The Electron Affinities of the Selenium Fluorides SeF_n ($n = 1-7$)

Qian-shu Li and Wen-guo Xu

The School of Chemical Engineering and Materials Science, Institute of Bejing Technology, Beijing, China, 100081

Yaoming Xie and Henry F. Schaefer III*

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

Received: March 5, 1999; In Final Form: June 1, 1999

The molecular structures, electron affinities, and dissociation energies of the SeF_n/SeF_n^- ($n = 1-7$) species were examined using hybrid Hartree−Fock/density functional theory (DFT). The three different types of electron affinities reported in this work are the adiabatic electron affinity (EA_{ad}), the vertical electron affinity (EA_{vert}), and the vertical detachment energy (VDE). The first Se−F dissociation energies of the SeF_n and SeF_n^- species were also been reported. The basis set used in this work is of double-ζ plus polarization quality with additional *s*- and *p*-type diffuse functions, and is denoted as DZP++. Four different density functionals (BHLYP, B3LYP, BP86, and BLYP) were used in this work. Among these, the best for predicting molecular structures and energies was found to be BHLYP, whereas other methods generally overestimated bond lengths. Neutral SeF_7 was found to have no structures that were significantly bound with respect to dissociation. SeF_7^- structures with D_{5h}, C_{4v}, and C_{3v} symmetry were found to lie very close in energy. The most reliable adiabatic electron affinities, obtained at the DZP++ BHLYP level of theory, are 1.99 eV (Se), 2.37 eV (SeF), 2.21 eV (SeF_2), 3.39 eV (SeF_3), 2.50 eV (SeF_4), 5.23 eV (SeF_5), and 3.13 eV (SeF_6). The BHLYP adiabatic electron affinities of the Se atom, SeF_5, and SeF_6 molecules predicted by this work are in good agreement with the experimental results, but the predicted electron affinities for SeF_4 are much larger than the experimental value (1.7 ± 0.1 eV) obtained by the electron impact appearance energy (EIAE) method, which usually gives lower EA_{ad} values. The other molecular electron affinities (SeF_n, $n = 1, 2, 3, 7$) are unknown experimentally. The predicted vertical detachment energy for SeF_7^- is very large, 8.01 eV. The neutral bond dissociation energies $D_e(F_{n-1}Se-F)$ are largely unknown experimentally. For SeF_5, the DFT methods predict $D_e(F_4Se-F) = 0.88-1.67$ eV, which is lower than the experimental estimated value of 2.8 eV. The DZP++ BLYP bond dissociation energy value, $D_e(F_5Se-F) = 3.15$ eV, is slightly lower than the dissociation energies predicted by the other methods (DZP++ BHLYP, 3.34 eV; DZP++ B3LYP, 3.31 eV; DZP++ BP86, 3.44 eV). Except for the DZP++ BP86 result, theory matches the experimental estimate 3.15 ± 0.2 eV based on thermochemical data. Excluding the DZP++ BHLYP results, the dissociation energy for diatomic SeF ranges from 3.4 to 3.80 eV among which the DZP++ B3LYP result (3.40 eV) is in best agreement with the experimental value (3.5 eV). For the bond dissociation value of the anion $D_e(SeF_5^- -F)$ the DZP++ BHLYP method gives $D_e(SeF_5^- -F) = 1.23$ eV, whereas the DZP++ B3LYP, DZP++ BP86, and DZP++ BLYP methods predict dissociation energies (B3LYP, 1.83 eV; BP86, 2.26 eV; BLYP, 2.13 eV) that are larger than experiment (1.09 ± 0.1 eV). It is concluded that the density functional methods, although very useful in establishing trends, must be used very carefully. Moreover, additional ($SeF_n^-SeF_n^-$) experiments are required to precisely establish the reliability of the different density functional methods.

Introduction

The 1978 study by Compton, Reinhardt, and Cooper[1] on the negative ion−molecule reactions of SeF_6 concluded that the adiabatic electron affinity (EA_{ad}) of SeF_6 molecule is 2.9 ± 0.2 eV, and that of $SeF_5 \geq 5.1 \pm 0.4$ eV. Earlier, Harland and Thynne reported experimental values for SeF_5 (3.3 eV) and SeF_4 (1.7 eV) through their negative ion electron impact study.[2] Although the electron affinity of Se has been experimentally determined to within ±0.00003 eV,[3] the EA_{ad} values of the SeF_n molecules are much more in doubt. Very little is known theoretically or experimentally about the electron affinities and other fundamental properties of the SeF_n molecules. The only theoretical prediction of the SeF_n electron affinities is the 1970 study of O'Hare and Wahl,[4] who predicted a vertical electron affinity (EA_{vert}) ≤ 2.8 ± 0.5 eV for diatomic SeF.

The purpose of the present study is to systematically apply several modern forms of density functional theory (DFT)[5] to determine the electron affinities of the SeF_n series. Of specific interest are (a) the accuracy of the electron affinities as determined by comparison with experimental results; (b) the variation in the predicted electron affinities between the different DFT methods; (c) the importance of the presence of diffuse functions in the basis set; and (d) the relationships between the EA_{ad}, EA_{vert}, and vertical detachment energy (VDE) values. Most important is to establish reliable theoretical predictions in the absence of experimental results and in some cases to challenge existing experiments.

---

* To whom correspondence should be addressed.

10.1021/jp9907894 CCC: $18.00

DFT[6] has evolved into a widely applicable computational technique on a par with modest level ab initio methods (e.g., second-order perturbation theory); DFT often requires less computational effort. The application of gradient-corrected DFT has been shown to be effective for a range of inorganic species such as the SF_n/SF_n^-, PF_n/PF_n^-, ClF_n/ClF_n^-, SiF_n/SiF_n^-, $C_2F_n/C_2F_n^-$, and BrF_n/BrF_n^- molecules.[7-12] In addition, although the prediction of an electron affinity is generally difficult, being the result of a small difference between two very large energies, these previous studies have shown that DFT can be a dependable source for EA predictions. For a general discussion of the reliability of DFT studies of negative ions, the reader is referred to the 1996 work of Galbraith and Schaefer.[7b] The primary objective of this study, therefore, is to provide theoretical data for the electron affinities of the selenium fluorides.

Computational Methods

The four different density functional or hybrid Hartree–Fock/density functional forms used here are Becke's 1988 exchange functional[13] with Lee, Yang, and Parr's correlation functional (BLYP);[14] Becke's half-and-half exchange functional[15] with the LYP correlation functional (BHLYP); Becke's three-parameter semiempirical exchange functional[16] with the LYP correlation functional (B3LYP); and Becke's 1988 exchange functional with the Perdew correlation functional (BP86).[17] Unrestricted wave functions were employed for all open-shell species. All of the electron affinities and molecular structures were determined using the Gaussian 94 program.[18] As is known to some, the BHLYP method used here, namely that implemented in the Gaussian programs, is not the half-and-half method proposed originally by Becke.[16] The default integration grid (75, 302) of Gaussian 94 was applied. The integrals evaluated in this study should be accurate to 10^{-5} E_h, the density-based convergence for the self-consistent field (SCF) iterations was 10^{-8} E_h, and Cartesian gradients were converged to at least 10^{-6} au.

A standard double-ζ plus polarization (DZP) basis set for fluorine was utilized, which is constructed from the Huzinaga–Dunning–Hay[19] contracted double-ζ Gaussian basis set by adding a set of five pure angular momentum *d*-like polarization functions on each atom. The contraction scheme for this basis is F(9s5p1d/4s2p1d). The DZP basis set for selenium used the double-ζ contracted Gaussian functions Se(14s11p5d/8s6p2d) plus a set of five pure *d*-type polarization functions $\alpha_d(\text{Se}) = 0.338$ generated by Schäfer–Horn–Ahlrichs.[20] These basis sets are either identical to or consistent with our large body of previous and yet unpublished work on electron affinities.

To determine the significance of diffuse function in the description of the anions, the above DZP basis was augmented with diffuse functions; each atom received one additional *s*-type and one additional set of *p*-type functions. The diffuse function orbital exponents were determined in an "even-tempered sense" as a mathematical extension of the primitive set, according to the prescription of Lee and Schaefer.[21] The diffuse function exponents were taken to be $\alpha_s = 0.03888$, $\alpha_p = 0.03819$ for selenium and $\alpha_s = 0.1049$, $\alpha_p = 0.0826$ for fluorine. The final basis set may be designated Se(15s12p6d/9s7p3d), F(10s6p1d/5s3p1d). This extended basis will be denoted as "DZP++". The total number of DZP++ basis functions ranged from 64 for SeF/SeF^- to 178 for SeF_7/SeF_7^-.

