THEORETICAL STUDY ON THE ADDUCTS OF SF₄ WITH AsF₅ AND SbF₅HONG-CHEN DU^{1*}, ZHI-KUN WANG, YU WANG, JIAN-ZHONG GUO

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ABSTRACT

Two adducts SF₄·AsF₅ and SF₄·SbF₅ have been studied in this work. Their structures, thermodynamic functions, and heats of formation were studied using density functional theory (DFT) method in gas phase and using the force field method and the DFT GGA-RPBE method in crystal state. The obtained crystal structures have the *P2₁/c* space group. The lattice energies, sublimation enthalpies and heats of formation in crystal state were estimated. Based on the optimized crystal structures, the electronic energy band and density of state were predicted and the results indicate that they are semiconductors with the band gap between 2.3 ~ 2.5 eV.

Keywords: SF₄·AsF₅, SF₄·SbF₅, crystal structure, theoretical study

INTRODUCTION

Sulfur tetrafluoride (SF₄) is a highly reactive compound. It can be used as a fluorinating agent in the preparation of a wide range of inorganic fluorine-containing compounds, such as IF₃, SeF₄, SnF₄, MoF₆ and UF₆ in high yields by fluorination of I₂O₃, SeO₂, SnS₂, MoO₃ and UO₃ respectively at 250-350°C in pressure vessels.¹ The reactions are characterized by replacing O or S with F to produce corresponding fluorides or in some cases oxyfluorides. Bartlett et al reported that SF₄ can form solid complexes with a number of inorganic fluorides, e.g., SF₄·BF₃, SF₄·AsF₅, SF₄·SbF₅.^{2,3} These complexes were supposed to be ionic salts or fluorine-bridged complexes (SF₃⁺BF₄⁻, SF₃⁺AsF₆⁻, SF₃⁺SbF₆⁻) rather than electron pair donor-acceptor compounds.^{1,2,4,5} The hypothesis is supported by the fact that these inorganic fluorides (BF₃, AsF₅, SbF₅) are strong fluorine acceptors and can form stable fluoro anions, i.e., BF₄⁻, AsF₆⁻, SbF₆⁻.

Several studies had been performed to validate the above hypothesis. Seel and Detmer observed the IR spectrum of [SF₃]⁺[BF₄]⁻.⁵ They found a band at 1050cm⁻¹ raised by BF₄⁻ and bands at 908 and 940 cm⁻¹ assigned to SF₃⁺. Evans and Long reported the Raman spectrum of the molten complex SF₄·SbF₅ at 250°C and the structure was interpreted as an ionic form [SF₃]⁺[SbF₆]⁻.⁶ In 1969, Azeem et al reported that at the room temperature, the adduct of [SF₃]⁺[BF₄]⁻ is in equilibrium with its components in the gas state and has a vapor pressure of approximately 100 mmHg.⁷ It seems reasonable to suppose that exchange of F exists when the adduct is a fluorine-bridged or an ionic compound, but if the adduct is a simple donor-acceptor complex, there would not exist obvious mechanism for exchange.

Up to date, the investigations on the molecular and crystal structures of SF₄·AsF₅ and SF₄·SbF₅ are very limited. Since many physical and chemical properties are tightly related with the structure, therefore, the prediction of molecular and crystal structure is of great value. In this work, this has been done with the help of quantum chemistry and molecular mechanics calculations.

Calculation Methods

The title compounds, SF₄·AsF₅ and SF₄·SbF₅ were optimized at the PBE1PBE/aug-cc-pvtz level of density functional theory (DFT) using Gaussian 03 program⁸ and confirmed to be the energy minima with no imaginary frequency by vibrational analysis. The natural bond orbital (NBO) analyses were performed to obtain the atomic charge and bond population. The gas-phase heats of formation (ΔH_{gas}^o) were calculated from the following reactions:

The changes in enthalpy (ΔH₂₉₈^o) of the above reactions were evaluated using the following equation:

$$\Delta H_{298}^o = \sum \Delta_f H_{298,P}^o - \sum \Delta_f H_{298,R}^o = \Delta E_0 + \Delta E_{ZPE} + \Delta H_T + \Delta nRT$$
 where $\sum \Delta_f H_{298,P}^o$ and $\sum \Delta_f H_{298,R}^o$ are the sum of the heats of formation of the products and reactants, respectively; ΔE₀ is the difference between the total energies of the products and the reactants at 0 K; ΔE_{ZPE} is the difference between the zero-point vibrational energy of the products and the reactants; ΔH_T^o is the difference between the thermal correction from 0 K to 298 K of the products and the reactants, Δn is the change in the quantity of gaseous substances, which is -1 here. In the reactions (1) and (2), the experimental heats of formation of all reactants (SF₄, AsF₅, SbF₅) are known,⁹ the heats of formation of the adducts can then be obtained with the calculated ΔH₂₉₈^o.

The widely-used flexible Dreiding force field¹⁰ was adopted to predict the

crystal structure employing the Polymorph module in Materials Studio.¹¹ Since the most of crystals belong to 7 space groups, *P2₁/c*, *P-1*, *P2₁2₁2₁*, *Pbca*, *C2/c*, *P2₁*, and *Pna2₁* according to the statistical data of crystals in the Cambridge Crystallographic Data Centre (CCDC),¹²⁻¹⁷ the searching of possible packings are carried out within these space groups.

The predicted crystals were further optimized using the DFT GGA-RPBE method in CASTEP.¹⁸ The cutoff energy of plane waves was set to 300.0 eV. Brillouin zone sampling was performed using the special Monkhost-Pack scheme with the k-point grid of 1×1×1. The values of the kinetic energy cutoff and the k-point grid were determined to ensure the convergence of total energy. The band gap (ΔE_g) and density of state (DOS) were then predicted based on the optimized crystal structure.

RESULTS AND DISCUSSION

Molecular structures

Figure 1 shows the optimized molecular structures of SF₄·AsF₅ and SF₄·SbF₅ at the PBE1PBE/aug-cc-pvtz level, together with NBO charges in parentheses. The total charges on the SF₃ unit of them are 0.772e and 0.807e respectively, showing that they have ionic forms, i.e., [SF₃]⁺[AsF₆]⁻ and [SF₃]⁺[SbF₆]⁻. Which is consistent the experimental results from Azeem et al.⁷

Figure 1: The molecular structures of SF₄·AsF₅ (left) and SF₄·SbF₅ (right) optimized at the PBE1PBE/aug-cc-pvtz level (Bond length in Å and charges in e)

Table 1: The bond populations from Mulliken analyses.

	Bond	Population	Bond	Population
[SF ₃] ⁺ [AsF ₆] ⁻	S-F1	0.201	As-F4	0.080
	S-F2	0.184	As-F5	0.257
	S-F3	0.210	As-F6	0.299
	S-F4	-0.013	As-F7	0.335
			As-F8	0.281
			As-F9	0.221
[SF ₃] ⁺ [SbF ₆] ⁻	S-F1	0.177	Sb-F4	0.078
	S-F2	0.186	Sb-F5	0.133
	S-F3	0.198	Sb-F6	0.173
	S-F4	-0.039	Sb-F7	0.179
			Sb-F8	0.168
			Sb-F9	0.113

Bond population is a measure of the strength of a bond between two atoms. The higher value of the bond population indicates a stronger bond. From Table 1, we can see that the bond populations of S-F4 are -0.013 and -0.039 in two structures, while the bond populations of other S-F bonds are in 0.177~0.210, implying the strength of S-F4 is much weaker than other S-F bonds, which is consistent with the situation of bond lengths, e.g., in [SF₃]⁺[AsF₆]⁻, the bond length of S-F4 (1.992 Å) is much longer than other S-F bonds (1.540~1.597 Å). Meanwhile, the similar conclusion can also be obtained for As-F or Sb-F bonds, i.e., As-F4 or Sb-F4 is much weaker than other As-F or Sb-F bonds.

