

Organo-Germynes: Structures, Electron Affinities and Singlet-Triplet Gaps of the $\text{Ge}(\text{CH}_3)_2$, $\text{CH}_3\text{GeSiH}_3$, $\text{CH}_3\text{GeGeH}_3$, XGeCY_3 (X; Y = H, F, Cl, Br) Species

¹Ashwini Bundhun, ²Hassan H. Abdallah, ¹Ponnadurai Ramasami and ³Henry F. Schaefer III

¹Department of Chemistry, University of Mauritius, Réduit, Mauritius

²Universiti Sains Malaysia, Penang, Malaysia

³Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

Abstract

A systematic investigation of the $\text{Ge}(\text{CH}_3)_2$, $\text{CH}_3\text{GeSiH}_3$, $\text{CH}_3\text{GeGeH}_3$, XGeCY_3 (X; Y = H, F, Cl, Br) species was carried out using the DFT functionals BLYP, B3LYP and BHLYP. Predicted are the singlet-triplet energy gaps and four types of neutral-anion separations: adiabatic electron affinity (EA_{ad}), zero-point vibrational energy corrected $\text{EA}_{\text{ad}(\text{ZPVE})}$, vertical electron affinity (EA_{vert}), and vertical detachment energy (VDE). The basis sets used for all atoms are of double- ζ plus polarization quality with additional s- and p-type diffuse functions denoted DZP++. The geometries are fully optimized with each functional independently. Vibrational frequency analyses are performed to compute zero-point energy corrections and to determine the nature of the stationary points. The $\text{EA}_{\text{ad}(\text{ZPVE})}$ values (eV) obtained with the BHLYP functional is $\text{Ge}(\text{CH}_3)_2 = 0.46$ eV, $\text{CH}_3\text{GeSiH}_3 = 1.22$ eV and $\text{CH}_3\text{GeGeH}_3 = 1.26$ eV, and $\text{FGeCCl}_3 = 1.66$ eV. The singlet-triplet splittings range from 1.28 eV (HGeCF_3) to 2.22 eV (FGeCCl_3). The XGeCY_3 (Y = Br) species are most often characterized by three-membered cyclic systems involving the divalent germanium atom, the carbon atom and a halogen atom. The predicted results are helpful for the synthesis, characterizations, and applications of these germylene derivatives.

Myself

Name: Ashwini Bundhun E-mail: ashwinibilly@gmail.com

University of Mauritius
Faculty of Science
Department of Chemistry

Supervisors: Assoc. Prof. (Dr) P. Ramasami &
Prof. H. F Schaefer

The aim of my research is to study and characterize germylenes by means of computational chemistry. The obtained quantities are all calculated, none of them are experimental. First, we investigated a large number of germylene derivatives and compared to the analogous carbenes and silylenes.

The noteworthy relationships between singlet-triplet splittings and activation energies for the insertion of Ge-H bond of germane into germylene are studied.

These germylenes are extended to the study of organogermylenes, where it is found that the substitution of hydrogen atom by halogen atom may lead to either conventional or cyclic systems.

Further, the study of the isomers of germylene cyanides is also interesting. The building-up of the potential energy surface for the isomerization of these cyanides reveals cyclic isomers. And the study of these systems remains the most challenging part of my PhD research at the University of Mauritius.

I. Introduction

-  The study of germylene generation, reactivities, substituent effects, singlet–triplet energy gaps, and relative stabilities (using both experimental and theoretical methods [1]), is an area of active research.
-  Such studies are inevitably connected with the absolute rate constants of germylene insertion processes [2-4].
-  Notably, it has been observed that there is a strong correlation between singlet-triplet splittings for the divalent reactant species and barrier heights.
-  Previous research [5] shed light on the electron affinities and singlet-triplet gaps for the GeX_2 , GeHX , XGeMH_3 (where $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{and I}$; $\text{M} = \text{C}, \text{Si}, \text{and Ge}$) species.

II. Theoretical Methods

All computations are done with the Gaussian 03 program [6].

Three different density functionals namely B3LYP, B3LYP and BLYP [7-9].

In all cases an extended integration grid (199,974) was applied.

The four forms of the neutral-anion energy difference are evaluated by the following scheme.

The adiabatic electron affinities are determined by:

$$EA_{\text{ad}} = E(\text{optimized neutral}) - E(\text{optimized anion}) \quad [1]$$

vertical electron affinity by

$$EA_{\text{vert}} = E(\text{optimized neutral}) - E(\text{anion at optimized neutral geometry}) \quad [2]$$

and the vertical detachment energy of the anion,

$$VDE = E(\text{neutral at optimized anion geometry}) - E(\text{optimized anion}) \quad [3]$$

Zero-point vibrational energies (ZPVE) are evaluated at each level. The corrected adiabatic electron affinities $EA_{\text{ad(ZPVE)}}$ between the neutral and the anionic species are reported as follows:

$$EA_{\text{ad(ZPVE)}} = [E(\text{optimized neutral}) + ZPVE_{\text{neutral}}] - [E(\text{optimized anion}) + ZPVE_{\text{anion}}] \quad [4]$$

The singlet-triplet splittings are predicted as the energy differences between the neutral ground state and the lowest triplet state.

III. The Objectives of this Research

- 🖨 Providing reliable theoretical predictions for the properties of the tetra-halo organo-systems $XGeCY_3$.
- 🖨 Investigate the abilities of these organo-germylenes to bind an extra electron, and trends observed compared to simpler germylene derivatives.

IV. Results and Discussion

The equilibrium geometries of the 1A ground state $\text{Ge}(\text{CH}_3)_2$ (C_1 symmetry), the ground state anion $^2A'$ $\text{Ge}(\text{CH}_3)_2^-$ (C_s symmetry) and the 3A triplet state of $\text{Ge}(\text{CH}_3)_2$ (C_1 symmetry) are presented in Figure 1.

The $\text{EA}_{\text{ad}}(\text{ZPVE})$ values range from 0.46 eV to 0.62 eV, with BHLYP and B3LYP as the lower and upper bounds, respectively.

The $\text{EA}_{\text{(vert)}}$ is small, ranging from 0.35 eV (BHLYP) to 0.51 eV (B3LYP), and the VDE is slightly larger ranging from 0.50 eV to 0.66 eV.

The singlet-triplet splittings for $\text{Ge}(\text{CH}_3)_2$ increase from 1.26 eV to 1.38 eV in the order BHLYP < B3LYP < BLYP.

Inductive effect of the two CH_3 moieties in $\text{Ge}(\text{CH}_3)_2$ is pronounced.

The electron-donor ability of the methyl groups causes the electron density near the central germanium to increase.

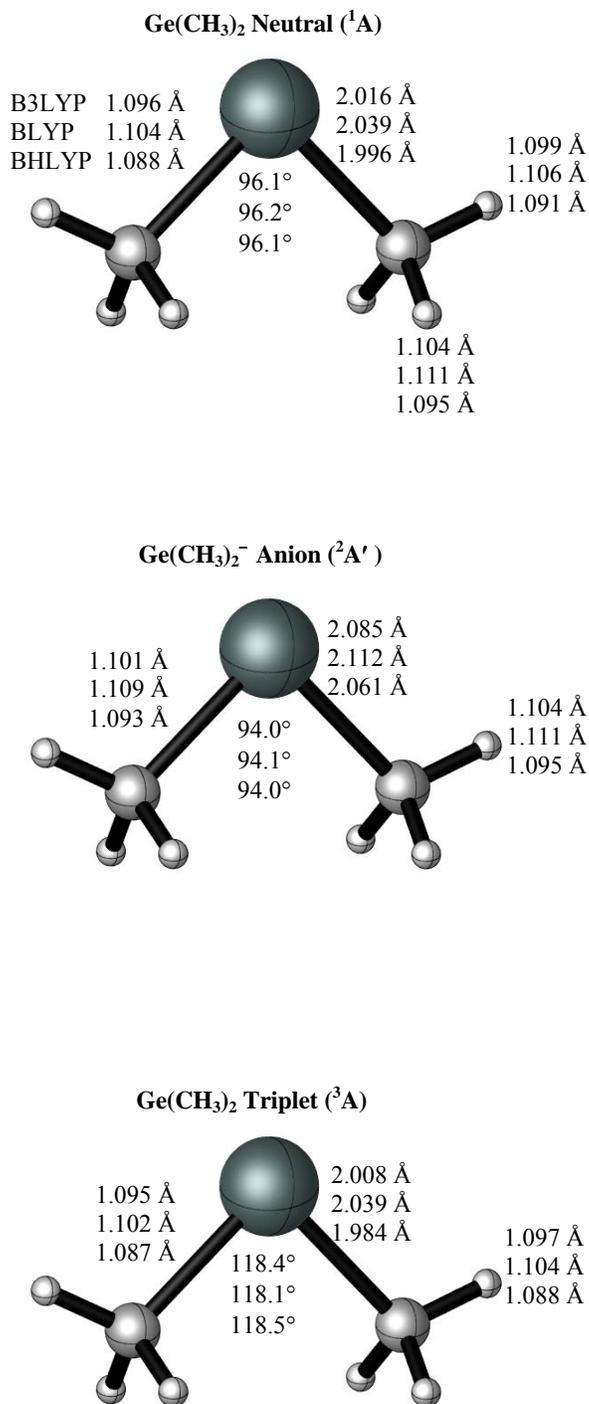


Figure 1. Equilibrium geometries for the 1A state of $\text{Ge}(\text{CH}_3)_2$, $^2A'$ state of the $\text{Ge}(\text{CH}_3)_2^-$ anion, and 3A state of the $\text{Ge}(\text{CH}_3)_2$.

To allow a comparative analysis of the halogen species, the electron affinities for $X\text{GeCH}_3$ are examined for $X = \text{H}, \text{F}, \text{Cl}$ and Br .

Relative to HGeCH_3 , a single fluoro substituent X decreases the $\text{EA}_{\text{ad(ZPVE)}}$ by 0.05 eV and the VEA by 0.11 eV, with a small increase in the VDE of 0.03 eV.

From these predicted values, it is noted that there is a more pronounced effect on the $\text{EA}_{\text{ad(ZPVE)}}$ by electron donating CH_3 group, thus causing the positive charge density of the central atom to decrease considerably.

Hence the ability of the $X\text{GeCH}_3$ ($X = \text{H}, \text{F}, \text{Cl}$, and Br) species to accommodate an extra electron is even weaker. As found earlier for $\text{Si}(\text{CH}_3)_2$, no neutral structure of C_{2v} symmetry was found for $\text{Ge}(\text{CH}_3)_2$ to be a minimum on the potential energy surface.

It is noted that the singlet-triplet splittings for the germylenes are consistently larger than those for the methylene and silylene analogues.

