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$Ge_3H_n^-$ Anions ($n = 0-5$) and Their Neutral Analogues: A Theoretical Investigation on the Structure, Stability, and Thermochemistry

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The structure, stability, and thermochemistry of various $Ge_3H_n^-$ isomers ($n = 0-5$) and of their neutral analogues have been investigated at the B3LYP/6-311+G(d), MP2(full)/6-31G(d), and Gaussian-2 (G2) level of theory. For Ge_3H^-, both the B3LYP and the G2/MP2 methods predict the cyclic, H-bridged structure **1a**$^-$ as the global minimum, more stable than another cyclic isomer and an open-chain isomer by ca. 10 and 25 kcal mol^{-1}, respectively. For $Ge_3H_2^-$, the B3LYP and the G2/MP2 methods provide a somewhat different description of the potential energy surface. At the G2/MP2 level of theory, the global minimum is the cyclic, H_2Ge-bridged structure **2a**$^-$, separated by other three nearly degenerate isomers by ca. 10 kcal mol^{-1}. On the other hand, at the B3LYP level of theory, the cyclic, H-bridged structure **2e**$^-$, not located at the MP2 level of theory, is more stable than **2a**$^-$ by ca. 1 kcal mol^{-1}. For $Ge_3H_3^-$, both the B3LYP and the G2/MP2 methods predict the cyclic, H_3Ge-bridged isomer **3a**$^-$ as the global minimum, but the energy differences with the other five located isomeric structures predicted by the two methods are quantitatively different. Similar to $Ge_3H_2^-$, the B3LYP and the G2/MP2 theoretical levels provide a somewhat different description of the $Ge_3H_4^-$ potential energy surface. At the G2/MP2 level of theory, the global minimum is the cyclic structure **4b**$^-$ of C_{2v} symmetry, featuring a Ge_2H_4 moiety and a Ge-bridged atom, which is more stable than other three located isomers by 3, 9, and 17 kcal mol^{-1}. On the other hand, at the B3LYP level of theory, the open-chain isomer **4a**$^-$ of $H_3Ge-Ge-GeH^-$ connectivity is more stable than **4b**$^-$ by ca. 1 kcal mol^{-1} and nearly degenerate with the alternative open-chain isomer $H_3Ge-GeH-Ge^-$. For $Ge_3H_5^-$, both the B3LYP and the G2/MP2 methods predict the 2-propenyl-like isomer $H_3Ge-Ge-GeH_2^-$ as the global minimum, with energy differences with other four isomeric structures which range from ca. 1−2 to 13−17 kcal mol^{-1}. At the G2 level of theory and 298.15 K, the electron affinities of Ge_3H_n are computed as 2.17 ($n = 0$), 2.57 ($n = 1$), 1.70 ($n = 2$), 2.41 ($n = 3$), 2.07/1.80 ($n = 4$), and 2.71/2.46 eV ($n = 5$). The two alternative values reported for Ge_3H_4 and Ge_3H_5 reflect the alternative conceivable choice for the structure of the involved neutrals and ions. The G2 enthalpies of formation of Ge_3H_n and $Ge_3H_n^-$ ($n = 0-5$) have also been calculated using the atomization procedure. Finally, we have briefly discussed the implications of our calculations for previously performed mass spectrometric experiments on the negative ion chemistry of GeH_4.

1. Introduction

Simple neutrals and ions containing germanium atoms are intensively investigated[1] not only for fundamental reasons but also for their role in vapor deposition processes, in film formation, and in the synthesis of ceramic materials.[2−4] Exemplary species in this regard are the neutral and ionic germanium hydrides involved in the formation of amorphous group 14 semiconductors by chemical vapor deposition from gaseous mixtures containing GeH_4.[5,6] Experimental studies[7] have demonstrated that the neutral GeH_n ($n = 1-3$) are relevant intermediates in the laser-initiated formation of Ge_n films from GeH_4, and the extensive mass spectrometric experiments performed in the past years by our group[8] have clearly established the role of cationic germanium hydrides GeH_n^+ ($n \geq 1$) and germanium cluster hydrides $Ge_mH_n^+$ ($m > 1$, $n \geq 1$) in the early steps of the sequences which eventually lead to the deposition of doped germanium carbides from gas-phase mixtures of GeH_4 and hydrocarbons, NH_3, or PH_3. More recently, preliminary experiments by our group[9] on the self-condensation reactions occurring in negatively charged GeH_4 have shown the formation of $Ge_mH_n^-$ cluster ions ($m = 1-9$, $n = 0 - m$), which can be considered as precursors of amorphous Ge:H materials with low hydrogen content and good photoelectric properties. From a fundamental point of view, the active role of neutral and ionic $GeH_n^{+/0/-}$ and $Ge_mH_n^{+/0/-}$ in the vapor deposition processes stimulates interest in their detailed structure, stability, and thermochemistry. In this regard, numerous experimental and theoretical studies have been reported, over the years, on the neutral and cationic germanium hydrides and germanium cluster hydrides.[10−33] On the other hand, the information about anionic germanium hydrides is less abundant and includes few studies on GeH_n^- ($n = 1-3$),[25,30−40] GeH_5^-,[41] $Ge_2H_6^-$,[42] and the systematic DFT investigation by

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Schaefer and co-workers[43] on GeH_n^- ($n = 0-4$) and $Ge_2H_n^-$ ($n = 0-6$). More recently, to obtain theoretical support to the mass spectrometric experiments on the anionic self-condensation of GeH_4,[9] we have investigated the experimentally observed $Ge_2H_n^-$ ($n = 0-5$) at the DFT and ab initio level of theory.[44] As a further contribution to the study of the species involved in the negative ion chemistry of GeH_4, we report here density functional theory (DFT) and Gaussian-2 (G2) calculations on various $Ge_3H_n^-$ anions ($n = 0-5$) and on their neutral analogues. We have in particular investigated their structure, stability, and thermochemistry and the adiabatic electron affinities of the most stable Ge_3H_n isomers. The implications of our calculations for the previously performed mass spectrometric experiments on ionized GeH_4 [9] will be also briefly discussed.

2. Computational Details

All the calculations were performed with the Gaussian03 set of programs.[45] The recent work by Schaefer and co-workers[43] has shown that DFT[46,47] is adequate to describe the structure of the GeH_n^- ($n = 0-4$) and $Ge_2H_n^-$ ($n = 0-6$) anions. Therefore, the geometries of the Ge_3H_n ($n = 0-5$) neutrals and anions were first optimized using the hybrid exchange correlation functional B3LYP, which combines the three terms exchange functional proposed by Becke (B3)[48] with the correlation functional of Lee, Yang, and Parr (LYP),[49] in conjunction with the standard internal 6-311+G(d) basis set.[50] The obtained critical points, located by unconstrained gradient procedures,[51-53] were unambiguously characterized as energy minima or transition structures by calculating the corresponding harmonic vibrational frequencies. The geometries of the various Ge_3H_n neutrals and ions ($n = 0-5$) were also optimized at the MP2(full)/6-31G(d) level of theory, and their total energies were subsequently calculated using the composite G2 procedure.[54] The adiabatic electron affinities of the most stable Ge_3H_n isomers ($n = 0-5$) were computed as the difference between their B3LYP/6-311+G(d) or G2 absolute energies and the corresponding energies of $Ge_3H_n^-$. The enthalpies of formation at 298.15 K ($\Delta H_f°$(298.15 K)) of Ge_3H_n and $Ge_3H_n^-$ were calculated combining the G2 enthalpy changes at 298.15 K of the atomization reactions

$$Ge_3H_n \rightarrow 3Ge(^3P) + nH(^2S)$$

$$Ge_3H_n^- \rightarrow 2Ge(^3P) + Ge^-(^4S) + nH(^2S)$$

with the experimental enthalpies of formation[55] of Ge, 90 kcal mol^{-1}; Ge$^-$, 61.7 kcal mol^{-1}; and H, 52.1 kcal mol^{-1}.

3. Results and Discussion

3a. Ge_3 and Ge_3^-. Over the years, the structure, stability, and properties of Ge_3 and Ge_3^-, in their ground and excited electronic states, have been intensively investigated by various experimental and theoretical methods.[56-72] The first comprehensive theoretical study was performed in 1998 by Archibong and St-Amant,[67] who explored the Ge_3 and Ge_3^- potential energy surfaces at the B3LYP/6-311+G(3df) level of theory and performed CCSD(T)/6-311+G(3df) single-point calculations to evaluate the relative stability of the various located isomers and transition structures. In line with previous computational studies,[61,62] the unambiguous determination of the electronic ground state of Ge_3 proved to be a “formidable task”.[67] The only safe conclusion is that the $^1A_1$ state of C_{2v} symmetry and the $^3A_2'$ state of D_{3h} symmetry are nearly degenerate, and both are likely candidates for the ground state. On the other hand, the $^2A_1$ (C_{2v} symmetry) ground state of Ge_3^- resulted as more stable than a linear isomer of $D_{\infty h}$ symmetry ($^2\Pi_g$) and an equilateral minimum of D_{3h} symmetry ($^2A_1'$) by more than 19 and 25 kcal mol^{-1}, respectively. An additional ion of C_{2v} symmetry ($^2B_2$), nearly degenerate with the ground state, was characterized as a transition state for pseudorotation. The adiabatic electron affinities (EA) of Ge_3 (assumed in the $^1A_1$ ground state) resulted as 2.17 and 2.15 eV at the B3LYP/6-311+G(3df) and CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) levels of theory, respectively, in good agreement with the experimental value of 2.23 ± 0.01 eV determined by photoelectron spectroscopy.[64b] The B3LYP theory has been subsequently used by other groups[66,72] to explore the structure and stability of Ge_3 and Ge_3^- but never in conjunction with the 6-311+G(d) basis set presently employed to study the Ge_3H_n and $Ge_3H_n^-$ isomeric structures. Our B3LYP/6-311+G(d) parameters of the most stable Ge_3 and Ge_3^- isomers and those obtained previously[66] at the MP2(full)/6-31G(d) level of theory are shown in Figure 1.

