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A study of Ge_n^- and Ge_n ($n=2-6$) using B3LYP-DFT and CCSD(T) methods: The structures and electron affinities of small germanium clusters

Edet F. Archibong and Alain St-Amant

Department of Chemistry, University of Ottawa, 10 Marie Curie Street, Ottawa, Ontario K1N 6N5, Canada

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The structures of the anionic germanium Ge_n^- clusters and the corresponding neutral Ge_n clusters ($n=2-6$) have been investigated using B3LYP-DFT and CCSD(T) methods. The 6-311+G(3df) basis set is employed for the dimers and trimers, while the smaller 6-311+G(d) basis set is used for clusters with $n>3$. The most stable structures for the germanium cluster anions Ge_3^- , Ge_4^- , Ge_5^- , and Ge_6^- are found to be $C_{2v}(^2A_1)$, $D_{2h}(^2B_{2g})$, $D_{3h}(^2A_2'')$, and $D_{4h}(^2A_{2u})$, respectively. In the case of Ge_2^- , our calculations show that the low lying $^2\Pi_u$ and $^2\Sigma_g^+$ states are within 1 kcal/mol of each other and both states are candidates for the ground state of the anion. The adiabatic electron affinities calculated for the Ge_n clusters with $n=2,3,4,6$ are within 0.1 eV of the corresponding experimental values. Furthermore, the adiabatic excitation energies computed at the CCSD(T) level for the low lying states of Ge_3 and Ge_4 compare quite well with the assignments of the bands observed in the photoelectron spectra of Ge_3^- and Ge_4^- by Burton, Xu, Arnold, and Neumark [J. Chem. Phys. **104**, 2757 (1996)]. © 1998 American Institute of Physics. [S0021-9606(98)30327-X]

I. INTRODUCTION

Over the past few decades, extensive studies of small semiconductor clusters have been fuelled by technological and purely scientific interests. The structures of small clusters are known to be quite different from that of the bulk material. Consequently, the focus of most studies is towards understanding the changes in structural and electronic properties with increasing cluster size. In this pursuit, clusters of silicon, and to a lesser extent, germanium, have received considerable attention.

Ab initio quantum chemical calculations have been used to determine the geometries, electronic structures, and binding energies of neutral clusters of silicon (Si_n , $n=2-10$) (Refs. 1–24) and germanium (Ge_n , $n=2-7$).^{8,24–36} It has been established that Si_2 and Ge_2 have a $^3\Sigma_g^-$ ground state with a low-lying $^3\Pi_u$ state, while the trimers have a $^1A_1(C_{2v})$ ground state with a low-lying, nearly degenerate, $^3A_2'$ state of D_{3h} symmetry.^{3–6,10,24,35} A 1A_g ground state of D_{2h} symmetry (planar rhombus) has been predicted for Si_4 and Ge_4 ,^{8,9,23,31,34} and the ground states of Si_5 and Ge_5 were found to be $^3A_2'(D_{3h})$ in one study,⁸ but subsequent investigations^{9,36} reassigned their ground states as $^1A_1'$ of D_{3h} symmetry.

For larger clusters where $n \geq 5$, the existence of isomers with nearly identical energies seriously complicates definitive assignment of the most stable structures and the accurate determination of relative stabilities.^{9,16,23} Post-Hartree–Fock methods employing flexible one-particle basis sets are necessary in most cases for reliable calculations of ground state properties and relative energies. Unfortunately, the cluster size limits the use of sophisticated post-SCF methods to optimize and characterize structures as minima or saddle points. Consequently, computation of the geometries and properties of these clusters via *ab initio* quantum chemical

methods requires prudent selection of a theoretical model.

The numerous theoretical calculations on small clusters of silicon and germanium have primarily been on the neutral species, while a significant portion of the experimental data for these systems is obtained from the charged particles. Laser photoelectron spectroscopy of negative ions has particularly been a very useful technique for the determination of the electronic structures of mass-selected clusters.^{37,38} With this technique, a very accurate adiabatic electron affinity can be measured for an individual neutral cluster, and in addition, its low-lying electronic states can be investigated. Following the pioneering work of Smalley and co-workers on the anion photoelectron spectroscopy of Si_n^- and Ge_n^- ($n=3-12$),³⁹ Neumark's group has reported comprehensive studies of mass selected silicon and germanium clusters.^{40–45} Very recently, the group reported the photoelectron and zero electron kinetic energy spectroscopic (ZEKE) studies of Ge_n^- ($n=2-15$).⁴⁶ In that work, the electron affinities of the neutral clusters for $n=2-15$ are measured, the vibrational frequencies for several electronic states of Ge_2 and Ge_3 are determined, and vibrational structure is observed in the ZEKE spectrum for the $^3B_{3u}$ excited state of Ge_4 .⁴⁶ Noticeably, the interpretation of the photoelectron spectra of the germanium anionic clusters is also expedited by previous theoretical calculations on small neutral silicon and germanium clusters. Reports of the photoelectron experiments^{45,46} also expose the scarcity of geometric and electronic structure calculations for the Ge_n^- clusters. Such theoretical data on these anions may accelerate future experimental studies, and one objective of this work is to provide such complimentary data.

In this paper, we present the results of our computational studies on small anionic and neutral clusters of germanium (Ge_n^- and Ge_n , $n=2-6$). An attempt is made to correlate

some of our results with a segment of the data derived from the analysis of experimental photoelectron spectra^{45,46} of Ge_n^- . This study follows the first such investigation on Si_n^- clusters by Raghavachari and co-workers.^{20,22,47} Several studies on small clusters of silicon and germanium have indicated that theoretical methods that account for electron correlation are necessary for computing the properties of these clusters.^{16,32} In this regard, density functional theory (DFT) is perhaps the method of choice as it includes electron correlation at a very low computational cost.⁴⁸ The question then arises as to the appropriateness of DFT methods for studying the low-lying excited states, and also the extent of spin-contamination in the Kohn-Sham determinant for a doublet or a triplet. In fact, a general DFT procedure for treating excited states has not been firmly established. On the other hand, it has been demonstrated that for a given system, the Hohenberg-Kohn theorem⁴⁹ can be generalized to the lowest energy state of each symmetry.^{50–52} Furthermore, spin contamination has been reported to be relatively minimal in DFT,^{53,54} making it attractive for estimating singlet-triplet splittings.^{55,56} In this study, the geometries, harmonic vibrational frequencies, relative energies, and electron affinities have been calculated for Ge_n and Ge_n^- , with $n=2-6$, using gradient-corrected DFT and the coupled cluster method.

II. METHODS

The approach followed in this study is similar to that employed by Bauschlicher in computing the structures, relative energies, and detachment energies of Li_4^- , Li_7^- , and K_7^- .^{57,58} The geometries and vibrational frequencies are computed with B3LYP functional. Using the B3LYP geometries, the relative energies and electron affinities of the clusters are calculated with coupled cluster singles and doubles including a perturbative estimate of triple excitations [CCSD(T)].⁵⁹ The 6-311+G(3df) basis set is used for the dimers and trimers, while the smaller 6-311+G(d) basis is employed for the larger clusters. Two sets of CCSD(T) calculations are performed for the dimers. In one set, only the valence electrons are correlated. We label this as CCSD(T). Calculations in which the 18 lowest molecular orbitals are frozen are labeled as CCSD(T)-F18. In the latter calculations, the d -type orbitals of Ge are included in the correlation window. Only the valence electrons are correlated for clusters with $n \geq 3$. All calculations are performed with GAUSSIAN 94.⁶⁰

III. RESULTS AND DISCUSSION

In order to assess the reliability of the computational models employed in this study, a calibration calculation is performed on the neutral dimer and its anion. The spectroscopic parameters (R_e , ω_e , T_e), adiabatic electron affinity, and binding energy of Ge_2 are well known from experiment and theory.^{28,33,45,46} There are no theoretical reports on Ge_2^- , but there is a comprehensive experimental report on the anion's term energies and vibrational frequencies.^{45,46}

A. Ge_2^- and Ge_2

Experimental work by Neumark and co-workers assigns^{45,46} the ground state of Ge_2^- as $^2\Pi_u(\dots 2\sigma_g^2 1\pi_u^3)$ with

a very low-lying $^2\Sigma_g^+(\dots 2\sigma_g^1 1\pi_u^4)$ excited state ($T_e = 279 \text{ cm}^{-1}$). Two triplet states of Ge_2 , $^3\Sigma_g^-(\dots 2\sigma_g^2 1\pi_u^2)$ and $^3\Pi_u(\dots 2\sigma_g^1 1\pi_u^3)$, can be generated by the removal of an electron from the highest occupied molecular orbital of each of these two anionic states. Several studies have placed the $^3\Pi_u$ state above the $^3\Sigma_g^-$ with T_e ranging from 50 cm^{-1} to 800 cm^{-1} (0.14 kcal/mol–2.29 kcal/mol).^{28–30,32,33}

