOF_4^+$ cations are less likely to be preparable with F_2 loss exothermicities of −17.5 and −9.3 kcal/mol, respectively. On the basis of the F^- affinities of ClOF (45.4 kcal/mol), BrOF (58.7 kcal/mol), and BrO_2F_3 (65.7 kcal/mol) and their predicted stabilities against loss of F_2, the $ClOF_2^-$, $BrOF_2^-$, and $BrO_2F_4^-$ anions are excellent targets for synthesis. Our previous failure to prepare the $ClO_2F_4^-$ anion can be rationalized by the predicted high exothermicity of −17.4 kcal/mol for the loss of F_2.

■ INTRODUCTION

Halogen fluorides and oxofluorides have been studied extensively because they have a wide range of coordination numbers up to 8 and of formal oxidation states up to +VII.[1−4] They are strong oxidizing agents and are amphoteric as they can act as both fluoride ion donors and acceptors. Therefore, halogen fluorides offer a unique opportunity to study a wide range of coordination numbers and oxidation states and represent an ideal case for the study of the relationship of structure and bonding in hypervalent molecules. To this end, a better understanding of their structures and thermochemical properties, including heats of formation and fluoride affinities, is crucial.

There have been a number of experimental studies of the structures,[5−32] of XF_n (X = Cl and Br; n = 1−6) and XO_nF_m (X = Cl, Br, and I; n = 1−3, m = 0−6) compounds. The structures of ClF, ClF_3, and ClF_5 have been determined in the gas-phase using microwave spectroscopy and electron diffraction.[6,9,15,16] The structures of ClF_2^+,[33] ClF_4^+,[17] ClF_6^+,[20] $ClOF_2^+$,[30] and ClF_4^-[34] have been determined by X-ray diffraction. The molecular structures of $ClOF_3$ and ClO_3F have been determined by gas electron diffraction[13,24] and those of ClOF,[35] ClO_2F,[36] and ClO_3F[37] from their rotational spectra. The structures of BrF, BrF_3, and BrF_5 in the gas-phase have been determined by microwave spectroscopy and electron diffraction.[9,8,11,12] The structures of BrF_2^+,[38] BrF_4^+,[17] BrF_6^+,[20] BrF_4^-,[10] $BrOF_2^+$,[30] and BrF_6^-[39] have been determined by X-ray diffraction. The crystal structures of $BrOF_3$ and $BrOF_4^-$ were obtained from $[NO_2]^+[BrF_4]^-\cdot 2BrOF_3$ and $[NO]^+[BrOF_4^-]$, respectively.[22] The gas-phase structure of BrO_3F was determined using electron diffraction.[13] The structure of $BrO_3F_2^-$ was determined from an X-ray crystallography study of $[NO]_2[BrO_3F_2][F]$.[23] Solid-state structures of IOF_3 and IO_2F were determined by X-ray crystallography[25,26] and the gas-phase structure of IOF_5 by a combined microwave-electron diffraction study.[40] The structures of IOF_4^-, IOF_6^-, and $IO_2F_2^-$ have been determined by X-ray crystallography

Received: July 3, 2012
Published: September 25, 2012

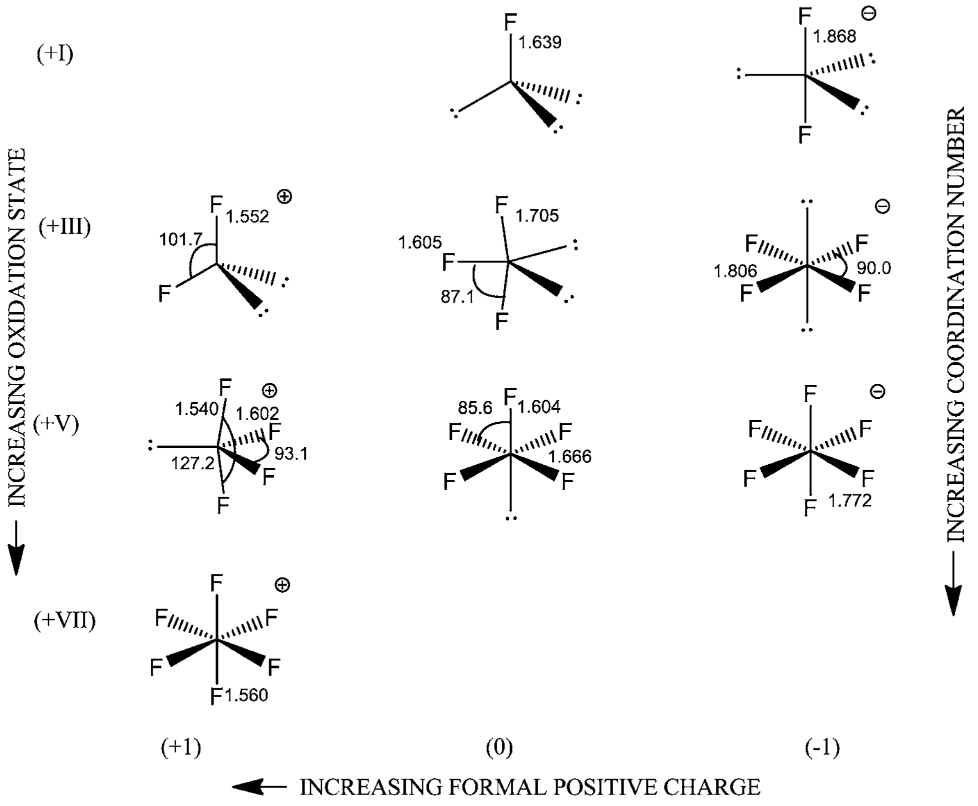

Figure 1. Calculated CCSD(T)/aVTZ geometries of the chlorine fluoride molecules and ions (bond lengths in Å and bond angles in degrees).

of $CsIOF_4$,[27] $N(CH_3)_4{}^+IOF_6{}^-$,[41] and $N(CH_3)_4{}^+IO_2F_2{}^-$,[28] respectively. Although a crystal structure has been reported for IO_2F_3,[42] the structure is that of an oxygen-bridged dimer. Because these compounds are difficult to synthesize and handle, they have often been characterized only by vibrational spectroscopy.[43−64] For example, the structure of ClO^+ was determined using spectroscopic techniques[65−67] in combination with high-level computational methods.[68] The $ClO_2{}^+$ and $BrO_2{}^+$ structures have also been determined by X-ray diffraction[69−72] and spectroscopic observations,[50,73−79] and have been studied theoretically.[21,80]

There are a number of summaries of the heats of formation of some of these compounds from experiment.[81−84] A number of theoretical studies[17−23,85−100] for these compounds are also available. The levels of theory used for these studies include density functional theory (DFT), the Gaussian-3 (G3) and Gaussian-3X (G3X) methods, and CCSD(T) (coupled-cluster singles and doubles substitutions with perturbatively connected triples) calculations extrapolated to the complete basis set (CBS) limit.

The direct prediction of reliable heats of formation[101] requires a high-level treatment of electron correlation using methods such as CCSD(T).[102] This approach has emerged as the most accurate computationally affordable method that can be applied to small to moderate sized systems and is considered the "gold standard" for chemical accuracy,[103,104] though it is unfortunately limited by its $O(N^7)$ complexity in its standard form where N is the number of basis functions. In collaboration with Washington State University, we have been developing a composite approach[101,105] for the prediction of the thermodynamic properties of molecules based on molecular orbital theory using coupled cluster methods at the CCSD(T) or higher levels with correlation-consistent basis sets.[106] These calculations have been extended to heavier elements using the new effective core potential/correlation consistent basis sets developed by Peterson and co-workers.[107] The resulting total energies are extrapolated to the CBS limit to minimize the basis set truncation error. Smaller corrections for the core−valence (CV) correlation, molecular scalar relativistic (SR) corrections, and atomic spin−orbit corrections (SO) are also included in the total atomization energy (TAE) calculations. A correction for zero-point vibrational energies (ZPEs) is included to obtain zero-point inclusive atomization energies (ΣD_0). Given ΣD_0 and the heats of formation of the elements, the heat of formation of a given compound can then be calculated. Our composite approach (with no empirical parameters for the electronic energies) assumes that the effects of the smaller corrections are additive to the extrapolated CBS "valence" electronic energies. 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 Feller's Computational Results Database.[101,108]

We have used such a computational approach to calculate heats of formation from total atomization energies for the closed shell compounds XF, $XF_2{}^-$, $XF_2{}^+$, XF_3, $XF_4{}^-$, $XF_4{}^+$, XF_5, $XF_6{}^-$, $XF_6{}^+$, XO^+, XOF, $XOF_2{}^-$, $XOF_2{}^+$, XOF_3, $XOF_4{}^-$, $XOF_4{}^+$, XOF_5, $XOF_6{}^-$, $XO_2{}^+$, XO_2F, $XO_2F_2{}^-$, $XO_2F_2{}^+$, XO_2F_3, $XO_2F_4{}^-$, $XO_3{}^+$, XO_3F, $XO_3F_2{}^-$ (X = Cl, Br, and I). A number of the values for the iodine compounds have been reported previously including IF_7 and $IF_8{}^-$.[88] These calculations enable the prediction of F^+ detachment energies (a measure of the oxidizer strength), fluoride affinities (a measure of Lewis acidity) with the fluoride affinity (FA) defined as the negative of the enthalpy of the reaction $A + F^- \rightarrow AF^-$, and F_2 binding energies.

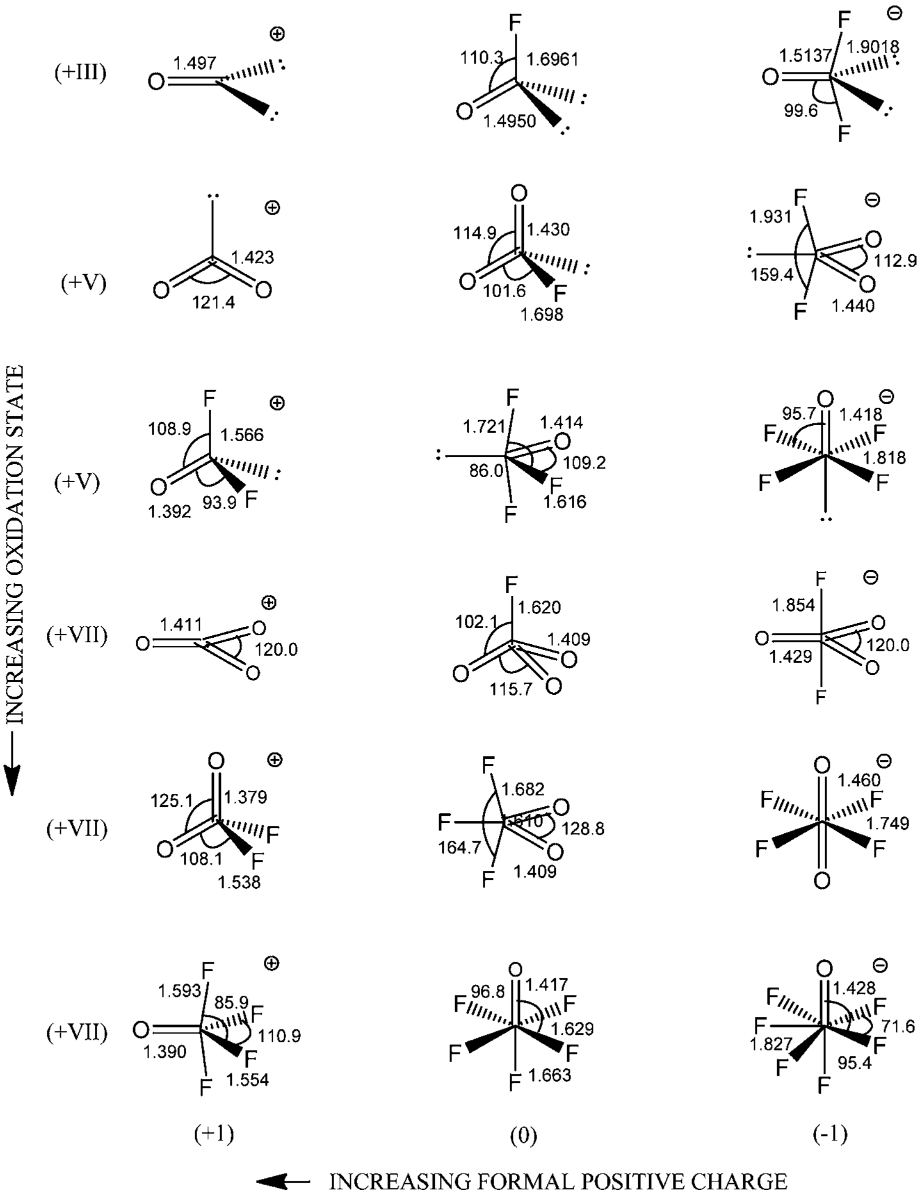

Figure 2. Calculated CCSD(T)/aVTZ geometries of the chlorine oxofluoride molecules and ions (bond lengths in Å and bond angles in degrees).