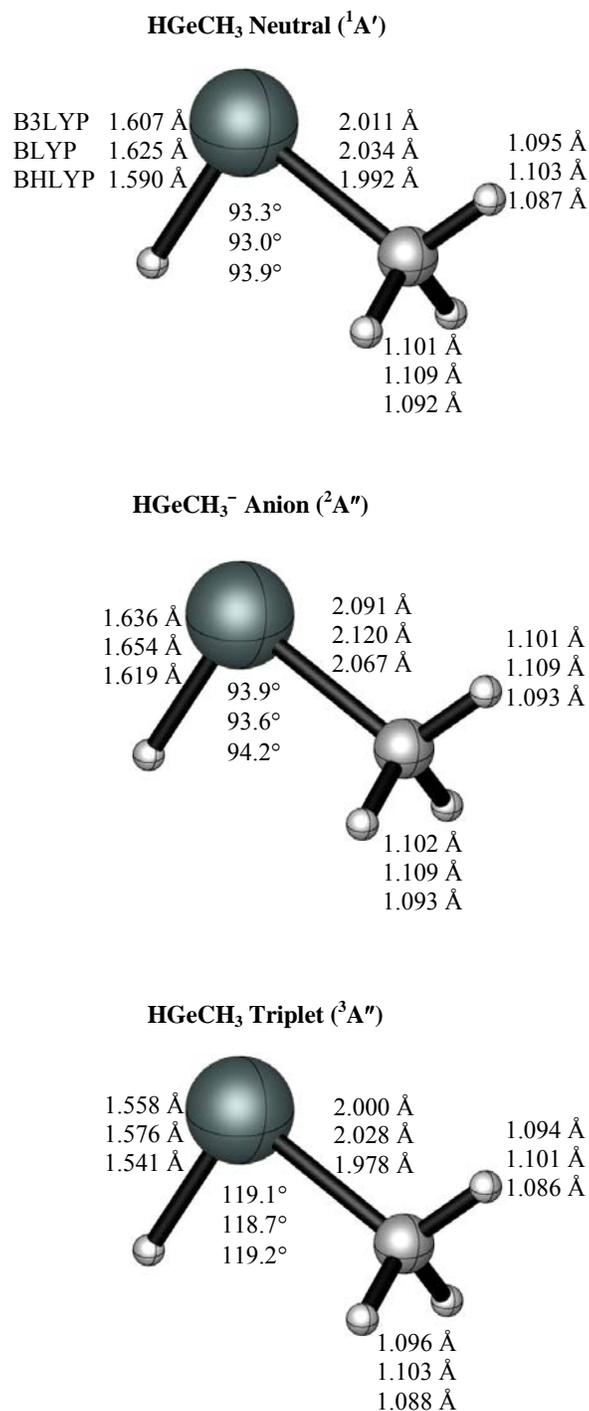


Figure 2. Equilibrium geometries for the $^1A'$ state of HGeCH_3 , $^2A''$ state of the HGeCH_3^- anion, and $^3A''$ state of the HGeCH_3 .

	BH&HLYP	BLYP	B3LYP
Ge(CH₃)₂	0.44 (0.46)	0.49 (0.52)	0.60 (0.62)
CH₃GeSiH₃	1.20 (1.22)	1.20 (1.23)	1.34 (1.37)
CH₃GeGeH₃	1.23 (1.26)	1.25 (1.29)	1.38 (1.41)
HGeCH₃	0.69 (0.71)	0.72 (0.75)	0.84 (0.86)
FGeCH₃	0.64 (0.66)	0.65 (0.67)	0.77 (0.79)
ClGeCH₃	1.07 (1.09)	1.01 (1.03)	1.17 (1.18)
BrGeCH₃	1.17 (1.19)	1.09 (1.10)	1.26 (1.27)
HGeCF₃	1.71 (1.74)	1.69 (1.72)	1.83 (1.86)
FGeCF₃	1.66 (1.69)	1.59 (1.62)	1.75 (1.78)
ClGeCF₃	2.00 (2.02)	1.88 (1.90)	2.06 (2.08)
BrGeCF₃	2.07 (2.08)	1.92 (1.94)	2.11 (2.13)
HGeCCl₃	1.67 (1.71)	1.64 (1.71)	1.78 (1.83)
FGeCCl₃	1.63 (1.66)	1.66 (1.69)	1.77 (1.80)
ClGeCCl₃	1.96 (1.99)	1.87 (1.93)	2.03 (2.06)
BrGeCCl₃	2.03 (2.05)	1.91 (1.95)	2.09 (2.11)
HGeCBr₃	1.63 (1.68)	2.94 (2.96)	3.17 (3.20)
FGeCBr₃	3.21 (3.24)	2.93 (2.96)	3.17 (3.20)
ClGeCBr₃	1.94 (1.96)	3.07 (3.09)	3.31 (3.34)
BrGeCBr₃	2.01 (1.82)	3.09 (3.12)	3.34 (3.37)

Table 1. Germylene adiabatic electron affinities EA_{ad} and zero-point corrected $EA_{ad(ZPVE)}$ values (in parentheses) in eV.

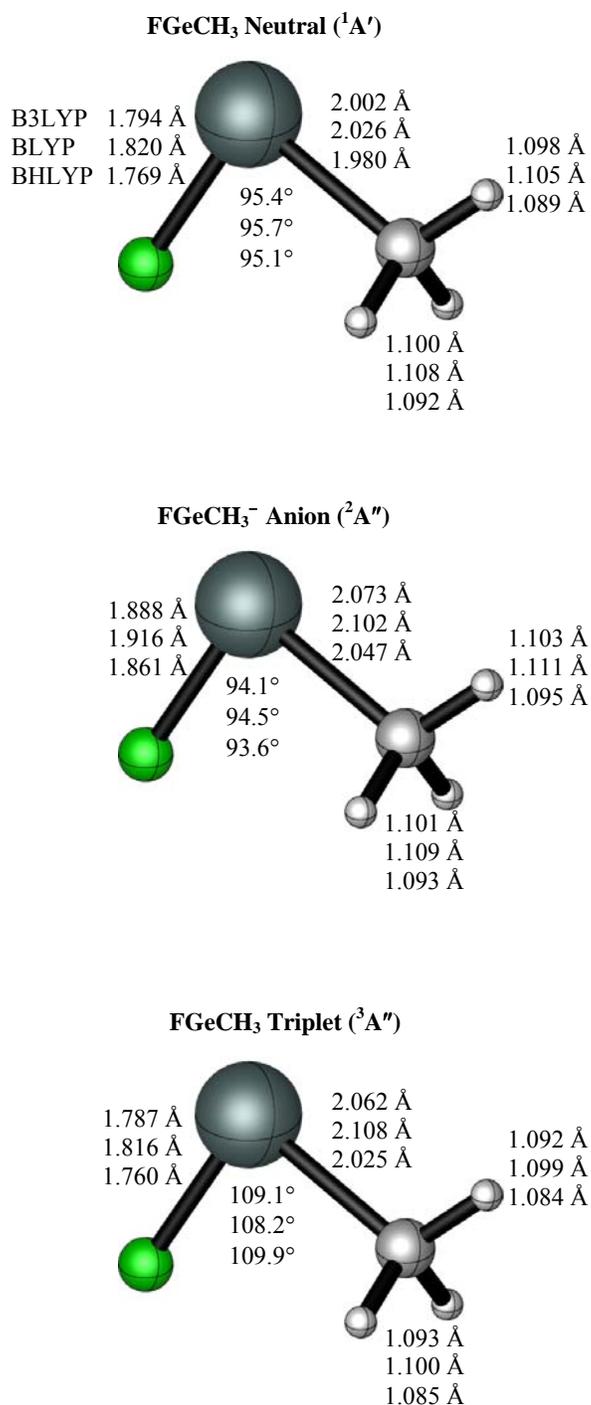


Figure 3. Equilibrium geometries for the ¹A' state of FGeCH₃, ²A'' state of the FGeCH₃⁻ anion, and ³A'' state of the FGeCH₃.

The predicted structural parameters show that the Ge-X, Ge-C, and C-Y bond distances lengthen in going from H→F→Cl→Br.

Expected trends are due to the change in atomic sizes and electronegativities (χ) of the halogen substituent.

The electronegativity (χ) can be used as a noteworthy reactivity descriptor, qualitatively defined by Pauling [10] as the power of the atom in a molecule to draw an electron to itself.

The standard Pauling electronegativities lie in the order $F(3.98) > Cl(3.16) > Br(2.96) > C(2.55) > H(2.20) > Ge(2.01)$.

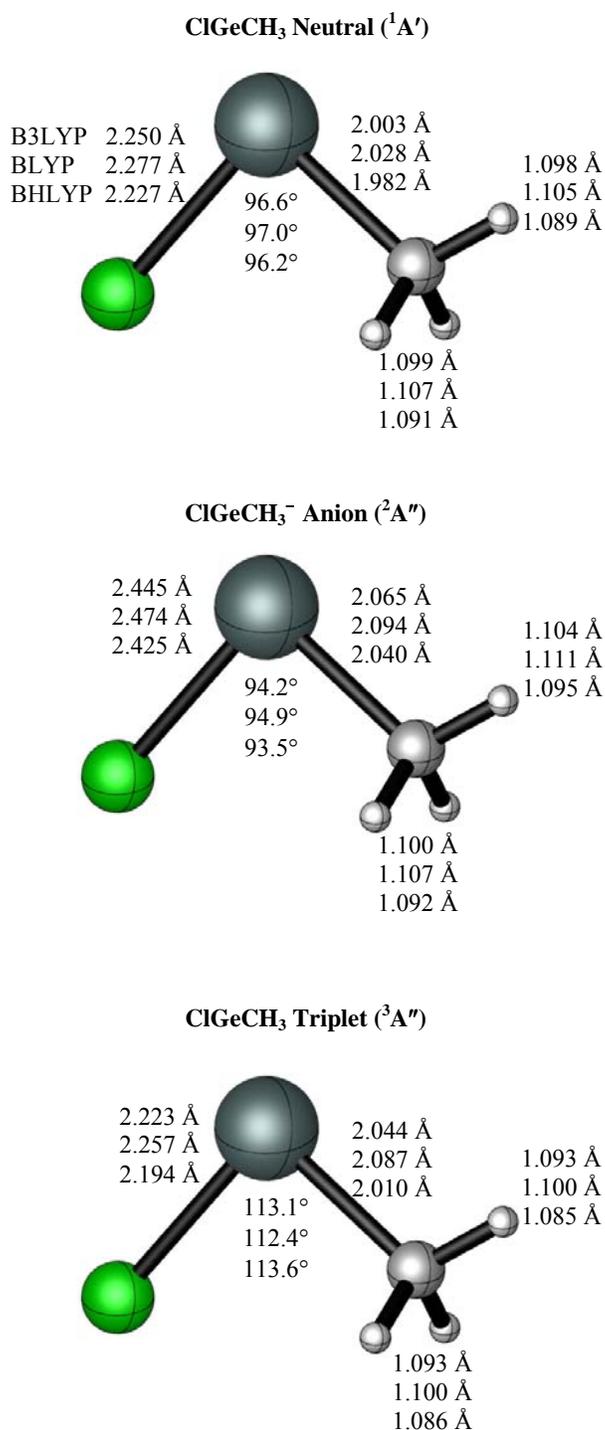


Figure 4. Equilibrium geometries for the ¹A' state of ClGeCH₃, ²A'' state of the ClGeCH₃⁻ anion, and ³A'' state of the ClGeCH₃.

