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Theoretical Study on the Thermochemistry of Chlorinated and Fluorinated Germanes and Their Radical Fragments

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The structures, vibrational frequencies, enthalpies of formation, and dissociation energies of germane, chlorinated and fluorinated germanes, and their radical fragments have been examined with density functional theory and quantum chemistry ab initio methods. The theoretical vibrational frequencies of the germanes at the B3LYP/6-31G(2df,p) level are in good agreement with the experimental data, but those of the germyl radicals largely disagree with the previous experimental assignments. The G3//DFT enthalpies of formation of GeH_4, $GeCl_4$, and $GeCl_2$ are within two times of the experimental uncertainties, while that of GeF_4 differs with the experiment by ∼10 kJ/mol. The calculated enthalpies of formation of the Ge-containing radicals have a large discrepancy with the available experimental data (which have large uncertainties). The bond dissociation energies of the Ge species and their trends with the F/Cl substitutions are evaluated at the G3 level as well. For dissociation of partially substituted F/Cl-germanes and germyl radicals, a propensity of diatomic elimination of H_2 or HF/HCl over single bond breaking is suggested, based on the low-energy barriers of the diatomic eliminations relative to the bond breakage to form Ge-containing radicals.

1. Introduction

Germane and its halogen substitutions have attracted considerable attention because of their potential roles in semiconductor productions.[1−5] For example, a $SiH_4/GeH_4/H_2$ mixture is commonly used as the precursor for growth of SiGe microcrystal; $GeCl_4$ has been proposed for deposition of germanium and growth of $Si_{1-x}Ge_x$ heterostructures on silicon surfaces;[6] GeF_4 is introduced as a guest molecule to reduce germanium-related dangling bond density in thin films in plasma-enhanced chemical vapor deposition (CVD) processes, in which GeF_x ($x = 1-3$) radicals are involved;[7,8] HCl is added to a SiH_2Cl_2/GeH_4 mixture for controlling growth of Si and SiGe,[9] etc.

The structural and thermodynamic parameters of simple germanes and their fragment radicals are important for understanding the CVD processes, and yet they are largely unknown in spite of decades of experimental and theoretical studies. The enthalpies of formation of gaseous Ge compounds are mostly derived based on those of the solid-state Ge compounds by using classical thermochemistry methods, as the standard state of germanium is crystal (cr) and the enthalpies of formation of some solid-state Ge compounds, such as GeO_2(s), are known with precision. For example, $\Delta_f H^\circ_{298}(GeH_4, g)$ has been determined to be 90.4 ± 2.1 kJ/mol from the heat of decomposition of GeH_4(g) to Ge(s) + $2H_2$,[10] $\Delta_f H^\circ_{298}(GeF_4, g) = -1190.3 \pm 0.8$ kJ/mol from F_2-bomb calorimetry,[11,12] and $\Delta_f H^\circ_{298}(GeCl_4, g) = -494.8 \pm 2.7$ kJ/mol from the third-law analysis of the equilibrium constant of $GeO_2(s) + 2Cl_2 = GeCl_4 + O_2$.[13] No measurements are available for the partially F/Cl-substituted germanes.

The classical thermodynamics has also been utilized to obtain the enthalpies of formation and bond dissociation energies (BDEs) of several fragment radicals of germanes. The enthalpy of formation of $GeCl_2$ has been determined from the chemical equilibrium $Ge(s) + GeCl_4(g) = 2GeCl_2(g)$. The enthalpy change of reaction at 723 K was first found to be 146.0 ± 2.1 kJ/mol;[14] with this value and $\Delta_f H^\circ_{298}(GeCl_4, g) = -510$ kJ/mol, Uy et al.[15] obtained $\Delta_f H^\circ_{298}(GeCl_2, g)$ of −170 ± 4 kJ/mol,[16] and $\Delta_f H^\circ_{298}(GeCl_2, g)$ can be revised to −162.8 ± 4 kJ/mol with a new $\Delta_f H^\circ_{298}(GeCl_4, g)$ of −494.8 ± 2.7 kJ/mol.[13] Two values of $\Delta_f H^\circ_f(GeF_2, g)$ have been published from the same group.[17,18] From the chemical equilibrium between CaF_2(g) and Ge, Ehlert et al. obtained a value in the range of −430 to −506 kJ/mol;[17] from the enthalpy of formation of GeF_2(cr) (−747.3 ± 4.2 kJ/mol, 298.15 K)[19] and the enthalpy of sublimation of GeF_2(cr) (85.8 kJ/mol, 298.15 K), Adams et al. obtained $\Delta_f H^\circ_{298}(GeF_2, g) = -572.8$ kJ/mol.[18] $D(Ge-Cl) = 387.0 \pm 9.6$ kJ/mol was determined from the gas-phase chemical equilibrium of GeCl, CuCl, Ge, and Cu.[20] $D(H_3Ge-H) = 346 \pm 10$ kJ/mol and $D(H_2IGe-H) = 332 \pm 10$ kJ/mol were derived from kinetic studies on the reaction between iodine and GeH_4 and GeH_3I.[21,22] $D(H_3Ge-H) \leq 326$ kJ/mol was also estimated from HF infrared chemiluminescence in the reaction of the F atom with GeH_4,[23] and it was revised to ∼339 kJ/mol.[24]

Photodissociation and photoionization with high-resolution light sources are other experimental methods for the determination of the bond dissociation energies and ionization energies. Up to now, the most precise determination of $D_0(H_3Ge-H) = 343.1 \pm 8.4$ kJ/mol is from the photoionization study;[24] and the ionization energies and bond dissociation energies of other GeH_x species are also obtained in the photoionization study. These experimental values of the GeH_x system from the photoionization study are reliable for testing the theoretical calculations. There have been a few photoionization and electron-bombardment studies on the substituted germanes, attempting for the BDEs of the germanes and fragment