■ COMPUTATIONAL PROCEDURE

Equilibrium geometries for all of the halogen and oxo-halogen compounds were optimized at the CCSD(T) level with the augmented correlation-consistent polarized valence double-ξ and triple-ξ basis sets.[109] Single point energies were calculated with the quadruple-ξ and quintuple-ξ basis sets at the triple-ξ geometries. The augmented correlation-consistent polarized weighted core–valence basis sets with Stuttgart small-core relativistic effective-core potentials (RECP) (aug-cc-pwCV*n*Z-PP) were used for I,[110] following our prior work on iodine complexes.[88] Augmented correlation-consistent polarized valence basis sets with effective core potentials (aug-cc-pV*n*Z-PP) and aug-cc-pwCV*n*Z-PP (CV calculations) were used for Br,[111] augmented correlation-consistence polarized valence basis sets with tight-d functions (aug-cc-pV(n+*d*)Z) were used for Cl,[112,113] and augmented correlation-consistent polarized valence basis sets (aug-cc-pV*n*Z)[109] were used for F and O. For Br, the RECP subsumes the ($1s^2$, $2s^2$, $2p^6$) orbital space into the 10-electron core set, leaving the ($3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4s^2$, $4p^5$) space with 25 electron to be handled explicitly, with the ($4s^2$, $4p^5$) electrons active in valence correlation space. The RECP for I subsumes the ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$) orbital space into the 28-electron core set, leaving the ($4s^2$, $4p^5$, $5s^2$, $4d^{10}$, and $5p^5$) space with 25 electrons to be handled explicitly. All CCSD(T) valence computations were performed with the core electrons frozen except for the compounds with Br and I. The calculations for the Br and I compounds had all of the electrons correlated and were performed with the aug-cc-pwCV*n*Z/aug-cc-pwCV*n*Z-PP basis sets. Additional single point "valence" energy calculations for compounds with Br were carried out with the aug-cc-pV*n*Z/aug-cc-pV*n*Z-PP basis set. The atomic energies were calculated at the R/UCCSD(T) level starting with a restricted open shell Hartree–Fock and an unrestricted CCSD(T).[114]

The converged energies were extrapolated to the CBS limit using two schemes. Feller et al. have discussed the different extrapolation schemes and evaluated them.[115] The aug-cc-pVnZ energies were extrapolated using a mixed exponential/Gaussian function of the form

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

as first proposed by Peterson et al.[116] with n = 2(D), 3(T), and 4(Q). In the second approach, the CBS limit was obtained by using a two-point extrapolation scheme,[117]

$$E(l_{\max}) = E_{\mathrm{CBS}} + B/l_{\max}{}^3 \qquad (2)$$

with $l_{\max}$ = Q, and 5.

Table 1. Calculated Geometry Parameters for Selected Compounds Compared to Experiment

molecule	parameter[a]	calculated[b]	experiment
ClF ($C_{\infty v}$)	r(Cl−F)	1.6396	1.628313[9,63]
ClF_3 (C_{2v})	$r(Cl-F_{ax})$	1.6052	1.598[15]1.584[16]
	$r(Cl-F_{eq})$	1.7054	1.698, 1.703
	$\angle F_{ax}-Cl-F_{eq}$	87.1	87.5[15]
ClF_2^+ (C_{2v})	r(Cl−F)	1.552	1.566(3)[33]
	∠F−Cl−F	101.7	96.4(3)
ClF_4^- (D_{4h})	r(Cl−F)	1.806	1.771−1.814(1)[34]
ClF_4^+ (C_{2v})	$r(Cl-F_{ax})$	1.602	1.618(2)[17]
	$r(Cl-F_{eq})$	1.540	1.530(2)
	$\angle F_{eq}-Cl-F_{eq}$	105.6	103.08(12)
	$\angle F_{ax}-Cl-F_{ax}$	173.9	173.92(13)
ClF_5 (C_{4v})	$r(Cl-F_{ax})$	1.6045	1.571[6]
	$r(Cl-F_{eq})$	1.6660	1.669
	$\angle F_{ax}-Cl-F_{eq}$	85.6	86.0
ClF_6^+ (O_h)	r(Cl−F)	1.5603	1.550(4)[20]
BrF ($C_{\infty v}$)	r(Br−F)	1.7713	1.758987[9,63]
BrF_2^+ (C_{2v})	r(Br−F)	1.6910	1.69(2)[38]
	∠F−Br−F	98.7	93.5(2.1)
BrF_3 (C_{2v})	$r(Br-F_{ax})$	1.7295	1.721[8]
	$r(Br-F_{eq})$	1.8167	1.810
	$\angle F_{ax}-Br-F_{eq}$	85.9	86.2
BrF_4^+ (C_{2v})	$r(Br-F_{ax})$	1.7214	1.728(3)[7,19]
	$r(Br-F_{eq})$	1.6704	1.664(3)
	$\angle F_{eq}-Br-F_{eq}$	104.4	97.5(2)
	$\angle F_{ax}-Br-F_{ax}$	168.8	168.9(2)
BrF_4^- (D_{4h})	r(Br−F)	1.8994	1.890,[10] 1.890(4)[39]
BrF_5 (C_{4v})	$r(Br-F_{ax})$	1.7071	1.680,[11] 1.699(6)[12]
	$r(Br-F_{eq})$	1.7713	1.780, 1.768(1)
	$\angle F_{ax}-Br-F_{eq}$	84.5	84.5, 85.05(43)
BrF_6^- (O_h)	r(Br−F)	1.8707	1.854(1)[39]
BrF_6^+ (O_h)	r(Br−F)	1.6767	1.666(11)[20]
$ClOF$ (C_s)	r(Cl−F)[c]	1.6961	1.6926(43)[35]
	r(Cl=O)[c]	1.4950	1.4878(46)
	∠O−Cl−F[c]	110.3	110.56(8)
$ClOF_2^+$(C_s)	r(Cl−F)	1.5665	1.522(2), 1.543(2)[30]
	r(Cl=O)	1.3921	1.455(2)
	∠O−Cl−F	108.9	105.5
	∠F−Cl−F	93.9	98.7
ClO_2F (C_s)	r(Cl−F)	1.6984	1.690(7)[36]
	r(Cl=O)	1.4299	1.419(9)
	∠O−Cl−O	114.9	115.0(3)
	∠O−Cl−F	101.6	101.6(9)
ClO_2^+ (C_{2v})	r(Cl=O)	1.4227	1.385(5),[21] 1.410(2)[78]
	∠O−Cl−O	121.4	117.8(4),[21] 118(9)[78]
$ClOF_3$ (C_s)	$r(Cl-F_{ax})$	1.7210	1.713(3)[24]
	$r(Cl-F_{eq})$	1.6159	1.603(4)
	r(Cl=O)	1.4137	1.405(3)
	$\angle O-Cl-F_{eq}$	109.2	108.9(0.9)
	$\angle O-Cl-F_{ax}$	96.2	94.7(2.0)
	$\angle F_{ax}-Cl-F_{eq}$	86.0	87.9(1.2)
	$\angle F_{ax}-Cl-F_{ax}$	166.8	170.5(4.1)
ClO_3F (C_s)	r(Cl=O)[d]	1.4091	1.404(2),[13] 1.4014(6)[37]
	r(Cl−F)[d]	1.6205	1.619(4),[13] 1.6195(9)[37]
	∠O−Cl−F[d]	102.1	100.8(8),[13] 101.99(4)[37]
	∠O−Cl−O[d]	115.7	116.6(5),[13] 115.80(3)[37]
$BrOF_2^+$(C_s)	r(Br−F)	1.7069	1.736(4), 1.733(4)
	r(Br=O)	1.5615	1.549(5)
	∠O−Br−F	106.5	102.8(3)
	∠F−Br−F	92.6	89.6(2)
$BrOF_3$ (C_s)	$r(Br-F_{ax})$	1.8108	1.820, 1.839[22]
	$r(Br-F_{eq})$	1.7419	1.725
	r(Br=O)	1.5784	1.569
	$\angle O-Br-F_{eq}$	107.2	103.3
	$\angle F_{ax}-Br-F_{ax}$	167.4	169.8
$BrOF_4^-$ (C_{4v})	r(Br−F)	1.8899	1.846(2), 1.912(2)[22]
	r(Br=O)	1.5857	1.575(3)
	$\angle O-Br-F_{eq}$	94.2	93.4, 92.1
BrO_2^+ (C_{2v})	r(Br=O)	1.6137	1.595(2),[21] 1.6135[78]
	∠O−Br−O	115.4	111.9(1),[21] 117.5[78]
BrO_3F (C_s)	r(Br−O)	1.5913	1.582(1)[14]
	r(Br−F)	1.7503	1.708(3)
	∠O−Br−F	101.8	103.3(3)
	∠O−Br−O	115.9	114.9(3)
$BrO_3F_2^-$ (D_{3h})	r(Br=O)	1.6150	1.602(6)[23]
	r(Br−F)	1.8553	1.861(16)
IOF_3 (C_s)	r(I=O)	1.7543	1.71(4)[25]
	$r(I-F_{ax})$	1.9266	1.91(3)
	$r(I-F_{eq})$	1.8701	1.84(3)
	$\angle O-I-F_{eq}$	104.7	99.5(1.8)
	$\angle O-I-F_{ax}$	94.3	91.2(1.4)
IOF_4^- (C_{4v})	r(I−F)	1.9938	1.98/1.95(1)[27]
	r(I=O)	1.7615	1.72(1)
	∠O−I−F	91.1	89.9/88.1(4)
IOF_5 (C_{4v})	$r(I-F_{ax})$	1.8454	1.863(4)[40]
	$r(I-F_{eq})$	1.8499	1.817(2)
	r(I=O)	1.7539	1.715(4)
	$\angle O-I-F_{eq}$	97.2	98.0(3)
IOF_6^- (C_{5v})	r(I=O)	1.8114	1.75−1.77[41]
	$r(I-F_{ax})$	1.90137	1.82
	$r(I-F_{eq})$	1.9654	1.88
	$\angle O-I-F_{eq}$	95.9	94−96
IO_2F (C_{2v})	r(I−F)	1.9196	1.903(5)[26]
	r(I=O)	1.7794	1.773(6)
	∠O−I−F	99.9	94.6(2)
$IO_2F_2^-$ (C_{2v})	r(I=O)	1.7927	1.774(2)[28a]
	r(I−F)	2.0238	2.0025(2)
	∠O−I−O	108.3	101.98(12)
	∠O−I−F	92.9	91.01(7)
$IO_2F_4^-$ (D_{4h})	r(I=O)	1.7775	1.771(1)[e]
	$r(I-F_{eq})$	1.9137	1.872(1)

[a] Bond lengths are given in angstroms (Å) and bond angles are given in degrees (deg). [b] Geometries optimized using CCSD(T) with the aug-cc-pVTZ/aug-cc-pVTZ-PP basis sets. [c] Experimental r_z value from microwave spectroscopy. [d] Second experimental is r_z value from microwave spectroscopy. [e] Haiges, R.; Christe, K., unpublished.

The following additional additive corrections to the TAE were used: zero-point vibrational energies (ΔE_{ZPE}), core−valence effects (ΔE_{CV}) for the Cl and Br compounds for the valence only calculations, a correction for scalar relativistic effects (ΔE_{SR}), and spin−orbit corrections (ΔE_{SO}). Zero-point vibrational energies were computed using second-order Møller−Plesset perturbation theory,[118] MP2/aug-cc-pVTZ. Core−valence (CV) corrections were calculated for all compounds containing Cl at the CCSD(T)/aug-cc-pwCVTZ[119,120] and at the CCSD(T)/aug-cc-pwCVTZ/aug-cc-pwCVTZ-PP[121] level for compounds containing Br. Scalar relativistic effects were evaluated by using expectation values for the two dominant terms in the Breit−Pauli Hamiltonian, the so-called mass-velocity and one-electron

Table 2. Observed and Calculated Frequencies (cm^{-1}) at the MP2/aug-cc-PVTZ/aug-cc-pVTZ Level

molecule	molecular symmetry	mode symmetry	frequency	experiment
ClF	$C_{\infty v}$	σ_g	795.1 (785.5)[a]	783[63]
ClF_2^+	C_{2h}	a_1	885.8	810,[43]806[44]
			364.4	406, 384
		b_1	891.6	818, 821
ClF_2^-	$D_{\infty h}$	σ_g^+	483.8	476[45]
		σ_u^+	459.0	470
		π_u	285.5	
ClF_3	C_{2v}	a_1	782.7	760,[47] 761[46]
			547.1	538, 535
			322.9	328, 332
		b_1	739.1	702, 703
			437.7	442, 434
		b_2	322.5	328, 364
ClF_4^+	C_{2v}	a_1	837.0	800,[48] 802[49]
			628.1	571, 574
			516.6	510, 515
			184.2	237, 235
		a_2	488.5	475, 475
		b_1	867.8	795, 803
			546.2	537, 534
		b_2	879.2	829, 822
			373.3	385, 386
ClF_4^-	D_{4h}	a_{1g}	507.6	505[52]
		a_{2u}	425.8	425
		b_{1g}	418.6	417
		b_{2g}	262.5	288
		b_{2u}	182.5	inactive
		e_u	635.0	590
			225.2	
ClF_5	C_{4v}	a_1	751.2	709,[53] 722[54]
			556.4	541, 539
			491.0	486, 493
		b_1	378.0	375, 375
			278.7	
		b_2	514.1	480, 487
		e	767.1	732, 725
			504.7	482, 484
			299.7	302, 299
ClF_6^+	O_h	a_{1g}	729.9	679,[50] 688[51]
		e_g	658.9	630, 631
		t_{1u}	934.6	890, 890
			598.0	582, 590
		t_{2g}	518.8	513, 517
		t_{2u}	348.0	353, 353
ClF_6^-	O_h	a_{1g}	526.8	525[55]
		e_g	377.8	384
		t_{1u}	746.4	
			307.1	
		t_{2g}	259.2	289
		t_{2u}	191.4	
BrF	$C_{\infty v}$	σ_g	672.4 (664.5)[a]	670[63]
BrF_2^-	$D_{\infty h}$	σ_g^+	456.1	460[45]
		σ_u^+	426.4	450
		π_u	224.7	236
BrF_3	C_{2v}	a_1	690.9	672,[47] 675[46]
			557.8	547, 552
			239.7	235, 242
		b_1	625.7	597, 614
			356.8	347, 350
		b_2	250.7	252, 242
BrF_4^+	C_{2v}	a_1	762.1	723[48]
			638.7	606
			383.8	385
			151.4	216
		a_2	403.7	
		b_1	748.6	704
			432.9	419
		b_2	764.3	736
			276.8	369
BrF_4^-	D_{4h}	a_{1g}	520.8	523[56]
		a_{2u}	322.6	317
		b_{1g}	233.5	246
		b_{2g}	446.6	449
		b_{2u}	173.6	i.a
		e_u	516.5	542
			181.5	183
BrF_5	C_{4v}	a_1	699.2	682[47]
			587.5	587
			373.5	369
		b_1	314.9	312
		b_2	555.2	535
			233.9	
		e	658.6	644
			420.2	415
			240.0	237
BrF_6^+	O_h	a_{1g}	692.8	658[20]
		e_g	682.0	668
		t_{1u}	793.2	775
			442.4	427,433
		t_{2g}	408.7	405
		t_{2u}	272.1	
BrF_6^-	O_h	a_{1g}	564.5	565,[55] 561[57]
		e_g	442.9	450, 445
		t_{1u}	575.9	
			211.3	
		t_{2g}	235.0	240,241
		t_{2u}	166.7	
ClOF	C_s	a′	1174.5 (1039.9)[a]	1038[58]
			585.6 (602.9)[a]	597
			324.7 (307.4)[a]	310
$ClOF_2^+$	C_s	a′	1443.3 (1371.6)[a]	1334, 1323[29]
			804.7 (801.0)[a]	734
			523.7 (499.9)[a]	512
			380.5 (369.8)[a]	405
		a″	756.7 (780.6)[a]	694
			393.7 (369.1)[a]	383
$ClOF_3$	C_s	a′	1315.2 (1233.3)[a]	1222[59]
			696.8 (681.1)[a]	694
			490.6 (494.5)[a]	482
			480.4 (484.8)[a]	489
			317.2 (324.1)[a]	319
			225.1 (227.7)[a]	224
		a″	696.7 (681.2)[a]	684
			511.3 (505.5)[a]	501
			419.1 (422.0)[a]	414
$ClOF_4^-$	C_{4v}	a_1	1281.7	1203[60]
			466.0	456
			368.6	339
		b_1	364.2	356
			192.8	

