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Thermochemical Properties of Selenium Fluorides, Oxides, and Oxofluorides

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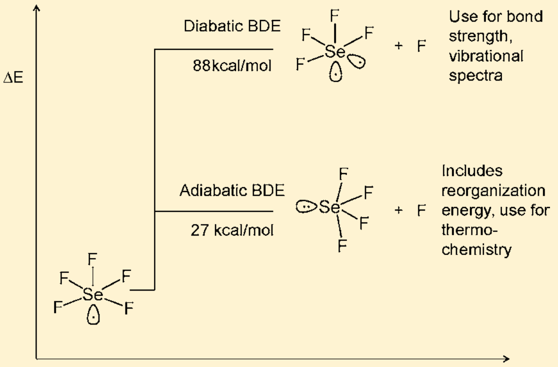
Supporting Information

ABSTRACT: The bond dissociation energies (BDEs), fluoride and fluorocation affinities, and electron affinities of SeF_n (n = 1−6), $SeOF_n$ (n = 0−4), and SeO_2F_n (n = 0−2) have been predicted with coupled cluster CCSD(T) theory extrapolated to the complete basis set limit. To achieve near chemical accuracy, additional corrections were added to the complete basis set binding energies based on frozen core coupled cluster theory energies. These included corrections for core−valence effects, scalar relativistic effects, for first-order atomic spin−orbit effects, and vibrational zero point energies. The adiabatic BDEs contain contributions from product reorganization energies and, therefore, can be much smaller than the diabatic BDEs and can vary over a wide range. For thermochemical calculations, the adiabatic values must be used, whereas for bond strength and kinetic considerations, the diabatic values should be used when only small displacements of the atoms without change of the geometry of the molecule are involved. The adiabatic Se−F BDEs of SeF_n (n = 1−6) are SeF_6 = 90, SeF_5 = 27, SeF_4 = 93, SeF_3 = 61, SeF_2 = 86, and SeF = 76 kcal/mol, and the corresponding diabatic values are SeF_6 = 90, SeF_5 = 88, SeF_4 = 93, SeF_3 = 74, SeF_2 = 86, and SeF = 76 kcal/mol. The adiabatic Se−O BDEs of SeO_n (n = 1−3), $SeOF_n$ (n = 1−4), and SeO_2F_n (n = 1,2) range from 23 to 107 kcal/mol, whereas the diabatic ones range from 62 to 154 kcal/mol. The adiabatic Se−F BDEs of $SeOF_n$ (n = 1−4) and SeO_2F_n (n = 1,2) range from 20 to 88 kcal/mol, whereas the diabatic ones range from 73 to 112 kcal/mol. The fluoride affinities of SeF_n, (n = 1−6), SeO_n, (n = 1−3), $SeOF_n$, (n = 1−4), and SeO_2F_n (n = 1,2) range from 15 to 121 kcal/mol, demonstrating that the Lewis acidity of these species covers the spectrum from very weak (SeF_6) to very strong (SeO_3) acids. The electron affinities which are a measure of the oxidizing power of a species, span a wide range from 1.56 eV in SeF_4 to 5.16 eV in SeF_5 and for the free radicals are much higher than for the neutral molecules. Another interesting feature of these molecules and ions stems from the fact that many of them possess both a Se free valence electron pair and a free unpaired valence electron, raising the questions of their preferred location and their influence on the Se−F and Se═O bond strengths.



INTRODUCTION

There is significant interest in the thermochemical properties including bond dissociation energies (BDEs) of compounds of the main group elements of the second- and higher-rows.[1,2] There have been a number of structural and spectroscopic studies of the binary selenium fluorides SeF_4,[2−7] SeF_5^-,[2,8,9] and SeF_6^{2-},[10,11] and the selenium oxofluorides including $SeOF_2$,[2,12−16] SeO_2F^-,[2,17−21] and $SeOF_3^-$.[2,22−24] Octahedral SeF_6 has been studied extensively, and its geometry,[25] heat of formation,[26] vibrational frequencies,[27] and ^{77}Se NMR chemical shifts[28−30] have been reported. The crystal structure of a compound of the form RSeF with R a phenyl ring with large bulky substituents was just reported.[31] Schaefer and co-workers have reported the geometries and electron affinities of SeF_x (x = 1−7).[32] Wang[33] predicted the heats of formation for $SeF_n^{0/\pm}$ for n = 1−6 using the G3 method.[34] In addition, Wang recommended a revised value of 57.90 ± 0.3 kcal/mol for ΔH_f(Se) at 0 K based on the ionization chemistry of H_2Se.[35] This value differs substantially from the value given by Wagman et al.[36] of ΔH_f(Se) = 54.11 kcal/mol at 0 K.

Because there is only a limited amount of information available on the above compounds as well as other selenium fluorides and oxofluorides, we have calculated the thermodynamic properties of a broad range of selenium fluorides, oxofluorides, and oxides using high level correlated molecular orbital theory. In this paper, we report the ΔH_f's, BDEs, fluoride affinities of SeF_n (n = 1−6), $SeOF_n$ (n = 1−4), SeO_2F_n

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Table 1. CCSD(T) Optimized Bond Lengths (Å) and Angles (degrees) for SeF_xO_y Geometries[a]

molecule	basis set	R_{SeF}	R_{SeO}	∠FSeF	∠FSeO	∠OSeO	∠FSeF
$SeF^+(^3\Sigma^-, C_{\infty v})$	aVQZ	1.663					
$SeF(^2\Pi, C_{\infty v})$	aVQZ	1.744					
	exp[b,c]	1.742					
$SeF^-(^1\Sigma^+, C_{\infty v})$	aVQZ	1.851					
$SeF_2^+(^2B_1, C_{2v})$	aVTZ	1.665		98.4			
$SeF_2(^1A_1, C_{2v})$	aVQZ	1.738		96.2			
$SeF_3^+(^1A_1, C_{3v})$	aVQZ	1.648		97.3			
$SeF_3(^2B_1,C_{2v})$	aVQZ	1.699eq		86.0			
		1.795ax					
$SeF_3^-(^1A_1,C_{2v})$	aVQZ	1.769eq		86.3			
		1.916ax					
$SeF_4\ (^1A_1,C_{2v})$	aVTZ	1.691eq		100.4eq			
		1.777ax		168.6ax			
$SeF_4^+(^2A_1,C_{2v})$	aVTZ	1.645eq		100.8eq			
		1.723ax		161.5ax			
$SeF_5^+(^1A_1,C_{2v})$	aVTZ	1.643eq		120.0			
		1.663ax		180.0			
$SeF_5(^2A_1,C_{4v})$	aVTZ	1.741eq		91.0			90.0
		1.674ax					
$SeF_5^-\ (^1A_1,C_{4v})$	aVTZ	1.721eq		84.3			89.4
		1.841ax					
$SeF_6(^1A_{1g},O_h)$	aVQZ	1.683		90.0			90.0
	Exp[d]	1.678					
$SeF_6^-\ (^2A_{1g},O_h)$	aVTZ	1.819		90.0			90.0
$SeF_6^{2-}\ (^1A_{1g},O_h)$	aVQZ	1.948		90.0			90.0
$SeF_7^-\ (^1A_1,D_{5h})$	aVTZ	1.817eq		72.0			90.0
		1.704ax		180.0			
$SeO^+(^2\Pi,C_{\infty v})$	aVTZ		1.597				
$SeO^-(^2\Pi,C_{\infty v})$	aVQZ		1.722				
	exp		1.726 ± 0.010[f]				
$SeO(^3\Sigma^-,C_{\infty v})$	aVQZ		1.644				
	exp		1.648[e]				
$SeOF^+(^1A',C_s)$	aVTZ	1.679	1.576		106.7		
$SeOF(^2A''C_s)$	aVQZ	1.753	1.607		105.6		
$SeOF^-\ (^1A',C_s)$	aVQZ	1.868	1.680		104.3		
$SeOF_2\ (^1A',C_s)$	aVTZ	1.738	1.585	92.6	104.9		
$SeOF_2^+(^2A',C_s)$	aVTZ	1.667	1.720	95.5	99.8		
$SeOF_2^-(^1A_1,C_{2v})$	aVTZ	1.953	1.640	167.7	96.2		
$SeOF_2^{2-}(^1A_1,C_{2v})$	aVTZ	2.202	1.703	158.0	101.0		
$SeOF_3^+(^1A_1,C_{3v})$	aVTZ	1.643	1.561	99.5	118.2		
$SeOF_3(^2A'',C_s)$	aVTZ	1.701	1.733		103.9		
		1.789					
$SeOF_3^-\ (^1A_1,C_s)$	aVTZ	1.771eq	1.606		104.5		
		1.903ax					
$SeOF_4^+(^2B_2,C_{2v})$	aVTZ	1.642eq	1.713	110.8	124.6		
		1.675ax		174.2	87.1		
$SeOF_4\ (^1A_1,C_{2v})$	aVQZ	1.682eq	1.575	111.6	124.2		
		1.714ax		162.8	98.6		
$SeOF_4^-\ (^1A_1,C_{4v})$	aVTZ	1.839	1.597	158.4	100.8		
				88.0			
$SeOF_5^-\ (^1A_1,C_{4v})$	aVTZ	1.753eq	1.614		96.9		
		1.757ax					
$SeO_2F^+\ (^1A',C_s)$	aVTZ	1.666	1.581		111.4	137.2	
$SeO_2F(^2A',C_s)$	aVQZ	1.734	1.617		104.0	120.2	
$SeO_2F^-(A',C_s)$	aVQZ	1.850	1.632		100.3	110.9	
$SeO_2F_2\ (^1A_1,C_{2v})$	aVTZ	1.696	1.582	90.5	107.8	126.9	
$SeO_2F_2^-\ (^2A_1,C_{2v})$	aVTZ	1.902	1.624	141.7	100.0	116.3	
$SeO_2F_3^-\ (^1A_1,C_{2v})$	aVTZ	1.740eq	1.609	82.1	114.9	130.1	
		1.802ax					
$SeO_2^+\ (^2A',C_s)$	aVTZ		1.592			104.2	
			1.732				

Table 1. continued

molecule	basis set	R_{SeF}	R_{SeO}	∠FSeF	∠FSeO	∠OSeO	∠FSeF
SeO_2 ($^1A_1,C_{2v}$)	aVTZ		1.618			114.3	
SeO_2^- ($^2B_1,C_{2v}$)	aVTZ		1.682			111.9	
SeO_3 ($^1A_1',D_{3h}$)	aVQZ		1.597			120.0	
SeO_3F ($^1A',C_s$)	aVTZ	1.657	1.573, 1.718		106.3, 114.1	58.6, 129.7	

[a] CCSD(T) optimizations on SeF, SeO, and SeF_xO_y compounds; ax = axial and eq = equatorial. [b] Ref 26. [c] Ref 54. [d] Ref 55. [e] Ref 27b. [f] Ref 69b.

(n = 1,2), and SeO_n (n = 1−3), the fluorocation affinities of SeF_n (n = 1−6), $SeOF_n$ (n = 1−4), SeO_2F_n (n = 1,2), and SeO_n (n = 1−3), and the electron affinities of SeF_n (n = 1−6), $SeOF_n$ (n = 1−4), and SeO_2F_n (n = 0−2) predicted at the coupled cluster CCSD(T) theory level[37] extrapolated to the complete basis set limit[38] using the correlation-consistent basis sets.[39] In addition, we report the ionization potentials of many of these species.

COMPUTATIONAL METHODS

Geometries were initially optimized at the density functional theory level with the Becke's three-parameter exchange functional with the LYP correlation functional (B3LYP),[40,41] and the standard augmented correlation consistent basis sets aug-cc-pVnZ, with n = D and T, were used for O and F. A small core relativistic effective core potential (RECP) was used for Se, which subsumes the ($1s^2$, $2s^2$, $2p^6$) orbital space into the 10-electron core, and a 24 electron space ($3s^2$, $3p^6$, $4s^2$, $3d^{10}$ and $4p^4$) where the electrons are treated explicitly together with the appropriate aug-cc-pVnZ basis set.[42] We denote this combination of basis sets as aug-cc-pVnZ-PP. Only the spherical component subset (e.g., 5-term d functions, 7-term f functions, etc.) of the Cartesian polarization functions were used. The B3LYP/aug-cc-pVTZ-PP optimized geometries were then used as starting geometries for second-order Møller−Plesset perturbation theory (MP2)[43] optimizations which were in turn used as starting points for high accuracy CCSD(T) optimizations with the aug-cc-pVnZ-PP basis sets for n = D, T, and in some cases Q.

