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The gas-phase thermochemistry of SeF_n, SeF_n^+, and SeF_n^- ($n = 1$–6) from Gaussian-3 calculations

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Abstract

Quantum chemistry calculations have been carried out on selenium fluorides $SeF_{1–6}$ at Gaussian-3 level for thermodynamic properties including the enthalpies of formation, adiabatic ionization potentials, electron affinities, and the appearance energies of cation fragments in the photoionization of SeF_6. The G3 calculations on $SeH_{0–2}{}^{0,\pm1}$ and enthalpy of formation of SeF_6 are in excellent agreement with experiments; however, the appearance energies of $SeF_{2–5}{}^+$ fragments from photoionization of SeF_6 and other quantities are in large disagreement with the existing experimental measurement and previous theoretical predictions.

Keywords: Selenium fluoride; Enthalpy of formation; Ionization potential; Electron affinity

1. Introduction

Little information is available on the thermochemistry of selenium fluorides and their ionic forms. The main interest is on their hypervalent structures analogous to sulfur fluorides, even though the SeF_6/Ar plasma has been used to modify the surface of TeSe alloy [1] and been used as the reagents for the synthesis of their perfluoroalkyl derivatives [2]. The gas-phase enthalpy of formation of SeF_6 has been determined from the fluorine bomb calorimetric measurement [3]; while the attempts for SeF_4 using classical thermodynamic techniques have obtained values with high uncertainties [4,5], largely due to the difficulty in preparing pure substances and measuring the enthalpy change for phase transition, and lack of the accurate values for the accompany compounds. Measurements from ion chemistry studies yielded satisfied results for selenium compounds neither [6–11], except for H_2Se system [12].

There have been only a few theoretical studies on this system, including the MP4 and G2 calculations on H_2Se, SeH, and ions [13,14], and density functional theory (DFT) studies on electron affinities of SeF_n ($n = 0$–6) and dissociation energies of Se–F bonds in neutrals and anions [15]. For H_2Se system, the G2 calculations and photoionization studies on H_2Se are in reasonable agreement. For $SeF_n{}^{0,-1}$, the DFT electron affinities and dissociation energies are in large discrepancy with the available experimental values, where the uncertainties can be as large as tens or more than 100 kJ/mol. It is also noticed the disagreement between different (hybrid HF-)DFT calculations on the electron affinities, and no preferential can be given to certain method [15]. The purpose of the present study is to provide the thermodynamic properties for selenium sulfides and their ionic forms from high-level quantum chemistry calculations, and to assess the reliability of the experimental data.

2. Computational methods

The molecular orbital theory and density functional theory (DFT) calculations are performed using Gaussian 98 suite of programs [16]. The geometries are optimized at DFT-B3LYP level of theory [17,18] with basis 6–31G(2df,p) augmented by diffuse functions to give proper description for anions, i.e., 6–31 + G(2df,p) [19,20]. Vibrational frequencies are evaluated at the same level of theory for zero-point energy corrections with scale factor of 0.9854. The single point electronic energies are calculated at Gaussian-3 (G3) level of theory [20,21] which approximates QCISD(T,Full)/G3Large level of electron correlation. First-order spin–orbit interactions are added only to atomic and linear species with degenerate electronic

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ground states. Second-order spin–orbit and non-scalar relativistic effects are presumably embedded in the G3 high-level correction parameters, therefore not included [14]. These terms have been found to be of minor importance for small species; while they will surely be significant for species containing heavy atoms.

The enthalpies of formation are obtained from the G3 atomization energies. $\Delta_f H^\circ_{0\,\mathrm{K}}$ of Se(g) is taken as