All SeF_n ($n = 1-6$) geometries were determined to be minima by the evaluation of their harmonic vibrational frequencies at the DZP++ BHLYP and the DZP++ B3LYP levels of theory. Structures with very small vibrational frequencies were confirmed to be minima by the further evaluation of their vibrational frequencies using the other functionals. Zero-point vibrational energies (ZPVE) evaluated at the DZP++ BHLYP and the DZP++ B3LYP levels are presented in Table 1. The ZPVE differences between SeF_n and SeF_n^- ($n = 1-6$) fall in the range of 0.01–0.18 eV. Note that the ZPVE differences between SeF_4 and SeF_4^- (0.083 or 0.076 eV with BHLYP and B3LYP methods, respectively) and between SeF_6 and SeF_6^- (0.180 or 0.145 eV, respectively) are quite large. These differences may be used as corrections to the EA_{ad} values, as will be discussed.

TABLE 1: Zero-Point Vibrational Energies within the Harmonic Approximation for the SeF_n/SeF_n^- ($n = 1-6$) at the DZP++ BHLYP and DZP++ B3LYP Levels of Theory in eV (or kcal/mol, in parentheses)

compounds	BHLYP	B3LYP
SeF	0.044 (1.02)	0.042 (0.97)
SeF^-	0.035 (0.80)	0.032 (0.75)
SeF_2	0.104 (2.40)	0.098 (2.26)
SeF_2^-	0.071 (1.65)	0.067 (1.54)
SeF_3	0.164 (3.79)	0.153 (3.53)
SeF_3^-	0.142 (3.28)	0.131 (3.02)
SeF_4	0.269 (6.21)	0.246 (5.67)
SeF_4^-	0.186 (4.28)	0.170 (3.91)
SeF_5	0.344 (7.94)	0.309 (7.13)
SeF_5^-	0.299 (6.89)	0.272 (6.26)
SeF_6	0.493 (11.37)	0.450 (10.39)
SeF_6^-	0.313 (7.21)	0.305 (7.04)

The electron affinities are evaluated as the difference of total energies in the following manner. The EA_{ad} values are determined by

$$EA_{ad} = E(\text{optimized neutral}) - E(\text{optimized anion})$$

The vertical electron affinities are determined by

$$EA_{vert} = E(\text{optimized neutral}) - E(\text{anion at optimized neutral geometry})$$

and the vertical detachment energies of the anions by

$$VDE = E(\text{neutral at optimized anion geometry}) - E(\text{optimized anion})$$

The dissociation energies for SeF_n/SeF_n^- are determined from differences in total energies in the following manner: the first dissociation energies for the neutrals refer to the reaction

$$SeF_n \rightarrow SeF_{n-1} + F \tag{1}$$

whereas the first dissociation energies for the anions refer to the two different reactions,

$$SeF_n^- \rightarrow SeF_{n-1}^- + F \tag{2}$$

$$SeF_n^- \rightarrow SeF_{n-1} + F^- \tag{3}$$

Results and Discussion

A. Se and Se^-. The electron affinities of the ^3P state of the Se atom at various levels of theory, as well as experimental electron affinity data, are reported in Table 2. Values are determined from total energies of the Se atom and the Se^- ion. The four functionals predict the experimental electron affinity of the Se atom within a deviation of at most 0.28 eV. The EA values from the DZP++ BHLYP (1.99 eV) and DZP++ BLYP (2.11 eV) methods are closest to the very precise experimental value of 2.02069(3) eV given by Hotop and Lineberger's laser-photodetachment threshold spectroscopy study of the Se anion.[3]

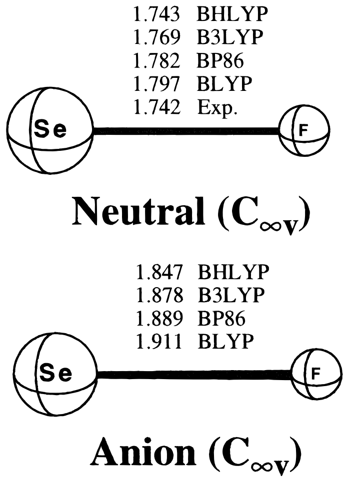

Figure 1. The molecular geometries of the X $^2\Pi$ state of neutral SeF and the X $^1\Sigma^+$ state of anion SeF$^-$. All bond lengths are in angstroms. All results were obtained with the DZP++ basis set.

TABLE 2: The Electron Affinities of Se in eV (All Results Obtained with the DZP++ Basis Set)

method	EA
BHLYP	1.99
B3LYP	2.21
BP86	2.30
BLYP	2.11
experimental	2.02069 (3)[a]

[a] Ref 3.

The DZP++ BHLYP value is only 0.03 eV lower than the experiment. The predictions of the B3LYP and BP86 methods are at least 0.2 eV larger than the experimental value. The fact that BHLYP gives the best predictions for electron affinities was also noted in the earlier work on the second-row fluorides[7−11] and bromine fluorides.[12]

B. SeF and SeF$^-$. The first unequivocal synthesis of SeF was obtained by Carrington and co-workers[22] by reacting carbonyl selenide with fluorine atoms generated in a microwave discharge. The geometries of the ground state of SeF and its anion are given in Figure 1. The SeF radical has a $^2\Pi$ ground state, and its experimental bond length is $r_o = 1.742 \pm 0.05$ Å.[22] The DZP++ BHLYP bond length (1.743 Å) compares most favorably with experiment, whereas the other methods predict longer bond distances by as much as 0.055 Å. Here we note the general trend for bond lengths for the selenium fluorides is BLYP > BP86 > B3LYP > BHLYP. The $^1\Sigma^+$ ground state of the anion has bond lengths which vary among the different DFT methods by about 0.06 Å, and the DZP++ BHLYP bond length, deemed to be the most reliable, is 1.847 Å, longer by roughly 0.10 Å than that of the neutral species.

The DZP++ electron affinities of SeF are given in Table 3. The electron affinities computed using the DZP++ basis are greater than those computed using the DZP basis (without diffuse). For example, EA$_{ad}$ was predicted as 2.37 eV at the DZP++ BHLYP level, but as 1.77 eV at DZP BHLYP. This is not surprising because the stabilization of the anion due to the addition of diffuse functions will be greater than the stabilization of the neutral species. Clearly, using a basis set including diffuse functions in the computation of electron affinities is of paramount importance. Therefore, the electron affinities computed with the DZP basis are not discussed further.

TABLE 3: Adiabatic and Vertical Electron Affinities of the Neutral and Vertical Detachment Energies of the Anionic SeF, SeF$_2$, SeF$_3$, SeF$_4$, SeF$_5$, and SeF$_6$ in eV (or kcal/mol in Parentheses) (Values Are Obtained with the DZP++ Basis Set, and Are Not Corrected for ZPVE; See Table 1 for ZPVE Corrections)

compound	method	EA$_{ad}$	EA$_{vert}$	VDE
SeF	BHLYP	2.37 (54.7)	2.21 (51.0)	2.53 (58.3)
	B3LYP	2.52 (58.1)	2.35 (54.2)	2.68 (61.8)
	BP86	2.53 (58.3)	2.35 (54.2)	2.68 (61.8)
	BLYP	2.39 (55.1)	2.21 (51.0)	2.54 (58.6)
SeF$_2$	BHLYP	2.21 (51.0)	0.31 (7.1)	4.86 (112.1)
	B3LYP	2.40 (55.3)	0.55 (12.7)	4.58 (105.6)
	BP86	2.42 (55.8)	0.61 (14.1)	4.49 (103.5)
	BLYP	2.32 (53.5)	0.50 (11.5)	4.18 (96.4)
SeF$_3$	BHLYP	3.39 (78.2)	2.97 (68.5)	3.83 (88.3)
	B3LYP	3.41 (78.6)	2.96 (68.3)	3.80 (87.6)
	BP86	3.22 (74.3)	2.83 (65.3)	3.56 (82.1)
	BLYP	3.14 (72.4)	2.75 (63.4)	3.47 (80.0)
SeF$_4$	BHLYP	2.50 (57.7)	0.69 (15.9)	5.05 (116.5)
	B3LYP	2.87 (66.2)	0.99 (22.8)	4.78 (110.2)
	BP86	2.89 (66.6)	1.03 (23.8)	4.69 (108.2)
	BLYP	2.92 (67.3)	1.01 (23.3)	4.67 (107.7)
	Expt	1.7[a]		
SeF$_5$	BHLYP	5.23 (120.6)	4.01 (92.5)	6.16 (142.0)
	B3LYP	5.44 (125.4)	4.45 (102.6)	6.19 (142.7)
	BP86	5.30 (122.2)	4.41 (101.7)	5.84 (134.7)
	BLYP	5.30 (122.2)	4.49 (103.5)	5.90 (136.1)
	Expt	3.3 ± 0.1[a]		
		$\geq 5.1 \pm 0.4$[b]		
SeF$_6$	BHLYP	3.13 (72.2)	1.37 (31.6)	4.72 (108.8)
	B3LYP	3.95 (91.1)	2.45 (56.5)	5.24 (120.8)
	BP86	4.11 (94.8)	2.79 (64.3)	5.24 (120.8)
	BLYP	4.39 (101.2)	3.01 (69.4)	5.35 (123.4)
	Expt	2.9 ± 0.2[b]		
		3.0 ± 0.2[c]		

[a] Ref 2. [b] Ref 1. [c] Ref 30.