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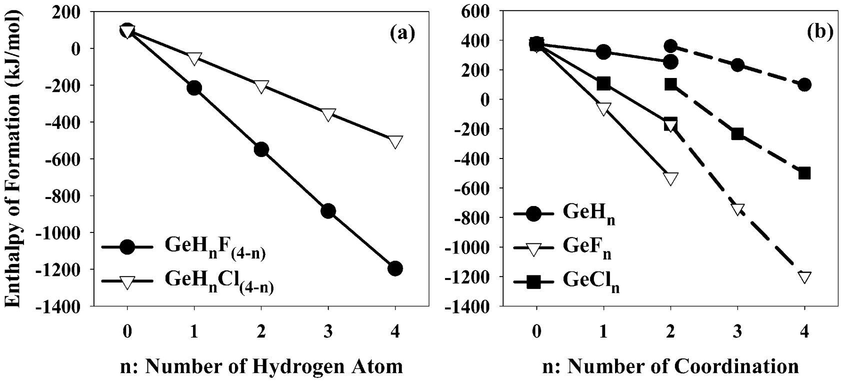

Figure 1. Enthalpies of formation of (a) $GeH_nF_{(4-n)}$ and $GeH_nCl_{(4-n)}$ and (b) GeH_n, GeF_n, and $GeCl_n$ at 0 K at the G3//DFT level of theory (singlet GeX_2 connects to the solid lines, and triplet GeX_2 to the dash lines).

radicals.[25−27] However, the low-energy resolution (due to the spectral resolution of the light sources and the sensitivity of ion detection) has limited the reliability and accuracy of these measurements.

The experimental enthalpies of formation are known accurately only for GeH_4, GeF_4, $GeCl_4$, and $GeCl_2$, and several measurements for only a few Ge-containing radicals have large uncertainties. The lack of experimental thermodynamic and kinetic data for the Ge compounds has hampered a better understanding of the precursors and their chemistry in the CVD processes, and it is desirable to determine these properties from the first principle calculations. Quantum chemistry calculations have been able to provide reasonably accurate estimations on the structural and thermodynamic parameters,[28] and to clarify the gas-phase reaction mechanisms in the CVD and etching processes.[29−31] The $D(H-GeH_3)$ has been determined to be 354.8 kJ/mol at the G1 level by Binning and Curtiss,[32] 354.5 kJ/mol at the G2 level by Mayer et al.,[33] 350.5 kJ/mol at the RCCSD(T)-CBS level (with scalar relativistic effect and spin−orbital effects included) by Ricca and Bauschlicher,[34] and 339.3 kJ/mol at the QCISD(T)/GCM+/ECP level by Morgon and Riveros.[35] The Dirac-HF calculation has obtained the reaction energy of $GeH_4 \rightarrow GeH_2 + H_2$ of 195.4 kJ/mol.[36] The BDEs of $GeX_{2,4}$ (X = F, Cl) have been attempted with DFT methods.[37] There have been several spectroscopic and theoretical studies on the singlet−triplet separations of the germylene radicals.[38−49] In this work, theoretical studies with the density functional method and high-level ab initio methods are carried out on the structural and thermodynamic properties of germane, its F/Cl substitutions, and their fragment radicals. The results are compared with the available experimental data and theoretical values.

2. Computational Details

All quantum chemistry calculations are performed with the Gaussian 98 program.[50] Geometries of germanes and their radicals are optimized at B3LYP and MP2(Full) levels of theory with 6-31G(2df,p) basis sets. Zero-point energy (ZPE) corrections are calculated from the B3LYP/6-31G(2df,p) vibrational frequencies with a scale factor of 0.9854.[51] The newly developed 6-31G(d) basis set with the 3d-shell included as the valence shell for germanium is employed here.[52] All the B3LYP and MP2(Full) geometries are subjected to G3 single-point calculations[53,54] (denoted G3//DFT and G3//MP2 here) with high-level correction parameters (in mhartree) of $A = 6.688$, $B = 3.007$, $C = 6.763$, and $D = 1.107$.[51] The enthalpies of formation are determined by the atomization energy procedure.[55] The enthalpies of formation and their thermal corrections $[H^{298.15}-H^0]$ of H, F, and Cl atoms are taken from the JANAF-NIST table.[56] The $\Delta_f H_0^\circ$(Ge, g) of 373.8 ± 8 kJ/mol and the thermal correction of 4.623 kJ/mol for Ge(cr) from the CRC handbook[57] are used in this study.

3. Results and Discussion

The geometry parameters, vibrational frequencies, G3 energies and enthalpies of formation, and bond dissociation energies (BDEs) of the title species are listed in Tables 1−4, respectively. The variations of enthalpies of formation and BDEs upon F/Cl substitution are depicted in Figures 1 and 2.

3.1. Geometry and Vibrational Frequencies. Most experimental geometries are obtained from the spectroscopic studies, and are limited to GeX and several germylene radicals for which rotationally resolved spectra have been recorded. These values are summarized in Table 1.

MP2(FU) and B3LYP predict similar geometries, with the MP2(FU) bond lengths systematically shorter than the B3LYP ones, up to 0.06 Å in $GeCl_3$. Experimental bond lengths, if available, are usually in between. For example, the $r(Ge-H)$ of GeH is 1.564 Å by MP2(FU), 1.588 Å from experiment, and 1.604 Å by B3LYP. These values for Ge−F are 1.736, 1.745, and 1.752 Å, respectively. Similar trends are expected for other species. Despite the bond length differences, the G3 energies based on the MP2(FU) and B3LYP geometries are in close agreement, within a maximum difference of 1.2 kJ/mol (for GeF_4). Discussions in the following will be based on the G3//DFT calculations unless otherwise stated.

