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Heats of Formation for GeH_n ($n = 1-4$) and Ge_2H_n ($n = 1-6$)

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Heats of formation, accurate to 2 kcal/mol or better, have been computed for GeH_n ($n = 1-4$) and Ge_2H_n ($n = 1-6$). The effects of basis set saturation, Ge 3d correlation, spin−orbit, and scalar relativity have been accounted for. The results show that the experimental heats of formation of GeH_4 and Ge_2H_6 are likely in error by up to 4 and 9 kcal/mol, respectively. However, for individual bond energies, the computed results agree with some experimental determinations.

I. Introduction

Germanium hydrides such as GeH_4 and Ge_2H_6 are common precursors used in chemical vapor deposition (CVD) to produce semiconductor devices. Modeling of such processes requires accurate thermochemical data on GeH_n and Ge_2H_n systems. Of these species, the GeH_4 heat of formation[1] of 21.6 ± 0.5 kcal/mol (at 298 K) has the smallest uncertainty. Unfortunately, there has been only one determination of the GeH_4 value, made in 1961, and it would be useful to have a confirmation of this value. Ruscic, Schwarz, and Berkowitz (RSB)[2] have deduced probable values for the heat of formation of GeH_3, GeH_2, and GeH. They reported a GeH_3 heat of formation of 54.7 ± 2.0 kcal/mol, a GeH_2 heat of formation of 61.8 kcal/mol, and a GeH heat of formation of 76.8 kcal/mol. The value for GeH_3 is in good agreement with the result of Noble and Walsh.[3] However, the value for GeH has a large uncertainty, and its accuracy needs to be determined. Almost no experimental heats of formation are available for Ge_2H_n ($n = 1-6$) species with the exception of Ge_2H_6, for which a value of 38.7 kcal/mol (at 298 K) has been measured by Gunn and Green.[1]

Several theoretical studies have been reported for the GeH_n ($n = 1-4$) species. The modified G1 results of Binning and Curtiss (BC)[4] for GeH_3 and GeH_4 are in good agreement with the G2 results of Mayer, Gal, and Radom (MGR).[5] The G1 and G2 values are in good agreement with experiment for GeH_3 but are somewhat smaller than experiment for GeH_4. The MP2 results of Simka, Hierlemann, Utz, and Jensen (SHUJ)[6] are smaller than the G1 and the G2 results and also smaller than experiment. We should also note that Schaefer and co-workers[7] and Das and Balasubramanian[8] have computed some Ge−H bond energies. The level of theory used by these groups is expected to predict correctly the trends in the bond energies, but not yield highly accurate thermochemistry.

Given the uncertainty in the heats of formation, it is useful to study these species using higher levels of theory. We use the coupled cluster singles and doubles approach,[9] including a perturbational estimate of the triple excitations,[10] CCSD(T), in conjunction with extrapolation to the complete basis set (CBS) limit. The extrapolated results are corrected for scalar relativistic effects, computed using the one-electron Douglas Kroll (DK) approach,[11] spin−orbit and thermal effects, and for zero-point energy.

II. Methods

Geometries are optimized using density functional theory (DFT), in conjunction with the hybrid[12] B3LYP[13] approach. All our geometries are optimized using the 6-311++G(2df,2p) basis set[14−17] and a grid with 96 radial shells and 974 angular points per shell. The zero-point energy is computed as one-half the sum of the B3LYP/6-31G* harmonic frequencies, which are not scaled and computed using the grid mentioned above.