Note that the EA$_{ad}$ values in Table 3 are not corrected for zero-point vibrational energy. Relying upon BHLYP, we report 2.37 eV as the most trustworthy EA$_{ad}$ value for SeF based on previous studies of other main group fluorides.[7−12] The DZP++ EA$_{vert}$ values calculated with the DZP++ BHLYP (2.21 eV), DZP++ B3LYP (2.35 eV), DZP++ BP86 (2.35 eV) and DZP++ BLYP (2.21 eV) methods are in broad agreement with the previous estimated theoretical value ($\leq 2.8 \pm 0.5$ eV) by O'Hare and Wahl.[4a] The O'Hare−Wahl prediction would appear to be about 0.5 eV too high. The DFT range for EA$_{vert}$ is 2.21−2.35 eV and the range of the VDE for (SeF$^-$) is 2.53−2.68 eV, and thus, the anion is quite stable with respect to electron detachment. The EA$_{ad}$, EA$_{vert}$, and VDE values are similar due to the small difference in geometry between neutral and anion.

C. SeF$_2$ and SeF$_2^-$. The equilibrium geometries of the $^1A_1$ ground state of neutral SeF$_2$ and the $^2\Pi$ ground state of SeF$_2^-$ are displayed in Figure 2. The neutral Se−F bond length is in the range from 1.733 to 1.794 Å. As was the case for SeF, the DZP++ BHLYP method gives the shortest bond length for SeF$_2$, and provides the most reliable value. The SeF$_2$ radical has a bent structure with a bond angle of 96.6−99.2° as predicted by the four different functions. Kraatz and co-workers reported the theoretical bond lengths to be 1.757 Å and the bond angle as 96° in 1993.[23] They used the local density approximation (LDA) along with a double-ζ Slater-type orbitals (STO) basis set augmented with a single 3d-type polarization function. Our BHLYP results are the closest to those from Kraatz and co-workers. The other functionals predict longer bond distances and larger bond angles.

SeF$_2^-$ is linear ($D_{\infty h}$), with Se−F bond distances predicted from 1.954 to 2.018 Å, which are about 0.2 Å longer than their neutral counterparts. We note that SeF$_2^-$, with its $^2\Pi_u$ ground state is a Renner−Teller molecule. Specifically, it falls in the

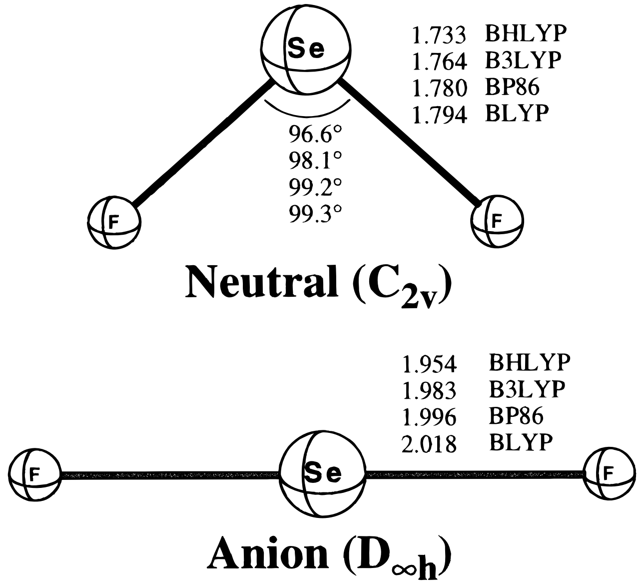

Figure 2. The molecular geometries in C_{2v} symmetry of the X $^1A_1$ state of neutral SeF_2 and the $D_{\infty h}$ symmetry geometries of the X $^2\Pi_u$ state of the anion, SeF_2^-. Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

case A category of Lee and co-workers,[24] with bending vibrational frequencies of both Renner−Teller components being real (235 and 76 cm^{-1}, respectively) and of differing magnitudes.

The theoretical EA_{ad}, EA_{vert}, and VDE are listed in Table 3. The predicted range of EA_{ad} is from 2.21 to 2.42 eV, among which the DZP++ BHLYP method predicts the smallest value (2.21 eV). The range of EA_{vert} is from 0.31 to 0.61 eV and the range of VDE is from 4.18 to 4.86 eV. The DZP++ BHLYP EA_{ad} and EA_{vert} are lower than those obtained with the other functionals, as is often the case for the other SeF_n and related main group fluorides. Note that the values for EA_{ad}, EA_{vert}, and VDE are significantly different due to the large differences in geometries between the neutral and the anion (vide infra).

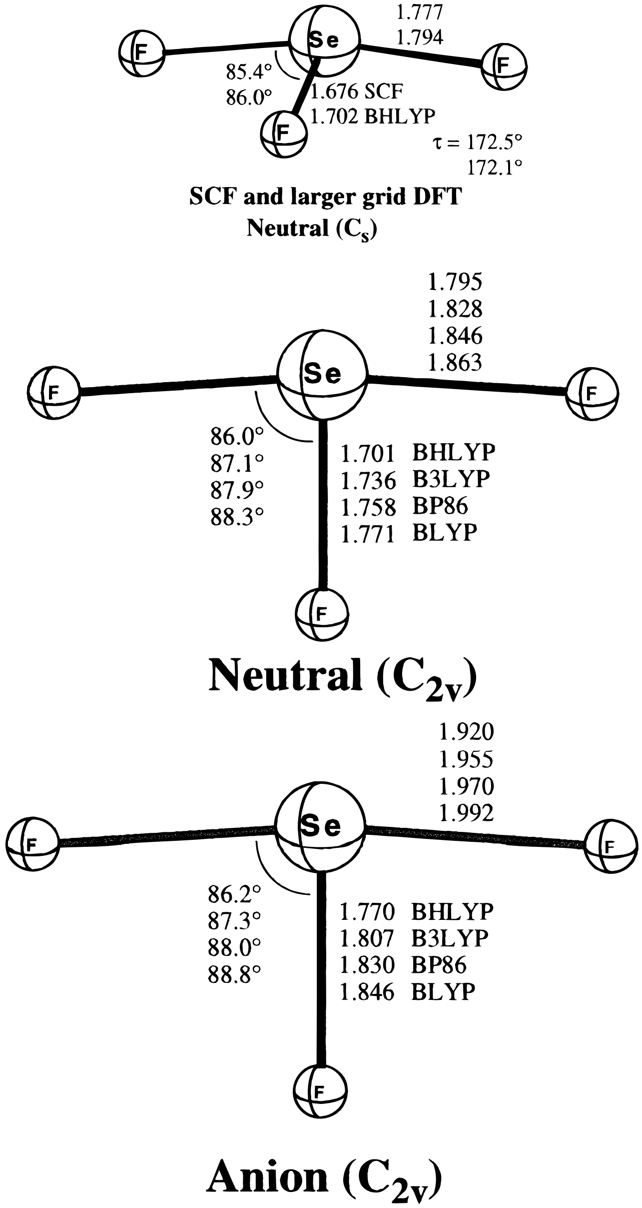

Figure 3. The molecular geometries in C_{2v} symmetry of the X $^2B_1$ state of neutral SeF_3 and the C_{2v} symmetry geometries of the X $^1A_1$ state of the anion, SeF_3^-. Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