Frequencies including the IR and Raman intensities were calculated with the B3LYP and MPW1PW91 exchange-correlation functionals and frequencies at the CCSD(T)/aug-cc-pVDZ-PP level. The unscaled vibrational frequencies from the CCSD(T)/aug-cc-pVDZ-PP calculations were used to calculate the vibrational zero point energies (ZPEs).

Only the 4s and 4p electrons on Se and the 2s and 2p electrons in O and F were correlated in the CCSD(T) valence electron correlation calculations. For the open shell atomic calculations, we used the R/UCCSD(T) (restricted method for the starting Hartree−Fock wave function and then relaxed the spin restriction in the coupled cluster portion of the calculation) approach.[44] The CCSD(T)/aug-cc-pVnZ-PP valence energies were extrapolated to the complete basis set (CBS) limit by using a mixed exponential/Gaussian function of the form:

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

with n = 2 (aug-cc-pVDZ-PP), 3 (aug-cc-pVTZ-PP), and 4 (aug-cc-pVQZ-PP). We abbreviate these basis sets as AVDZ, AVTZ, and AVQZ. Core−valence corrections, ΔE_{CV}, were obtained as the difference between valence-only and all active electrons correlated calculations at the CCSD(T)/cc-pwCVTZ-PP level.[45] A scalar relativistic correction, ΔE_{SR}, due to the F and O atoms was evaluated from the expectation values for the two dominant terms in the Breit−Pauli Hamiltonian (the mass-velocity, and one-electron Darwin (MVD) corrections)[46] from configuration interaction singles and doubles (CISD) calculations with a cc-pVTZ basis set at the CCSD(T)/ aug-cc-pVTZ-PP geometry. Any "double counting" of the relativistic effect on the Se when applying a MVD correction to an energy, which already includes most of the relativistic effects via the RECP, is small. A second relativistic correction is due to the neglect of atomic spin orbit effects in our calculations, and spin orbit atomic corrections of 0.22 (O), 0.39 (F), and 2.70 (Se) kcal/mol were taken from the excitation energies compiled by Moore.[47] By combining our computed $\sum D_0$ values given by the following expression:[48]

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

with the known atomic heats of formation[33,49] at 0 K for the elements, $\Delta H_f(O)$ = 58.99 kcal/mol, $\Delta H_f(F)$ = 18.47 ± 0.07 kcal/mol, and $\Delta H_f(Se)$ = 57.90 ± 0.3 kcal/mol,[33] we can derive ΔH_f values for the molecules under study. Heats of formation at 298 K were obtained by following the procedures outlined by Curtiss et al.[50]

Calculations of the NMR chemical shifts were done using the gauge invariant atomic orbital (GIAO) approach to deal with the gauge invariance issue.[51] All NMR calculations were done with the B3LYP/aVTZ-PP geometries. The NMR chemical shift calculations were done with the B3LYP functional and the Ahlrichs TZ2P[52] Gaussian basis set on F and O and the aug-cc-pVTZ-PP on Se (labeled as TZ2P). Additional NMR chemical shift calculations were done with the BLYP[41,53] functional with the TZP ADF basis set with and without using ZORA (zeroth-order regular approximation) for the relativistic effects[54−59] with the ADF code.[60] The ^{77}Se chemical shifts were calculated relative to the reference standard $Se(CH_3)_2$ and the ^{19}F shifts relative to $CFCl_3$.

All of the CCSD(T) calculations were performed with the MOLPRO program system[61] on the Dell Intel or Penguin AMD clusters at The University of Alabama. The DFT geometry optimizations and B3LYP NMR chemical shift calculations were done with the Gaussian program system.[62] Molecular visualization was done using the AGUI graphics program from the AMPAC program package.[63]

RESULTS AND DISCUSSION

Geometries. The optimized geometry parameters for the selenium fluorides, oxides and oxofluorides are given in Table 1 together with the point group and ground-state symmetry labels. Drawings of all molecules and ions are given in Figure 1. We briefly discuss the $SeF_n^{0/\pm}$ geometries. The calculated CCSD(T)/AVQZ Se−F bond distance in SeF agrees well with the experimental value within 0.002 Å.[64] As expected, SeF_2 has a C_{2v} geometry with a CCSD(T)/aVQZ calculated F−Se−F bond angle of 96.2°, which is much smaller than that of H_2O.[65] Our predicted geometry for SeF_3 at the CCSD(T)/aVQZ level is a planar, T-shaped molecule with C_{2v} symmetry. SeF_4 is a pseudotrigonal bipyramid, and SeF_5 is predicted to have C_{4v} symmetry, derived from a distorted octahedron. In octahedral SeF_6, the Se−F bond length is in excellent agreement with experiment within 0.005 Å at the CCSD(T)/aVQZ level. The DFT BHLYP calculated geometries of Li et al.[32] for the SeF_n compounds agree best with our higher level values. Starting from an initial structure with seven F atoms bonded to the Se, the SeF_7^+ cation dissociates to form SeF_5^+ plus difluorine (Figure 1) with a bond distance of 1.40 Å which suggests that it forms molecular fluorine which has an F−F bond length of 1.417 ± 0.001 Å.[66]

Two selenium oxofluoride cations have interesting geometries. Starting from a structure with five F atoms and one O atom bonded to the Se, the $SeOF_5^+$ cation undergoes an isomerization (Figure 1) where an Se−F bond is transferred from the Se to the oxygen to form an O−F bond. A similar type of isomerization is predicted for the $SeO_2F_3^+$ cation starting

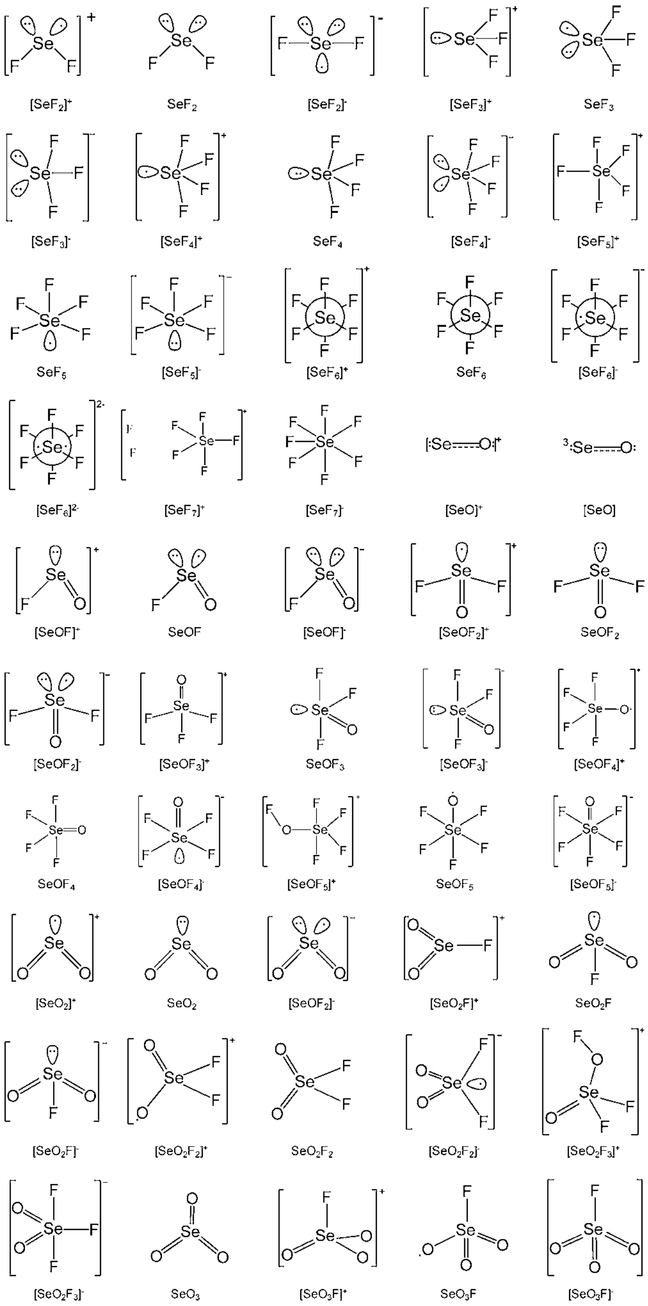

Figure 1. Lewis dot structures for the selenium fluorides, oxides, and oxofluorides of SeF_n (n = 2–6) $^{+,0,-}$, $SeOF_n$ (n = 0–4) $^{+,0,-}$, and SeO_2F_n (n = 0–2) $^{+,0,-}$ molecules.

from a structure with three F atoms and two O atoms bonded to the Se. On the basis of these results, we carefully investigated the structure of SeO_3F^+. Starting from the pseudotetrahedral structure did not change the basic framework. We moved the F to bind to an O leading to a planar structure with C_s symmetry. The C_s structure is 17.0 kcal/mol higher in energy than the pseudotetrahedral structure with the 3 O and 1 F atoms bonded to the Se.

Vibrational Frequencies. Table 2 shows the comparison between theory and experiment for SeF_2, SeF_2^+, SeF_6, and SeO_2^-. For SeF_2, the calculated symmetric and antisymmetric Se–F stretching modes at the CCSD(T)/aVTZ level are within 10 cm^{-1} of experiment,[67] which is excellent agreement considering that our calculated values do not include anharmonic corrections. For SeF_2^+, the symmetric Se–F stretching mode at the CCSD(T)/aVTZ level is within 50 cm^{-1} of experiment.[68] For SeF_6 our CCSD(T)/aVDZ stretching modes are too small, for the a_g mode by ~30 cm^{-1} and for the e_g and t_{1u} modes by ~10 cm^{-1}. This is consistent with the fact that, at this level, the bond distance is 0.045 Å too long as compared to experiment. The t_{2g} bending mode is almost the same as experiment, but the other two bending modes are smaller than experiment with the largest difference found for the t_{1u} mode. The lower values of the calculated bending frequencies are also consistent with the longer predicted bond distance as the repulsion between fluorine ligands decreases with increasing bond length. For SeO_2^-, the symmetric Se–O stretching mode at the CCSD(T)/aVTZ level is within 10 cm^{-1} of the value of 810 ± 80 cm^{-1} derived from a photoelectron spectroscopy experiment.[69]

Table 2. Calculated CCSD(T)/aug-cc-pVDZ (-PP on Se) Vibrational Frequencies, for SeF_2, SeF_2^+, SeF_6, and SeO_2^-

molecule	CCSD(T)	experiment
SeO	869.5(σ)	914.7(σ)^h
SeO^-	683.2(σ)	730 ± 25^g
SeF_2	689.9 (a_1)	699 (a_1)^a
	245.8 (a_1)	
	669.3 (b_2)	672 (b_2)^a
SeF_2^+	811.1 (a_1)	780 ± 50 (a_1)^b
	297.1 (a_1)	
	803.5 (b_2)	
SeF_6	676.5 (a_g)	707 (a_g)^{c,d}
	648.9 (e_g)	659 (e_g)^c
	410.7 (t_{2g})	405 (t_{2g})^e
	769.8 (t_{1u})	780 (t_{1u})^e
	372.6 (t_{1u})	437 (t_{1u})^e
	247.7 (t_{2u})	264 (t_{2u})^f
SeO_2^-	836.2 (b_2)	
	820.8 (a_1)	810 ± 80 (a_1)^g
	326.2 (a_1)	

[a] Ref 67. [b] Ref 68. [c] 1–3 cm^{-1} uncertainty, [d] Ref 27. [e] 3–6 cm^{-1} uncertainty. [f] 15–30 cm^{-1} uncertainty. [g] Ref 69. [h] Ref 27b.