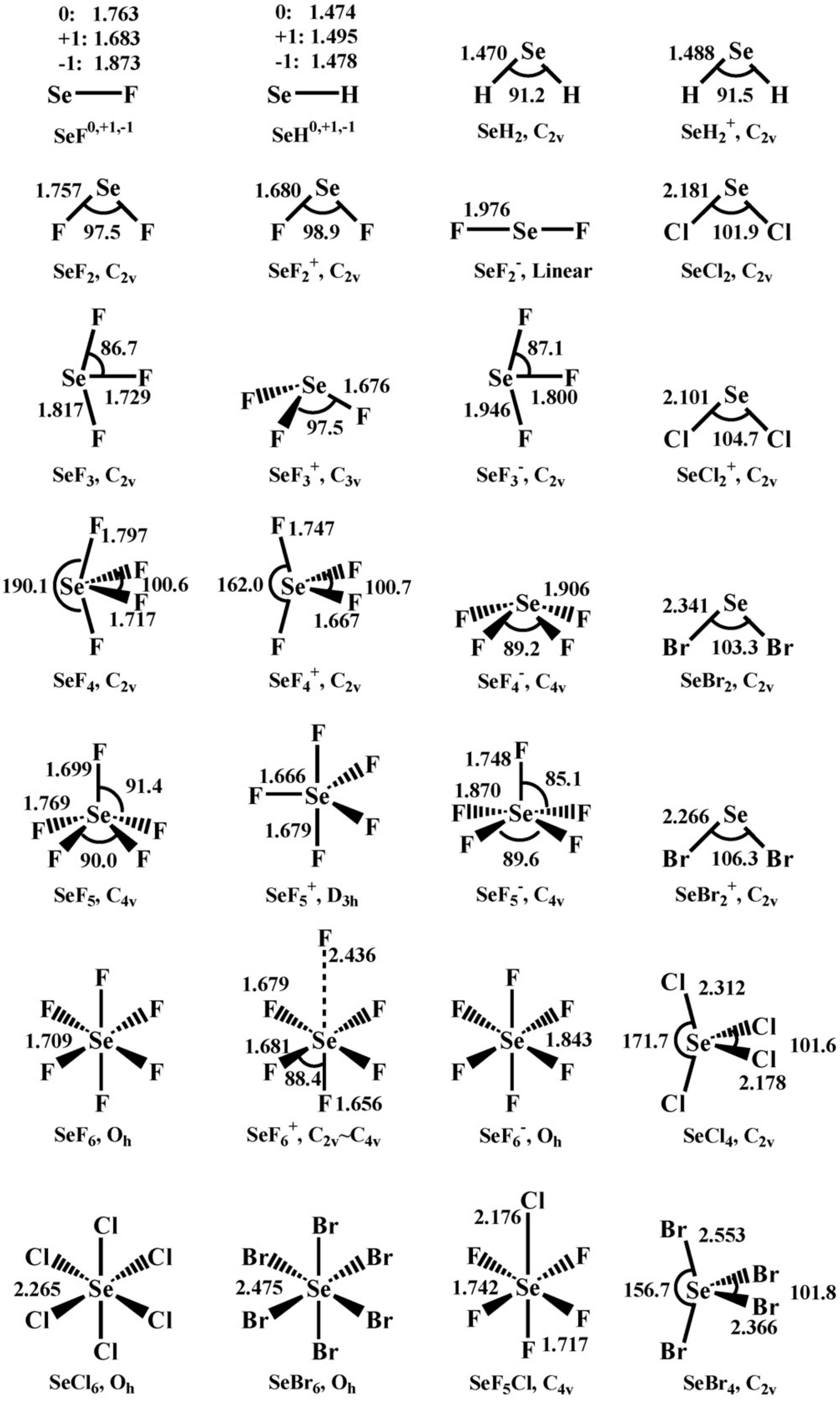

Fig. 1. Theoretical equilibrium structures optimized at B3LYP/6–31 + G(2df,p) level.

242.25 ± 1.26 kJ/mol, which was obtained from the appearance energy of Se^+ from photoionization of H_2Se (11.916 ± 0.006 eV) [12], the ionization potential of Se(g) (9.752 eV), and the enthalpy of formation of H_2Se(g) (33.5 kJ/mol) [22]. The thermal correction H^{298}–H^0 for Se(s) is taken from CODATA (5.52 kJ/mol) [23].

3. Results and discussion

Fig. 1 depicts the equilibrium structures of SeF_n, SeF_n^+, and SeF_n^- ($n = 1$–6) and a few selenium chlorides and bromides optimized at B3LYP/6–31 + G(2df,p) level. Compared with the experimental structures of SeF_2, SeF_4, and SeF_6, the theoretical model over-predicts the bond lengths by ca. 0.02 Å [24–27]. The species have the same symmetry as their sulfur analogs optimized at MP2(full)/6–31G(d) level [28–32], except for SeF_3, and the structures can be rationalized by VESPR model as well. For SeF_n, all the SOMOs in $SeF_{1,3,5}$ and the LUMOs in $SeF_{2,4,6}$ have antibonding characteristics; thereafter the Se–F bonds are lengthened from cations to neutrals to anions. Table 1 lists the G3 electronic energies, from which the enthalpies of formation($\Delta_f H^\circ$), ionization potentials (IPs), electron affinities (EAs), appearance energies (AEs) of ion fragments, and bond dissociation energies (D_0) can be readily derived (Tables 1, 2 and Fig. 2). The calculated G3 EAs agree closely with DFT ones on $SeF_{1,3,5}$, while they are always lower than the DFT ones for $SeF_{2,4,6}$ [15]. The G3 results are also used to interpret the dissociative photoionization experiment on SeF_6 and its reactions with several anions and cations. For comparison, the corresponding D_0, IPs, and EAs for SF_n system is also given in Fig. 2.