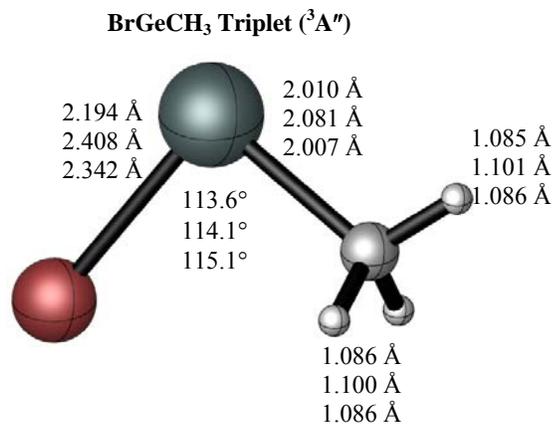
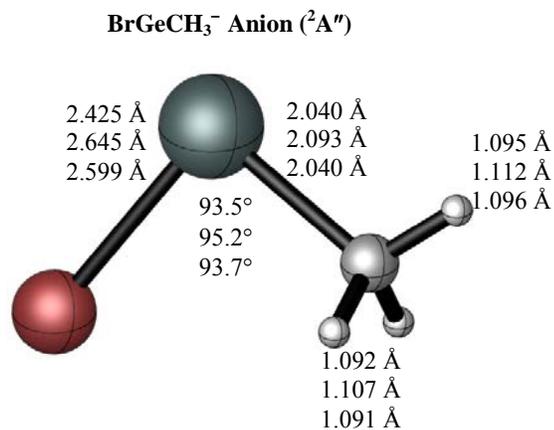
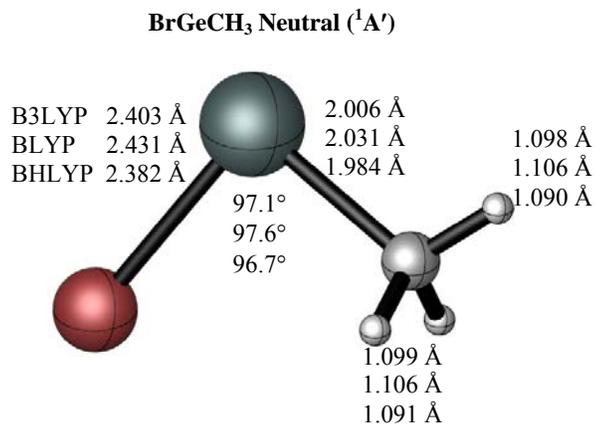


Figure 5. Equilibrium geometries for the ¹A' state of BrGeCH₃, ²A'' state of the BrGeCH₃⁻ anion, and ³A'' state of the BrGeCH₃.

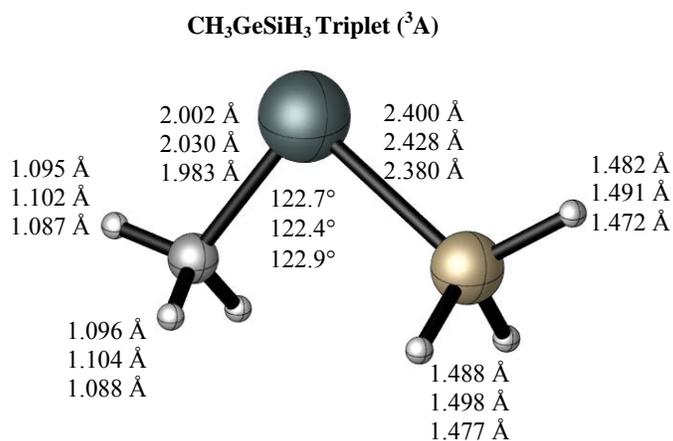
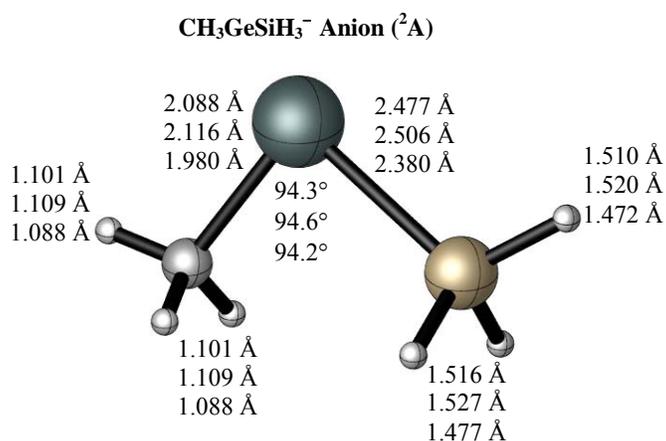
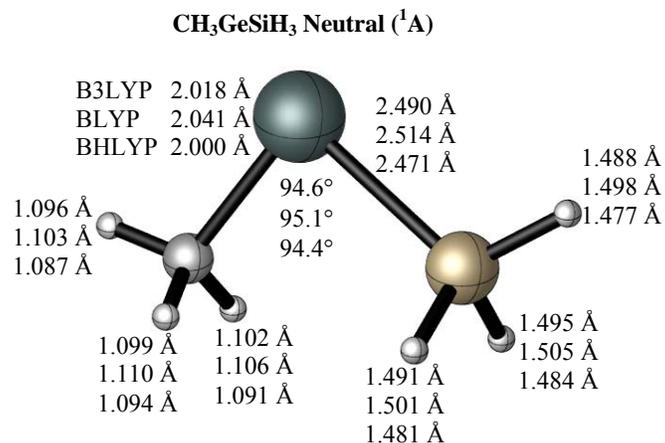
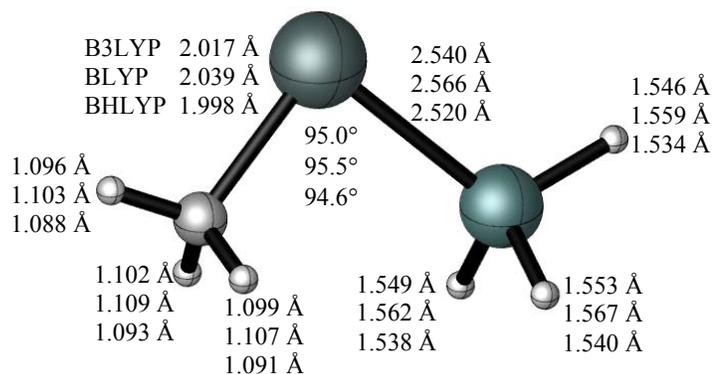
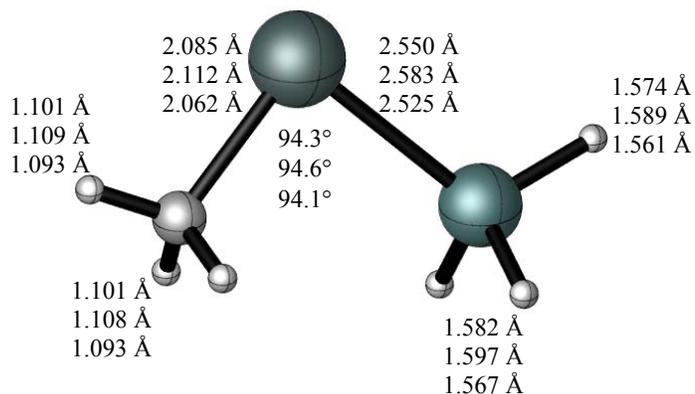


Figure 6. Equilibrium geometries for the ¹A state of CH₃GeSiH₃, ²A state of the CH₃GeSiH₃⁻ anion, and ³A state of the CH₃GeSiH₃.

CH₃GeGeH₃ Neutral (¹A)



CH₃GeGeH₃⁻ Anion (²A)



CH₃GeGeH₃ Triplet (³A)

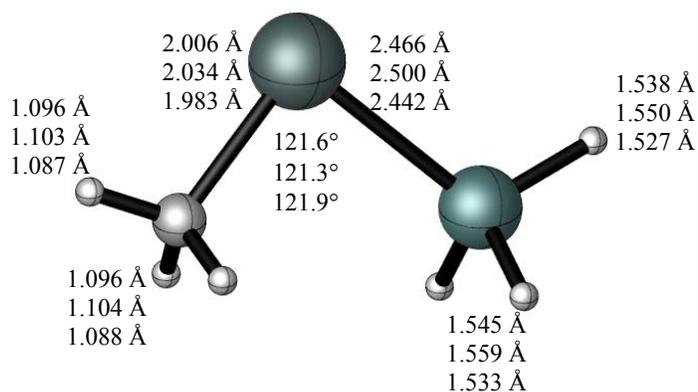


Figure 7. Equilibrium geometries for the ¹A state of CH₃GeGeH₃, ²A state of the CH₃GeGeH₃⁻ anion, and ³A state of the CH₃GeGeH₃.

In extending the electronegativities of atoms to functional groups, Geerlings and coworkers [11] have suggested $\chi_{\text{CH}_3} = 5.72$, $\chi_{\text{CF}_3} = 6.28$, $\chi_{\text{CCl}_3} = 5.63$, $\chi_{\text{CBr}_3} = 5.49$.

We expect to observe similar trends in the geometrical parameters, electron affinities and singlet-triplet splittings for the X-Ge-CY₃ systems.

As a function of the halogen atom, the X-Ge-CY₃ systems should display trends in geometrical parameters, electron affinities and singlet-triplet gaps, compared to the XGeCH₃ systems.

Halogen substitution appears to increase the favorability of the singlet states, and the magnitude of this stabilization follows the electronegativity.

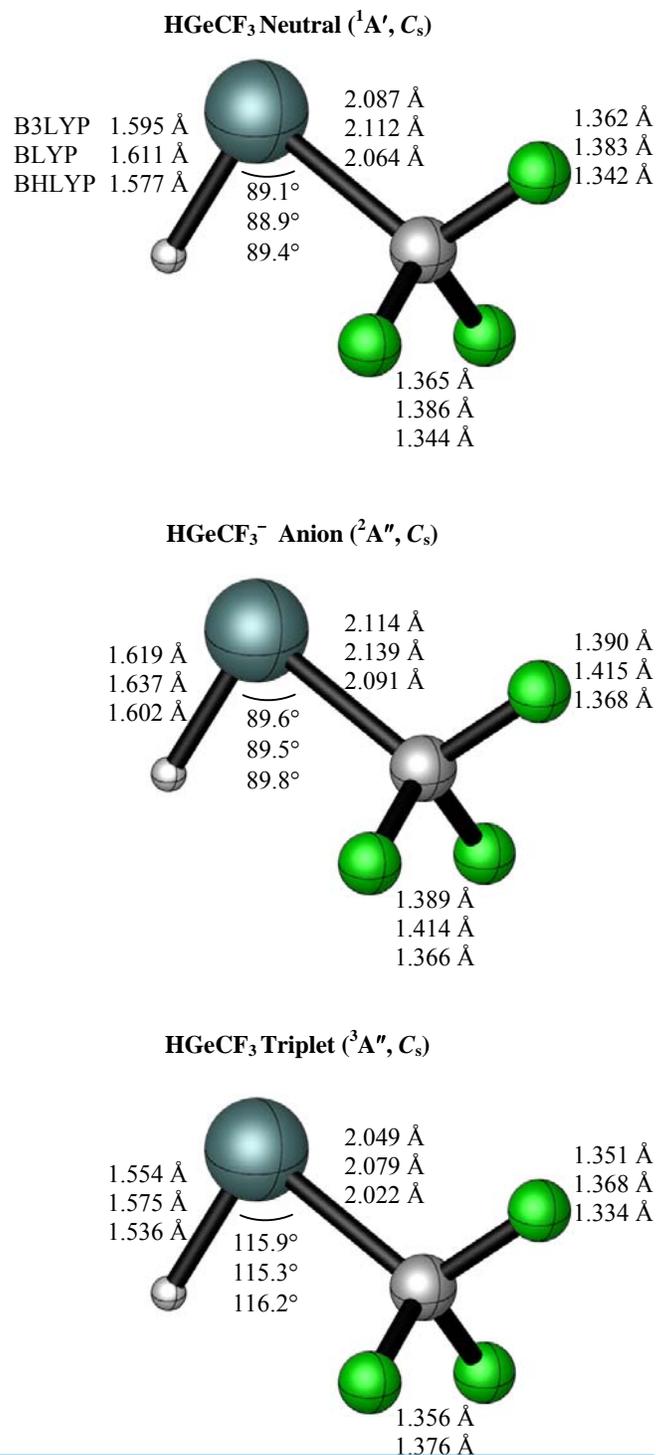


Figure 8. Equilibrium geometries for the ¹A' state of HGeCF₃, ²A'' state of the HGeCF₃⁻ anion and ³A'' state of the HGeCF₃.

