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Quantum Chemistry Study on Cation Structures of Fluorinated and Chlorinated Germanes and Their Radicals

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The structures and vibrational frequencies of cations of fluorinated and chlorinated germanes and radicals ($GeH_xX_y^+$, X = F, Cl; $x + y = 1-4$) and protonated germanes are investigated theoretically at B3LYP/6-31+G(2df,p) level. For GeH_2, GeHX, GeH_2X, $GeHX_2$, and germanes, the most stable cationic structures are largely distorted from their neutral ones and all can be viewed as ion complexes between a Ge-centered cation and a neutral atom or diatom. The ionization potentials, appearance energies, and proton affinities are obtained at Gaussian-3(CC) levels. Cations with the lowest energy (and adiabatic ionization potentials (in eV)) are Ge^+-H_2 ($^2B_2$, 8.94), Ge^+-FH (9.42), Ge^+-ClH (9.45), GeH_3^+ (8.01), GeF^+-H_2 (7.71), $GeCl^+-H_2$ (8.01), GeF^+-FH (7.69), $GeCl^+-ClH$ (7.80), $GeH_2^+-H_2$ (10.45), GeH_2^+-FH (10.32), $GeHF^+-FH$ (10.64), GeF_2^+-FH (11.40), GeF_4^+ (15.22), GeH_2^+-ClH (10.29), $GeHCl^+-ClH$ (10.33), $GeCl_2^+-ClH$ (10.43), and $GeCl_4^+$ (11.48). The most stable protonated germanes (and proton affinities (in kJ/mol, 0 K)) are $GeH_3^+-H_2$ (658.3), GeH_3^+-FH (672.5), GeH_2F^+-FH (634.2), $GeHF_2^+-FH$ (583.4), GeF_3^+-FH (516.3), GeH_3^+-ClH (672.7), GeH_2Cl^+-ClH (652.6), $GeHCl_2^+-ClH$ (637.5), and $GeCl_3^+-ClH$ (624.4), respectively. The G3 atomization energies of fluorinated Ge-species are found to be significantly different from G3X and G4 ones, and this may merit further investigation.

I. Introduction

The ion chemistry of germane, its F/Cl substitutents, and their fragment radicals are of interest in chemical vapor deposition (CVD) of germanium. In particular, gas-phase reactions involving germanium molecules, radicals, and ionic species can play important roles in deposition and etching of amorphous germanium film in radio frequency or plasma-enhanced CVD,[1,2] where radical fragments and ions are created by discharge. The ionic germanium species are of great interest in structural chemistry, where theoretical studies[3−8] on CH_4^+, SiH_4^+, GeH_4^+, and SnH_4^+ have revealed large distortions from their neutrals with floppy bonds. The elusive Ge-centered organic cations are important reactive intermediates in organic chemistry as well.[9]

Thermodynamic study of phase equilibrium during CVD processes has provided useful guideline for selection of processing conditions.[10,11] With limited experimental studies, quantum chemistry calculations have been carried out to predict the enthalpies of formation of fluorinated and chlorinated germanes and radicals.[12−15] However, knowledge on the structures, energetics, and reactivities of their ionic forms remains largely unknown. While experimental measurement on the GeH_x system is available with high accuracy using vacuum ultraviolet (VUV) photoionization,[16,17] studies on other Ge species have used relatively low-resolution techniques such as electron impact ionization or He(I)-photoelectron spectroscopy (PES) to measure the ionization potentials (IPs), electron affinities (EAs), and appearance energies (AEs) of ion fragments.[18−31] Radicals and ion fragments have also been observed following photoexcitation of GeH_4, GeF_4, and $GeCl_4$ in photoionization using tunable VUV radiation.[16,17,32−35] Thermodynamic properties obtained from majority of these experiments carry considerable uncertainties. The IPs and AEs are often overestimated due to poor detection sensitivity at the threshold energies, large structural distortions of cations from their neutrals, exit barriers in fragmentation process, and internal excitation of fragments, etc. Alternatively, these properties can be predicted with chemical accuracy (∼1 kcal/mol) using medium-level quantum chemistry theory. In this paper, Gaussian-3 (G3) model chemistry[36−38] is employed to calculate cationic structures of simple Ge-containing cations, including cations of fluoro- and chlorogermanes and radicals, and protonated germanes. IPs, proton affinities (PAs) of germanes, and AEs from germanes are derived and compared with the previous experimental results.

II. Computational Details

All density functional theory (DFT) and molecular orbital calculations are carried out using Gaussian 03 suite of programs.[39] Following the performance of Gaussian-4 (G4)[40] on hydrogen-bonded species, G3 calculations[36,37] in the present study are based on the improved geometries and zero-point energy (ZPE) corrections at B3LYP/6-31+G(2df,p) levels, and the QCISD(T) calculation is replaced by CCSD(T). No relativistic effects are included except the spin−orbit corrections, which are obtained from spectroscopic data[41] and applied to atomic and diatomic species only. The spin−orbit interaction is important for open-shell nonlinear molecules with at least a 3-fold axis,[42] i.e., GeH_3, GeF_3, and $GeCl_3$ only in the present study. However, the ground states of these species are nondegenerate, namely, the spin−orbit interaction is negligible. Previous studies on the G2/97 test set have also shown little

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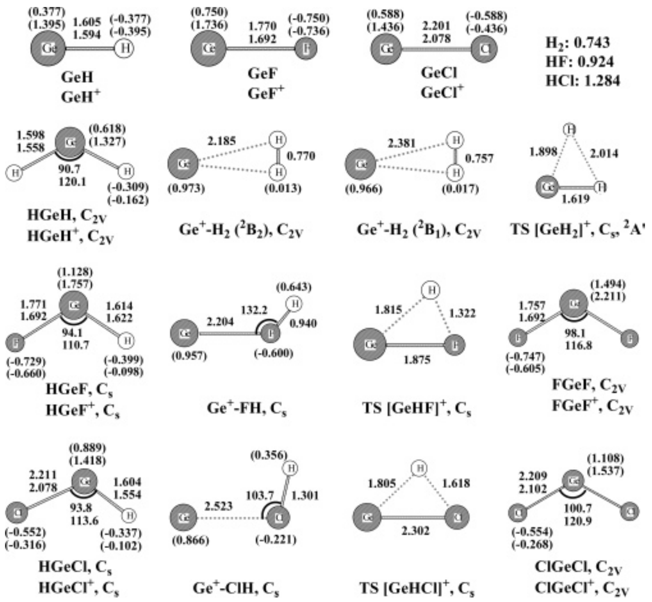

Figure 1. Geometries at B3LYP/6-31+G(2df,p) level (bond lengths in Å and angles in deg) and NBO charges (in parentheses, at the CCSD(T)/6-31G(d) level).

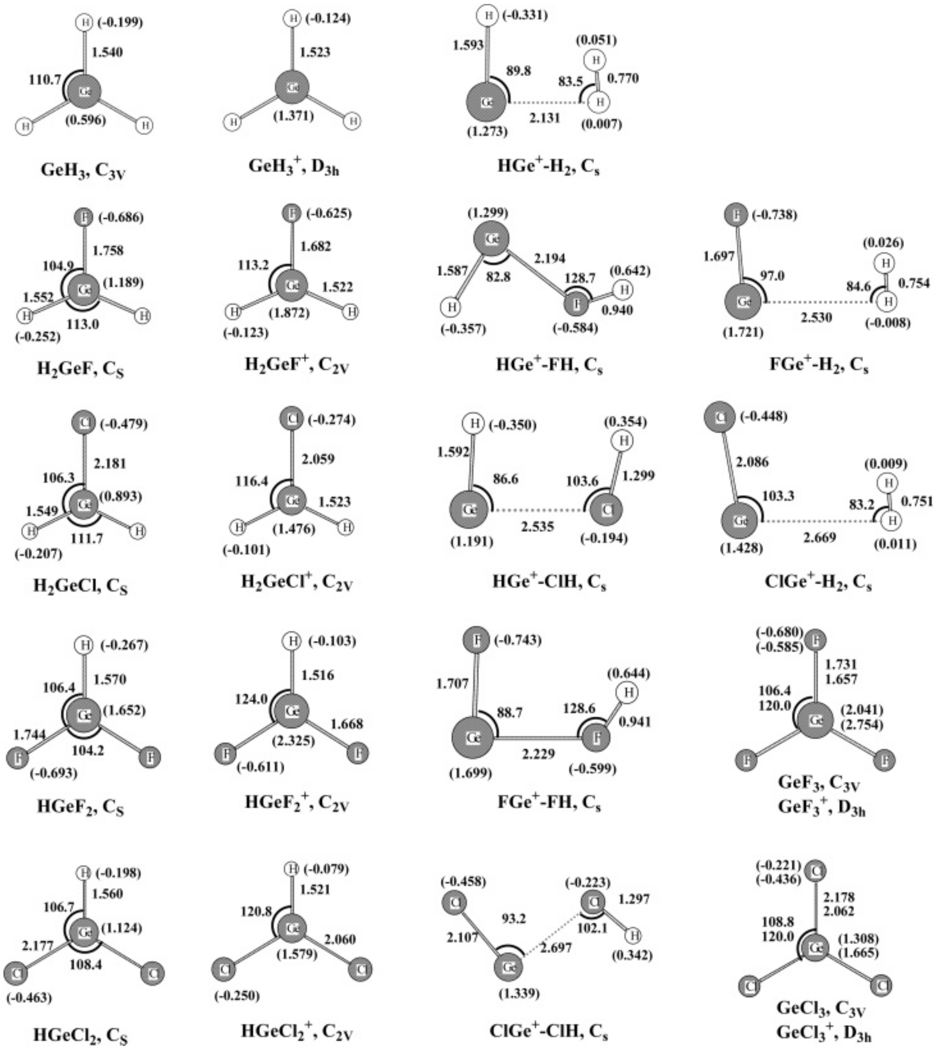

Figure 2. Geometrical parameters and NBO charges of cations of fluorinated and chlorinated germylenes and germyls.