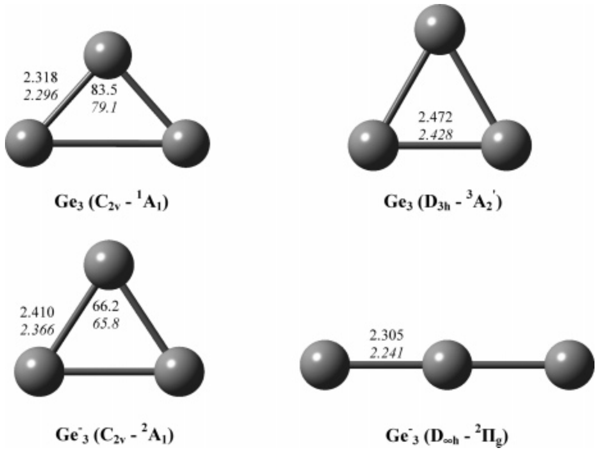


Figure 1. B3LYP/6-311+G(d) and MP2(full)/6-31G(d) (italics) optimized geometries (angstroms and degrees) of Ge_3 and Ge_3^-.

The B3LYP/6-311+G(d) calculations confirm the near degeneracy of the $^1A_1$ and $^3A_2'$ states of Ge_3, with the appreciable structural differences with ground-state Ge_3^- ($^2A_1$) already noted in previous studies[66b,67,72] and the existence of a linear Ge_3^- isomer of $D_{\infty h}$ symmetry less stable than the ground state by 16.5 kcal mol^{-1}. In addition, the B3LYP/6-311+G(d) EA of Ge_3 (assumed in the $^1A_1$ ground state) is computed as 2.18 eV, in good agreement with the experiment.

The MP2(full)/6-31G(d) structure of Ge_3 ($^1A_1$ and $^3A_2'$) and Ge_3^- ($^2A_1$) and their G2 stability and thermochemistry have already been investigated by Deutsch, Curtiss, and Blaudeau.[66] We extended here the investigation to the linear Ge_3^- isomer of $D_{\infty h}$ symmetry ($^2\Pi_g$). This species confirmed to be a minimum on the doublet MP2(full)/6-31G(d) potential energy surface and less stable than the cyclic ground state ($^2A_1$) by 21.0 kcal mol^{-1} at the G2 level of theory. We note also from Figure 1 that the MP2(full)/6-31G(d) geometries of Ge_3 and Ge_3^- and their structural differences are qualitatively similar to those predicted at the B3LYP/6-311+G(d) level of theory.

The thermochemistry of Ge_3 and Ge_3^- predicted at the G2 level of theory is in very good agreement with the experiment. Thus, the adiabatic EA of Ge_3 ($^1A_1$) amounts to 2.17 eV, and the previously computed[66a] atomization enthalpy of 141.7 kcal mol^{-1} compares quite favorably with the most recent experimental value of 141.0 ± 4.6 kcal mol^{-1} from Gingerich et al.[57c] This suggests that G2 theory should be adequate to predict the thermochemistry of the presently investigated Ge_3H_n neutrals

TABLE 1: Adiabatic Electron Affinities (electronvolts) of Ge_3H_n (n = 0−5)[a]

species	B3LYP/6-311+G(d)(0 K)	G2(298.15 K)
Ge_3 ($^1A_1/^2A_1$)	2.18	2.17[b]
Ge_3H (1a/1a$^-$)	2.40	2.57
Ge_3H_2 (2a/2a$^-$)	1.79	1.70
Ge_3H_3 (3b/3b$^-$)	2.18	2.41
Ge_3H_4 (4b/4b$^-$)	2.04	2.07
(**4c**/**4c**$^-$)	1.97	1.80
Ge_3H_5 (5a/5a$^-$)	2.46	2.71
(**5b**/**5b**$^-$)	2.62	2.46

[a] The involved neutrals and anions (see Figures 1−6) are given in parentheses. [b] The experimental value is 2.23 ± 0.01 eV (ref 64b).

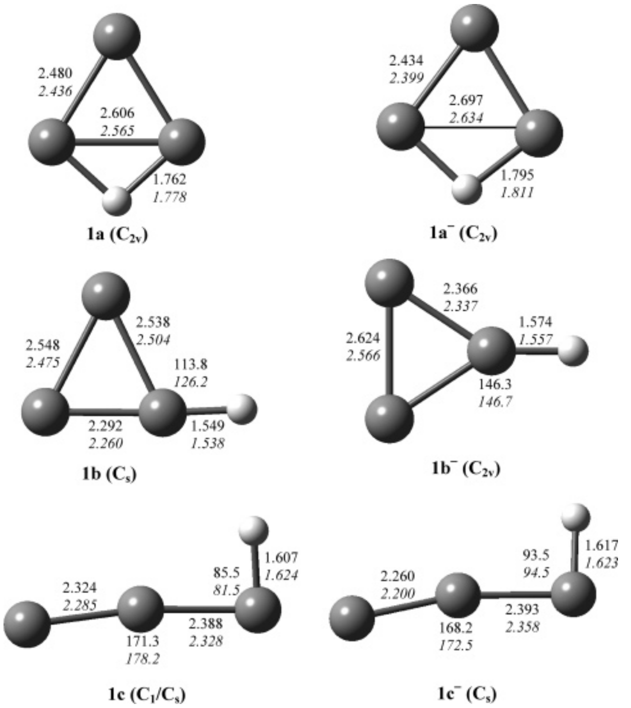


Figure 2. B3LYP/6-311+G(d) and MP2(full)/6-31G(d) (italics) optimized geometries (angstroms and degrees) of the Ge_3H and Ge_3H^- isomeric structures **1a**−**1c** and **1a**$^-$−**1c**$^-$.

and ions. The adiabatic EA of Ge_3 and of the most stable Ge_3H_n isomeric structures (n = 1−5) (vide infra) are reported in Table 1.

3b. Ge_3H and Ge_3H^-. The relevant optimized parameters of the Ge_3H and Ge_3H^- isomeric structures **1a**−**1c** and **1a**$^-$−**1c**$^-$ are shown in Figure 2, and their relative stabilities and absolute enthalpies of formation are reported in Table 2.

On the singlet Ge_3H^- potential energy surface, we have located three distinct minima, namely, the two cyclic isomers of C_{2v} symmetry **1a**$^-$ ($^1A_1$) and **1b**$^-$ ($^1A_1$), and the open-chain isomer of C_s symmetry **1c**$^-$ ($^1A'$). At the G2 level of theory and 298.15 K, the global minimum **1a**$^-$ is more stable than **1b**$^-$ and **1c**$^-$ by 11.1 and 26.3 kcal mol^{-1}, respectively, and similar energy differences are computed at the B3LYP/6-311+G(d) level of theory. We note also from Figure 2 that, similar to the cyclic Ge_3^-, the B3LYP values of the bond distances of these three structures are typically slightly longer than the MP2.

We have also investigated the triplet Ge_3H^- potential energy surface, but the four structures (not included in Figure 2), located as energy minima at the B3LYP/6-311+G(d) level of theory (becoming three at the MP2(full)/6-31G(d) level of theory), resulted as invariably less stable than **1a**$^-$ by ca. 40−45 kcal mol^{-1} at the G2 level of theory. In addition, they suffered from strong spin contamination, with spin-state eigenvalues of up to ca. 2.5.

TABLE 2: Relative Energies, Zero-point Energies (ZPE), and G2 Enthalpies of Formation (kcal mol^{-1}) of the Ge_3H and Ge_3H^- Isomeric Structures 1a−1c and 1a$^-$−1c$^-$ (see Figure 2)

species	B3LYP[a]	ZPE[b]	$\langle S^2 \rangle$[c]	G2(298.15 K)	ΔH_f°(298.15 K)
			Ge_3H		
1a ($^2B_2$)	0.0	4.6	0.755	0.0	112.2
1b ($^2A'$)	6.2	4.8	0.755	6.6	118.8
1c ($^2A/^2A'$)[d]	19.2	4.3	0.802	25.4	137.6
			Ge_3H^-		
1a$^-$ ($^1A_1$)	0.0	4.7	0.0	0.0	55.4
1b$^-$ ($^1A_1$)	11.6	4.5	0.0	11.1	66.5
1c$^-$ ($^1A'$)	22.4	4.3	0.0	26.3	81.8

[a] With the 6-311+G(d) basis set and not including the ZPE. [b] At the B3LYP/6-311+G(d) level of theory. [c] B3LYP/6-311+G(d) eigenvalues of the spin operator. [d] B3LYP/6-311+G(d)/MP2(full)/6-31G(d) electronic state.

The cyclic isomers **1a** and **1b** and the open-chain isomer **1c** located as energy minima on the doublet B3LYP/6-311+G(d) and MP2(full)/6-31G(d) Ge_3H potential energy surfaces are the neutral analogues of the anions **1a**$^-$, **1b**$^-$, and **1c**$^-$. From Figure 2 and Table 2, the geometries and the relative stabilities of these molecules do not differ appreciably from their corresponding anions. In particular, at the G2 level of theory and 298.15 K, the global minimum **1a** of C_{2v} symmetry ($^2B_2$) is more stable than **1b** ($^2A'$) and **1c** ($^2A'$) by 6.6 and 25.4 kcal mol^{-1}, respectively, and these energy differences are not significantly different from the B3LYP/6-311+G(d) (at this computational level, the H atom of **1c** resulted as slightly distorted out from the symmetry plane).