Table I lists the energies, equilibrium bond lengths (R_e), and harmonic vibrational frequencies (ω_e) for Ge_2 and Ge_2^- calculated at different levels of theory. Consider first the spectroscopic properties of the Ge_2 dimer. The results in Table I confirm a $^3\Sigma_g^-$ ground state for the neutral dimer. The B3LYP functional predicts the ground state to be separated from the low-lying $^3\Pi_u$ excited state by 4.6 kcal/mol. At the CCSD(T) level, the energy separation is only 2.0 kcal/mol, in excellent agreement with the 2.03 kcal/mol value suggested from experiment. The B3LYP equilibrium bond lengths of 2.404 Å and 2.286 Å for the $^3\Sigma_g^-$ ground state and the $^3\Pi_u$ state are, respectively, within 0.005 Å and 0.025 Å of the CCSD(T) values. These bond lengths are also in reasonable agreement with previous calculations that predict R_e values of 2.42–2.46 Å for the $^3\Sigma_g^-$ state, and 2.33 to 2.39 Å for the $^3\Pi_u$ state.^{28–30,32,33} Furthermore, the B3LYP harmonic vibrational frequency of 281 cm^{-1} for the $^3\Sigma_g^-$ ground state compares well with the 277 cm^{-1} value determined from Raman matrix studies,⁶¹ and the 286 cm^{-1} value assigned from the ZEKE spectrum.^{45,46}

The calculations on Ge_2^- suggest two nearly degenerate doublet states as candidates for the ground state. B3LYP predicts the $^2\Pi_u$ state to lie 2.6 kcal/mol below the $^2\Sigma_g^+$ state. Based on the results for Ge_2 , the B3LYP error in the relative energy could easily be as large as 2.5 kcal/mol, meaning that these two states could in fact still be nearly degenerate. Indeed, calculations at the CCSD(T) level predict virtually identical energies for the two states. An important observation is the fact that the CCSD(T)-F18 calculations (with Ge $3d$ orbitals active) predict the adiabatic energy separation between the $^2\Sigma_g^+$ state and the $^2\Pi_u$ states as 0.5 kcal/mol, with the $^2\Sigma_g^+$ as the ground state. This contradicts the experimental results which place the $^2\Sigma_g^+$ above the $^2\Pi_u$ state with $T_e = 279 \pm 10 \text{ cm}^{-1}$ ($\approx 0.8 \text{ kcal/mol}$). It should be noted, however, that the very small energy separation involved prevents unequivocal establishment of the ground state of Ge_2^- with the computational methods employed in this study. It can only be inferred from this work that the $^2\Sigma_g^+$ and the $^2\Pi_u$ low-lying states of Ge_2^- are most likely within 1.0 kcal/mol of each other.

The B3LYP bond lengths for the $^2\Sigma_g^+$ state and the $^2\Pi_u$ state deviate from those computed with CCSD(T) by less than 0.035 Å. Note also that the B3LYP equilibrium bond lengths are within 0.007 Å of the CCSD(T)-F18 values. The present CCSD(T)-F18 calculations on the dimer predict smaller R_e values ($\Delta R_e \approx -0.027 \text{ Å}$) compared to the CCSD(T) frozen core calculations. The B3LYP harmonic vibrational frequencies of 333 cm^{-1} for the $^2\Sigma_g^+$ state and 309 cm^{-1} for the $^2\Pi_u$ state are within 7 wave numbers of the experimental values listed in Table I.

TABLE I. Total energies (a.u.), equilibrium distances (R_e , Å), harmonic vibrational frequencies (ω_e , cm^{-1}), and relative energies (ΔE , kcal/mol) of the lowest-lying states of Ge_2 and Ge_2^- .

| | State | Method | Total energy | R_e | ω_e | ΔE |
|-----------------|----------------|-------------------------|--------------|-------|------------------|------------|
| Ge_2 | $^3\Pi_u$ | SCF | -4150.597239 | 2.268 | 336 | 11.6 |
| | | B3LYP | -4153.959763 | 2.286 | 307 | 4.6 |
| | | CCSD(T) | -4150.795158 | 2.311 | | 2.0 |
| | | CCSD(T)-F18 | -4151.130035 | 2.284 | | 1.6 |
| | | CCSD(T) ^a | -4150.795003 | | | 2.1 |
| | | EXPERIMENT ^b | | | 308 | 2.03 |
| | $^3\Sigma_g^-$ | SCF | -4150.615787 | 2.352 | 325 | 0.0 |
| | | B3LYP | -4153.966963 | 2.404 | 281 | 0.0 |
| | | CCSD(T) | -4150.798401 | 2.409 | | 0.0 |
| | | CCSD(T)-F18 | -4151.132557 | 2.382 | | 0.0 |
| | | CCSD(T) ^a | -4150.798396 | | | 0.0 |
| | | EXPERIMENT | | | 286 ^b | 0.0 |
| Ge_2^- | $^2\Sigma_g^+$ | SCF | -4150.634212 | 2.214 | 358 | 8.7 |
| | | B3LYP | -4154.034063 | 2.226 | 333 | 2.6 |
| | | CCSD(T) | -4150.870365 | 2.260 | | 0.0 |
| | | CCSD(T)-F18 | -4151.206866 | 2.233 | | -0.5 |
| | | CCSD(T) ^a | -4150.870041 | | | 0.1 |
| | | EXPERIMENT ^b | | | 326 | 0.80 |
| | $^2\Pi_u$ | SCF | -4150.648093 | 2.276 | 349 | 0.0 |
| | | B3LYP | -4154.038100 | 2.313 | 307 | 0.0 |
| | | CCSD(T) | -4150.870323 | 2.339 | | 0.0 |
| | | CCSD(T)-F18 | -4151.206142 | 2.312 | | 0.0 |
| | | CCSD(T) ^a | -4150.870165 | | | 0.0 |
| | | EXPERIMENT ^b | | | 309 | |
| | | | | | 277 ^c | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
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| | | | | | | |

^aComputed at the B3LYP/6-311+G(3df) geometry.^bReference 45.^cReference 61.

A few heartening results emerge from the results presented in Table I. The CCSD(T) relative energies computed using B3LYP bond lengths [CCSD(T)//B3LYP] are within 0.1 kcal/mol of those calculated with CCSD(T) bond lengths [CCSD(T)//CCSD(T)]. The electron affinity of Ge_2 calculated at the CCSD(T)//B3LYP level is 1.95 eV, in good agreement with the CCSD(T) value of 1.96 eV, and the experimental electron affinity of 2.035 eV. In addition, the dissociation energy of Ge_2 ($D_e = 61.9$ kcal/mol; $D_0 = 61.5$ kcal/mol using the B3LYP zero-point energy) computed at the CCSD(T)//B3LYP level is identical to the CCSD(T) prediction, and in good agreement with the experimental result ($D_0^0 = 62.2 \pm 1.7$ kcal/mol) of Kingcade *et al.*²⁸ The agreement between the CCSD(T)//B3LYP and the pure CCSD(T) results is very encouraging and justifies the use of B3LYP geometries in computing CCSD(T) energies for the larger clusters.

B. Ge_3^- and Ge_3

To date, the most comprehensive computational studies on Ge_3 are those reported by Dixon and Gole²⁴ and by Balasubramanian and co-workers.³⁵ In the latter work, the potential energy surfaces of eight electronic states of Ge_3 were investigated using multiconfigurational methods, but vibrational frequencies were not reported. Dixon and Gole studied²⁴ only two states (the 1A_1 state with C_{2v} symmetry and a $^3A_2'$ state with D_{3h} symmetry) within the local density functional approximation and also computed the harmonic

vibrational frequencies. These previous theoretical studies suggest a $^1A_1(C_{2v})$ ground state, with a very low-lying $^3A_2'$ state (D_{3h}) within 1–5 kcal/mol above.

Our results in Table II confirm the $\dots(a_1)^2(b_2)^2(a_1)^2(b_1)^2(b_2)^2(a_1)^0$ (1A_1) state (C_{2v} symmetry) and the $\dots(a_1')^2(e')^4(a_1')^2(a_2')^2(e')^2$ ($^3A_2'$) state (D_{3h} symmetry) to be the lowest states of Ge_3 , with the 1A_1

TABLE II. Total energies (a.u.), geometries (Å, deg), and relative energies (ΔE , eV) of Ge_3 and Ge_3^- .

| | State | B3LYP/6-311+G(3df) | | CCSD(T)/6-311+G(3df) ^a | |
|-----------------|----------------|--------------------|------------------|-----------------------------------|--------------|
| | | R (1-2) | θ (2-1-3) | Total energy | ΔE^b |
| Ge_3 | 3A_2 | 2.650 | 55.2 | -6226.239776 | 0.92 (3.07) |
| | 3B_1 | 2.493 | 67.8 | -6226.240722 | 0.89 (3.05) |
| | 3A_1 | 2.424 | 65.7 | -6226.243383 | 0.82 (2.97) |
| | $^1\Sigma_g^+$ | 2.280 | 180. | -6226.255193 | 0.50 (2.65) |
| | 1B_2 | 2.483 | 58.3 | -6226.265042 | 0.23 (2.38) |
| | $^3A_2'$ | 2.465 | 60.0 | -6226.272291 | 0.04 (2.19) |
| | 1A_1 | 2.312 | 83.2 | -6226.273583 | 0.00 (2.15) |
| Ge_3^- | 4A_2 | 2.635 | 53.4 | -6226.303678 | (1.33) |
| | $^2A_1'$ | 2.490 | 60.0 | -6226.312662 | (1.09) |
| | $^2\Pi_g$ | 2.299 | 180. | -6226.321844 | (0.84) |
| | 2B_2 | 2.522 | 56.2 | -6226.351854 | (0.02) |
| | 2A_1 | 2.407 | 66.0 | -6226.352682 | (0.00) |