change in overall performance of G3 when relativistic effects are included.[43] The calculations closely resemble the so-called G3(CC)//B2df level,[44] and are denoted here as G3(CC)/B2df+ or as G3 in brief. The same high-level correction parameters are adopted as $A = 6.688$, $B = 3.007$, $C = 6.763$, and $D = 1.107$ in mhartree. For germylene radicals, unrestricted wave-

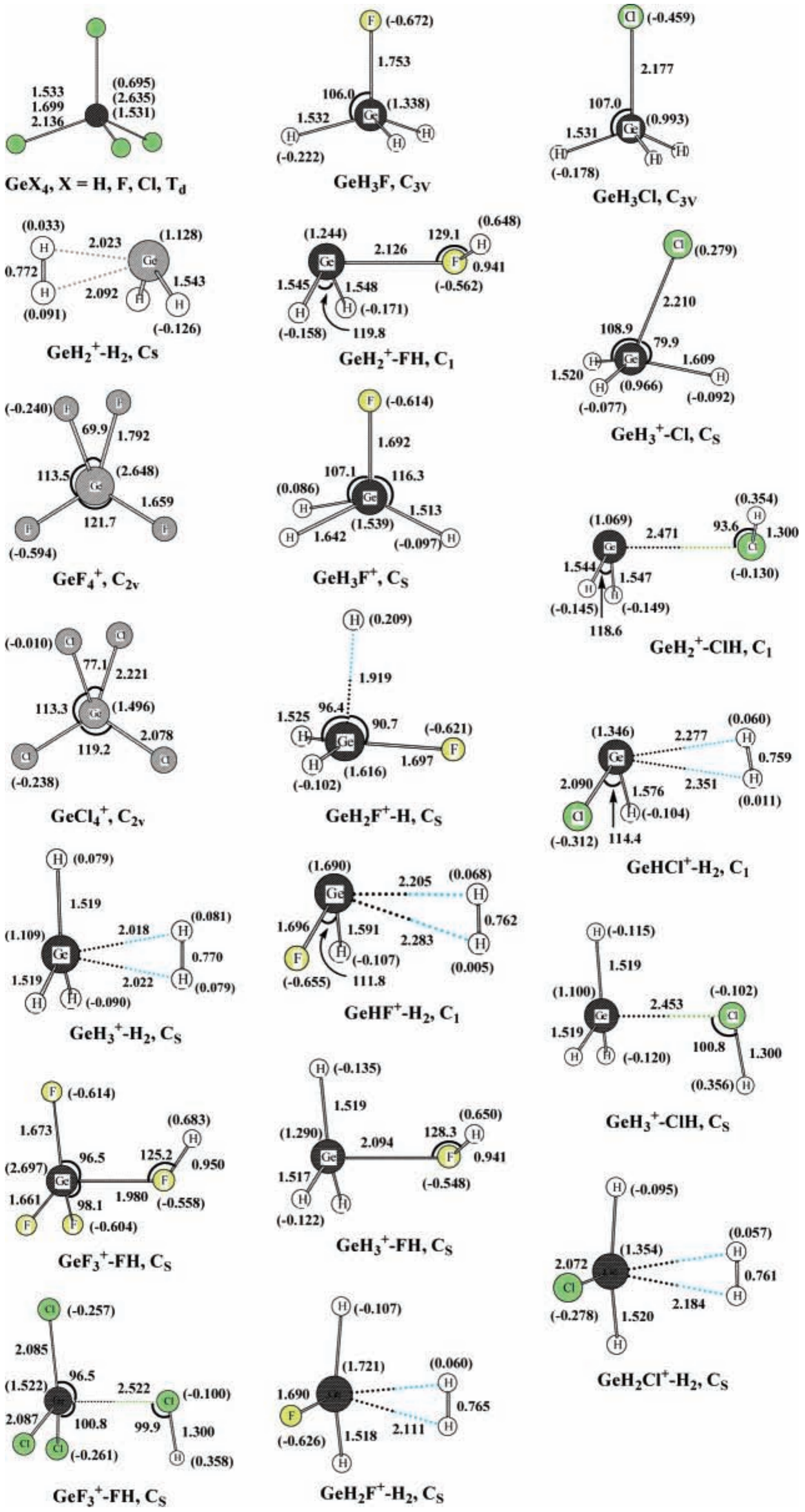

Figure 3. Geometrical parameters and NBO charges of cations of GeX_4 and GeH_3X (X = H, F, Cl).

functions are used for post-Hartree−Fock calculations whenever RHF-wavefunction instability is found. The bonding, charges, and orbital interactions are analyzed using natural bond orbital package NBO 3.0 as implemented in Gaussian 03.[45]

III. Results and Discussion

The optimized B3LYP/6-31+G(2df,p) geometries are displayed in Figures 1−4. The calculated vibrational frequencies are listed in Tables 1 and 2, and ZPE corrections and G3(CC)/B2df+ electronic energies in Tables 3 and 4. As noticed in our previous study,[12] B3LYP tends to predict bond lengths longer than the experimental measurements and other correlation methods such as MP2 and CCSD(T). For example, the Ge−F bond length of 1.757 Å in GeF_2 at B3LYP level is longer than that of 1.731 Å at CCSD(T,Full)/cc-pVTZ level[14] and 1.732 Å from microwave spectroscopy.[46] However, the G3 electronic

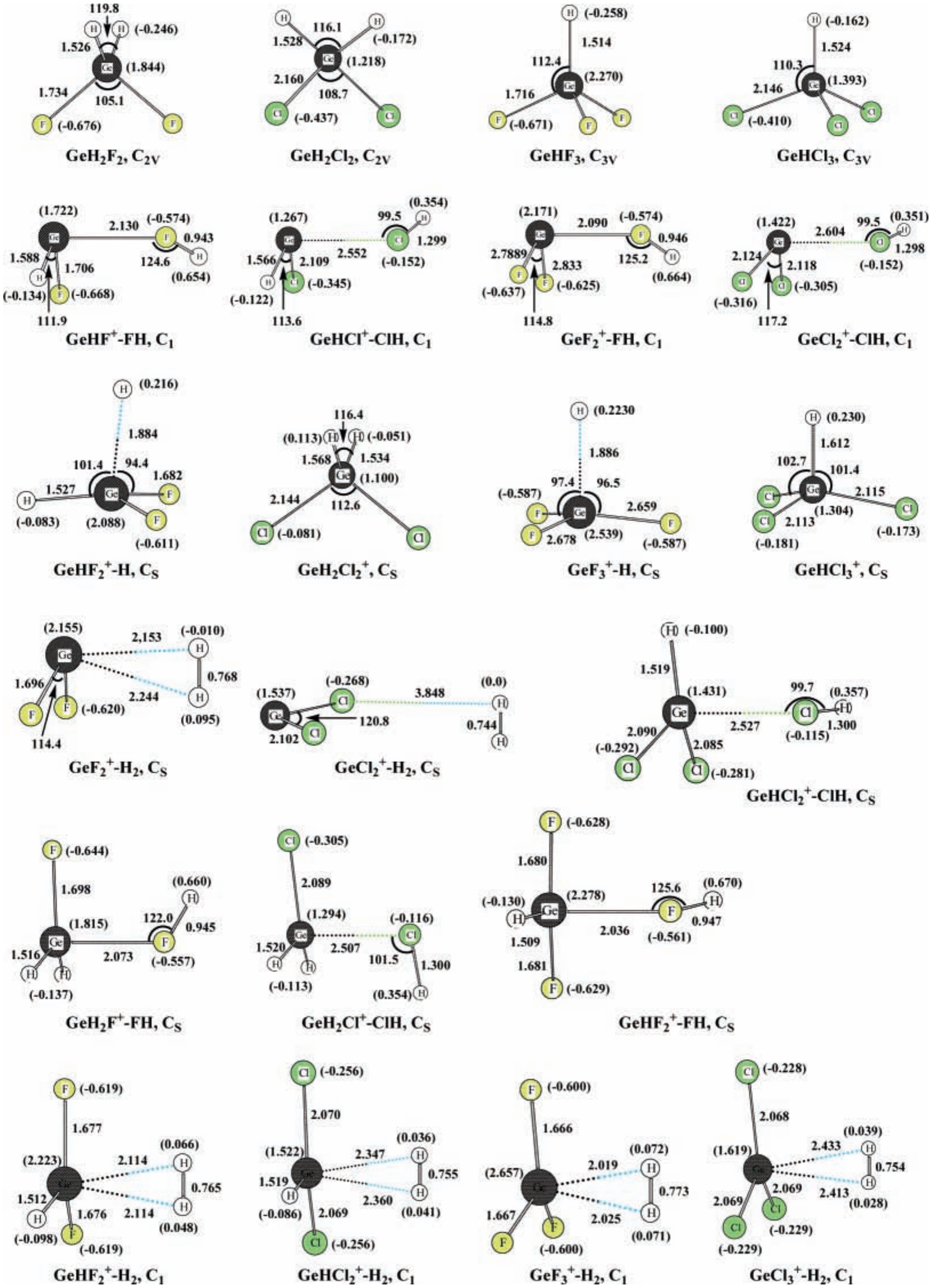

Figure 4. Geometrical parameters and NBO charges of cations of GeH_2X_2 and $GeHX_3$ ($X = F, Cl$).