3.1. Comparison of G3 calculations and photoionization study on H_2Se

The results from G3 calculations are first compared with the photoionization studies on H_2Se and with previous theoretical studies. In the photoionization study of H_2Se, Gibson et al. obtained AE(Se^+) = 11.876 ± 0.006 eV and IP(Se) = 9.7524 eV [12], with which the corresponding G3 values of 11.841 and 9.727 eV agree within 0.04 eV. The G3 IPs of H_2Se and SeH of 9.847 and 9.901 eV agree excellently with the experimental ones of 9.845 ± 0.003 and 9.886 ± 0.003 eV, respectively [12]; but the predicted AE(SeH^+) = 13.19 eV from H_2Se ($H_2Se \rightarrow SeH^+ + H$) is slightly lower than the experiment (13.266 ± 0.007 eV) by ca. 7 kJ/mol. This difference propagates to the D_0(HSe–H) = 322.6 and D_0(Se–H) = 315.4 kJ/mol at G3 level versus 330.49 ± 0.75 and 310.75 ± 0.96 kJ/mol by Gibson et al. However, the summation of these two D_0s, namely, the atomization energy of H_2Se (637.9 kJ/mol at 0 K by G3) agrees with the experimental

Table 1
Gaussian-3 total energies at 0 K (ZPE included, in Hartree) and the enthalpies of formation of neutrals using G3 atomization energies (in kJ/mol), ionization potentials and electron affinities (in eV)

Species	Neutrals			Cations		Anions	
	E	$\Delta_f H^\circ_{0\,K}$	$\Delta_f H^\circ_{298\,K}$	E	IP	E	EA
F	−99.68576	77.28	79.39	−99.04612	17.465	−99.81136	3.418
Se	−2400.91421	242.25	242.93	−2400.55675	9.727	−2400.99230	2.125
SeH	−2401.53525	142.9	141.9	−2401.17736	9.847	−2401.61741	2.236
H_2Se	−2402.15903	36.4	32.4	−2401.79518	9.901	−2402.13717	−0.595
SeF	−2500.72227	−1.6	−2.5	−2500.36166	9.813	−2500.81199	2.442
						2.38–2.54 [15]	
SeF_2	−2600.54135	−274.3	−276.7	−2600.17362	10.006	−2600.61603	2.032
						2.24–2.45 [15]	
SeF_3	−2700.31974	−440.3	−443.5	−2699.99842	8.744	−2700.97208	3.385
						3.16–3.43 [15]	
SeF_4	−2800.15088	−744.7	−750.6	−2799.69157	12.499	−2800.23346	2.247
						2.58–3.00 [15], 1.7 [44]	
SeF_5	−2899.88251	−787.8	−795.3	−2899.49384	10.576	−2900.07495	5.236
						5.28–5.29 [15], ≥5.1 ± 0.4 [7]	
SeF_6	−2999.71926	−1107.0	−1118.6	−2999.18625	14.504	−2999.82269	2.815
						3.31–4.57 [15], 2.9 ± 0.2 [7]	
SeCl	−2861.00670	112.5	111.8	−2860.66037	9.424	−2861.09940	2.522
$SeCl_2$	−3321.08922	−17.3	−18.8	−3320.74525	9.360	−3321.17758	2.404
$SeCl_3$	−3781.11434	16.7	14.5	−3780.82253	7.941	−3781.26812	4.185
$SeCl_4$	−4241.18298	−63.5	−64.8				
$SeCl_5$	−4701.19397	7.6	6.8				
$SeCl_6$	−5161.23537	−1.2	−4.1				
SeBr	−4974.51955	133.5	125.5	−4974.18036	9.230	−4974.61444	2.582
$SeBr_2$	−7548.11333	55.2	39.3	−7547.77857	9.109	−7548.20517	2.499
$SeBr_3$	−10121.65577	130.4	89.9				
$SeBr_4$	−12695.22576	95.7	66.9				
$SeBr_5$	−15268.75539	185.8	150.4				
$SeBr_6$	−17842.29687	244.7	201.5				
SeF_5Cl	−3359.96909	−915.2	−925.4				

Table 2
G3 enthalpies of reactions of anions with SeF_6 (0 K, in kJ/mol)