^aComputed at the B3LYP/6-311+G(3df) geometries.^bIn the photoelectron spectra of Ge_3^- , at least five bands are observed with origins at binding energies of 2.23, 2.44, 3.04, 3.2 and 3.83 eV. The electron affinity of Ge_3 is determined to be 2.23 ± 0.010 eV (see Ref. 46).

state appearing to be slightly more stable by less than 1 kcal/mol. Again, like the dimers discussed above, the small energy separation between the two lowest-lying states of Ge_3 is within the margin of error of the theoretical methods employed in this study. Consequently, and in accord with past studies,³⁵ unambiguous determination of the ground state of Ge_3 is a formidable task. It can only be concluded that the 1A_1 state (C_{2v}) and the $^3A'_2$ state (D_{3h}) are nearly degenerate, and both are likely candidates for the ground state.

A few comments need to be made concerning the present results for Ge_3 and the previous ones. First, an impressive testimonial for the relatively computationally inexpensive DFT method is that B3LYP geometries for the lowest 1A_1 (C_{2v}) and the $^3A'_2$ (D_{3h}) states are in very good agreement with the multireference singles+doubles configuration interaction results of Dai and Balasubramanian.³⁵ The difference is less than 0.02 Å for bond lengths and 0.2° for the included bond angle in the C_{2v} structure. However, the relative energies and the energy ordering computed at the CCSD(T)/B3LYP level for the 3A_1 , 3B_1 and 3A_2 electronic states are slightly different from their results. The present ordering of the electronic states places the 3A_1 state below the 3B_1 and 3A_2 states with an energy separation in the 0.1 eV range. Their study places the 3A_1 state above the 3B_1 and 3A_2 states.³⁵ The latter assignment may be correct when taking into consideration the small energy separations between these states, and the excellent reputation of multiconfigurational methods in dealing with such problems. Nevertheless, as will be discussed below, the CCSD(T) ordering of the 3B_1 and 3A_2 states relative to the lowest 1A_1 (C_{2v}) state appears to agree better with experiment. We note also that B3LYP harmonic vibrational frequencies for the lowest states are within 15 cm^{-1} of those computed by Dixon and Gole.²⁴

There are no reports of computational studies on Ge_3^- . Table II lists the energies and geometries for this anion. The harmonic vibrational frequencies are included in Table III. The anion has a $...(a_1)^2(b_2)^2(a_1)^2(a_1)^2(b_1)^2(b_2)^2(a_1)^1$ (2A_1) ground state with C_{2v} symmetry. The geometry of the anion 2A_1 ground state ($\text{Ge1}-\text{Ge2}=2.407$ Å, $\text{Ge1}-\text{Ge2}-\text{Ge3}=66.0^\circ$) is noticeably different from the neutral C_{2v} 1A_1 structure ($\text{Ge1}-\text{Ge2}=2.312$ Å, $\text{Ge1}-\text{Ge2}-\text{Ge3}=83.2^\circ$) of Ge_3 , but is closer to the D_{3h} $^3A'_2$ geometry ($\text{Ge1}-\text{Ge2}=2.465$ Å). This difference in geometries could be useful in interpreting the photoelectron spectra of Ge_3^- . Three other stationary points were located on the potential energy surface of the anion. An acute-triangle 2B_2 (C_{2v}) transition state for pseudorotation is 0.52 kcal/mol (≈ 0.02 eV) above the anion 2A_1 ground state. The linear ($^2\Pi_g, D_{\infty h}$) structure is a minimum at 0.84 eV above, and the equilateral ($^2A'_1, D_{3h}$) structure, also a local minimum, lies 1.09 eV higher in energy.

Recently, Neumark and co-workers reported⁴⁶ the photoelectron spectra of Ge_3^- . Six bands labeled X and A–E have been assigned to one-electron photodetachment transitions from the anion ground state to various electronic states of neutral Ge_3 . The authors⁴⁶ indicate that the photoelectron spectrum shows significant overlap of the (X,A) bands, suggesting two overlapping electronic transitions. Vibrational progressions are also observed for the (X,A), B, and E

TABLE III. Harmonic vibrational frequencies $\omega_e(\text{cm}^{-1})$ of Ge_3 and Ge_3^- and calculated isotopic shifts at the B3LYP/6-311+G(3df) level.

| | Symmetry | State | Vibrational frequencies (mode) | Isotopomer | Isotopic shift |
|-----------------|----------|-------------|--|------------|----------------|
| Ge_3 | C_{2v} | 1A_1 | 99 (a_1) | | |
| | | | 299 (a_1) | 74-74-74 | 0.0 |
| | | | | 72-72-72 | +4.1 |
| | | | | 70-70-70 | +8.5 |
| | | | | 74-72-74 | +2.1 |
| | | | | 74-74-72 | +0.6 |
| | | | | 74-70-74 | +4.2 |
| | | | | 74-74-70 | +0.7 |
| | | $301 (b_2)$ | | 74-74-74 | 0.0 |
| | | | | 74-72-74 | +1.9 |
| | | | | 74-74-72 | +1.6 |
| | | | | 74-70-74 | +4.0 |
| | | | | 74-74-70 | +3.7 |
| | D_{3h} | $^3A'_2$ | 171 (e') | 74-74-74 | 0.0 |
| | | | | 72-72-72 | +2.3 |
| | | | | 70-70-70 | +4.8 |
| | | | | 72-74-74 | +0.8 |
| | | | | 70-74-74 | +1.6 |
| Ge_3^- | C_{2v} | 3A_1 | 275 (a'_1) | | |
| | | | 158(a_1)220(b_2)282(a_1) | | |
| | | | 140(a_1)168(b_1)267(a_1) | | |
| | | | 136i(b_2)189(a_1)268(a_1) | | |
| | | | 3(π_u)224(σ_g)391(σ_u) | | |
| | D_{3h} | $^2\Pi_g$ | 155(a_1)165(b_2)284(a_1) | | |
| | | | 150i(b_2)212(a_1)291(a_1) | | |
| | | | 211(e')275(a'_1) | | |
| | | | (34,54)(π_u)213(σ_g)327(σ_u) | | |
| | | | | | |

bands with frequencies of 150 cm^{-1} , 355 cm^{-1} , and 266 cm^{-1} respectively. Assuming a $^3A'_2$ ground state for Ge_3 , the electron affinity (EA) given by the origin of the (X,A) band was determined as 2.23 ± 0.010 eV.

The correlation between the CCSD(T) excitation energies in Table II and the corresponding experimental values⁴⁶ is reasonable. First, recall the ground state (2A_1) of Ge_3^- has the valence electron configuration $...(a_1)^2(b_2)^2(a_1)^2(a_1)^2(b_1)^2(b_2)^2(a_1)^1$. Formation of the neutral 1A_1 (C_{2v}) ground state involves removal of the single electron from the highest occupied molecular orbital (a_1) of the anion, while removal of an electron from the occupied b_2 , b_1 , and a_1 orbitals immediately below the HOMO results in triplet and singlet combinations of the B_2 , B_1 and A_1 excited states, respectively. The CCSD(T) calculations place the 1B_2 , 3A_1 , and 3B_1 states 0.23 (0.19) eV, 0.82 (0.78) eV, and 0.89 (0.85) eV, respectively, above the 1A_1 ground state of Ge_3 (the values in parentheses are with respect to the neutral $^3A'_2$ state). The B–E bands were assigned by Neumark and co-workers⁴⁶ to the 1B_2 , 3A_1 , 3B_1 , and 1B_1 states lying 0.21 eV, 0.81 eV, 1.00 eV, and 1.69 eV, respectively, above the $^3A'_2$ state.⁴⁶ It is noteworthy that the computed energy ordering is in accord with experimental data. The calculated excitation energies for the 1B_2 (B) and 3A_1 (C) states are also in good agreement with those obtained from the photoelectron experiments.⁴⁶ Furthermore, the experimental observation that photoelectron spectrum of Ge_3^- shows a very sharp peak for the C (3A_1) band⁴⁶ is consistent with the similarity in the calculated geometries of

the latter state and that of the anion 1A_1 C_{2v} ground state (see Table II). In the case of the 3B_1 state, the calculated excitation energy differs from the experimental counterpart by 0.11 eV. Overall the relative electronic energies and the calculated energy ordering of the states appear to be in agreement with experiment. Additionally, the ω_2 (e') harmonic vibrational frequency computed at 171 cm^{-1} (not scaled) for the $^3A_2'$ (D_{3h}) state is in reasonable agreement with the observed spacing of 150 cm^{-1} in the (X,A) band.⁴⁶ For future studies, computed isotopic frequency shifts relative to the 171 cm^{-1} (e') band of the 74-74-74 isotopomer are listed in Table III. The table also contains isotopic shifts relative to the calculated 299 cm^{-1} (a_1) and 301 cm^{-1} (b_2) bands of the 74-74-74 isotopomer for the 1A_1 (C_{2v}) state of Ge_3 .