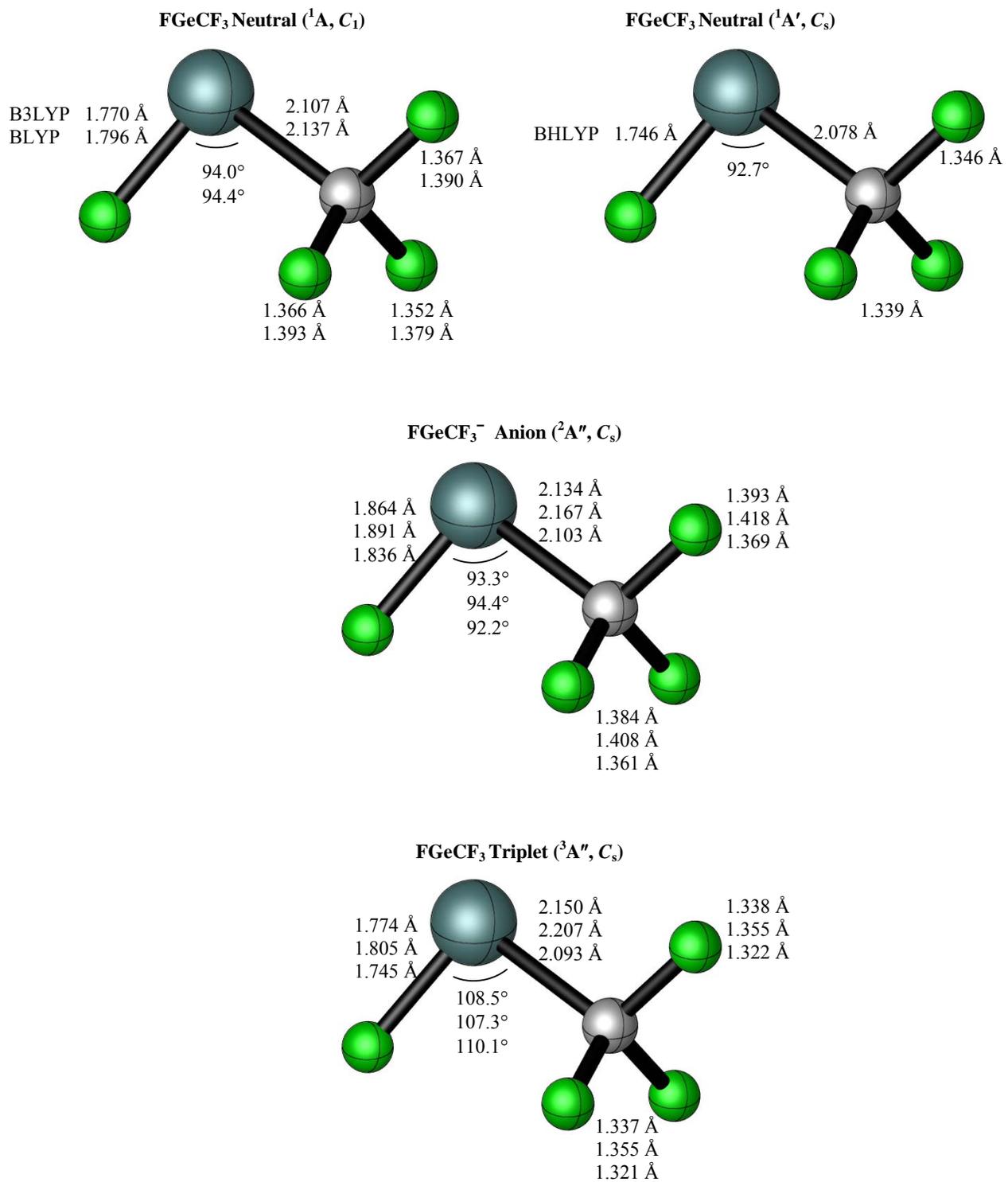


Figure 9. Equilibrium geometries for the ¹A/¹A' states of FGeCF₃, ²A'' state of the FGeCF₃⁻ anion and ³A'' state of the FGeCF₃.

- Bond angles for all molecules in their singlet neutral ground states lie in the range $89.1^\circ - 102.3^\circ$.
- The lone pair on the germanium atom causes a larger repulsion compared to the analogous repulsion of the bonding pair of electrons; hence the ideal angle of 120° is decreased significantly.
- This lone pair “occupies” a large space, and consequently results in divalent angles less than 120° .
- The values of the divalent angles in the series $X\text{-Ge-CY}_3$ ($X = \text{H, F, Cl, and Br}$; $Y = \text{F and Cl}$), with respect to substituent X, show a larger effect compared to varying the halide substituent on the $-\text{CY}_3$ moiety.
- While fixing either the Ge-X bond or the $-\text{CY}_3$ moiety, the divalent bond angles fall in the order $\text{F} < \text{Cl} < \text{Br}$.
- Experimentally determined $r(\text{Ge-C}) = 1.95 \text{ \AA} - 2.00 \text{ \AA}$ [12] of organogermanium derivatives

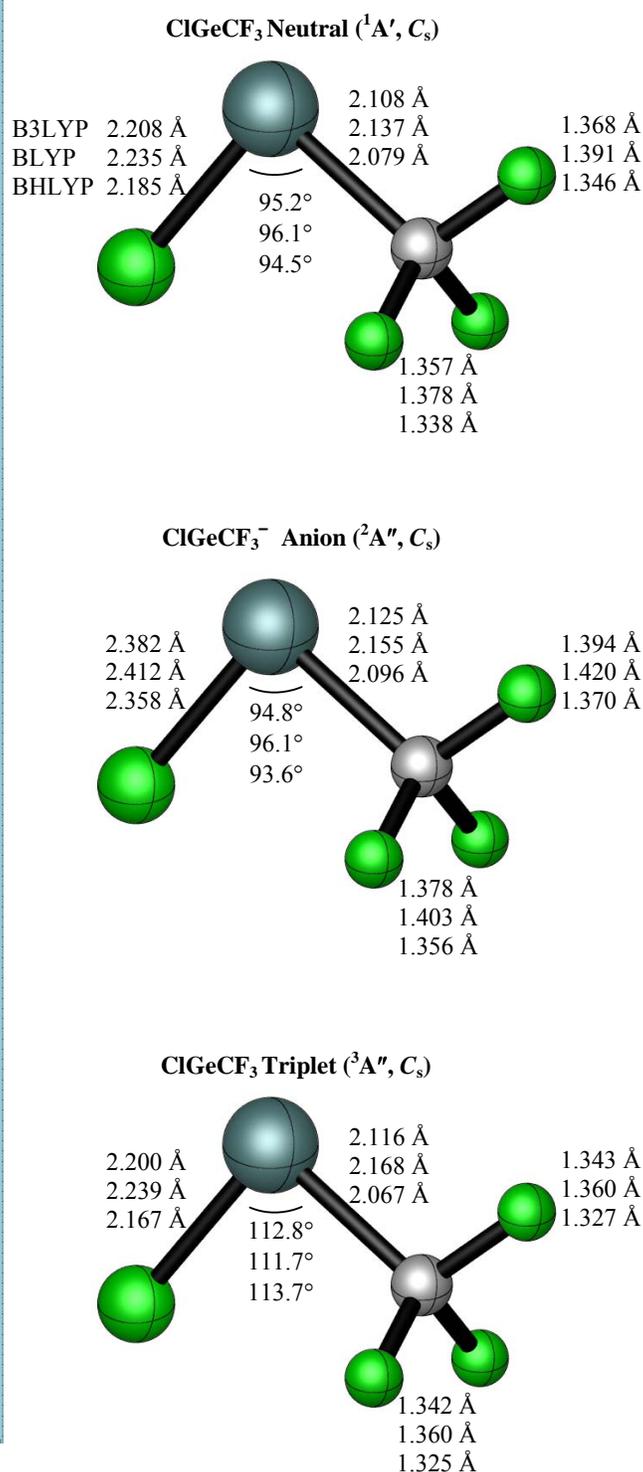


Figure 10. Equilibrium geometries for the $^1\text{A}'$ state of ClGeCF_3 , $^2\text{A}''$ state of the ClGeCF_3^- anion and $^3\text{A}''$ state of the ClGeCF_3 .

	BH&HLYP	BLYP	B3LYP
Ge(CH ₃) ₂	0.35	0.36	0.51
CH ₃ GeSiH ₃	1.06	1.05	1.19
CH ₃ GeGeH ₃	1.10	1.11	1.24
HGeCH ₃	0.64	0.67	0.79
FGeCH ₃	0.53	0.55	0.67
ClGeCH ₃	0.89	0.85	1.00
BrGeCH ₃	1.00	0.93	1.09
HGeCF ₃	1.61	1.58	1.73
FGeCF ₃	1.49	1.42	1.58
ClGeCF ₃	1.78	1.67	1.85
BrGeCF ₃	1.85	1.72	1.91
HGeCCl ₃	1.20	0.94	1.14
FGeCCl ₃	1.24	1.43	1.56
ClGeCCl ₃	1.52	1.30	1.53
BrGeCCl ₃	1.60	1.40	1.62

Table 2. Germylene vertical electron affinities (VEA) in eV.