Electronic structure

The molecular electrostatic potential (MEP) is used commonly in analyzing molecular reactivity and is very useful since it provides information about local polarity due to the charge density distribution. After having chosen some sort of region to be visualized, a color-coding convention is chosen to depict the MEP. Figure 2 illustrates the MEP for the 0.001 electron/bohr³ isosurface of electron density at the PBE1PBE/aug-cc-pvtz level for the two compounds. The colors ranging from -0.02~0.05 hartrees denoting the most negative potential and the most positive potential. It can be seen from Figure 2 that the most obvious feature of the MEP in appears in the region over the fluoride atoms and the sulfur atoms, the positive regions are mainly the SF₃ unit, and the negative regions are located on AsF₆ and SbF₆ units, which is consistent with the conclusion from part "Molecular Structures".

Figure 2: Molecular electrostatic potential (MEP) surfaces mapped onto 0.001 electron/bohr³ contour of the electronic density for the bridged triazines calculated at the PBE1PBE/aug-cc-pvtz level. Color range: from -0.02 to 0.05

Thermodynamic Properties

The standard thermodynamic functions of the title compounds are shown in Figure 3. Under the room temperature, the calculated $C_{p,m}^{\circ}$, S_m° , and H_m° of [SF₃]⁺[SbF₆]⁻ are 199.66 J•K⁻¹•mol⁻¹, 464.13 J•K⁻¹•mol⁻¹, and 38.69 kJ•mol⁻¹, respectively, and those of [SF₃]⁺[AsF₆]⁻ are 193.17 J•K⁻¹•mol⁻¹, 446.72 J•K⁻¹•mol⁻¹, and 39.19 kJ•mol⁻¹. With the increase in temperature, all the thermodynamic functions increase, which is mainly because that the vibrational movement is intensified at the higher temperature and therefore makes more contributions to the thermodynamic functions. The relationships between the

thermodynamic functions and temperature for, for example [SF₃]⁺[SbF₆]⁻ are (the units of $C_{p,m}^{\circ}$, S_m° , and H_m° are J•K⁻¹•mol⁻¹, J•K⁻¹•mol⁻¹, and kJ•mol⁻¹, and the correlation coefficients are 0.9844, 0.9995, and 0.9999, respectively):

$$C_{p,m}^{\circ} = 105.38 + 0.40T - (2.81 \times 10^{-4})T^2$$

$$S_m^{\circ} = 229.70 + 0.91T - (4.15 \times 10^{-4})T^2$$

$$H_m^{\circ} = -16.77 + 0.17T + (5.37 \times 10^{-5})T^2$$

From these equations, we have

$$\frac{dC_{p,m}^{\circ}}{dT} = 0.40 - (5.62 \times 10^{-4})T$$

$$\frac{dS_m^{\circ}}{dT} = 0.91 - (8.30 \times 10^{-4})T$$

$$\frac{dH_m^{\circ}}{dT} = 0.17 + (10.74 \times 10^{-5})T$$

Obviously, with the increase in temperature, the increments of $C_{p,m}^{\circ}$ and S_m° decrease, while that of H_m° increases.

Figure 3: The thermodynamic functions of [SF₃]⁺[AsF₆]⁻ (left) and [SF₃]⁺[SbF₆]⁻ (right)

Heat of formation is an important thermochemical property. The obtained $\Delta_f H^\circ_{\text{gas}}$ are -2305.83 and -2442.34 kJ·mol⁻¹ for [SF₃]⁺[AsF₆]⁻ and [SF₃]⁺[SbF₆]⁻ respectively (Table 2) at PBE1PBE/aug-cc-pvtz level.

Table 2: Total energies E (a.u.) and $\Delta_f H^\circ_{\text{gas}}$ (kJ·mol⁻¹) of the title compounds

	E					$\Delta_f H^\circ_{\text{gas}}$	
	AsF ₅	SbF ₅	SF ₄	SF ₄ ·AsF ₅	SF ₄ ·SbF ₅	SF ₄ ·AsF ₅	SF ₄ ·SbF ₅
PBE1PBE/aug-cc-pvtz	-2734.65745	-504.449166	-797.055527	-3531.82992	-1301.637s92	-2305..83	-2442.34

Crystal structure

Tables 3 and 4 present the predicted energies (E), cell parameters (a , b , c , α , β , γ), and densities (ρ) of the most possible crystal structure in seven space groups using the Dreiding force field. We see that for [SF₃]⁺[AsF₆]⁻ and [SF₃]⁺[SbF₆]⁻, the energies of various structures are 167.33~173.48 and 168.99~175.15 kcal·mol⁻¹·cell⁻¹, respectively. According to the principle that the possible stable polymorph usually possesses a lower energy, the structures with the $P2_1/c$ symmetry which are lower in energy than others are the most possible stable polymorphs for both compounds.