Table 2. continued

molecule	molecular symmetry	mode symmetry	frequency	experiment
		b_2	257.0	278
		e	640.2	600
			444.6	414
			201.8	194
$ClO_2F_2^+$	C_{2v}	a_1	1317.3	1241[29]
			791.2	756
			545.2	514
			387.5	390
		a_2	383.9	390
		b_1	1579.6	1479
			534.0	530
		b_2	848.7	830
			527.9	514
$ClO_2F_2^-$	C_{2v}	a_1	1149.1	1191[59]
			564.6	510
			363.8	363
			187.2	198
		a_2	338.0	337
		b_1	1277.0	1225
			241.5	
		b_2	561.1	
			370.0	378
ClO_3F	C_{3v}	a_1	1118.3 (1067.9)[a]	1063[61]
			705.2 (715.7)[a]	717
			553.3 (549.1)[a]	549
		e	1376.8 (1324.6)[a]	1314
			587.4 (583.3)[a]	573
			403.7 (402.4)[a]	414
ClO_2^+	C_{2v}	a_1	1065.7	1065[23]
			481.4	519
		b_2	1335.1	1308
$BrOF_3$	C_s	a′	1102.3 (1009.5)[a]	995[59]
			628.8 (636.5)[a]	625
			531.6 (538.9)[a]	531
			367.1 (357.2)[a]	345
			237.7 (243.7)[a]	236
			185.8 (187.6)[a]	201
		a″	617.7 (611.7)[a]	601
			414.4 (401.6)[a]	394
			344.0 (345.5)[a]	330
$BrOF_4^-$	C_{4v}	a_1	1044.8	930,[59] 930[60]
			492.2	500, 499
			285.5	302, 299
		b_1	417.6	417, 413
			173.0	205, 178
		b_2	228.4	235, 236
		e	529.3	505, 505
			385.8	395, 395
			170.9	179, 178
BrO_2^+	C_{2v}	a_1	984.4	878[23]
			331.3	372
		b_2	1009.8	943
IOF_4^-	C_{4v}	a_1	958.4	887[60]
			518.7	537
			256.9	279
		b_1	471.2	480
			167.2	
		b_2	199.4	219
		e	513.0	482
			335.1	374
			132.9	140
IOF_5	C_{4v}	a_1	985.7	927[62]
			690.7	681
			645.7	640
			356.4	329
		b_1	646.5	647
			292.3	
		b_2	235.2	307
		e	717.5	712
			368.4	375
			346.6	341
			201.3	208
$IO_2F_4^-$	D_{4h}	a_{1g}	863.4	824[64]
			560.3	569
		a_{2u}	945.3	885
			354.6	349
		b_{1g}	544.7	555
		b_{2g}	242.4	255
		b_{2u}	240.9	
		e_g	374.9	380
		e_u	608.1	590
			380.4	
			166.0	

[a] Values in parentheses calculated at the CCSD(T)/aug-cc-pVTZ level.

Darwin (MVD)[122] corrections from configuration interaction singles and doubles (CISD)[123] calculations. The CISD(MVD)/aug-cc-pVTZ expectation values are generally in good agreement with spin-free one-electron Douglass–Kroll–Hess computations, for most calculations. Since we employed a RECP for Br and I atoms, there is a possibility of "double counting" the relativistic effects when computing MVD corrections to the energy which already includes most of the relativistic effects. Because the MVD operators mainly sample the core region where the pseudo-orbitals are small, it could be assumed that any double counting is very small.[124] Molecular spin orbit corrections (second-order as the molecules are all closed shell singlets) for the I containing molecules were carried out using density functional theory (DFT)[125] with the B3LYP exchange correlation functional[126,127] and the aug-cc-pVTZ-PP-SO basis set for I[128] and the aug-cc-pVTZ for F and O. The atomic spin–orbit corrections are $\Delta E_{SO}(O) = -0.22$ kcal/mol, $\Delta E_{SO}(F) = -0.39$ kcal/mol, $\Delta E_{SO}(Cl) = -0.84$ kcal/mol, $\Delta E_{SO}(Br) = -3.50$ kcal/mol, and $\Delta E_{SO}(I) = -7.24$ kcal/mol from Moore.[129]

The calculated ΣD_0 values are obtained from the following expression

$$\Sigma D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO} \qquad (3)$$

for the Cl compounds and with the valence only CBS extrapolation for the Br compounds. Equation 4 was used to calculate ΣD_0 for the compounds with Br and I when the core–valence corrections are included in the CBS extrapolation,

$$\Sigma D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{SR} + \Delta E_{SO} \qquad (4)$$

By combining the ΣD_0 with the known heats of formation[81] ΔH^0_f at 0 K for elements, ΔH^0_f (O) = 58.99 ± 0.02 kcal/mol, ΔH^0_f (F) = 18.47 ± 0.07 kcal/mol, ΔH^0_f (Cl) = 28.59 ± 0.01 kcal/mol, ΔH^0_f (Br) = 28.18 ± 0.01 kcal/mol, ΔH^0_f (I) = 25.61 ± 0.01 kcal/mol, gas-phase ΔH^0_f values can be derived for compounds in the current

Table 3. Components for CCSD(T) Atomization Energies for XF_n (X = Cl and Br; n = 1−6) in kcal/mol[a]

	CBS							ΣD_0 (0 K)[i]		
reaction	DTQ[b]	Q5[c]	DTQ_{CV}[d]	ΔE_{ZPE}[e]	ΔE_{CV}[f]	ΔE_{SR}[g]	ΔE_{SO}[h]	DTQ	Q5	DTQ_{CV}
$ClF \rightarrow Cl + F$	62.54	62.67		−1.14	0.12	−0.25	−1.23	60.17	60.05	
$ClF_2^+ + e \rightarrow Cl + 2F$	−168.45	−167.98		−3.06	0.61	−0.42	−1.62	−172.47	−172.94	
$ClF_2^- \rightarrow Cl + 2F + e$	188.95	188.76		−2.16	0.18	−0.26	−1.62	184.90	185.09	
$ClF_3 \rightarrow Cl + 3F$	127.97	128.25		−4.51	0.26	−0.72	−2.01	121.27	121.00	
$ClF_4^+ + e \rightarrow Cl + 4F$	−111.57	−110.67		−7.61	−0.22	−1.58	−2.40	−122.48	−123.38	
$ClF_4^- \rightarrow Cl + 4F + e$	265.15	264.82		−5.03	1.02	−0.24	−2.40	258.18	258.51	
$ClF_5 \rightarrow Cl + 5F$	186.01	186.39		−8.74	0.27	−1.80	−2.79	173.33	172.95	
$ClF_6^+ + e \rightarrow Cl + 6F$	−46.17	−45.05		−13.22	−0.12	−4.03	−3.18	−65.61	−66.73	
$ClF_6^- \rightarrow Cl + 6F + e$	311.66	310.95		−8.28	0.58	0.03	−3.18	300.10	300.81	
$BrF \rightarrow Br + F$	63.40	63.36	63.23	−0.96	−0.03	−0.04	−3.89	58.48	58.44	58.35
$BrF_2^+ + e \rightarrow Br + 2F$	−148.25	−148.43	−149.96	−2.57	−1.04	0.22	−4.28	−155.92	−156.09	−156.56
$BrF_2^- \rightarrow Br + 2F + e$	199.79	199.37	199.41	−1.90	0.02	−0.24	−4.28	193.39	192.98	192.99
$BrF_3 \rightarrow Br + 3F$	151.65	151.17	150.04	−3.89	−0.83	0.05	−4.67	142.30	141.83	141.53
$BrF_4^+ + e \rightarrow Br + 4F$	−68.25	−68.84	−72.34	−6.52	−2.69	0.60	−5.06	−81.92	−82.52	−83.33
$BrF_4^- \rightarrow Br + 4F + e$	301.81	300.74	300.44	−4.42	−0.25	−0.28	−5.06	291.80	290.73	290.68
$BrF_5 \rightarrow Br + 5F$	239.99	238.94	236.20	−7.72	−2.23	0.29	−5.45	224.88	223.83	223.32
$BrF_6^+ + e \rightarrow Br + 6F$	−1.48	−2.33	−9.26	−11.16	−5.59	1.06	−5.84	−23.00	−23.86	−25.20
$BrF_6^- \rightarrow Br + 6F + e$	383.05	380.86	380.90	−7.17	0.02	−0.28	−5.84	369.78	367.59	367.61

[a] The atomic asymptotes were calculated with R/UCCSD(T). [b] Extrapolated by using eq 1 with aVDZ, aVTZ, and aVQZ (frozen core). [c] Extrapolated by using eq 2 with aVQZ and aV5Z (frozen core). [d] Extrapolated by using eq 1 with awCVDZ, awCVTZ, and awCVQZ without frozen core approximation. [e] The zero point energies for the polyatomics were taken as 0.5 of the sum of the CCSD(T) with aug-cc-pVTZ or aug-cc-pVTZ-PP harmonic frequencies. [f] 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) with aug-cc-pwCVTZ or aug-cc-pwCVTZ-PP. [g] 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 relativistic effective core potential. [h] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables. Cf. ref 129. [i] The theoretical value of ΔD_0 (0 K) was computed with the CBS estimates.

study. We obtain enthalpies of formation at 298 K by following the procedures outlined by Curtiss et al.[86] Heats of formation at 298 K were obtained by combining the atomic thermal corrections (1.04 kcal/mol (O), 1.05 kcal/mol (F), 1.10 kcal/mol (Cl), 2.93 kcal/mol (Br), and 1.58 kcal/mol (I)) with the molecular thermal corrections in the appropriate statistical mechanical expressions.[130]

All calculations were performed with the MOLPRO2010[131] package of ab initio programs. Molecular spin orbit correction computations were carried out with NWCHEM[132] program. The DFT transition state calculations for ClF_7 and BrF_7 were done with the Gaussian09 program system.[133]

RESULTS AND DISCUSSION

Geometries. The calculated geometries are summarized in Figures 1 and 2 for compounds where the center atom is Cl. The basic molecular shapes are the same for the XF_n (X = Cl, Br, and I; n = 1−8) and XO_nF_m (X = Cl, Br, and I; n = 1−3, m = 1−6) compounds with respect to their central atom, so only the structures of the chlorine fluorides and oxofluorides are illustrated. The only difference between the chlorine and bromine couple and the iodine is the steric activity of the lone valence electron pair on the central atom in the XF_6^- anions. In ClF_6^- and BrF_6^- it is sterically inactive, and the anions are octahedral, whereas in IF_6^- it is sterically active and the anion is distorted from O_h symmetry.[88] Detailed calculated geometry parameters for all compounds are given in the Supporting Information.

A comparison of the calculated geometries with those experimentally observed is given in Table 1. ClF has a $^1\Sigma^+$ ground state with an experimental bond distance of 1.628313 Å.[9,63] The calculated bond length improves systematically from 1.6396 Å to 1.6284 from CCSD(T)/aug-cc-pV(T+d)Z to CCSD(T)/ aug-cc-pV(6+d)Z, and the latter value is in excellent agreement with experiment. The computed geometry parameters for ClF_3 are in good agreement with the experimental values, with the predicted bond lengths being within 0.007 Å and the bond angle within 0.4°. The structure of the ClF_4^+ cation from the X-ray crystal structure[17] of $ClF_4^+SbF_6^-$ is a pseudo trigonal bipyramid. The four fluorine atoms occupy the two axial and two of the equatorial positions with a sterically active lone valence electron pair occupying the third equatorial position. The calculated geometry of the free ion is in very good agreement with the experimental structure. For ClF_5, the predicted $Cl-F_{ax}$ bond length is 0.033 Å longer than experiment and the $Cl-F_{eq}$ bond length is 0.004 Å shorter than experiment;[6] the calculated bond angle is 0.4° smaller than experiment. The calculated geometry of ClO_2^+ agrees with the experimental values, with the bond length and bond angle only differing by 0.01 Å and 2.0°, respectively.[21,78] For ClF_6^+ and BrF_6^+, the experimental[21] and predicted bond lengths agree within 0.01 Å. The calculated geometry of $ClOF_2^+$ agrees with the X-ray crystallographic determination with the bond length and angle differing by 0.05 Å and 3.0°, respectively.[30] For ClOF, ClO_2F, and ClO_3F, the calculated and experimental[35−37] bond lengths and angles are in good agreement with the experimental microwave structures within 0.01 Å for the bond distances and better than 1° for the bond angles.