Table 3 shows the vibrational stretching frequencies calculated at the CCSD(T)/aVDZ level for SeF_n (n = 1,3,4,5), SeF_n^- (n = 1–4, 7), SeF_3^+, $SeOF_n$ (n = 0, 1–5), $SeOF_n^-$ (n = 1,2,3,5), SeO_2F_n (n = 1,2), $SeO_2F_n^-$ (n = 1–3), and SeO_3. These calculated values can be used to interpret new experimental results when they become available. Calculated frequencies for other molecules can be found in our previous report.[2]

NMR Chemical Shifts. The chemical shifts are given in Table 4 with different exchange-correlation functionals and basis sets: B3LYP/AhlrichsVTZP, BLYP/TZ2P, and at the ZORA-BLYP/TZ2P level. Our predicted ^{77}Se chemical shift for SeF_2, using the B3LYP/AhlrichsVTZP method, differs by 45 ppm from Poleschner and Seppelt's[70] value of 3723.5 ppm, calculated at the MP2/6-311+G(d,p)//MP2/6-311+G(d,p) level. Their calculated ^{19}F chemical shift (−208.9 ppm) differs from our value by approximately 9 ppm. They also used B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) to predict a ^{77}Se chemical shift of 4368.0 ppm which differs significantly from our value by approximately 600 ppm because of their apparent neglect of relativistic effects. Their DFT value of −204.2 for the ^{19}F chemical shift differs from our value by only 1.2 ppm. For SeF_6, we predict ^{77}Se chemical shift values of 555

Table 3. Calculated CCSD(T)/aug-cc-pVDZ-PP Se−F and Se−O Vibrational Stretching Frequencies[a]

molecule	symmetric and antisymmetric stretches, cm^{-1}			
SeF^+	808.1(σ)			
SeF	670.2(σ)			
SeF^-	534.9(σ)			
SeF_2^+	811.12(a$_1$)	803.5(b$_2$)		
SeF_2^-	443.9(a$_1$)	405.0(b$_2$)		
SeF_3^+	785.6(a′)	782.5(a″)	782.5(a′)	
SeF_3	709.4(a$_1$)	611.4(b$_2$)	569.7(a$_1$)	
SeF_3^-	619.5(a$_1$)	455.0(a$_1$)	440.8(b$_2$)	
SeF_4^+	883.8(b$_2$)	865.4(a$_1$)	657.74(b$_1$)	651.2(a$_1$)
SeF_4	710.8(a$_1$)	705.8(b$_2$)	615.5(b$_1$)	572.6(a$_1$)
SeF_4^-	580.0(a$_1$)	504.0(b$_2$)	477.0(a$_1$)	
SeF_5^+	909.8(b$_2$)	909.8(a$_1$)	898.7(b$_1$)	787.5(a$_1$)
	765.0(a$_1$)			
SeF_5	739.7(a$_1$)	639.3(b$_2$)	639.3(b$_1$)	592.2(a$_1$)
	585.4(a$_1$)			
SeF_5^-	673.8(a$_1$)	526.8(a$_1$)	525.8(e)	474.8(b$_1$)
SeF_6^+	870.6(a$_1$)	847.2(b$_2$)	846.1(b$_1$)	754.5(a$_1$)
	718.0(a$_1$)			
SeF_6^-	585.2(a$_g$)	538.7(b$_u$)	538.7(b$_u$)	538.6(a$_u$)
	502.5(a$_u$)	502.0(a$_g$)		
SeF_6^{2-}	514.2 (a$_{1g}$)	424.3(t$_{1u}$)	424.3(t$_{1u}$)	380.9(e$_g$)
SeF_7^-	725.5(a$_2$″)	615.2(a$_1$′)	575.9(e$_1$′)	563.1(a$_1$′)
	401.3(e′)			
SeO^+	948.2(σ)			
$SeOF^+$	1051.8(a′) (Se−O)	771.7(a′) (Se−F)		
SeOF	985.3(a′) (Se−O)	745.0(a′) (Se−F)		
$SeOF^-$	780.4(a′) (Se−O)	467.7(a′) (Se−F)		
$SeOF_2^+$	841.6(a″) (Se−F)	841.5(a′) (Se−F)	740.4(a′) (Se−O)	
$SeOF_2$	1000.4(a′) (Se−O)	652.3(a′) (Se−F)	625.3(a″) (Se−F)	
$SeOF_2^-$	886.1(a$_1$) (Se−O)	427.5(a$_1$) (Se−F)	409.1(b$_2$) (Se−F)	
$SeOF_2^{2-}$	775.6(a$_1$) (Se−O)	250.4(b$_2$) (Se−F)	235.9(a$_1$) (Se−F)	
$SeOF_3^+$	1098.1(a$_1$) (Se−O)	833.0(e) (Se−F)	775.9(a$_1$) (Se−F)	
$SeOF_3$	711.9(a′) (Se−O)	698.3(a′) (Se−F)	617.2(a″) (Se−F)	561.2(a′) (Se−F)
$SeOF_3^-$	933.5(a′) (Se−O)	580.9(a′) (Se−F)	455.3(a″) (Se−F)	439.9(a′) (Se−F)
$SeOF_4^+$	869.0(a$_1$) (Se−O)	865.4(b$_1$) (Se−F)	832.1(b$_2$) (Se−F)	761.8(a$_1$) (Se−F)
	717.6(a$_1$) (Se−F)			
$SeOF_4$	974.2(a$_1$) (Se−O)	728.5(b$_1$) (Se−F)	703.5(b$_2$) (Se−F)	677.2(a$_1$) (Se−F)
	603.2(a$_1$) (Se−F)			
$SeOF_5^+$	984.2(a) (O−F)	856.6(a) (Se−F)	823.9(a) (Se−F)	816.1(a) (Se−F)
	718.1(a) (Se−F)	685.9(a) (Se−O)		
$SeOF_5$	784.8(a$_1$) (Se−O)	778.4(b$_2$) (Se−F)	769.9(b$_1$) (Se−F)	710.1(a$_1$) (Se−F)
	667.4(a$_1$) (Se−F)	653.3(a$_1$) (Se−F)		
$SeOF_5^-$	877.4(a$_1$) (Se−O)	637.9(b$_1$) (Se−F)	637.9(b$_2$) (Se−F)	620.3(a$_1$) (Se−F)
	539.8(a$_1$) (Se−F)	539.5(a$_1$) (Se−F)		
SeO_2^+	999.0(a′)	684.3(a′)		
SeO_2	922.1(b$_2$)	874.9(a$_1$)		
SeO_2^-	836.2(a$_1$)	820.8(a$_1$)		
SeO_2F^+	1080.0(b$_2$) (Se−O)	958.8(a$_1$) (Se−O)	760.5(a$_1$) (Se−F)	
SeO_2F	815.9(a′) (Se−O)	769.5(a″) (Se−O)	620.6(a′) (Se−F)	
SeO_2F^-	868.6(a″) (Se−O)	856.5(a′) (Se−O)	464.0(a′) (Se−F)	
$SeO_2F_2^+$	1190.2(a′) (Se−O)	821.6(a″) (Se−F)	816.4(a′) (Se−F)	756.7(a′) (Se−O)
SeO_2F_2	1011.7(b$_1$) (Se−O)	927.4(a$_1$) (Se−O)	684.6(b$_2$) (Se−F)	681.7(a$_1$) (Se−F)
$SeO_2F_2^-$	859.7(b$_2$) (Se−O)	838.7(a$_1$) (Se−O)	442.6(b$_1$) (Se−F)	438.5(a$_1$) (Se−F)
$SeO_2F_3^-$	932.8(b$_1$) (Se−O)	853.4(a$_1$) (Se−O)	618.6(a$_1$) (Se−F)	561.5(b$_1$) (Se−F)
	493.4(a$_1$) (Se−F)			
SeO_3	1017.5(e)	893.2(a$_1$′)		
SeO_3F^+ (C_s)	1074.6(a′) (Se−O)	957.7(a′) (O−F)	900.0(a″) (Se−O)	625.2(a′) (Se−F)
SeO_3F^+ (“T_d”)	1201.0(a′) (Se−O)	859.5(a′) (Se−O)	812.3(a″) (Se−O)	780.2(a′) (Se−F)
SeO_3F	1904.0(a″) (Se−O)	1127.1(a′) (Se−O)	982.7(a′) (Se−O)	706.1(a′) (Se−F)
SeO_3F^-	912.1(a′) (Se−O)	912.0(a″) (Se−O)	829.3(a′) (Se−O)	559.5(a′) (Se−F)

[a] Harmonic and anharmonic values at the CCSD(T)/aVQZ level from a 5-point Dunham fit for the diatomics $SeO^{+/0/-}$ and $SeF^{+/0/-}$ given in the Supporting Information.

and 534 ppm at the BLYP/TZ2P and ZORA-BLYP/TZ2P levels, respectively. These values differ from the two reported experimental values of 600 and 610 ppm by 45 and 75 ppm. Our ^{19}F chemical shift values calculated at the same levels differ from the experimental value of 49.6[70] by 61 and 98 ppm, respectively.

Calculated Heats of Formation. Table 5 lists the calculated contributions to the total atomization energy (TAE). The core valence corrections have a range of 7.7 kcal/mol with SeF_7^- having the largest correction of −7.41 kcal/mol and SeO having the smallest correction of 0.11 kcal/mol. The scalar relativistic corrections are significantly smaller than both the core valence corrections with a range 1.8 kcal/mol.

The heats of formation at 0 and 298 K (Table 6) were calculated from the total atomization energies. Our predicted heat of formation for SeF_6 (O_h) of −267.7 kcal/mol is in excellent agreement with experiment when using Wang's recommended value of 57.9 kcal/mol for the heat of formation of the Se atom. Use of the Wagman et al. value[36] for ΔH_f(Se) at 0 K leads to an error of almost 4 kcal/mol. The experimental heat of formation of SeF_6 was obtained from the reaction of solid Se with F_2 so it does not involve the heat of formation of the gaseous Se atom. Compared to the best experimental value for ΔH_f(SeF_6) of −267.18 kcal/mol at 298 K,[71] our calculated value of −267.7 kcal/mol is in excellent agreement. Using our calculated TAE, we predict a value of 58.43 kcal/mol for ΔH_f(Se) at 0 K. To obtain another estimate of ΔH_f(Se) at 0 K, we calculated the TAE of SeF_6 at the CCSD(T)/aug-cc-pVQZ-PP and CCSD(T)/aug-cc-pV5Z-PP levels and extrapolated these values to the complete basis set limit using the following

Table 4. Calculated $\delta(^{19}F)$/ppm[a] and $\delta(^{77}Se)$/ppm[b] NMR Chemical Shifts

		chem shift		
molecule	atom	B3LYP/ TZVP	BLYP/ TZ2P	ZORA-BLYP/ TZVP
SeF^-	Se	3751.7	3760.3	3605.8
	F	−841.6	−832.4	−839.5
SeF_2	Se	3768.5	3844.3	3667.0
	F (2)	−217.5	−203.0	−197.9
SeF_3^+	Se	1295.4	1277.8	1203.0
	F (3)	79.7	60.2	69.5
SeF_3^-	Se	2957.4	3219.2	3098.3
	F (2) ax	−74.3	−38.5	−36.7
	F eq	−303.9	−280.2	−279.4
SeF_5^+	Se	898.5	734.9	696.4
	F eq	166.2	140.5	175.7
	F (2) eq	167.3	141.5	167.8
	F (2) ax	195.8	200.0	245.9
SeF_6	Se	694.0	554.9	534.4
	F	104.6	110.4	147.8
SeF_7^-	Se	675.4	582.2	559.8
	F (5) eq	431.1	531.2	667.3
	F (2) ax	155.6	177.9	225.6
$SeOF^-$	Se	3940.7	4024.6	3862.9
	F	−403.2	−373.1	−378.6
$SeOF_2^{2-}$	Se	3629.4	3826.1	3642.2
	F	−264.8	−233.6	−240.0
SeO_2F_2	Se	943.7	784.7	739.3
	F	93.6	68.8	87.6
$SeOF_3^+$	Se	872.6	703.4	654.3
	F	144.1	110.1	138.1
$SeOF_4$	Se	793.3	633.7	593.1
	F (2) ax	154.3	157.1	191.2
	F (2) eq	133.6	121.9	152.4
$SeOF_5^-$	Se	662.6	504.9	471.7
	F (4) eq	116.5	123.1	154.2
	F ax	173.0	203.9	248.7
SeO_2F^+	Se	1119.1	943.2	886.9
	F	325.6	285.1	314.1
$SeO_2F_3^-$	Se	862.1	718.2	680.9
	F (2) ax	98.2	98.3	118.6
	F eq	94.3	89.3	111.3
SeO_3F^-	Se	1060.2	892.6	846.9
	F	51.7	44.9	57.8

[a] ^{19}F chemical shifts relative to $CFCl_3$. Absolute ^{19}F chemical shift = 156.1 ppm at the GIAO B3LYP/AhlrichsVTZP level. Absolute ^{19}F chemical shift = 135.3 ppm at the GIAO BLYP/TZ2P level. Absolute ^{19}F chemical shift = 134.5 ppm at the GIAO BLYP-ZORA/TZ2P level. [b] ^{77}Se chemical shifts relative to $Se(CH_3)_2$. Absolute ^{77}Se chemical shift = 1698.8 ppm at the GIAO B3LYP/AhlrichsVTZP level. Absolute ^{77}Se chemical shift = 1616.2 ppm at the GIAO BLYP/TZ2P level. Absolute ^{77}Se chemical shift = 1747.9 ppm at the GIAO BLYP-ZORA/TZ2P level.

expression.[72,73]

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

This gives a TAE of 432.80 kcal/mol at 0 K, resulting in a value of 57.54 kcal/mol for $\Delta H_f(Se)$. We can average our two calculated values for $\Delta H_f(Se)$ to give 58.0 ± 0.5 kcal/mol for $\Delta H_f(Se)$ at 0 K, which is in excellent agreement with Wang's value[33] of 57.9 kcal/mol, derived from experiment. As a consequence, we used Wang's value[33] of 57.9 kcal/mol for all of the heats of formation predictions.