C. Ge_4^- and Ge_4

Previous computational studies on Ge_4 found the most stable structure to be a planar rhombus (1A_g) with D_{2h} symmetry.^{31,34} In addition, Dai and Balasubramanian computed vertical energy separations of several electronic states with the rhombus (D_{2h}) and linear ($D_{\infty h}$) geometries.³⁴ None of the earlier work determined the vibrational frequencies of the Ge_4 structures, and characterization of the species as minima, transition states, or higher order critical points still remains.

Experimentally, the photoelectron spectrum of Ge_4^- obtained by Burton *et al.*⁴⁶ shows three bands at 2.0 eV, 2.8 eV, and 3.7 eV, corresponding to transitions to various electronic states of Ge_4 . The measured electron affinity of the Ge_4 ground state is 1.94 ± 0.05 eV, and the data suggest that two excited states lie 0.8 eV and 1.7 eV above the ground state of Ge_4 . Though the 2.8 eV band is quite broad, the authors⁴⁶ were able to observe vibrational structure with a characteristic frequency of 173 cm^{-1} in the ZEKE spectrum.

In the present study, all of the geometries of Ge_4 shown in Fig. 1, including those of the low-lying triplet states are fully optimized, and the nature of the stationary points characterized via their Hessian indices. The geometrical parameters are presented in Table IV and the harmonic vibrational frequencies are listed in Table V. Note that computed vibrational frequencies listed in Table V are not scaled. For the rhomboidal structure (molecular plane is the yz plane), the 1A_g (D_{2h}) and the $^3B_{3u}$ (D_{2h}) states are minima. The 1A_g (D_{2h}) is found to be the ground state of Ge_4 , with the $^3B_{3u}$ (D_{2h}) state lying 0.83 eV above. The square (D_{4h} , $^3A_{1g}$) structure located 1.51 eV above the 1A_g (D_{2h}) state is a transition state with an imaginary frequency of $177i\text{ cm}^{-1}$ (b_{2u}). Following the eigenvector for this imaginary frequency leads to a distorted-tetrahedron (D_{2d} , 3A_2) structure lying 0.80 eV above the 1A_g (D_{2h}) ground state. Other minima located above the ground state are the following: a planar (C_{2h} , 3B_g) structure at 1.43 eV, a C_2 (3B) structure at 1.44 eV, and a tetrahedron (T_d , 1A_1) at 1.76 eV. It should be noted that the C_{2h} (3B_g) and the C_2 (3B) structures mentioned above are obtained via geometric distortion of the rhombus D_{2h} ($^3B_{2g}$) and D_{2h} ($^3B_{1u}$) structures respectively. The optimized geometry of the Y-shape (C_{2v} , 3B_1) structure possesses one imaginary frequency at $49i\text{ cm}^{-1}$ (b_2). Fol-

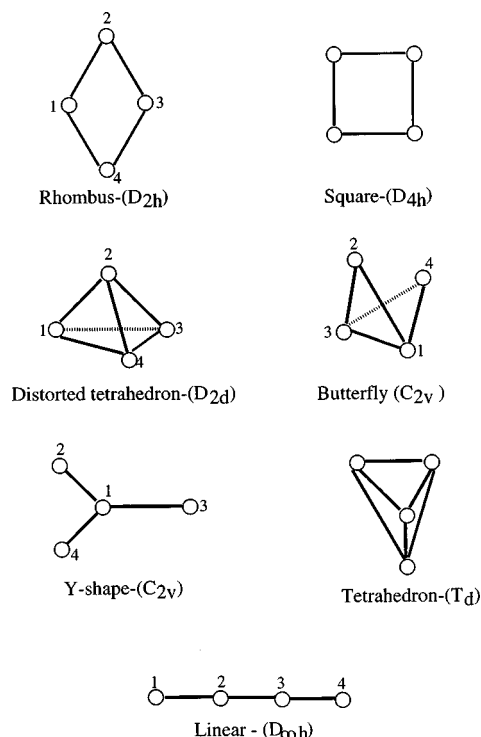


FIG. 1. Structures of Ge_4 and Ge_4^- investigated in this work. Optimized geometrical parameters are listed in Table III.

lowing this mode leads to the rhombus (D_{2h} , $^3B_{3u}$) structure discussed above.

There are some differences in the CCSD(T) energy separations listed in Table IV and the CASSCF vertical energy separations computed in earlier studies.³⁴ These computed relative energies are obviously important for the correct interpretation of the photoelectron spectra of the anions. Previously, a vertical excitation energy of 1.41 eV was estimated³⁴ for the $^3B_{3u}$ (D_{2h}) state. In this work, the $^3B_{3u}$ (D_{2h}) state is located 0.83 eV above the 1A_g (D_{2h}) ground state, in good agreement with the interpretation of the photoelectron spectrum⁴⁶ of Ge_4^- placing the $^3B_{3u}$ state of neutral Ge_4 0.8 eV above the 1A_g ground state (see discussion below). Additionally, the present calculations place the $^3B_{2g}$ (D_{2h}) state 0.18 eV lower in energy than the $^3B_{1u}$ (D_{2h}) state, whereas earlier studies³⁴ suggest the latter to be lower in energy by 0.33 eV.

The lowest energy structure determined for Ge_4^- in this study is a planar rhombus with D_{2h} symmetry (see Table IV). The geometry of the $^2B_{2g}$ [$\dots(a_g)^2(b_{1u})^2(b_{2u})^2(a_g)^2(b_{3g})^2(b_{3u})^2(a_g)^2(b_{1u})^2(b_{2g})^1; D_{2h}$] ground state of Ge_4^- closely resembles that of neutral Ge_4 which is formed by the removal of an electron from the highest occupied b_{2g} orbital of the anion. Compared to neutral Ge_4 (1A_g), each of the four equal sides (e.g., $\text{Ge1}-\text{Ge2}$) of the rhombic Ge_4^- ($^2B_{2g}$) is 0.01 Å longer, the $\text{Ge1}-\text{Ge3}$ short diagonal is 0.06 Å shorter, and the acute $\text{Ge1}-\text{Ge2}-\text{Ge3}$ angle is 2° smaller. At 0.28 eV above the $^2B_{2g}$ (D_{2h}) ground state lies the 2B_2 (C_{2v}) state with a butterfly structure. Vibrational frequency analysis indicates that this butterfly (C_{2v}) structure of the anion is a minimum. Another rhombic D_{2h} ($^2B_{1g}$) structure with geometrical parameters very close to that of the butter-

TABLE IV. Total energies (a.u.), geometries (Å, deg), relative energies (ΔE , eV) of Ge_4 and Ge_4^- .

| | Point group/(geometry) | State | B3LYP/6-311+G(d) | | | CCSD(T)/6-311+G(d) ^a | | H.I. ^c |
|-----------------|----------------------------------|----------------|------------------|----------------|------------------|---------------------------------|--------------|-------------------|
| | | | <i>R</i> (1-2) | <i>R</i> (1-3) | θ (1-2-3) | Total energy | ΔE^b | |
| Ge_4 | $D_{\infty h}$ (linear) | $^3\Sigma_g^-$ | 2.306 | 4.580 | | -8301.592 047 | 2.70 (4.50) | 2 |
| | D_{2h} (rhombus) | $^3B_{1g}$ | 2.505 | 2.685 | 64.8 | -8301.609 706 | 2.22 (4.02) | 0 |
| | C_{2v} (Y-shape) | 3B_1 | 2.447 | 2.337 | 149.2 | -8301.621 950 | 1.89 (3.69) | 1 |
| | T_d (tetrahedron) | 1A_1 | 2.668 | | | -8301.626 576 | 1.76 (3.56) | 0 |
| | D_{2h} (rhombus) | $^3B_{1u}$ | 2.568 | 2.668 | 62.6 | -8301.628 364 | 1.71 (3.51) | 1 |
| | C_{2v} (Y-shape) | 1A_1 | 2.468 | 2.300 | | -8301.630 625 | 1.65 (3.45) | 2 |
| | D_{2h} (rhombus) | $^3B_{2g}$ | 2.532 | 2.442 | 57.7 | -8301.635 220 | 1.53 (3.33) | 1 |
| | D_{4h} (square) | $^3A_{1g}$ | 2.475 | | | -8301.636 214 | 1.51 (3.30) | 1 |
| | C_2 (butterfly) ^d | 3B | 2.460 | 2.678 | 63.8 | -8301.638 352 | 1.44 (3.24) | 0 |
| | C_{2h} (parallelogram) | $^3B'_g$ | 2.415 | 2.465 | 57.3 | -8301.638 764 | 1.43 (3.23) | 0 |
| | D_{2h} (rhombus) | $^3B_{3u}$ | 2.443 | 2.770 | 69.1 | -8301.660 684 | 0.83 (2.63) | 0 |
| | D_{2d} (distorted tetrahedron) | 3A_2 | 2.444 | 3.265 | 83.8 | -8301.661 860 | 0.80 (2.60) | 0 |
| | D_{2h} (rhombus) | 1A_g | 2.475 | 2.619 | 63.9 | -8301.691 354 | 0.00 (1.80) | 0 |
| Ge_4^- | $D_{\infty h}$ (linear) | $^2\Pi_g$ | 2.260 | 4.594 | | -8301.678 465 | (2.15) | 0 |
| | C_{2v} (Y-shape) | 2B_1 | 2.488 | 2.311 | 150.8 | -8301.714 539 | (1.17) | 1 |
| | D_{2d} (distorted tetrahedron) | 2B_1 | 2.542 | 2.901 | 69.6 | -8301.720 824 | (1.00) | 0 |
| | D_{2h} (rhombus) | $^2B_{1g}$ | 2.472 | 2.843 | 70.2 | -8301.723 084 | (0.94) | 1 |
| | C_{2v} (butterfly) | 2B_2 | 2.469 | 2.844 | 70.3 | -8301.747 251 | (0.28) | 0 |
| | D_{2h} (rhombus) | $^2B_{2g}$ | 2.485 | 2.556 | 61.9 | -8301.757 504 | (0.00) | 0 |