The calculated geometry parameters for BrF and BrF_3 are in good agreement with experiment within 0.01 Å and 0.3°.[8,9,63] The calculated geometry of BrF_4^+ is in good agreement with the experimental crystal structure values reported by Christe et al.,[7,19] except for the $F_{eq}-Br-F_{eq}$ bond angle which is

Table 4. Components for CCSD(T) Atomization Energies for XO_nF_m (X = Cl and Br; n = 1–3, m = 1– 6) in kcal/mol[a]

	CBS							ΣD_0 (0 K)[i]		
reaction	DTQ[b]	Q5[c]	DTQ_{CV}[d]	ΔE_{ZPE}[e]	ΔE_{CV}[f]	ΔE_{SR}[g]	ΔE_{SO}[h]	DTQ	Q5	DTQ_{CV}
$ClOF \rightarrow Cl + O + F$	103.78	104.61		−2.98	0.31	−0.66	−1.45	99.00	99.83	
$ClOF_2^+ + e \rightarrow Cl + O + 2F$	−98.72	−97.26		−6.15	0.22	−1.20	−1.84	−107.69	−106.23	
$ClOF_2^- \rightarrow Cl + O + 2F + e$	228.74	229.29		−3.96	0.41	−0.72	−1.84	222.62	223.18	
$ClOF_3 \rightarrow Cl + O + 3F$	182.45	183.61		−7.37	0.44	−1.61	−2.23	171.68	172.85	
$ClOF_4^+ + e \rightarrow Cl + O + 4F$	−73.03	−71.29		−11.05	0.46	−3.27	−2.62	−89.51	−87.77	
$ClOF_4^- \rightarrow Cl + O + 4F + e$	316.49	317.04		−7.87	0.60	−1.37	−2.62	305.23	305.78	
$ClOF_5 \rightarrow Cl + O + 5F$	222.08	223.45		−12.52	0.26	−4.14	−3.01	202.67	204.05	
$ClOF_6^- \rightarrow Cl + O + 6F + e$	294.11			−12.15	0.09	−4.18	−3.40	274.47		
$ClO_2F \rightarrow Cl + 2O + F$	179.05	181.06		−6.38	0.61	−1.64	−1.67	169.97	171.98	
$ClO_2F_2^+ + e \rightarrow Cl + 2O + 2F$	−51.50	48.51		−9.89	0.59	−2.84	−2.06	−65.69	−63.11	
$ClO_2F_2^- \rightarrow Cl + 2O + 2F + e$	302.46	304.07		−7.22	0.72	−1.74	−2.06	292.16	293.77	
$ClO_2F_3 \rightarrow Cl + 2O + 3F$	218.97	221.14		−11.05	0.53	−3.57	−2.45	202.42	204.59	
$ClO_2F_4^- \rightarrow Cl + 2O + 4F + e$	328.14	329.71		−11.49	0.47	−3.78	−2.84	310.50	312.07	
$ClO_3F \rightarrow Cl + 3O + F$	235.71	238.70		−10.17	0.88	−3.29	−1.89	221.24	224.23	
$ClO_3F_2^- \rightarrow Cl + 3O + 3F + e$	344.50	347.01		−10.89	0.85	−3.59	−2.28	328.58	331.09	
$BrOF \rightarrow Br + O + F$	103.44	103.77	102.54	−2.60	−0.46	0.13	−4.11	96.40	96.72	95.96
$BrOF_2^+ + e \rightarrow Br + O + 2F$	−88.69	−88.59	−91.72	−5.07	−1.99	0.63	−4.50	−99.62	−99.52	−99.84
$BrOF_2^- \rightarrow Br + O + 2F + e$	241.39	241.37	240.36	−3.48	−0.35	−0.14	−4.50	232.92	232.90	232.24
$BrOF_3 \rightarrow Br + O + 3F$	205.13	204.93	202.21	−6.33	−1.75	0.37	−4.89	192.53	192.33	191.35
$BrOF_4^+ + e \rightarrow Br + O + 4F$	−54.71	−55.06	−61.06	−9.23	−4.56	1.05	−5.28	−72.72	−73.07	−73.25
$BrOF_4^- \rightarrow Br + O + 4F + e$	355.41	354.57	352.82	−6.88	−1.10	−0.03	−5.28	342.11	341.28	340.63
$BrOF_5 \rightarrow Br + O + 5F$	261.14	260.67	254.62	−10.85	−4.57	0.74	−5.67	240.79	240.32	238.84
$BrOF_6^- \rightarrow Br + O + 6F + e$	366.76		359.93	−11.43	−4.49	0.26	−6.06	345.05		342.70
$BrO_2F \rightarrow Br + 2O + F$	168.77	169.43	166.4	−5.21	−1.58	0.52	−4.33	158.16	158.82	157.38
$BrO_2F_2^+ + e \rightarrow Br + 2O + 2F$	−74.20	−73.83	−79.33	−7.69	−3.76	1.10	−4.72	−89.27	−88.90	−89.98
$BrO_2F_2^- \rightarrow Br + 2O + 2F + e$	309.51	309.26	306.86	−6.11	−1.38	0.17	−4.72	297.23	297.47	296.20
$BrO_2F_3 \rightarrow Br + 2O + 3F$	224.79	224.88	219.38	−9.21	−3.82	0.80	−5.11	207.44	207.53	205.85
$BrO_2F_4^- \rightarrow Br + 2O + 4F + e$	369.86	369.65	364.32	−10.24	−3.70	0.38	−5.50	350.79	350.58	348.95
$BrO_3F \rightarrow Br + 3O + F$	201.40	202.30	196.95	−7.85	−3.31	0.95	−4.55	186.64	187.54	185.49
$BrO_3F_2^- \rightarrow Br + 3O + 3F + e$	343.38	343.86	338.48	−9.11	−3.43	0.57	−4.94	326.49	326.96	325.01

[a]The atomic asymptotes were calculated with R/UCCSD(T). [b]Extrapolated by using eq 1 with aVDZ, aVTZ, and aVQZ (frozen core). [c]Extrapolated by using eq 2 with aVQZ and aV5Z (frozen core). [d]Extrapolated by using eq 1 with awCVDZ, awCVTZ, and awCVQZ without frozen core approximation. [e]The zero point energies for the polyatomics were taken as 0.5 of the sum of the CCSD(T) with aug-cc-pVTZ or aug-cc-pVTZ-PP harmonic frequencies. [f]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) with aug-cc-pwCVTZ or aug-cc-pwCVTZ-PP. [g]The scalar relativistic correction is based on a CISD(FC)/aug-cc-pVTZ or aug-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. [h]Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables. Cf. ref 129. [i]The theoretical value of ΔD_0 (0 K) was computed with the CBS estimates.

compressed in the solid state by fluorine bridges to the anions. For BrF_4^-, the calculated bond length is 0.009 Å longer than that from the X-ray crystal structure[10] of $KBrF_4$. For BrF_5, the calculated triple-ζ geometry is in good agreement with the X-ray crystal structure[11] and the electron diffraction and microwave gas-phase structure.[12] The calculated structure for BrO_3F is in good agreement with the electron diffraction structure[14] within 0.01 Å for the bond lengths and 1° for the bond angles. The calculated geometry of $BrOF_2^+$ agrees with the X-ray crystallography determination with the bond length and angle differing by 0.02 Å and 3.0°, respectively.[30] The calculated geometry of BrO_2^+ agrees with experiment with the bond length and angle differing by 0.01 Å and 2.0°, respectively.[21,78]

For IOF_3, the calculated structure is in reasonable agreement with the experimental one, considering the size of the experimental error bars.[25] The calculated bond lengths of IO_2F and $IO_2F_2^-$ are in excellent agreement with the experimental values.[26,28] The calculated structure for IOF_4^- is in fair agreement with the average experimental values[27] for the I−F bond distance and the ∠O−I−F bond angle, considering the large experimental error bars. However, the calculated I−O bond distance is somewhat surprisingly 0.04 Å longer than experiment. We only report the structure for *trans*-$IO_2F_4^-$ as the *cis*-isomer is ∼10 kcal/mol higher in energy.

Vibrational Frequencies. The harmonic vibrational frequencies for the molecules with experimental values calculated at the MP2/AVTZ level are given in Table 2, where they are compared with experiment. The harmonic vibrational frequencies for all of the XF_n and XO_nF_m compounds are listed in the Supporting Information. The overall agreement between the computed and the experimental frequencies is very good, especially considering that the calculated values are harmonic values and the experimental values include an anharmonic component. Although the calculated values for ClF_2^+, ClF_4^+, ClF_6^+, and BrF_4^+ show considerable deviations from experiment, the experimental data are strongly affected by fluorine bridging in the solid state.[48−51]

Table 5. Components for CCSD(T) Atomization Energies for IO_nF_m (n = 1−3, m = 1− 6) in kcal/mol[a]

	CBS				ΔE_{SO}		ΣD_0 (0 K)[g]	
reaction	DTQ[b]	Q5[c]	ΔE_{ZPE}[d]	ΔE_{SR}[e]	atomic[f]	molecular	DTQ	Q5
$IOF \rightarrow I + O + F$	120.65	120.79	−2.46	−0.48	−7.85	1.40	111.26	110.00
$IOF_2^+ + e \rightarrow I + O + 2F$	−36.78	−35.63	−4.37	−0.39	−8.24	1.21	170.1	
$IOF_2^- \rightarrow I + O + 2F + e$	270.73	270.80	−3.34	−0.60	−8.24	1.01	259.56	258.61
$IOF_3 \rightarrow I + O + 3F$	267.05		−5.92	−0.69	−8.63	1.41	253.22	
$IOF_4^+ + e \rightarrow I + O + 4F$	37.50		−8.45	−0.72	−9.02	2.50	136.7	
$IOF_4^- \rightarrow I + O + 4F + e$	428.82		−6.48	−1.04	−9.02	1.38	413.66	
$IOF_5 \rightarrow I + O + 5F$	369.30		−10.18	−1.06	−9.41	2.81	351.46	
$IOF_6^- \rightarrow I + O + 6F + e$	511.85		−11.36	−1.55	−9.80	2.53	491.66	
$IO_2F \rightarrow I + 2O + F$	199.89	200.22	−4.75	−0.43	−8.07	1.20	187.83	186.96
$IO_2F_2^+ + e \rightarrow I + 2O + 2F$	−20.15		−6.87	−0.44	−8.46	1.58	214.9	
$IO_2F_2^- \rightarrow I + 2O + 2F + e$	357.73		−5.73	−0.78	−8.46	1.32	344.08	
$IO_2F_3 \rightarrow I + 2O + 3F$	294.81		−8.00	−0.76	−8.85	2.09	279.30	
$IO_2F_4^- \rightarrow I + 2O + 4F + e$	478.33		−9.73	−1.20	−9.24	2.62	460.78	
$IO_3F \rightarrow I + 3O + F$	240.05		−7.00	−0.52	−8.29	1.65	225.89	
$IO_3F_2^- \rightarrow I + 3O + 3F + e$	412.63		−8.42	−0.92	−8.68	2.08	396.69	

[a] The atomic asymptotes were calculated with R/UCCSD(T). [b] Extrapolated by using eq 1 with awCVDZ, awCVTZ, and awCVQZ without frozen core approximation. [c] Extrapolated by using eq 2 with awCVQZ, and awCV5Z without frozen core approximation. [d] The zero point energies for the polyatomics were taken as 0.5 of the sum of the CCSD(T) with aug-cc-pVTZ or aug-cc-pVTZ-PP harmonic frequencies. [e] The scalar relativistic correction is based on a CISD(FC)/ aug-cc-pVTZ or aug-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. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables. Cf. ref 129. [g] The theoretical value of ΔD_0 (0 K) was computed with the CBS estimates.

Table 6. Components for CCSD(T) Atomization Energies for XO_n^+ and XO_n^- (X = Cl, Br, I; n = 1−3) in kcal/mol[a]

	CBS					ΔE_{SO}		ΣD_0 (0 K)[h]	
Reaction	DTQ[b]	Q5[c]	ΔE_{ZPE}[d]	$\Delta E cv$[e]	ΔE_{SR}[f]	atomic[g]	molecular	DTQ	Q5
$ClO^+ + e \rightarrow Cl + O$	−211.97	−211.30	−1.47	−0.13	0.00	−1.06		−214.63	−213.96
$ClO_2^+ + e \rightarrow Cl + 2O$	−113.13	−111.17	−4.12	0.33	−0.79	−1.28		−118.99	−117.03
$ClO_3^+ + e \rightarrow Cl + 3O$	−84.91	−82.17	−7.26	0.47	−2.00	−1.50		−95.19	−92.46
$ClO^- \rightarrow Cl + O + e$	117.64	118.10	−0.96	0.17	−0.50	−1.06		115.29	115.74
$ClO_2^- \rightarrow Cl + 2O + e$	175.17	176.43	−2.91	0.44	−0.96	−1.28		170.45	171.71
$ClO_3^- \rightarrow Cl + 3O + e$	262.29	264.66	−6.43	0.75	−1.89	−1.50		253.22	255.59
$BrO^+ + e \rightarrow Br + O$	−204.23 (−205.38)	−203.81	−1.50	−0.74	0.20	−3.72		−209.99	−209.57
$BrO_2^+ + e \rightarrow Br + 2O$	−126.42 (−128.35)	−125.57	−3.20	−1.23	0.64	−3.94		−134.15	−133.29
$BrO_3^+ + e \rightarrow Br + 3O$	−119.87 (−123.50)	−118.71	−6.20	−2.61	1.04	−4.16		−131.80	−130.64
$BrO^- \rightarrow Br + O + e$	114.02 (113.97)	114.35	−0.93	0.07	−0.09	−3.72		109.35	109.68
$BrO_2^- \rightarrow Br + 2O + e$	168.99 (168.19)	169.77	−2.61	−0.46	0.03	−3.94		162.01	162.79
$BrO_3^- \rightarrow Br + 3O + e$	249.42 (247.10)	250.55	−5.37	−1.63	0.39	−4.16		238.64	239.78
$IO^+ + e \rightarrow I + O$	−184.97	−184.80	−1.41		−0.05	−7.46	1.05	−192.84	−193.72
$IO_2^+ + e \rightarrow I + 2O$	−104.65	−104.17	−3.00		−0.15	−7.68	1.07	−114.41	−115.00
$IO_3^+ + e \rightarrow I + 3O$	−93.17	−92.42	−5.64		−0.17	−7.90	1.48	−105.41	−106.13
$IO^- \rightarrow I + O + e$	117.14	117.46	−0.97		−0.16	−7.46	1.68	110.24	108.87
$IO_2^- \rightarrow I + 2O + e$	182.29	182.90	−2.61		−0.34	−7.68	1.98	173.64	172.27
$IO_3^- \rightarrow I + 3O + e$	278.75	279.53	−5.08		−0.54	−7.90	1.32	266.55	266.00

[a] The atomic asymptotes were calculated with R/UCCSD(T). [b] Extrapolated by using eq 1 with aV(D+d)Z, aV(T+d)Z, and aV(Q+d)Z for Cl and aVDZ, aVTZ, and aVQZ for O in Cl compounds (frozen core); with aVDZ-PP, aVTZ-PP, and aVQZ-PP for Br and aVDZ, aVTZ, and aVQZ for O in Br compounds (frozen core); with awCVDZ-PP, awCVTZ-PP, and awCVQZ-PP for Br and awCVDZ, awCVTZ, and awCVQZ for O in Br compounds without frozen core approximation given in parentheses; with awCVDZ-PP, awCVTZ-PP, and awCVQZ-PP for I and awCVDZ, awCVTZ, and awCVQZ for O in I compounds without frozen core approximation. [c] Extrapolated by using eq 2 with appropriate QZ and 5Z type basis as stated in footnote *b*. [d] The zero point energies for the polyatomics were taken as 0.5 of the sum of the CCSD(T) with aug-cc-pVTZ or aug-cc-pVTZ-PP harmonic frequencies. [e] 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) with aug-cc-pwCVTZ or aug-cc-pwCVTZ-PP. [f] The scalar relativistic correction is based on a CISD(FC)/ aug-cc-pVTZ or aug-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 C. Moore's Tables. Cf. ref 129. [h] The theoretical value of ΔD_0 (0 K) was computed with the CBS estimates.