We can compare our calculated value for ΔH_f (SeF_4) at 298 K with that obtained from the experimental heat of formation of liquid SeF_4 at 298 K of −203 ± 6 kcal/mol and its estimated heat of vaporization[74] of 11 kcal/mol giving an estimated $\Delta H_f^{298}(SeF_4)$ = −192 ± 6 kcal/mol. Our value of −185.9 kcal/mol is in good agreement with this estimated value.

Our calculated value for the ΔH_f's at 298 K of SeF_3^- and SeF_6^- are in excellent agreement with the respective experimentally derived values.[75,76] In contrast, our calculated value for $\Delta H_f(SeF_4^-)$ at 298 K is 23 kcal more negative than that derived from experiment.[75]

We can compare the predicted G3 values[34] for ΔH_f (SeF_n) for n = 1−6 with our higher level values which do not incorporate empirical corrections to the electronic energy (Table 6). The G3 value for $\Delta H_f(SeF)$ is within 0.2 kcal/mol of our value. The G3 value for ΔH_f (SeF_2) differs from our value by 2.1 kcal/mol, the G3 value for $\Delta H_f(SeF_3)$ differs from our value by 4.7 kcal/mol, and the G3 value for ΔH_f (SeF_5) differs from ours by 4.7 kcal/mol. The G3 value for $\Delta H_f(SeF_4)$ differs from our value by 6.5 kcal/mol and is far outside the error bars of the estimated experimental value. Considering these differences, it is surprising that the G3 value for $\Delta H_f(SeF_6)$ differs from our value by only 0.3 kcal/mol.

Bond Dissociation Energies. There is little experimental information available for the BDEs for the range of selenium fluorides, selenium oxofluorides, and oxides, except for SeF_6, SeF_5, SeF, and SeO.[77] Table 7 shows the various Se−F and Se−O BDEs calculated from the heats of formation as well as those for the comparable sulfur compounds. We can define two types of BDEs:[78,79] (a) adiabatic, dissociating to the ground states of the separated species and (b) diabatic, dissociating to electronic configurations appropriate for forming the bonds in the parent molecule. The adiabatic and diabatic BDEs can differ by varying amounts depending on the nature of the electronic states of the products. The diabatic BDE is always equal to or larger than the adiabatic BDE, and the difference between the adiabatic and diabatic BDEs corresponds to any reorganization energy of the product(s) and can be substantial. Considering these very large possible differences, it is important to use the appropriate values in thermodynamic calculations. For thermochemical calculations, such as Born−Haber cycles, the adiabatic values must be used, whereas for simple kinetic models, the diabatic values can be more appropriate. The inappropriate use of adiabatic and diabatic bond dissociation energies can lead to large errors and the wrong conclusions. In order to estimate the diabatic values, we calculated the singlet−triplet splittings of the appropriate products at the CCSD(T)/aVDZ level.

Our calculated SeF_6 adiabatic Se−F BDE is larger by 17.8 kcal/mol than the reported experimental value.[77,76] Our calculated SeF_5 adiabatic Se−F BDE is smaller than the experimental value[76,77] by 37.6 kcal/mol. This suggests that the experimental estimate for $\Delta H_f(SeF_5)$ used in the BDE calculations is far too negative. Our SeF adiabatic BDE is consistent with the experimental value.[77,80]

The adiabatic and diabatic Se−F BDEs of SeF_6, SeF_4, SeF_2, and SeF are the same (see Table 7) and involve no reorganization energies. All of the values are substantial and range from 93.0 kcal/mol in SeF_4 to 76.1 kcal/mol in SeF. As noted above, the adiabatic BDEs can include possible reorganization energies and, therefore, are not always a measure of the bond strengths. For the evaluation of bond strengths

Table 5. Components for Calculating the Atomization Energies in kcal/mol[a]

molecule	(CBS)[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	$\sum D_0$ (0 K)[g]
SeF^+	−143.53	1.18	−1.10	0.10	−3.09	−148.81
SeF	80.49	0.96	−0.26	−0.08	−3.09	76.10
SeF^-	135.95	0.76	−0.01	−0.19	−3.09	131.89
SeF_2^+	−59.01	2.73	−1.67	0.12	−3.48	−66.78
SeF_2	169.03	2.29	−0.71	−0.08	−3.48	162.47
SeF_2^-	212.70	1.33	−0.15	−0.35	−3.48	207.40
SeF_3^+	33.78	4.60	−2.72	0.16	−3.87	22.74
SeF_3	232.28	3.53	−1.48	−0.12	−3.87	223.29
SeF_3^-	306.41	3.12	−0.76	−0.46	−3.87	298.20
SeF_4^+	40.55	6.07	−4.10	0.28	−4.26	26.40
SeF_4	328.77	5.38	−2.73	−0.14	−4.26	316.26
SeF_4^-	364.79	4.30	−1.89	−0.42	−4.26	353.93
SeF_5^+	110.62	9.08	−7.00	0.46	−4.65	90.36
SeF_5	359.89	7.38	−4.51	−0.02	−4.65	343.32
SeF_5^-	478.85	6.56	−2.37	−0.55	−4.65	464.76
SeF_6^+	115.29	9.72	−7.15	0.23	−5.04	93.62
SeF_6	456.41	10.54	−7.22	0.08	−5.04	433.70
SeF_6^-	517.54	7.40	−2.22	−0.60	−5.04	502.28
SeF_6^{2-}	492.40	5.45	0.33	−1.10	−5.04	481.15
SeF_7^+	156.45	11.08	−7.15	0.01	−5.43	132.81
SeF_7^-	551.17	11.00	−7.41	−0.40	−5.43	526.92
SeO^+	−125.10	1.46	−0.56	0.21	−2.92	−129.84
SeO	105.29	1.24	0.11	0.03	−2.92	101.27
SeO^-	136.85	0.75	0.30	−0.12	−2.92	133.36
$SeOF^+$	−37.55	3.07	−1.46	0.29	−3.31	−45.10
SeOF	187.54	2.90	−0.38	0.00	−3.31	180.95
$SeOF^-$	222.77	2.10	−0.38	−0.19	−3.31	216.79
$SeOF_2^+$	1.19	4.49	−2.36	0.18	−3.70	−9.18
$SeOF_2$	278.86	4.48	−1.72	0.06	−3.70	269.02
$SeOF_2^-$	318.58	3.34	−0.50	−0.30	−3.70	310.74
$SeOF_2^{2-}$	240.22	2.35	−0.26	−0.54	−3.70	233.37
$SeOF_3^+$	69.04	7.19	−5.31	0.58	−4.09	53.03
$SeOF_3$	301.04	5.58	−2.33	−0.09	−4.09	288.95
$SeOF_3^-$	418.35	5.30	−1.72	−0.31	−4.09	406.93
$SeOF_4^+$	94.96	8.95	−6.42	0.50	−4.48	75.61
$SeOF_4$	380.11	8.45	−5.60	0.22	−4.48	361.80
$SeOF_4^-$	457.81	6.47	−2.93	−0.30	−4.48	443.62
$SeOF_5^+$	135.87	10.86	−6.20	0.20	−4.87	114.15
$SeOF_5$	420.37	10.78	−6.72	0.14	−4.87	398.13
$SeOF_5^-$	545.95	9.88	−6.01	−0.18	−4.87	525.00
SeO_2^+	−65.37	2.72	−1.06	0.31	−3.14	−71.98
SeO_2	207.33	3.05	−0.86	0.28	−3.14	200.56
SeO_2^-	249.04	2.84	−0.60	0.02	−3.14	242.49
SeO_2F^+	−8.24	5.14	−3.30	0.61	−3.53	−19.60
SeO_2F	249.81	4.34	−1.98	0.25	−3.53	240.21
SeO_2F^-	352.29	4.38	−1.51	0.00	−3.53	342.88
$SeO_2F_2^+$	39.58	7.08	−4.77	0.59	−3.92	24.40
SeO_2F_2	335.60	6.88	−4.20	0.40	−3.92	321.01
$SeO_2F_2^-$	395.31	5.37	−2.26	−0.05	−3.92	383.71
$SeO_2F_3^+$	83.49	8.88	−4.54	0.34	−4.31	66.10
$SeO_2F_3^-$	485.44	8.23	−4.66	0.00	−4.31	468.24
SeO_3	259.57	5.55	−2.59	0.53	−3.36	248.59
SeO_3F^+ (C_s)	11.96	6.72	−2.71	0.38	−3.75	−0.85
SeO_3F^+("T_d")	28.04	7.55	−4.04	0.65	−3.75	13.35
SeO_3F	302.97	9.14	−3.80	0.50	−3.75	286.78
SeO_3F^-	435.76	6.90	−3.70	0.26	−3.75	421.67

[a] $\sum D_0 = \Delta E_{elec}(CBS) - \Delta E_{ZPE} + \Delta E_{CV} + \Delta E_{SR} + \Delta E_{SO}$. [b] Valence electron dissociation energy extrapolated to the CBS limit by using eq 1 with n = D, T, Q. [c] ΔE_{ZPE} calculated at the CCSD(T)/aug-cc-pVDZ-PP level. [d] Core/valence corrections were obtained with the cc-pwCVTZ basis sets at the optimized geometries. [e] The scalar relativistic correction is based on a CISD(FC)/cc-pVTZ MVD calculation. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on Moore's tables.[47] [g] The theoretical value of the dissociation energy to atoms $\sum D_0$(0 K).

near the minimum, the diabatic values should be used as they describe the bonding when only small displacements of the atoms from their equilibrium positions are made. The adiabatic Se−F BDE of SeF_6 is 2.6 kcal/mol less than that in SeF_4 consistent with the lower steric interactions in the latter. The adiabatic Se−F BDE in SeF_2 is ∼4 kcal/mol lower than that in SeF_6. The Se−F BDE in diatomic SeF is about 10 kcal/mol less than that in SeF_2. It is more appropriate to compare the diabatic Se−F BDEs in SeF_5, and SeF_3 with the above adiabatic values. The diabatic Se−F BDE in SeF_5 is between those of SeF_4 and SeF_2 and that for SeF_3 is ∼2 kcal/mol less than that of SeF. The adiabatic Se−F BDE in SeF_5 is very low because of the stability of SeF_4. The adiabatic Se−F BDE in SeF_3 is surprisingly high suggesting that the SeF_3 radical is quite stable thermodynamically.

The SeF_n BDEs follow the same patterns previously found for the SF_n BDEs.[1] As would be expected from periodic trends, the Se−F adiabatic BDE in SeF_6 is 14.4 kcal/mol smaller than that of SF_6. We note that the calculated adiabatic S−F BDE in SF_6 is 12.6 kcal/mol larger than the experimental value[49] of 92.2 ± 3.8 kcal/mol, similar to what is found for SeF_6. The adiabatic Se−F BDE in SeF_5 is 10.7 kcal/mol smaller than that in SF_5. The Se−F BDEs of SeF_4 and SeF_2 are only 2.5 to 3 kcal/mol smaller than the corresponding S−F BDEs in SF_4 and SF_2. The adiabatic Se−F BDEs in SeF_3 and Se−F are 6 to 7 kcal/mol smaller than the S−F BDEs in SF_3 and SF.

We can compare the predicted G3 BDEs in SeF_n for n = 1−6 with our CCSD(T)/CBS adiabatic BDEs in kcal/mol at 298 K. The G3 value for SeF_6 (94.8 kcal/mol)[33] is 4.4 kcal/mol larger than our value. The G3 value for SeF_5 (28.8 kcal/mol)[33] differs by 1.8 kcal/mol. The G3 value for SeF_4 (91.2 kcal/mol)[33] is smaller than our value by 1.8 kcal/mol. The G3 value for SeF_3 (58.1 kcal/mol)[33] is smaller than ours by 2.7 kcal/mol. The G3 value for SeF_2 (83.7 kcal/mol)[33] is smaller than our value by 2.7 kcal/mol. The G3 value for SeF (76.7 kcal/mol)[33] is in excellent agreement with our value within 1.0 kcal/mol.