For open-shell molecules, energetics are computed using the restricted coupled cluster singles and doubles approach,[9,18] including the effect of connected triples determined using perturbation theory,[10,19] RCCSD(T). In these RCCSD(T) calculations, only the valence electrons (the Ge 4s and 4p and H 1s) are correlated. For H we use the augmented-correlation-consistent polarized valence (aug-cc-pV) sets developed by Dunning and co-workers,[20−22] namely, the triple-ζ (TZ), quadruple-ζ (QZ), and quintuple-ζ (5Z) sets. For Ge, we have derived a valence basis set from the (21s 16p 10d) primitive set optimized by Partridge.[23] This set is contracted to [6s, 5p, 3d] by contracting the inner 19 s primitives to four functions, the inner 14 p primitives to three functions, and the 10 d primitives to one function. The two d primitives (3.412662 and 1.6194) with the largest coefficients in the atomic Ge 3d orbital are uncontracted. All contraction coefficients are taken from nonrelativistic self-consistent-field calculations. This valence basis set is fixed in all calculations. Polarization functions are optimized at the RCCSD(T) level with the 4s and 4p electrons correlated. The TZ, QZ, and 5Z sets are obtained by adding (2d1f), (3d2f1g), and (4d3f2g1h) polarization sets, respectively, to the valence basis. The (2d1f) set corresponds to two even-tempered d functions (center = 0.227, $\beta = 2.757$) and one *f* function with an exponent of 0.338; the (3d2f1g) set to three even-tempered d functions (center = 0.224, $\beta = 2.264$), two even-tempered *f* functions (center = 0.336, $\beta = 2.483$), and one g function with an exponent of 0.466; and the (4d3f2g1h) set to four even-tempered d functions (center = 0.257, $\beta = 2.082$), three even-tempered *f* functions (center = 0.347, $\beta = 2.069$), two even-tempered g functions (center = 0.494, $\beta = 2.244$), and one h function with an exponent of 0.564.

To compute the effect of Ge 3d correlation on the atomization energies, a series of calculations are performed by including the Ge 3d orbitals in the CCSD(T) treatment. The Ge basis sets used in these calculations are derived from the valence basis sets. The innermost 15 s primitives are contracted to three functions, the innermost 10 p primitives to two functions, and the innermost six d primitives to one function. Since the outermost d primitives overlap with the valence d polarization functions, the valence d polarization functions, described above, are deleted. For the TZ basis set, one even-tempered d with a β of

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2.757 is added. For the QZ and 5Z sets, the outermost 4 d primitives are removed and replaced with six and seven even-tempered ($\beta = 2.0$) functions, respectively. The valence polarization functions, excluding the d functions, are added to this new contraction, and a series of tight even-tempered polarization functions are optimized correlating 14 electrons. The following polarization sets are obtained: for the TZ set, a two-term f with a center of 4.372 and a β of 3.553 and a g function with an exponent of 5.636; for the QZ set, a three-term f with a center of 5.152 and a β of 2.76, a two-term g with a center of 5.189 and a β of 3.189, and an h function with an exponent of 6.404; for the 5Z set, a four-term f with a center of 6.299 and a β of 2.27, a three-term g with a center of 6.058 and a β of 2.486, a two-term h with a center of 6.125 and a β of 2.927, and an i function with an exponent of 7.78. We denote these basis sets as val+3d.

To improve the accuracy of the results, several extrapolation techniques are used. We use the two-point (n^{-3}) scheme described by Helgaker et al.[24] We also use the two-point (n^{-4}), three-point ($n^{-4} + n^{-6}$), and variable α ($n^{-\alpha}$) schemes described by Martin.[25]

The scalar relativistic effect is computed at the modified coupled pair functional[26] (MCPF) level of theory using the triple-ζ (TZ) basis set as the difference between the results using the nonrelativistic and the Douglas Kroll (DK) approaches. In the DK calculations, the same primitive basis sets are used and it is contracted in the same manner as in the nonrelativistic calculations, but the contraction coefficients are taken from DK atomic calculations.

The effect of spin−orbit coupling on the dissociation energy is computed using experiment. For GeH, the spin−orbit effect is taken as half the splitting between the $^2\Pi$ sublevels given in Huber and Herzberg.[27] For all the other systems, the spin−orbit effect is obtained by using the accurately known spin−orbit splittings in the atoms[28] and we use the difference between the lowest J component and the weighted average energy.