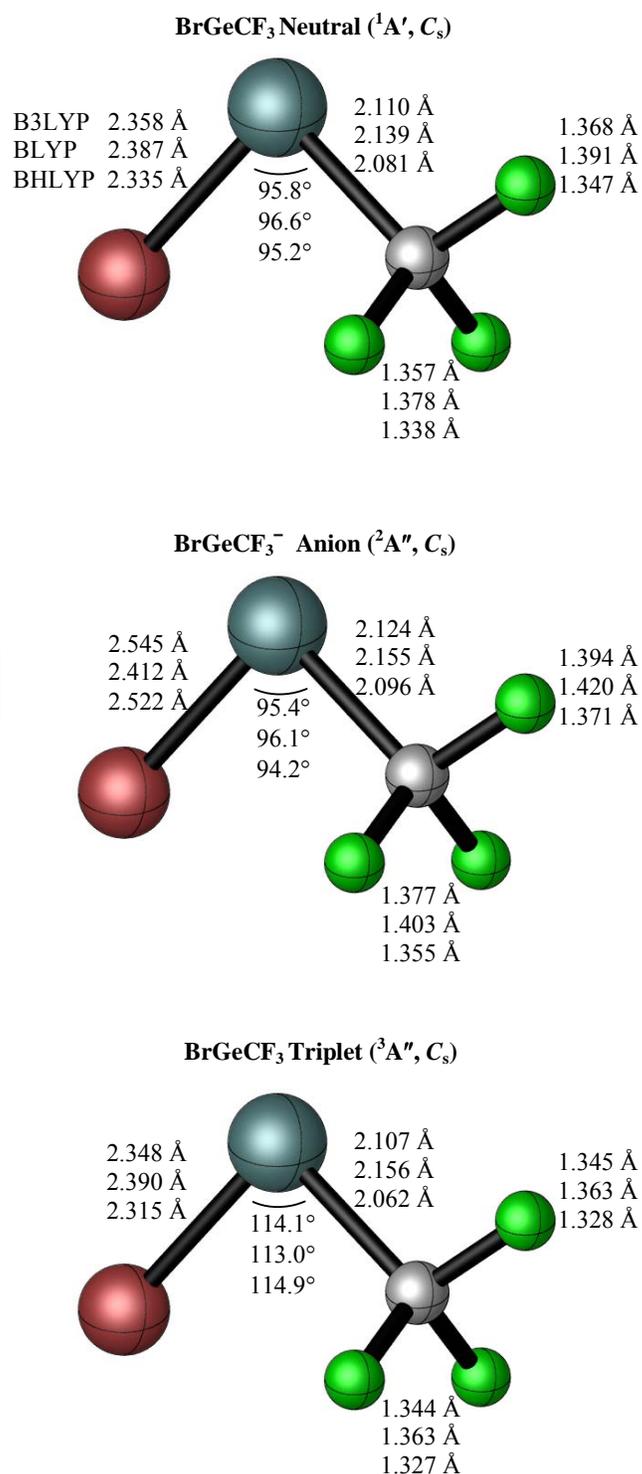


Figure 11. Equilibrium geometries for the ¹A' state of BrGeCF₃, ²A'' state of the BrGeCF₃⁻ anion and ³A'' state of the BrGeCF₃.

However, the same effect is not observed in going from $\text{HGeCF}_3 \rightarrow \text{FGeCF}_3$.

The large electronegativity of the fluoro substituent gives rise to strong Coulombic repulsion, acting against the decrease in the bond angle. In going from the singlet ground state to the lowest lying triplet state, similar trends in the change of the structural parameters are predicted.

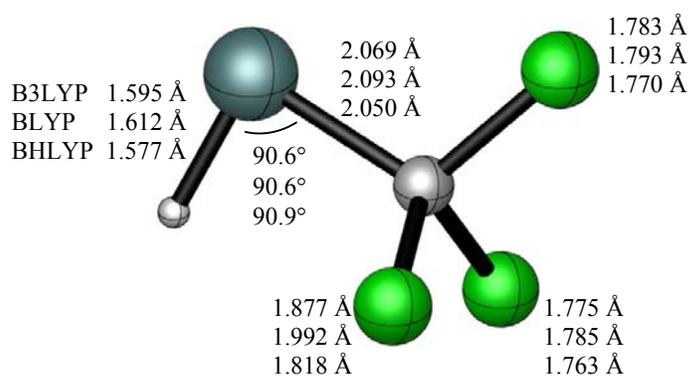
The importance of the ligand–ligand interactions is also one of the factors driving the increase in the bond angles, which depend on the electronegativity of the ligand, independently of the size of the halogen.

	BH&HLYP	BLYP	B3LYP
Ge(CH₃)₂	0.50	0.53	0.66
CH₃GeSiH₃	1.32	1.31	1.45
CH₃GeGeH₃	1.35	1.36	1.49
HGeCH₃	0.74	0.77	0.89
FGeCH₃	0.77	0.76	0.89
ClGeCH₃	1.29	1.19	1.37
BrGeCH₃	1.40	1.27	1.46
HGeCF₃	1.81	1.56	1.93
FGeCF₃	1.85	1.78	1.94
ClGeCF₃	2.25	2.11	2.31
BrGeCF₃	2.31	2.15	2.35
HGeCCl₃	1.84	1.97	2.01
FGeCCl₃	1.86	1.93	1.99
ClGeCCl₃	2.23	2.19	2.31
BrGeCCl₃	2.30	2.22	2.36

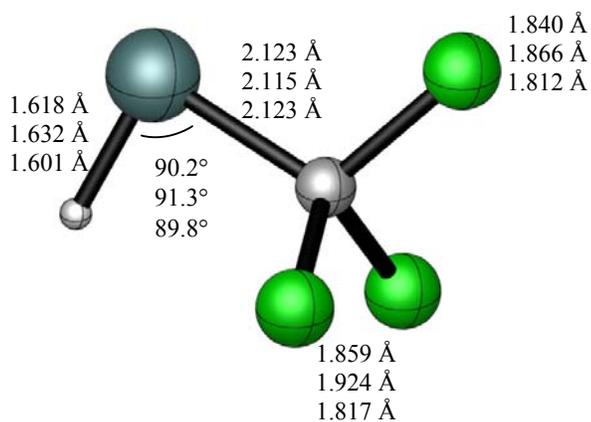
Table 3. Germylene vertical detachment energies (VDE) in eV.

- ❏ Comparing the geometrical parameters of the lowest singlet and triplet states of the same molecule, the most noticeable difference is that the bond angles of the triplet states are larger by 10–20°, for all XGeCF_3 and XGeCCl_3 ($X = \text{H, F, Cl, and Br}$).
- ❏ In the singlet state the HOMO is of a' symmetry, corresponding to the lone pair of electrons lying in the molecular plane.
- ❏ Consequently, in the triplet state an electron is moved to an orbital of a'' symmetry, in a simple picture an out-of-plane atomic p orbital of the divalent germanium atom.
- ❏ As a result, of the valence shell electrons in the molecular plane, only one electron remains at the germanium centre, leading to a large decrease in the repulsion, opening the bond angle in the triplet states.
- ❏ Another remarkable difference between the neutral ground and the lowest lying triplet states is that the Ge–X bond length is shorter in the triplet state.
- ❏ Analysis of the geometrical parameters reveals a regular trend, similar to the GeHX ($X = \text{H, F, Cl, and Br}$) series with respect to the substituent electronegativity.

HGeCCl₃ Neutral (¹A, C₁)



HGeCCl₃⁻ Anion (²A", C_s)



HGeCCl₃ Triplet (³A", C_s)

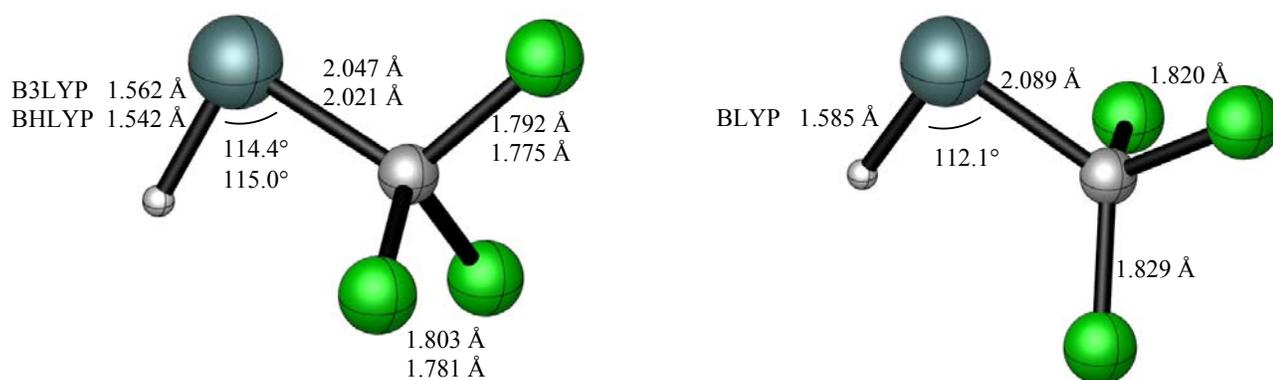


Figure 12. Equilibrium geometries for the ¹A state of HGeCCl₃, ²A" state of the HGeCCl₃⁻ anion and ³A" state of the HGeCCl₃.