D. SeF_3 and SeF_3^-. The geometries of the $^2B_1$ ground state of SeF_3 radical and the $^1A_1$ ground state of SeF_3^- are displayed in Figure 3. SeF_3 was initially found to have a planar C_{2v} symmetry structure (T-shaped), unlike the isovalent SF_3, which has a nonplanar C_s symmetry structure with a $F_{eq}-S-F_{ax}-F_{eq}$ torsion angle of 158−167°.[7a] With the standard Gaussian grid, the DZP++ BHLYP method predicts 1.795 and 1.701 Å for the $Se-F_{eq}$, $Se-F_{ax}$ bond distances, respectively, and 86.0° for the $F_{eq}-Se-F_{ax}$ angle. The other functionals predict longer bond distances, showing the same trend as for SeF_2/SeF_2^- and SeF/SeF^-. All four theoretical methods do a reasonable job in predicting that the equatorial Se−F bond distances are longer than the axial distance by about 0.09 Å. However, the SeF_3 molecule lies on a very flat potential curve with respect to the $F_{eq}-Se-F_{ax}-F_{eq}$ torsion angle. With the standard Gaussian integration grid, a C_s symmetry structure ($^2A'$ state) with a torsion angle of 172° (and all other geometrical parameters fixed at the C_{2v} equilibrium values) was found to be only 0.0003 eV (0.006 kcal/mol) higher in energy than the planar form (C_{2v} symmetry), and the C_{3v} symmetry pyramidal structure was found to be 0.58 eV (13.5 kcal/mol) higher than the C_s symmetry structure at the above level. The above results mandated that the SeF_3 and SeF_3^- investigation be repeated with a larger numerical integration grid, in this case the (99, 590) grid. With the BHLYP method, the total energies are −2700.918287 and −2700.918105 hartree for SeF_3 (C_{2v}, C_s) with the standard and larger grid, respectively. The analogous results for SeF_3^- are −2701.042791 (standard grid) and −2701.042661 (large grid) hartree. Not entirely surprisingly and similar to the case of SF_3,[7] the C_{2v} planar structure turned out to be a transition state with a very small imaginary vibrational frequency 34i cm^{-1}, and the minimum becomes a butterfly-shape structure (C_s symmetry) with a dihedral angle 172.1°. The C_s structure lies 0.00043 eV (0.0099 kcal/mol) in energy lower than the C_{2v} structure. At the DZP++ SCF level of theory, with which all integrals are computed analytically, the C_{2v} structure, once again, has a small imaginary vibrational frequency (32i cm^{-1}), and the C_s structure with the torsion angle of 172.5° is a minimum. The latter has an energy 0.00033 eV (0.0076 kcal/mol) lower than the C_{2v} stationary point. The electron affinity EA_{ad} at the SCF level is predicted to be 2.73 eV (63.0 kcal/mol), which is slightly smaller than the DFT results. However, the B3LYP, BP86, and BLYP methods still predict the C_{2v} structure as the minimum, even when the larger (99, 590) integration grid is used. The electron affinity is not significantly affected for all four DFT methods using this larger (99, 590) grid with the change less than 0.01 eV. Our general conclusion is that with presently available DFT procedures, energy differences less than 0.1 kcal/mol are of dubious numerical stability.

For the SeF_3^- ion, which is planar with C_{2v} symmetry, there are likewise no experimental data with which to compare. The bonds have been elongated from the neutral structure, but the F−Se−F bond angle has remained virtually constant. The DZP++ BHLYP method predicts the geometrical parameters as 1.920 Å, 1.770 Å, and 86.2° for $Se-F_{eq}$, $Se-F_{ax}$, and <FSeF, respectively. The $Se-F_{eq}$ distance is significantly longer than that for the neutral species. Clearly, the character of the bonding in the SeF_3^- anion is quite different from that of the neutral one. The trend for the bond lengths with the different theoretical methods is similar to the neutral radical.

The theoretical EA_{ad}, EA_{vert}, and VDE values are listed in Table 3. The predicted range of EA_{ad} is from 3.14 to 3.41 eV, among which the DZP++ BHLYP method predicts the value 3.39 eV. In previous work on the sulfur analogues, for which many experimental EA values exist, it was found that DFT may slightly overestimate (<0.6 eV) the electron affinities of the larger species (SF_n, $n = 5,6$); however the DZP++ BHLYP method provided excellent agreement for the $n = 1-4$ series and was usually within 0.2 eV of experiment. Therefore, the EA_{ad} value from the BHLYP method for SeF_3 should be regarded as dependable. The EA_{ad} values obtained for SeF_3 from the other functionals are in a good agreement with BHLYP, showing deviation of about (or less than) 0.2 eV. The range of EA_{vert} is from 2.75 to 2.97 eV and the range of VDE is from 3.47 to 3.83 eV. The DZP++ BLYP EA_{ad} and EA_{vert} are lower than those obtained with the other functionals. Compared with SeF_2/SeF_2^-, these smaller differences between EA_{ad}, EA_{vert}, and VDE values are due to the minor changes in geometry between SeF_3 and SeF_3^-.

E. SeF_4 and SeF_4^-. The C_{2v} symmetry geometry of the $^1A_1$ ground state for SeF_4 and the C_{4v} symmetry geometry of the $^2A_1$ ground state of SeF_4^- are given in Figure 4. The geometries vary by as much as 0.08 Å from the experimental geometry of Brown's group.[25] As expected, the BHLYP method gives the shortest and most accurate bond lengths, within 0.006 Å of experiment. The BLYP method predicted the worst geometry with bond lengths 0.08 Å too long as well as an axial−equatorial angle in error by 4°. For comparison with other theoretical work done on the SeF_4 molecule, $Se-F_{eq}$ and $Se-F_{ax}$ bond distances, and $F_{eq}-Se-F_{eq}$ bond angles obtained by Bühl et al.[26] at the SCF/641(d), MP2/541(d), and MP2/962(d) levels of theory were 1.670, 1.713, and 1.707 Å; 1.747, 1.781, and 1.796 Å; and 102.1, 101.6, and 100.0°, respectively. Their SCF bond lengths are less than our DZP++ BHLYP results (1.688 and 1.774 Å). Their MP2 bond distances are longer than our DZP++ BHLYP results. This difference is due to the widely known fact that second-order perturbation theory almost always yields long equilibrium bond distances, even in the complete basis set limit.[27] Therefore, the most reliable Se−F bond distances are thought to be the present BHLYP results.

The electron affinities of SeF_4 are given in Table 3. The DZP++ BHLYP method gives the lowest EA_{ad} (2.50 eV) and EA_{vert} (0.69 eV). After ZPVE correction, the BHLYP value of EA_{ad} is 2.42 eV, which is in poor agreement with Harland and Thynne's (1973) experimental value of EA_{ad} (SeF_4) = 1.7 eV[2]. All of our theoretical electron affinities lie significantly above this experimental value, with the BHLYP being the lowest value. On the basis of our earlier extensive comparisons with experiment for related systems, it seems likely that the experimental EA for SeF_4 is incorrect. The EA_{vert} ranges from 0.69 to 1.03 eV and the VDE ranges from 4.67 to 5.05 eV, and thus the anion is quite stable on the basis of large electron detachment energy. Again, these large differences between EA_{ad}, EA_{vert}, and VDE values are due to the large differences in geometry between SeF_4 and SeF_4^-.

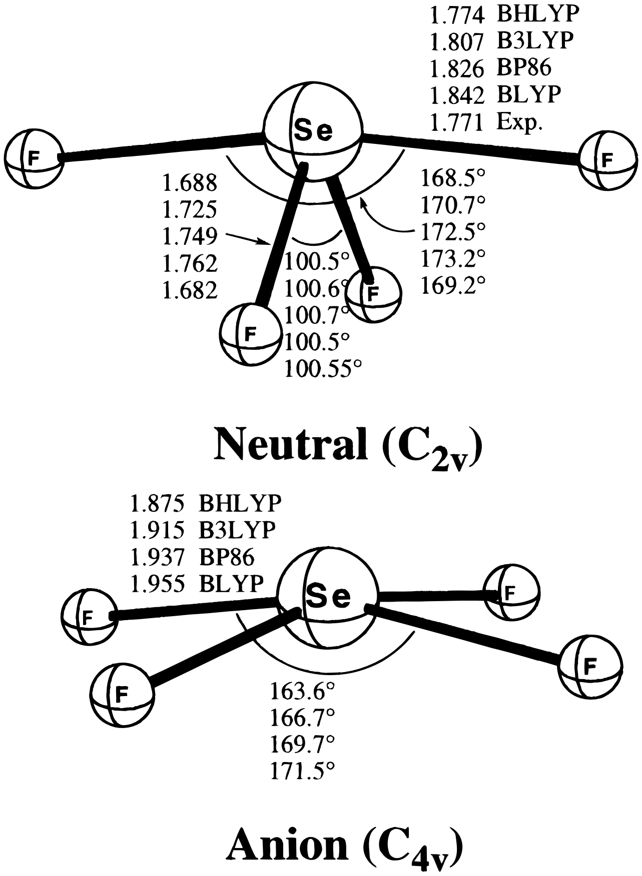

Figure 4. The molecular geometries in C_{2v} symmetry of the X $^1A_1$ state of neutral SeF_4 and the C_{4v} symmetry geometries of the X $^2A_1$ state of the anion, SeF_4^-. Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

F. SeF_5 and SeF_5^-. The C_{4v} symmetry geometry of the $^2A_1$ ground state of SeF_5 and the similar C_{4v} symmetry structure of the $^1A_1$ ground state of SeF_5^- are given in Figure 5. For the neutral SeF_5, the DZP++ BHLYP method predicts 1.740 and 1.671 Å for the $Se-F_{eq}$ and $Se-F_{ax}$ bond distances and 90.9° for the $F_{ax}-Se-F_{eq}$ angle, respectively. Analogous to SeF^- and SeF_3^-, the SeF_5^- ion has longer Se−F bond distances than the neutral. It is clear that the bonding in the anion (SeF_5^-) must be quite different from that for neutral species.