When the formation of **1a** and **1a**$^-$ is assumed, the adiabatic EA of Ge_3H is computed as 2.40 eV at the B3LYP/6-311+G(d) level of theory and 0 K and 2.57 eV at the G2 level of theory and 298.15 K. No experimental data are yet available for comparison. It is however of interest to note that this value is quite close to the EA of Si_3H, experimentally obtained as 2.530 ± 0.010 eV[55] and theoretically predicted by DFT methods to range from 2.37 to 2.64 eV.[73]

3c. Ge_3H_2 and $Ge_3H_2^-$. The relevant optimized parameters of the singlet Ge_3H_2 and of the doublet $Ge_3H_2^-$ isomeric structures **2a**, **2b**, and **2a**$^-$−**2f**$^-$ are shown in Figure 3, and their relative stabilities and absolute enthalpies of formation are reported in Table 3.

At variance with the Ge_3H^- isomers, the B3LYP/6-311+G(d) and G2//MP2(full)/6-31G(d) levels of theory provide a somewhat different description of the $Ge_3H_2^-$ potential energy surface. At the MP2(full)/6-31G(d) level of theory, we have located four distinct energy minima of the doublet electronic state, namely, the cyclic structure **2a**$^-$ of C_1 symmetry featuring two hydrogen atoms bound to the same germanium atom, the open-chain H-bridged structure **2b**$^-$ of C_s symmetry, the cyclic structure **2c**$^-$ of C_1 (actually pseudo-C_s) symmetry, featuring two hydrogen atoms bound to adjacent germanium atoms, and the open-chain structure **2d**$^-$ of C_s symmetry with two hydrogen atoms bound to the same germanium atom. At the G2 level of theory, the global minimum **2a**$^-$ is more stable than the nearly degenerate **2b**$^-$ and **2c**$^-$ by ca. 9.5 kcal mol^{-1}, and it is also more stable than **2d**$^-$ by 11.4 kcal mol^{-1}. At the B3LYP/6-311+G(d) level of theory, the geometry of the isomer **2a**$^-$ is predicted to be quite similar to that obtained at the MP2(full)/6-31G(d). However, the structure of isomer **2c**$^-$ becomes strongly asymmetric and features in particular two nonequivalent

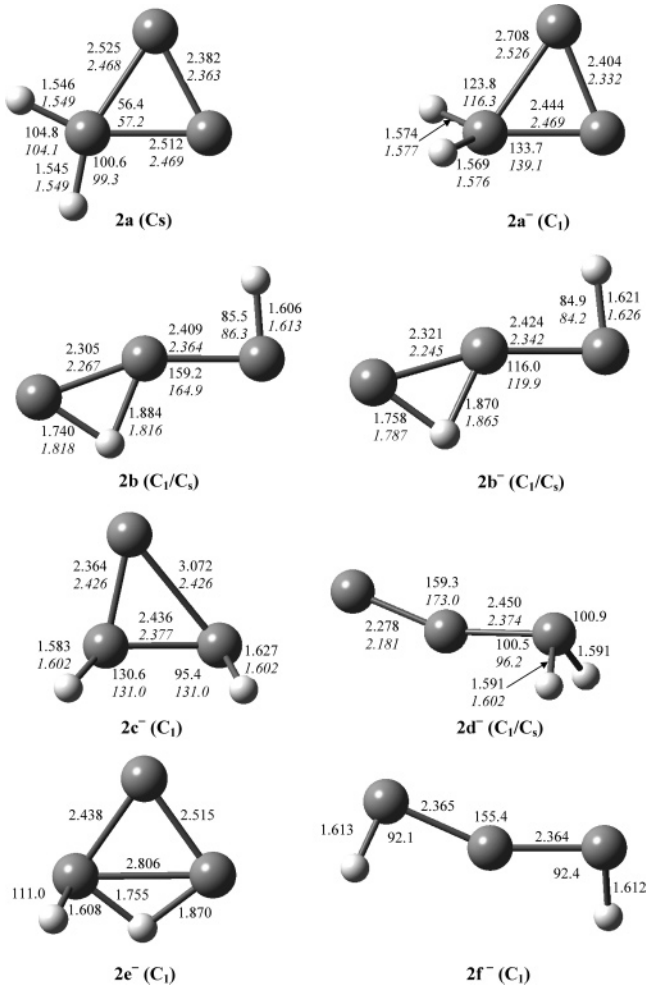


Figure 3. B3LYP/6-311+G(d) and MP2(full)/6-31G(d) (italics) optimized geometries (angstroms and degrees) of the Ge_3H_2 and $Ge_3H_2^-$ isomeric structures **2a**, **2b**, and **2a**⁻−**2f**⁻. The doubly specified symmetries are B3LYP/MP2.

TABLE 3: Relative Energies, Zero-point Energies (ZPE), and G2 Enthalpies of Formation (kcal mol⁻¹) of the Ge_3H_2 and $Ge_3H_2^-$ Isomeric Structures 2a, 2b, and 2a⁻−2f⁻ (see Figure 3)

species	B3LYP[a]	ZPE[b]	$\langle S^2\rangle$[c]	G2(298.15 K)	$\Delta H_f°$(298.15 K)
			Ge_3H_2		
2a ($^1A'$)	0.0	9.4	0.0	0.0	108.6
2b ($^1A/^1A'$)[d]	7.9	8.3	0.0	11.7	120.3
			$Ge_3H_2^-$		
2a⁻ (^2A)	1.0	9.0	0.758	0.0	72.0
2b⁻ ($^2A/^2A''$)[d]	7.4	7.8	0.785	9.2	81.3
2c⁻ (^2A)	10.5	8.0	0.763	9.5	81.5
2d⁻ ($^2A/^2A'$)[d]	5.3	8.8	0.757_5	11.4	83.4
2e⁻ (^2A)	0.0	8.3	0.757		
2f⁻ (^2A)	7.9	7.9	0.773		

[a] With the 6-311+G(d) basis set and not including the ZPE. [b] At the B3LYP/6-311+G(d) level of theory. [c] B3LYP/6-311+G(d) eigenvalues of the spin operator. [d] B3LYP/6-311+G(d)/MP2(full)/6-31G(d) electronic state.

Ge−Ge distances of 2.364 and 3.072 Å, respectively. In addition, under the constraint of C_s symmetry, structures **2b**⁻ and **2d**⁻ revealed first-order saddle points, unstable with respect to slight distortions from the symmetry plane. We note also that, although **2a**⁻ is still more stable than **2b**⁻, **2c**⁻, and **2d**⁻, the B3LYP/6-311+G(d) order of stability, namely, **2a**⁻ > **2d**⁻ > **2b**⁻ > **2c**⁻, is slightly different from G2. Most importantly, isomer **2a**⁻ is not the global minimum on the doublet B3LYP/6-311+G(d) $Ge_3H_2^-$ potential energy surface. In fact, at this computational level, we have located two novel structures, namely, the H-bridged cyclic species **2e**⁻ of C_1 symmetry, which is more stable than **2a**⁻ by 1.0 kcal mol⁻¹, and the open-chain isomer **2f**⁻ of C_1 symmetry and HGe−Ge−GeH⁻ connectivity, which is however less stable than **2e**⁻ by 7.9 kcal mol⁻¹ and nearly degenerate with **2b**⁻.

Concerning the neutral Ge_3H_2, at both the B3LYP/6-311+G(d) and MP2(full)/6-31G(d) level of theory, we have located only two energy minima on the singlet potential energy surface, namely, the cyclic structure **2a** of C_s symmetry with two hydrogen atoms bound to the same germanium atom and the open-chain H-bridged isomer **2b**, whose structure is fully planar at the MP2, but slightly distorted from planarity (C_1 symmetry) at the B3LYP level of theory. These two isomers are the neutral analogues of **2a**⁻ and **2b**⁻, and overall, we note from Figure 3 and Table 3 only minor differences with the geometries and the relative stabilities of the two anions. Thus, at the G2 level of theory and 298.15 K, isomer **2a** is more stable than **2b** by 11.7 kcal mol⁻¹, and this energy difference reduces by less than 4 kcal mol⁻¹ at the B3LYP/6-311+G(d) level of theory.

When the formation of **2a** and **2a**⁻ is assumed, the adiabatic EA of Ge_3H_2 is computed as 1.79 eV at the B3LYP/6-311+G(d) level of theory and 0 K and 1.70 eV at the G2 level of theory and 298.15 K. No experimental data are yet available for comparison.

3d. Ge_3H_3 and $Ge_3H_3^-$. The relevant optimized parameters of the Ge_3H_3 and $Ge_3H_3^-$ isomeric structures **3a**−**3d** and **3a**⁻−**3f**⁻ are shown in Figure 4, and their relative stabilities and absolute enthalpies of formation are reported in Table 4.