The adiabatic and diabatic Se−F BDEs in $SeOF_4$ and $SeOF_2$ SeOF, and SeO_2F_2 are the same. The Se−F BDE in SeF_4O is lower than that in Se−F, but the Se−F BDE in SeF_2O is comparable to that of SeF_6. The Se−F BDEs in SeOF and SeO_2F_2 are near 80 kcal/mol. The diabatic Se−F BDE in SeO_2F is similar to that in SeF_6. The highest diabatic Se−F BDE is found for $SeOF_3$ at 112 kcal/mol, although the adiabatic BDE is very low at 20 kcal/mol. The Mulliken atomic spin densities for the triplet state of $SeOF_2$ are mainly localized on the O (1.01e) and the Se atom (0.78e), with spin densities of only 0.11e on the two F atoms. In the doublet state of $SeOF_3$ the Mulliken atomic spin density is essentially localized on the O atom (0.95e).

The Se−O BDE in $SeOF_2$ (106.5 kcal/mol) is the largest adiabatic BDE of the SeO_xF_x and SeF_x compounds, and the Se−F BDE in $SeOF_3$ is the smallest at 19.9 kcal/mol.

Table 6. Calculated CCSD(T)/CBS Heats of Formation (kcal/mol) at 0 and 298 K

molecule	ΔH_f(0 K) CCSD(T)/CBS	ΔH_f(298 K) CCSD(T)/CBS	ΔH_f(298 K) Expt	ΔH_f(0 K) G3[f]	ΔH_f(298 K) G3[f]
Se^+	281.1	281.2			
Se			58.1 (57.9@0K)		
Se^-	13.1	13.3			
SeF^+	225.2	225.0			
SeF	−0.5	−0.8		−0.4	−0.6
SeF^-	−55.5	−55.7			
SeF_2^+	161.6	161.0			
SeF_2	−67.6	−68.2		−65.6	−66.1
SeF_2^-	−112.6	−112.7			
SeF_3^+	90.6	89.4			
SeF_3	−110.0	−110.7			
SeF_3^-	−184.9	−185.5	−185.0[a,g]		
SeF_4^+	105.4	104.0			
SeF_4	−184.5[b]	−185.9[b]	−203 ± 6[d]	−178.0	−179.4
SeF_4^-	−222.1	−223.5	−190 ± 10[a]		
SeF_5^+	59.9	58.2			
SeF_5	−193.1	−194.8		−188.3	−190.1
SeF_5^-	−314.5[b]	−315.9[b]	−331.1 ± 9.6[c]		
SeF_6^+	75.1	72.4			
SeF_6	−265.0	−267.7	−267.18 ± 0.12[e]	−264.6	−267.4
SeF_6^-	−333.6	−334.9	−333.9 ± 6.8[c]		
SeF_6^{2-}	−312.4[b]	−313.8[b]			
SeF_7^+	54.4	51.9			
SeF_7^-	−339.7	−342.3			
SeO^+	246.7	246.5			
SeO	15.6	15.4	15.4 ± 1.6 0K[h]		
SeO^-	−16.5	−16.7			
$SeOF^+$	180.5	179.8			
SeOF	−45.6	−46.2			
$SeOF^-$	−81.4	−81.9			
$SeOF_2^+$	163.0	161.9			
$SeOF_2$	−115.2[b]	−116.3[b]			
$SeOF_2^-$	−156.9	−157.5			
$SeOF_2^{2-}$	−79.5	−79.8			
$SeOF_3^+$	119.3	118.0			
$SeOF_3$	−116.6	−117.9			
$SeOF_3^-$	−234.6	−235.7			
$SeOF_4$	−171.0	−173.1			
$SeOF_4^-$	−252.9	−254.9			
$SeOF_5^+$	95.1	92.6			
$SeOF_5$	−188.9	−191.4			
$SeOF_5^-$	−315.8	−318.3			
SeO_2^+	247.9	247.1			
SeO_2	−24.7[b]	−25.4[b]			
SeO_2^-	−66.6	−67.4			
SeO_2F^+	214.0	212.9			
SeO_2F	−45.9	−46.9			
SeO_2F^-	−148.5[b]	−149.6[b]			
$SeO_2F_2^+$	188.4	186.8			
SeO_2F_2	−108.2	−109.2			
$SeO_2F_2^-$	−170.9	−171.9			
$SeO_2F_3^+$	165.2	163.2			
$SeO_2F_3^-$	−236.9	−239.6			
SeO_3	−13.7	−15.0			
$SeO_3F^+(T_d)$	240.0	238.3			
SeO_3F	−33.4	−35.1			
SeO_3F^-	−168.3	−170.0			

[a] Ref 75. [b] Revised values from the original ones in ref 2. [c] Ref 76. [d] Ref 74. [e] Ref 71. [f] Ref 33. [g] Ref 49. [h] Ref 69 b,c.

Table 7. Calculated CCSD(T)/CBS Adiabatic and Diabatic BDEs in kcal/mol

reactions	adiabat Se 0 K	diabat Se 0 K	adiabat S 0 K[a]
$^1SeF_6 \rightarrow {}^2SeF_5 + {}^2F$	90.4	90.4	104.8
$^2SeF_5 \rightarrow {}^1SeF_4 + {}^2F$	27.0	88.1 ($^3SeF_4$)	37.7
$^1SeF_4 \rightarrow {}^2SeF_3 + {}^2F$	93.0	93.0	95.5
$^2SeF_3 \rightarrow {}^1SeF_2 + {}^2F$	60.8	74.4 ($^3SeF_2$)	54.8
$^1SeF_2 \rightarrow {}^2SeF + {}^2F$	86.4	86.4	89.1
$^2SeF \rightarrow {}^3Se + {}^2F$	76.1	76.1	83.2
$^1SeOF_4 \rightarrow {}^2SeOF_3 + {}^2F$	72.9	72.9	89.7
$^1SeOF_4 \rightarrow {}^1SeF_4 + {}^3O$	45.5	96.3 ($^3SeF_4$)	88.2
$^2SeOF_3 \rightarrow {}^1SeOF_2 + {}^2F$	19.9	112.2 ($^3SeOF_2$)	20.0
$^2SeOF_3 \rightarrow {}^2SeF_3 + {}^3O$	65.7	111.0 (^1O)	94.0
$^1SeOF_2 \rightarrow {}^2SeOF + {}^2F$	88.1	88.1	93.6
$^1SeOF_2 \rightarrow {}^1SeF_2 + {}^3O$	106.5	125.9 ($^3SeF_2$)	128.8
$^2SeOF \rightarrow {}^3SeO + {}^2F$	79.7	79.7	85.4
$^2SeOF \rightarrow {}^2SeF + {}^3O$	104.0	138.4 (^4SeF)	124.3
$^3SeO \rightarrow {}^3Se + {}^3O$	101.3	101.3	123.1
$^1SeO_2F_2 \rightarrow {}^1SeOF_2 + {}^3O$	52.0	129.7 ($^3SeOF_2$)	98.7
$^1SeO_2F_2 \rightarrow {}^2SeO_2F + {}^2F$	80.8	80.8	106.9
$^2SeO_2F \rightarrow {}^2SeOF + {}^3O$	59.3	154.4 (^4SeOF)	85.4
$^2SeO_2F \rightarrow {}^1SeO_2 + {}^2F$	39.7	88.9 ($^3SeO_2$)	40.4
$^1SeO_3 \rightarrow {}^1SeO_2 + {}^3O$	48.0	97.2 ($^3SeO_2$)	
$^2SeO_3F \rightarrow {}^1SeO_3 + {}^2F$	38.2		
$^1SeO_2 \rightarrow {}^3SeO + {}^3O$	99.3		131.1

[a] Ref 1.

The adiabatic Se−F BDE in SeF_5 is small as expected because of the instability of SeF_5 and the stability of SeF_4. The Se−O BDE in SeO_2F has the largest diabatic BDE of the SeO_xF_x and SeF_x compounds.

The Se−F adiabatic BDE in $SeOF_4$ is 16.8 kcal/mol smaller than the S−F BDE in SF_4O. The Se−O BDE in $SeOF_4$ is 42.7 kcal/mol smaller than the S−F BDE in SF_4O. The Se−F adiabatic BDE in $SeOF_3$ is only 0.1 kcal/mol smaller than the S−F BDE in SF_3O, and the Se−O BDE in $SeOF_3$ is 28.3 kcal/mol smaller than the S−O BDE of SF_3O. The Se−F BDE in $SeOF_2$ is 5.5 kcal/mol smaller than the S−F BDE in SF_2O, whereas the Se−O BDE in $SeOF_2$ is 22.3 kcal/mol smaller than the S−O BDE in SF_2O. In SeOF, the same trend continues with the Se−F adiabatic BDE 5.7 kcal/mol which is smaller than the S−F BDE in SFO and the Se−O BDE of SeOF is 20.3 kcal/mol smaller than the S−O BDE in SFO. The adiabatic Se−O BDE of SeO is 21.8 kcal/mol smaller than that of SO. In SeO_2F_2 the Se−F adiabatic BDE is 26.1 kcal/mol smaller than the S−F BDE in SF_2O_2 and the Se−O BDE is 46.7 kcal/mol smaller than the S−O BDE in SF_2O_2. The Se−F BDE in SeO_2F is only 0.7 kcal/mol smaller than the S−F BDE in SO_2F. The Se−O BDE in SeO_2F is 26.1 kcal/mol smaller that the S−O BDE in SO_2F. Overall, there is a much larger difference in the Se−O/S-O BDEs than in the Se−F/S-F BDEs.

The Se−O BDEs show the need to consider the diabatic values. As expected from comparing the bond lengths and vibrational frequencies, the diabatic Se−O BDE in $SeOF_4$ is greater than the Se−F BDE. The adiabatic Se−O BDE is quite low because of the stability of SeF_4. The diabatic Se−F BDE in $SeOF_3$ is essentially the same as the diabatic Se−O BDE. The diabatic Se−O BDEs increase from 96 kcal/mol in $SeOF_4$ to 111 kcal/mol in $SeOF_3$ to 126 kcal/mol in $SeOF_2$ to 138 kcal/mol in SeOF. The Se−O BDE for diatomic SeO is at the low end. In contrast, the diabatic Se−O BDE in SeO_2F_2 is in the upper range of Se−O BDEs, and that for SeO_2F is even higher. The diabatic Se−F BDE in SeO_2F is surprisingly low at 89 kcal/mol, about 10 kcal/mol lower than the diabatic value for SeO_3. The diabatic Se−O BDE for SeO_3 is comparable to the adiabatic (and diabatic) BDEs for SeO_2 and SeO. The adiabatic Se−O BDEs are comparable, 45 to 52 kcal/mol, and low in $SeOF_4$, SeO_2F_2, and SeO_3.

Table 8. CCSD(T)/CBS Fluoride Affinities in kcal/mol at 298 K

reactions	CCSD(T)[a]
$Se + F^- \rightarrow SeF^-$	56.9
$SeF + F^- \rightarrow SeF_2^-$	52.5
$SeF_2 + F^- \rightarrow SeF_3^-$	57.8 (47.2)
$SeF_3 + F^- \rightarrow SeF_4^-$	53.3
$SeF_4 + F^- \rightarrow SeF_5^-$	70.5
$SeF_5 + F^- \rightarrow SeF_6^-$	80.7
$SeF_6 + F^- \rightarrow SeF_7^-$	15.0
$SeO + F^- \rightarrow SeOF^-$	37.8
$SeOF + F^- \rightarrow SeOF_2^-$	51.8
$SeOF_2 + F^- \rightarrow SeOF_3^-$	60.0 (43.5)
$SeOF_3 + F^- \rightarrow SeOF_4^-$	77.5
$SeOF_4 + F^- \rightarrow SeOF_5^-$	85.7 (62.3)
$SeO_2 + F^- \rightarrow SeO_2F^-$	64.6
$SeO_2F + F^- \rightarrow SeO_2F_2^-$	65.5
$SeO_2F_2 + F^- \rightarrow SeO_2F_3^-$	69.6 (39.8)
$SeO_3 + F^- \rightarrow SeO_3F^-$	95.5

[a] Fluoride affinities for corresponding sulfur compound in parentheses.