^aComputed at the B3LYP/6-311+G(d) geometries.^bIn the photoelectron spectra of Ge_4^- , at least three distinct bands are observed at binding energies of 2.0, 2.8, 3.7 eV (see Ref. 46).^cHessian index (H.I.)-the number of imaginary vibrational frequencies.^d $R(1-4) = 1.618 \text{ \AA}$.

fly (C_{2v}) form is located 0.98 eV above the $^2B_{2g}$ ground state of Ge_4^- . The D_{2h} ($^2B_{1g}$) structure has one imaginary frequency corresponding to an out-of-plane bending (butterfly) motion. This planar transition state structure connects two equivalent forms of the puckered C_{2v} (2B_2) structure. The barrier to this interconversion is 0.7 eV (16 kcal/mol). The distorted tetrahedron (D_{2d} , 2B_1) is a minimum lying 1.0 eV above the ground state, and the optimized geometry of the Y-shape (C_{2v} , 2B_1) structure has one imaginary frequency and collapses to the D_{2h} ($^2B_{2g}$) structure upon distortion.

Experimental vibrational frequency data for the ground states of Ge_4 (1A_g) and Ge_4^- ($^2B_{2g}$) have not been reported. However, in their ZEKE spectrum of Ge_4^- , Burton *et al.*⁴⁶ observed that the band at 2.8 eV [Fig. 3(b) of Ref. 46] shows vibrational progression with a characteristic frequency of 173 cm^{-1} . Our results listed in Table V indicate that the B3LYP harmonic vibrational frequency at 168 cm^{-1} [$\omega_2(a_g)$] for the $^3B_{3u}$ (D_{2h}) state of neutral Ge_4 , though slightly lower, is in accord with the 173 cm^{-1} progression observed in the ZEKE spectrum. Note that the $^3B_{3u}$ state results from the removal of an electron from the in plane bonding b_{1u} molecular orbital [essentially located on Ge1–Ge3 (see Fig. 1)] of the anion ground state. The broad feature observed in the ZEKE spectrum is consistent with a pronounced geometry change between the neutral $^3B_{3u}$ (D_{2h}) state and the ground $^2B_{2g}$ (D_{2h}) state of the anion. The results in Table IV show that the Ge1–Ge3 distance and the Ge1–Ge2–Ge3 bond angle in the $^2B_{2g}$ ground state of Ge_4^- are 0.214 \AA and 7.2° larger in the $^3B_{3u}$ state of Ge_4 . Consequently, the $\omega_2(a_g)$ frequency in the $^3B_{3u}$ state is lowered compared to the 191 cm^{-1} value computed for the anion. For the purpose of

future experimental studies on this cluster, Table V contains harmonic vibrational frequencies for the neutral 1A_g (D_{2h}) ground state, including isotopic frequency shifts. These shifts are computed relative to the 282 cm^{-1} (b_{1u}) band (which has the highest intensity) of the 74-74-74-74 isotopomer.

D. Ge_n^- and Ge_n , $n=5,6$

The results of geometry optimizations at the B3LYP/6-311+G(d) level, and CCSD//B3LYP energies for the germanium pentamer and its anion are presented in Table VI. The B3LYP harmonic vibrational frequencies (not scaled) are listed in Table VII for all the structures considered. Each of the two previous studies^{8,36} on the neutral germanium pentamer predict a different ground state for Ge_5 . An earlier *ab initio* pseudopotential configuration interaction (CI) calculation⁸ suggests a $^3A'_2$ (D_{3h}) ground state, while a recent multiconfiguration self-consistent-field calculation³⁶ predicts a $^1A'_1$ (D_{3h}) ground state with the $^3A'_2$ (D_{3h}) state lying 1.2 eV above. Qualitatively, the latter result is in accord with ours. Using CCSD//B3LYP with 6-311+G(d) basis set, we find the $^1A'_1$ (D_{3h}) state 1.88 eV below the $^3A'_2$ (D_{3h}) state, as indicated in Table VI. Both states are found to be minima at the B3LYP/6-311+G(d) level. Other structures considered for Ge_5 are presented in Fig. 2. The bipyramid (C_{2v} , 3B_1) structure and the trapezoidal structure (C_{2v} , 1A_1) are 0.7 eV and 1.36 eV, respectively, above the trigonal bipyramid (D_{3h} , $^1A'_1$) ground state structure. The square pyramid (C_{4v} , 1A_1) with a relative energy of 1.05 eV is a transition state, and distortion of this geometry leads to the stable D_{3h} ($^1A'_1$) structure.

Our calculations predict a $^2A''_2$ (D_{3h}) ground state for

TABLE V. Harmonic vibrational frequencies $\omega_e(\text{cm}^{-1})$ of Ge_4 and Ge_4^- , and the calculated isotopic shifts (cm^{-1}) at the B3LYP/6-311+G(d) level.

| | Symmetry | State | Vibrational frequencies | ZPE | Isotopomers | Mode | Isotopic shift |
|-----------------|----------------|----------------|---|------|-------------|----------|----------------|
| Ge_4 | D_{2h} | 1A_g | 55(b_{3u})125(b_{2u})188(a_g) | 1.64 | 74-74-74-74 | b_{1u} | 0.0 |
| | | | 237(b_{3g})262(a_g)282(b_{1u}) | | 72-72-72-72 | | +3.9 |
| | | | | | 70-70-70-70 | | +8.0 |
| | | | | | 72-74-74-74 | | +1.0 |
| | | | | | 74-72-74-74 | | +1.0 |
| | | | | | 70-74-74-74 | | +2.1 |
| | | | | | 74-70-74-74 | | +2.2 |
| | D_{2h} | $^3B_{3u}$ | 93(b_{3u})153(b_{2u})168(a_g) | 1.54 | | | |
| | | | 181(b_{3g})233(b_{1u})254(a_g) | | | | |
| | D_{2h} | $^3B_{2g}$ | 945i(b_{3g})56(b_{3u})129(b_{2u}) | 1.36 | | | |
| | | | 189(a_g)265(a_g)313(b_{1u}) | | | | |
| | D_{2h} | $^3B_{1u}$ | 125i(b_{3u})63(b_{3g})110(b_{2u}) | 1.16 | | | |
| | | | 174(a_g)231(b_{1u})236(a_g) | | | | |
| | D_{2h} | $^3B_{1g}$ | 122(b_{2u})175(a_g)191(b_{3u}) | 1.78 | | | |
| | | | 240(a_g)256(b_{1u})264(b_{3g}) | | | | |
| | D_{2d} | 3A_1 | 97(a_1)110(b_2)208(e) | 1.40 | | | |
| | | | 209(b_1)260(a_1) | | | | |
| | C_{2h} | 3B_g | 53(a_u)89(b_u)143(a_g) | 1.31 | | | |
| | | | 200(a_g)226(b_u)268(a_g) | | | | |
| | C_2 | 3B | 53(a)117(a)143(b) | 1.10 | | | |
| | | | 166(a)221(b)250(a) | | | | |
| | D_{4h} | $^3A_{1g}$ | 177i(b_{2u})113(b_{1g})210(e_u) | 1.45 | | | |
| | | | 238(a_{1g})254(b_{2g}) | | | | |
| | C_{2v} | 1A_1 | 49i(b_2)20i(b_1)158(a_1) | 1.31 | | | |
| | | | 170(b_2)239(a_1)347(a_1) | | | | |
| | C_{2v} | 3B_1 | 49i(b_2)47(b_2)48(b_1) | 1.10 | | | |
| | | | 141(a_1)210(a_1)323(a_1) | | | | |
| | T_d | 1A_1 | 119(e)175(t_2)249(a_1) | 1.45 | | | |
| | $D_{\infty h}$ | $^3\Sigma_g^-$ | 37(π_u)31(π_g)276(σ_u) | 1.35 | | | |
| | | | 381(σ_g) | | | | |
| Ge_4^- | D_{2h} | $^2B_{2g}$ | 81(b_{3u})126(b_{2u})170(b_{3g}) | 1.54 | | | |
| | | | 191(a_g)247(b_{1u})263(a_g) | | | | |
| | D_{2h} | $^2B_{1g}$ | 233i(b_{3u})128(b_{2u})170(a_g) | 1.61 | | | |
| | | | 248(a_g)276(b_{1u})302(b_{3g}) | | | | |
| | C_{2v} | 2B_2 | 85(a_1)142(a_1)173(a_2) | 1.56 | | | |
| | | | 175(b_2)257(b_1)260(a_1) | | | | |
| Ge_4^- | D_{2d} | 2B_1 | 96(b_1)115(a_1)134(b_2) | 1.85 | | | |
| | | | 259(a_1)344(e) | | | | |
| | C_{2v} | 2B_1 | 31i(b_2)56(b_1)155(a_1) | 1.35 | | | |
| | | | 164(b_2)250(a_1)319(a_1) | | | | |