On the singlet $Ge_3H_3^-$ potential energy surface, at both the B3LYP/6-311+G(d) and MP2(full)/6-31G(d) levels of theory, we have located four energy minima, namely, the two cyclic isomers **3a**⁻ and **3b**⁻ and the two open-chain isomers **3c**⁻ and **3d**⁻. The global minimum resulted in isomer **3a**⁻, separated however by **3b**⁻ by only 1.6 kcal mol⁻¹ at the G2 level of theory. The open-chain isomers **3c**⁻ and **3d**⁻ are as well nearly degenerate but less stable than **3a**⁻ by ca. 13−14 kcal mol⁻¹ at the G2 and ca. 9 kcal mol⁻¹ at the B3LYP/6-311+G(d) level of theory. The comparable stability of **3a**⁻ and **3b**⁻ and **3c**⁻ and **3d**⁻ does not reflect however in structural similarities. Thus, **3a**⁻ is a cyclic species with a GeH_3 group bridged on a Ge−Ge double bond, whereas the unsymmetrical isomer **3b**⁻ features a H atom bridged between two relatively distant Ge atoms. Similarly, isomer **3c**⁻ has a HGe−Ge−GeH_2^- connectivity and two different Ge−Ge bond distances, whereas isomer **3d**⁻ has a HGe−GeH−GeH⁻ connectivity and two equivalent distances between adjacent Ge atoms. We note also that, at the B3LYP/6-311+G(d) level of theory, both **3c**⁻ and **3d**⁻ resulted as slightly distorted with respect to the symmetry plane identified at the MP2(full)/6-31G(d) level of theory.

We have also investigated the triplet $Ge_3H_3^-$ potential energy surface and located, at both the B3LYP and MP2 levels of theory, the open-chain isomer **3e**⁻ and the cyclic H-bridged isomer **3f**⁻. These two structures are however significantly higher in energy than the singlet isomers, and in particular, they are less stable than **3a**⁻ by 26.7 and 30.7 kcal mol⁻¹, respectively, at the G2 level of theory.

The four isomeric structures **3a**, **3b**, **3c**, and **3d** located as distinct energy minima on both the B3LYP/6-311+G(d) and MP2(full)/6-31G(d) doublet Ge_3H_3 potential energy surface are the neutral analogues of ions **3a**⁻, **3b**⁻, **3c**⁻, and **3d**⁻. Apart from some appreciable differences between some Ge−Ge bond distances of **3a** and **3a**⁻ and **3b** and **3b**⁻, the geometries of

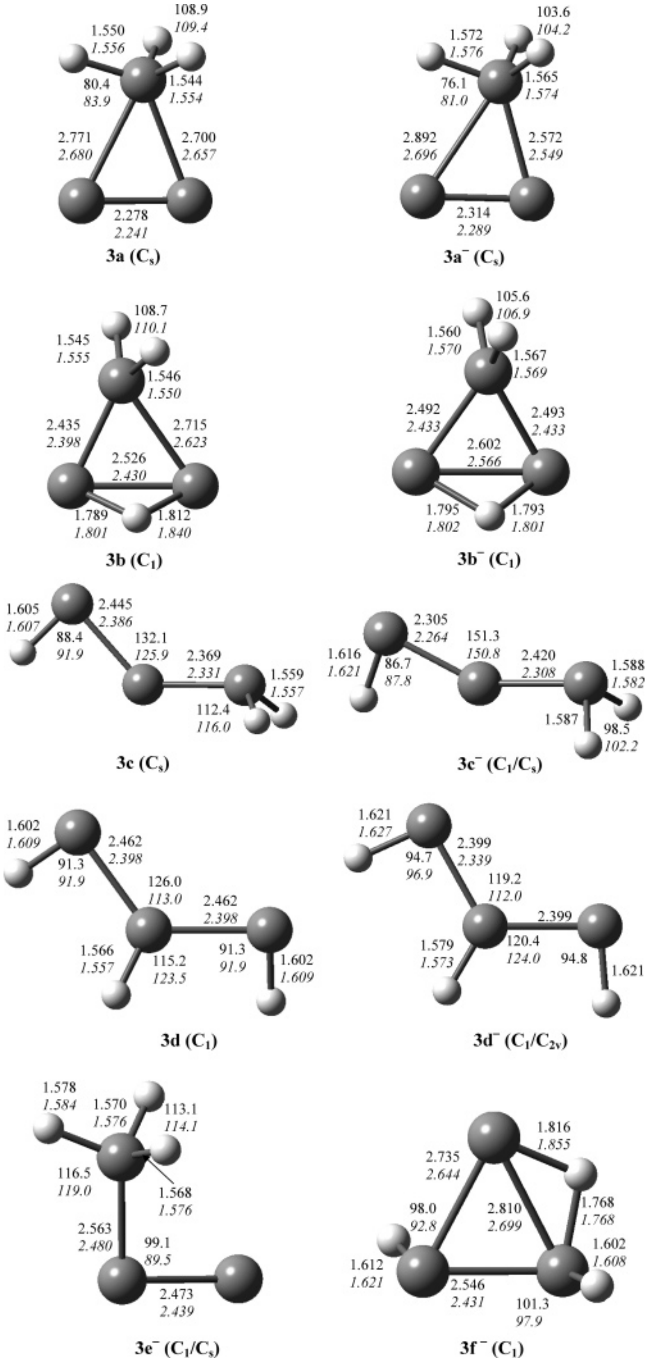


Figure 4. B3LYP/6-311+G(d) and MP2(full)/6-31G(d) (italics) optimized geometries (angstroms and degrees) of the Ge_3H_3 and $Ge_3H_3^-$ isomeric structures **3a**−**3d** and **3a**$^-$−**3f**$^-$. The doubly specified symmetries are B3LYP/MP2.

these molecules are essentially similar to their anionic counterparts. However, their order of stability follows a different trend, and isomer **3b** is in particular the global minimum, more stable than **3a** by only 2.7 kcal mol^{-1} at the B3LYP/6-311+G(d) level of theory but by ca. 11 kcal mol^{-1} at the G2 level of theory. Isomers **3c** and **3d** are even less stable and are predicted to lie, at the G2 level of theory, 19.6 and 25.2 kcal mol^{-1}, respectively, above the global minimum.

Assuming the formation of **3b** and **3b**$^-$, the adiabatic EA of Ge_3H_3 is computed as 2.18 eV at the B3LYP/6-311+G(d) level of theory and 0 K and 2.41 eV at the G2 level of theory and 298.15 K. No experimental data are yet available for comparison.

TABLE 4: Relative Energies, Zero-point Energies (ZPE), and G2 Enthalpies of Formation (kcal mol^{-1}) of the Ge_3H_3 and $Ge_3H_3^-$ Isomeric Structures 3a−3d and 3a$^-$−3f$^-$ (see Figure 4)

species	B3LYP[a]	ZPE[b]	$\langle S^2\rangle$[c]	G2(298.15 K)	$\Delta H_f°$(298.15 K)
			Ge_3H_3		
3a ($^2A'$)	2.7	14.8	0.755	10.8	119.7
3b (^2A)	0.0	13.4	0.757	0.0	108.9
3c ($^2A''$)	13.1	12.9	0.768	19.6	128.5
3d (^2A)	17.7	11.6	0.798	25.2	134.1
			$Ge_3H_3^-$		
3a$^-$ ($^1A'$)	0.0	14.3	0.0	0.0	54.2
3b$^-$ (^1A)	3.8	13.3	0.0	1.6	55.7
3c$^-$ ($^1A/^1A'$)[d]	9.7	12.5	0.0	13.4	67.6
3d$^-$ ($^1A/^1A_1$)[d]	9.1	12.2	0.0	14.3	68.5
3e$^-$ ($^3A/^3A''$)[d]	18.9	13.9	2.004	26.7	80.8
3f$^-$ (^3A)	24.8	11.9	2.010	30.7	84.9

[a] With the 6-311+G(d) basis set and not including the ZPE. [b] At the B3LYP/6-311+G(d) level of theory. [c] B3LYP/6-311+G(d) eigenvalues of the spin operator. [d] B3LYP/6-311+G(d)/MP2(full)/6-31G(d) electronic state.

3e. Ge_3H_4 and $Ge_3H_4^-$. The relevant optimized parameters of the **4a**−**4e** isomers located on the singlet Ge_3H_4 potential energy surface and of their corresponding anions **4a**$^-$−**4e**$^-$ located on the doublet $Ge_3H_4^-$ potential energy surface are shown in Figure 5. Their relative stabilities and absolute enthalpies of formation are reported in Table 5.

Similar to Ge_3H_2 and $Ge_3H_2^-$, the B3LYP/6-311+G(d) and G2//MP2(full)/6-31G(d) levels of theory provide a somewhat different description of the structure and stability of the Ge_3H_4 and $Ge_3H_4^-$ isomeric structures. At the B3LYP/6-311+G(d) level of theory, we have located five distinct $Ge_3H_4^-$ energy minima, namely, the three open-chain structures **4a**$^-$, **4c**$^-$, and **4d**$^-$ of C_s or C_1 symmetry, the Ge-bridged structure **4b**$^-$ of C_{2v} symmetry, and the open-chain H-bridged structure **4e**$^-$ of C_1 symmetry. From Table 5, the global minimum is **4a**$^-$, which is however nearly degenerate with **4b**$^-$ and **4c**$^-$ and more stable than **4d**$^-$ by only 2.8 kcal mol^{-1}. On the other hand, isomer **4e**$^-$ is less stable than **4a**$^-$ by 12.0 kcal mol^{-1}. The five isomers **4a**−**4e**, which are the neutral analogues of **4a**$^-$−**4e**$^-$, have been as well located as energy minima at the B3LYP level of theory. The global minimum is the open-chain structure **4c** of C_s symmetry, more stable than **4b** and **4d** by 2.8 and 4.7 kcal mol^{-1}, respectively. Isomers **4a** and **4e** are even higher in energy and less stable than **4c** by 7.3 and 13.5 kcal mol^{-1}, respectively. Passing to the MP2(full)/6-31G(d) level of theory, no critical points corresponding to the neutral **4a** were located on the Ge_3H_4 potential energy surface and the anion **4a**$^-$ resulted in a first-order saddle point, with a small imaginary frequency of 42.6*i* cm^{-1} and a highly contaminated spin eigenvalue of 1.25. A similar contamination problem ($\langle S^2\rangle = 1.02$) has been found for the anion **4d**$^-$, confirmed however to be a true energy minimum on the MP2 surface. In addition, from Figure 5, whereas the B3LYP/6-311+G(d) and MP2(full)/6-31G(d) optimized geometries of the $Ge_3H_4^-$ isomers **4b**$^-$−**4e**$^-$ are not significantly different, the geometries of their neutral analogues feature appreciable differences. This is especially true for isomers **4c** and **4e**. In the former species, the B3LYP value of the Ge−Ge−Ge angle, 126.1°, becomes 78.2° at the MP2 level, and the open-chain skeleton of **4e**, featuring a Ge−Ge−Ge bond angle of 123.7° and two nearly equivalent Ge−Ge bonds of 2.47−2.48 Å, becomes cyclic at the MP2 level, with a Ge−Ge−Ge bond angle of 67.8° and two nonequivalent Ge−Ge bond lengths of 2.318 (corresponding to a double bond) and 2.555 Å, respectively. At the G2 level of theory, the global minimum among the $Ge_3H_4^-$ isomeric structures results in the