The EA_{ad}, EA_{vert}, and VDE values are reported in Table 3. The experimental EA_{ad} was reported as 3.3 eV in 1973,[2] but it was reported as ≥ 5.1 ± 0.4 eV 5 years later.[1] Our theoretical EA_{ad} values predicted by all functionals are larger than 5.1 eV. The DZP++ BHLYP method gives the closest EA_{ad} (5.23 eV) to the 1978 Compton experiment.[1] With correction for ZPVE, the BHLYP result (5.18 eV) is even closer to the Compton experiment. Thus it would appear that the 1973 experiment is in error. The EA_{vert} values range from 4.01 to 4.49 eV and the range for VDE is from 5.84 to 6.19 eV.

G. SeF_6 and SeF_6^-. The octahedral geometry of the $^1A_{1g}$ ground state of SeF_6 and the octahedral geometry of the $^2A_{2g}$ ground state of SeF_6^- are given in Figure 6. Again the DZP++

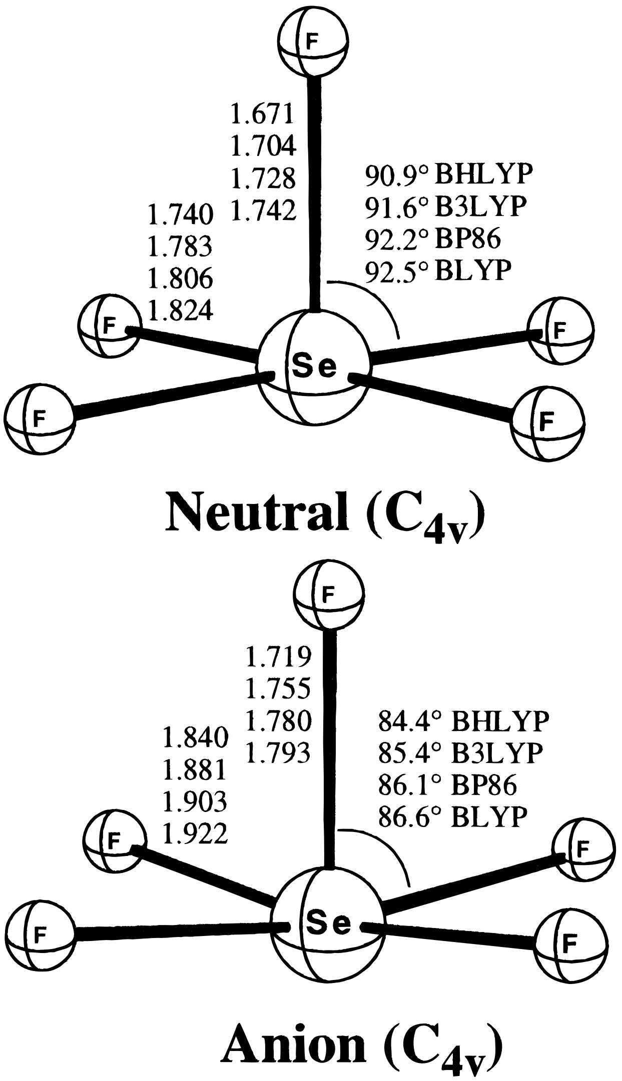

Figure 5. The molecular geometries in C_{4v} symmetry of the X $^2A_1$ state of neutral SeF_5 and the C_{4v} symmetry geometries of the X $^1A_1$ state of the anion, SeF_5^-. Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

BHLYP bond length (1.686 Å) is in the best agreement with the experimental result ($r_e = 1.678$ Å [28]). The DZP++ BLYP method predicted the poorest geometry, with a bond distance that is 0.08 Å too long. Compared with earlier theoretical work on SeF_6, the bond lengths obtained by SCF theory range from 1.652 to 1.675 Å, and with MP2 from 1.707 to 1.716 Å,[29] respectively. The SCF bond lengths are less than our DZP++ BHLYP (1.686 Å) distance, while the MP2 internuclear separations are larger than our DZP++ BHLYP results. As mentioned above, this difference between theoretical methods is due to the widely known fact that second-order perturbation theory often provides equilibrium bond distances that are too long, even in the complete basis set limit.[27]

The EA_{ad}, EA_{vert}, and VDE values are reported in Table 3. Again, The DZP++ BHLYP method gives the lowest EA_{ad} and EA_{vert}. The experimental values for EA_{ad} are 2.9 ± 0.2 eV by Compton et al.,[1] and 3.0 ± 0.2 eV by Boring et al.[30] The DZP++ BHLYP method predicted the smallest $EA_{ad} = 3.13$ eV, which is in satisfactory agreement with the experimental values. Even better agreement with experiment is found for the ZPVE corrected BHLYP result (2.95 eV). The BHLYP EA is also close to an earlier theoretical value (2.9 eV) obtained by Boring[31] with the multiple scattering (MS) X_α method. The other DFT methods predict too large EA values, in the range 3.95−4.39 eV. The EA_{vert} values range from 1.37 to 3.01 eV and the range for VDE is 4.72 to 5.35 eV.

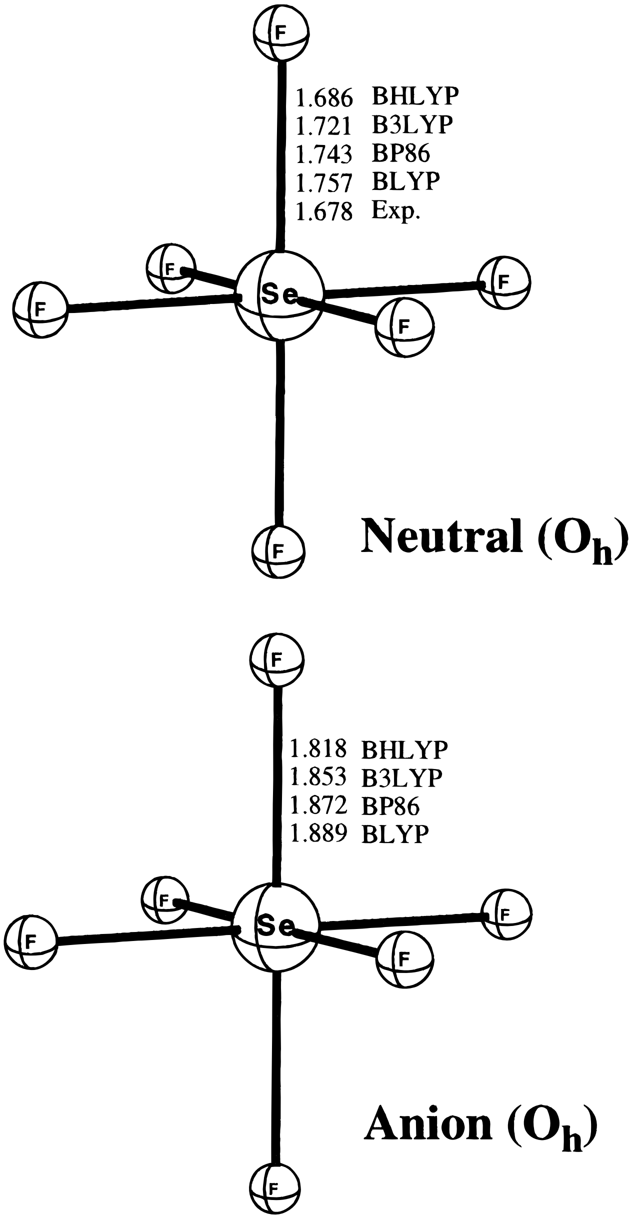

Figure 6. The molecular geometries in O_h symmetry of the X $^1A_{1g}$ state of neutral SeF_6 and the O_h symmetry geometries of the X $^2A_{2g}$ state of the anion, SeF_6^-. Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

H. SeF_7 and SeF_7^-. The molecular geometries of SeF_7 and SeF_7^- were also investigated. No significant minimum was found on the potential energy surface for the neutral SeF_7 species. However, similar to TeF_7^-,[32] a minimum D_{5h} symmetry structure was found for the SeF_7^- anion with all four DFT methods, and its geometry is shown in Figure 7. The DZP++ VDE for the D_{5h} structure is predicted as 8.01 eV(BHLYP), 7.05 eV(B3LYP), 6.23 eV (BP86), or 6.15 eV (BLYP). Two other structures with C_{4v} and C_{3v} symmetries (both of the $^1A_1$ ground state) were also found (Figure 7). The C_{4v} symmetry structure was confirmed to be a minimum by the evaluation of its harmonic vibrational frequencies with all four functionals, whereas the C_{3v} symmetry structure is confirmed as a minimum at only the DZP++ BHLYP level. At the DZP++ BHLYP level, the C_{3v} structure lies 0.36 eV (8.2 kcal/mol) higher in energy than the D_{5h} structure, and the C_{4v} structure is 0.07 eV (1.6 kcal/mol) higher than the C_{3v} structure.