The theoretical vibrational frequencies are listed in Table 2 along with the available experimental values. Vibrational spectra are available for most of the germanes concerned here from IR and Raman spectroscopy.[58−63] Photolysis of chlorogermanes in matrix has been used to produce the radicals and to study their IR absorption spectra.[64−66] The calculated B3LYP/6-31G(2df,p) vibrational frequencies of germanes agree well with the experimentally observed transitions, with the Ge−H stretching frequencies usually overestimated by about 1−2%. However, our calculation results cast doubt on some of the assignments for several radicals. For example, the calculations support the experimental assignments for GeH_4 and the GeH_2 radical, but they are not consistent with those for the GeH_3 radical. The 850 cm^{-1} experimental transition can be assigned to the deformation mode of GeH_3, while the 928, 1813, and 1839 cm^{-1} transitions observed in the experiment do not match with the calculated frequencies of GeH_3.[66] The calculations agree with the experimental assignments for $GeCl_3$ and $GeCl_2$,[64] but disagree with the assignments for the GeH_2Cl radical. The observed transition at 385 cm^{-1} may correspond to the

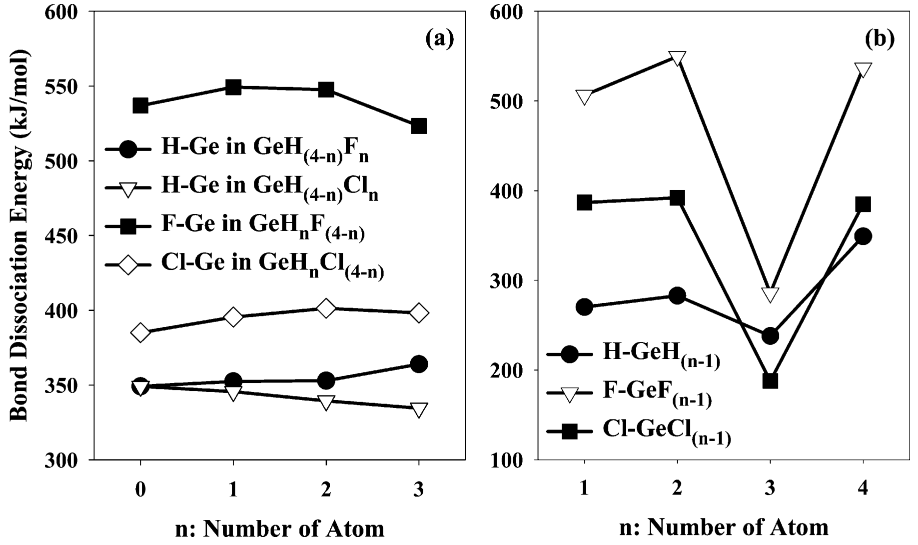

Figure 2. Bond dissociation energies (in kJ/mol) in (a) F- and Cl-substituted germanes and (b) GeH_n, GeF_n, and $GeCl_n$ at 0 K at the G3//DFT level of theory.

TABLE 1: Geometrical Parameters at the MP2(FU) and B3LYP (in parentheses) Levels of Theory and Available Experimental Values (in curly braces)[a]

species	sym	Ge−H	Ge−X	H−Ge−H	H−Ge−X	X−Ge−X
Ge−H		1.564 (1.604) {1.588}				
Ge−F			1.736 (1.752) {1.745}			
Ge−Cl			2.148 (2.198)			
$^1GeH_2$	C_{2v}	1.559 (1.596) {1.591}[48]		91.9 (90.4) {91.2}[48]		
$^3GeH_2$	C_{2v}	1.508 (1.544)		119.9 (119.5)		
^1GeHF	C_s	1.573 (1.616)	1.737 (1.753)		94.8 (94.6)	
^3GeHF	C_s	1.521 (1.572)	1.728 (1.745)		113.7 (112.6)	
$^1GeF_2$	C_{2v}		1.727 (1.742) {1.7320}[82]			97.8 (98.1) {97.148}[82]
$^3GeF_2$	C_{2v}		1.719 (1.744)			112.2 (113.2)
^1GeHCl	C_s	1.563 (1.603)	2.154 (2.207)		94.3 (93.7)	
^3GeHCl	C_s	1.517 (1.565)	2.123 (2.176)		115.5 (114.4)	
$^1GeCl_2$	C_{2v}		2.152 (2.206)			100.2 (100.7)
$^3GeCl_2$	C_{2v}		2.120 (2.187)			117.6 (119.8)
GeH_3	C_{3v}	1.510 (1.540)		111.9 (110.7)		
GeH_2F	C_s	1.518 (1.555)	1.729 (1.743)	113.5 (112.6)	106.2 (105.6)	
$GeHF_2$	C_s	1.528 (1.573)	1.717 (1.733)		107.5 (106.3)	104.3 (104.2)
GeF_3	C_{3v}		1.706 (1.723)			106.6 (106.4)
GeH_2Cl	C_s	1.515 (1.549)	2.131 (2.179)	112.9 (111.7)	107.5 (106.2)	
$GeHCl_2$	C_s	1.521 (1.561)	2.123 (2.176)		108.0 (106.6)	108.4 (108.5)
$GeCl_3$	C_{3v}		2.118 (2.177)			108.7 (108.8)
GeH_4	T_d	1.510 (1.534)				
GeH_3F	C_{3v}	1.510 (1.533)	1.728 (1.738)	112.3 (112.4)	106.4 (106.4)	
GeH_2F_2		1.515 (1.530)	1.713 (1.723)	118.5 (119.0)	108.1 (108.0)	105.2 (105.2)
$GeHF_3$	C_{3v}	1.496 (1.519)	1.698 (1.708)		112.2 (112.2)	106.6 (106.5)
GeF_4	T_d		1.685 (1.694)			
GeH_3Cl	C_{3v}	1.507 (1.532)	2.133 (2.174)	111.7 (111.8)	107.1 (107.0)	
GeH_2Cl_2		1.504 (1.529)	2.117 (2.158)	115.6 (116.0)	108.2 (108.0)	108.2 (108.8)
$GeHCl_3$	C_{3v}	1.501 (1.526)	2.105 (2.145)		110.4 (110.2)	108.5 (108.7)
$GeCl_4$	T_d		2.095 (2.136)			

[a] Bond lengths in Å and bond angles in deg.

calculated 402 cm^{-1} of GeH_2Cl, while those observed at 685, 715, 734, 1810, and 1856 cm^{-1} cannot be matched to the theoretical values here.[65]