The heat capacity, entropy, and temperature dependence of the heat of formation, are computed for 300−4000 K using a rigid rotor/harmonic oscillator approximation. We include the effect of electronic excitation for the atoms using the data from Moore.[28] These results are fit in two temperature ranges, 300−1000 K and 1000−4000 K using the Chemkin[29] fitting program and following their constrained three-step procedure. The B3LYP calculations are performed using Gaussian94,[30] the RCCSD(T) are performed using Molpro,[31] and the MCPF calculations are performed using Molecule-Sweden.[32] The DK integrals are computed using a modified version of the program written by Hess.

III. Results and Discussion

The geometries of the GeH$_n$ ($n = 1-4$) and Ge$_2$H$_n$ ($n = 1-6$) species are reported in Table 1, and the structures of the Ge$_2$H$_n$ ($n = 1-6$) molecules are shown in Figure 1. For H$_3$GeGeH$_3$, the Ge−H bond length is slightly underestimated with respect to experiment[33] (1.541 Å), whereas the Ge−Ge bond length is larger than the experimental value of 2.403 Å.[33] Despite these small differences, the agreement between DFT and experiment is quite satisfactory for Ge$_2$H$_6$, as already noted by Leszczynski et al.,[34] and the computational cost is not prohibitive for the large Ge$_2$H$_n$ systems. Removing an H from H$_3$GeGeH$_3$ does not significantly affect the structure of H$_3$GeGeH$_2$, which has C_s symmetry and closely resembles H$_3$GeGeH$_3$. It is worth mentioning that the default grid in Gaussian 94 (75 radial shells and 302 angular points per shell) incorrectly yields an imaginary frequency for the H$_3$GeGeH$_2$ C_s structure. It is necessary to use the large grid with 96 radial shells and 974 angular points per shell to obtain correct vibrational frequencies. To obtain consistent results, we optimize all the geometries and compute all the frequencies using the large grid. H$_2$GeGeH$_2$ has a trans-bent geometry with C_{2h} symmetry. The out-of-plane angle of 47.8° and the Ge−Ge bond length of 2.293 Å are in good agreement with the DFT values of 47.3° and 2.245 Å reported by Jacobsen and Ziegler.[35] H$_2$GeGeH$_2$ clearly differs from H$_2$CCH$_2$, and the deviation from planarity of Ge$_2$H$_4$ has been attributed[35] to larger intra-atomic, as well as, interatomic Pauli repulsion for Ge atoms. The H$_3$GeGeH isomer has C_s symmetry and is derived from the interaction of GeH$_3$ (^{2}A$_1$) with GeH ($^2\Pi$). It is only 0.9 kcal/mol higher in energy than the H$_2$GeGeH$_2$ structure. As for H$_3$GeGeH$_2$, the default grid in Gaussian 94 incorrectly yields an imaginary frequency for the H$_3$GeGeH C_s

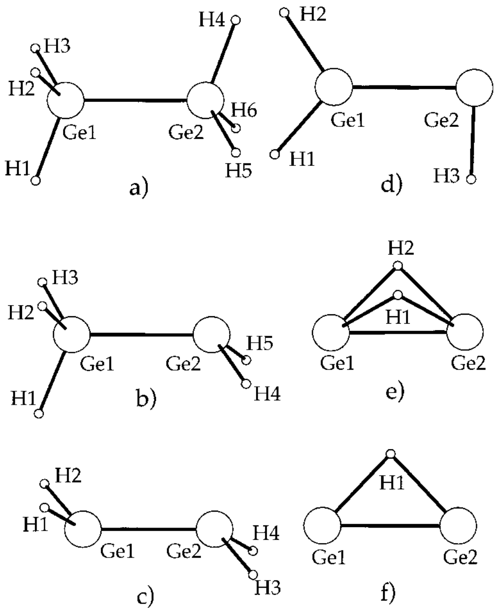

Figure 1. Geometric structure of the Ge$_2$H$_n$ ($n = 1-6$) species: (a) H$_3$GeGeH$_3$; (b) H$_3$GeGeH$_2$; (c) H$_2$GeGeH$_2$; (d) H$_2$GeGeH; (e) GeHHGe; (f) GeHGe.