For the SeF_7^- ion with D_{5h} symmetry structure, the DZP++ dissociation energies $D_e(F_6Se{-}F^-)$ are predicted as 0.67, 0.91, 1.11, and 1.11 eV by using the BHLYP, B3LYP, BP86, and BLYP methods, respectively. Those for the C_{4v} structure are 0.25, 0.95, 1.55, and 1.71 eV. Thus one has the peculiar result that the pentagonal bipyramid D_{5h} structure lies lower in energy with the BHLYP method, while the C_{4v} structure lies lower with the other DFT methods (B3LYP, BP86, and BLYP). When the larger integration grid (99, 590) is used, this unusual energetic ordering is unchanged. This exercise demonstrates the importance of using a range of such DFT methods for chemical problems for which the answer is not known in advance from experiment. Even better, one might use convergent quantum mechanical methods (e.g., coupled cluster theory with large basis sets).

I. Dissociation Energies. The neutral and anionic bond dissociation energies for SeF_n/SeF_n^- ($n = 1-6$) are given in Tables 4 and 5. The DZP++ BHLYP dissociation energies are much lower than those from the other three methods. It was found in the previous studies[7−12] that the DZP++ BHLYP predictions for dissociation energies were the worst of the four functionals employed. This highlights the necessity of being very selective in choosing DFT results for final theoretical predictions. Although the BHLYP method is excellent for the structures and electron affinities of these main group fluorides, the thermochemistry predicted by this method is unreliable. Because the DFT/HF hybrid BHLYP functional incorporates standard Hartree−Fock theory to the greatest degree of all the functionals used in this study, this finding is not surprising. It is well-known that Hartree−Fock (without the inclusion of dynamic or nondynamic correlation) performs poorly for bond-breaking processes.[33] The Hartree−Fock method seriously under-predicts dissociation energies, so the inclusion of 50% exact exchange in the BHLYP method transfers this Hartree−Fock problem to DFT.

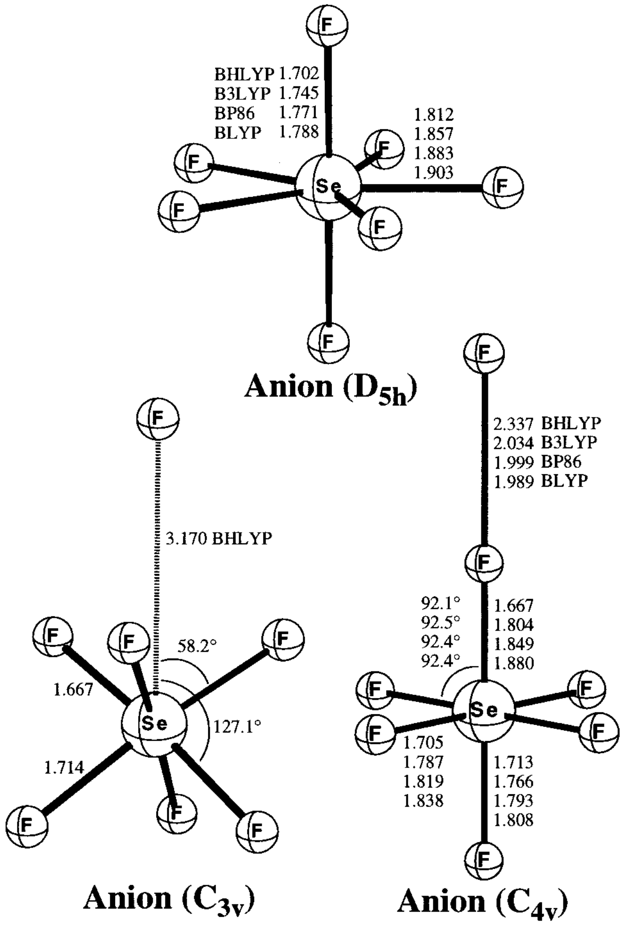

Figure 7. The molecular geometries of SeF_7^- with D_{5h}, C_{4v}, and C_{3v} symmetries. Bond lengths and bond angles are in angstroms and degrees, respectively. All results were obtained with the DZP++ basis set.

Table 4 shows the dissociation energies (for the process $SeF_n \rightarrow SeF_{n-1} + F$) pertaining to the neutral molecules. Excluding the DZP++ BHLYP results, the dissociation energy

TABLE 4: Dissociation Energies $D_e(SeF_n)$ for the Neutral Members of the Series in eV (or kcal/mol in parentheses) (Values Are Obtained with the DZP++ Basis Set, and Are Not Corrected for ZPVE)

dissociation	BHLYP	B3LYP	BP86	BLYP	expt
$SeF \rightarrow Se+F$	2.82 (65.6)	3.40 (78.4)	3.80 (87.6)	3.71 (85.6)	3.5[a]
$SeF_2 \rightarrow SeF+F$	3.01 (69.4)	3.50 (80.7)	3.87 (89.2)	3.78 (87.2)	
$SeF_3 \rightarrow SeF_2+F$	2.21 (48.9)	2.71 (62.5)	3.21 (74.0)	3.10 (71.5)	
$SeF_4 \rightarrow SeF_3+F$	3.26 (75.2)	3.56 (82.1)	3.84 (88.6)	3.67 (84.6)	
$SeF_5 \rightarrow SeF_4+F$	0.88 (20.3)	1.27 (29.3)	1.67 (38.5)	1.52 (35.1)	2.8[b]
$SeF_6 \rightarrow SeF_5+F$	3.34 (77.0)	3.31 (76.3)	3.44 (79.3)	3.15 (72.6)	3.15 ± 0.2[b]

[a] Ref 4a−b. [b] Ref 1.

TABLE 5: Dissociation Energies $D_e(SeF_n^-)$ for the Anionic Members of the Series in eV (or kcal/mol in parentheses) (Values Are Obtained with the DZP++ Basis Set, and Are Not Corrected for ZPVE)

dissociation	BHLYP	B3LYP	BP86	BLYP	expt[a]
$SeF^- \rightarrow Se^-+F$	3.19 (73.6)	3.71 (85.6)	4.04 (93.2)	3.98 (91.8)	
$SeF_2^- \rightarrow SeF^-+F$	2.85 (65.7)	3.38 (77.9)	3.75 (86.5)	3.70 (85.3)	
$SeF_3^- \rightarrow SeF_2^-+F$	3.79 (75.9)	3.71 (85.6)	4.01 (92.5)	3.93 (90.6)	
$SeF_4^- \rightarrow SeF_3^-+F$	2.37 (54.7)	3.02 (69.6)	3.52 (81.2)	3.46 (79.8)	
$SeF_5^- \rightarrow SeF_4^-+F$	3.61 (83.2)	3.84 (88.6)	4.08 (94.1)	3.89 (87.7)	
$SeF_6^- \rightarrow SeF_5^-+F$	1.23 (28.6)	1.83 (42.2)	2.26 (52.1)	2.13 (49.2)	1.09 ± 0.1
$SeF^- \rightarrow Se+F^-$	2.25 (51.8)	2.38 (54.8)	2.56 (59.1)	2.42 (55.9)	
$SeF_2^- \rightarrow SeF^+F^-$	2.28 (52.5)	2.36 (54.4)	2.52 (58.1)	2.42 (55.9)	
$SeF_3^- \rightarrow SeF_2+F^-$	2.56 (59.1)	2.57 (59.3)	2.66 (61.4)	2.57 (59.3)	
$SeF_4^- \rightarrow SeF_3^+F^-$	2.82 (65.0)	2.88 (66.5)	2.97 (68.6)	2.92 (67.4)	
$SeF_5^- \rightarrow SeF_4^+F^-$	3.17 (73.1)	3.17 (73.0)	3.20 (73.9)	3.14 (72.4)	
$SeF_6^- \rightarrow SeF_5^+F^-$	3.53 (81.3)	3.72 (85.8)	3.79 (87.5)	3.76 (86.7)	

[a] Ref 1.

for SeF ranges from 3.4 to 3.80 eV. This is in good agreement with the experimental value 3.5 eV, which was derived by O'Hare et al.,[4a−b] based on the heats of formation for Se, F, and SeF_2. Our DFT results are also in reasonable agreement with the early theoretical dissociation of energy of 3.2 ± 0.1 eV from O'Hare.[4c]

The theoretical dissociation energies for SeF_2 increase to the range of 3.50−3.87 eV. Table 4 shows that this value decreases for SeF_3 and increases for SeF_4 again. The same trend continues for SeF_5 and SeF_6. In other words, the dissociation energies are larger for SeF_n when n is even than when n is an odd number. This zigzag phenomenon can be readily explained. The SeF_n molecules with odd number n are radicals, and are less stable than those with even number n, which have closed-shell electronic structures. Another trend is that when the even number increases (i.e., from 2, 4, to 6), the dissociation energy decreases. The molecules with odd numbers show the same trend. This indicates in a qualitative way that the larger SeF_n molecules are less stable than the smaller ones, due to their increasing hypervalency. For SeF_5, our predicted neutral bond dissociation energies $D_e(F_4Se{-}F) =$ (BHLYP, 0.88 eV; B3LYP, 1.27 eV; BP86, 1.67 eV; BLYP, 1.52 eV) are lower than the experimental estimated value of 2.8 eV.[1] For SeF_6, the dissociation energy values are $D_e(F_5Se{-}F) =$ (BHLYP, 3.34 eV; B3LYP, 3.31 eV; BP86, 3.44 eV; BLYP, 3.15 eV). Except for the DZP++ BP86 results, the other methods match the experimental estimate 3.15 ± 0.2 eV of Compton[1] based on previous thermochemical data,[34] and the DZP++ BLYP method gives the "best" value of 3.15 eV.