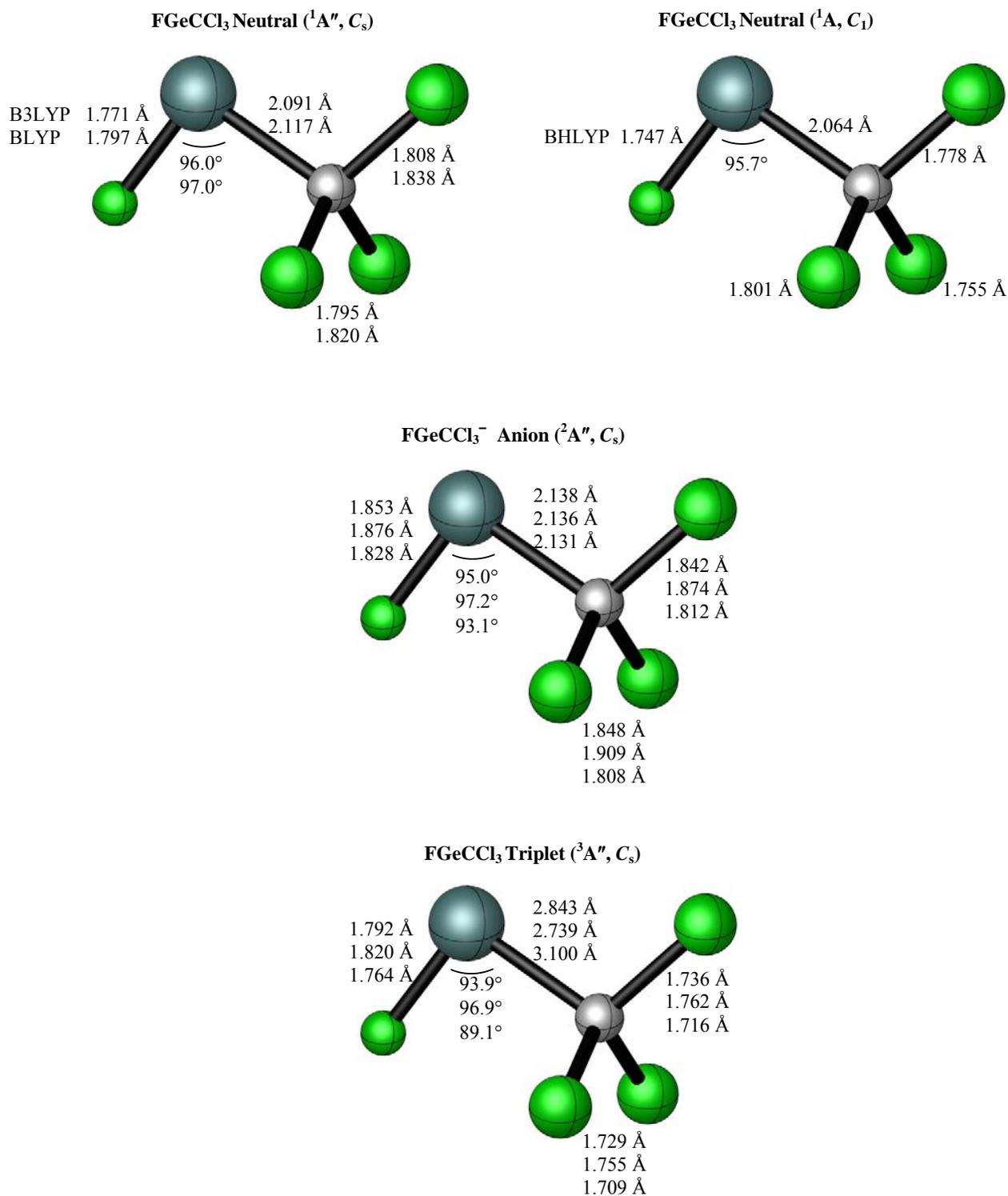


Figure 13. Equilibrium geometries for the ¹A/¹A' state of FGeCCl₃, ²A" state of the FGeCCl₃⁻ anion and ³A" state of the FGeCCl₃.

	BH&HLYP	BLYP	B3LYP
Ge(CH₃)₂	1.26	1.38	1.34
CH₃GeSiH₃	0.78	0.95	0.88
CH₃GeGeH₃	0.85	1.02	0.96
HGeCH₃	1.14	1.29	1.24
FGeCH₃	2.01	2.09	2.08
ClGeCH₃	1.81	1.91	1.89
BrGeCH₃	1.74	1.83	1.81
HGeCF₃	1.28	1.42	1.37
FGeCF₃	2.18	2.21	2.22
ClGeCF₃	1.94	2.00	2.00
BrGeCF₃	1.85	1.91	1.91
HGeCCl₃	1.47	1.63	1.57
FGeCCl₃	2.22	2.20	2.23
ClGeCCl₃	2.12	2.10	2.14
BrGeCCl₃	2.02	2.02	2.05

Table 4. Germylene singlet-triplet gaps (eV).

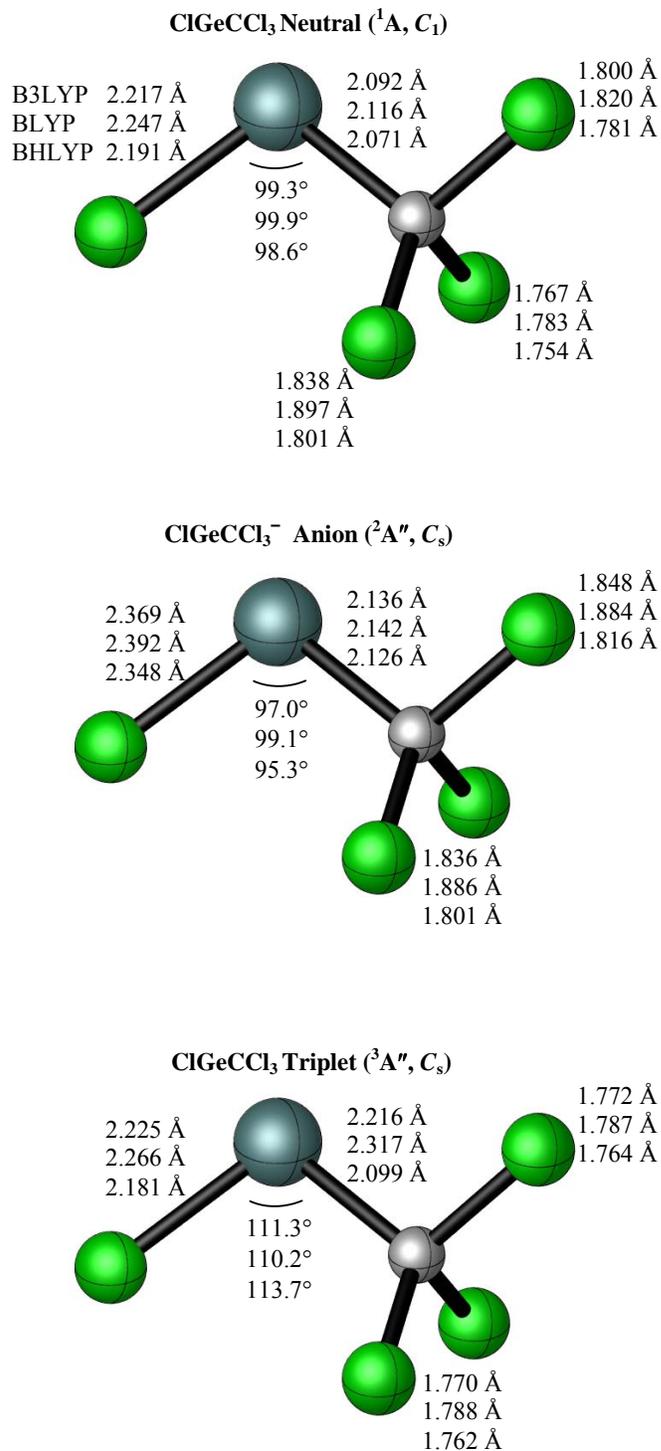


Figure 14. Equilibrium geometries for the ¹A state of ClGeCCl₃, ²A" state of the ClGeCCl₃⁻ anion and ³A" state of the ClGeCCl₃.

To study the influence of a given halide substituent on the bond length, R , it is useful to plot the values of the Ge–C bond distance for fixed $-\text{CF}_3$ in the series XGeCY_3 ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{and Br}$) as a function of the Pauling electronegativity of the second substituent X.

Similarly, in keeping the $R(\text{Ge}-\text{X})$ bond distance fixed, the trend in the Ge–C bond elongation can be analyzed.

The decreases in the repulsive interaction of the ligands from the singlet to the triplet state are illustrated in the trends shown in the Ge–X bond length along the series.

It is observed that the Ge–C bond length increases monotonically.

These structural changes may be related to the decreasing electron density around the divalent germanium centre in the molecular plane from the singlet state to its corresponding triplet species. The ligand gets closer to the germanium atom and achieves a better screening of the bonding electrons.

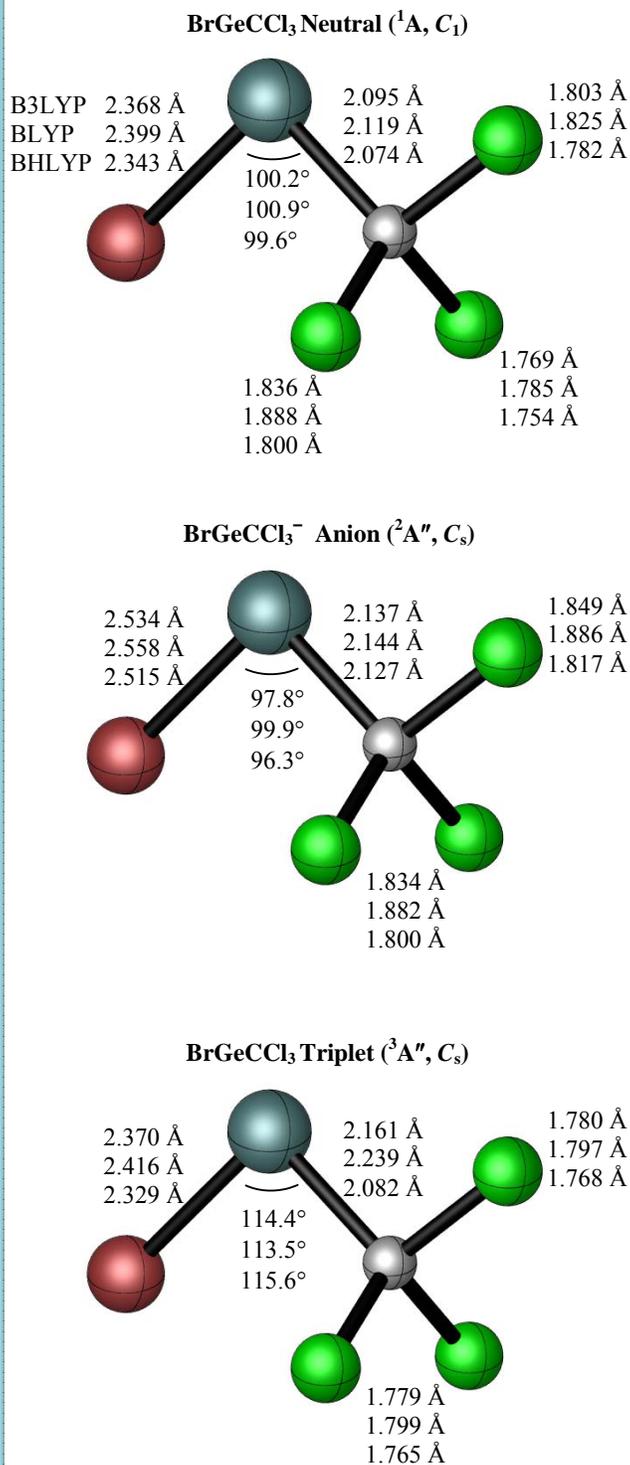
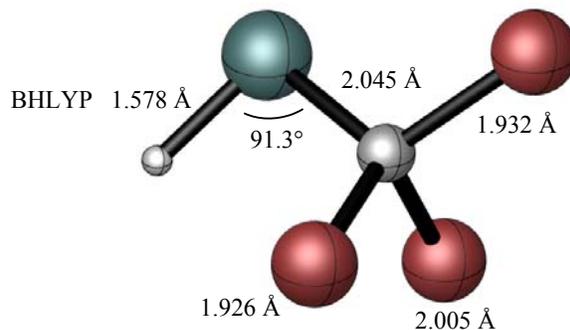
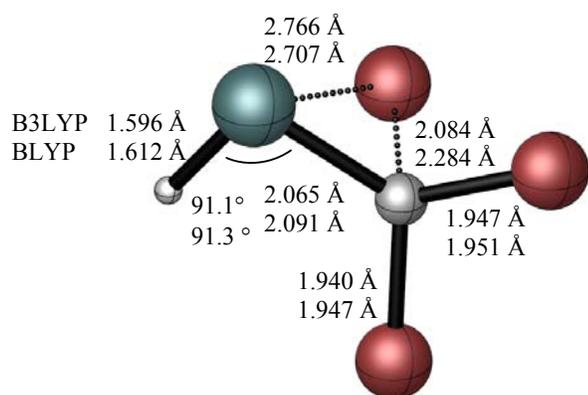


Figure 15. Equilibrium geometries for the ¹A state of BrGeCCl₃, ²A'' state of the BrGeCCl₃⁻ anion and ³A'' state of the BrGeCCl₃.