Reactions	$\Delta_r H^\circ_{0\,K}$	Reactions	$\Delta_r H^\circ_{0\,K}$
$CF_3^- + SeF_6 \rightarrow CF_3 + SeF_6^-$	−97.4	$CF_3^+ + SeF_6 \rightarrow CF_4 + SeF_5^+$	−0.9
$CF_3^- + SeF_6 \rightarrow CF_4 + SeF_5^-$	−475.8		
$CF_3^- + SeF_6 \rightarrow CF_3 + SeF_5^- + F$	65.3	$CF_2^+ + SeF_6 \rightarrow CF_3 + SeF_5^+$	−35.6
		$CF_2^+ + SeF_6 \rightarrow CF_4 + SeF_4^+$	−270.8
$O_2^- + SeF_6 \rightarrow O_2 + SeF_6^-$	−234.4	$CF_2^+ + SeF_6 \rightarrow CF_4 + SeF_3^+ + F$	−251.4
$O_2^- + SeF_6 \rightarrow FO_2 + SeF_5^-$	−123.6		
$O_2^- + SeF_6 \rightarrow O_2 + SeF_5^- + F$	−72.6	$H_2O^+ + SeF_6 \rightarrow H_2O + SeF_5^+ + F$	201.4
		$H_2O^+ + SeF_6 \rightarrow HO + HF + SeF_5^+$	124.4
$O^- + SeF_6 \rightarrow O + SeF_6^-$	−140.9		
$O^- + SeF_6 \rightarrow FO + SeF_5^-$	−191.3	$O^+ + SeF_6 \rightarrow O + SeF_5^+ + F$	108.0
$O^- + SeF_6 \rightarrow O + SeF_5^- + F$	21.9	$O^+ + SeF_6 \rightarrow OF + SeF_5^+$	−105.2
$OH^- + SeF_6 \rightarrow OH + SeF_6^-$	−100.6	$F^+ + SeF_6 \rightarrow 2F + SeF_5^+$	−262.6
$OH^- + SeF_6 \rightarrow FOH + SeF_5^-$	−132.8	$F^+ + SeF_6 \rightarrow F_2 + SeF_5^+$	−411.5
$OH^- + SeF_6 \rightarrow OH + SeF_5^- + F$	62.1		
		$CO^+ + SeF_6 \rightarrow CO + SeF_5^+ + F$	62.8
$F^- + SeF_6 \rightarrow F + SeF_6^-$	58.2	$CO^+ + SeF_6 \rightarrow FCO + SeF_5^+$	−76.8
$F^- + SeF_6 \rightarrow 2F + SeF_5^-$	221.0		
$F^- + SeF_6 \rightarrow F_2 + SeF_5^-$	72.0	$h\nu + SeF_6 \rightarrow SeF_6^+ + e$	1399.4
		$h\nu + SeF_6 \rightarrow SeF_5^+ + F + e$	1416.8
$e^- + SeF_6 \rightarrow SeF_6^-$	−271.5	$h\nu + SeF_6 \rightarrow SeF_4^+ + F_2 + e$	1573.8
$e^- + SeF_6 \rightarrow F + SeF_5^-$	−108.8	$h\nu + SeF_6 \rightarrow SeF_4^+ + 2F + e$	1722.8
		$h\nu + SeF_6 \rightarrow SeF_3^+ + F_2 + F + e$	1593.2
		$h\nu + SeF_6 \rightarrow SeF_3^+ + 3F + e$	1742.2
		$h\nu + SeF_6 \rightarrow SeF_2^+ + 2F_2 + e$	1809.3
		$h\nu + SeF_6 \rightarrow SeF_2^+ + F_2 + 2F + e$	1958.3
		$h\nu + SeF_6 \rightarrow SeF_2^+ + 4F + e$	2107.2

value of 640.8 kJ/mol within 4 kJ/mol. The resulted G3 $\Delta_f H^\circ_{298\,K}$ (H_2Se) of 32.4 kJ/mol is in better agreement with the reference 29.3 kJ/mol than G2 and modified G1 predictions of 38.1 and 41.0 kJ/mol, respectively [13,14].

3.2. *Enthalpies of formation of selenium fluorides, chlorides, and bromides*

Unlike the SF_n system on which extensive theoretical and experimental studies are available, there are much less studies on SeF_n system. Furthermore, the experimental results for $SeF_n^{0,\pm1}$ species usually have fairly large uncertainties, except for SeF_6 where $\Delta_f H^\circ_{298\,K}$ (g) with chemical accuracy has been obtained from the fluorine-bomb calorimetry study [3]. Unfortunately, this technique could not be applied to the partially fluorinated SeF_4 or SeF_2. The main purpose of present G3 calculations is therefore to assess the reliability of the previous experiments and to provide a set of values for future comparison.

The theoretical enthalpies of formation of SeF_n are determined from the G3 atomization energies. For comparison, values for $SeCl_n$ and $SeBr_n$ are also calculated at the same level of theory. The G3 $\Delta_f H^\circ_{298\,K}$ (SeF_6) = −1118.6 kJ/mol