3.2. Germanium Hydrides (GeH_x, $x = 1-4$). As the previous experimental and theoretical studies have obtained accurate and reliable BDEs only for the GeH_x system, it is worthwhile to examine the performance of the G3 method on this system first. From the photoionization studies, Ruscic et al. obtained the 0 K BDEs of the Ge−H bond to be <357.7, >236.0, <288.3, and >224.7 kJ/mol from GeH_4 to GeH, respectively.[24] At the RCCSD(T)-CBS level with scalar relativistic effects and spin−orbital effects included, Ricca et al. calculated BDEs of 350.5, 238.9, 286.4, and 269.9 kJ/mol correspondingly.[34] A previous G2 study obtained BDE(GeH_3−H) of 354.5 kJ/mol.[33] Our G3//DFT values of 349.1, 237.5, 282.9, and 270.5 kJ/mol (Table 4) are in excellent agreement with Ricca et al.'s theoretical results, but with much less computational demand. The G3 calculations are also consistent with the experimental BDEs by Ruscic et al.,[24] which were obtained from the measurements of adiabatic ionization poten-

TABLE 2: Vibrational Frequencies (in cm^{-1}) at the B3LYP/6-31G(2df,p) Level, Compared with the Available Experimental Values

species	frequencies (in cm^{-1})
GeH	1875 (exptl: 1834)
GeF	710 (exptl: 666)
GeCl	390 (exptl: 408)
^{1}GeH$_2$	935, 1903, 1912 (exptl: 920, 1864, 1887[66])
^{3}GeH$_2$	817, 2026, 2117
^{1}GeHF	702, 775, 1830
^{3}GeHF	545, 710, 1852
^{1}GeF$_2$	250, 689, 709 (exptl: 265, 677, 707[60]) (exptl: 263.9[47])
^{3}GeF$_2$	197, 661, 704 (exptl: 192.4, 673.1[47])
^{1}GeHCl	386, 724, 1878 (exptl: 439, 706, 1862[65])
^{3}GeHCl	396, 532, 1909
^{1}GeCl$_2$	152, 374, 393 (exptl: 160, 391.2 [46]) (exptl: 356/362, 383/388[64])
^{3}GeCl$_2$	108, 346, 394 (exptl: 118, 393 [46])
GeH$_3$	701, 855, 855, 2090, 2137, 2137 (exptl: 850, 928/920, 1813, 1839[66])
GeH$_2$F	627, 697, 721, 834, 2017, 2081
GeHF$_2$	236, 613, 616, 717, 725, 1913
GeF$_3$	209, 209, 260, 703, 739, 739
GeH$_2$Cl	calcd: 402, 585, 654, 830, 2042, 2101 exptl: 385, 685, 715, 734, 1810, 1856[65]
GeHCl$_2$	135, 389, 404, 569, 632, 1993
GeCl$_3$	126, 126, 159, 362, 401, 401 (exptl: 356/362, 383/388[64])
GeH$_4$	calcd: 821, 821, 821, 926, 926, 2149, 2158, 2158, 2158 exptl: 819, 819, 819, 931, 931, 2106, 2114, 2114, 2114[61] exptl: 812/820, 2097, 2106, 2134[66]
GeH$_3$F	calcd: 634, 634, 723, 869, 871, 871, 2157, 2169, 2169 exptl: 643, 643, 689, 859, 874, 874, 2121, 2132, 2132[62]
GeH$_2$F$_2$	calcd: 243, 586, 634, 737, 748, 801, 858, 2181, 2199 exptl: 596, 720, 720, 813.5, 860.0, 2154.5, 2174.4 [58]
GeHF$_3$	calcd: 228, 228, 281, 695, 695, 749, 783, 783, 2242
GeF$_4$	calcd: 200, 200, 267, 267, 267, 736, 823, 823, 823 exptl: 203, 203, 273, 273, 273, 735, 800, 800, 800 [61]
GeH$_3$Cl	calcd: 410, 588, 588, 841, 871, 871, 2164, 2179, 2179 exptl: 422, 602, 602, 848, 874, 874, 2120, 2129, 2129[62] exptl: 414. 601/612, 839/842/844, 866/782, 2104/2116/2139, 2151 [65]
GeH$_2$Cl$_2$	calcd: 145, 411, 424, 512, 644, 774, 849, 2173, 2193 exptl: 414, 429, 537, 773/780/787, 840/845/867, 1996/2000, 2112/2125[64]
GeHCl$_3$	calcd: 139, 139, 176, 403, 433, 433, 703, 703, 2201 exptl: 414/417, 439/444/454/455, 699/700/714/720/723, 2139/2160[64]
GeCl$_4$	calcd: 121, 121, 165, 165, 165, 380, 443, 443, 443 exptl: 125, 125, 171, 171, 171, 397, 459, 459, 459[63]

tials (IPs) and fragment ion appearance energies. The photoionization studies have obtained two close values for the IP of GeH$_4$: $\leq$10.52 eV by Ruscic et al.[24] and 10.54 eV by Wu et al.,[67] compared to our G3//DFT value of 10.45 eV. The G3//DFT IPs of GeH$_3$ and GeH$_2$ are 8.05 and 9.19 eV, compared to Ruscic et al.'s values of $\leq$7.94 and $\leq$9.25 eV.[24] Furthermore, the G3//DFT predicts the appearance energies of GeH$_3^+$ and GeH$_2^+$ from photoionization of GeH$_4$ to be 11.66 and 10.78 eV, which are within the experimental uncertainty ($<$11.65$_7$ $\pm$ 0.01 and $\leq$10.77$_2$ $\pm$ 0.009 eV[24]).