energies based on considerably different geometries at B3LYP and MP2 levels agree closely within 1.5 kJ/mol for the neutrals.[12]

A. Performance of G3(CC)/B2df+, G3X(CC), and G4. The performance of G3(QCI)/B2df has been demonstrated in our previous study on the ion chemistry of GeH_x ($x = 0-4$) system and the prediction of enthalpies of formation of GeH_4, GeF_4, $GeCl_4$, and $GeCl_2$.[12] The calculated IPs of GeH_x and enthalpies of formation of GeH_4, $GeCl_4$, and $GeCl_2$ are within the range of the experimental uncertainties. The present G3(CC)/B2df+ calculation virtually reproduces our previous results on the neutral species. The present G3(CC)/B2df+ atomization energy of GeH_4 (1142 kJ/mol) also agrees excellently with the recent CCSD(T)/CBS result (1140 kJ/mol), while ~ 10 kJ/mol of discrepancy is found for GeF_4, e.g., 1876.5 kJ/mol *vs* 1867 kJ/mol.[13] The predicted accuracies on the atomization energies, ionization potentials, and proton affinities are approximately 1 kcal/mol.[37,40]

Recently, G3X,[44] an improved version of G3 with larger basis set extrapolation, was extended to the third-row compounds,[38] and further improved version G4 was also released.[40] Both G3X and G4 perform better than G3 in predicting the enthalpy of formation, IPs, and PAs for the test sets of molecules and ions, which, however, contains only three molecular Ge-species, GeH_4, GeO, and GeS_2. The performances of G3X(CC) and G4 are tested here on the Ge-species. The G3(CC), G3X(CC) and

TABLE 1: Unscaled Vibrational Frequencies (in cm^{-1}) of Radicals and Cations at B3LYP/6-31+G(2df,p) Level[a]

neutrals	vibrational frequencies (cm^{-1})[b]	cations	vibrational frequencies (cm^{-1})
H_2	4462		
HF	4082		
HCl	2947		
GeH	1862	GeH^+	1986
GeF	661	GeF^+	789
GeCl	384	$GeCl^+$	491
GeH_2	932, 1891, 1900	GeH_2^+	826, 1983, 2086
		Ge^+-H_2 ($^2B_2$)	509, 726, 3992
		Ge^+-H_2 ($^2B_1$)	460, 521, 4242
		TS	1793*i*, 684, 1816
GeHF	654, 754, 1832	$GeHF^+$	512, 782, 1549
		Ge^+-FH	242, 455, 3837
		TS	1154*i*, 609, 1308
GeF_2	238, 635, 664	GeF_2^+	195, 710, 763
GeHCl	380, 717, 1868	$GeHCl^+$	477, 528, 1739
		Ge^+-ClH	201, 492, 2796
		TS	840*i*, 391, 1343
$GeCl_2$	151, 368, 389	$GeCl_2^+$	125, 399, 454
GeH_3	703, 854(2), 2084, 2132(2)	GeH_3^+	790, 850(2), 2180, 2251(2)
		GeH^+-H_2	517, 528, 628, 820, 1978, 4015
GeH_2F	614, 669, 690, 829, 2018, 2086	GeH_2F^+	578, 678, 777, 816, 2180, 2261
		GeF^+-H_2	161, 176, 315, 448, 779, 4280
		GeH^+-FH	249, 323, 496, 599, 2002, 3843
$GeHF_2$	229, 602, 609, 683, 684, 1916	$GeHF_2^+$	238, 495, 627, 806, 851, 2218
		GeF^+-FH	143, 235, 278, 464, 753, 3829
GeF_3	200(2), 251, 675, 702(2)	GeF_3^+	197, 205(2), 761, 884(2)
GeH_2Cl	398, 580, 652, 828, 2038, 2097	GeH_2Cl^+	508, 549, 641, 804, 2186, 2251
		GeH^+-ClH	208, 311, 472, 641, 1973, 2825
		$GeCl^+-H_2$	113, 137, 274, 391, 484, 4319
$GeHCl_2$	133, 385, 400, 567, 628, 1990	$GeHCl_2^+$	153, 456, 471, 528, 679, 2210
		$GeCl^+-ClH$	94, 163, 173, 455, 485, 2843
$GeCl_3$	124(2), 158, 359, 397(2)	$GeCl_3^+$	143(2), 147, 416, 527(2)

[a] Experimental values for neutrals and references can be found in ref 12. [b] Numbers in parentheses are the degeneracy.

G4 electronic energies and the atomization energies of neutral species are listed in Table 5. Close agreement is found among G3(CC)/B2df+, G3X(CC)/B2df+, and G4/B2df+ for GeH_x and chlorinated species; e.g., the atomization energies of GeH_4 are 1142.4, 1143.3, and 1142.4 kJ/mol and those of $GeCl_4$ are 1353.0, 1355.7, and 1357.4 kJ/mol from the three model chemistries, respectively. However, predictions on fluorinated species have fairly large discrepancies between different model chemistries, e.g., atomization energies of 1876.5, 1890.9, and 1890.3 kJ/mol for GeF_4. Values from G3X and G4 are significantly larger than those from G3 and CCSD(T)/CBS of 1867 kJ/mol.[13] Close examination into the basis set additivity scheme reveals the over-correction to Hartree−Fock (HF) extension of basis set effects in G3X and G4 calculations. With G3X, $\Delta E(\text{HF}, \text{GeF}_4) = E(\text{HF/G3eXtraLarge}) - E(\text{HF/G3Large}) = -7.1$ mhartree is considerably larger than other species with similar number of valence electrons, e.g., $\Delta E(\text{HF}, \text{Ge(OH)}_4) = -4.4$ mhartree and $\Delta E(\text{HF}, \text{GeCl}_4) = -2.6$ mhartree. Thereafter, discussions have been based on G3(CC)/B2df+ calculations, instead of G3X or G4, even though close agreement between G3X and G4 is found for all species.

B. GeX^+ (X = H, F, and Cl) (Figure 1, Tables 1 and 3). The unpaired p-electron in Ge/GeH/GeF/GeCl is removed upon ionization. From neutral Ge-atom to GeH radical, the unpaired p-orbital is perturbed slightly, resulting a small change in its charge, and consequently small change of IP from Ge-atom (7.90 eV) to GeH (7.83 eV by G3). In GeCl and GeF radicals, the energy of the p-orbital is shifted up slightly by intramolecular orbital interaction with the doubly occupied p-orbital of F/Cl-atom, leading to reduced IPs for GeF (7.58 eV) and GeCl (7.43 eV, Table 3). Ionization leaves the positive charge almost localized on Ge-atom, e.g., NBO charge of 0.75 *e* on Ge in GeF, and 1.74 *e* in GeF^+. The removal of unpaired electron shrinks the bond lengths from the neutrals (1.605, 1.770, and 2.201 Å for GeH, GeF, and GeCl) to cations (1.594, 1.692, and 2.078 Å), and increases the vibrational frequencies from 1862, 661, and 384 cm^{-1} to 1986, 789, and 491 cm^{-1}, respectively.

The calculated IP of Ge is in excellent agreement with the experimental value (7.899 eV[41]), and IP(GeF) = 7.58 eV is higher than the value of 7.46 eV obtained from extrapolation of observed Rydberg series[47] and the recent CCSD(T,Full)/cc-pVTZ prediction of 7.3 eV.[14] Bond dissociation energy (BDE) of Ge^+-F = 536.1 kJ/mol is in close agreement with CASSCF/SOCI calculation (544 kJ/mol);[48] and BDE(Ge^+-Cl) = 431.7 kJ/mol is about 30 kJ/mol higher than the CASSCF/SOCI calculation (402.3 kJ/mol).[49]

C. $GeH_xF_y^+$ and $GeH_xCl_y^+$ ($x + y = 2$) (Figure 1). Ground states of all neutral germylenes considered here are singlet, even if unrestricted wavefunctions are required to describe GeH_2 and GeHCl. Ionization of germylene radicals removes mostly one of the Ge 4s lone-pair electrons, forming divalent germylene cations with sp^2-like bond angles. Predictions of adiabatic IPs of germylenes at G3 level are listed in Table 3.