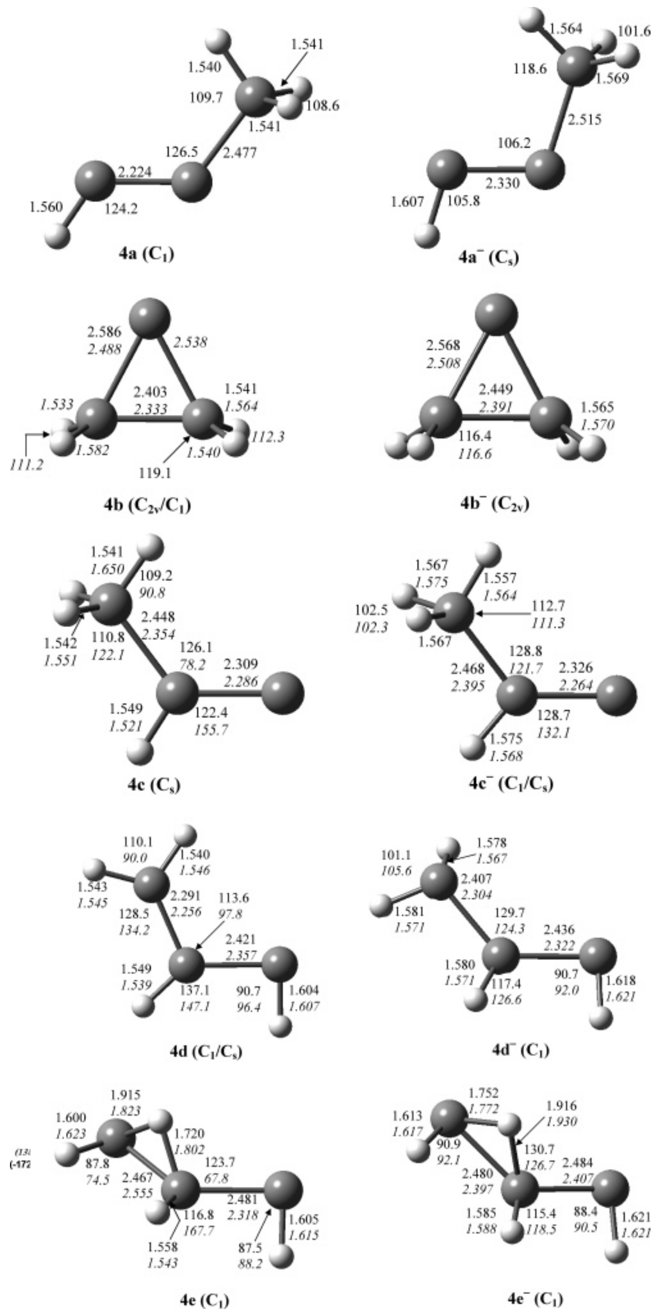


Figure 5. B3LYP/6-311+G(d) and MP2(full)/6-31G(d) (italics) optimized geometries (angstroms and degrees) of the Ge_3H_4 and $Ge_3H_4^-$ isomeric structures **4a**−**4e** and **4a**$^-$−**4e**$^-$. The doubly specified symmetries are B3LYP/MP2.

cyclic isomer **4b**$^-$, more stable than isomers **4c**$^-$ and **4d**$^-$ by 3.0 and 9.0 kcal mol^{-1}, respectively. In addition, isomer **4e**$^-$ confirmed the least stable species, higher in energy than **4b**$^-$ by 16.5 kcal mol^{-1}. The G2 order of stability of the four Ge_3H_4 isomers **4b**−**4e** is similar to B3LYP/6-311+G(d). The global minimum **4c** is more stable than **4b** and **4d** by 3.2 and 7.8 kcal mol^{-1}, respectively. In addition, **4e** was confirmed to be a high-energy minimum, less stable than **4c** by 19.6 kcal mol^{-1}.

Assuming the formation of **4b**$^-$, which is the global minimum on the G2//MP2(full)/6-31G(d) $Ge_3H_4^-$ potential energy surface, the adiabatic EA of Ge_3H_4 is computed as 2.07 eV at the G2 level of theory and 2.04 eV at the B3LYP/6-311+G(d) level. On the other hand, assuming the formation of **4c**, which is the global minimum on the neutral Ge_3H_4 G2//MP2(full)/6-31G(d) potential energy surface, the adiabatic EA of Ge_3H_4 is computed as 1.80 eV at the G2 level of theory and 1.97 eV at the B3LYP/6-311+G(d). No experimental data are yet available for comparison.

TABLE 5: Relative Energies, Zero-point Energies (ZPE), and G2 Enthalpies of Formation (kcal mol^{-1}) of the Ge_3H_4 and $Ge_3H_4^-$ Isomeric Structures 4a−4e and 4a$^-$−4e$^-$ (see Figure 5)

species	B3LYP[a]	ZPE[b]	$\langle S^2\rangle$[c]	G2(298.15 K)	$\Delta H_f°$(298.15 K)
			Ge_3H_4		
4a (^{1}A)	7.3	18.7	0.0		
4b ($^1A_1$/^{1}A)[d]	2.8	18.3	0.0	3.2	102.9
4c (^{1}A′)	0.0	19.1	0.0	0.0	99.7
4d (^{1}A/^{1}A′)[d]	4.7	17.8	0.0	7.8	107.5
4e (^{1}A)	13.5	17.0	0.0	19.6	119.3
			$Ge_3H_4^-$		
4a$^-$ (^{2}A′)	0.0	17.8	0.756		
4b$^-$ ($^2B_1$)	1.1	17.8	0.753	0.0	57.6
4c$^-$ (^{2}A/^{2}A′)[d]	0.2	18.2	0.767	3.0	60.6
4d$^-$ (^{2}A)	2.8	16.8	0.771	9.0	66.6
4e$^-$ (^{2}A)	12.0	16.0	0.754_5	16.5	74.1

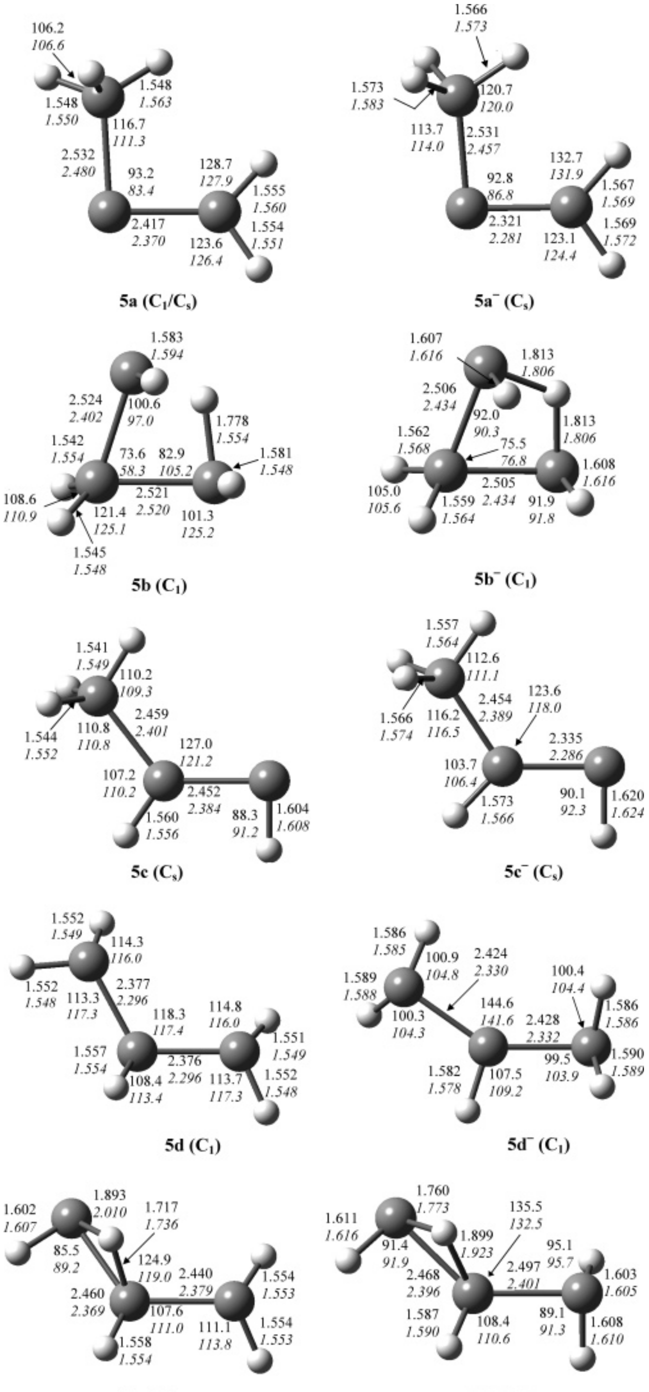
[a] With the 6-311+G(d) basis set and not including the ZPE. [b] At the B3LYP/6-311+G(d) level of theory. [c] B3LYP/6-311+G(d) eigenvalues of the spin operator. [d] B3LYP/6-311+G(d)/MP2(full)/6-31G(d) electronic state.