3.3. Enthalpies of Formation. The enthalpies of formation of the germanium species are calculated by using the atomization energy procedure,[55] and the results are listed in Table 3, along with the limited experimental data. Note that the uncertainty of $\pm$8 kJ/mol in $\Delta_f H^\circ_0$(Ge, g) is transferred to the G3//DFT $\Delta_f H^\circ_{298}$ values of all the Ge-containing species in this work. Thus the enthalpies of formation obtained here from the atomization procedure should be considered as the more probable values, instead of the exact prediction. To improve the theoretical $\Delta_f H^\circ_{298}$ values, a more accurate $\Delta_f H^\circ$(Ge, g) is desirable. A possible approach is via a high-resolution photoionization/fragmentation study of GeF$_4$, which is the only gaseous Ge compound with a highly accurate and reliable enthalpy of formation, using an advanced synchrotron light source and photoionization and mass spectrometry methods.[68-70]

As mentioned in the introduction, the accurate experimental $\Delta_f H^\circ_{298}$ is available only for GeH$_4$ (90.4 $\pm$ 2.1 kJ/mol),[10] GeF$_4$ ($-$1190.3 $\pm$ 0.8 kJ/mol),[11,12] GeCl$_4$ ($-$494.8 $\pm$ 2.7 kJ/mol),[13] and GeCl$_2$ ($-$162.8 $\pm$ 4 kJ/mol).[16] Our G3//DFT $\Delta_f H^\circ_{298}$ values for these species are 87.2, $-$1199.6, $-$500.4, and $-$166.9 kJ/mol, respectively. The agreements for GeH$_4$, GeCl$_4$, and GeCl$_2$ are within twice of the experimental uncertainties, while the G3//DFT $\Delta_f H^\circ_{298}$ of GeF$_4$ differs with the experiment by $\sim$10 kJ/mol. At the same level, the predicted $\Delta_f H^\circ_{298}$ of SiF$_4$ is about 5.0 kJ/mol lower than the experimental value, and the deviation for CF$_4$ is less than 1 kJ/mol.[51] The large deviation for GeF$_4$ might be due to the reduction of atomization energy caused by the exclusion of the scalar relativistic effect that is only partially accounted for by the high-level correction.[54]

The experimental data on the enthalpies of formation for other Ge species are limited. As mentioned before, the values for several free radicals have been measured, but with large uncertainties. The theoretical results from the G3 calculations, however, should be reliable based the good performance of the G3 model calculations on GeH$_x$, GeF$_4$, GeCl$_4$, and GeCl$_2$. For the enthalpy of formation of GeF$_2$(g), the large discrepancy between G3 ($-$529.5 kJ/mol, 298.15 K) and experiment ($-$430 to $-$506, or $-$573 kJ/mol[17,18]) is out of the theoretical uncertainty range. In the first experimental study, Ehlert et al obtained $-$506 kJ/mol for enthalpy of formation of GeF$_2$(g), which was detected as GeF$_2^+$ with the appearance potential of 11.6 $\pm$ 0.3 eV.[17] In the later study of GeF$_2$(cr) sublimation from the same group, GeF$_2^+$ was detected with an appearance potential of 12.9 $\pm$ 0.3 eV.[18] Our calculated IPs of GeF$_2$ at the G3//DFT level (adiabatic: 11.6 eV; vertical: 11.9 eV[71]) indicate that the GeF$_2^+$ observed in the later study might come from dissociation of other parent ions, possibly (GeF$_2$)$_2^+$. The experimental $\Delta_f H^\circ$(GeF$_3$) of $-$753 kJ/mol was obtained from the appearance energies of F$^-$ and GeF$_3^-$ from electron bombardment of GeF$_4$ and an estimation on the electronic excitation energy of GeF$_3$ from the spectroscopic data of CF$_3$ and SiF$_3$;[26] the experimental value is close to the G3//DFT value of $-$738.5 kJ/mol (298 K). $\Delta_f H^\circ_{298}$(GeCl$_3$, g) of $-$268 $\pm$ 50 kJ/mol estimated by Gurvich et al.[72] has a large uncertainty, and it is reasonably close to the G3//DFT value of $-$234.4 kJ/mol at 298 K.

The trends of the enthalpies of formation are shown in Figure 1. The enthalpies of formation of GeH$_n$F/Cl$_{(4-n)}$ decrease approximately linearly with the successive substitution of Ge$-$H bonds with Ge$-$F/Cl bonds (Figure 1a). The linearity is less perfect for the first and last F substitutions, with [$\Delta_f H^\circ_0$(GeH$_4$) $-$ $\Delta_f H^\circ_0$(GeH$_3$F)] = 312.7 kJ/mol, followed by 333.8, 334.8, and 311.4 kJ/mol. The linearity is better in the GeH$_n$Cl$_{(4-n)}$ series with $\Delta(\Delta_f H^\circ_0)$ of 145.8, 152.2, 152.2, and 147.6 kJ/mol. The variation of the enthalpy of formation in GeX$_n$ (X = H, F, and Cl) reflects the changes from sp^3 hybridization of the Ge atom in GeX$_4$, GeX$_3$, and triplet GeX$_2$ to the nearly localized p orbital of the Ge atom in singlet GeX$_2$, GeX, and Ge(^{3}P). The enthalpy of formation decreases approximately linearly with additional coordination within the same hybridization (Figure 1b). Similar trends have been observed in the previous theoretical studies on SiH$_n$X$_{(4-n)}$ (X = F, Cl, OH),[73-76] with larger average decrease in the enthalpy of formation upon subsequent substitution of about 413 kJ/mol for F substitution and 176 kJ/mol for Cl substitution.

TABLE 3: ZPEs, Thermal Corrections, Total Energies, and Enthalpies of Formation (G3//DFT)[a]