Close examination on the orbital energies of Ge−H, Ge−F, and Ge−Cl σ-bonds and the lone pair orbital of Ge has been carried out on the neutral germylene radicals using NBO orbital energy analysis. The small differences between Ge−H bond orbital and Ge 4s orbital in singlet germylene radicals (−0.5246 *vs* −0.5465 hartree in GeH_2, −0.5265 *vs* −0.5465 hartree in GeHF, and −0.5392 *vs* −0.5860 hartree in GeHCl from NBO analysis) suggest the orbital mixing between them after ionization. The weakening in Ge−H bonds is apparent in the reduction of Ge−H stretching vibrational frequencies from GeHF and GeHCl (1832 and 1868 cm^{-1}) to $GeHF^+$ and $GeHCl^+$ (1549 and 1739 cm^{-1}, respectively). The orbital mixing between the Ge−X bond orbital and Ge 4s orbital is relatively small due to

TABLE 2: Unscaled Vibrational Frequencies (in cm^{-1}) of Neutral, Ionized, and Protonated Germanes at B3LYP/6-31+G(2df,p) Level[a]

species	vibrational frequencies (cm^{-1})[b]
GeH_4	819(3), 924(2), 2151, 2159(3)
$GeH_2^+-H_2$	147, 542, 555, 640, 808, 854, 2057, 2147, 4002
$GeH_3^+-H_2$	19, 570, 570, 636, 814, 814, 846, 849, 917, 2200, 2255, 2262, 4084
GeH_3F	624(2), 681, 860, 868(2), 2159, 2174(2)
GeH_2^+-FH	125, 275, 453, 544, 586, 824, 2032, 2132, 3829
GeH_3F^+	222, 486, 496, 616, 782, 794, 1304, 1711, 2255
GeH_2F^+-H	231, 241, 567, 583, 754, 781, 813, 2151, 2216
GeH_3^+-FH	111, 291, 471, 489, 590, 824, 855, 857, 2204, 2259, 2267, 3827
$GeHF^+-H_2$	127, 238, 405, 444, 551, 620, 772, 1755, 4155
$GeH_2F^+-H_2$	191, 286, 521, 533, 573, 736, 779, 794, 808, 2194, 2261, 4127
GeH_2F_2	236, 582, 625, 703, 706, 796, 848, 2188, 2210
$GeHF^+-FH$	141, 223, 268, 413, 548, 552, 752, 1761, 3793
$GeHF_2^+-H$	227, 237, 251, 498, 602, 758, 820, 832, 2143
$GeF_2^+-H_2$	48, 189, 218, 235, 525, 620, 719, 767, 4075
GeH_2F^+-FH	155, 194, 301, 459, 583, 599, 741, 773, 810, 2215, 2281, 3777
$GeHF_2^+-H_2$	57, 230, 285, 295, 513, 640, 668, 770, 796, 839, 2247, 4137
$GeHF_3$	222(2), 276, 691(2), 724, 748(2), 2251
GeF_2^+-FH	129, 150, 171, 214, 293, 569, 719, 770, 3753
GeF_3^+-H	198, 198, 206, 230, 233, 714, 841, 843, 880
$GeHF_2^+-FH$	71, 178, 189, 239, 320, 572, 639, 648, 789, 825, 2262, 3747
$GeF_3^+-H_2$	84, 206, 207, 235, 300, 309, 734, 771, 855, 870, 886, 4027
GeF_4	193(2), 262(3), 719, 786(3)
GeF_4^+	133, 176, 196, 198, 319, 415, 656, 813, 885
GeF_3^+-FH	127, 148, 167, 215, 227, 235, 362, 641, 752, 857, 865, 3697
GeH_3Cl	405, 586(2), 838, 869(2), 2161, 2176(2)
GeH_2^+-ClH	141, 226, 446, 559, 647, 816, 2046, 2138, 2819
GeH_3^+-Cl	250, 363, 523, 641, 672, 795, 1722, 2188, 2234
$GeHCl^+-H_2$	157, 211, 355, 427, 467, 545, 560, 1879, 4194
GeH_3^+-ClH	120, 233, 455, 506, 652, 795, 852, 854, 2202, 2254, 2256, 2818
$GeH_2Cl^+-H_2$	171, 266, 439, 490, 499, 559, 708, 708, 810, 2188, 2243, 4173
GeH_2Cl_2	143, 408, 418, 512, 639, 769, 847, 2171, 2192
$GeHCl^+-ClH$	84, 113, 195, 434, 447, 560, 588, 1942, 2825
$GeH_2Cl_2^+$	111, 144, 237, 347, 478, 584, 628, 1867, 2097
$GeCl_2^+-H_2$	11, 27, 54, 97, 124, 148, 399, 454, 4437
GeH_2Cl^+-ClH	65, 107, 206, 467, 477, 563, 565, 714, 816, 2201, 2251, 2819
$GeHCl_2^+-H_2$	41, 150, 219, 238, 304, 465, 515, 554, 574, 682, 2224, 3262
$GeHCl_3$	138(2), 175, 401, 429(2), 697(2), 2203
$GeCl_2^+-ClH$	73, 92, 116, 133, 182, 396, 440, 520, 2828
$GeHCl_3^+$	126, 129, 130, 156, 166, 372, 488, 490, 1594
$GeHCl_2^+-ClH$	54, 115, 125, 156, 195, 448, 493, 562, 608, 689, 2226, 2819
$GeCl_3^+-H_2$	34, 136, 139, 140, 232, 238, 308, 416, 506, 520, 525, 4286
$GeCl_4$	119(2), 164(3), 379, 439(3)
$GeCl_4^+$	99, 133, 138, 139, 176, 279, 369, 463, 511
$GeCl_3^+-ClH$	89, 98, 122, 145, 147, 155, 190, 406, 498, 498, 589, 2817

[a] Experimental values for neutrals and references can be found in ref 12. [b] Numbers in parentheses are the degeneracy.

the relative large energy differences. Final results of the calculated adiabatic IPs depend on the orbital energies of the neutrals, orbital mixing in cations, and the structure relaxation in cations, and the overall effect is seen in the increasing IPs upon successive halogen substitutions.

Besides the divalent cations, structural rearrangement of GeH_2^+ to Ge^+-H_2 upon collision has been proposed previously from the mass spectrometry study and DFT and *ab initio* calculations,[50] and structure Ge^+-FH has been found to be more stable than the divalent $GeHF^+$ cation.[51] The present B3LYP/6-31+G(2df,p) study finds similar structures for $[GeH_2]^+$, $[GeHF]^+$, and $[GeHCl]^+$ as well (Figure 1). These structures can be viewed as the complexes Ge^+-H_2, Ge^+-FH, and Ge^+-ClH, where the positive charge is mostly localized on the Ge-atom. Two electronic states of Ge^+-H_2, $^2B_2$ and $^2B_1$, are below GeH_2^+ by 18.1 and 11.5 kJ/mol at G3 level, and Ge^+-FH and Ge^+-ClH are below divalent $GeHF^+$ and $GeHCl^+$ by 43.6 and 4.6 kJ/mol, respectively. The relative stability of Ge^+-FH^+ and $GeHF^+$ at G3 level is significantly different from that of −4.2 kJ/mol at CCSD(T,Full)/aug-cc-pVTZ (AVTZ) level.[51] Note that divalent GeH_2^+ is slightly above the $Ge^+ + H_2$ dissociation limit by 3.4 kJ/mol, while the dissociations of Ge^+-H_2 ($^2B_2$), Ge^+-FH, and Ge^+-ClH into $Ge^+ + H_2/HF/HCl$ require energies of 14.7, 68.7, and 84.9 kJ/mol, respectively. The G3 dissociation energies of the cations are given in Table 3.

The barrier heights for isomerizations from GeH_2^+, $GeHF^+$ and $GeHCl^+$ to Ge^+-H_2, Ge^+-FH, and Ge^+-ClH are 124.4, 103.6, and 71.6 kJ/mol, respectively. Levels of the barriers for GeH_2^+ and $GeHF^+$, 10.41 and 10.95 eV relative to their neutrals, are above the dissociation limits of 9.09 and 10.13 eV for $Ge^+ + H_2$ and $Ge^+ + HF$, respectively; thereafter, the Ge^+-H_2 or Ge^+-FH complex cations cannot be observed from direct photoionization of GeH_2 and GeHF. While the barrier of 10.187 eV for $GeHCl^+$ is below $Ge^+ + HCl$ limit of 10.278 eV, therefore there is a small window in photon energy to produce Ge^+-ClH from direct photoionization of GeHCl. Alternatively, formation of these complex cations may be allowed in ion reactions, chemical ionization, or neutralization−reionization.