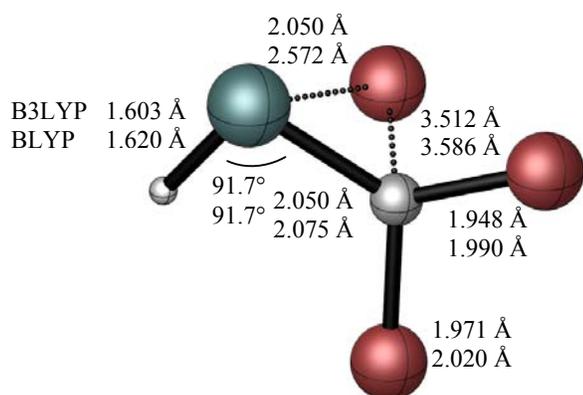
V. The Surprising XGeCBr₃ (X = H, F, Cl and Br) Germylenes

- Unlike the XGeCF₃ (X = H, F, Cl and Br) molecules, the heavier XGeCBr₃ and XGeCl₃ (X = H, F, Cl, and Br) molecules converged to unexpected structures.
- For the bromine substituents at the carbon centre, it is observed that in some cases the expected structures collapse to three-membered cyclic systems with the formation of weak bonds involving the divalent germanium centre, the carbon atom and one of the bromine atoms.
- In some cases, the molecules are optimized to yield structures where the carbon moiety is rotated or one of the halogen atoms is completely bonded to the divalent germanium center.
- Following the (3n-6) rule for the number of fundamentals in these polyatomic molecules, 12 real vibrational frequencies are found in all cases.

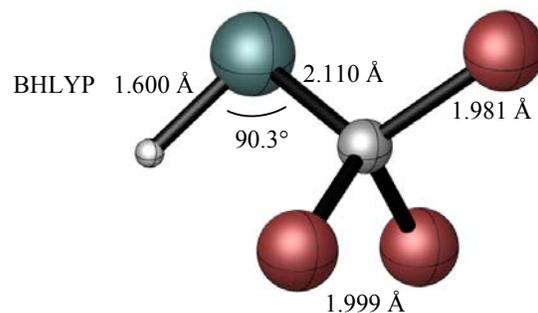
HGeCBr₃ Neutral (¹A, C₁)



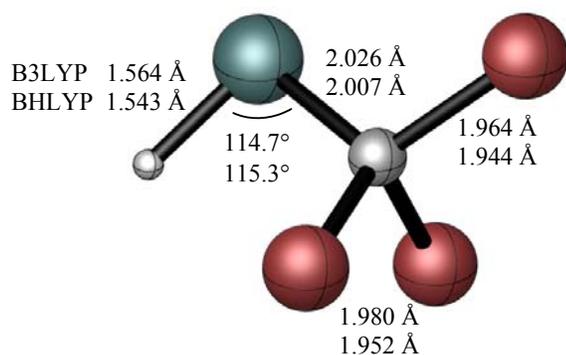
HGeCBr₃⁻ Anion (²A, C₁)



HGeCBr₃⁻ Anion (²A", C_s)



HGeCBr₃ Triplet (³A", C_s)



HGeCBr₃ Triplet (³A, C₁)

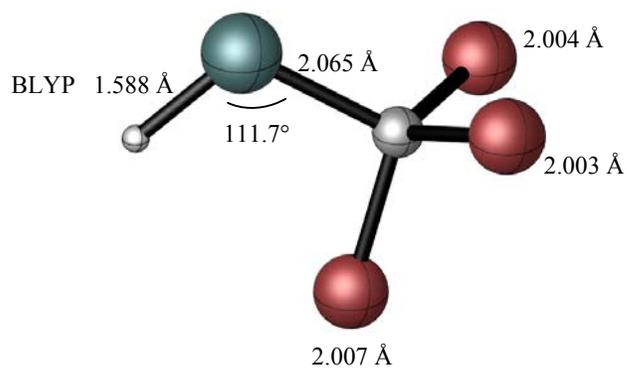


Figure 16. Equilibrium geometries for the ¹A state of HGeCBr₃, ²A/²A" state of the HGeCBr₃⁻ anion and ³A/³A" state of the HGeCBr₃.

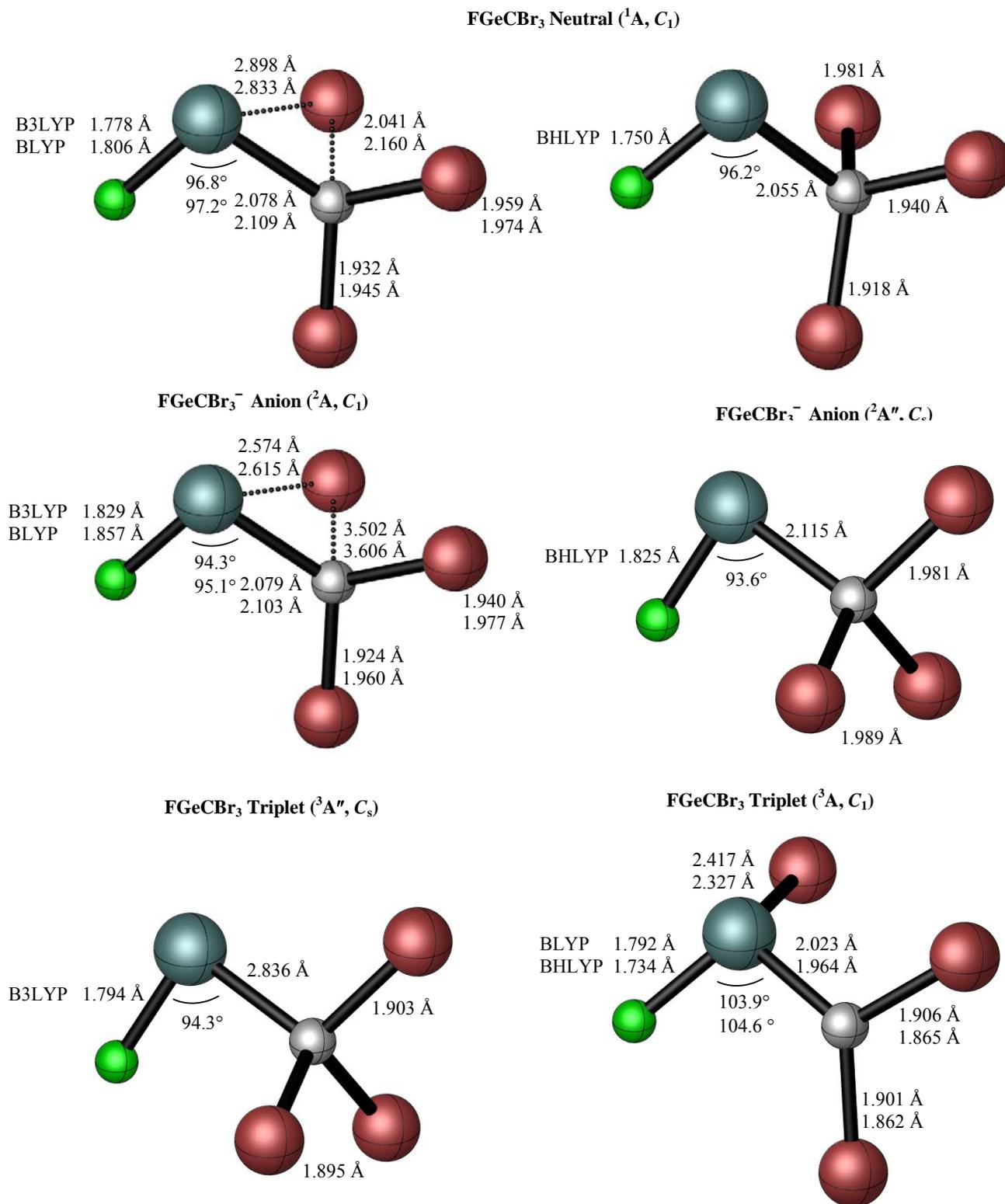


Figure 17. Equilibrium geometries for the ¹A state of FGeCBr₃, ²A/²A'' state of the FGeCBr₃⁻ anion and ³A/³A'' state of the FGeCBr₃.

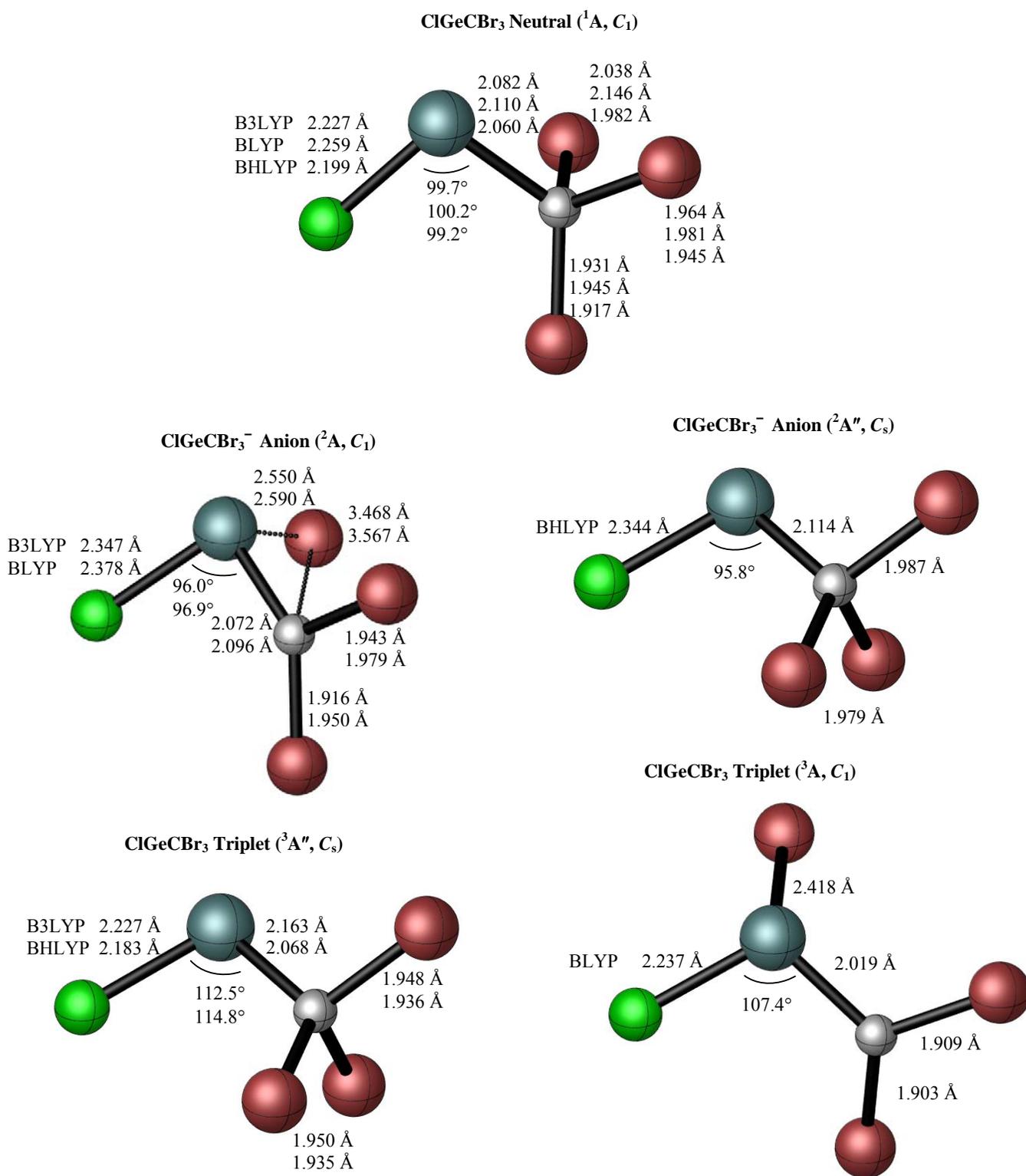


Figure 18. Equilibrium geometries for the ¹A state of ClGeCBr₃, ²A/²A" state of the ClGeCBr₃⁻ anion and ³A/³A" state of the ClGeCBr₃.