Fluoride Affinities. Table 8 gives the fluoride affinities predicted at the coupled cluster CCSD(T) theory level extrapolated to the complete basis set limit of selenium compared to those of the same reaction with sulfur when possible. An experimental value of $\Delta H_f^{298}(F^-) = -59.50$ kcal/mol was used.[49] The fluoride affinities for the SeF_x compounds span a range of 66 kcal/mol, with SeF_5 having the highest fluoride affinity of 80.7 kcal/mol and SeF_6 having the lowest one of 15.0 kcal/mol. The fluoride affinities for the SeO_x and SeO_xF_x compounds cover a range of 83 kcal/mol with SeO having the lowest fluoride affinity of 37.8 kcal/mol and SeO_3 having the highest one of 121.0 kcal/mol. A comparison of the fluoride affinities (FAs) of the Se and S compounds shows that the selenium compounds are stronger Lewis acids than the corresponding sulfur compounds, in accord with the general trends in the periodic table.

Fluorocation Affinities. Table 9 gives our CCSD(T)/CBS fluorocation affinities obtained using the experimental value $\Delta H_f^{298}(F^+) = 420.75$ kcal/mol.[49] The fluorocation affinities for the SeF_x compounds differ by up to 162 kcal/mol, with SeF_2 having the largest fluorocation affinity of 263.1 kcal/mol and SeF_6 having the smallest of 101.2 kcal/mol. The small value for SeF_6 is consistent with the substantial steric hindrance in this compound for adding an additional fluorine, as well as the fact that the Se is in the +6 oxidation state leading to the formation of an SeF_5^+ complex with F_2.

The fluorocation affinities for the SeO_x and SeO_xF_x compounds differ by up to 109 kcal/mol with SeO_2F_2 having the smallest fluorocation affinity of 147.7 kcal/mol and SeO having the largest of 256.3 kcal/mol. Again, the compound with the least steric hindrance and lowest formal positive charge on the Se has the highest fluorocation affinity. The two compounds with the lowest F^+ affinities are $SeOF_4$ and SeO_2F_2 which

Table 9. CCSD(T)/CBS Fluorocation Affinities (FCA) in kcal/mol at 298 K

reactions	FCA
$Se + F^+ \rightarrow SeF^+$	256.6
$SeF + F^+ \rightarrow SeF_2^+$	259.0
$SeF_2 + F^+ \rightarrow SeF_3^+$	263.1
$SeF_3 + F^+ \rightarrow SeF_4^+$	206.1
$SeF_4 + F^+ \rightarrow SeF_5^+$	176.7
$SeF_5 + F^+ \rightarrow SeF_6^+$	122.0
$SeF_6 + F^+ \rightarrow SeF_7^+$	101.2
$SeO + F^+ \rightarrow SeOF^+$	256.3
$SeOF + F^+ \rightarrow SeOF_2^+$	212.6
$SeOF_2 + F^+ \rightarrow SeOF_3^+$	186.5
$SeOF_3 + F^+ \rightarrow SeOF_4^+$	189.7
$SeOF_4 + F^+ \rightarrow SeOF_5^+$	155.1
$SeO_2 + F^+ \rightarrow SeO_2F^+$	182.4
$SeO_2F + F^+ \rightarrow SeO_2F_2^+$	187.0
$SeO_2F_2 + F^+ \rightarrow SeO_2F_3^+$	147.7
$SeO_3 + F^+ \rightarrow SeO_3F^+$	167.4

undergo a rearrangement so that the F is actually bonded to an O. The lowest F^+ affinity for the F bonded to Se is SeO_3 with the largest formal positive charge on the Se.

Electron Affinities and Ionization Potentials. The calculated electron affinities and ionization potentials are given in Tables 10 and 11. The electron affinity values predicted for Se, SeF_4, SeF_5, SeF_6, SeO, and SeO_2 are all in good agreement with the reported experimental values,[25,67,69,81,82] as well as the ionization energies predicted for Se, SeF_2, and SeO_2 are also all in good agreement with the reported experimental values.[68,81,83,69]

Table 10. CCSD(T)/CBS Electron Affinities at 0 K in eV

molecule	CCSD(T)	expt	G3[a]
Se	2.05	$2.020682 \pm 0.000044^{b}$	2.125
SeF	2.40		2.442
SeF_2	1.93		2.032
SeF_3	3.24		3.385
SeF_4	1.63	$1.7 \pm 0.10^{c,d,e}$	2.247
SeF_5	5.25	$3.3 \pm 0.2^{d,e}$, $\geq 5.1 \pm 0.4^{d,f}$	5.236
SeF_6	2.92	$2.9 \pm 0.2^{d,f}$, $3.0 \pm 0.2^{d,g}$	2.815
SeO	1.39	1.465 ± 0.020^{h}	
SeOF	1.55		
$SeOF_2$	1.79		
$SeOF_3$	5.11		
$SeOF_4$	3.55		
SeO_2	1.82	1.823 ± 0.050^{h}	
SeO_2F	4.45		
SeO_2F_2	2.69		

BDEs in the Cations and Anions. Table 12 gives the Se−F and Se−O anion BDEs of SeF_n^- (n = 1−7), $SeOF_n^-$ (n = 1−4), and $SeO_2F_n^-$ (n = 1−2) calculated from the heats of formation at the CCSD(T)/CBS level. The SeF_n^- (n = 1−7) BDEs differ by up to 85 kcal/mol at 298 K with SeF_5^- having the largest BDE and SeF_7^- having the smallest BDE. The high BDE in SeF_5^- suggests the SeF_5^- anion is quite stable thermodynamically. The $SeOF_n^-$ (n = 1−4) and $SeO_2F_n^-$ (n = 1−2) Se−F BDEs differ by up to 59 kcal/mol at 298 K with $SeOF_3^-$ having the largest Se−F BDE and $SeOF_4^-$ having the smallest Se−F BDE. The $SeOF_n^-$ (n = 1−4) and $SeO_2F_n^-$ (n = 1−2) Se−O BDEs differ by up to 53 kcal/mol at 298 K with SeO_2F^- having the largest BDE and $SeO_2F_2^-$ having the smallest BDE. The values of the BDEs in $SeOF_2^-$, $SeOF_3^-$, and SeO_2F^- suggests that these anions are also quite stable thermodynamically in terms of loss of an $^2F\bullet$ or ^3O atomic radical.

Table 11. CCSD(T)/CBS Ionization energies at 0 K in eV

molecule	CCSD(T)	expt	G3[c]
Se	9.67 (9.69)[f]	9.75238[a]	9.727
SeF	9.79		9.813
SeF_2	9.94	10.20[b]	10.006
SeF_3	8.68		8.744
SeF_4	12.57		12.499
SeF_5	10.97		10.576
SeF_6	14.75		14.504
SeO	10.02		
SeOF	9.80		
$SeOF_2$	12.06		
$SeOF_3$	10.23		
$SeOF_4$	12.41		
$SeOF_5$	12.31		
SeO_2	11.82	11.5 ± 0.5^{d}, 11.76^{e}	
SeO_2F	11.27		
SeO_2F_2	12.86		
SeO_3F	11.86		

[a] Ref 81. [b] Ref 68. [c] Ref 33. [d] Ref 83. [e] Ref 69. [f] TAE value in parentheses represents Se calculated at the CCSD(T)/aug-cc-pVQZ-PP and CCSD(T)/aug-cc-pV5Z-PP levels extrapolated to complete basis set limit using the expression in eq 3.

Table 12. CCSD(T)/CBS Adiabatic Anion BDEs in kcal/mol at 0 and 298 K

reactions	0 K	298 K	(298 K) G3[a]
$SeF_7^- \rightarrow SeF_6^- + F$	24.6	26.3	
$SeF_6^- \rightarrow SeF_5^- + F$	37.6	38.0	38.9
$SeF_5^- \rightarrow SeF_4^- + F$	110.8	111.3	97.7
$SeF_4^- \rightarrow SeF_3^- + F$	55.7	57.0	65.0
$SeF_3^- \rightarrow SeF_2^- + F$	90.8	91.8	89.3
$SeF_2^- \rightarrow SeF^- + F$	75.5	76.0	74.2
$SeF^- \rightarrow Se^- + F$	86.9	90.0	84.0
$SeOF_4^- \rightarrow SeOF_3^- + F$	36.7	38.1	
$SeOF_4^- \rightarrow SeF_4^- + O$	89.7	90.9	
$SeOF_3^- \rightarrow SeOF_2^- + F$	96.2	97.2	
$SeOF_3^- \rightarrow SeF_3^- + O$	108.7	109.8	
$SeOF_2^- \rightarrow SeOF^- + F$	94.0	94.6	
$SeOF_2^- \rightarrow SeF_2^- +O$	103.6	104.3	
$SeOF^- \rightarrow SeF^- + O$	83.3	81.9	
$SeO_2F_2^- \rightarrow SeO_2F^- + F$	40.8	41.3	
$SeO_2F_2^- \rightarrow SeOF_2^- + O$	73.0	73.9	
$SeO_2F^- \rightarrow SeO_2^- + F$	96.2	97.2	
$SeO_2F^- \rightarrow SeOF^- + O$	126.1	127.2	

[a] Ref 33.

Table 13 gives the Se−F and Se−O cation BDEs of SeF_n^+ (n = 1−7), $SeOF_n^+$ (n = 1−4) and $SeO_2F_n^+$ (n = 1−2), calculated from the heats of formation at the CCSD(T)/CBS level. The SeF_n^+ (n = 1−7) BDEs differ by up to 91 kcal/mol at 298 K with SeF_3^+ having the largest BDE. SeF_6^+ is predicted to be unstable with respect to loss of an F atom on ionization of SeF_6, consistent with the fact that this ion has not been

Table 13. CCSD(T)/CBS Adiabatic Cation BDEs in kcal/mol at 0 and 298 K

reactions	0 K	298 K	298 K G3[a]
$SeF_7^+ \rightarrow SeF_6^+ + F$	39.2	39.5	
$SeF_6^+ \rightarrow SeF_5^+ + F$	3.3	4.8	4.2
$SeF_5^+ \rightarrow SeF_4^+ + F$	64.0	64.8	73.1
$SeF_4^+ \rightarrow SeF_3^+ + F$	3.7	4.4	4.6
$SeF_3^+ \rightarrow SeF_2^+ + F$	89.5	90.6	87.3
$SeF_2^+ \rightarrow SeF^+ + F$	76.1	77.0	79.2
$SeF^+ \rightarrow Se^+ + F$	72.2	73.1	74.8
$SeOF_4^+ \rightarrow SeOF_3^+ + F$	22.6	23.9	
$SeOF_4^+ \rightarrow SeF_4^+ + O$	49.2	50.4	
$SeOF_3^+ \rightarrow SeOF_2^+ + F$	62.2	62.9	
$SeOF_3^+ \rightarrow SeF_3^+ + O$	30.3	31.0	
$SeOF_2^+ \rightarrow SeOF^+ + F$	35.9	36.9	
$SeOF_2^+ \rightarrow SeF_2^+ + O$	57.6	58.7	
$SeOF^+ \rightarrow SeF^+ + O$	84.7	85.6	
$SeO_2F_2^+ \rightarrow SeO_2F^+ + F$	44.0	45.0	
$SeO_2F_2^+ \rightarrow SeOF_2^+ + O$	33.6	34.7	
$SeO_2F^+ \rightarrow SeO_2^+ + F$	62.2	62.9	
$SeO_2F^+ \rightarrow SeOF^+ + O$	25.5	26.5	

[a] Ref 33.

Table 14. CCSD(T)/CBS Adiabatic Heterolytic Se−F BDEs in kcal/mol at 0 and 298 K to Form a Cation and F⁻

reactions	0 K	298 K
$SeF \rightarrow Se^+ + F^-$	219.9	220.3
$SeF_2 \rightarrow SeF^+ + F^-$	233.3	233.7
$SeF_3 \rightarrow SeF_2^+ + F^-$	212.1	212.3
$SeF_4 \rightarrow SeF_3^+ + F^-$	215.5	215.8
$SeF_5 \rightarrow SeF_4^+ + F^-$	238.9	239.3
$SeF_6 \rightarrow SeF_5^+ + F^-$	265.4	266.4
$SeOF \rightarrow SeO^+ + F^-$	232.8	233.2
$SeOF_2 \rightarrow SeOF^+ + F^-$	236.1	236.6
$SeOF_3 \rightarrow SeOF_2^+ + F^-$	220.2	220.3
$SeOF_4 \rightarrow SeOF_3^+ + F^-$	230.8	231.6
$SeOF_5 \rightarrow SeOF_4^+ + F^-$	244.5	245.0
$SeO_2F \rightarrow SeO_2^+ + F^-$	234.2	234.5
$SeO_2F_2 \rightarrow SeO_2F^+ + F^-$	262.6	263.2

reported. The $SeOF_n^+$ (n = 1−4) and $SeO_2F_n^+$ (n = 1−2) Se−F BDEs differ by up to 39 kcal/mol at 298 K with $SeOF_3^+$ having the largest BDE and $SeOF_4^+$ having the smallest BDE. The $SeOF_n^+$ (n = 1−4) and $SeO_2F_n^+$ (n = 1−2) Se−O BDEs differ by up to 59 kcal/mol at 298 K with $SeOF^+$ having the largest and SeO_2F^+ having the smallest BDE.