3f. Ge_3H_5 and $Ge_3H_5^-$. The relevant optimized parameters of the **5a**−**5e** isomers located on the doublet Ge_3H_5 potential energy surface and of their corresponding anions **5a**$^-$−**5e**$^-$ located on the singlet $Ge_3H_5^-$ potential energy surface are shown in Figure 6. Their relative stabilities and absolute enthalpies of formation are reported in Table 6.

Concerning the $Ge_3H_5^-$ potential energy surface, we first note that the B3LYP/6-311+G(d) and G2//MP2(full)/6-31G(d) levels of theory furnish a qualitatively and also quantitatively similar description. The predicted global minimum is the 2-propenyl-like isomer **5a**$^-$ of C_s symmetry, which features a single and a double Ge−Ge bond with B3LYP and MP2 distances of 2.531 and 2.321, and 2.457 and 2.281 Å, respectively. The Ge−Ge−Ge angle is around 90°, but the long Ge1−Ge3 distance of ca. 3.5 Å is still suggestive of an open chain rather than a cyclic structure. Quite close in energy to **5a**$^-$ is the cyclic isomer **5b**$^-$, which lies 1.7 kcal mol^{-1} above the global minimum at the G2 level of theory and only 0.9 kcal mol^{-1} at the B3LYP/6-311+G(d) level of theory. This isomer features a quadrangular disposition, only slightly distorted from planarity, of three germaniums and one hydrogen atom (at the B3LYP level of theory, we have also located an additional isomer, not included in Figure 6, structurally analogous to the cyclopropyl anion but less stable than **5a**$^-$ by more than 30 kcal mol^{-1}). The 1-propenyl-like isomer **5c**$^-$ of C_s symmetry is still close in energy to **5a**$^-$, being less stable by only 2.9 and 3.6 kcal mol^{-1}, respectively, at the B3LYP/6-311+G(d) and G2 levels of theory.

Searching for allyl-like $Ge_3H_5^-$ isomers of C_{2v} symmetry, we located a second-order saddle point, unstable with respect to the distortion from planarity of the two GeH_2 groups. The corresponding energy minimum is the C_1 symmetry isomer **5d**$^-$, which is less stable than **5a**$^-$ by 8.1 and 12.2 kcal mol^{-1}, respectively, at the B3LYP/6-311+G(d) and G2 levels of theory. Isomer **5e**$^-$ is the least stable among the singlet $Ge_3H_5^-$ isomeric structures and is still perceivable as an allyl-like species with a H atom bridged between two adjacent germanium atoms. It is less stable than **5d**$^-$ by 5.2 and 4.7 kcal mol^{-1}, respectively, at the B3LYP/6-311+G(d) and G2 levels of theory.

We have also investigated the triplet $Ge_3H_5^-$ potential energy surface and located five distinct isomeric structures, not included in Figure 6, which resulted however as significantly less stable



5a (C_1/C_s) **5a**$^-$ (C_s)

5b (C_1) **5b**$^-$ (C_1)

5c (C_s) **5c**$^-$ (C_s)

5d (C_1) **5d**$^-$ (C_1)

5e (C_1) **5e**$^-$ (C_1)

Figure 6. B3LYP/6-311+G(d) and MP2(full)/6-31G(d) (italics) optimized geometries (angstroms and degrees) of the Ge_3H_5 and $Ge_3H_5^-$ isomeric structures **5a**−**5e** and **5a**$^-$−**5e**$^-$. The doubly specified symmetries are B3LYP/MP2.

than **5a**$^-$. For example, at the B3LYP/6-311+G(d) level of theory, the two lowest-energy species, structurally analogous to **5a**$^-$ and **5c**$^-$ but with hydrogen atoms distorted out from planarity, are less stable than **5a**$^-$ by 16.9 and 18.9 kcal mol^{-1}, respectively.

At variance with $Ge_3H_5^-$, the B3LYP/6-311+G(d) and G2//MP2(full)/6-31G(d) description of the doublet Ge_3H_5 potential energy surface is somewhat different, especially for the three lowest-energy isomers **5a**, **5b**, and **5c**. At the B3LYP level of theory, the 2-propenyl-like isomer **5a** and the 1-propenyl-like isomer **5c** are nearly degenerate and more stable than isomer **5b** by 4.6 kcal mol^{-1}. The latter species features a quadrangular disposition of three germaniums and one hydrogen atom, which is bridged between two terminal GeH groups. On the other hand, at the MP2(full)/6-31G(d) level of theory, **5b** collapses to a cyclopropyl-like structure and is predicted by G2 theory to be the global minimum on the Ge_3H_5 surface, more stable than the still nearly degenerate **5a** and **5c** by almost 4 kcal mol^{-1}.

TABLE 6: Relative Energies, Zero-point Energies (ZPE), and G2 Enthalpies of Formation (kcal mol^{-1}) of the Ge_3H_5 and $Ge_3H_5^-$ Isomeric Structures 5a−5e and 5a$^-$−5e$^-$ (see Figure 6)

species	B3LYP[a]	ZPE[b]	$\langle S^2\rangle$[c]	G2(298.15 K)	$\Delta H_f°$(298.15 K)
			Ge_3H_5		
5a ($^2A/^2A''$)[d]	0.0	23.1	0.760	4.0	98.6
5b (^2A)	4.6	22.2	0.758	0.0	94.6
5c ($^2A''$)	0.02	22.5	0.752	4.4	99.0
5d (^2A)	5.4	22.8	0.814	7.6	102.2
5e (^2A)	14.0	22.0	0.758	16.0	110.6
			$Ge_3H_5^-$		
5a$^-$ ($^1A'$)	0.0	22.6	0.0	0.0	38.6
5b$^-$ (^1A)	0.9	21.8	0.0	1.7	40.3
5c$^-$ ($^1A'$)	2.9	22.2	0.0	3.6	42.3
5d$^-$ (^1A)	8.1	21.4	0.0	12.2	50.8
5e$^-$ (^1A)	13.3	20.9	0.0	16.9	55.5

[a] With the 6-311+G(d) basis set and not including the ZPE. [b] At the B3LYP/6-311+G(d) level of theory. [c] B3LYP/6-311+G(d) eigenvalues of the spin operator. [d] B3LYP/6-311+G(d)/MP2(full)/6-31G(d) electronic state.

Concerning the trygermaallyl radical **5d**, its germanium atoms are more pyramidalized than the corresponding anion **5d**$^-$ and the two equivalent Ge−Ge bond distances are also slightly shorter. It is less stable than **5a** by 5.4 and 3.6 kcal mol^{-1}, respectively, at the B3LYP/6-311+G(d) and G2 levels of theory. Finally, isomer **5e**, structurally analogous to anion **5e**$^-$, is invariably predicted as the least stable among the various Ge_3H_5 isomeric structures and results as less stable than **5a** by 14.0 and 12.0 kcal mol^{-1}, respectively, at the B3LYP/6-311+G(d) and G2 levels of theory.

At the B3LYP/6-311+G(d) level of theory, assuming the formation of the neutral ground-state **5a**, the adiabatic EA of Ge_3H_5 is predicted as 2.46 eV. At the G2 level of theory, the neutral ground-state Ge_3H_5 isomer results as **5b** and its adiabatic EA is computed as 2.46 eV. No experimental data are yet available for comparison.

3g. Implications for Mass Spectrometric Experiments. As already pointed out in the Introduction, the mass spectrometric investigation of the negative ion chemistry of GeH_4 [9] has disclosed the formation of germanium clusters hydrides, up to $Ge_9H_n^-$, whose stability and relative abundance strictly depends on the total pressure and the observation time. In particular, all the presently investigated $Ge_3H_n^-$ ($n = 0-5$) anions, with only the exception of $Ge_3H_4^-$, have been experimentally observed and ascertained to arise from the following ion−molecule reactions

$$Ge_2^- + GeH_4 \rightarrow Ge_3H_2^- + H_2 \qquad (1)$$

$$Ge_2H^- + GeH_4 \rightarrow Ge_3H^- + 2H_2 \qquad (2a)$$

$$\rightarrow Ge_3H_3^- + H_2 \qquad (2b)$$

$$Ge_2H_2^- + GeH_4 \rightarrow Ge_3H_2^- + 2H_2 \qquad (3)$$

$$Ge_2H_3^- + GeH_4 \rightarrow Ge_3H_5^- + H_2 \qquad (4)$$

The employed mass spectrometric techniques do not provide however information on the detailed structure of the observed