	ZPE	$H^{298}-H^0$	G3//DFT	G3//MP2	$\Delta_f H°$	$\Delta_f H^°_{298}$	$\Delta_f H°$ (exptl)
H	0.0	6.2	−0.50092	−0.50092	216.04	218.00	
F	0.0	6.5	−99.68589	−99.68589	77.28	79.39	
Cl	0.0	6.3	−459.99262	−459.99262	119.62	121.30	
Ge(g)	0.0	7.4	−2076.37975	−2076.37975	373.8	376.6	
H_2	26.3	8.7	−1.16713	−1.16709	−1.9	−1.7	0
F_2	6.3	8.8	−199.42840	−199.42859	5.9	5.8	0
Cl_2	3.2	9.2	−920.07368	−920.07354	7.0	7.1	0
HF	24.2	8.7	−100.40249	−100.40248	−273.0	−272.9	−273.25
HCl	17.4	8.7	−460.65587	−460.65590	−90.5	−90.7	−92.31
GeH	11.0	8.7	−2076.98369	−2076.98361	319.4	319.2	
GeF	4.2	9.0	−2176.25863	−2176.25851	−55.3	−55.4	
GeCl	2.3	9.5	−2536.51990	−2536.51970	106.6	106.9	
$^1GeH_2$	28.0	10.1	−2077.59237	−2077.59223	252.5	249.5	
$^3GeH_2$	29.2	10.1	−2077.55172	−2077.55170	359.2	356.3	
^1GeHF	19.5	10.5	−2176.86441	−2176.86432	−114.9	−117.7	
^3GeHF	18.3	10.7	−2176.79189	−2176.79178	75.5	73.0	
$^1GeF_2$	9.7	11.8	−2276.15382	−2276.15376	−527.9	−529.5	−572.8
$^3GeF_2$	9.2	12.1	−2276.01791	−2276.01809	−171.1	−172.4	
^1GeHCl	17.6	11.1	−2537.12405	−2537.12375	51.1	48.7	
^3GeHCl	16.7	11.3	−2537.05846	−2537.05831	223.3	221.2	
$^1GeCl_2$	5.4	13.3	−2996.66190	−2996.66164	−165.5	−166.9	−162.9
$^3GeCl_2$	5.0	13.6	−2996.55944	−2996.55940	102.5	102.3	
GeH_3	51.7	10.6	−2078.18377	−2078.18382	231.0	224.2	
GeH_2F	41.1	11.1	−2177.43375	−2177.43385	−78.5	−84.9	
$GeHF_2$	28.4	12.7	−2276.69282	−2276.69299	−411.8	−416.8	
GeF_3	16.8	14.9	−2375.94823	−2375.94856	−735.5	−738.5	−753
GeH_2Cl	39.0	11.7	−2537.69556	−2537.69552	81.8	75.9	
$GeHCl_2$	24.3	14.2	−2997.21088	−2997.21081	−76.6	−80.4	
$GeCl_3$	9.3	17.8	−2345.72570	−2345.72575	−233.7	−234.4	−268 ± 50
GeH_4	76.3	10.8	−2078.81766	−2078.81768	97.9	87.2	90.3 ± 2.0
GeH_3F	65.4	11.5	−2178.06887	−2178.06900	−214.8	−225.0	
GeH_2F_2	53.0	13.0	−2277.32811	−2277.32831	−548.6	−557.5	
$GeHF_3$	39.4	15.2	−2376.58777	−2376.58807	−883.4	−890.3	
GeF_4	25.8	17.5	−2475.83847	−2475.83892	−1194.8	−1199.6	−1190.2 ± 0.5
GeH_3Cl	63.0	12.1	−2538.32818	−2538.32807	−47.9	−57.7	
GeH_2Cl_2	47.9	14.6	−2997.84111	−2997.84100	−200.1	−207.8	
$GeHCl_3$	31.4	17.9	−3457.35407	−3457.35406	−352.3	−357.0	
$GeCl_4$	14.4	21.5	−3916.86488	−3916.86498	−498.9	−500.4	−495.8

[a] ZPE, thermal correction to 298 K and enthalpies of formation are in kJ/mol; G3 energies in hartree (ZPE included; HLC parameters (in mhartree): $A = 6.688$, $B = 3.007$, $C = 6.763$, $D = 1.107$; the 6-31G(d) basis sets using five Cartesian components for d functions); experimental values are taken from the JANAF table for HF and HCl; see text for details of the experimental values of the Ge-containing species.

The singlet−triplet (S−T) separation of the germylene radicals is an important parameter to assess their reactivity, and has been subject to several theoretical studies at theoretical levels of Hartree−Fock, DFT, CAS-MCSCF, MRSDIS(+Q), CCSD(T), etc.[38−40,42−45,77] The ground states of the germylene radicals are all singlet. The transition from the singlet ground state to the triplet excited state has been observed by laser-induced fluorescence spectroscopy for GeF_2 ($T_{00} = 30582.1$ cm^{-1} = 365.85 kJ/mol)[46] and $GeCl_2$ ($T_{00} = 22315$ cm^{-1} = 266.95 kJ/mol),[47] compared to the calculated G3//DFT values of 356.8 and 268.4 kJ/mol, respectively. The S−T splittings of GeH_2, GeHF, and GeHCl at the G3//DFT level are 106.7, 190.4, and 172.2 kJ/mol, respectively. The previous calculations, all using effective core potential, obtained smaller S−T separations than our G3 values. For example, the previous MRCISD(+Q) and CCSD(T) studies on GeF_2 predicted the S−T splitting between 330 and 350 kJ/mol,[45,77] below the experimental value. However, the previous DFT calculations with nonlocal functional for exchange-correlation energy predicted the S−T separations of GeF_2 and $GeCl_2$ that agreed with the experiments,[44] and in the present study, the B3LYP/6-31G(2df,p) calculations provide the S−T separations (GeH_2: 112.0 kJ/mol; GeHF: 190.8 kJ/mol; GeF_2: 352.3 kJ/mol; GeHCl: 172.4 kJ/mol; $GeCl_2$: 264.7 kJ/mol) that are in close agreement with G3.

3.4. Bond Dissociation Energies (BDEs). The calculated BDEs have, in principle, higher accuracy and less uncertainty than the calculated enthalpies of formation from atomization energy procedure [whose uncertainty is due to that of $\Delta_f H^°_0$(Ge, g)]. The calculated dissociation energies are listed in Table 4. The agreement among our G3//DFT BDEs, the previous theoretical results, and the experimental data for the GeH_x system have been demonstrated in Section 3.2. Experimental data besides those of GeH_x are limited. The experimental BDE of GeCl is determined to be 387.0 ± 9.6 kJ/mol from the gas-phase equilibrium of GeCl, CuCl, Ge, and Cu.[20] Our G3//DFT value of 386.8 kJ/mol at 0 K is in agreement with this experimental value. The study on GeF_2 and GeF[17] has been discussed in the previous section.