TABLE 1: Geometries of GeH$_n$ (n = 1−4) and Ge$_2$H$_n$ (n = 1−6) Computed at the B3LYP/6-311++G(2df,2p) Level of Theory (in Angstroms and Degrees)

	r(Ge−H)	∠(HGeH)
GeH$_4$ $^1A_1$ (T_d)	1.533	109.47
GeH$_3$ $^2A_1$ (C_{3v})	1.540	110.93
GeH$_2$ $^1A_1$ (C_{2v})	1.596	90.84
GeH $^2\Pi$ ($C_{\infty v}$)	1.603	

	r(Ge−H)	r(Ge−Ge)	angles
H$_3$GeGeH$_3$ ^{1}A$_{1g}$ (D_{3d})	1.537	2.435	108.43 (HGeH)
			110.49 (GeGeH)
H$_3$GeGeH$_2$ ^{2}A′ (C_s)	1.541 (Ge$_1$H$_1$)	2.439	108.57 (H$_1$Ge$_1$H$_2$)
	1.536 (Ge$_1$H$_2$)		108.43 (H$_4$Ge$_2$H$_5$)
	1.545 (Ge$_2$H$_4$)		108.83 (H$_2$Ge$_1$H$_3$)
			113.10 (Ge$_1$Ge$_2$H$_4$)
			111.95 (Ge$_2$Ge$_1$H$_1$)
H$_2$GeGeH$_2$ ^{1}A$_g$ (C_{2h})	1.542	2.293	108.19 (HGeH)
			115.92 (GeGeH)
H$_2$GeGeH ^{2}A″ (C_s)	1.549 (Ge$_1$H$_1$)	2.429	105.94 (H$_1$Ge$_1$H$_2$)
	1.549 (Ge$_1$H$_2$)		123.63 (Ge$_2$Ge$_1$H$_2$)
	1.597 (Ge$_2$H$_3$)		88.22 (Ge$_1$Ge$_2$H$_3$)
GeHHGe ^{1}A$_1$ (C_{2v})	1.832	2.338	79.29 (GeHGe)
			50.35 (GeGeH)
GeHGe ^{2}B$_1$ (C_{2v})	1.789	2.384	83.57 (GeHGe)
			48.21 (GeGeH)

TABLE 2: Effect of Ge 3d Correlation on the Atomization Energy (in kcal/mol) of GeH_4, Computed at the CCSD(T) Level of Theory and without Including Zero-Point Energies

	val[a]	val+3d	Δ
	TZ		
AE	291.605	293.991	2.386
BSSE Ge(H_4) ^3P	0.841	2.371	1.530
BSSE Ge(H_4) ^5S	0.399	1.714	1.714
AE−BSSE[b]	290.765	291.621	0.856
	QZ		
AE	294.326	296.529	2.203
BSSE Ge(H_4) ^3P	0.426	1.158	0.731
BSSE Ge(H_4) ^5S	0.159	0.835	0.835
AE−BSSE	293.899	295.371	1.472
	5Z		
AE	294.922	297.141	2.219
BSSE Ge(H_4) ^3P	0.262	0.685	0.424
BSSE Ge(H_4) ^5S	0.093	0.487	0.487
AE−BSSE	294.661	296.456	1.795
	CBS $n^{-4} + n^{-6}$		
AE	295.233	297.513	2.280

[a] The type of correlation, both the valence and valence plus Ge 3d treatments use the val + 3d basis set. [b] Indicates that the atomization has been correct for BSSE.