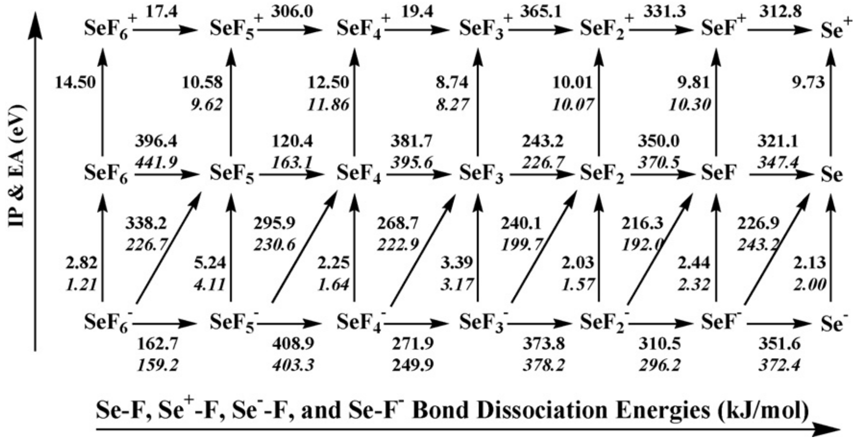

Fig. 2. Schematic diagram for G3 adiabatic ionization potentials, electron affinities of SeF_n and bond dissociations of Se–F, Se^+–F, Se^-–F, and Se–F^- in $SeF_n^{0,\pm1}$ (n = 0–6), and comparisons with their sulfur counterparts (in italics, from [30] at G3 level for D_0 and electron affinities, and from [29] at G2MP2 level for ionization potentials).

is in excellent agreement with the experimental value of −1118.0 ± 0.5 kJ/mol [3]; while discrepancies between theory and experiments for other species are fairly large. $\Delta_f H^\circ_{298\,\mathrm{K}}$ (SeF_4, g) = −802 kJ/mol could be derived from the measured $\Delta_f H^\circ_{298\,\mathrm{K}}$ (SeF_4, l) = −849.4 ± 24.3 kJ/mol and the estimated ΔH_{Vap} = 47 kJ/mol by Carre et al. [4,5]. The value is much lower than the G3 prediction of −750.6 kJ/mol. Similarly, a rough estimation $\Delta_f H^\circ_{298\,\mathrm{K}}$ ($SeCl_4$, g) = −10 kJ/mol can be obtained from the measured $\Delta_f H^\circ_{298\,\mathrm{K}}$ ($SeCl_4$, l) = −184.4 ± 4.8 kJ/mol [33] and ΔH_{Vap} = 175 kJ/mol from the vapor pressure measurements between 347 and 465 K [34]. The value is ca. 55 kJ/mol higher than the G3 prediction of −64.5 kJ/mol. The large discrepancy arises likely from the almost complete decomposition of $SeCl_4$(g) to $SeCl_2$(g) + Cl_2(g) at the experimental temperatures, which imposes difficulty in obtaining the actual vapor pressure of $SeCl_4$. Attempt on ΔH_{Vap} ($SeCl_4$, l) obtained indeed the enthalpy change for $SeCl_4(l) \rightarrow SeCl_2(g) + Cl_2(g)$ [35], and gas-phase electron diffractions of $SeCl_4$ have produced the structure of $SeCl_2$(g) instead [36–38]. The measurement for ΔH_{Vap} obtained likely $\Delta H_{\mathrm{Vap}} + \Delta_r H$ for reaction $SeCl_4(g) \rightarrow SeCl_2(g) + Cl_2(g)$. With $\Delta_r H$(G3) = 55.3 kJ/mol, ΔH_{Vap} would be ca. 120 kJ/mol, and experimental $\Delta_f H^\circ_{298\,\mathrm{K}}$ ($SeCl_4$, g) is ca. −64 kJ/mol, agreeing with G3 calculation. $\Delta_f H^\circ$ ($SeCl_2$, g) = −45 kJ/mol has also been estimated from the decomposition of $SeCl_4$(s) by Yost and Kircher [35], compared to the G3 values of −17.3 kJ/mol at 0 K and −18.8 kJ/mol at 298 K.

There has been no experimental observation of SeF_5 or SeF_3 radical; while SeF radical was first observed by Carrington et al. in reaction of CSe_2 with F-atom [39]. The ground state of SeF is $^2\Pi$ with spin-orbital interaction of $-560\ \mathrm{cm}^{-1}$ and bond length of 1.742 Å [40], compared to B3LYP value of 1.763 Å. No experimental measurement is available on its heat of formation, IP, or EA. D_0(Se–F) has been estimated as 309 ± 10 kJ/mol (3.2 ± 0.1 eV) from the corrected Hartree–Fock value of 3.29 eV as upper limit and average of Se–F bond strength of 3.1 eV in SeF_6 as the lower limit [41]. DFT calculations have also yielded values from 272 to 367 kJ/mol (2.82–3.80 eV) [15]. The G3 dissociation energy is 321.1 kJ/mol, which results in $\Delta_f H^\circ_0$ (SeF, g) = −1.6 kJ/mol and $\Delta_f H^\circ_{298\,\mathrm{K}}$ = −2.5 kJ/mol.