Ge_5^- , with a 2B_2 (C_{2v}) state (also a minimum) 0.44 eV above. The results in Table VI show that the geometry of the $^2A_2''$ (D_{3h}) ground state of the anion is significantly different from that of the neutral $^1A_1'$ (D_{3h}) state. For example, the Ge1–Ge4 distance in the anion is about 0.03 Å longer than in the neutral system, and the three Ge–Ge (e.g., Ge1–Ge2) distances in the Ge1–Ge2–Ge3 (equatorial) plane are shorter by roughly 0.34 Å in the anion.

Definitive determination of the most stable structure of the Ge_6 cluster is a difficult task. Preliminary calculations at the B3LYP/6-31+G(d) level reveal that the potential energy surface of the hexamer is very shallow. Among several structures optimized at the B3LYP/6-31+G(d) level, the edge-capped trigonal bipyramid C_{2v} (1A_1) and the square bipyramid D_{4h} ($^1A_{1g}$) structures (see Fig. 2) appear to have the lowest energy. It should be pointed out that Pacchioni and Koutecky find a 1A_1 (C_{2v}) ground state for Ge_6 ,⁸ and

Raghavachari's work suggests a $^1A_{1g}$ (D_{4h}) ground state for Si_6 .⁶² However, the face-capped trigonal bipyramid (C_{2v}) structure located by Pacchioni and Koutecky for Ge_6 turned out to be a transition state at the B3LYP/6-311+G(d) level in this work. Further optimization at the B3LYP/6-311+G(d) level does not introduce a significant energy separation between the edge-capped trigonal bipyramid C_{2v} (1A_1) and the square bipyramid D_{4h} ($^1A_{1g}$) structures. However, the edge-capped trigonal bipyramid structure is a genuine minimum whereas the optimized geometry of the square bipyramid structure possesses one doubly degenerate imaginary frequency ($20i \text{ cm}^{-1}$, e_u) as shown in Table IX. It should be noted that the energy difference between the C_{2v} and D_{4h} structures is less than the computed zero point vibrational energy (2.8 kcal/mol) of the former. The D_{4h} structure is further stabilized at the CCSD/6-311+G(d) level [CCSD/B3LYP], and the energy

TABLE VI. Total energies (a.u.), geometries (Å, deg), and relative energies (ΔE , eV) of Ge_5 and Ge_5^- .

| | Point group/(geometry) | State | B3LYP/6-311+G(d) | | | | CCSD/6-311+G(d) ^a | |
|-----------------|-------------------------------|-----------|------------------|---------|---------|---------|------------------------------|-------------|
| | | | R (1-2) | R (2-3) | R (1-4) | R (4-5) | Total energy | ΔE |
| Ge_5 | T_d (tetrahedron) | 1A_1 | 2.369 | | | | -10376.907901 | 5.35 (7.45) |
| | D_{3h} (trigonal bipyramid) | $^3A_2''$ | 3.028 | | 2.545 | 3.698 | -10377.035157 | 1.88 (3.98) |
| | C_{2v} (trapezoid) | 1A_1 | 2.585 | 2.385 | 2.559 | | -10377.054472 | 1.36 (3.46) |
| | C_{4v} (square pyramid) | 1A_1 | 2.468 | | | 2.707 | -10377.065680 | 1.05 (3.15) |
| | C_{2v} (bipyramid) | 3B_1 | 2.863 | 3.052 | 2.440 | 3.135 | -10377.078571 | 0.70 (2.80) |
| | D_{3h} (trigonal bipyramid) | 1A_1 | 3.320 | | 2.476 | 3.135 | -10377.104429 | 0.00 (2.10) |
| Ge_5^- | C_{2v} (bipyramid) | 2B_2 | 2.526 | 2.953 | 3.137 | 3.938 | -10377.165438 | (0.44) |
| | D_{3h} (trigonal bipyramid) | $^2A_2''$ | 2.976 | | 2.509 | | -10377.181581 | (0.00) |

^aComputed at the B3LYP/6-311+G(d) geometries.

separation is lowered below 0.05 kcal/mol. The flatness and the congestion in the potential energy surface of Ge_6 probably requires more extensive studies and even more reliable theoretical methods. Such a project is beyond the resources currently available to us. The most stable triplet found in this work is the $^3A_{1g}$ (D_{4h}) state. This state is predicted to be 0.67 eV above the 1A_1 (C_{2v}) state at the B3LYP/6-311+G(d). The most stable structure found for Ge_6^- is the square bipyramid D_{4h} ($^2A_{2u}$). The geometrical parameters for Ge_6^- are listed in Table VIII and the harmonic frequencies for the anion are included in Table IX.

E. Electron affinities

The computed vertical electron detachment energies (VEDE) of the anions and adiabatic electron affinities (AEA) of the neutral clusters are presented in Table X. The table also includes electron affinities obtained from photoelectron

experiments. The VEDE correspond to transitions from the ground electronic state of the anion to the identical geometry in the neutral molecule ground electronic state.

The results in Table X indicate that there is good agreement between the electron affinities computed by the B3LYP-DFT and CCSD(T) methods. A slight discrepancy between the two methods occurs for the tetramers where the computed detachment energies differ by as much as 0.14 eV. The AEA calculated for clusters with $n=2, 3, 4, 6$ also compare very well with the experimental values.^{46,63} In case of Ge_3 , there are two low lying, nearly degenerate, 1A_1 (C_{2v}) and $^3A_2'$ (D_{3h}) states within 1 kcal/mol of each other. The AEA calculated for the 1A_1 (C_{2v}) ground state (2A_1 $C_{2v} \rightarrow ^1A_1$ C_{2v}) is 2.15 eV at the CCSD(T) level. The B3LYP value is higher by 0.02 eV. These computed values are within 0.08 eV of the experimental value of 2.23 ± 0.01 eV, which assumes a $^3A_2'$ (D_{3h}) ground state for

TABLE VII. Harmonic vibrational frequencies $\omega_e(\text{cm}^{-1})$ of Ge_5 and Ge_5^- , and the isotopic shifts (cm^{-1}) at the B3LYP/6-311+G(d) level.

| | Point group | State | Vibrational frequencies | ZPE | Isotopomers | Frequency (mode) | Isotopic shift |
|-----------------|-------------|-----------|---|------|----------------|------------------|----------------|
| Ge_5 | D_{3h} | 1A_1 | 99(e')133(a_1')188(e'') | 2.41 | 74-74-74-74-74 | 211(a_2'') | 0.0 |
| | | | 211(a_2'')250(e')265(a_1') | | 72-72-72-72-72 | | 2.9 |
| | | | | | 70-70-70-70-70 | | 5.9 |
| | | 3B_1 | 56(b_2)88(a_1)132(b_2) | 2.05 | 74-74-74-74-74 | 250(e') | 0.0 |
| | | | 136(a_2)153(b_1)164(a_1) | | 72-72-72-72-72 | | 3.5 |
| | | | 190(a_1)257(a_1)257(b_1) | | 70-70-70-70-70 | | 7.0 |
| | C_{2v} | 1A_1 | 173(i)120(b_2)129(e) | 2.11 | | | |
| | | | 185(a_1)220(e)224(b_1) | | | | |
| | | | 250(a_1) | | | | |
| | | $^3A_2''$ | 110(e')120(a_1')207(e') | 2.36 | | | |
| | | | 210(e'')233(a_2'')243(a_1') | | | | |
| | | | 243(a_1)274(b_2)280(a_1) | | | | |
| Ge_5^- | D_{3h} | $^2A_2''$ | 43(b_2)49(b_1)77(a_2) | 1.99 | | | |
| | | | 86(a_1)167(a_1)173(b_2) | | | | |
| | | | 204(e')238(a_2'')255(a_1') | | | | |
| | C_{2v} | 2B_2 | 67(a_1)82(b_2)134(b_1) | 2.18 | | | |
| | | | 145(a_1)182(a_2)194(b_1) | | | | |
| | | | 220(a_1)242(b_2)260(a_1) | | | | |