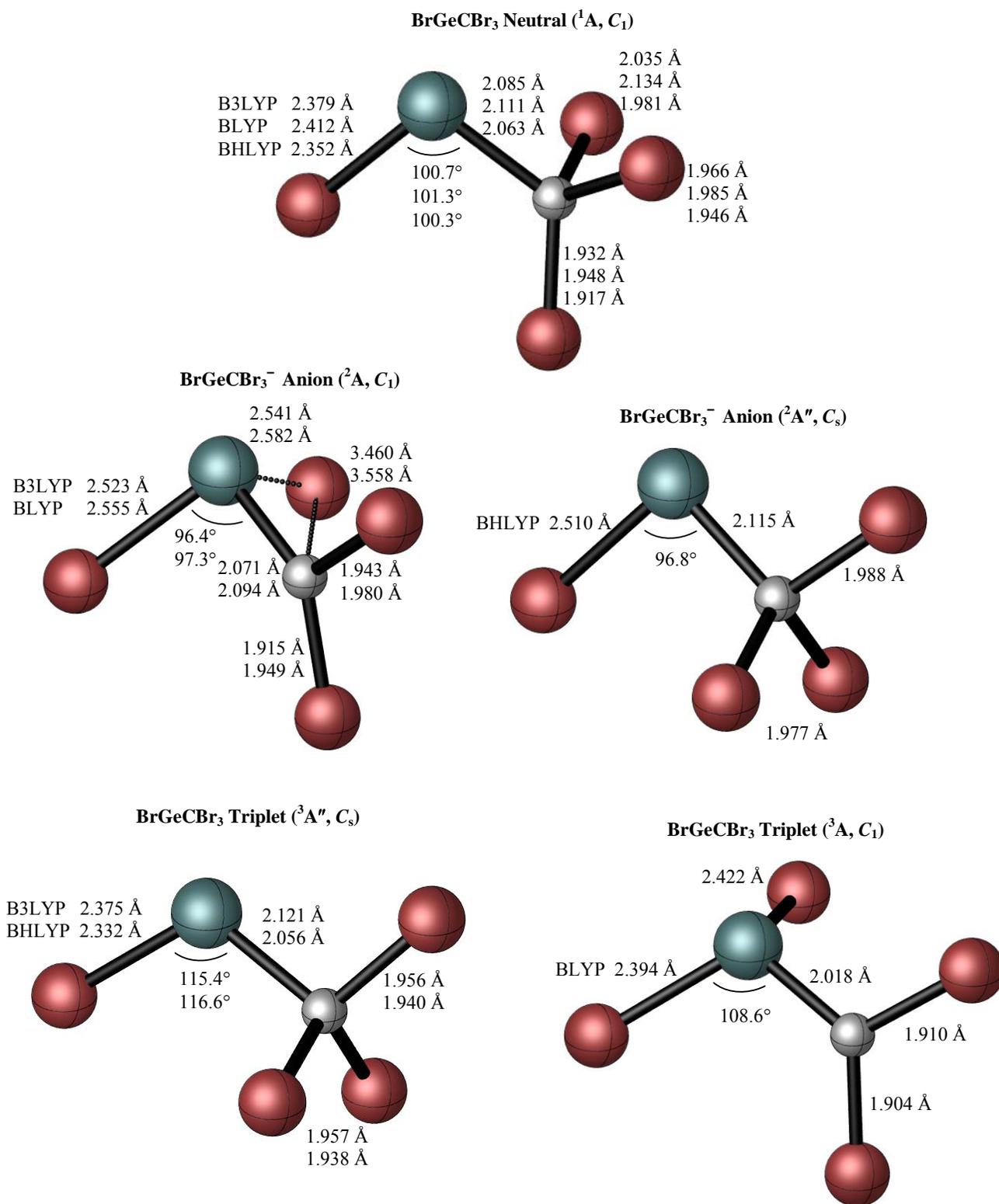


Figure 19. Equilibrium geometries for the ¹A state of BrGeCBr₃, ²A/²A'' state of the BrGeCBr₃⁻ anion and ³A/³A'' state of the BrGeCBr₃.

Although these tribromo-substituted species show different trends in their geometrical parameters, their zero-point corrected electron affinities for the $X\text{GeCBr}_3$ ($X = \text{H}, \text{F}, \text{Cl}$ and Br) molecules are included in Table 1.

- It is noted that all EA_{ad} and $EA_{\text{ad(ZPVE)}}$ are larger than those for the $X\text{GeCF}_3$ and $X\text{GeCCl}_3$ molecules ($X = \text{H}, \text{F}, \text{Cl}$ and Br).
- Exceptions are for the computed zero-point corrected electron affinities values of (1.68 eV) HGeCBr_3 and ClGeCBr_3 (1.96 eV) which are irregularly predicted by the BHLYP functional.

- 🖼️ A plausible explanation for the atypical characteristics of these species is that the carbon-halogen bonds are σ -acceptors; hence hyperconjugative effects are particularly sensitive to changes in substituent effects.
- 🖼️ The $\sigma_{\text{C-F}}^*$ bonds have higher acceptor abilities, while the anomeric effect predominates for the bromo- and iodo-substituents. The anomeric effect contributes to the electronic and steric factors.
- 🖼️ Acceptor ability of the carbon-halogen bonds, where the substituents $X = \text{F, Cl, and Br}$ are closely associated with their electronegativity.
- 🖼️ Another factor that contributes may be reflected by the carbon-halogen bond strengths of carbon-bromine.

-  The σ energy levels increase from $\sigma(\text{C-F}) < \sigma(\text{C-Cl}) < \sigma(\text{C-Br})$, whereas the σ^* energy levels decrease from $\sigma^*(\text{C-F}) > \sigma^*(\text{C-Cl}) > \sigma^*(\text{C-Br})$.
-  This implies that the $\sigma(\text{C-Y}) \rightarrow \sigma^*(\text{C-Y})$, the energy of the $-\text{CY}_3$ fragment becomes smaller as one proceeds along the series from fluorine to bromine.
-  Even with a decrease in the electronegativity of the halogen substituents $\text{F} > \text{Cl} > \text{Br}$, the acceptor abilities of the $\sigma^*_{(\text{C-Y})}$ orbitals increase in the order $\sigma^*_{(\text{C-F})} < \sigma^*_{(\text{C-Cl})} < \sigma^*_{(\text{C-Br})}$.
-  These results are intriguing in light of the higher donor abilities of the $\sigma_{\text{C-Cl}}$ and $\sigma_{\text{C-Br}}$ bond.
-  The order of the acceptor ability toward the C-F orbital is $\text{C-Br} > \text{C-Cl}$, while the order of acceptor abilities toward the C-Cl orbital is $\text{C-Br} > \text{C-F}$.
-  With respect to the carbon-halogen bond, the hyperconjugative interactions are lower, because the carbon-halogen bonds are weaker donors than C-H bonds.
-  Though the difference in the acceptor ability of the $\sigma^*(\text{C-Cl})$ and $\sigma^*(\text{C-Br})$ bonds is not very large, it is susceptible to the nature of X substitution.
-  The C-F bonds are more polarized toward the halogen than C-Cl/C-Br bonds.

VI. Conclusions

- ❏ The structural parameters, four different neutral-anion energy differences (namely EA_{ad} , $EA_{ad(ZPVE)}$, VEA, and VDE), plus the singlet-triplet gaps of the smaller $XGeCY_3$ ($X = H, F, Cl$ and Br ; $Y = F$ and Cl) systems have been investigated.
- ❏ It has been observed that these structures are conventional when the halogens attached to the carbon centre are fluorine or chlorine substituents, but this is not the case for bromine and iodine.
- ❏ For the tribromo germylene derivatives an unexpected three membered cyclic system is observed. It is also observed that the breaking of the halogen-carbon bond increases with decreasing halide electronegativity.
- ❏ All halogens stabilize the trihalo-substituted germylenes relative to $HGeCH_3$, since carbon is a strong π acceptor in the $-CY_3$ substituent and a σ acceptor with $-CCl_3$ and $-CBr_3$. The ability to bind an extra electron by the $XGeCY_3$ ($X = H, F, Cl$ and Br ; $Y = F$ and Cl) molecules has been predicted.
- ❏ It is observed that a related trend in the predicted electron affinities and singlet-triplet gaps is followed compared to the simple $XGeCH_3$ species.

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VIII. References

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Publications

Germylene Energetics: Electron Affinities and Singlet-Triplet Gaps of GeX_2 and GeXY Species ($X, Y = \text{H}, \text{CH}_3, \text{SiH}_3, \text{GeH}_3, \text{F}, \text{Cl}, \text{Br}, \text{I}$)

Ashwini Bundhun, Ponnadurai Ramasami and Henry F. Schaefer III
J. Phys. Chem. A, 2009, 113 (28), pp 8080–8090

Density functional theory study of the carbon chains

$\text{C}_n\text{X}, \text{C}_n\text{X}^+$ and C_nX^- ($X = \text{O}$ and $\text{Se}; n = 1-10$)

A. Bundhun and P. Ramasami
Eur. Phys. J. D 57 3 (2010) 355-364

Quantum Mechanical Modeling for the $\text{GeX}_2/\text{GeHX} + \text{GeH}_4$ Reactions ($X = \text{H}, \text{F}, \text{Cl},$ and Br)

Ashwini Bundhun, Paul Blowers, Ponnadurai Ramasami and
Henry F. Schaefer III
J. Phys. Chem. A, 2010, 114 (12), pp 4210–4223

Germynes: Structures, Electron Affinities and Singlet-Triplet Gaps of the Conventional XGeCY_3 ($X = \text{H}, \text{F}, \text{Cl}, \text{Br},$ and $\text{I}; Y = \text{F}$ and Cl) Species and the Unexpected Cyclic XGeCY_3 ($Y = \text{Br}$ and I) Systems

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