Calculations show that $SeCl_4$ and $SeBr_4$ are thermodynamically unstable in decomposition to $SeX_2 + X_2$ (X = Cl, Br) at 298 K; while SeF_4 is stable with tremendous endothermicity of 479 kJ/mol for decomposition $SeF_4 \rightarrow SeF_2 + F_2$. The calculations are consistent with the stability of SeF_4 and the virtually complete decomposition of $SeCl_4$ and $SeBr_4$ at room temperature [42]. Similarly, we would not expect the existence of $SeCl_6$ or $SeBr_6$ in the gas phase, while SeF_6 and SeF_5Cl are thermodynamically stable:

$$SeF_6(g) \rightarrow SeF_4(g) + F_2(g), \quad \Delta_r H^\circ_{298\,\mathrm{K}} = +373.5\ \mathrm{kJ/mol}$$

$$SeF_5(g) \rightarrow SeF_4(g) + FCl_2(g), \quad \Delta_r H^\circ_{298\,\mathrm{K}} = +124.4\ \mathrm{kJ/mol}$$

$$SeCl_6(g) \rightarrow SeCl_4(g) + Cl_2(g), \quad \Delta_r H^\circ_{298\,\mathrm{K}} = -53.4\ \mathrm{kJ/mol}$$

$$SeBr_6(g) \rightarrow SeBr_4(g) + Br_2(g), \quad \Delta_r H^\circ_{298\,\mathrm{K}} = -101.5\ \mathrm{kJ/mol}$$

Because of their instability of the neutrals, ionic species from $SeCl_x$ and $SeBr_x$ will not be considered except for $SeCl_2^+$ and $SeBr_2^+$.

3.3. Ionization potentials and electron affinities of SeF_n

The adiabatic IPs and EAs can be readily obtained from the G3 electronic energies (Table 1). It is not surprised to find that IPs of $SeF_{2,4,6}$ are higher than those of $SeF_{1,3,5}$ and EAs of $SeF_{1,3,5}$ are higher than those of $SeF_{2,4,6}$. Experimentally, only the vertical IP of SeF_2 [43] and EAs of SeF_4, SeF_5, and SeF_6 have been reported [7,44]. Alternatively, Li et al. [15] have predicted the adiabatic EAs of SeF_n at DFT level. The G3 EAs are within the relatively narrow ranges of DFT results for $SeF_{1,3,5}$, while being much lower than the DFT results for $SeF_{2,4,6}$.

Even though the experimental heat of formation of SeF_6 is well established, the adiabatic IP for SeF_6 is unknown from previous studies. SeF_6^+ has not been observed in photoionization or electron bombard experiment. This is consistent with our calculation here. At B3LYP level, SeF_6^+ can be viewed as weak SeF_5^+–F complex with pseudo C_{4v} symmetry, with the longest Se–F bond length of 2.436 Å and others from 1.656 to 1.681 Å. The G3 adiabatic ionization potential of SeF_6 is 14.50 eV, and SeF_6^+ is only 0.18 eV below the dissociation limit $SeF_5^+ + F$. Even though SeF_6^+ can be observed in principle if the excess internal energy can be relaxed, it is not expected from photoionization of SeF_6 [10] nor from reactions of SeF_6 with cations [9] because of the large structural change from neutral to cation. Note that experimental studies show that SF_6^+ is unstable as well, and theoretical attempts to determine the SF_6^+ structure were unsuccessful.

For SeF_2, the vertical IP(SeF_2) = 10.2 eV has been obtained by De Leeuw et al. from He(I) photoelectron spectroscopy study [43]. The vertical IP is slightly higher than the G3 adiabatic value of 10.01 eV because of the small structural change from neutral to cation (Fig. 1). Similarly, the experiment has obtained vertical IPs of 9.52 and 9.07 eV for $SeCl_2$ and $SeBr_2$, respectively, and a later study also yielded vertical IP($SeBr_2$) of 9.17 eV using the same technique [45]. The measured vertical IPs of $SeCl_2$ and $SeBr_2$ are also only slightly higher than G3 adiabatic IPs of 9.36 and 9.11 eV.

On the other hand, SeF_6^- and SF_6^- have been observed experimentally. The experimental adiabatic EA(SeF_6) = 2.9 ± 0.2 eV was obtained by Compton et al. [7] from the electron transfer reactions between alkali metal atoms and SeF_6. The values are supported by our G3 prediction of 2.81 eV and the BHLYP/DZP++ calculation 3.13 eV [15]. However, it should be pointed out that the alkali-metal atom threshold measurements are difficult to interpret correctly. The same experiment yielded incorrect EA of 0.46 ± 0.2 eV for SF_6 and lower limit of ∼5 eV for WF_6, which are significantly different from the recently accepted values of 1.05 ± 0.1 eV [29,30,46–49] and 3.5 ± 0.2 eV [50,51] for SF_6 and WF_6, respectively.