The dissociation energies of Ge−H in the germanes show different trends upon F and Cl substitutions (Figure 2a). Small increases in Ge−H BDE for fluorogermanes are often attributed to the large electronegativity of fluorine and electron withdrawing from the Ge−H bonds, while small decreases of Ge−H BDE in chlorogermanes are attributed to the high polarizability of the Cl atom and electron returning back to the Ge−H bonds via hyperconjugation (for example, Ge−H BDE in GeH_3I is 332 ± 10 kJ/mol,[21] compared to 349.1 kJ/mol in GeH_4 from G3//DFT). These effects can be understood by the natural bond orbital analysis.[78] The H atom in GeH_4 is negatively charged by −0.181e. The F substitution increases the negative charges on the H atoms (−0.233e in GeH_3F, −0.260e in GeH_2F_2, and −0.270e in $GeHF_3$) and the positive charge on the central Ge

TABLE 4: Dissociation Energies (kJ/mol) at the G3//DFT Level at 0 K

dissociation	BDE	dissociation	BDE
GeH → Ge + H	270.5		
GeF → Ge + F	506.7	GeCl → Ge + Cl	387.3
GeH_2 → GeH + H	282.9	GeH_2 → Ge + H_2	119.5
GeHF → GeH + F	511.6	GeHCl → GeH + Cl	387.4
GeHF → GeF + H	275.4	GeHCl → GeCl + H	270.8
GeHF → Ge + HF	215.5	GeHCl → Ge + HCl	231.3
GeF_2 → GeF + F	549.7	$GeCl_2$ → GeCl + Cl	392.0
GeF_2 → Ge + F_2	906.9	$GeCl_2$ → Ge + Cl_2	547.0
GeH_3 → GeH_2 + H	237.5	GeH_3 → GeH + H_2	86.5
GeH_2F → GeHF + H	180.1	GeH_2Cl → GeHCl + H	186.0
GeH_2F → GeH_2 + F	408.9	GeH_2Cl → GeH_2 + Cl	290.6
GeH_2F → GeH + HF	125.4	GeH_2Cl → GeH + HCl	147.1
GeH_2F → GeF + H_2	21.7	GeH_2Cl → GeCl + H_2	23.0
$GeHF_2$ → GeF_2 + H	100.5	$GeHCl_2$ → $GeCl_2$ + H	126.7
$GeHF_2$ → GeHF + F	374.8	$GeHCl_2$ → GeHCl + Cl	247.9
$GeHF_2$ → GeH + F_2	717.6	$GeHCl_2$ → GeH + Cl_2	403.5
$GeHF_2$ → GeF +HF	83.9	$GeHCl_2$ → GeCl + HCl	92.4
GeF_3 → GeF_2 + F	285.9	$GeCl_3$ → $GeCl_2$ + Cl	187.7
GeF_3 → GeF + F_2	686.4	$GeCl_3$ → GeCl + Cl_2	347.9
GeH_4 → GeH_3 + H	349.1	GeH_4 → GeH_2 + H_2	253.1
GeH_3F → GeH_3 + F	523.3	GeH_3Cl → GeH_3 + Cl	398.2
GeH_3F → GeH_2F + H	352.4	GeH_3Cl → GeH_2Cl + H	345.6
GeH_3F → GeH_2 + HF	195.2	GeH_3Cl → GeH_2 + HCl	209.9
GeH_3F → GeHF + H_2	98.7	GeH_3Cl → GeHCl + H_2	97.9
GeH_2F_2 → GeH_2F + F	547.6	GeH_2Cl_2 → GeH_2Cl + Cl	401.3
GeH_2F_2 → $GeHF_2$ + H	352.9	GeH_2Cl_2 → $GeHCl_2$ + H	339.4
GeH_2F_2 → GeH_2 + F_2	807.4	GeH_2Cl_2 → GeH_2 + Cl_2	460.1
GeH_2F_2 → GeF_2 + H_2	19.5	GeH_2Cl_2 → $GeCl_2$ + H_2	32.1
GeH_2F_2 → GeHF + HF	161.6	GeH_2Cl_2 → GeHCl + HCl	161.1
$GeHF_3$ → GeF_3 + H	363.9	$GeHCl_3$ → $GeCl_3$ + H	334.5
$GeHF_3$ → $GeHF_2$ + F	549.3	$GeHCl_3$ → $GeHCl_2$ + Cl	395.5
$GeHF_3$ → GeF_2 + HF	83.6	$GeHCl_3$ → $GeCl_2$ + HCl	95.9
$GeHF_3$ → GeHF + F_2	773.0	$GeHCl_3$ → GeHCl + Cl_2	411.6
GeF_4 → GeF_3 + F	536.9	$GeCl_4$ → $GeCl_3$ + Cl	385.0
GeF_4 → GeF_2 + F_2	673.7	$GeCl_4$ → $GeCl_2$ + Cl_2	340.8

atom (0.723e in GeH_4, 1.375e in GeH_3F, 1.885e in GeH_2F_2, and 2.313e in $GeHF_3$). Therefore, the Ge−H bond(s) in $GeH_{(4-n)}F_n$ become more polarized and stronger with F substitution (Figure 2a). The Cl substitution, on the other hand, keeps the charge on the H atoms nearly constant (−0.181e in GeH_4, −0.188e in GeH_3Cl, −0.185e in GeH_2Cl_2, and −0.179e in $GeHCl_3$), and increases a smaller amount of the positive charge on the central Ge atom (0.723e, 1.022e, 1.250e, and 1.434e, correspondingly), resulting in slightly decreasing Ge−H BDE in $GeH_{(4-n)}Cl_n$ with Cl substitution (Figure 2a). The increase of the positive charge on the Ge atom upon F/Cl substitution increases the polarity of the Ge−F/Ge−Cl bonds, as well as the electrostatic repulsion between the negatively charged halogen atoms. The Ge−F BDE increases from GeH_3F (523.3 kJ/mol) to GeH_2F_2 (547.6 kJ/mol) to $GeHF_3$ (549.3 kJ/mol), and decreases from $GeHF_3$ to GeF_4 (536.9 kJ/mol) (Figure 2a). The Ge−Cl BDE increases from GeH_3Cl (398.2 kJ/mol) to GeH_2Cl_2 (401.3 kJ/mol) and decreases from GeH_2Cl_2 to $GeHCl_3$ (395.5 kJ/mol) to $GeCl_4$ (385.0 kJ/mol). In addition, due to the increased bond polarity, the Ge−H and Ge−X bond lengths decrease upon F/Cl substitution.