$Ge_3H_n^-$ ($n = 1-3$, 5) and also do not furnish arguments to speculate why the $Ge_3H_4^-$ ions are not experimentally detected. These questions can be at least partially addressed using the results of our calculations. In the quadrupole ion trap experiments performed to investigate reactions 1−4,[9] the precursor $Ge_2H_n^-$ ions ($n = 0-3$) are preliminarily thermalized by unreactive collisions with buffer helium and it is therefore reasonable to assume that the $Ge_3H_n^-$ ($n = 1-3,5$) products arise from exothermic or nearly thermoneutral reactions. Therefore, using the experimental enthalpy of formation of Ge_2^-, 65.7 ± 2.4;[74] Ge_3^-, 61.5 ± 0.5;[64b] and GeH_4, 21.7 kcal mol^{-1},[55] and our previously calculated[44] G2(298.15 K) enthalpies of formation of Ge_2H^-, 49.8; $Ge_2H_2^-$, 54.0; and $Ge_2H_3^-$, 37.1 kcal mol^{-1}, the following upper limits for the enthalpies of formation of $Ge_3H_n^-$ ($n = 1-3$, 5) are predicted: Ge_3H^- and $Ge_3H_3^- \leq 71.5$, $Ge_3H_2^- \leq 75.7$ or 87.4, and $Ge_3H_5^- \leq 58.8$ kcal mol^{-1}. Therefore, the comparison with the theoretical values reported in Tables 2, 3, 4, and 6 suggests, for example, that the Ge_3H^- ions formed in reaction 2a should possess the cyclic structure **1a**$^-$ or **1b**$^-$, whereas the open-chain isomer **1c**$^-$ should not be accessible. The structural assignment of the $Ge_3H_2^-$ ions from reaction 3 is apparently even less ambiguous, since only the cyclic isomer **2a**$^-$ has a calculated enthalpy of formation, 72.0 kcal mol^{-1}, which is compatible with a nearly thermoneutral reaction. On the other hand, all four $Ge_3H_2^-$ isomers **2a**$^-$−**2d**$^-$ could be formed from reaction 1, and only the two triplet isomers **3e**$^-$ and **3f**$^-$ can probably be safely ruled out from reaction 2b. In addition, from Table 6, any of the presently investigated $Ge_3H_5^-$ isomeric structures **5a**$^-$−**5e**$^-$ could be obtained as the product of reaction 4. Therefore, especially for the $Ge_3H_3^-$ and $Ge_3H_5^-$ ions, additional experiments are required to disclose in more detail their connectivity and structure.

Concerning the not observed $Ge_3H_4^-$ ions, their formation could be expected, for example, by a process such as

$$Ge_2H_2^- + GeH_4 \rightarrow Ge_3H_4^- + H_2$$

which is analogous to reactions 1, 2b, 3, and 4 and is predicted to be exothermic or nearly thermoneutral for all the $Ge_3H_4^-$ isomeric structures **4b**$^-$−**4d**$^-$ reported in Table 5. Although speculative, it is therefore tempting to suggest that their actual observation is prevented by kinetic factors and/or by decomposition processes which are faster than the observation time window of the mass spectrometric experiments.

4. Conclusions

The results of B3LYP, MP2, and G2 calculations reveal that the germanium cluster hydrides $Ge_3H_n^-$ ($n = 1-5$) may possess various cyclic or open-chain isomeric structures, whose energy differences may be sometimes as large as up to 20 or 30 kcal mol^{-1}. These thermochemical data may help to assign the plausible connectivity of the $Ge_3H_n^-$ ions ($n = 1-3,5$) experimentally observed in the negative ion chemistry of GeH_4. We suggest in particular that the experimentally observed Ge_3H^- and $Ge_3H_2^-$ should possess a cyclic rather than an open-chain isomeric structure, whereas the connectivity of the $Ge_3H_3^-$ and $Ge_3H_5^-$ observed ions cannot be unambiguously assigned on simple thermochemical grounds, and additional experiments are required to disclose in more detail their connectivity and structure. The identification of the observed ions is also complicated by the fact that, for species such as $Ge_3H_2^-$ and $Ge_3H_4^-$, the B3LYP and the G2/MP2 levels of theory furnish a somewhat different description of their structure and stability, especially for the lowest-energy isomers. At least in principle, the B3LYP structures, obtained using the more flexible 6-311+G(d) basis set, should be more accurate than the MP2/6-31G(d). This is in line with the conclusions from a recent study[43] which indicates that, for the $Ge_2H_n^-$ anions ($n = 1-5$), various DFT methods used in conjunction with basis sets including diffuse functions predict geometries close to the few available experimental structures. In any case, a stronger interplay between theory and experiment is probably still required to assess which computational level has to be used to perform accurate predictions of the structure and stability of large-size anionic germanium hydrides.

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Supporting Information Available: Full list of the Cartesian coordinates (angstroms) of all the presently investigated Ge_3H_n and $Ge_3H_n^-$ ($n = 1-5$) anions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Riveros, J. M. *Int. J. Mass Spectrom.* **2002**, *221*, 177.

(2) Ehrlich, D. J.; Tsao, J. Y. *J. Vac. Sci. Technol., B* **1983**, *1*, 969.

(3) Barrau, J.; Escudié, J.; Satgé, J. *Chem. Rev.* **1990**, *90*, 283.

(4) Pola, J.; Taylor, R. *J. Organomet. Chem.* **1992**, *437*, 271.

(5) *Chemical Vapor Deposition: Principles and Applications*; Hitchman, M. L., Jensen, K. F., Eds.; Academic Press Limited: London, 1993.

(6) Antoniotti, P.; Benzi, P.; Castiglioni, M.; Volpe, P. *Eur. J. Inorg. Chem.* **1999**, 323.

(7) Osmundsen, J. F.; Abels, C. C.; Eden, J. G. *J. Appl. Phys.* **1985**, *57*, 2921.

(8) Operti, L.; Splendore, M.; Vaglio, G. A.; Franklin, A. M.; Todd, J. F. J. *Int. J. Mass Spectrom. Ion Processes* **1994**, *136*, 25. (b) Castiglioni, M.; Operti, L.; Rabezzana, R.; Vaglio, G. A.; Volpe, P. *Int. J. Mass Spectrom.* **1998**, *179/180*, 277. (c) Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *J. Organomet. Chem.* **1988**, *354*, 39. (d) Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *J. Organomet. Chem.* **1988**, *373*, 289. (e) Benzi, P.; Operti, L.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Gabrielli, R. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 647. (f) Operti, L.; Splendore, M.; Vaglio, G. A.; Volpe, P.; Speranza, M.; Occhiucci, G. *J. Organomet. Chem.* **1992**, *433*, 35. (g) Operti, L.; Splendore, M.; Vaglio, G. A.; Volpe, P. *Organometallics* **1993**, *12*, 4516. (h) Benzi, P.; Operti, L.; Rabezzana, R.; Splendore, M.; Volpe, P. *Int. J. Mass Spectrom. Ion Processes* **1996**, *52*, 61. (i) Antoniotti, P.; Operti, L.; Rabezzana, R.; Vaglio, G. A. *Int. J. Mass Spectrom.* **1999**, *182/183*, 63. (j) Benzi, P.; Operti, L.; Rabezzana, R. *Eur. J. Inorg. Chem.* **2000**, 505. (k) Antoniotti, P.; Canepa, C.; Maranzana, A.; Operti, L.; Rabezzana, R.; Tonachini, G.; Vaglio, G. A. *Organometallics* **2001**, *20*, 382. (l) Benzi, P.; Operti, L.; Rabezzana, R.; Vaglio, G. A. *J. Mass Spectrom.* **2002**, *37*, 603. (m) Benzi, P.; Bottizzo, E.; Operti, L.; Rabezzana, R.; Vaglio, G. A.; Volpe, P. *Chem. Mater.* **2002**, *14*, 2506. (n) Operti, L.; Rabezzana, R.; Vaglio, G. A. *Int. J. Mass Spectrom.* **2003**, *228*, 403.

(9) Antoniotti, P.; Operti, L.; Rabezzana, R.; Vaglio, G. A.; Guarini, A. *Rapid Commun. Mass Spectrom.* **2002**, *16*, 185. (b) Operti, L.; Rabezzana, R.; Turco, F.; Vaglio, G. A. *Rapid Commun. Mass Spectrom.* **2005**, *19*, 1963.

(10) Gunn, S. R.; Green, G. L. *J. Phys. Chem.* **1961**, *65*, 779.

(11) Saalfeld, F. E.; Svec, H. J. *Inorg. Chem.* **1963**, *2*, 46. (b) Saalfeld, F. E.; Svec, H. J. *Inorg. Chem.* **1963**, *2*, 50. (c) Saalfeld, F. E.; Svec, H. J. *J. Phys. Chem.* **1966**, *70*, 1753.

(12) Northrop, J. K.; Lampe, F. W. *J. Phys. Chem.* **1973**, *77*, 30. (b) Senzer, S. N.; Abernathy, R. N.; Lampe, F. W. *J. Phys. Chem.* **1980**, *84*, 3066.

(13) Nagase, S.; Kudo, T. *J. Mol. Struct. (THEOCHEM)* **1983**, *12*, 35. (b) Kudo, T.; Nagase, S. *Chem. Phys. Lett.* **1988**, *148*, 73.

(14) Balasubramanian, K. *J. Chem. Phys.* **1988**, *89*, 5731. (b) Balasubramanian, K.; Li, J. *J. Mol. Spectrosc.* **1988**, *128*, 413. (c) Das, K. K.; Balasubramanian, K. *J. Chem. Phys.* **1990**, *93*, 5883.

(15) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (b) Trinquier, G. *J. Am. Chem. Soc.* **1992**, *114*, 6807.

(16) Ruscic, B.; Schwarz, M.; Berkovitz, J. *J. Chem. Phys.* **1990**, *92*, 1865.