In the same study, Compton et al. [7] also derived EA(SeF_5) = 5.1 ± 0.4 eV, assuming D_0(SeF_5–F) of 3.15 eV as the average Se–F bond strength in SeF_6 and $D_0(SeF_5{}^-–F)$ of 1.1 eV as the difference between onsets of $SeF_6{}^-$ and $SeF_5{}^-$:

$$\mathrm{EA}(SeF_5) = \mathrm{EA}(SeF_6, \cdot 3.05\ \mathrm{ev}) + D_0(SeF_5F, \cdot 3.15\ \mathrm{ev}) - D_0(SeF_5^-F, \cdot 1.1\ \mathrm{ev})$$

The EA value is supported by G3 value of 5.24 eV in present study and DFT values of 5.28–5.49 eV by Li et al. [15]. However, this agreement on $\mathrm{EA}(SeF_5)$ is fortuitous since the G3 $D_0(SeF_5–F) = 4.11$ eV and $D_0(SeF_5{}^-–F) = 1.69$ eV. The experimental $D_0(SeF_5{}^-–F)$ is questionable as well, since the $D_0(SF_5{}^-–F)$ ∼97 kJ/mol measured by the same technique is also considerably lower than the recent measurement of $\leq 178 \pm 12$ kJ/mol by energy-resolved collision-induced dissociation study [52], and the G2 and G3 calculations of 175 and 159 kJ/mol [29,30], respectively. The fact that $D_0(SeF_5{}^-–F)$ is smaller than the $\mathrm{EA}(SeF_6)$ leads to significant yield of $SeF_5{}^-$ in the low energy electron attachment of SeF_6 [8].

The crude measurement of $\mathrm{EA}(SeF_5) = 1.7$ eV from electron bombard [44] is much lower than G3 prediction of 2.25 eV. However, the experiment cannot be considered reliable. The G3 $\mathrm{EA}(SeF_4)$ is lower than the DFT ones of 2.58–3.00 eV [15].

There has been no experimental report on IPs of $SeF_{1–5}$ and EAs of $SeF_{1,2,3}$. Given the scarcity and unreliability of the experimental measurements, the G3 theoretical predictions of IPs and EAs are preferred and recommended. Note that $SeF_2{}^-$ is linear in its ground state of $^2\Pi$, and the Renner–Teller effect and the spin-orbital interaction are not considered here. The ionization of SeF removes one electron from the anti-Π bond, leading to a $^3\Sigma$ ground state for the cation SeF^+ and the shortening of the bond length; while the anion SeF^- is in its singlet state $^1\Sigma$. From the G3 energies, the IP(SeF) = 9.81 eV and EA(SeF) = 2.44 eV can be determined. The G3 EA agrees with the DFT values of 2.37–2.53 eV [15].

3.4. Enthalpies of formation of $SeF_n{}^+$ and comparison to photoionization of SeF_6

$\Delta_f H_0^\circ$ of $SeF_n{}^+$ ($n = 2–5$) has been obtained from their appearance energies (AEs) in the photoionization study of SeF_6 by Jarvis et al. [10] and from the G3 atomization energies here. However, the experimental values carry uncertainties as large as 52 kJ/mol for $SeF_5{}^+$. The large uncertainty is due to the difficulties in determining the kinetic energy release and the possible internal excitation of fragments.

The observed appearance energy [10] of $SeF_5{}^+$ from dissociative photoionization of SeF_6 is 15.3 ± 0.2 eV; however, the fragments carry ∼0.4 eV of kinetic energy and ∼0.7 eV of internal excitation. After extrapolation to zero kinetic energy, the threshold of $SeF_5{}^+ + F + e$ is. 14.1 ± 0.5 eV, from which $\Delta_f H_0^\circ (SeF_5{}^+) = 166 \pm 52$ kJ/mol was derived. The G3 AE is 14.68 eV; consequently, the G3 $\Delta_f H^\circ$ of $SeF_5{}^+$ (232.6 kJ/mol at 0 K and 224.2 kJ/mol at 298 K) is just outside the experimental estimation of 166 ± 52 kJ/mol.

$SeF_4{}^+$ has been observed in photoionization of SeF_6 [10]. From its appearance energy, the upper limit of $\Delta_f H_0^\circ (SeF_4{}^+) = 426 \pm 36$ kJ/mol is estimated with the following reaction:

$$SeF_6 + hv \rightarrow SeF_4^+ + 2F + e, \quad \mathrm{AE(Expt.)} = 17.6 \pm 0.2\ \mathrm{ev}$$

This experimental AE is not corrected for the kinetic energy and the possible internal excitation of $SeF_4{}^+$, even though it agrees with the G3 AE of 17.86 eV. At energy of 17.6 ± 0.2 eV, the $SeF_4{}^+ + F_2 + e$ channel is also accessible with G3 AE = 16.31 eV. It is difficult to identify the origin of $SeF_4{}^+$; however, it may be proposed as the secondary decomposition of $SeF_5{}^+$ as for the origin of $SF_4{}^+$ from photoionization of SF_6 [53]. It is noticed that $SeF_4{}^+$ is unstable with $D_0(SeF_3{}^+–F) = 0.20$ eV only. This is probably the reason that the abundance of $SeF_4{}^+$ is smaller than those of $SeF_{2,3,5}{}^+$ ions, and direct ionization of SeF_4 does not lead to formation of $SeF_4{}^+$ as for SeF_6.