Table 3: Possible molecular packings of [SF₃]⁺[AsF₆]⁻ in various space groups.

	$P2_1/c$	$P2_12_12_1$	$P-1$	$Pbca$	$C2/c$	$Pna2_1$	$P2_1$
Z	4	4	2	8	8	4	2
$E(\text{kcal}\cdot\text{mol}^{-1}\cdot\text{cell}^{-1})$	167.33	172.83	173.29	168.73	169.29	173.48	169.01
$\rho(\text{g}\cdot\text{cm}^{-3})$	2.68	2.84	2.81	2.79	2.72	2.78	2.76
$a(\text{\AA})$	13.92	14.38	8.82	27.62	15.78	16.68	5.21
$b(\text{\AA})$	14.64	8.57	9.90	5.28	5.41	5.31	8.91
$c(\text{\AA})$	9.96	5.27	5.44	9.09	15.93	7.49	7.35
$\alpha(^{\circ})$	90.00	90.00	56.99	90.00	90.00	90.00	90.00
$\beta(^{\circ})$	160.15	90.00	121.58	90.00	94.14	90.00	78.55
$\gamma(^{\circ})$	90.00	90.00	95.84	90.00	90.00	90.00	90.00

Table 4: Possible molecular packings of [SF₃]⁺[SbF₆]⁻ in various space groups.

	$P2_1/c$	$P2_12_12_1$	$P-1$	$Pbca$	$C2/c$	$Pna2_1$	$P2_1$
Z	4	4	2	8	8	4	2
$E(\text{kcal}\cdot\text{mol}^{-1}\cdot\text{cell}^{-1})$	168.99	170.41	174.80	174.81	169.77	175.15	169.63
$\rho(\text{g}\cdot\text{cm}^{-3})$	2.94	2.81	3.08	3.08	2.87	3.06	2.87
$a(\text{\AA})$	20.49	20.22	6.44	8.59	27.84	8.52	5.55
$b(\text{\AA})$	5.36	5.29	6.33	16.71	5.56	14.72	12.34
$c(\text{\AA})$	27.40	7.18	10.99	9.76	23.99	5.62	5.68
$\alpha(^{\circ})$	90.00	90.00	58.29	90.00	90.00	90.00	90.00
$\beta(^{\circ})$	165.91	90.00	66.80	90.00	156.13	90.00	104.88
$\gamma(^{\circ})$	90.00	90.00	76.69	90.00	90.00	90.00	90.00

Table 5: The unit cell parameters obtained with the DFT-GGA-RPBE method.

	[SF ₃] ⁺ [AsF ₆] ⁻	[SF ₃] ⁺ [SbF ₆] ⁻
Z	4	4
E (eV)	-24135.65	-24069.50
$\rho(\text{g}\cdot\text{cm}^{-3})$	3.13	2.46
$a(\text{\AA})$	7.74	9.16
$b(\text{\AA})$	11.14	10.78
$c(\text{\AA})$	6.89	16.10
$\alpha(^{\circ})$	90.00	90.00
$\beta(^{\circ})$	96.68	146.47
$\gamma(^{\circ})$	90.00	90.00