TABLE 3: Atomization Energies (in kcal/mol) Computed at the CCSD(T) Level of Theory and without Including Zero-Point Energies

	TZ	QZ	5Z	CBS
GeH_4	291.78	294.88	295.59	295.98[a]
GeH_3	203.28	205.74	206.31	206.64[a]
GeH_2	139.45	141.39	141.94	142.35[a]
GeH	66.75	67.90	68.27	68.58[a]
Ge_2H_6	476.26	482.34		485.86[b]
Ge_2H_5	390.27	395.74		398.90[b]
Ge_2H_4	327.34	332.58		335.60[b]
Ge_2H_3	252.00	256.53		259.14[b]
Ge_2H_2	200.46	204.57	206.05	207.35[a]
Ge_2H	129.44	132.93	134.29	135.55[a]

[a] Extrapolated using the three-point Martin ($n^{-4} + n^{-6}$) scheme. [b] Extrapolated using the two-point Martin (n^{-4}) scheme.

TABLE 4: Extrapolated Atomization Energies (in kcal/mol)

basis	n^{-3}		n^{-4}		$n^{-4} + n^{-6}$	variable α[a]
set	TZ,QZ	QZ,5Z	TZ,QZ	QZ,5Z	TZ,QZ,5Z	TZ,QZ,5Z
GeH_4	297.14	296.33	296.67	296.16	295.98	295.95 (5.411)
GeH_3	207.53	206.91	207.15	206.77	206.64	206.61 (5.340)
GeH_2	142.80	142.52	142.51	142.39	142.35	142.32 (4.480)
GeH	68.74	68.67	68.57	68.58	68.58	68.58 (3.937)
Ge_2H_6	486.78		485.86			
Ge_2H_5	399.73		398.90			
Ge_2H_4	336.40		335.60			
Ge_2H_3	259.83		259.14			
Ge_2H_2	207.57	207.60	206.95	207.25	207.35	207.50 (3.488)
Ge_2H	135.47	135.71	134.94	135.39	135.55	135.83 (3.136)

[a] The α values are reported in parentheses.

structure. We do not report the results for H_3GeGeH as we focus on the lowest isomer having a given number of Ge atoms and of H atoms. The H_2GeGeH structure is derived from the interaction of GeH_2 with GeH in its ground state. The GeH lone pair is in-plane and the unpaired electron is in an out-of-plane π orbital. The promotion energy required to excite GeH from its ground state to a quartet state (49 kcal/mol) is higher than the energy to form a Ge−Ge double bond (33 kcal/mol).[35] For Ge_2H_2, several isomers are possible and searches on the potential energy hypersurface of Ge_2H_2 have been computed at the MP2 level by Boone et al.[36] We also consider several isomers, and at the B3LYP level of theory, the lowest isomer is GeHHGe with a C_{2v} dibridged structure derived from the interaction of two GeH ($^2\Pi$) fragments. The planar trans HGeGeH with C_{2h} symmetry is 18.3 kcal/mol higher in energy, the HGeHGe cis-monobridged planar structure is 8.4 kcal/mol higher in energy, and the $GeGeH_2$ planar C_{2v} isomer is 9.8 kcal/mol higher in energy. Removing one H from GeHHGe leads to GeHGe which has C_{2v} symmetry.

In Table 2, we report the CCSD(T) atomization energies of GeH_4 for treatments that correlate the valence (val) electrons and correlate the valence plus Ge 3d electrons (val+3d). The effect of Ge 3d correlation on the atomization energy using the TZ basis set is 2.39 kcal/mol. Also given are the basis set superposition error (BSSE) for both the Ge ^3P and ^5S states. Correcting the atomization energy for ^3P BSSE reduces the size of the Ge 3d effect to only 0.86 kcal/mol. As the basis sets are improved from TZ to QZ and on to 5Z, the atomization energy increases and the BSSE decreases. It is interesting to note that the 5Z Ge 3d effect, corrected for BSSE, is closer to the uncorrected TZ value than to the corrected value. At the bottom of the table, we report the CBS values for the valence and valence plus Ge 3d correlation treatments; the difference of the CBS values is very close to the uncorrected TZ value. Since the val+3d calculations using the val+3d QZ and 5Z basis sets are very large and could not be performed for most systems, we compute the atomization energies correlating only the valence electrons using the valence basis sets, then in a subsequent step we compute the Ge 3d effect as the difference between val and val+3d correlation treatments using the TZ val+3d basis set and add this effect to our best valence treatment.