Experimentally, adiabatic IP(GeF_2) can be estimated as the appearance potentials of 11.6 ± 0.3[18] and 11.8 ± 0.1 eV[19] for GeF_2^+ from electron impact ionization of GeF_2 and of 11.65 eV from He(I)-PES,[20] and vertical IP of 11.98 ± 0.03 eV from He(I)-PES.[20] These values are supported by our G3 adiabatic IP of 11.63 eV and vertical IP of 12.02 eV. The G3 adiabatic

TABLE 3: Zero-Point Energy Corrections and G3(CC)/B2df+ Energies (in Hartree) of Neutral Radicals and Cations, the Adiabatic Ionization Potentials (in eV), and Dissociation Energies of Complex Ions (DE, in kJ/mol)[a]

neutrals	ZPE	G3(CC)	cations	ZPE	G3(CC)	IP(G3)	DE	IP(others)
H	0.000 00	−0.50092						
F	0.000 00	−99.68566						
Cl	0.000 00	−459.99250						
Ge	0.000 00	−2076.37852	Ge^+	0.000 00	−2076.08811	7.90		7.899[b]
H_2	0.010 02	−1.17714						
HF	0.009 16	−100.41132						
HCl	0.006 62	−460.66231						
F_2	0.002 35	−199.43048						
Cl_2	0.001 22	−920.07452						
GeH	0.004 18	−2076.98679	$Ge-H^+$	0.004 46	−2076.69915	7.83		
Ge−F	0.001 48	−2176.25810	$Ge-F^+$	0.001 77	−2175.97972	7.58		7.46,[c] 7.3[d]
Ge−Cl	0.000 86	−2536.51910	$Ge-Cl^+$	0.001 10	−2536.24614	7.43		
GeH_2	0.010 60	−2077.59988	$HGeH^+$	0.010 99	−2077.26491	9.13		9.25[e]
			Ge^+-H_2 ($^2B_2$)	0.011 73	−2077.27257	8.94	14.7	
			Ge^+-H_2 ($^2B_1$)	0.011 73	−2077.27007	9.01	8.1	
			TS	0.005 61	−2077.21217			
GeHF	0.007 27	−2176.86994	$HGeF^+$	0.006 38	−2176.50620	9.87		
			Ge^+-FH	0.010 18	−2176.52662	9.42	68.7	
			TS	0.004 31	−2176.46467			
GeF_2	0.003 45	−2276.15459	GeF_2^+	0.003 75	−2275.72763	11.63		11.2,[d] 11.6 ± 0.3[f] 11.8 ± 0.1[g] 11.65,[h] 11.98[i] 11.24,[j] 11.67[k]
GeHCl	0.006 66	−2537.12816	$HGeCl^+$	0.006 16	−2536.78057	9.45		
			Ge^+-ClH	0.007 83	−2536.78399	9.40	84.9	
			TS($HGeCl^+$)	0.003 89	−2536.75103			
$GeCl_2$	0.002 04	−2996.66191	$GeCl_2^+$	0.002 20	−2996.28763	10.19		≤ 7.94,[e] 10.21[k] 10.20 ± 0.05[l] 10.55 ± 0.03[m]
GeH_3	0.019 66	−2078.20304	GeH_3^+	0.020 59	−2077.90814	8.01		
			GeH^+-H_2	0.019 05	−2077.88878	8.53	20.8	
GeH_2F	0.015 52	−2177.44826	GeH_2F^+	0.016 37	−2177.14424	8.30		
			FGe^+-H_2	0.013 82	−2177.16315	7.71	11.2	
			HGe^+-FH	0.016 87	−2177.14260	8.35	75.8	
$GeHF_2$	0.010 60	−2276.70167	$GeHF_2^+$	0.011 75	−2276.37315	8.97		
			FGe^+-FH	0.012 80	−2276.42124	7.69	74.4	
GeF_3	0.006 13	−2375.95190	GeF_3^+	0.007 04	−2375.58354	10.05		≤ 10.3,[n] 9.7[d]
GeH_2Cl	0.014 80	−2537.70973	GeH_2Cl^+	0.015 58	−2537.41601	8.01		
			$ClGe^+-H_2$	0.012 84	−2537.42759	7.62	6.2	
			HGe^+-ClH	0.014 44	−2537.39944	8.43	90.9	
$GeHCl_2$	0.009 21	−2997.21916	$GeHCl_2^+$	0.010 09	−2996.92001	8.16		
			$ClGe^+-ClH$	0.009 46	−2996.93268	7.80	59.0	
$GeCl_3$	0.003 50	−3456.72793	$GeCl_3^+$	0.004 27	−3456.41936	8.42		

[a] Spin orbit corrections in mhartrees: Ge (^3P) = −4.41, Ge^+ (^2P) = −5.37, GeH = −2.03, GeF = −2.13, and GeCl = −2.22. [b] From *NIST WebBook*.[41] [c] Huber et al. from spectroscopic study.[47] [d] CCSD(T,Full)/cc-pVTZ.[14] [e] Photoionization study.[16] [f] Adiabatic IP from electron impact ionization.[18] [g] Adiabatic IP from electron impact.[19] [h] Adiabatic IP from He(I) photoelectron spectroscopy.[20] [i] Vertical IP from He(I) PES.[20] [j] MRSDCI+Q).[52] [k] DFT-LSD.[22] [l] Adiabatic IP from He(I) PES.[21] [m] Vertical IP from He(I) PES.[21] [n] Adiabatic IP from electron impact ionization.[23]

IP(GeF_2) is higher than a previous MRSDCI(+Q) estimation of 11.24 eV[52] and recent CCSD(T,Full)/cc-pVTZ prediction of 11.2 eV.[14] Adiabatic IP($GeCl_2$) = 10.20 ± 0.05 eV and vertical IP($GeCl_2$) = 10.55 ± 0.03 eV[21] were also obtained from He(I)-PES of $GeCl_2$. These values are supported here by our G3 predictions of 10.19 and 10.60 eV, respectively. A previous DFT-LSD prediction yields IPs of 11.67 and 10.21 eV for GeF_2 and $GeCl_2$,[22] agreeing excellently with the present G3 values. The adiabatic G3 IP(GeH_2) = 9.13 eV agrees with experimental result of ≤9.25 eV from the photoionization study.[16] No previous study can be found for the structure or the energetics for $[GeHCl]^+$.

D. $GeH_xF_y^+$ and $GeH_xCl_y^+$ ($x + y = 3$) (Figure 2). All germyl radicals are pyramidal, and direct ionization leads to planar trivalent germyl cations. The G3 adiabatic IPs are listed in Table 3. There have been no direct experimental measurement on the ionization energies of germyl radicals except for GeH_3, for which the adiabatic IP from G3 prediction (8.01 eV) agrees with the photoionization value (7.94_8 ± 0.005 eV[16]). F-substitution on germyl radicals increases the adiabatic IP significantly to 10.05 eV for GeF_3, while Cl-substitution changes the values only slightly to 8.42 eV for $GeCl_3$. Appearance of GeF_3^+ has been observed from electron impact ionization of GeF_4 at energy of 15.7 ± 0.2 eV,[23] which is consistent with our G3 prediction of 15.61 eV. The G3 adiabatic IP(GeF_3) is higher than the CCSD(T,Full)/cc-pVTZ value of 9.7 eV.[14] It is noticed that our G3 IPs for GeF, GeF_2, and GeF_3 are systematically higher than the CCSD(T,Full)/cc-pVZ ones by 0.2−0.3 eV, and it is suspected that the cc-pVTZ basis set may not be large enough to obtain highly accurate results. With cc-pVTZ basis set for Ge, the CCSD(T) calculations is appropriate for correlating 4s and 4p electrons only.[53]

For the $[GeH_3]^+$ species, ion complex structure have also been found as GeH^+-H_2, which is above the trivalent GeH_3^+ by 54 kJ/mol at B3LYP/6-311++G(d,p) level[50] and by 47.6 kJ/mol at G3 level. The G3 dissociation energies of GeH_3^+ to $GeH^+ + H_2$ and $GeH_2^+ + H$ are 20.8 and 348.4 kJ/mol, respectively. The dissociation to $GeH^+ + H_2$ is mediated by the GeH^+-H_2 complex, and a transition state is located at 223.1 kJ/mol above GeH_3^+ from GeH_3^+ to GeH^+-H_2. The barrier is below the

TABLE 4: Calculated Results for Neutral, Ionized, and Protonated Germanes and Proton Affinities of Germanes (ZPEs and G3 Energies in Hartree, IPs in eV, DEs and PAs in kJ/mol)[a]