The fact that in many oxofluorides the observed X═O stretching frequencies at MP2/AVTZ level tend to be about 50 to 100 cm^{-1} lower than the calculated ones, appears to be quite general. To determine if this is due to the computational

Table 7. Calculated Heats of Formation (kcal/mol) at 298 K

molecule	DTQ[a]	Q5	Δ(DTQ-Q5)	experiment
ClF	−13.0	−13.1	0.1	−13.3 ± 0.1,[b] −12.0 ± 0.1,[c] −14.3 ± 2.9[e,f]
ClF_2^+	237.9	237.5	0.4	
ClF_2^-	−119.8	−119.6	−0.2	
ClF_3	−38.0	−38.3	0.3	−39.3 ± 1.2,[b] −38.0 ± 0.7[c]
ClF_4^+	224.1	223.2	0.9	
ClF_4^-	−157.0	−156.6	−0.4	
ClF_5	−54.1	−54.5	0.4	−56.9 ± 1.7,[b] −59.9 ± 3.9,[d] −57.2 ± 4.2,[e] −56 ± 4.5,[f] −59.2 ± 4.2[e,f]
ClF_6^+	202.8	201.7	1.1	
ClF_6^-	−163.0	−162.2	−0.7	
ClF_7	20.9	20.7	0.2	
BrF	−13.7 (−13.5)	−13.6	0.1	−14.0 ± 0.4[c]
BrF_2^+	218.2 (−218.8)	218.4	−0.2	
BrF_2^-	−130.2 (−129.8)	−129.8	−0.4	
BrF_3	−61.3 (−60.5)	−60.8	−0.5	−61.1 ± 0.7[c]
BrF_4^+	180.7 (182.1)	181.3	−0.6	
BrF_4^-	−192.2 (−191.1)	−191.2	−1.0	
BrF_5	−107.9 (−106.4)	−106.9	−1.0	−102.5 ± 0.5[c]
BrF_6^+	157.5 (159.6)	158.3	−0.8	
BrF_6^-	−233.7 (−231.5)	−231.5	−2.2	
BrF_7	−62.8(−60.3)	−61.2	−1.6	
IF[g]	−19.7(−19.7)	−19.4	−0.3	−22.6 ± 0.9[c]
IF_2^+[g]	176.3(177.2)	176.7	−0.4	
IF_2^-[g]	−143.6(−143.1)	−143.3	−0.3	
IF_3[g]	−104.3(−102.9)	−103.7	0.6	
IF_4^+[g]	89.6(91.7)	90.6	−1.0	
IF_4^-[g]	−239.6(−238.5)	−238.8	−0.8	
IF_5[g]	−205.0(−202.6)	−203.7	−1.3	−200.8 ± 0.4[c]
IF_6^+[g]	22.5(27.8)			
IF_6^-[g]	−326.1(−323.3)			
IF_7[g]	−234.6(−229.0)			−229.7 ± 0.6[c]
$ClOF$	6.6	5.8	0.8	
$ClOF_2^+$	231.0	229.5	1.5	
$ClOF_2^-$	−98.7	−99.3	0.6	
$ClOF_3$	−30.3	−31.4	1.2	−35.4 ± 1.5[e,f]
$ClOF_4^+$	248.5	246.7	2.2	
$ClOF_4^-$	−145.3	−145.8	0.5	
$ClOF_5$	−25.8	−27.2	1.4	
$ClOF_6^-$	−78.8	−79.5	0.7	
ClO_2F	−6.2	−8.2	2.0	−7.8 ± 2.5[e,f]
$ClO_2F_2^+$	247.2	244.5	2.7	
$ClO_2F_2^-$	−110.0	−111.6	1.6	
ClO_2F_3	−2.9	−5.1	2.2	
$ClO_2F_4^-$	−92.6	−94.2	1.6	
ClO_3F	0.7	−2.3	3.0	−5.12 ± 0.68,[c,h] −5.3 ± 4,[c,i] −5.6 ± 1.2[e,f]
$ClO_3F_2^-$	−88.4	−90.9	2.5	
ClO^+	302.2	301.5	0.7	
ClO_2^+	264.9	263.0	1.9	
ClO_3^+	299.4	296.7	2.7	
ClO^-	−27.7	−28.1	0.4	
ClO_2^-	−24.4	−25.6	1.2	
ClO_3^-	−49.0	−51.4	2.4	
$BrOF$	7.0 (7.5)	6.7	0.3	
$BrOF_2^+$	221.0(221.2)	220.9	0.9	
$BrOF_2^-$	−111.1 (−110.5)	−111.1	0.0	
$BrOF_3$	−53.1 (−51.9)	−52.9	−0.2	
$BrOF_4^+$	229.9(230.5)	230.3	−0.4	
$BrOF_4^-$	−184.1 (−182.6)	−183.3	−0.8	
$BrOF_5$	−65.7 (−63.8)	−65.2	−0.5	
$BrOF_6^-$	−151.5 (−149.2)			
BrO_2F	3.7 (4.5)	3.0	0.7	
$BrO_2F_2^+$	269.0(269.8)	268.7	0.3	

Table 7. continued

molecule	DTQ[a]	Q5	Δ(DTQ-Q5)	experiment
$BrO_2F_2^-$	−117.1 (−116.0)	−117.3	0.2	
BrO_2F_3	−9.7 (−8.1)	−9.8	0.1	
$BrO_2F_4^-$	−134.9 (−133.1)	−134.7	−0.2	
BrO_3F	33.5 (34.7)	32.6	0.9	
$BrO_3F_2^-$	−88.2 (−86.8)	−88.7	0.5	
BrO^+	295.3 (295.7)	294.9	0.4	
BrO_2^+	278.0 (278.7)	277.1	0.9	
BrO_3^+	334.1 (335.1)	332.9	1.2	
BrO^-	−24.0 (−23.9)	−24.3	0.3	
BrO_2^-	−18.1 (−17.8)	−18.9	0.8	
BrO_3^-	−36.4 (−35.8)	−37.6	1.2	
IOF	−9.0	−7.8	−1.3	
IOF_2^+	168.9			
IOF_2^-	−139.0			
IOF_3	−114.8			
IOF_4^+	134.6			
IOF_4^-	−256.7			
IOF_5	−177.2			
IOF_6^-	−299.3			
IO_2F	−27.1	−26.2	−0.9	
$IO_2F_2^+$	213.2			
$IO_2F_2^-$	−165.0			
IO_2F_3	−82.4			
$IO_2F_4^-$	−245.8			
IO_3F	−6.6			
$IO_3F_2^-$	−159.4			
IO^+	276.9	277.8	−0.9	
IO_2^+	257.1	257.7	−0.6	
IO_3^+	306.7	307.4	−0.7	
IO^-	−26.1	−24.7	−1.4	
IO_2^-	−30.9	−29.6	−1.4	
IO_3^-	−66.3	−65.7	−0.5	

[a] Calculations from DTQ_{CV} extrapolated results are given in parentheses for compounds with Br. [b] Reference 82. [c] Reference 81. [d] Reference 83. [e] Reference 84a. [f] Reference 84b [g] Values obtained from reference 88a. [h] Reference 135. [i] Reference 136.

method, frequency calculations at the CCSD(T)/AVTZ level were performed on ClOF, $ClOF_2^+$, $ClOF_3$, ClO_3F, and $BrOF_3$. The agreement with experiment is substantially improved showing that this high level method provides reliable predictions of the frequencies. However, it is too computationally expensive to apply this approach to all of the compounds that have been studied.

Heats of Formation. The total energies used in this study are given in the Supporting Information. The energy components for computing TAEs for XF_n (X = Cl and Br; $n = 1-6$) are given in Table 3, and for XO_nF_m (X = Cl, Br, and I; $n = 1$, 2 and $m = 1-6$) are given in Tables 4 and 5. The results for $XO_n^{\pm}$ are given in Table 6. The CBS extrapolated values from both eq 1 (DTQ) and eq 2 (Q5) are reported for comparison.

We first describe some trends in the various components for the TAE. For the ClF_n and ClO_nF_m compounds, the ΔE_{CV} values are all positive with the highest value being 1.02 kcal/mol for ClF_4^-. The only exceptions are ClF_4^+ and ClF_6^+ which have values of −0.22 and −0.12 kcal/mol, respectively. The opposite trend is found for the BrF_n and XO_nF_m compounds. All ΔE_{CV} values are negative, except for both BrF_2^- and BrF_6^- which are slightly positive with a value of 0.02 kcal/mol. The ΔE_{SR} corrections are generally larger than the ΔE_{CV} corrections. There is a significant correlation between the ΔE_{SR} correction and the oxidation state of the central atom of the molecule, with the corrections increasing with increasing oxidation state. The ΔE_{SR} corrections for Cl in the formal +VII oxidation state are in the range of −3.3 to −4.2 kcal/mol.

For the CCSD calculations, an estimate of the potential for significant multireference character in the wave function can be obtained from the T_1 diagnostic.[134] The values for the T_1 diagnostics are small (<0.028) for all compounds showing that the wave function is dominated by a single configuration.

The predicted heats of formation (both DTQ and Q5 extrapolation values) at 298 K and the available experimental values of XF_n and XO_nF_m are given in Table 7. For most cases, the DTQ and Q5 extrapolated heats of formation agree within ~0.5 kcal/mol. We estimate that the error bars for the computed heats of formation are ±1.5 kcal/mol, considering the errors in the CBS extrapolations, zero-point energies, and other molecular electronic structure energetic components. Quantities, such as the fluorides affinities, should be good to ±1.0 kcal/mol as the errors for adding F^- are smaller.

Experimental thermodynamic data are available only for the following chlorine compounds: ClF, ClF_3, ClF_5, BrF, BrF_3, BrF_5, $ClOF_3$, ClO_2F, and ClO_3F. Three experimental heats of formation that differ by 2 kcal/mol have been reported for ClF.[81,82] Feller and Peterson[85] reported a value of −13.2 kcal/mol using a similar CCSD(T)/CBS approach as did Ricca[94]

Table 8. Fluoride Affinities at 298 K (kcal/mol)

reaction	DTQ[a]	Q5
$ClF + F^- \rightarrow ClF_2^-$	46.9	47.0
$ClF_3 + F^- \rightarrow ClF_4^-$	59.0	58.9
$ClF_5 + F^- \rightarrow ClF_6^-$	48.9	48.3
$BrF + F^- \rightarrow BrF_2^-$	57.1 (56.8)	56.7
$BrF_3 + F^- \rightarrow BrF_4^-$	71.0 (71.1)	70.9
$BrF_5 + F^- \rightarrow BrF_6^-$	65.8 (65.7)	64.7
$IF + F^- \rightarrow IF_2^-$	64.0[b]	
$IF_3 + F^- \rightarrow IF_4^-$	76.1[b]	
$IF_5 + F^- \rightarrow IF_6^-$	61.2[b]	
$ClOF + F^- \rightarrow ClOF_2^-$	45.4	45.6
$ClOF_3 + F^- \rightarrow ClOF_4^-$	55.0	54.9
$ClOF_5 + F^- \rightarrow ClOF_6^-$	−6.5	
$ClO_2F + F^- \rightarrow ClO_2F_2^-$	43.9	44.0
$ClO_2F_3 + F^- \rightarrow ClO_2F_4^-$	29.7	29.6
$ClO_3F + F^- \rightarrow ClO_3F_2^-$	29.1	29.2
$BrOF + F^- \rightarrow BrOF_2^-$	58.7 (58.5)	58.4
$BrOF_3 + F^- \rightarrow BrOF_4^-$	71.6 (71.3)	71.0
$BrOF_5 + F^- \rightarrow BrOF_6^-$	26.4 (26.0)	
$BrO_2F + F^- \rightarrow BrO_2F_2^-$	61.3 (61.0)	60.9
$BrO_2F_3 + F^- \rightarrow BrO_3F_4^-$	65.7 (65.7)	65.4
$BrO_3F + F^- \rightarrow BrO_3F_2^-$	62.3 (62.0)	61.9
$IOF + F^- \rightarrow IOF_2^-$	70.5	70.8
$IOF_3 + F^- \rightarrow IOF_4^-$	82.4	
$IOF_5 + F^- \rightarrow IOF_6^-$	62.6	
$IO_2F + F^- \rightarrow IO_2F_2^-$	78.5	
$IO_2F_3 + F^- \rightarrow IO_2F_4^-$	103.9	
$IO_3F + F^- \rightarrow IO_3F_2^-$	93.3	

[a] Calculations from DTQ_{CV} extrapolated results are given in parentheses for compounds with Br. [b] Values obtained from reference 88a.