The variation of BDEs upon the number of coordination is shown in Figure 2b. The dip for the germyl radicals is the reflection of change of hybridization. For GeF_2, breaking the first Ge−F bond requires more energy than the second one, presumably due to the higher polarity of Ge−F bonds in GeF_2 than in GeF. The change is mild in $GeCl_2$ and GeH_2 where the bonds are less polarized.

It has often been assumed in early data analysis that the average bond strengths of the GeX_3 species is the average of those of GeX_4 and GeX_2. This approach could be a source of error for many of the previous studies because of the different hybridization of GeX_2. The G3//DFT calculations show that this assumption would cause an error of 18.5 kJ/mol per Ge−H bond (263.7 kJ/mol for GeH_3 versus 282.2 kJ/mol for the average of GeH_4 and GeH_2), 41.9 kJ/mol per Ge−F bond (447.3 kJ/mol versus 489.2 kJ/mol for the average), and 32.9 kJ/mol per Ge−Cl bond (322.2 kJ/mol versus 355.1 kJ/mol for the average). The G3//DFT calculations, however, indicate that it is sound to approximate the average bond strength of GeX_3 to the average bond strength of $^1GeX_2$, $^3GeX_2$, and GeX_4 (263.7 versus 267.5 kJ/mol for H, 447.3 versus 454.2 kJ/mol for F, and 322.2 versus 330.2 kJ/mol for Cl).

3.5. Dissociations of Substituted Germanes. As in their silicon analogues, the single bond dissociations of germanes except GeF_4 are not the most energetically favored dissociation channels. Eliminations of H_2 and HF/HCl usually require less energy, but with energy barriers.

It is known that the initial decomposition step of SiH_4/GeH_4 is SiH_4/GeH_4 → SiH_2/GeH_2 + H_2 in high-temperature pyrolysis.[79,80] At the G3//DFT level (Table 4), the GeH_4 → GeH_2 + H_2 channel requires only 153.1 kJ/mol, and the energy barrier for this GeH_2 + H_2 channel is 207.8 kJ/mol by G3//DFT. Both are far below the energy of 349.1 kJ/mol required for the GeH_3 + H dissociation channel. For the halogen-substituted germanes, the strong Ge−F and H−F/H−Cl bonds favor the dissociation channels with the H_2 product, followed by the HF/HCl product when available. The product channels with the lowest dissociation energies and energy barrier heights (E_a) are

$$GeH_3F \rightarrow GeHF + H_2: \quad \Delta_r H_0^\circ = 98.7 \text{ kJ/mol}, E_a = 235.5 \text{ kJ/mol}$$

$$GeH_2F_2 \rightarrow GeF_2 + H_2: \quad \Delta_r H_0^\circ = 19.5 \text{ kJ/mol}, E_a = 304.2 \text{ kJ/mol}$$

$$GeHF_3 \rightarrow GeF_2 + HF: \quad \Delta_r H_0^\circ = 83.6 \text{ kJ/mol}, E_a = 224.8 \text{ kJ/mol}$$

$$GeH_3Cl \rightarrow GeHCl + H_2: \quad \Delta_r H_0^\circ = 97.9 \text{ kJ/mol}, E_a = 224.4 \text{ kJ/mol}$$

$$GeH_2Cl_2 \rightarrow GeCl_2 + H_2: \quad \Delta_r H_0^\circ = 32.1 \text{ kJ/mol}, E_a = 265.4 \text{ kJ/mol}$$

$$GeHCl_3 \rightarrow GeCl_2 + HCl: \quad \Delta_r H_0^\circ = 95.9 \text{ kJ/mol}, E_a = 188.8 \text{ kJ/mol}$$

where the enthalpy changes of reaction are calculated at the G3//DFT level, and the energy barrier heights are at the B3LYP/6-31G(2df,p) level. All the energy barrier heights are far below the Ge−H bond strengths in germanes (∼350 kJ/mol); therefore the diatomic eliminations would be favored over the bond breakages. This is partially the reason for using SiH_2Cl_2 in Si−CVD processes.[81] The propensity to dissociation into H_2 or HF/HCl channels holds true for most of the germyl and germylene radicals as well. For example, the dissociation GeH_2X → GeX + H_2 has a small energy threshold (21.7 kJ/mol for GeH_2F and 23.0 kJ/mol for GeH_2Cl).

4. Conclusion

The present work provides a systematic theoretical study on the structures, vibrational frequencies, enthalpies of formation, and dissociation energies of germane, fluorogermanes, chlorogermanes, and their fragment radicals. While the B3LYP/6-31G(2df,p) vibrational frequencies of the germanes agree with the observed experimental values in the gas phase and matrix spectra, the calculations cast some doubts on the previous experimental assignments for several germyl radicals. The G3//DFT calculations on the GeH$_x$ system, which up to now has the most accurate experimental measurements and theoretical calculations, can provide reliable bond dissociation energies, ionization potentials, and cation appearance potentials, and are in good agreement with the experimental data (within the experimental uncertainties) and the previous theoretical studies. The G3//DFT enthalpies of formation of GeH$_4$, GeCl$_4$, and GeCl$_2$ and the singlet−triplet separation of GeCl$_2$ fall within twice of the experimental uncertainties, while the G3//DFT enthalpy of formation of GeF$_4$ and singlet−triplet separation of GeF$_2$ differ with the experimental values by about 10 kJ/mol. For the Ge-containing free radicals, only a few experimental enthalpies of formation (with large uncertainties) are available; the G3//DFT enthalpies of formation of the Ge radicals should be more reliable compared with the currently available experimental values, and can be useful in reaction mechanism studies of the Ge radicals.

The bond dissociation energies of germane, fluorogermanes, chlorogermanes, and their fragment radicals, as well as the trends of BDEs with the F/Cl substitutions, are examined. The Ge−H BDE in GeH$_{(4-n)}$F$_n$ increases with the F substitution, while that in GeH$_{(4-n)}$Cl$_n$ decreases with the Cl substitution. For dissociation of the partially substituted F/Cl germanes and germyl radicals, diatomic elimination of H$_2$ or HF/HCl is preferred over single bond breaking due to the low-energy barriers of the diatomic eliminations relative to the bond breakage to the atom and Ge-containing radicals.

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