For the anions, SeF_n^-, there are two forms of dissociation: either to a neutral SeF_{n-1} plus an F^- ion, or to SeF_{n-1}^- ion plus a neutral F atom. Excluding the DZP++ BHLYP dissociation energies, which are significantly smaller than the others, Table 5 shows that, for the dissociation to "$SeF_{n-1}^- + F$", the zigzag phenomenon is similar to that shown in Table 4. The amplitude of the zigzag is significant and the general trend is downward. The difference is that the molecules with odd number n are more stable because they have closed shell electronic structures. This may also be related to the fact that when n is even, the additional electron of the anion is residing in an antibonding orbital (primarily a σ^* orbital), lengthening and destabilizing those σ bonds. However, for the dissociation to $SeF_{n-1} + F^-$, the zigzag feature is not as obvious, and the general trend is upward. This indicates that when the size of the molecule increases, dissociation to a SeF_{n-1}^- plus a neutral F atom becomes preferable. The 1978 experiment by Compton, Reinhardt, and Cooper[1] measured $D_e(F_5Se{-}F) = 1.09 \pm 0.1$ eV. The DZP++ BHLYP method gives the result $D_e(F_5Se{-}F) = 1.23$ eV, while the other functionals predict the dissociation energies that are larger than experimental value (B3LYP, 1.83 eV; BP86, 2.26 eV; BLYP, 2.13 eV). If the dissociation trends discussed earlier hold up, the experimental $F_5Se{-}F$ dissociation energy may be too small.

The theoretical electron affinities for the F atom with the same methods used in this paper are 2.94 eV (BHLYP), 3.54 eV (B3LYP), 3.76 eV (BP86), and 3.68 eV (BLYP). These data are relevant to the dissociation in terms of the different dissociation channels, and they should suggest the accuracy of the results.

J. Bond Distances and Molecular Orbitals. For the previously studied BrF_n systems,[12] the bond length differences between neutral and anionic species which contain an odd number of F atoms are greater than the corresponding differences in those BrF_n with even numbers of F atoms. However, the situation for SeF_n is just opposite. To explain why the SeF_n systems is different from BrF_n, we need to investigate those molecular orbitals to which an electron is added in going from the neutral molecules to the anions.

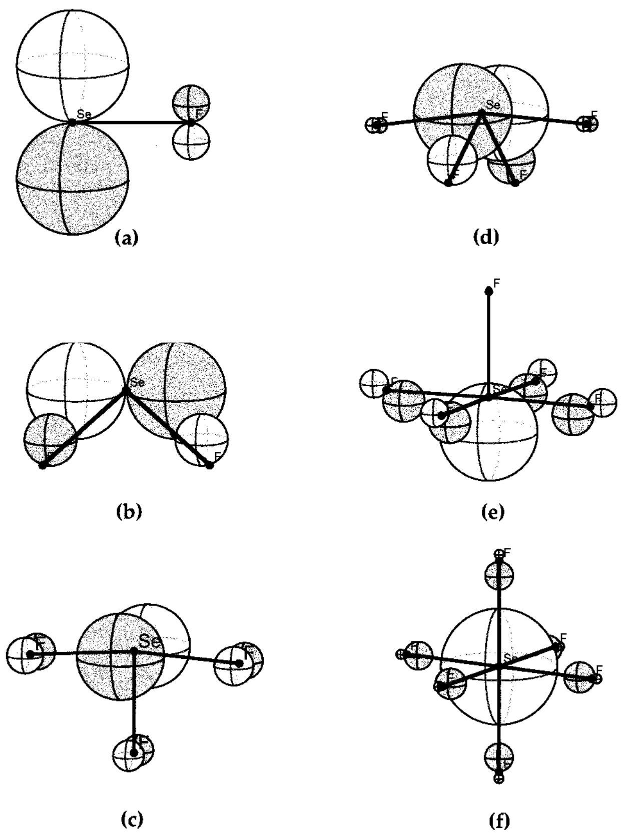

Figure 8. The singly occupied (SeF, SeF_3, and SeF_5) and the lowest unoccupied (SeF_2, SeF_4, and SeF_6) molecular orbitals: (a) 5π, SOMO of SeF; (b) 8b_2, LUMO of SeF_2; (c) 6b_1, SOMO of SeF_3; (d) 9b_1, LUMO of SeF_4 (e) 14a_1, SOMO of SeF_5; (b) 7a_{1g}, LUMO of SeF_6.

Figure 8 shows the singly occupied (SeF, SeF_3, and SeF_5) and the lowest unoccupied (SeF_2, SeF_4, and SeF_6) molecular orbitals (SOMO and LUMO, respectively). All of these are antibonding molecular orbitals. Adding an electron to these orbitals will thus decrease the bond order, and accordingly lengthen the bond distances. However, because there is one less electron in the SeF_n system than in BrF_n, the SOMOs and LUMOs in SeF_n are quite different from those in BrF_n. (Compare Figure 8 in this paper to Figure 6 in ref 12). The SeF_n molecules containing an odd number of F atoms have a SOMO with antibonding π character, while those with an even number of F atoms have a σ-type LUMO. The latter has a stronger effect on the bond distance when an electron is added than the former (π-type). Therefore, contrary to the situation of BrF_n, the bond length differences between neutral and anionic species for SeF_n which contain an odd number of F atoms are smaller than the corresponding differences in those SeF_n with even numbers of F atoms.

Note also that the symmetries for anionic SeF_2^- and SeF_4^- are different from those for their neutral species, and thus the order of the molecular orbitals would change. The bond distances could similarly be influenced.

Conclusions

On the basis of the experimental EA_{ad} values for the Se atom, SeF_5, and SeF_6 molecules, and the previous work on the SF_n/SF_n^-, PF_n/PF_n^-, ClF_n/ClF_n^-, SiF_n/SiF_n^-, C_2F_n/$C_2F_n^-$, and BrF_n/

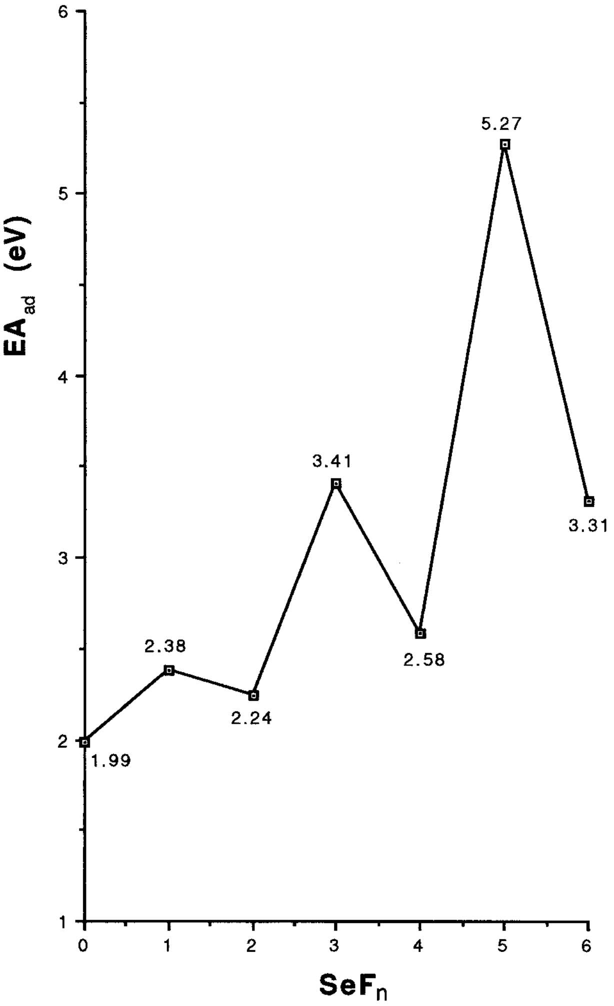

Figure 9. The plot of "the best theoretical adiabatic electron affinities", which are BHLYP results after ZPVE correction, for SeF$_n$ ($n = 0-6$).