Table 9. F^+ Affinities at 298 K in kcal/mol

reaction	DTQ[a]	Q5
$ClF + F^+ \rightarrow ClF_2^+$	−169.8	−170.2
$ClF_3 + F^+ \rightarrow ClF_4^+$	−158.7	−159.3
$ClF_5 + F^+ \rightarrow ClF_6^+$	−163.8	−164.6
$ClOF + F^+ \rightarrow ClOF_2^+$	−196.4	−197.0
$ClOF_3 + F^+ \rightarrow ClOF_4^+$	−142.0	−142.6
$ClO_2F + F^+ \rightarrow ClO_2F_2^+$	−167.4	−168.0
$BrF + F^+ \rightarrow BrF_2^+$	−188.9 (−188.4)	−188.8
$BrF_3 + F^+ \rightarrow BrF_4^+$	−178.7 (−178.1)	−178.6
$BrF_5 + F^+ \rightarrow BrF_6^+$	−155.4 (−154.1)	−154.6
$BrOF + F^+ \rightarrow BrOF_2^+$	−206.8 (207.0)	−206.6
$BrOF_3 + F^+ \rightarrow BrOF_4^+$	−137.7 (−138.4)	−137.6
$BrO_2F + F^+ \rightarrow BrO_2F_2^+$	−155.4 (−155.5)	−155.1
$IF + F^+ \rightarrow IF_2^+$	−223.8[b]	
$IF_3 + F^+ \rightarrow IF_4^+$	−226.1[b]	
$IF_5 + F^+ \rightarrow IF_6^+$	−190.3[b]	
$IOF + F^+ \rightarrow IOF_2^+$	−242.9	
$IOF_3 + F^+ \rightarrow IOF_4^+$	−171.4	
$IO_2F + F^+ \rightarrow IO_2F_2^+$	−180.5	

[a] Calculations from DTQ_{CV} extrapolated results are given in parentheses for compounds with Br. [b] Values calculated using heat of formations form reference 88a.

Table 10. Heterolytic Bond Energies Producing F^- (kcal/mol) at 298 K

reaction	DTQ[a]	Q5
$ClF \rightarrow Cl^+ + F^-$	280.7	281.3
$ClF_3 \rightarrow ClF_2^+ + F^-$	215.9	216.2
$ClF_5 \rightarrow ClF_4^+ + F^-$	218.3	218.3
$BrF \rightarrow Br^+ + F^-$	253.4 (253.2)	253.3
$BrF_3 \rightarrow BrF_2^+ + F^-$	219.5 (219.9)	219.7
$BrF_5 \rightarrow BrF_4^+ + F^-$	228.7 (229.0)	228.8
$IF \rightarrow I^+ + F^-$	226.7[b]	
$IF_3 \rightarrow IF_2^+ + F^-$	220.6[b]	
$IF_5 \rightarrow IF_4^+ + F^-$	234.8[b]	
$IF_7 \rightarrow IF_6^+ + F^-$	197.3[b]	
$ClOF \rightarrow ClO^+ + F^-$	236.1	236.3
$ClOF_3 \rightarrow ClOF_2^+ + F^-$	261.3	261.0
$ClOF_5 \rightarrow ClOF_4^+ + F^-$	274.3	274.0
$ClO_2F \rightarrow ClO_2^+ + F^-$	211.6	211.7
$ClO_2F_3 \rightarrow ClO_2F_2^+ + F^-$	250.1	249.7
$ClO_3F \rightarrow ClO_3^+ + F^-$	239.3	239.5
$BrOF \rightarrow BrO^+ + F^-$	228.8 (228.8)	228.7
$BrOF_3 \rightarrow BrOF_2^+ + F^-$	274.0 (273.0)	273.7
$BrOF_5 \rightarrow BrOF_4^+ + F^-$	295.6 (294.2)	295.5
$BrO_2F \rightarrow BrO_2^+ + F^-$	214.0 (214.7)	217.6
$BrO_2F_3 \rightarrow BrO_2F_2^+ + F^-$	278.8 (277.9)	278.5
$BrO_3F \rightarrow BrO_3^+ + F^-$	241.1 (241.0)	240.8
$IOF \rightarrow IO^+ + F^-$	226.5	
$IOF_3 \rightarrow IOF_2^+ + F^-$	283.7	
$IOF_5 \rightarrow IOF_4^+ + F^-$	311.8	
$IO_2F \rightarrow IO_2^+ + F^-$	224.7	
$IO_2F_3 \rightarrow IO_2F_2^+ + F^-$	295.7	
$IO_3F \rightarrow IO_3^+ + F^-$	253.9	

[a] Calculations from DTQ_{CV} extrapolated results are given in parentheses for compounds with Br. [b] Values obtained from reference 88a.

who found a value of −13.1 kcal/mol. Curtiss et al.[86] reported a value of −14.0 kcal/mol using the G2 method and Law et al.[87] reported values of −12.5 kcal/mol and −13.86 kcal/mol using G3 and G3X methods, respectively. The present values for ΔH_f^{298}(ClF) differ by only 0.1 kcal/mol for the DTQ and Q5 extrapolations and are in very good agreement with the experiments[82,84] and the above theoretical results. The JANAF value[81] is apparently too positive by about 1 kcal/mol.

The computed values for ΔH_f^{298} (ClF_3) from the DTQ and Q5 CBS extrapolations, which differ by 0.3 kcal/mol, are in good agreement with the experimental values[81,82,84] and theoretical values of −38.4(G2),[86b] −39.6(G2),[86c] −37.3-(G3X),[85] −35.8(G3),[99] and −39.1(CCSD(T)/CBS)[94] kcal/mol. For ClF_5, two experimental values, −59.9 ± 3.9 and −59.2 ± 4.2 kcal/mol have been reported.[83,84] Law et al.[87] reported values of −50.4 and −53.2 kcal/mol using the G3 and G3X methods, respectively, and Du et al.[99] reported a value of −50.3 kcal/mol at the G3 level as well. Our calculated values for ClF_5 differ by only 0.4 kcal/mol between the DTQ and Q5 CBS extrapolations and are more negative than the G3 and G3X values. The best calculated value (Q5) is more positive than the experimental values and just outside of the error bars. For ClO_3F, three experimental values have been reported for the heat of formation.[81,84,135,136] Our best computed value for the heat of formation is −2.3 kcal/mol from the Q5 CBS extrapolation, which is too positive as compared to experiment by about 3 kcal/mol and just outside the error bars of the calculation and experiment. Du et al.[99] reported the heat of formation of ClO_3F as 1.5 kcal/mol at the G3 level, slightly more positive than our DTQ extrapolated value of 0.7 kcal/mol. For $ClOF_3$, the experimental value is about 4 kcal/mol more negative than the calculated value and again the calculated value is just outside

Table 11. F_2 Elimination Reaction Energies (kcal/mol) at 298 K

reaction	DTQ[a]	Q5
$ClF_7 \rightarrow ClF_5 + F_2$	−75.1	−75.2
$ClF_5 \rightarrow ClF_3 + F_2$	16.2	16.3
$ClF_3 \rightarrow ClF + F_2$	25.0	25.1
$ClF_6^- \rightarrow ClF_4^- + F_2$	6.0	5.6
$ClF_4^- \rightarrow ClF_2^- + F_2$	37.1	37.0
$ClF_2^- \rightarrow Cl^- + F_2$	65.3	65.5
$ClF_6^+ \rightarrow ClF_4^+ + F_2$	21.3	21.5
$ClF_4^+ \rightarrow ClF_2^+ + F_2$	13.8	14.3
$ClF_2^+ \rightarrow Cl^+ + F_2$	90.6	90.1
$BrF_7 \rightarrow BrF_5 + F_2$	−45.1	−45.6
$BrF_5 \rightarrow BrF_3 + F_2$	46.6 (45.8)	46.1
$BrF_3 \rightarrow BrF + F_2$	47.6 (47.0)	47.2
$BrF_6^- \rightarrow BrF_4^- + F_2$	41.5 (40.4)	40.4
$BrF_4^- \rightarrow BrF_2^- + F_2$	62.0 (61.3)	61.4
$BrF_2^- \rightarrow Br^- + F_2$	79.0 (79.0)	79.4
$BrF_6^+ \rightarrow BrF_4^+ + F_2$	23.3 (22.5)	23.0
$BrF_4^+ \rightarrow BrF_2^+ + F_2$	37.4 (36.7)	37.0
$BrF_2^+ \rightarrow Br^+ + F_2$	80.8 (80.3)	81.0
$IF_7 \rightarrow IF_5 + F_2$	25.4[b]	
$IF_5 \rightarrow IF_3 + F_2$	98.8[b]	
$IF_3 \rightarrow IF + F_2$	82.6[b]	
$IF_6^- \rightarrow IF_4^- + F_2$	84.8[b]	
$IF_4^- \rightarrow IF_2^- + F_2$	94.9[b]	
$IF_2^- \rightarrow I^- + F_2$	97.7[b]	
$IF_6^+ \rightarrow IF_4^+ + F_2$	63.0[b]	
$IF_4^+ \rightarrow IF_2^+ + F_2$	84.8[b]	
$IF_2^+ \rightarrow I^+ + F_2$	88.5[b]	
$ClOF_5 \rightarrow ClOF_3 + F_2$	−4.4	−4.2
$ClOF_3 \rightarrow ClOF + F_2$	36.9	37.2
$ClO_2F_3 \rightarrow ClO_2F + F_2$	−3.3	−3.1
$ClOF_2^+ \rightarrow ClO^+ + F_2$	71.2	72.0
$ClO_2F_2^+ \rightarrow ClO_2^+ + F_2$	17.8	18.4
$ClOF_4^+ \rightarrow ClOF_2^+ + F_2$	−17.5	−17.2
$ClOF_6^- \rightarrow ClOF_4^- + F_2$	−66.4	
$ClOF_4^- \rightarrow ClOF_2^- + F_2$	46.5	46.5
$ClOF_2^- \rightarrow ClO^- + F_2$	71.0	71.1
$ClO_2F_4^- \rightarrow ClO_2F_2^- + F_2$	−17.4	−17.4
$ClO_2F_2^- \rightarrow ClO_2^- + F_2$	85.6	85.9
$ClO_3F_2^- \rightarrow ClO_3^- + F_2$	39.4	39.5
$BrOF_5 \rightarrow BrOF_3 + F_2$	12.7 (11.9)	12.4
$BrOF_3 \rightarrow BrOF + F_2$	60.1 (59.3)	59.6
$BrO_2F_3 \rightarrow BrO_2F + F_2$	13.4 (12.6)	12.8
$BrOF_2^+ \rightarrow BrO^+ + F_2$	74.1 (74.5)	
$BrO_2F_2^+ \rightarrow BrO_2^+ + F_2$	8.2 (8.9)	
$BrOF_4^+ \rightarrow BrOF_2^+ + F_2$	−9.3 (−9.3)	
$BrOF_6^- \rightarrow BrOF_4^- + F_2$	−32.6 (−33.4)	
$BrOF_4^- \rightarrow BrOF_2^- + F_2$	73.0 (72.2)	72.1
$BrOF_2^- \rightarrow BrO^- + F_2$	87.2 (86.6)	86.8
$BrO_2F_4^- \rightarrow BrO_2F_2^- + F_2$	17.9 (17.1)	17.4
$BrO_2F_2^- \rightarrow BrO_2^- + F_2$	98.9 (98.3)	98.4
$BrO_3F_2^- \rightarrow BrO_3^- + F_2$	51.8 (51.0)	51.1
$IOF_5 \rightarrow IOF_3 + F_2$	62.4	
$IOF_3 \rightarrow IOF + F_2$	123.8	
$IO_2F_3 \rightarrow IO_2F + F_2$	55.4	
$IOF_2^+ \rightarrow IO^+ + F_2$	108.0	
$IO_2F_2^+ \rightarrow IO_2^+ + F_2$	43.9	
$IOF_4^+ \rightarrow IOF_2^+ + F_2$	34.3	
$IOF_6^- \rightarrow IOF_4^- + F_2$	42.6	
$IOF_4^- \rightarrow IOF_2^- + F_2$	117.7	
$IOF_2^- \rightarrow IO^- + F_2$	112.8	
$IO_2F_4^- \rightarrow IO_2F_2^- + F_2$	80.8	
$IO_2F_2^- \rightarrow IO_2^- + F_2$	134.1	
$IO_3F_2^- \rightarrow IO_3^- + F_2$	93.1	

[a] Calculations from DTQ_{CV} extrapolated results are given in parentheses for compounds with Br. [b] Values obtained from reference 88a.

the sum of the error bars. In contrast, for ClO_2F, the agreement between the calculated and the experimental values is good. It is useful to note that the largest differences with the limited experimental data tend to be for the compounds with central atoms having a higher formal oxidation number, although this is not always the case. We have previously seen such an effect in the prediction of the heat of formation of H_2SO_4 and note that large basis sets are needed to deal with this issue.[137]

The calculated heats of formation for BrF and BrF_3, are in good agreement with the experimental values.[81] The DTQ and Q5 extrapolated values differ by only 0.1 kcal/mol for BrF and 0.5 kcal/mol for BrF_3. In contrast to the case for ClF_5 where the calculated value is too positive as compared to experiment, the calculated heat of formation for BrF_5 is 4.5 kcal/mol more negative than experiment. We would expect the calculated value to be more positive so we suggest that the experimental value for BrF_5 may need to be reinvestigated. No additional experimental or computational work has been cited in the literature for the other bromine fluorides and bromine oxofluorides.

The heats of formation of the iodine fluorides are included for completeness. We have previously compared the heats of formation of the iodine fluorides with experimental values[88a] and note that we suggested that the heat of formation of IF should be reinvestigated.

Fluoride Ion and Fluorine Cation Affinities and Heterolytic X^+-F^- Bond Dissociation Energies. The computed heats of formation can be utilized to predict the fluoride (F^-) affinities (FA) for the XF_n and XO_nF_m compounds (Table 8). Of the neutral halogen fluorides, IF_3 has the highest FA of 76.1 kcal/mol, about 5 kcal/mol higher than that of BrF_3, and 17 kcal/mol higher than that of ClF_3.[88a] Thus, these compounds have fluoride affinities in the mid to low range of the Lewis acidity scale.[138] $ClOF_5$ is predicted not to bind an F^- ion because the maximum coordination number of Cl(+VII) toward F is 6. This has previously been demonstrated experimentally by the failure of ClF_6^+ to form ClF_7 when reacted with F^-.[50,139] $BrOF_5$ is predicted to bind an F^- ion, although the value is at the low end of the FA scale. Increasing the size of the central atom to I leads to a much larger FA so that IOF_5 has a significant FA, as demonstrated by the existence of IOF_6^-.[45]

The F^+ affinities of XF, XF_3, XF_5, XOF, XOF_3, and XO_2F_2 are given in Table 9. As expected, the F^+ affinities of the halogen fluorides decrease with increasing coordination number and formal oxidation state of the halogen central atom except for the ClF_3/ClF_5 couple. In this case, the F^+ affinity increases by about 5 kcal/mol, in contrast to the corresponding Br and I compounds where a decrease is observed. The F^+ affinities of the halogen oxofluorides also decrease with the increasing the coordination number and the formal oxidation state.