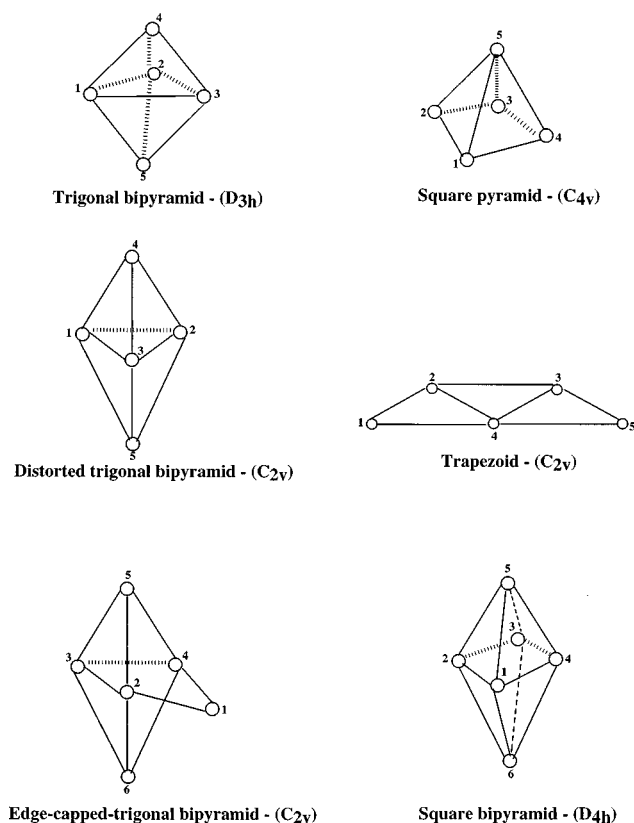


FIG. 2. Structures of Ge_5 and Ge_6 investigated in this work. Optimized geometrical parameters are listed in Table V. Some of the structures are also considered for the anions.

Ge_3 .⁴⁶ Note that the calculated electron affinity of 2.19 eV for the $^3A'_2$ (D_{3h}) state (2A_1 $C_{2v} \rightarrow ^3A'_2$ D_{3h}) at the CCSD(T) level is closer to the experimental value. Nonetheless, our results place the $^3A'_2$ (D_{3h}) slightly above the 1A_1 (C_{2v}) state as discussed above. For $n=4$, the B3LYP prediction of 1.94 eV is in excellent agreement with the electron affinity determined from photoelectron spectroscopy by Neumark and co-workers⁴⁶ (also 1.94 eV), while the CCSD(T) value of 1.80 eV agrees better with 1.81 eV measured by Negishi *et al.*⁶³ It has been reported that photoelectron spectrum of Ge_4^- shows a very narrow band for the 1A_g $D_{4h} \leftarrow ^2B_{2g}$ D_{4h} transition.⁴⁶ As shown in Table X, there is a small difference of 0.02 eV between the calculated VEDE of Ge_4^- and the AEA of Ge_4 , consistent with very little geometrical relaxation accompanying detachment of an electron from the ground state of Ge_4^- . The close similarity in the equilibrium geometries of the ground state of the anion and

TABLE IX. Harmonic vibrational frequencies ω_e (cm^{-1}) of Ge_6 and Ge_6^- at the B3LYP/6-311+G(d) level.

| | Point group | State | Vibrational frequencies | ZPE |
|-----------------|-------------|------------|---|------|
| Ge_6 | C_{2v} | 1A_1 | 18(b_2)35(a_1)62(b_1) | 2.80 |
| | | | 143(b_2)168(b_1)173(a_1) | |
| | | | 201(a_1)202(a_2)210(b_1) | |
| | D_{4h} | $^1A_{1g}$ | 244(b_2)245(a_1)256(a_1) | 2.73 |
| | | | 20i(e_u)60(b_{2u})140(b_{2g}) | |
| | | | 171(a_{2u})172(a_{1g})206(b_{1g}) | |
| Ge_6^- | D_{4h} | $^3A_{1g}$ | 209(e_g)246(e_u)253(a_{1g}) | 2.79 |
| | | | 27(b_{2u})61(e_u)172(b_{1g}) | |
| | | | 174(e_g)192(a_{1g})207(e_u) | |
| | D_{4h} | $^2A_{2u}$ | 208(a_{2u})221(b_{2g})246(a_{1g}) | 2.83 |
| | | | 56(e_u)77(b_{2u})161(b_{2g}) | |
| | | | 172(a_{1g})194(e_g)195(b_{1g}) | |

the neutral species explains the observed sharp peak in the lowest energy band of the Ge_4^- photoelectron spectrum.⁴⁶ The largest discrepancy between the calculated and experimental electron affinities occurs when $n=5$. The electron affinity of Ge_5 ($^2A''_2$ $D_{3h} \rightarrow ^1A'_1$ D_{3h}) computed at the CCSD level is 2.10 eV and differs by 0.48 eV and 0.57 eV from the results of Refs. 46 and 63, respectively. As noted above, the optimal geometry of Ge_5^- ground state is noticeably different from the ground state geometry of Ge_5 , consequently, a large difference of 0.67 eV in the computed VEDE and the AEA is not unexpected. For Ge_6 , the B3LYP computed AEA ($^2A_{2u}$ $D_{4h} \rightarrow ^1A_1$ C_{2v}) is 2.01 eV, in very good agreement with experimental values of 2.06 eV and 2.04 eV.^{46,63}

IV. CONCLUSIONS

The B3LYP and CCSD(T) calculations reported in this study find the most stable structures of the germanium cluster anions, Ge_3^- , Ge_4^- , Ge_5^- , and Ge_6^- to be C_{2v} (2A_1), D_{2h} ($^2B_{2g}$), D_{3h} ($^2A''_2$), and D_{4h} ($^2A_{2u}$), respectively. In the case of Ge_2^- , our calculations show that the low lying $^2\Pi_u$ and $^2\Sigma_g^+$ states are within 1 kcal/mol of each other and both states are possible candidates for the ground state of the anion. We also confirm the ground state geometries previously determined for Ge_2 – Ge_5 , while the structure of Ge_6 is determined to be edge-capped trigonal bipyramid (C_{2v} , 1A_1) in our limited search of the potential energy surface of this system.

The adiabatic energy separation calculated at the CCSD(T) level for the low lying excited states of Ge_3 and Ge_4 , as well as the energy ordering of the states are in good

TABLE VIII. Total energies (a.u.), geometries (\AA , deg), and relative energies (ΔE , eV) of Ge_6 and Ge_6^- .

| | Point group | State | B3LYP/6-311+G(d) | | | | | CCSD/6-311+G(d) ^a | |
|-----------------|-------------|------------|------------------|---------|---------|---------|----------------|------------------------------|----------------|
| | | | R (1-2) | R (2-3) | R (2-6) | R (5-6) | Total energy | ΔE | Total energy |
| Ge_6 | D_{4h} | $^3A_{1g}$ | 2.545 | | 2.715 | 4.066 | −12462.158 091 | 0.67 (2.68) | −12452.534 759 |
| | D_{4h} | $^1A_{1g}$ | 2.941 | | 2.553 | 2.964 | −12462.182 513 | 0.00 (2.01) | −12452.560 439 |
| | C_{2v} | 1A_1 | 2.792 | 3.107 | 2.563 | 2.954 | −12462.182 626 | 0.00 (2.01) | −12452.560 484 |
| Ge_6^- | D_{4h} | $^2A_{2u}$ | 2.787 | | 2.608 | 3.416 | −12462.256 532 | (0.00) | |

^aComputed at the B3LYP/6-311+G(d) geometries.

TABLE X. Vertical detachment energies (eV) of Ge_n^- and adiabatic electron affinities (eV) of Ge_n ($n=2-6$).

| $\text{Ge}_n^-/\text{Ge}_n$ | Method | Vertical detachment energy of Ge_n^- | Adiabatic electron affinity of Ge_n | Experimental electron affinity |
|-----------------------------|-----------------------------------|---|--|--------------------------------|
| 2 | B3LYP/6-331+G(3df) | 1.98 | 1.93 | 2.035±0.001 |
| | CCSD(T)/6-311+G(3df) | 1.99 | 1.96 | |
| | CCSD(T)/6-311+G(3df) ^a | 2.01 | 1.95 | |
| 3 | B3LYP/6-311+G(3df) | 2.49 | 2.17 | 2.23±0.01 |
| | CCSD(T)/6-311+G(3df) ^a | 2.39 | 2.15 | |
| 4 | B3LYP/6-311+G(d) | 1.96 | 1.94 | 1.94±0.05 |
| | CCSD(T)/6-311+G(d) ^a | 1.82 | 1.80 | 1.81±0.09 |
| 5 | B3LYP/6-311+G(d) | 2.86 | 2.19 | 2.51±0.05 |
| | CCSD/6-311+G(d) ^a | 2.77 | 2.10 | 2.67±0.17 |
| 6 | | | | 2.06±0.05 |
| | B3LYP/6-311+G(d) | 2.60 | 2.01 | 2.04±0.08 |

^aComputed at the B3LYP geometry.

agreement with the assignment of the bands observed in the photoelectron spectra of Ge_3^- and Ge_4^- .⁴⁶ In the case of Ge_5 , an excited 3B_1 (C_{2v}) state 0.70 eV above the $^1A_1'$ (D_{3h}) ground state is most likely the second band observed in the photoelectron spectrum of Ge_5^- . For Ge_6 , a $^1A_{1g}$ (D_{4h}) state is found to be nearly degenerate with the 1A_1 (C_{2v}) ground state, and our calculations suggest an excited state ($^3A_{1g}$, D_{4h}) at 0.67 eV.