The crystal structures predicted from force field method were refined with the DFT GGA-RPBE method. The results are shown in Table 5 and Figures 4 and 5. In the crystal cell of both compounds, there are 4 symmetry equivalent molecules. The density of $[\text{SF}_3]^+[\text{AsF}_6]^-$ is $3.13 \text{ g}\cdot\text{cm}^{-3}$, much larger than that of $[\text{SF}_3]^+[\text{SbF}_6]^-$. S-F has a length of $1.689\sim 1.870 \text{ \AA}$ in $[\text{SF}_3]^+[\text{AsF}_6]^-$, while $1.642\sim 3.338 \text{ \AA}$ in $[\text{SF}_3]^+[\text{SbF}_6]^-$. S-F4 in $[\text{SF}_3]^+[\text{SbF}_6]^-$ ($3.338 \text{ \AA}$) is much longer than other S-F bonds and that in $[\text{SF}_3]^+[\text{AsF}_6]^-$ ($1.723 \text{ \AA}$), implying that $[\text{SF}_3]^+[\text{SbF}_6]^-$ has a more obvious ionic character which has already been shown by the more severe charge separation in this system. This also shows that SbF_5 is a stronger fluorine acceptor than AsF_5 . This conclusion is demonstrated by the changes of enthalpy (ΔH) and free energy (ΔG) of the following reactions (3) and (4). At the PBE1PBE/aug-cc-pvtz level, the ΔH s are -427.86 and $-480.32 \text{ kJ}\cdot\text{mol}^{-1}$ respectively for reactions (3) and (4), the corresponding ΔG s are -392.40 and $-445.88 \text{ kJ}\cdot\text{mol}^{-1}$. Reaction (4) is more exothermic and spontaneous. This indicates that SbF_6^- can be formed more readily than AsF_6^- and SbF_5 is a stronger fluorine acceptor.

Compared with the molecular structure in gas phase, most bonds in crystal are longer, for example, in the crystal of $[\text{SF}_3]^+[\text{SbF}_6]^-$, the bond length of S-F ($1.642\sim 3.338 \text{ \AA}$) is much longer than that in gas phase ($1.539\sim 2.058 \text{ \AA}$). For $[\text{SF}_3]^+[\text{AsF}_6]^-$, all bonds except for S-F4 are longer in crystal than in gas phase.

Figure 4: The DFT optimized crystal structures of the adducts with the $P2_1/c$ space group.

Figure 5: The bond lengths ($\text{\AA}$) of the molecule in crystals.

For a crystal, the lattice energy (E_{latt}) is important for predicting its structural and physicochemical properties such as polymorphism and growth morphology. E_{latt} can be calculated from the energy difference between the crystal (E_{crystal}) and the isolated molecules (E_{molecule}), i.e.,

$$E_{\text{latt}} = E_{\text{crystal}} - Z E_{\text{molecule}}$$

where Z is the number of molecules in unit cell. E_{latt} is therefore the energy required for vaporizing a crystal and represents the strength of cohesion or interaction between molecules in the solid state. A negative value of E_{latt} indicates an attractive intermolecular interaction in a crystal. The lattice energies of $[\text{SF}_3]^+[\text{AsF}_6]^-$ and $[\text{SF}_3]^+[\text{SbF}_6]^-$ obtained at DFT LDA/CA-PZ level are -623.79 and $-872.49 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, indicating that the intermolecular interactions are much stronger in the bulk $[\text{SF}_3]^+[\text{SbF}_6]^-$ than in $[\text{SF}_3]^+[\text{AsF}_6]^-$.

E_{latt} was further used to evaluate the enthalpy of sublimation (ΔH_{sub}) using the following relationship:¹⁹

$$-\Delta H_{\text{sub}} = E_{\text{latt}} + E_{\text{ZPE}} + ZRT$$

A rough estimation of the ΔH_{sub} is obtained by neglecting the E_{ZPE} term, and the solid phase heat of formation ($\Delta_f H_{\text{solid}}^\circ$) is then predicted from $\Delta_f H_{\text{gas}}^\circ$:

$$\Delta_f H_{\text{solid}}^\circ = \Delta_f H_{\text{gas}}^\circ - \Delta H_{\text{sub}}$$

The calculated $\Delta_f H_{\text{solid}}^\circ$ of $[\text{SF}_3]^+[\text{AsF}_6]^-$ and $[\text{SF}_3]^+[\text{SbF}_6]^-$ are -2881.69 and $-3269.71 \text{ kJ}\cdot\text{mol}^{-1}$ respectively.

To evaluate the reliability of the method for predicting ΔH_{sub} , benzene which has the experimental $\Delta H_{\text{sub}}^{20}$ ($44.52 \text{ kJ}\cdot\text{mol}^{-1}$) was tested and the calculated result was $49.70 \text{ kJ}\cdot\text{mol}^{-1}$, showing that the method we used is reliable and the calculated ΔH_{sub} is reasonable.