(17) Grev, R. S.; Deleeuw, B. J.; Schaefer, H. F. *Chem. Phys. Lett.* **1990**, *165*, 257. (b) Grev, R. S.; Schaefer, H. F.; Baines, K. M. *J. Am. Chem.*

Soc. **1990**, *112*, 9458. (c) Grev, R. S. *Adv. Organomet. Chem.* **1991**, *33*, 125. (d) Grev, R. S.; Schaefer, H. F. *Organometallics* **1992**, *11*, 3489. (e) Horner, D. A.; Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 2093.

(18) Palágyi, Z.; Schaefer, H. F.; Kapuy, E. *J. Am. Chem. Soc.* **1993**, *115*, 6901.

(19) Schreiner, P. R.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1994**, *101*, 2141. (b) Kapp, J.; Schreiner, P. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *118*, 12154.

(20) Archibong, E. F.; Leszczyñski, J. *J. Phys. Chem.* **1994**, *98*, 10084. (b) Archibong, E. F.; Schreiner, P. F.; Leszczyñski, J.; Schleyer, P. v. R.; Schaefer, H. F.; Sullivan, R. *J. Chem. Phys.* **1995**, *102*, 3667. (c) Boone, A. J.; Magers, D. H.; Leszczyñski, J. *Int. J. Quantum Chem.* **1998**, *70*, 925. (d) Roszak, S.; Babinec, P.; Leszczyñski, J. *Chem. Phys.* **2000**, *256*, 177.

(21) Jemmis, E. D.; Srinivas, G. N.; Leszczyñski, J.; Kapp, J.; Korkin, A. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1995**, *117*, 11361. (b) Srinivas, G. N.; Kiran, B.; Jemmis, E. D. *J. Mol. Struct. (THEOCHEM)* **1996**, *361*, 205.

(22) Mineva, T.; Russo, N.; Sicilia, E.; Toscano, M. *Int. J. Quantum Chem.* **1995**, *56*, 669.

(23) So, S. P. *J. Phys. Chem.* **1996**, *100*, 8250. (b) So, S. P. *Chem. Phys. Lett.* **1998**, *291*, 523. (c) So, S. P. *Chem. Phys. Lett.* **1999**, *313*, 587.

(24) Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Mol. Struct. (THEOCHEM)* **1998**, *455*, 101.

(25) Morgon, N. H.; Riveros, J. M. *J. Phys. Chem. A* **1998**, *102*, 10399.

(26) Becerra, R.; Boganov, S. E.; Egorov, M. P.; Faustov, V. I.; Nefedov, O. M.; Walsh, R. *J. Am. Chem.* Soc. **1998**, *120*, 12657.

(27) Ricca, A.; Bauschlicher, C. W. *J. Phys. Chem. A* **1999**, *103*, 11121.

(28) Jackson, P.; Diefenbach, M.; Srinivas, R.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1445. (b) Jackson, P.; Sändig, N.; Diefenbach, M.; Schröder, D.; Schwarz, H.; Srinivas, R. *Chem.−Eur. J.* **2001**, *7*, 151.

(29) Chambreau, S. D.; Zhang, J. *Chem. Phys. Lett.* **2002**, *351*, 171.

(30) Li, S.-D.; Yu, H.-L.; Wu, H.-S.; Jin, Z.-H. *J. Chem. Phys.* **2002**, *117*, 9543.

(31) Wang, X.; Andrews, L.; Kushto, G. P. *J. Phys. Chem. A* **2002**, *106*, 5809. (b) Wang, X.; Andrews, L.; Chertihin, G. V.; Souter, P. F. *J. Phys. Chem. A* **2002**, *106*, 6302. (c) Wang, X.; Andrews, L. *J. Am. Chem. Soc.* **2003**, *125*, 6581.

(32) Su, M.-D. *J. Phys. Chem. A* **2004**, *108*, 823.

(33) Lein, M.; Krapp, A.; Frenking, G. *J. Am. Chem. Soc.* **2005**, *127*, 6290.

(34) Reed, K. J.; Brauman, J. I. *J. Chem. Phys.* **1974**, *61*, 4830.

(35) Eades, R. A.; Dixon, D. A. *J. Chem. Phys.* **1980**, *72*, 3309.

(36) Ortiz, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 5072.

(37) Mayer, P. M.; Gal, J.-F.; Radom, L. *Int. J. Mass Spectrom. Ion Processes* **1997**, *167/168*, 689.

(38) Morgon, N. H.; Riveros, J. M. *Int. J. Mass Spectrom.* **2001**, *210/211*, 173.

(39) Bruna, P. J.; Grein, F. *J. Mol. Struct.* **2001**, *599*, 261.

(40) Woon, D. E.; Beck, D. R. *Chem. Phys. Lett.* **2001**, *347*, 255.

(41) Moc, J. *J. Mol. Struct. (THEOCHEM)* **1999**, *461−462*, 249.

(42) Tada, T.; Yoshimura, R. *J. Phys. Chem.* **1993**, *97*, 1019.

(43) Li, Q.-S.; Lü, R.-H.; Xie, Y.; Schaefer, H. F. *J. Comput. Chem.* **2002**, *23*, 1642.

(44) Antoniotti, P.; Operti, L.; Rabezzana, R.; Vaglio, G. A. *J. Mol. Struct. (THEOCHEM)* **2003**, *663*, 1.

(45) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(46) Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

(47) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley: New York, 2001.

(48) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *ACS Symp. Ser.* **1989**, *394*, 165. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(49) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(50) Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(51) Pople, J. A.; Gill, P. M. W.; Johnson, B. G. *Chem. Phys. Lett.* **1992**, *199*, 557.

(52) Schlegel, H. B. In *Computational Theoretical Organic Chemistry*; Csizsmadia, I. G., Daudel, R., Eds.; Reidel Publ. Co.: Dordrecht, The Netherlands, 1981; pp 129−159.

(53) Schlegel, H. B. *J. Chem. Phys.* **1982**, *77*, 3676. (b) Schlegel, H. B.; Binkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1984**, *80*, 1976. (c) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

(54) Curtiss, A. L.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(55) All thermochemical data are taken from NIST Chemistry WebBook, NIST Standard Reference Database Number 69, June 2005 Release. http://webbook.nist.gov.

(56) Kant, A.; Strauss, B. H. *J. Chem. Phys.* **1966**, *45*, 822.

(57) Kingcade, J. E., Jr.; Choudary, U. V.; Gingerich, K. A. *Inorg. Chem.* **1979**, *18*, 3094. (b) Gingerich, K. A.; Shim, I.; Gupta, S. K.; Kingcade, J. E. *Surf. Sci.* **1985**, *156*, 495. (c) Gingerich, K. A.; Baba, M. S.; Schmude, R. W., Jr.; Kingcade, J. E., Jr. *Chem. Phys.* **2000**, *262*, 65.

(58) Froben, F. W.; Schulze, W. *Surf. Sci.* **1985**, *156*, 765.

(59) Cheshnovsky, O.; Yang, S. H.; Pettiette, C. L.; Craycraft, M. J.; Liu, Y.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *138*, 119.

(60) Islam, M. S.; Ray, A. K. *Chem. Phys. Lett.* **1988**, *153*, 496.

(61) Dixon, D. A.; Gole, J. L. *Chem. Phys. Lett.* **1992**, *188*, 560.

(62) Dai, D.; Sumathi, K.; Balasubramanian, K. *Chem. Phys. Lett.* **1992**, *193*, 251.

(63) Lanza, G.; Millefiori, S.; Millefiori, A.; Dupuis, M. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2961.

(64) Burton, G. R.; Xu, C.; Neumark, D. M. *Surf. Rev. Lett.* **1996**, *3*, 383. (b) Burton, G. R.; Xu, C.; Arnold, C. C.; Neumark, D. M. *J. Chem. Phys.* **1996**, *104*, 2757.

(65) Jackson, P.; Fisher, K. J.; Gadd, G. E.; Dance, I. G.; Smith, D. R.; Willett, G. D. *Int. J. Mass Spectrom. Ion Processes* **1997**, *164*, 45.

(66) Deutsch, P. W.; Curtiss, L. A.; Blaudeau, J. P. *Chem. Phys. Lett.* **1997**, *270*, 413. (b) Deutsch, P. W.; Curtiss, L. A.; Blaudeau, J. P. *Chem. Phys. Lett.* **2001**, *344*, 101.

(67) Archibong, E. F., St-Amant, A. *J. Chem. Phys.* **1998**, *109*, 962.

(68) Lu, Z.-Y.; Wang, C.-Z.; Ho, K.-M. *Phys. Rev. B* **2000**, *61*, 2329.

(69) Li, B.-x.; Cao, P.-l. *Phys. Rev. B* **2000**, *62*, 15788.

(70) Li, S.-D.; Zhao, Z.-G.; Wu, H.-S.; Jin, Z.-H. *J. Chem. Phys.* **2001**, *115*, 9255.

(71) Wang, J.; Wang, G.; Zhao, J. *Phys. Rev. B* **2001**, *64*, 205411. (b) Wang, J.; Yang, M.; Wang, G.; Zhao, J. *Chem. Phys. Lett.* **2003**, *367*, 448.

(72) Xu, W.; Zhao, Y.; Li, Q.; Xie, Y.; Schaefer, H. F. *Mol. Phys.* **2004**, *102*, 579.

(73) Xu, W.; Yang, J.; Xiao, W. *J. Phys. Chem. A* **2004**, *108*, 11345.

(74) Arnold, C. C.; Xu, C.; Burton, G. R.; Neumark, D. M. *J. Chem. Phys.* **1995**, *102*, 6982.