The computed and extrapolated atomization energies are reported in Tables 3 and 4. Increasing the size of the basis set increases the atomization energy for all the systems. All the extrapolation schemes give consistent results. The very good agreement between the three-point ($n^{-4} + n^{-6}$) and the variable α ($n^{-\alpha}$) results indicates that our Ge basis set is of systematic quality, and we adopt the three-point ($n^{-4} + n^{-6}$) values as our CBS results. For the largest systems, for which the three-point values are not available, we select the two-point (n^{-4}) values instead, since this two-point approach agrees best with the three-point ($n^{-4} + n^{-6}$) approach for the smaller systems. We note that the extrapolated value for GeH_4 using the val+3d basis set is 0.75 kcal/mol smaller than using the valence basis (compare the results in Tables 2 and 3). On this basis, we assume that the extrapolated values are accurate to approximately 1 kcal/mol. We suspect that using the B3LYP geometries and zero-point energies and other approximations could increase the uncertainty in our values to approximately 2 kcal/mol.

The extrapolated results are corrected for Ge 3d correlation, scalar relativistic effects (rel), spin−orbit effects (SO), zero-point energy (ZPE), and thermal effects (therm), and the values are reported in Table 5. The AE(0) and AE(298) values are computed as follows:

$$AE(0) = AE\ CBS + Ge\ 3d + rel + SO + ZPE$$

and

$$AE(298) = AE(0) + therm$$

The effect of Ge 3d correlation grows with the number of Ge−H bonds and varies inversely with the Ge−Ge bond length. The Ge−Ge bond length effect seems to be the larger of the two, as the Ge 3d contribution to the Ge_2H_5 atomization energy is smaller than for Ge_2H_4, even though there is one more Ge−H

TABLE 5: Atomization Energies (in kcal/mol) Computed at 0 and 298 K and Corrected for Ge 3d Correlation, Scalar Relativistic Effects, Spin−Orbit Effects, Zero-Point Energy, and Thermal Effects

	AE CBS[a]	Ge 3d	rel	SO	ZPE	therm	AE(0)	AE(298)
GeH_4	295.98	2.39	−3.58	−2.77	−18.18	+5.12	273.84	278.96
GeH_3	206.64	1.52	−3.10	−2.77	−12.23	+3.69	190.06	193.75
GeH_2	142.35	0.92	−1.00	−2.77	−6.55	+2.33	132.95	135.28
GeH	68.58	0.44	−0.46	−1.49	−2.56	+1.17	64.51	65.68
Ge_2H_6	485.86	4.97	−6.88	−5.54	−28.09	+8.39	450.32	458.71
Ge_2H_5	398.90	3.93	−6.38	−5.54	−22.49	+6.98	368.41	375.39
Ge_2H_4	335.60	4.28	−5.11	−5.54	−17.56	+5.82	311.67	317.49
Ge_2H_3	259.14	2.89	−3.27	−5.54	−11.96	+4.29	241.26	245.55
Ge_2H_2	207.35	3.15	−1.23	−5.54	−7.67	+3.69	196.06	199.75
Ge_2H	135.55	2.43	−0.79	−5.54	−3.47	+2.32	128.18	130.50

[a] Taken from Table 3.