Band gap

The band gap (ΔE_g) is an important parameter to characterize the electronic structure of the crystals, it refers to the energy difference between the top of the valence band (HOCO) and the bottom of the conduction band (LUCO). Insulators have large band gaps, semiconductors have smaller band gaps, while conductors have either very small or none band gaps. ΔE_g is also related with the impact sensitivity of energetic materials with similar structure.

Based on the equilibrium crystal structures at the GGA-RPBE level, the self-consistent band structure along different symmetry directions of the Brillouin zone was predicted and shown in Figure 6. We can see that in the direction of reciprocal vector of Brillouin area of $[\text{SF}_3]^+[\text{AsF}_6]^-$ and $[\text{SF}_3]^+[\text{SbF}_6]^-$, the variations of the frontier band with the k values are relatively smooth, which indicates that the energy states of the molecular orbital in crystal have little influence on the crystal field. The band gaps of them are 2.302 and 2.425 eV , respectively, which implies that they are all semiconductors.

Figure 6: The energy bands along different symmetric directions of the Brillouin zone at ambient pressure. The Fermi energy is shown as a dashed horizontal line.

Density of states

To obtain more information about the bond nature of the title compounds, the total electronic density of states (DOS) and partial DOS (PDOS) are calculated and shown in Figure 6. DOS can reveal the composition of HOCO and LUCO, while PDOS in which DOS is projected on atom-centered orbital reflects the constitution of energy bands. From Figure 6, we see that the upper valence bands of the title compounds have a sharp peak near the Fermi level, indicating the flatness of these bands.²¹ All the peaks are predominately from the *p* states. The HOCO of $[\text{SF}_3]^+[\text{AsF}_6]^-$ is mainly contributed from the *p* state of F in SF_3^+ and AsF_6^- , while the HOCO of $[\text{SF}_3]^+[\text{SbF}_6]^-$ is mainly contributed from the *p* state of F atom in SbF_6^- . The LUCOs of both compounds are mainly composed of the *p* states of S atom. The conduction bands are also dominated by the *p* states, these indicate that the *p* states play an important role in their chemical reaction.

The S-F bonds are the reaction center since the frontier bands are dominated by the *p* states of S and F atoms and F4 is the most active atom among all F atoms, as depicted in Figures 1 and 4. The transfer of F4 between SF_4 and AsF_5 (or SbF_5) results in the formation or dissociation of the adduct, which supports the previous hypothesis.

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Figure 7: The calculated DOS at ambient pressure. The Fermi energy is shown as a dashed vertical line

CONCLUSIONS

In this study, DFT calculations have been performed to study the molecular, crystal, and electronic structures and thermodynamic properties of the adducts $\text{SF}_4 \cdot \text{AsF}_5$ and $\text{SF}_4 \cdot \text{SbF}_5$. Results show that the adducts exist in ionic forms $[\text{SF}_3]^+[\text{AsF}_6]^-$ and $[\text{SF}_3]^+[\text{SbF}_6]^-$. Their most possible packings predicted with the force field method belongs to the $P2_1/c$ space group. The unit cell parameters at the DFT GGA-RPBE level are $a=13.92 \text{ \AA}$, $b=14.04 \text{ \AA}$, $c=9.96 \text{ \AA}$, $\beta=160.15^\circ$ and $a=20.49 \text{ \AA}$, $b=5.36 \text{ \AA}$, $c=27.40 \text{ \AA}$, $\beta=165.91^\circ$, respectively, with the corresponding band gaps of 2.30 and 2.43 eV. The S-F bonds are the reaction center and the bridged F atom may exchange between SF_4 and AsF_5 or SbF_5 units. The heats of formation of the adducts have also been predicted, and they are -2267.82 and -2407.14 $\text{kJ} \cdot \text{mol}^{-1}$ in gas phase and -2881.69 and -3269.71 $\text{kJ} \cdot \text{mol}^{-1}$ in solid state for $[\text{SF}_3]^+[\text{AsF}_6]^-$ and $[\text{SF}_3]^+[\text{SbF}_6]^-$ respectively.