The heterolytic X^+-F^- bond dissociation energies (BDEs) are given in Table 10. The heterolytic BDEs for XF_n with X = Cl, Br, I and n = 1, 3, 5 lie between 215 to 280 kcal/mol. Because of steric crowding, IF_7 has the lowest heterolytic BDE, just below 200 kcal/mol. Excluding the diatomics ClF and BrF whose cations cannot readily stabilize a positive charge, the largest heterolytic BDEs are for XOF_5 and XO_2F_3 for X = I and Br which have the halogen central atom in the +VII oxidation state.

F_2 Binding Energies. The calculated heats of formations can also be used to predict the enthalpies for the loss of a F_2 molecule for both neutral and ionic fluorides and oxofluorides. The F_2 elimination reaction energies are given in Table 11. 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, except for ClF_7 and BrF_7 which are exothermic. The instabilities of the latter two compounds are attributed to steric crowding. The F_2 elimination reaction enthalpies increase from the chlorine fluorides to the bromine fluorides and iodine fluorides in accord with the increasing strength of their X-F bonds.[88a] Within each group of compounds (same central atom and formal charge), the F_2 elimination reaction enthalpies decrease with increasing number of fluorine ligands because of increasing mutual ligand repulsion, so that loss of F_2 becomes more favorable. The sterically most crowded compound, ClF_6^-, is predicted to lose F_2 most readily with a dissociation energy of less than 10 kcal/mol.

To better understand the stabilities of ClF_7 and BrF_7, we calculated the transition states for elimination of F_2 from two equatorial fluorines. The high exothermicities of the reactions suggests that the transition states should more closely resemble the starting species XF_7 following Hammond's postulate.[140] The transition states were found at the B3LYP level with the DZVP2 basis sets for F and Cl and the DZVP basis set for Br.[141] The DFT transition state is similar to the original ClF_7 molecule with the Cl−F bond distances for the departing F_2 elongated by 0.22 Å as compared to the minimum and a very long F−F interaction of 2.12 Å as compared to a value of 1.41 Å for the minimum of F_2. At the DFT level, the transition state for ClF_7 is 4.7 kcal/mol above the minimum for the electronic energy difference and 2.9 kcal/mol above the minimum with the zero point energy included; the imaginary frequency at the transition state is $574i$ cm^{-1}. A single point CCSD(T)/aug-cc-pVDZ calculation at the optimized DFT geometries gives an electronic barrier height of 4.7 kcal/mol. For BrF_7, the exothermicity to lose F_2 is smaller so a larger barrier is expected. The DFT electronic barrier height is 15.4 kcal/mol and the zero point energy corrected value is 13.4 kcal/mol. The corresponding CCSD(T)/aug-cc-pVDZ-PP electronic barrier height is 20.9 kcal/mol and the difference with respect to the DFT value is somewhat larger for BrF_7 than for ClF_7. The geometry distortions are an elongation of 0.28 Å for the Br−F bonds and an F_2 distance of 2.03 Å; the imaginary frequency at the transition state is $481i$ cm^{-1}. Thus as expected from the reaction energies, BrF_7 is more stable with respect to F_2 loss than is ClF_7 in terms of the barrier heights (kinetics) for this loss as well.

By analogy with the halogen +VII fluorides, ClF_7 and BrF_7, the following +VII oxofluorides are also thermodynamically not stable with respect to loss of F_2: $ClOF_4^+$, $ClOF_5$, $ClOF_6^-$, ClO_2F_3, $ClO_2F_4^-$, $BrOF_4^+$, and $BrOF_6^-$. The exothermicity of the F_2 loss is largest for the sterically most crowded XOF_6^- ions. As found for the XF_n compounds, F_2 loss in the XO_nF_m compounds is facilitated by ligand crowding, and the stability against F_2 loss increases from the chlorine to the bromine and iodine compounds. In fact, all of the iodine compounds are predicted to be stable with respect to loss of F_2.

CONCLUSIONS

A self-consistent set of the most reliable available thermodynamic parameters has been calculated for the halogen fluorides and oxofluorides using a composite electronic structure approach based on CCSD(T) calculations extrapolated to the complete basis set limit. Of greatest interest are our predictions for the possible syntheses of hitherto unknown molecules and ions. $BrOF_5$ and BrO_2F_3 are predicted to be stable against spontaneous loss of F_2 and should be preparable, whereas BrF_7, ClF_7, $BrOF_6^-$, and $ClOF_6^-$ are unstable by a very wide margin. The stability of $ClOF_5$ is a borderline case. Although its predicted reaction enthalpy toward F_2 loss, −4.4 kcal/mol, is slightly exothermic, this value is comparable to the value of −3.3 kcal/mol calculated for ClO_2F_3, a compound which has been successfully synthesized and characterized.[50,139,142] (The vibrational frequencies for $ClOF_5$ are given in the Supporting Information.) On the basis of the F^- affinities of ClOF (45.4 kcal/mol), BrOF (58.7 kcal/mol), and BrO_2F_3 (65.7 kcal/mol) and their predicted stabilities against loss of F_2, the $ClOF_2^-$, $BrOF_2^-$, and $BrO_2F_4^-$ anions are excellent targets for synthesis. The main challenge for their synthesis is the preparation of the parent compounds. Our previous failure to prepare the $ClO_2F_4^-$ anion[142] can be rationalized by the predicted high exothermicity of −17.4 kcal/mol for the loss of F_2. We note that these stability arguments are based on thermodynamics, not on kinetics. The fact that a molecule such as ClO_2F_3 can be synthesized shows that a kinetic barrier to loss of F_2 is present. This barrier is expected to decrease as the exothermicity of the reaction increases, hence our prediction that $ClOF_5$ might be able to be synthesized but not reactions which are more exothermic for loss of F_2.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete citations for references 105b, 131, 132, and 133. Geometry information for the Cl, Br, and I compounds including Cartesian (x, y, z) coordinates in angstrom. The harmonic vibrational frequencies for all of the XF_n and XO_nF_m compounds. The total energies to calculate the TAE. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dadixon@bama.ua.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported, in part, by the U.S. Department of Energy, Office of Basis Energy Research, Chemical Sciences, in the catalysis program and by the National Science Foundation (CTS-0608896) through the NIRT program. Calculations were done at the Alabama Supercomputer Center or on the massively parallel HP Linux cluster in the Molecular Science Computing Facility (MSCF) in the William R. Wiley Environmental Molecular Sciences Laboratory at the Pacific Northwest National Laboratory.

The MSCF is a national user facility funded by the Office of Biological and Environmental Research in the U.S. Department of Energy. The Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute. K.O.C. is indebted to the Air Force Office of Scientific Research, the Office of Naval Research, the Defense Threat Reduction Agency, and the National Science Foundation for financial support.

■ REFERENCES

(1) Christe, K. O.; Curtis, E. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1520−1526.

(2) Christe, K. O.; Wilson, W. W.; Drake, G. W.; Dixon, D. A.; Boatz, J. A.; Gnann, R. Z. *J. Am. Chem. Soc.* **1998**, *120*, 4711−4716.

(3) Banks, E. R., Ed.; *Fluorine chemistry at the millennium: fascinated by fluorine*; Elsevier Science Ltd.: Oxford, U.K., 2000.

(4) Thrasher, J. S., Strauss, S. H., Eds.; *Inorganic Fluorine Chemistry: Toward the 21st Century*, ACS Symposium Series 555; Americal Chemical Society: Washington, DC, 1994.

(5) Christe, K. O.; Zhang, X.; Sheehy, J. A.; Bau, R. *J. Am. Chem. Soc.* **2001**, *123*, 6338−6348.

(6) Al'tman, A. B.; Myakshin, I. N.; Sukhoverkov, V. F.; Romanov, G. V.; Spiridonov, V. P. *Dokl. Nauk, SSSR* **1978**, *241*, 360−363; *Proc. Acad. Sci. USSR (English Tansl.)* **1978**, *241*, 333−336.

(7) Lind, M. D.; Christe, K. O. *Inorg. Chem.* **1972**, *11*, 608−612.

(8) Magnuson, D. W. *J. Chem. Phys.* **1957**, *27*, 223−226.

(9) Willis, R. E., Jr.; Clark, W. W., III *J. Chem. Phys.* **1980**, *72*, 4946−4950.

(10) Edwards, A. J.; Jones, G. R. *J. Chem. Soc. A* **1969**, 1936−1938.

(11) Burbank, R. D.; Bensey, F. N. *J. Chem. Phys.* **1957**, *27*, 982−983.

(12) (a) Robiette, A. G.; Bradley, R. H.; Brier, P. N. *J. Chem. Soc. D* **1971**, 1567−1568. (b) Georghiou, C.; Brier, P. N.; Baker, J. G.; Jones, S. R. *J. Mol. Spectrosc.* **1978**, *72*, 282−292. (c) Heenan, R. K.; Robliette, A. G. *J. Mol. Struct.* **1979**, *54*, 1375−144.

(13) Clark, A. H.; Beagley, B.; Cruickshank, D. W. J.; Hewitt, T. G. *J. Chem. Soc. A* **1970**, 872−875.

(14) Appelman, E. H.; Beagley, B.; Cruickshank, D. W. J.; Foord, A.; Rustad, s.; Ulbrecht, V. *J. Mol. Struct.* **1976**, *35*, 139−148.

(15) Smith, D. F. *J. Chem. Phys.* **1953**, *21*, 609−614.

(16) Madelung, O. *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology*; Springer: Berlin, Germany, 1987; Vol *II/15*.

(17) Christe, K. O.; Zhang, X.; Sheehy, J. A.; Bau, R. *J. Am. Chem. Soc.* **2001**, *123*, 6338−6348.

(18) Christe, K. O.; Wilson, W. W.; Drake, G. W.; Petrie, M. A.; Boatz, J. A. *J. Fluorine Chem.* **1998**, *88*, 185−189.

(19) Vij, A.; Tham, F. S.; Vij, V.; Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **2002**, *41*, 6397−6403.

(20) Lehmann, J. F.; Schrobilgen, G. J.; Christe, K. O.; Kornath, A.; Suontamo, R. J. *Inorg. Chem.* **2004**, *43*, 6905−6921.

(21) Lehmann, J. F.; Riedel, S.; Schrobilgen, G. J. *Inorg. Chem.* **2008**, *47*, 8343−8356.

(22) Ellern, A.; Boatz, J. A.; Christe, K. O.; Drews, T.; Seppelt, K. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1991−1999.

(23) Lehmann, J. F.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **2005**, *127*, 9416−9427.

(24) Oberhammer, H.; Christe, K. O. *Inorg. Chem.* **1982**, *21*, 273−275.

(25) (a) Edwards, A. J.; Taylor, P. *J. Fluorine Chem.* **1974**, *4*, 173−179. (b) Viers, J. W.; Baird, H. W. *Chem. Commun. (London)* **1967**, 1093−1094.

(26) Minkwitz, R.; Berkei, M.; Ludwig, R. *Inorg. Chem.* **2001**, *40*, 6493−6495.

(27) Ryan, R. R.; Asprey, L. B. *Acta Crystallogr.* **1972**, *B28*, 979−981.

(28) (a) Gerken, M.; Mack, J. P.; Schrobilgen, G. J.; Suontamo, R. J. *J. Fluorine Chem.* **2004**, *125*, 1663−1670. (b) Laval, J.-P.; Jennene Boukharrata, N. *Acta Crystallogr.* **2008**, *C64*, i47−i49. (c) Abrahams, S. C.; Bernstein, J. L. *J. Chem. Phys.* **1976**, *64*, 3254−3260. (d) Helmholz, L. *J. Am. Chem. Soc.* **1940**, *62*, 1537−1542.

(29) Christe, K. O.; Schack, C. J. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus, H. J., Sharpe, A. G., Eds.; Academic Press: New York, 1976; Vol. *18*; pp 319−339.

(30) (a) Bougon, R.; Huy, T. B.; Charpin, P.; Gillespie, R. J.; Spekkens, P. H. *J. Chem. Soc., Dalton Trans.* **1979**, 6−12. (b) Brock., D. S.; de Pury, J. J. C.; Mercier, H. P. A.; Schrobilgen, G. J.; Silvi, B. *Inorg. Chem.* **2010**, *49*, 6673−6689.

(31) Christe, K. O.; Curtis, E. C.; Schack, C. J. *Inorg. Chem.* **1972**, *11*, 2212−2215.

(32) Christe, K. O.; Wilson, R. D.; Curtis, E. C. *Inorg. Chem.* **1973**, *12*, 1358−1362.

(33) Bougon, R.; Cicha, W. V.; Lance, M.; Meublat, L.; Nierlich, M. *Inorg. Chem.* **1991**, *30*, 102−109.

(34) Zhang, X.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1997**, *623*, 491−500.

(35) Müller, H. S. P.; Cohen, E. A. *J. Chem. Phys.* **2002**, *116*, 2407−2416.

(36) (a) Müller, H. S. P. *J. Mol. Struct.* **2000**, *517/518*, 335−350. (b) Robiette, A. G.; Parent, C. R.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1981**, *86*, 455−464.

(37) Müller, H. S. P.; Gerry, M. C. L. *J. Mol. Spectrosc.* **1996**, *175*, 120−132.

(38) Edwards, A. J.; Jones, G. R. *J. Chem. Soc. A* **1969**, 1467−1470.

(39) Mahjoub, A. R.; Hoser, A.; Fuchs, J.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1526−1527.

(40) Bartell, L. S.; Clippard, F. B.; Jacob, E. J. *Inorg. Chem.* **1976**, *15*, 3009−3013.

(41) Christe, K. O.; Dixon, D. A.; Mahjoub, A. R.; Mercier, H. P. A.; Sanders, J. C. P.; Seppelt, K.; Schrobilgen, G. J.; Wilson, W. W. *J. Am. Chem. Soc.* **1993**, *115*, 2696−2706.

(42) Smart, L. E. *Chem. Commun. (London)* **1977**, 519−520.