BrF$_n^-$ molecules,[7-12] we have concluded that the DZP++ BHLYP method is the most reliable method for predicting the electron affinities [1.99 eV (Se), 2.37 eV (SeF), 2.21 eV (SeF$_2$), 3.39 eV (SeF$_3$), 2.50 eV (SeF$_4$), 5.23 eV (SeF$_5$), 3.13 eV (SeF$_6$)] and molecular structures of the selenium fluorides. After ZPVE corrections, the EA$_{ad}$ values are predicted to be 1.99 eV (Se), 2.38 eV (SeF), 2.24 eV(SeF$_2$), 3.41 eV (SeF$_3$), 2.58 eV (SeF$_4$), 5.27 eV (SeF$_5$), 3.31 eV (SeF$_6$). A plot of "the best" theoretical results are shown in Figure 9. The experimental EA for SeF$_4$ appears to be incorrect.

Compared with available experimental geometrical parameters (SeF, SeF$_4$, and SeF$_6$), the mean errors of the bond distance for the four density functionals are 0.003 Å (BHLYP), 0.033 Å (B3LYP), 0.053 Å (BP86), and 0.067 Å (BLYP). Similarly, for the bond angle (only SeF$_4$ is reliably known from experiment), the errors of the DFT methods are 0.4° (BHLYP), 0.8° (B3LYP), 1.7° (BP86), and 2.0° (BLYP), respectively. The DZP++ BHLYP structures clearly provide the best agreement with experiment.

Unlike the geometries and EA values for these molecules, the DZP++ BHLYP method is considered to yield the least reliable predictions of dissociation energies, as shown earlier for related molecules.[7-12] This may be correlated with the fact that the BHLYP functional incorporates the largest fraction of the Hartree−Fock method; thus, similar to the SCF method, its performance for dissociation energies is less than desirable. The dissociation energy range for the neutral members of these chalcogen fluorides, excluding the DZP++ BHLYP values, are 3.40−3.80 eV (SeF), 3.50−3.87 eV (SeF$_2$), 2.71−3.21 eV (SeF$_3$), 3.56−3.84 eV (SeF$_4$), 1.27−1.67 eV (SeF$_5$), and 3.15−3.44 eV (SeF$_6$). The general trend for dissociation energy values is BP86 $\sim$ BLYP $>$ B3LYP $\gg$ BHLYP. Compared to the experimental dissociation energy for SeF$_6$ (3.15 ± 0.2 eV), our predictions are reasonable, but the experimental dissociation energy for SeF$_5$ (2.8 eV) appears to be too large. The dissociation energy ranges for losing F from the SeF$_n^-$ anions are 3.19−4.04 eV (SeF$^-$), 2.85−3.75 eV (SeF$_2^-$), 3.71−4.01 eV (SeF$_3^-$), 2.37−3.52 eV (SeF$_4^-$), 3.61−4.08 eV (SeF$_5^-$), and 1.23−2.26 eV (SeF$_6^-$). The general trend is BP86 $>$ BLYP $>$ B3LYP $\gg$ BHLYP. The dissociation energy ranges for losing F$^-$ from the SeF$_n^-$ anions are 2.25−2.56 eV (SeF$^-$), 2.28−2.52 eV (SeF$_2^-$), 2.56−2.66 eV (SeF$_3^-$), 2.82−2.97 eV (SeF$_4^-$), 3.14−3.20 eV (SeF$_5^-$), and 3.53−3.79 eV (SeF$_6^-$), and the general trend is BP86 $\sim$ BLYP $>$ B3LYP $\sim$ BHLYP. Thus, except for SeF$_6^-$, the lower energy dissociation limit is always to the F$^-$ anion. The lone experimental dissociation energy, for $SeF_6^- \rightarrow SeF_5^- + F$, appears to be too small.

The range of selenium−fluorine bond distances predicted here is of special interest. For this purpose we consider only the more reliable BHLYP predictions. The neutral Se−F bond distances are 1.743 Å (SeF), 1.733 Å (SeF$_2$), 1.701 and 1.795 Å (SeF$_3$), 1.688 and 1.774 Å (SeF$_4$), 1.671 and 1.740 Å (SeF$_5$), and 1.686 Å (SeF$_6$). Thus, the entire range, from 1.671 to 1.795 Å, is 0.124 Å. The negative ion Se−F bond distances are 1.847 Å (SeF$^-$), 1.954 Å (SeF$_2^-$), 1.770 and 1.920 Å (SeF$_3^-$), 1.875 Å (SeF$_4^-$), 1.719 and 1.840 Å (SeF$_5^-$), 1.818 Å (SeF$_6^-$), and 1.702 and 1.812 Å (SeF$_7^-$, D_{5h}). We see that the closed-shell SeF$^-$, SeF$_3^-$, and SeF$_5^-$ have Se−F bond distances longer than the neutral selenium fluorides by within 0.1 Å, but the distances for SeF$_2^-$, SeF$_4^-$, and SeF$_6^-$ are all much longer (around 0.2 Å) than those observed for the neutral selenium fluorides. One is tempted via ideas such as Badger's Rule to suggest that unusually long bond distances might be associated with low electron affinities. Such an argument may be applied to the SeF$_2$, SeF$_4$, and SeF$_6$ systems, which have smaller EA values and longer anion bond distances. However, one should be careful about invoking Badger's rule with F compounds and ionic dissociation limits.

We hope that our theoretical predictions will provide strong motivation for future experimental studies of these important chalcogen fluorides and their anions.

Acknowledgment. This research was supported by Key Laboratory of Theoretical and Computational Chemistry of Jilin University, National Science Foundation in China, and the US National Science Foundation, Grant CHE-9815397.

References and Notes

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

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

(3) Hotop, H.; Lineberger, W. C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 731.

(4) (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. (c) O'Hare, P. A. G. *J. Chem. Phys.* **1974**, *60*, 4084.

(5) (a) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *B 136*, 864. (b) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *A 140*, 1133. (c) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford: New York, 1989. (d) Jones, R. O.; Gunnarsson, O. *Rev. Mod. Phys.* **1989**, *61*, 689. (e) *Density Functional Methods in Chemistry*; Labanowski J. K.; Andzelm, J., Eds.; Springer-Verlag: New York, 1989. (f) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(6) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 5612.

(7) (a) King, R. A.; Galbraith, J. M.; Schaefer, H. F. *J. Phys. Chem*. **1996**, *100*, 6061. (b) Galbraith, J. M.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 863.

(8) Tschumper, G. S.; Fermann, J. T.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *104*, 3676.

(9) Van Huis, T. J.; Galbraith, J. M.; Schaefer, H. F. *Mol. Phys*. **1996**, *89*, 607.

(10) King, R. A.; Mastryukov, V. S.; Schaefer, H. F. *J. Chem. Phys.* **1996**, *105*, 6880.

(11) King, R. A., Pettigrew, N. D.; Schaefer, H. F. *J. Chem. Phys.* **1997**, *107*, 8536.

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

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

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1993**, *B 37*, 785.

(15) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

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

(17) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822; *34*, 7046.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P., Head-Gordon, M., Gonzalez, C.; Pople, J. A.; GAUSSION 94 (Revisions E. 1 and C. 3) Gaussian, Inc., Pittsburgh, PA, 1995.

(19) (a) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. (b) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823. (c) Huzinaga, S. *Approximate Atomic Wave functions*; Department of Chemistry, University of Alberta:??, 1971; Vol. II. (d) Dunning, T. H.; Hay, P. J. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; pp 1−27.

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

(21) Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1985**, *83*, 1784.

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

(23) Kraatz, H.-B.; Jacobsen, H.; Ziegler, T.; Boorman, P. M. *Organometallics* **1993**, *12*, 76.

(24) (a) Herzberg, G.; Teller, E. *Z. Phys. Chem. Abt*. **1933**, *B 21*, 410. (b) Renner, R. *Z. Phys.* **1934**, *92*, 172. (c) Lee, T. J.; Fox, D. J.; Schaefer, H. F.; Pitzer, R. M. *J. Chem. Phys.* **1984**, *81*, 356.

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

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

(27) Peterson, K. A.; Dunning, T. H. *J. Mol. Struct. (THEOCHEM)* **1997**, *400*, 93.

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

(29) Klobukowski M. *J. Comput. Chem*. **1993**, *14*, 1234.

(30) Boring, M.; Wood, J. H.; Moskowitz, J. W. *J. Chem. Phys*. **1974**, *61*, 3800.

(31) Boring, M. *Chem. Phys. Lett*. **1977**, *46*, 242.

(32) Selig, H.; Sarig, S.; Aramowitz, S. *Inorg. Chem.* **1974**, *13*, 1508.

(33) Roos, B. O. In *Ab Initio methods in Quantum Chemistry*; Lawley, K. P., Ed.; John Wiley & Sons: New York, 1987; pp 399−445.

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