neutrals	ZPE	G3(CC)	cations	ZPE	G3(CC)	IP(G3)PA(G3)	DE(G3)	IP[b](others)
GeH_4	0.029 03	−2078.84639	$GeH_2^+{-}H_2$	0.026 37	−2078.45972	10.45	32.3	≤10.52[c]
			$GeH_3^+{-}H_2$	0.035 89	−2079.10518	*658.3*	38.4	10.54[d]
GeH_3F	0.024 76	−2178.09282	$GeH_2^+{-}FH$	0.024 24	−2177.71312	10.32	86.1	12.3[e]
			GeH_3F^+	0.019 46	−2177.65627	11.73		
			$GeH_2F^+{-}H$	0.018 71	−2177.65924	11.63	30.8	
			$GeHF^+{-}H_2$	0.020 36	−2177.69452	10.72	18.9	
			$GeH_3^+{-}FH$	0.033 78	−2178.35916	*672.5*	93.6	
			$GeH_2F^+{-}H_2$	0.030 99	−2178.33703	*621.7*	29.0	
GeH_2F_2	0.019 97	−2277.34659	$GeHF^+{-}FH$	0.018 97	−2276.95454	10.64	88.2	13.0 ± 0.1[e]
			$GeHF_2^+{-}H$	0.014 29	−2276.88880	12.30	32.0	
			$GeF_2^+{-}H_2$	0.016 60	−2276.91948	11.53	31.2	
			$GeH_2F^+{-}FH$	0.028 93	−2277.59831	*634.2*	103.3	
			$GeHF_2^+{-}H_2$	0.025 77	−2277.56726	*561.0*	34.1	
$GeHF_3$	0.014 76	−2376.60037	$GeF_2^+{-}FH$	0.015 19	−2376.18206	11.40	107.2	
			$GeF_3^+{-}H$	0.009 75	−2376.10396	13.37	44.1	
			$GeHF_2^+{-}FH$	0.023 52	−2376.83252	*583.4*	119.3	
			$GeF_3^+{-}H_2$	0.021 29	−2376.78544	*465.6*	53.9	
GeF_4	0.009 54	−2475.84543	GeF_4^+	0.008 51	−2475.28497	15.22		15.5,[f] 15.69[g] 16.1,[h] 16.56[i]
			$GeF_3^+{-}FH$	0.018 62	−2476.05234	*516.3*	144.5	
GeH_3Cl	0.023 94	−2538.35165	$GeH_3^+{-}Cl$	0.021 07	−2537.93808	11.18	97.0	11.3 ± 0.02[e]
			$GeHCl^+{-}H_2$	0.019 75	−2537.96577	10.39	11.8	11.34[j]
			$GeH_2^+{-}ClH$	0.022 08	−2537.97172	10.29	105.1	
			$GeH_3^+{-}ClH$	0.031 42	−2538.61652	*672.7*	109.9	
			$GeH_2Cl^+{-}H_2$	0.029 76	−2538.60429	*644.9*	18.3	
GeH_2Cl_2	0.018 18	−2997.85863	$GeHCl^+{-}ClH$	0.016 14	−2997.47680	10.33	80.2	11.42[e]
			$GeH_2Cl_2^+$	0.014 57	−2997.43160	11.52		
			$GeCl_2^+{-}H_2$	0.012 91	−2997.46587	10.54	1.1	
			$GeH_2Cl^+{-}ClH$	0.025 26	−2998.10468	*652.6*	89.5	
			$GeHCl_2^+{-}H_2$	0.022 96	−2998.11547	*630.4*	12.3	
$GeHCl_3$	0.011 91	−3457.36512	$GeHCl_3^+$	0.008 20	−3456.98063	11.72		
			$GeCl_2^+{-}ClH$	0.010 73	−3456.93055	10.43	75.5	
			$GeHCl_2^+{-}ClH$	0.019 06	−3457.61627	*637.5*	83.0	
			$GeCl_3^+{-}H_2$	0.016 79	−3457.60296	*608.5*	10.4	
$GeCl_4$	0.005 45	−3916.86928	$GeCl_4^+$	0.005 18	−3916.44712	11.48		11.6 ± 0.3,[k] 11.68[l] 11.88 ± 0.02[m] 11.7[n]
			$GeCl_3^+{-}ClH$	0.012 90	−3917.11499	*624.4*	82.2	

[a] Proton affinities are calculated at 0 K, using $\Delta_f H^\circ_{0K}(H^+) = 1528.1$ kJ/mol. [b] Adiabatic IP unless being denoted by v as vertical IP. [c] Photoionization.[16] [d] Photoionization.[17] [e] Vertical IP from He(I) PES.[30] [f] Adiabatic IP using He(I) PES.[24] [g] Adiabatic IP using He(I) PES.[25] [h] Vertical IP using He(I) PES.[24−27] [i] Vertical IP using He(I) PES.[24] [j] Vertical IP using He(I) PES.[31] [k] Electron impact.[28] [l] Electron impact.[29] [m] From He(I) PES.[25] [n] From He(I) PES.[32]

dissociation limit for $GeH_2^+ + H$, and this is consistent with the observation of H_2 loss being the main channel in collision-activated dissociation of GeH_3^+ cation.[50] Similar ion complexes are also located for $[GeH_2X]^+$ and $[GeHX_2]^+$ (X = F, Cl) in previous[51] and present studies. The ion complexes can be viewed as $XGe^+{-}H_2$, $HGe^+{-}XH$, and $XGe^+{-}XH$, of which $GeH^+{-}FH$ and $GeH^+{-}ClH$ are energetically less stable than their trivalent counterparts. At G3 level, $FGe^+{-}H_2$, and $ClGe^+{-}H_2$ are more stable than GeH_2F^+ and GeH_2Cl^+ by 56.4 and 37.6 kJ/mol, and $FGe^+{-}FH$ and $ClGe^+{-}ClH$ by 123.5 and 35.0 kJ/mol, respectively. The relative stabilities of $GeH^+{-}FH$ and $GeF^+{-}FH$ at G3 level are significantly different from those of 10.0 and 72.8 kJ/mol at CCSD(T,Full)/AVTZ level. Again, the AVTZ basis set for Ge are appropriate for correlating the electrons in the valence 4s and 4p orbitals only.[53]

It is also noticed that trivalent GeH_2F^+, $GeHF_2^+$, and GeH_2Cl^+ are above the dissociation limits of $GeF^+ + H_2$, $GeF^+ + HF$, and $GeCl^+ + H_2$, respectively. However, energy barriers are expected for isomerizations from trivalent to complex ions, and loss of H_2, HF, or HCl is also expected from collision-activated processes, even though the possible transition states are not pursued here. The G3 dissociation energies of germyl cations are listed in Table 3.

E. Cations of Germanes $GeH_xF_y^+$ and $GeH_xCl_y^+$ ($x + y = 4$) (Figures 3 and 4; Tables 2 and 4). Of this class of cations, $[GeH_4]^+$ has been observed in high-resolution photoionizaton studies with the adiabatic IP of ≤10.52[16] or 10.54 eV,[17] with which the G3 prediction of 10.45 eV agrees. Structure of GeH_4^+ has a C_s symmetry at the B3LYP level (Figure 3), similar to those in previous studies.[6,7,54] The cation can be viewed as a $H_2Ge^+{-}H_2$ complex, largely different from the neutral GeH_4. Similar large structural distortion from the neutral has also been found in $[SiH_4]^+$, $[SnH_4]^+$, and fluorinated silane cations,[3−8] and C_{2v} structure for CH_4^+.[55] The structural changes are due to spin−orbit coupling and/or the Jahn−Teller effect.[42] For GeF_4 and $GeCl_4$, the HOMOs have triple degeneracy (t_1). In cations, the degeneracy is lifted by a change in molecular shape (the Jahn−Teller effect), and symmetries are reduced to C_{2v} (Figure 3). Two F/Cl atoms with less negative charge experience less repulsion to each other, leading to a small FGeF angle of 69.9° in GeF_4^+ and ClGeCl angle of 77.1°. At the CASSCF/MRSDCI level, Das et al.[6] obtained an adiabatic IP of 10.73 eV at C_{2v} symmetry without ZPE correction (∼ −6.9 kJ/mol). The C_{2v} structure is indeed a first-order saddle point at B3LYP level. $GeH_3^+{-}H$ structure with C_{3v} symmetry, as found for

TABLE 5: ZPE, G3(CC)/B2df+, G3X(CC)/B2df+, and G4//B2df+ Electronic Energies (in Hartree) and Atomization Energies (in kJ/mol) of Germanes and Radicals[a]

	electronic energy			atomization energy			
neutrals	ZPE	G3	G3X	G4	G3	G3X	G4
H	0.000 00	−0.50092	−0.50097	−0.50142			
F	0.000 00	−99.68566	−99.68635	−99.70498			
Cl	0.000 00	−459.99250	−459.99319	−460.01505			
Ge	0.000 00	−2076.37852	−2076.37887	−2076.44070			
H_2	0.010 02	−1.17714	−1.17724	−1.17804	433.9	433.9	433.7
HF	0.009 16	−100.41132	−100.41170	−100.43155	566.0	565.1	567.1
HCl	0.006 62	−460.66231	−460.66279	−460.68534	426.0	425.4	426.0
F_2	0.002 35	−199.43048	−199.43114	−199.47026	149.1	147.3	152.1
Cl_2	0.001 22	−920.07452	−920.07597	−920.12153	231.8	232.0	236.8
GeH	0.004 18	−2076.98679	−2076.98718	−2077.04872	270.9	270.9	268.9
Ge−F	0.001 48	−2176.25810	−2176.26018	−2176.34083	505.2	508.0	508.5
Ge−Cl	0.000 86	−2536.51910	−2536.52019	−2536.60413	386.5	386.7	387.3
GeH_2	0.010 60	−2077.59988	−2077.60036	−2077.66274	548.5	548.6	547.7
GeHF	0.007 27	−2176.86994	−2176.87210	−2176.95288	781.2	784.1	783.7
GeF_2	0.003 45	−2276.15459	−2276.15862	−2276.25773	1053.6	1059.7	1059.7
GeHCl	0.006 66	−2537.12816	−2537.12931	−2537.21340	655.2	655.4	655.2
$GeCl_2$	0.002 04	−2996.66191	−2996.66373	−2996.76951	778.1	778.3	778.9
GeH_3	0.019 66	−2078.20304	−2078.20375	−2078.26644	793.1	793.7	792.4
GeH_2F	0.015 52	−2177.44826	−2177.45070	−2177.53241	962.8	966.2	967.1
$GeHF_2$	0.010 60	−2276.70167	−2276.70599	−2276.80656	1156.0	1162.7	1165.4
GeF_3	0.006 13	−2375.95190	−2375.95819	−2376.07753	1339.7	1349.9	1354.1
GeH_2Cl	0.014 80	−2537.70973	−2537.71115	−2537.79633	845.6	846.3	847.9
$GeHCl_2$	0.009 21	−2997.21916	−2997.22133	−2997.32885	907.1	908.2	912.1
$GeCl_3$	0.003 50	−3456.72793	−3456.73085	−3456.86049	967.3	968.6	974.4
GeH_4	0.029 03	−2078.84639	−2078.84725	−2078.91052	1142.4	1143.3	1142.4
GeH_3F	0.024 76	−2178.09282	−2178.09548	−2178.17711	1315.6	1319.5	1319.0
GeH_2F_2	0.019 97	−2277.34659	−2277.35120	−2277.45105	1509.5	1516.8	1516.4
$GeHF_3$	0.014 76	−2376.60037	−2376.60703	−2376.72498	1704.4	1715.5	1714.8
GeF_4	0.009 54	−2475.84543	−2475.85401	−2475.99013	1876.5	1890.9	1890.3
GeH_3Cl	0.023 94	−2538.35165	−2538.35325	−2538.43840	1191.8	1192.9	1193.1
GeH_2Cl_2	0.018 18	−2997.85863	−2997.86103	−2997.96800	1247.3	1248.9	1250.2
$GeHCl_3$	0.011 91	−3457.36512	−3457.36839	−3457.49698	1303.0	1305.1	1307.0
$GeCl_4$	0.005 45	−3916.86928	−3916.87344	−3917.02337	1353.0	1355.7	1357.4