There is good agreement between the electron affinities computed with B3LYP-DFT and the CCSD(T) methods. The largest discrepancy between the two methods occurs for $n=4$ with the computed detachment energies differing by as much as 0.14 eV. The electron affinities calculated for clusters with $n=2,3,4,6$ compare very well with experimental values.^{46,63} The largest discrepancy between the calculated and the experimental results occurs when $n=5$. The CCSD(T) value of 2.01 eV computed for Ge_5 differs by 0.48 eV and 0.57 eV from the results of Refs. 46 and 63, respectively.

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- ¹P. J. Bruna, S. D. Peyerimhoff, and R. J. Buenker, J. Chem. Phys. **72**, 5437 (1980).
- ²A. D. McLean, B. Liu, and G. S. Chandler, J. Chem. Phys. **80**, 5130 (1984).
- ³K. Raghavachari, J. Chem. Phys. **83**, 3520 (1985).
- ⁴G. H. F. Diercksen, N. E. Grüner, J. Oddershede, and J. R. Sabin, Chem. Phys. Lett. **117**, 29 (1985).
- ⁵R. S. Grev and H. F. Schaefer III, Chem. Phys. Lett. **119**, 111 (1985).
- ⁶R. O. Jones, Phys. Rev. A **32**, 2589 (1985).
- ⁷J. R. Sabin, J. Oddershede, G. H. F. Diercksen, and N. E. Grüner, J. Chem. Phys. **84**, 354 (1986).
- ⁸G. Pacchioni and J. Koutecký, J. Chem. Phys. **84**, 3301 (1986).
- ⁹K. Raghavachari, J. Chem. Phys. **84**, 5672 (1986).
- ¹⁰K. Balasubramanian, Chem. Phys. Lett. **125**, 400 (1986).
- ¹¹D. Tomanek and M. A. Schluter, Phys. Rev. B **36**, 1208 (1987).
- ¹²K. Balasubramanian, Chem. Phys. Lett. **135**, 283 (1987).
- ¹³H. P. Luthi and A. D. McLean, Chem. Phys. Lett. **135**, 352 (1987).

- ¹⁴C. W. Bauschlicher, Jr. and S. R. Langhoff, J. Chem. Phys. **87**, 2919 (1987).
- ¹⁵K. Raghavachari, Chem. Phys. Lett. **143**, 428 (1988).
- ¹⁶K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **89**, 2219 (1988).
- ¹⁷F. Müller-Plathe and L. Laaksonen, Chem. Phys. Lett. **160**, 175 (1989).
- ¹⁸K. Raghavachari, Chem. Phys. Lett. **167**, 559 (1990).
- ¹⁹C. H. Patterson and R. P. Messmer, Phys. Rev. B **42**, 7530 (1990).
- ²⁰K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **94**, 3670 (1991).
- ²¹U. Röthlisberger, W. Andreoni, and P. Giannozzi, J. Chem. Phys. **96**, 1248 (1992).
- ²²L. A. Curtiss, P. W. Deutsch, and K. Raghavachari, J. Chem. Phys. **96**, 6868 (1992).
- ²³R. Fournier, S. B. Sinnott, and A. E. DePristo, J. Chem. Phys. **97**, 4149 (1992).
- ²⁴D. A. Dixon and J. L. Gole, Chem. Phys. Lett. **188**, 560 (1992).
- ²⁵A. B. Anderson, J. Chem. Phys. **63**, 4430 (1975).
- ²⁶J. Harris and R. O. Jones, Phys. Rev. A **18**, 2159 (1978).
- ²⁷J. E. Northrup and M. L. Cohen, Chem. Phys. Lett. **102**, 440 (1983).
- ²⁸J. E. Kingcade, H. M. Nagarathna-Naik, I. Shim, and K. A. Gingerich, J. Phys. Chem. **90**, 2830 (1986).
- ²⁹J. Andzelm, N. Russo, and D. R. Salahub, J. Chem. Phys. **87**, 6562 (1987).
- ³⁰K. Balasubramanian, J. Mol. Spectrosc. **123**, 228 (1987).
- ³¹M. S. Islam and A. K. Ray, Chem. Phys. Lett. **153**, 496 (1988).
- ³²K. Balasubramanian, Chem. Rev. **90**, 93 (1990).
- ³³P. J. Bruna and F. Grein, Mol. Phys. **74**, 1133 (1991).
- ³⁴D. Dai and K. Balasubramanian, J. Chem. Phys. **96**, 8345 (1992).
- ³⁵D. Dai, K. Sumathi, and K. Balasubramanian, Chem. Phys. Lett. **193**, 251 (1992).
- ³⁶D. Dai and K. Balasubramanian, J. Chem. Phys. **105**, 5901 (1996).
- ³⁷D. G. Leopold, J. Ho, and W. C. Lineberger, J. Chem. Phys. **86**, 1715 (1987).
- ³⁸R. D. Mead, A. E. Stevens, and W. C. Lineberger, in *Gas Phase Ion Chemistry*, edited by M. T. Bowers (Academic, New York, 1984), Vol. III, pp. 213–248.
- ³⁹O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu, and R. E. Smalley, Chem. Phys. Lett. **138**, 119 (1987).
- ⁴⁰T. N. Kitsopoulos, C. J. Chick, A. Weaver, and D. M. Neumark, J. Chem. Phys. **93**, 6108 (1990).
- ⁴¹T. N. Kitsopoulos, C. J. Chick, Y. Zhao, and D. M. Neumark, J. Chem. Phys. **95**, 1441 (1991).
- ⁴²C. C. Arnold, T. N. Kitsopoulos, and D. M. Neumark, J. Chem. Phys. **99**, 766 (1993).
- ⁴³C. C. Arnold and D. M. Neumark, J. Chem. Phys. **99**, 3353 (1993).
- ⁴⁴C. C. Arnold and D. M. Neumark, J. Chem. Phys. **100**, 1797 (1994).
- ⁴⁵C. C. Arnold, C. Xu, G. R. Burton, and D. M. Neumark, J. Chem. Phys. **102**, 6982 (1995).
- ⁴⁶G. R. Burton, C. C. Arnold, C. Xu, and D. M. Neumark, J. Chem. Phys. **104**, 2757 (1996).
- ⁴⁷K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **96**, 2114 (1992).
- ⁴⁸T. Ziegler, Chem. Rev. **91**, 651 (1991).
- ⁴⁹P. Hohenberg and W. Kohn, Phys. Rev. B **134**, 864 (1964).
- ⁵⁰O. Gunnarson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

- ⁵¹T. Ziegler, A. Rauk, and E. J. Baerends, *Phys. Rev. B* **43**, 261 (1977).
- ⁵²R. O. Jones and O. Gunnarson, *Rev. Mod. Phys.* **61**, 689 (1989).
- ⁵³J. Baker, A. Scheiner, and J. Andzelm, *Chem. Phys. Lett.* **216**, 380 (1993).
- ⁵⁴C. W. Murray, N. C. Handy, and R. D. Amos, *J. Chem. Phys.* **98**, 7145 (1993).
- ⁵⁵C. J. Cramer, F. J. Dulles, and D. E. Falvey, *J. Am. Chem. Soc.* **116**, 9787 (1994).
- ⁵⁶C. J. Cramer and S. E. Worthington, *J. Phys. Chem.* **99**, 1462 (1995).
- ⁵⁷C. W. Bauschlicher, Jr., *Chem. Phys.* **206**, 35 (1996).
- ⁵⁸C. W. Bauschlicher, Jr., *Chem. Phys. Lett.* **260**, 309 (1996).
- ⁵⁹K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- ⁶⁰M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN 94*, Gaussian, Inc., Pittsburgh, Pennsylvania, 1995.
- ⁶¹F. W. Froben and W. Schelze, *Surf. Sci.* **156**, 765 (1985).
- ⁶²E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, *Nature (London)* **366**, 42 (1993).
- ⁶³Y. Negishi, H. Kawamata, T. Hayase, M. Gomei, R. Kishi, F. Hayakawa, A. Nakajima, and K. Kaya, *Chem. Phys. Lett.* **269**, 199 (1997).