TABLE 6: Selected Bond Energies, in kcal/mol

	0 K	298 K
$GeH_4 \rightarrow GeH_3 + H$	83.78	85.21
$GeH_3 \rightarrow GeH_2 + H$	57.11	58.47
$GeH_2 \rightarrow GeH + H$	68.44	69.60
$GeH \rightarrow Ge + H$	64.51	65.68
$Ge_2H_6 \rightarrow Ge_2H_5 + H$	81.91	83.32
$Ge_2H_5 \rightarrow Ge_2H_4 + H$	56.75	57.90
$Ge_2H_4 \rightarrow Ge_2H_3 + H$	70.41	71.94
$Ge_2H_3 \rightarrow Ge_2H_2 + H$	45.20	45.80
$Ge_2H_2 \rightarrow Ge_2H + H$	67.88	69.25
$Ge_2H_6 \rightarrow GeH_3 + GeH_3$	70.20	71.21
$Ge_2H_5 \rightarrow GeH_3 + GeH_2$	45.41	46.36
$Ge_2H_4 \rightarrow GeH_2 + GeH_2$	45.77	46.93
$Ge_2H_3 \rightarrow GeH_2 + GeH$	43.80	44.59
$Ge_2H_2 \rightarrow GeH + GeH$	67.04	68.39
$Ge_2H \rightarrow GeH + Ge$	63.67	64.82

TABLE 7: Heats of Formation (in kcal/mol)

	0 K					298 K	
	theory				exptl	theory	
	PW[a]	MGR[b]	BC[c]	SHUJ[d]	RSB[e]	PW[a]	exptl
GeH_4	20.0	20.1	19.6	16.2		17.4	21.6 ± 0.5[f]
GeH_3	52.1	53.2	52.8	49.7	50.2 ± 2.0	50.5	47.9 ± 2.4[g]
GeH_2	57.6		59.2	57.2	57.6	56.8	
GeH	74.4		76.0	75.1	72.6	74.3	
Ge	[87.25]					[87.91]	
Ge_2H_6	34.0			25.7		29.7	38.7 ± 0.3[f]
Ge_2H_5	64.3					60.9	
Ge_2H_4	69.4			62.8		66.7	
Ge_2H_3	88.1					86.6	
Ge_2H_2	81.7					80.3	
Ge_2H	98.0					97.4	

[a] Present work. The values given in square brackets for Ge are taken from Gurvich,[37] whereas the H heats of formation (51.634 at 0 K and 52.103 at 298 K) are taken from JANAF.[38] [b] Mayer et al.[5] [c] Binning and Curtiss.[4] The values include estimates of spin−orbit corrections. [d] Simka et al.[6] [e] Ruscic et al.[2] Their most probable values are corrected using our GeH_4 heat of formation. [f] Reference 1. [g] Noble and Walsh[3] value corrected using our GeH_4 heat of formation.

bond in Ge_2H_5. The scalar relativistic effect increases when the Ge atoms hybridize to form more than two bonds. Thus, the scalar relativistic effect for GeH_3 is more than 3 times that for GeH_2. There are sizable increases in the series from Ge_2H_2 to Ge_2H_5 as the Ge hybridization changes, whereas from Ge_2H to Ge_2H_2 and from Ge_2H_5 to Ge_2H_6 there is only a small effect associated with little change in the Ge hybridization.

In Table 6, we summarize some selected bond energies. The HGe−H bond energy is slightly larger than the Ge−H bond because there is no loss of atomic exchange with the second bond, however this effect is relatively small. Unlike the small change due to atomic exchange, the H_2Ge−H bond is significantly weaker than the first two, since the Ge must hybridize to form a third bond. The H_3Ge−H bond is the largest because the Ge sp^3 hybrid bonds are stronger than the Ge p bonds. The Ge_2H_5−H bond is very similar to that in GeH_4 since the only change is substituting a Ge−H spectator bond for a Ge−Ge spectator bond. The Ge_2H_4−H bond is weak since the resulting Ge_2H_4 is stabilized by a Ge−Ge interaction, however, from the structure shown in Figure 1, it is clearly not a strong π bond. This oscillation in Ge−H bond energies continues for subsequent H loss. The Ge−Ge bonds are also interesting. The largest Ge−Ge bond energy is for Ge_2H_6 but drops dramatically for the next three, where each case involves a GeH_2 fragment, which must hybridize to form the Ge−Ge bond. For Ge_2H_2 and Ge_2H, the Ge−Ge bond can form without a change in the Ge or GeH fragment hybridization, and hence the bond energies are larger than for Ge_2H_3 to Ge_2H_5. Thus, all of the bond energies follow the expected trends.