(43) Christe, K. O.; Sawodny, W. *Inorg. Chem.* **1967**, *6*, 313−318.

(44) Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* **1970**, *9*, 616−618.

(45) Christe, K. O.; Sawodny, W.; Guertin, J. P. *Inorg. Chem.* **1967**, *6*, 1965−1968.

(46) Claassen, H. H.; Weinstock, B.; Malm, J. G. *J. Chem. Phys.* **1958**, *28*, 285−289.

(47) Selig, H.; Claassen, H. H.; Holloway, J. H. *J. Chem. Phys.* **1970**, *52*, 3517−3521.

(48) Christe, K. O.; Sawodny, W. *Inorg. Chem.* **1973**, *12*, 2879−2885.

(49) Christe, K. O.; Zhang, X.; Sheehy, J. A.; Bau, R. *J. Am. Chem. Soc.* **2001**, *123*, 6338−6348.

(50) Christe, K. O. *Inorg. Chem.* **1973**, *12*, 1580−1587.

(51) Christe, K. O.; Wilson, W. W.; Curtis, E. C. *Inorg. Chem.* **1983**, *22*, 3056−3060.

(52) Christe, K. O. *Z. Anorg. Allg. Chem.* **1970**, *374*, 306−309.

(53) Begun, G. M.; Fletcher, W. H.; Smith, D. F. *J. Chem. Phys.* **1965**, *42*, 2236−2242.

(54) Christe, K. O. *Spectrochim. Acta, Part A* **1971**, *27A*, 631−635.

(55) Christe, K. O.; Wilson, W. W.; Chirakal, R. V.; Sanders, J. C. P; Schrobilgen, G. J. *Inorg. Chem.* **1990**, *29*, 3506−3511.

(56) Christe, K. O.; Schack, C. J. *Inorg. Chem.* **1970**, *9*, 1852−1858.

(57) Bougon, R.; Charpin, P.; Soriano, J. C. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1971**, *272*, 565−568.

(58) Müller, H. S. P. *Chem. Phys. Lett.* **1999**, *314*, 396−402.

(59) (a) Christe, K. O.; Curtis, E. C. *Inorg. Chem.* **1972**, *11*, 2196−2201. (b) Christe, K. O.; Curtis, E. C.; Bougon, R. *Inorg. Chem.* **1978**, *17*, 1533−1539.

(60) Christe, K. O.; Wilson, R. D.; Curtis, E. C.; Kuhlmann, W.; Sawodny, W. *Inorg. Chem.* **1978**, *17*, 533−538.

(61) (a) Burczyk, K.; Bürger, H. *J. Mol. Spectrosc.* **1986**, *118*, 288−297. (b) Lide, D. R.; Mann, D. E. *J. Chem. Phys.* **1956**, *25*, 1128−1131.

(62) Christe, K. O.; Curtis, E. C.; Dixon, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 9655−9658.

(63) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules. IV*; Van Nostrand Reinhold: New York, 1979.

(64) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Chem.* **1981**, *20*, 2104−2114.

(65) Bulgin, D. K.; Dyke, J. M.; Jonathan, N.; Morris, A. *Mol. Phys.* **1976**, *32*, 1487−1489.

(66) Schwell, M.; Jochims, H.-W.; Wassermann, B.; Rockland, U.; Flesch, R.; Rühl, E. *J. Phys. Chem.* **1996**, *100*, 10070−10075.

(67) Wales, N. P. L.; Buma, W. J.; de Lange, C. A. *Chem. Phys. Lett.* **1996**, *259*, 213−218.

(68) Peterson, K. A.; Woods, R. C. *J. Chem. Phys.* **1990**, *93*, 1876−1888.

(69) Edwards, A. J.; Sills, R. J. C. *J. Chem. Soc., Dalton Trans.* **1974**, 1726−1729.

(70) Mallouk, T. E.; Rosenthal, G. L.; Müller, G.; Brusasco, R.; Bartlett, N. *Inorg. Chem.* **1984**, *23*, 3167−3173.

(71) Bougon, R.; Cicha, W. V.; Lance, M.; Meublat, L.; Nierlich, M.; Vigner, J. *Inorg. Chem.* **1991**, *30*, 102−109.

(72) Tobias, K. M.; Jansen, M. *Z. Anorg. Allg. Chem* **1987**, *550*, 16−26.

(73) Bougon, R.; Cicha, W. V.; Lance, M.; Meublat, L.; Nerlich, M.; Vigner, J. *Inorg. Chem.* **1991**, *30*, 102−109.

(74) Tobias, K. M.; Jansen, M. *Z. Anorg. Allg. Chem* **1987**, *550*, 16−26.

(75) Jacob, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 158; *Angew. Chem.* **1976**, *88*, 189−190.

(76) Spekkens, P. H. Ph.D. Dissertation, McMaster University, Hamilton, ON, Canada, 1977.

(77) Gillespie, R. J.; Spekkens, P. H. *Isr. J. Chem.* **1978**, *17*, 11−19.

(78) Dyke, J. M.; Gamblin, S. D.; Hooper, N.; Lee, E. P. F.; Morris, A.; Mok, D. K. W.; Chau, F. T. *J. Chem. Phys.* **2000**, *112*, 6262−6274.

(79) Nabiev, S. S. *Russ. Chem. Bull.* **1999**, *48*, 711−717.

(80) Francisco, J. S. *Chem. Phys. Lett.* **1998**, *288*, 307−310.

(81) Chase, M. W., Jr. NIST-JANAF Tables, 4th ed.; *J. Phys. Chem. Ref. Data, Monogr.* **1998**, *9*, 1−1951.

(82) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*; CRC Press: Boca Raton, FL, 1994.

(83) Bisbee, W. R.; Hamilton, J. V.; Gerhauser, J. M.; Rushworth, R. *J. Chem. Eng. Data* **1968**, *13*, 382−385.

(84) (a) Barberi, P.; Rigny, P. *J. Fluorine Chem.* **1976**, *8*, 125−132. (b) Barberi, P. Ph.D. Thesis, L'Universite de Provence, Aix Marseille I, France, 1974.

(85) Feller, D.; Peterson, K. A. *J. Chem. Phys.* **1999**, *110*, 8384−8396.

(86) (a) Curtiss, L. A.; Raghavachari, K.; Truck, G. W.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764−7776. (b) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 108−117. (c) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570−10579.

(87) Law, C.; Chien, S.; Li, W.; Cheung, Y. *J. Phy. Chem. A* **2002**, *106*, 11271−11276.

(88) (a) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1989**, *28*, 3275−3277. (b) Mahjoub, A. R.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 323−324. (c) Dixon, D. A.; Grant, D. J.; Christe, K. O.; Peterson, K. A. *Inorg. Chem.* **2008**, *47*, 5485−5494. (d) Grant, D. J.; Garner, E. B., III; Matus, M. H.; Nguyen, M. T.; Peterson, K. A.; Francisco, J. S.; Dixon, D. A. *J. Phys. Chem. A* **2010**, *114*, 4254−4265. (e) Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2009**, *113*, 777−787.

(89) Ungemach, S. R.; Schaefer, S. F., III *Chem. Phys. Lett.* **1976**, *38*, 407−409.

(90) Ungemach, S. R.; Schaefer, S. F., III *J. Am. Chem. Soc.* **1976**, *98*, 1658−1662.

(91) Pershin, V. L.; Boldyrev, A. I. *J. Mol. Struct. (THEOCHEM)* **1987**, *150*, 171−188.

(92) Pak, C.; Xie, Y.; Van Huis, T. J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1998**, *120*, 11115−11121.

(93) Ignatyev, I. S.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1999**, *121*, 6904−6910.

(94) Ricca, A. *Chem. Phys. Lett.* **2000**, *323*, 498−505.

(95) Law, C.-K.; Chien, S.-H.; Li, W.-K.; Cheung, Y.-S. *J. Phys. Chem. A* **2002**, *106*, 11271−11276.

(96) Gong, L.; Li, Q.; Xu, W.; Xie, Y.; Schaefer., H. F., III *J. Phys. Chem. A* **2004**, *108*, 3598−3614.

(97) Li, Q.; Gong, L.; Xie, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **2004**, *126*, 14950−14959.

(98) Chen, L.; Woon, D. E.; Dunning, T. H., Jr. *J. Phys. Chem. A* **2009**, *113*, 12645−12654.

(99) Du, H.; Liu, Y.; Wang, F.; Zhang, J.; Liu, H.; Gong, X. *Thermochim. Acta* **2011**, *523*, 79−83.

(100) Kalemos, A.; Mavridis, A. *J. Phys. Chem. A* **2011**, *115*, 2378−2384.

(101) (a) Peterson, K. A.; Feller, D.; Dixon, D. A. *Theor. Chem. Acc.* **2012**, *131* (1), 1079 (20 pages). (b) Feller, D.; Peterson, K. A.; Dixon, D. A. *Mol. Phys.* Online May 2012, DOI:10.1080/00268976.2012.684897.

(102) (a) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483. (c) Bartlett, R. J.; Watts, J. D.; Kucharski, S. A.; Noga, J. *Chem. Phys. Lett.* **1990**, *165*, 513−522; *erratum* **1990**, *167*, 479. (d) Watts, J. D.; Gauss, J.; Bartlett, R. J. *Chem. Phys. Lett.* **1992**, *200*, 1−7. (e) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718−8733.

(103) Lee, T. J.; Scuseria, G. E. Achieving Chemical Accuracy with Coupled-Cluster Theory. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995; pp 47−108.

(104) Dunning, T. H., Jr. *J. Phys. Chem. A* **2000**, *104*, 9062−9080.

(105) (a) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484−3496. (b) Ruscic, B.; Wagner, A. F.; Harding, L. B.; Asher, R. L.; Feller, D.; Dixon, D. A.; Peterson, K. A.; Song, Y.; Qian, X.; Ng, C.-Y.; et al. *J. Phys. Chem. A* **2002**, *106*, 2727−2747. (c) Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *129*, 204015 (32 pages).

(106) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796−6806. (c) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358−1371. (d) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244−9253. (e) Wilson, A. K.; Woon, D. E.; Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1999**, *110*, 7667−7676.

(107) (a) Peterson, K. A. *J. Chem. Phys.* **2003**, *119*, 11099−11112. (b) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113−11123.

(108) Feller, D. *J. Comput. Chem.* **1996**, *17*, 1571−1586.

(109) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796−6806.

(110) Peterson, K. A.; Shepler, B. C.; Figgen, D.; Stoll, H. *J. Phys. Chem. A* **2006**, *110*, 13877−13883.

(111) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113−11123.

(112) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244−9253.

(113) Wilson, A. K.; Dunning, T. H., Jr. *J. Phys. Chem. A* **2004**, *108*, 3129−3133.

(114) (a) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219−5227. (b) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321−327. (c) Erratum: *J. Chem. Phys.* **2000**, *112*, 3106−3107 .

(115) Feller, D.; Peterson, K. A.; Hill, J. G. *J. Chem. Phys.* **2011**, *135*, 044102−1−0 44102−18.

(116) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410−7415.

(117) Halkier, A.; Klopper, W.; Helgaker, T.; Jörgensen, P.; Taylor, P. R. *J. Chem. Phys.* **1999**, *111*, 9157−9167.

(118) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618−622. (b) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359−401.

(119) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548−10560.

(120) DeYonker, N. J.; Peterson, K. A.; Wilson, A. K. *J. Phys. Chem. A* **2007**, *111*, 11383−13893.

(121) Peterson, K. A.; Yousaf, K. E. *J. Chem. Phys.* **2010**, *133*, 174116 (6 pages).
(122) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett.* **1981**, *84*, 226–227.
(123) Sherrill, C. D.; Schaefer, H. F., III *Adv. Quantum Chem.* **1999**, *34*, 143–269.
(124) (a) Dixon, D. A.; de Jong, W. A.; Peterson, K. A.; Christe, K. O.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **2005**, *127*, 8627–8634. (b) Dixon, D. A.; Grant, D. J.; Peterson, K. A.; Christe, K. O.; Schrobilgen, G. J. *Inorg. Chem.* **2008**, *47*, 5485–5494. (c) Grant, D. J.; Wang, T. H-; Dixon, D. A.; Christe, K. O. *Inorg. Chem.* **2010**, *49*, 261–270. (d) Dixon, D. A.; Wang, T. H.; Grant, D. J.; Peterson, K. A.; Christe, K. O.; Schrobilgen, G. J. *Inorg. Chem.* **2007**, *46*, 10016–10021.
(125) Parr, R. G. Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989; Vol. *16*, International Series of Monographs on Chemistry.
(126) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
(127) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
(128) Hess, B. A.; Marian, C. M.; Whalgren, U.; Gropen, O. *Chem. Phys. Lett.* **1996**, *251*, 365–371.
(129) Moore, C. E. *Atomic energy levels as derived from the analysis of optical spectra, Volume 1, H to V*; U.S. National Bureau of Standards Circular 467; U.S. Department of Commerce, National Technical Information Service, COM-72-50282: Washington, D.C., 1949.
(130) McQuarrie, D. A. *Statistical Mechanics*; University Science Books: Sausalito, CA, 2000.
(131) *MOLPRO, a package of ab initio programs*, version 2010.1; Knowles, P. J.; Manby, F. R.; Schütz, M.; Celani, P.; Knizia, G.; Korona, T.; Lindh, R.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; et al.; see http://www.molpro.net.
(132) Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; et al. *Comput. Phys. Commun.* **2010**, *181*, 1477–1489.
(133) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.
(134) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *S23*, 199–207.
(135) Neugebaur, C. A.; Margrave, J. L. *J. Am. Chem. Soc.* **1957**, *79*, 1338–1340.
(136) Dibeler, V. H.; Reese, R. M.; Mann, D. E. *J. Chem. Phys.* **1957**, *27*, 176–179.
(137) Gutowski, K. E.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 12044–12054.
(138) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J.; Boatz, J. A. *J. Fluorine Chem.* **2000**, *101*, 151–153. *Chem. Eng. News*, March 3, **2003**, pp 48–49.
(139) (a) Christe, K. O. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 741–745.
(140) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.
(141) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–571.
(142) (a) Christe, K. O.; Wilson, R. D. *Inorg. Chem.* **1973**, *12*, 1356–1357. (b) Christe, K. O.; Curtis, E. C. *Inorg. Chem.* **1973**, *12*, 2245–2251.