Table 14 gives the Se^+−F^- heterolytic bond cleavage of SeF_n (n = 1−6), $SeOF_n$ (n = 1−5), and SeO_2F_n (n = 1−2) calculated from the heats of formation at the CCSD(T)/CBS level. The SeF_n (n = 1−6) heterolytic BDEs differ by up to 54 kcal/mol at 298 K with SeF_6 having the largest BDE and SeF_3 having the smallest. The $SeOF_n$ (n = 1−5) and SeO_2F_n (n = 1−2) Se−F heterolytic BDEs differ by up to 43 kcal/mol at 298 K with SeO_2F_2 having the largest BDE and $SeOF_3$ having the smallest.

Figure 2 gives a summary of the calculated CCSD(T)/CBS heats of formation (kcal/mol) of $SeOF_n$ at 298 K, the energy differences between the various species, the reaction enthalpies for the addition of either F^-, F, and F^+ to the neutral parent. The $SeOF^+$, $SeOF_3^+$, $SeOF_4^+$ cations, the $SeOF_2$ molecule, and

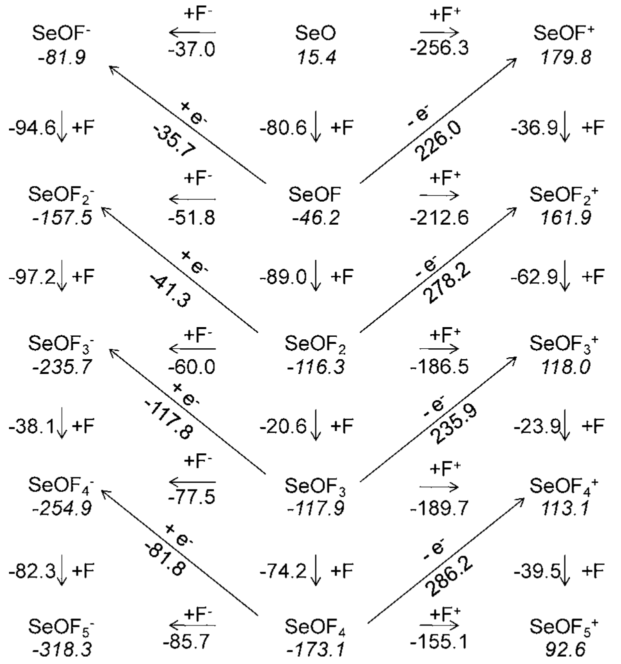

Figure 2. Heats of formation and the reaction enthalpies for the addition of F^+, F, and F^- at 298 K as well as ionization potentials($-e^-$) and electron affinities ($+e^-$) of $SeOF_n$. All values in kcal/mol. Heats of formation are given below each species *in italics*. Vertical arrows correspond to the addition of F to $SeOF_n$ to form $SeOF_{n+1}$ for the cation, neutral, and anion. Horizontal arrows to the left correspond to fluoride anion affinities. Horizontal arrows to the right correspond to the fluorocation affinities. Diagonal arrows to the right correspond to the ionization potential ($-e^-$). Diagonal arrows to the left correspond to the electron affinity ($+e^-$). The heat of formation of F^- at 298 K is −59.5 kcal/mol using the electron affinity of F.[49]

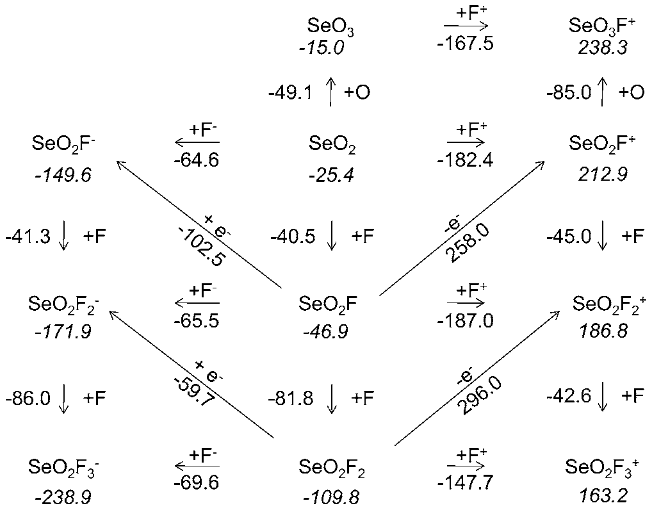

Figure 3. Heats of formation and the reaction enthalpies for the addition of F^+, F, and F^- at 298 K as well as ionization potentials ($-e^-$) and electron affinities ($+e^-$) of SeO_2F_n. All values in kcal/mol. Heats of formation are indicated below each species *in italics*. Vertical arrows correspond to the addition of F to SeO_2F_n to form SeO_2F_{n+1} in terms of the cation, neutral, and anion. Horizontal arrows to the left correspond to the fluorocation affinities. Horizontal arrows to the right correspond to fluoride anion affinities. Diagonal arrows to the right correspond to the ionization potential ($-e^-$). Diagonal arrows to the right correspond to the electron affinity ($+e^-$).

the $SeOF_3^-$ anion have the smallest enthalpies for addition of F in their series indicating that the addition of a F atom is less favored.

Figure 3 depicts the calculated CCSD(T)/CBS heats of formation (kcal/mol) of SeO_2F_n and SeO_3F_n at 298 K, the energy differences between the various species, the reaction enthalpies for the addition of either F^-, F, and F^+ to the neutral parent. The reaction enthalpy for the addition of the first F atom to to the neutral, cation, and anion are about the same, 40 to 45 kcal/mol. The exothermicity of the reaction to add F to SeO_2F_n increases for the neutral and the anion with the second addition almost double the value of the first. In contrast, the addition of the second F to the cation is essentially the same energy as the first. The addition of F to $SeO_2F_2^+$ to form $SeO_2F_3^+$ occurs by addition to an oxygen and not selenium (Figure 1).

In Figure 4 the reaction enthalpies for the addition of an F atom to $SeF_n^{0\pm1}$ (n = 1−7) to form $SeF_{n+1}^{0\pm1}$ range from −26.3 kcal/mol in SeF_6^- and −38.0 kcal/mol in SeF_5^- to −111.3 kcal/mol in SeF_4^-, suggesting that the addition of a fifth Se−F bond is strongly favored. The low values of −4.4 and −4.8 kcal/mol for the addition of F to SeF_3^+ and SeF_5^+, respectively, suggest that the oxidation of these two cations may prove to be difficult. We have already noted that SeF_6^+ will dissociate. The energies to add an O or an F to a compound are summarized in Figure 5.

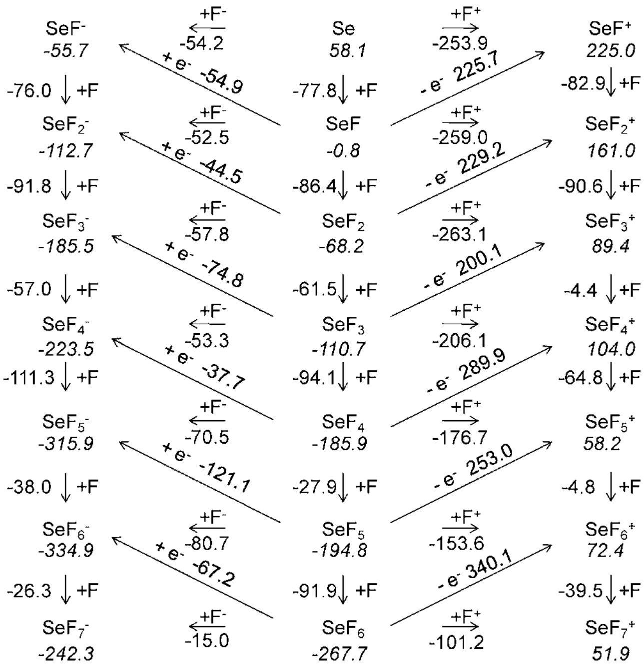

Figure 4. Heats of formation and the reaction enthalpies for the addition of F^+, F, and F^- at 298 K as well as ionization potentials ($-e^-$) and electron affinities ($+e^-$) of SeF_n. All values in kcal/mol. Heats of formation are indicated below each species *in italics*. Vertical arrows correspond to the addition of F to SeF_n to form SeF_{n+1} in terms of the cation, neutral, and anion. Horizontal arrows to the left correspond to fluoride anion affinities. Horizontal arrows to the right correspond to the fluorocation affinities. Diagonal arrows to the right correspond to the ionization potential ($-e^-$). Diagonal arrows to the left correspond to the electron affinity ($+e^-$).

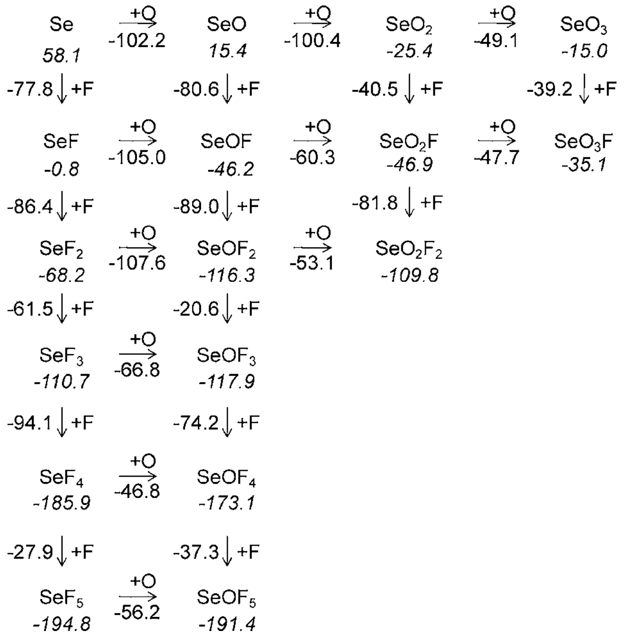

Figure 5. Heats of formation and reaction enthalpies for the addition of an F to SeF_n to form SeF_{n+1}, O to SeF_n to form $SeOF_n$, F to $SeOF_n$ to form $SeOF_{n+1}$, and O to SeO_2F_n to form SeO_3F_n at 298 K in kcal/mol. Heats of formation are indicated below each molecule *in italics*. Vertical arrows correspond to the addition of F to SeF_n or $SeOF_n$ to form SeF_{n+1} or $SeOF_{n+1}$. Horizontal arrows to the right correspond to the addition of O to SeF_n, $SeOF_n$, or SeO_2F_n to form $SeOF_n$, SeO_2F_n, and SeO_3F_n, respectively.

■ CONCLUSIONS

The bond dissociation energies (BDEs) and fluoride affinities of SeF_n (n = 1−6), $SeOF_n$ (n = 0−4), SeO_2F_n (n = 0−2), and SeO_3 and the electron affinities of SeF_n (n = 1−6) have been predicted with coupled cluster CCSD(T) theory and extrapolated to the complete basis set limit (Figure 5). The calculated heats of formation are dependent on the correct value of ΔH_f^0(Se). We used the value of 57.9 kcal/mol recommended by Wang,[33] and obtained excellent agreement with experiment for $\Delta H_f^{298}(SeF_6)$. Using the experimental heat of formation and our calculated TAEs, we predicted ΔH_f^0(Se) 57.98 ± 0.5 kcal/mol in excellent agreement with Wang's value derived from experimental appearance potentials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Total valence electronic energies at the CCSD(T) level in a.u., optimized bond lengths (Å) and angles (degrees) for SeF_xO_y geometries, and optimized CCSD(T) Cartesian coordinates in Å. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Grant, D. J.; Matus, M. H.; Switzer, J. R.; Dixon, D. A.; Francisco, J. S.; Christe, K. O. *J. Phys. Chem. A* **2008**, *112*, 3145.