Using our best atomization energies summarized in Table 5 and the experimental heat of formation of Ge[37] and of H,[38] we compute the heats of formation, which are reported in Table 7. Our heats of formation at 0 K for GeH_n are in good agreement with the modified G1 values of BC and the G2 values of MGR. However, part of this agreement comes from a cancellation of errors, as these approaches neglect the scalar relativistic and Ge 3d correlation effects. The MP2 values of SHUJ are in good agreement with the present work for GeH and GeH_2, but the error increases as the systems get larger so that the errors are quite large for Ge_2H_6 and Ge_2H_4.

Gunn and Green reported the heats of formation of GeH_4 and Ge_2H_6, and these values have been used by other workers to determine the heats of formation of other Ge-containing systems. We therefore first compare our computed values with the experimental values of Gunn and Green. As shown in Table 7, our value for GeH_4 is 4.2 kcal/mol smaller than their experimental value and our Ge_2H_6 value is 9 kcal/mol smaller. This means that our atomization energies are larger than those determined experimentally. Since most errors will result in the computed values being too small, we conclude that the experimental atomization energies are too small, which means that the GeH_4 and Ge_2H_6 experimental heats of formation are very likely about 4 and 9 kcal/mol, respectively, too large. For GeH_4, the very small difference between the best computed atomization energy and the extrapolated value supports this conclusion, even though we have assigned a conservative error bar of ±2 kcal/mol.

Ruscic et al. measured the energy of several reactions, which allowed them to determine the first three Ge−H bond energies. They converted these into heats of formation using the Gunn and Green result for GeH_4. Since we believe that our computed GeH_4 result is more accurate than the Gunn and Green result, we recomputed the heats of formation of Ruscic et al. using our GeH_4 heat of formation. The revised Ruscic et al. results are in good agreement with the computed results to within the combined error bars, although their values for GeH_3 and GeH would suggest that the true GeH_4 heat of formation falls between our value and that of Gunn and Green. Noble and Walsh also determined the first bond energy of GeH_4 and after revising their value for the new GeH_4 heat of formation, their value agrees with our value to within their mutual error bars. Like the value of Ruscic et al., the Noble and Walch value suggests that the true value lies between our value and that of Gunn and Green. However, we should note that Noble and Walch made some assumptions that could increase the uncertainty in their value.

We use our heats of formation at 298 K, the B3LYP optimized geometries, and vibrational frequencies to compute the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fit can be found on the Web.[39]

IV. Conclusions

The atomization energies of GeH_n ($n = 1-4$) and Ge_2H_n ($n = 1-6$) systems are computed using the CCSD(T) approach and a newly developed correlation-consistent basis set for Ge. To obtain high accuracy, the atomization energies are extrapolated to the CBS limit and corrected for Ge 3d correlation, scalar relativistic, spin−orbit, and thermal effects, and zero-point energy. The heats of formation of GeH_n and Ge_2H_n are obtained by combining the atomization energies with the experimental heats of formation of Ge and H. Our results suggest that the heats of formation of GeH_4 and Ge_2H_6 should be re-examined. A comparison of our computed heats of formation with the experimental results of Ruscic et al. and Noble and Walsh supports our contention that the GeH_4 heat of formation is too large. While the experimental work supports a reduction of about 2 kcal/mol, it is not inconsistent with our suggestion of an up to 4 kcal/mol reduction.

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