[a] High-level correction parameters for G3(CC)/B2df+: $A = 6.688$, $B = 3.007$, $C = 6.763$, $D = 1.107$. Parameters for G3X(CC)/B2df+: $A = 6.783$, $B = 3.083$, $C = 6.977$, $D = 1.152$. Parameters for G4/B2df+: $A = 6.947$, $A' = 7.128$, $B = 2.441$, $C = 7.116$, $D = 1.414$, $E = 2.745$ mhartree

SiH_3^+−H at HF/3-21G level,[5] is a second-order saddle point at the B3LYP level.

Multiple structures are identified for cations of GeH_3X, GeH_2X_2, and $GeHX_3$ (Figures 3 and 4). Almost all these structures can be viewed as ion complex between a Ge-containing cation and a neutral atom or diatom, except for one structure of GeH_3F^+, $GeH_2Cl_2^+$, and $GeHCl_3^+$. IPs to these ionic isomers and their dissociation energies of the corresponding fragments are calculated and listed in Table 4. For example, in addition to the “normal” GeH_3F^+, three other $[GeH_3F]^+$ structures are found to be $GeHF^+$−H_2, GeH_2^+−FH, and GeH_2F^+−H complexes with large separations between Ge atom and dissociating fragments. Only a small fraction of the charges are partitioned in the dissociating fragments, e.g., 0.073 *e* on H_2 of $GeHF^+$−H_2, 0.086 *e* on HF of GeH_2^+−FH, and 0.209 *e* on H of GeH_2F^+−H. The structures of GeH_2^+ and $GeHF^+$ moieties in GeH_2^+−FH and $GeHF^+$−H_2 resemble closely those of cations in free form (*see* Figures 1 and 3). The relative stability of the complex cations is determined by the interaction between the two fragments and the easiness of cationic fragment formation. For $[GeH_3F]^+$, the GeH_2^+−FH structure has the lowest energy among all four $[GeH_3F]^+$ isomers and its stability is due to the smaller IP of GeH_2 than that of GeHF and the strong bonding between the lone-pair on F atom and the empty Ge p-orbital on GeH_2^+. Dissociation of GeH_2^+−FH to GeH_2^+ + HF requires energy of 86.1 kJ/mol, being higher than those for $GeHF^+$−H_2 (18.9 kJ/mol) and GeH_2F^+−H (30.8 kJ/mol). For cations of GeH_3X, GeH_2X_2, and $GeHX_3$, the most stable structures are ion complexes between HF or HCl with a germylene cation.

The large structural distortion from neutral to the most stable cation imposes experimental difficulty in determination of adiabatic IP with photoionization because of the small Franck−Condon factor at the onset of ionization, especially for GeH_3X, GH_2X_2, and $GeHX_3$ in photoelectron spectroscopy. For GeH_3X, GeH_2X_2, and $GeHX_3$, the PES peaks correspond more likely to the ionic conformers which are structurally closest to the neutrals, instead of the ones with the lowest energies. For GeH_3F, the structure GeH_3F^+ is likely to have the largest Franck−Condon factor, and therefore, likely the ionic state observed in the PES studies, even though it has the highest energy among the ionic isomers (Table 4). The vertical IP of GeH_3F of 12.3 eV obtained using He(I)-PES[30] is much higher than the G3 adiabatic IP of 11.73 eV to GeH_3F^+ while being lower than the G3 vertical IP of 12.58 eV. For GeH_3Cl, the measured vertical IP of 11.30 ± 0.02[30] or 11.34 ± 0.05 eV[31] is higher than the calculated adiabatic IP to GeH_3^+−Cl (11.175 eV) but agrees with the calculated vertical value of 11.383 eV. The observed vertical IP of 13.0 ± 0.1 eV for GeH_2F_2[30] may correspond to $GeHF_2^+$−H, which is structurally closest to then neutral GeH_2F_2, and the observed vertical IP of 11.42 ± 0.02 eV for GeH_2Cl_2[30] to $GeHCl_2^+$−H.

On the other hand, the relatively smaller structural changes result in reasonable measurements for adiabatic IPs of GeF_4 and $GeCl_4$. The adiabatic IP(GeF_4) = 15.5[24] or 15.69 eV[25] and vertical IP(GeF_4) = 16.1[24−27] or 16.56 eV[24] have been obtained

TABLE 6: Appearance Energies of Cation Fragments at the G3(CC)//B2df+ Level (in eV)

neutral	fragments	AE	expt
GeH_4	$GeH_3^+ + H$	11.67	$\leq 11.65_7 \pm 0.01^{16}$
	$GeH_2^+ + H_2$	10.78	$10.77_2 \pm 0.009^{16}$
	$GeH^+ + H_2 + H$	12.37	$\leq 12.9^{16}$
	$Ge^+ + 2H_2$	10.75	$\leq 11.48^{16}$
GeF_2	$GeF^+ + F$	13.27	14.0 ± 0.3^{19}
	$Ge^+ + F_2$	17.28	
	$Ge^+ + 2F$	18.82	18.8 ± 0.3^{19}
GeHF	$Ge^+ + HF$	10.13	
	$GeF^+ + H$	10.44	
	$GeH^+ + F$	13.12	
GeH_2F	$GeF^+ + H_2$	7.83	
	$GeH^+ + HF$	9.14	
	$GeH_2^+ + F$	13.42	
	$GeHF^+ + H$	11.76	
$GeHF_2$	$GeF^+ + HF$	8.46	
	$GeH^+ + F_2$	15.46	
	$GeF_2^+ + H$	12.69	
	$GeHF^+ + F$	13.76	
GeF_3	$GeF^+ + F_2$	14.69	
	$GeF_2^+ + F$	14.59	
GeH_3F	$GeH_3^+ + F$	13.47	
	$GeH_2F^+ + H$	11.95	
	$GeH_2^+ + HF$	11.21	
	$GeHF^+ + H_2$	10.92	
	$GeF^+ + H_2 + H$	11.49	
	$GeH^+ + HF + H$	12.80	
	$Ge^+ + H_2 + HF$	11.17	
GeH_2F_2	$GeH_2F^+ + F$	13.96	
	$GeHF_2^+ + H$	12.63	
	$GeH_2^+ + F_2$	16.89	
	$GeF_2^+ + H_2$	11.85	
	$GeHF^+ + HF$	11.55	
	$GeH^+ + HF + F$	14.81	
	$GeF^+ + HF + H$	12.13	
	$Ge^+ + HF + HF$	11.82	
$GeHF_3$	$GeF_3^+ + H$	13.83	
	$GeHF_2^+ + F$	14.65	
	$GeF_2^+ + HF$	12.51	
	$GeHF^+ + F_2$	17.90	
	$GeH^+ + F_2 + F$	21.15	
	$GeF^+ + HF + F$	14.15	
	$Ge^+ + HF + F_2$	18.16	
GeF_4	$GeF_3^+ + F$	15.61	15.7 ± 0.2^{23}
	$GeF_2^+ + F_2$	18.61	
	$GeF_2^+ + 2F$	20.16	20.7 ± 0.3^{23}
	$GeF^+ + F_2 + F$	20.25	23.4 ± 0.4^{23}
	$Ge^+ + F_2 + F_2$	24.26	
	$Ge^+ + 4F$	27.35	29.4 ± 0.2^{23}
GeH_2	$Ge^+ + H_2$	9.09	
	$GeH^+ + H$	10.71	
	$Ge^+ + H + H$	13.59	
GeH_3	$GeH^+ + H_2$	8.75	
$GeCl_2$	$GeCl^+ + Cl$	11.49	11.5 ± 0.5^{28}
	$Ge^+ + Cl_2$	13.56	
	$Ge^+ + 2Cl$	15.97	16.8 ± 0.5^{28}
GeHCl	$Ge^+ + HCl$	10.28	
	$GeCl^+ + H$	10.22	
	$GeH^+ + Cl$	11.82	
GeH_2Cl	$GeCl^+ + H_2$	7.69	
	$GeH^+ + HCl$	9.38	
	$GeH_2^+ + Cl$	12.20	
	$GeHCl^+ + H$	11.42	
$GeHCl_2$	$GeCl^+ + HCl$	8.41	
	$GeH^+ + Cl_2$	12.03	
	$GeCl_2^+ + H$	11.53	
	$GeHCl^+ + Cl$	12.06	
$GeCl_3$	$GeCl^+ + Cl_2$	11.05	
	$GeCl_2^+ + Cl$	12.15	
GeH_3Cl	$GeH_3^+ + Cl$	12.18	
	$GeH_2Cl^+ + H$	11.60	
	$GeH_2^+ + HCl$	11.38	
	$GeHCl^+ + H_2$	10.51	
	$GeCl^+ + H_2 + H$	11.28	
	$GeH^+ + HCl + H$	12.96	
	$Ge^+ + H_2 + HCl$	11.34	
GeH_2Cl_2	$GeH_2Cl^+ + Cl$	12.18	
	$GeHCl_2^+ + H$	11.69	
	$GeH_2^+ + Cl_2$	13.97	
	$GeCl_2^+ + H_2$	10.56	
	$GeHCl^+ + HCl$	11.17	
	$GeH^+ + HCl + Cl$	13.54	
	$GeCl^+ + HCl + H$	11.94	
	$Ge^+ + HCl + HCl$	12.00	
$GeHCl_3$	$GeCl_3^+ + H$	11.90	
	$GeHCl_2^+ + Cl$	12.27	
	$GeCl_2^+ + HCl$	11.21	
	$GeHCl^+ + Cl_2$	13.76	
	$GeH^+ + Cl_2 + Cl$	16.13	
	$GeCl^+ + HCl + Cl$	12.52	
	$Ge^+ + HCl + Cl_2$	14.59	
$GeCl_4$	$GeCl_3^+ + Cl$	12.42	12.3 ± 0.3^{28} 12.12 ± 0.04^{29}
	$GeCl_2^+ + Cl_2$	13.74	
	$GeCl_2^+ + 2Cl$	16.15	$17. \pm 1.^{28}$
	$GeCl^+ + Cl_2 + Cl$	15.05	$18. \pm 1.^{28}$
	$Ge^+ + Cl_2 + Cl_2$	17.12	
	$Ge^+ + 4Cl$	21.93	$21. \pm 1.^{28}$