(2) Christe, K. O.; Dixon, D. A.; Haiges, R.; Hopinger, M.; Jackson, V. E.; Klapotke, T. M.; Krumm, B.; Scherr, M. *J. Fluor. Chem.* **2010**, *131*, 791.

(3) Nakanishi, W.; Hayashi, S. *J. Phys. Chem. A* **1999**, *103*, 6074.

(4) Kniep, R.; Korte, L.; Kryschi, R.; Poll, W. *Angew. Chem., Int. Ed.* **1984**, *23*, 388.

(5) Seppelt, K. *Z. Anorg. Allg. Chem.* **1975**, *415*, 12.

(6) Bowater, I. C.; Brown, R. D.; Burden, F. R. *J. Mol. Spectrosc.* **1968**, *28*, 454.

(7) Damerius, R.; Huppmann, P.; Lentz, D.; Seppelt, K. *J. Chem. Soc., Dalton Trans.* **1984**, 2821.

(8) Mahjoub, A. R.; Leopold, D.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1992**, *618*, 83.

(9) Christe, K. O.; Curtis, E. C.; Schack, C. J.; Pilipovich, D. *Inorg. Chem.* **1972**, *11*, 1679.

(10) Mahjoub, A. R.; Zhang, X.; Seppelt, K. *Chem.—Eur. J.* **1995**, *1*, 261.

(11) Moock, K. H.; Boere, R. T. J. *Fluorine Chem.* **1994**, *68*, 175.

(12) Bowater, I. C.; Brown, R. D.; Burden, F. R. *J. Mol. Spectrosc.* **1967**, *23*, 272.

(13) Paetzold, R.; Aurich, K. *Z. Anorg. Allg. Chem.* **1962**, *315*, 72.

(14) Rolfe, J. A.; Woodward, L. A. *Trans. Faraday Soc.* **1955**, *51*, 778.

(15) Prideaux, E. B. R.; Cox, C. B. *J. Chem. Soc.* **1928**, 739.

(16) Prideaux, E. B. R.; Cox, C. B. *J. Chem. Soc.* **1927**, 928.

(17) Feldmann, C.; Jansen, M. *Chem. Ber.* **1994**, *127*, 2173.

(18) Gillespie, R. J.; Spekkens, P.; Milne, J. B.; Moffett, D. *J. Fluorine Chem. 7* **1976**, *7*, 43.

(19) Baran, E. J. *J. Fluorine Chem.* **1977**, *10*, 255.

(20) Milne, J. *Inorg. Chem.* **1978**, *17*, 3592.

(21) Paetzold, R.; Aurich, K. *Z. Anorg. Allg. Chem.* **1965**, *335*, 281.

(22) Milne, J.; Lahaie, P. *Inorg. Chem.* **1983**, *22*, 2425.

(23) Paetzold, R.; Aurich, K. *Z. Anorg. Allg. Chem.* **1966**, *348*, 94.

(24) Paetzold, R.; Aurich, K. *Z. Chem.* **1966**, *6*, 152.

(25) Maggard, P.; Lobastov, V. A.; Schäfer, L.; Ewbank, J. D.; Ischenko, A. A. *J. Phys. Chem.* **1995**, *99*, 13115.

(26) O'Hare, P. A. G.; Settle, J. L.; Hubbard, W. N. *Trans. Faraday Soc.* **1966**, *62*, 558.

(27) (a) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; National Bureau of Standards: Gaithersburg, MD, 1972; Vol. *I*, pp 1−160. (b) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold Co.: New York, 1979.

(28) (a) Damerius, R.; Huppmann, P.; Lentz, D.; Seppelt, K. *J. Chem. Soc., Dalton Trans.* **1984**, 2821. (b) Seppelt, K. *Z. Anorg. Allg. Chem.* **1975**, *416*, 12.

(29) (a) Mason, J., Ed.; *Multinuclear NMR*; Plenum Press: New York, 1987. (b) Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*; Wiley: New York, 1981.

(30) Buhl, M.; Thiel., W.; Fleischer, U.; Kutzelnigg, W. *J. Phys. Chem.* **1995**, *99*, 4000.

(31) Poleschner, H.; Ellrodt, S.; Malischewski, M.; Nakatsuji, J.-y.; Rohner, C.; Seppelt, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 419.

(32) Xu, Q-s. Li, W.; Xie, Y.; Schaefer, H. F. III *J. Phys. Chem. A* **1999**, *103*, 7496.

(33) Wang, L. *Int. J. Mass Spectrom.* **2007**, *264*, 84.

(34) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764. Curtiss, L. A.; Redfern, P. C.; Rassolov, V.; Kedziora, G.; Pople, J. A. *J. Chem. Phys.* **2001**, *114*, 9287.

(35) Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1986**, *85*, 4815. Gunn, S. R. *J. Phys. Chem.* **1964**, *68*, 949.

(36) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *Suppl. 2*, 11.

(37) (a) Purvis, G. D. III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (b) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (c) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718. (d) Bartlett, R. J.; Musial, M. *Rev. Mod. Phys.* **2007**, *79*, 291.

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

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

(40) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(41) Lee, C.; Yang, C. W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

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

(43) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *Y- 10* (Suppl), 1−19.

(44) (a) Knowles, P. J.; Hampel, C.; Werner, H. -J. *J. Chem. Phys.* **1993**, *99*, 5219. (b) Deegan, M. J. O.; Knowles, P. J. *J. Chem. Phys. Lett.* **1994**, *227*, 321.

(45) (a) Peterson, K. A.; Dunning, T. H. Jr. *J. Chem. Phys.* **2002**, *117*, 10548. (b) Woon, D. E.; Dunning, T. H. Jr. *J. Chem. Phys.* **1993**, *98*, 1358. (c) Peterson, K. A.; Yousaf, K. E. *J. Chem. Phys.* **2010**, *133*, 174116.

(46) Davidson, E. R.; Ishikawa, Y.; Malli, G. L. *Chem. Phys. Lett.* **1981**, *84*, 226.

(47) Moore, C. E. *Atomic energy levels as derived from the analysis of optical spectra*; U.S. Department of Commerce, National Technical Information Service, COM-72-50282: Washington, DC, 1949; Vol. *1*, H to V, U.S. National Bureau of Standards Circular 467.

(48) (a) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2000**, *104*, 3048. (b) Feller, D.; Dixon, D. A. *J. Chem. Phys.* **2001**, *115*, 3484. (c) Dixon, D. A.; Feller, D.; Peterson, K. A. *J. Chem. Phys.* **2001**, *115*, 2576. (d) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2003**, *107*, 9641. (e) Dixon, D. A.; Feller, D.; Christe, K. O.; Wilson, W. W.; Vij, A.; Vij, V.; Jenkins, H. D. B.; Olson, R. M.; Gordon, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 834. (f) Dixon, D. A.; Gutowski, M. *J. Phys. Chem. A* **2005**, *109*, 5129. (g) Pollack, L.; Windus, T. L.; de Jong, W. A.; Dixon, D. A. *J. Phys. Chem. A* **2005**, *109*, 6934. (h) 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.; Liu, J.; Chen, W.; Schwenke, D. W. *J. Phys. Chem. A* **2002**, *106*, 27277.

(49) Chase, M. W., Jr. *NIST-JANAF Tables*, 4th ed.; *J. Phys. Chem. Ref. Data* **1998**, Mono. 9, Suppl. 1. See also: Linstrom, P. J.; Mallard, W. G., Eds.; *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, June 2005; National Institute of Standards and Technology: Gaithersburg, MD, 2005 (http://webbook.nist.gov/chemistry/).

(50) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(51) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(52) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(53) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(54) Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1995**, *99*, 606.

(55) Schreckenbach, G.; Ziegler, T. *Int. J. Quantum Chem.* **1997**, *61*, 899.

(56) Wolff, S. K.; Ziegler, T. *J. Chem. Phys.* **1998**, *109*, 895.

(57) Wolff, S. K.; Ziegler, T.; van Lenthe, E.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 7689.

(58) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.

(59) Autschbach, J.; Ziegler, T. In *Calculation of NMR and EPR Parameters: Theory and Application*; Kaupp, M., Buhl, M., Malkin, V. G., Eds.; Wiley-VCH & Co.: Weinheim, Germany, 2004; p 249.

(60) (a) *ADF 2004.01, ADF Users Guide*; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 2004; http://www.scm.com. (b) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(61) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklaß, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *MOLPRO, A Package of ab initio Programs*, Version 2009; University of Cardiff/Universität Stuttgart: Wales, U.K./Stuttgart, Germany, 2009.

(62) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb,M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.;Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.;Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.;Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li,X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.;Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich,S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.;Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham,M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.;Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03*, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(63) *AMPAC 9*; Semichem, Inc.: Shawnee, KS, 1992−2008.

(64) Carrington, A.; Currie, G. N.; Miller, T. A.; Levy, D. H. *J. Chem. Phys.* **1969**, *50*, 2726.

(65) Feller, D.; Peterson, K. A.; Dixon, D. A. *J. Chem. Phys.* **2008**, *129*, 204105.

(66) Sutton, L. E., Ed.; *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society: London, U.K., 1958.

(67) (a) Haas, A.; Willner, H. *Z. Anorg. Allg. Chem.* **1979**, *454*, 17. (b) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1998**, *27* (2), 115.

(68) de Leeuw, D. M.; Mooyman, R.; de Lange, C. A. *Chem. Phys.* **1979**, *38*, 21.

(69) (a) Snodgrass, J. T.; Coe, J. V.; McHugh, K. M.; Freidhoff, C. B.; Bowen, K. H. *J. Phys. Chem.* **1989**, *93*, 1249. (b) Coe, J. V.; Snodgrass, J. T.; Freidhoff, C. B.; McHugh, K. M.; Bowen, K. H. *J. Chem. Phys.* **1986**, *84*, 618. (c) Smoes, S.; Drowart, J. *J. Chem. Soc. Faraday Trans.* **1984**, *80*, 1171.

(70) Poleschner, H.; Seppelt, K. *Chem.—Eur. J.* **2004**, *10*, 6565.

(71) O'Hare, P. A. G. *J. Chem. Thermodyn.* **1986**, *18*, 555−562.

(72) (a) Helgaker, T.; Klopper, W.; Koch, H.; Noga, J. *J. Chem. Phys.* **1997**, *106*, 9639. (b) Halkier, A.; Helgaker, T.; Jørgensen, P.; Klopper, W.; Koch, H.; Olsen, J.; Wilson, A. K. *Chem. Phys. Lett.* **1998**, *286*, 243.

(73) Martin, M. L. *Chem. Phys. Lett.* **1996**, *259*, 699.

(74) Carre, J.; Claudy, P.; Letoffe, J. M.; Kolimannsberger, M.; Bousquet, E. J. *J. Fluorine Chem.* **1979**, *14*, 139. Carre, J.; Germain, P.; Kolimannsberger, M.; Perachon, G.; Thourey, J. *J. Fluorine Chem.* **1979**, *13*, 365.

(75) Brion, C. E. *Int. J. Mass Spectrom. Ion Phys.* **1969**, *3*, 197.

(76) Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 2023.

(77) Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, 2007.

(78) (a) Nicolaides, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750. (b) Wang, S. Y.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 7282. (c) Carter, E. A.; Goddard, W. A. III *J. Am. Chem. Soc.* **1988**, *110*, 4077. (d) Carter, E. A.; Goddard, W. A. III *J. Phys. Chem.* **1986**, *90*, 998.

(79) (a) Grant, D. J.; Dixon, D. A. *J. Phys. Chem. A* **2006**, *110*, 12955. (b) Grant, D. J.; Matus, M. H.; Switzer, J. K.; Dixon, D. A.; Francisco, J. S.; Christe, K. O. *J. Phys. Chem. A* **2008**, *112*, 3145.

(80) (a) O'Hare, P. A. G.; Wahl, A. C. *J. Chem. Phys.* **1970**, *53*, 2834. (b) O'Hare, P. A. G.; Hubbard, W. N.; Feder, H. M. IUPAC Thermodynamik Symposium, Heidelberg, Germany, September 1967; Paper No. II-5.

(81) Lide, D. R., Ed.; *CRC Handbook of Chemistry and Physics*, 86th ed.; Taylor and Francis: Boca Raton, FL, 2005; pp (10-202)−(10-222).

(82) Harland, P. W.; Thynne, J. C. *J. Inorg. Nucl. Chem. Lett.* **1973**, *9*, 265.

(83) Ficalora, P. J.; Thompson, J. C.; Margrave, J. L. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3771.