$\Delta_f H_0^\circ (SeF_3{}^+) = 368 \pm 28$ kJ/mol has been estimated from $\mathrm{AE}(SeF_3{}^+)$ in the photoionization of SeF_6, assuming the following process:

$$SeF_6 + hv \rightarrow SeF_4^+ + 3F + e, \qquad \mathrm{AE(Expt.)} = 17.6 \pm 0.2\ \mathrm{ev}$$

The experimental AE is slightly lower than G3 prediction of 18.06 eV, while much higher than the G3 AE of 16.51 eV for $SeF_3{}^+ + F_2 + F + e$ channel. Threshold photoelectron spectrum shows that the appearances of $SeF_3{}^+$ and $SeF_4{}^+$ are associated with the depletion of $SeF_5{}^+$; however, it is difficult to identify the decomposition channel.

$\Delta_f H_0^\circ (SeF_2{}^+) = 850$ kJ/mol has also been estimated as the upper limit from the observed $\mathrm{AE}(SeF_2{}^+ + 4F + e) = 23.6 \pm 0.2$ eV [10]. The enthalpy of formation is significantly higher than G3 prediction of 691.1 kJ/mol since the observed AE is above the predicted 21.84 eV. The higher-than-G3-prediction AE for $SeF_2{}^+$ indicates the uncertainty in the kinetic energy release, and the internal excitation of fragments, or the presence of possible barriers for dissociation $SeF_3{}^+ \rightarrow SeF_2{}^+ + F$. The G3 prediction is considered being more reliable. It is noticed that the $\Delta_f H_0^\circ (SF_2{}^+)$ obtained using the same technique from SF_6 is also significantly higher than the theoretical predictions [10,29].

3.5. Bond dissociation energies

The bond dissociation energies can be derived from the electronic energies (Fig. 2). For the neutrals, the G3 $D_0(SeF_n–F)$ are 321.1, 350.0, 243.2, 381.7, 120.4, and 396.4 kJ/mol for $n = 0–5$, respectively. The small BDEs of $SeF_4–F$ and $SeF_2–F$ reflect the stability of SeF_4 and SeF_2, similar to those of SF_4 and SF_2 [30]. These values have also been calculated by Li et al. [15] using several different hybrid DFT methods [15], of which B3LYP/DZP++ is in best agreement with G3. The assumption of $D_e(SeF_5–F$, 396.4 kJ/mol) as the average Se–F bond strength (302.1 kJ/mol) in SeF_6 [7] is certainly not valid, and neither for SF_6 [30]. $D_0(SeF_4–F)$ of 2.8 eV (270 kJ/mol) [7], deduced from the roughly estimated $\mathrm{EA}(SeF_4)$ of 164 kJ/mol (1.7 eV) [44] (2.25 eV at G3 level), is significantly higher than the G3 (120.4 kJ/mol) and DFT (78–154 kJ/mol) predictions. $\mathrm{BDE}(SeF_4{}^-–F)$ of 298 kJ/mol were also predicted at MP2/DZP level using effective core potentials [54], and the DFT values are in the range of 337 to 383 kJ/mol, all being lower than G3 value of 408.9 kJ/mol. For bond dissociation of SeF_n^-, the formation of $SeF_{n-1} + F^-$ is favored over $SeF_{n-1}^- + F$ for all anions except SeF_6^-.

3.6. Ion reactions with SeF_6

Reactions of SeF_6 with several ions have been studied [9,11]. The possible reaction types are electron transfer (R1), $F^\pm$-abstraction (R2), and dissociative electron transfer (R3):

$$A^- + SeF_6 \rightarrow A + SeF_6^- \qquad R1$$

$$A^\pm + SeF_6 \rightarrow AF + SeF_5^\pm \qquad R2$$

$$A^\pm + SeF_6 \rightarrow A + SeF_5^\pm \qquad R3$$

The enthalpy changes for reactions with several ions are listed in Table 2. The most energetic pathway forming $SeF_5^\pm$ is certainly the $F^\pm$-abstraction reactions. From the enthalpy changes of reactions and the relative yield of SeF_5^-, Jarvis et al. [9] suggest that SeF_5^- productions in reactions with O_2^-, O^-, and OH^- are from dissociative electron transfer. However, this is contradictory to current calculation, which shows that $R3$ reaction is exothermic only for O_2^-. Further studies on the possible energy barriers for these reactions are required to classify the reaction mechanism. For reactions with cations CF_3^+, CF_2^+, O^+, F^+, and CO^+ etc, the F^--abstractions are all exothermic, while the dissociative electron transfers are endothermic.

4. Conclusion

The enthalpies of formation of selenium halides, ionization potentials, and electron affinities for selected species have been obtained using G3 calculations. The patterns of these values are illustrated in Fig. 2. Good agreements with experiments are observed on the enthalpies of formation of H_2Se and SeF_6 and the photoionization study of H_2Se only. Large discrepancies exist for other available experimental values, and for these cases, our G3 calculations should be preferred.

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