from He(I)-PES study, and the values are between our G3 adiabatic and vertical values of 15.22 and 16.25 eV, respectively. Four values have been available for adiabatic IP($GeCl_4$), 11.6 ± 0.3 eV by Uy et al.[28] and 11.68 ± 0.05 eV by Tamas et al. with electron impact ionization,[29] 11.88 ± 0.02 eV by Bassett et al. with He(I/II)-PES,[25] and 11.7 eV by Smith et al. with threshold photoelectron spectrum.[32] All these values are slightly above the G3 adiabatic IP of 11.48 eV and far below the G3 vertical IP of 12.16 eV.

While ionizations of GeX_2 and GeX_4 remove electron from the paired orbital, those of Ge, GeX, and GeX_3 (X = H, F, Cl) remove the unpaired electrons. Consequently, the IPs of GeX_2 and GeX_4 are always higher than those of Ge, GeX, and GeX_3 radicals. There is no simple trend for the adiabatic IPs of germyl radicals and germanes containing both hydrogen and halogen atoms because of the structural rearrangement and the bonding between the empty p-orbital of the Ge atom and lone pairs of halogen atoms. Similar variations have been found for the Si−H−F system as well.[5]

F. Appearance Energies (AEs) of Ion Fragments from Ionization. The ion fragment appearance energy (AE) measurement from well-known precursor and well-defined neutral fragment counterparts, together with the ionization potentials, is one of the highly accurate methods in measuring bond dissociation energies and enthalpies of formation of free radicals,[56,57] although none of such measurement has been made on halogenated germanes. With the G3 results discussed in above sessions, the AEs of various possible fragmentation channels can be readily derived and are listed in Table 6.

AEs of ion fragments have been reported from electron bombardment on GeF_2,[19] GeF_4,[23] $GeCl_2$,[28] and $GeCl_4$[28,29] and from photoionization of GeH_4, GeF_4, and $GeCl_4$.[16,17,32−35] While the G3 AEs of GeH_3^+ and GeH_2^+ from GeH_4 are only 0.02 eV above the upper limits of the high-resolution photoionization study,[16] the other electron impact ionization and photoionization experiments have rather large uncertainties. Only a few channels can be assigned with confidence, e.g., GeF^+ from GeF_2, $GeCl^+$ from $GeCl_2$, GeF_3^+ from GeF_4, and $GeCl_3^+$ from $GeCl_4$, justified from the good agreement between the experimental observations and the theoretical G3 predictions. The measured AEs of other fragmentation channels are all considerably higher than the calculated G3 values of the possible channels. The excess energy is likely due to the translational energies and/or internal excitation of fragments, especially when transition states may exist for ion dissociation processes.

G. Protonation of Germanes (Figures 3 and 4). Proton affinity is one of the important parameters in gas-phase ion chemistry[56] and in generating germyl cations from germanes. Proton affinity of GeH_4 has been measured in the range of 678−686 kJ/mol from gas-phase proton-transfer reactions.[58] Theoretical study has assigned $GeH_3^+{-}H_2$ complexes for the structure of GeH_5^+, and the predicted PA and dissociation energy of the ion complex are 653 and 42 kJ/mol at CCSD/TZP+*f* level by Schreiner et al.,[59] in agreement with our G3 values of 658.3 and 38.4 kJ/mol at 0 K and PA of 662.0 kJ/mol at 298 K, respectively. PA(GeH_4, 298 K) = 672.8 kJ/mol has also been predicted at G2 level.[60] All the theoretical PAs are smaller than the experimental measurements. However, Schreiner et al. suggested that the experimental PA may need to be lowered by 10−20 kJ/mol with the redetermination of the usual standard PA of isobutene as 802 ± 3.6,[61] 802 ± 5.0,[62] or 801.7 ± 1.4 kJ/mol,[63] which agree excellently with the G2 prediction of 802 kJ/mol[64] but are markedly different from the earlier evaluation of 820 kJ/mol.[65] We are not aware of any studies on protonation of other halogenated germanes.

The structures of protonated germanes are displayed in Figures 3 and 4, and the G3 PAs are listed in Table 3. At the B3LYP/6-31+G(2df,p) level, structures similar to $GeH_3^+{-}H_2$ are also identified as $GeH_2X^+{-}H_2$, $GeHX_2^+{-}H_2$, and $GeX_3^+{-}H_2$ for protonated GeH_3X, GeH_2X_2, and $GeHX_3$ (X = F, Cl). The dissociation energies into germyl cations + H_2 are in the ranges 29 to 54 kJ/mol for fluorinated cations and 10 to 19 kJ/mol for chlorinated cations. The weak bonding between germyl cations and H_2 is also manifested in the almost planar geometry of the germyl cation moieties (summation of three bond angles is larger than 358°) and in the small partial charges on the H_2 moiety (from 0.06 *e* to 0.15 *e*). More stable structures for protonated germanes are again the ion complexes between germyl cations and HF or HCl, where the germyl cation moieties are less planar (summation of angles in the range of 352 to 357°) and the charge transfers are slightly larger, e.g., *ca.* 0.11 *e* on HF and *ca.* 0.25 *e* on HCl. The binding strength with HF increases from 93.6 kJ/mol with GeH_3^+ to 144.5 kJ/mol with GeF_3^+, while the one with HCl decreases from 109.9 kJ/mol with GeH_3^+ to 82.2 kJ/mol with $GeCl_3^+$.

The calculated PA decreases drastically from 672.5 kJ/mol for GeH_3F to 516.3 kJ/mol for GeF_4, while much more mildly from 672.7 kJ/mol for GeH_3Cl to 624.4 kJ/mol for $GeCl_4$. The trend is in line with the steep increase of IPs from 8.01 eV for GeH_3 to 10.05 eV for GeF_3 and the slight increase to 8.417 eV for $GeCl_3$.

IV. Concluding Remarks

A systematic study has been carried out on the cation structures and energetic of fluorinated and chlorinated germanes and radicals and protonated germanes at G3(CC)/B2df+ level. Cations are characterized by the existence of ion complexes between a Ge-containing cations and H_2, HF, or HCl, besides the "normal" divalent and trivalent structures for germylene and germyl cations. Adiabatic ionization potentials, appearance energies of ion fragments, and proton affinities of germanes are predicted. The calculations are compared to the previous experimental measurements. The G3 results for GeH_x^+ system are in excellent agreement with the previous experimental and theoretical values.[12,16,50] Reasonable agreements on adiabatic IPs of GeF_2 and $GeCl_2$ are also observed (Table 3), while the sparse measurements on other species are not accurate enough. Experimental measurements on adiabatic IPs of fluorogermanes and chlorogermanes are expected to be difficult due to the large structural distortion from neutral to ionic and hence small Franck−Condon factors for photoionization at the ionization threshold. The previous photoelectron and electron impact ionization studies on GeH_3F, GeH_3Cl, GeH_2F_2, and GeH_2Cl_2 obtained likely the vertical IPs to ionic configurations with high-energy configurations instead of the ground states. However, measurements of adiabatic IPs for these species may possibly be obtained by the advanced threshold photoionization method.[66]

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