



20 June 2002

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 359 (2002) 203–212

www.elsevier.com/locate/cplett

Theoretical studies on the structure of the endohedral CoGe_{10}^- cluster anion

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Received 26 November 2001; in final form 26 March 2002

Abstract

Theoretical studies have been carried out on the structure of the endohedral CoGe_{10}^- cluster anion using ab initio (HF) and density functional theory (DFT-B3LYP) methods in conjunction with effective core potential basis sets (LanL2DZ and LanL2DZ*). For the important structures, all-electron basis sets plus polarization and diffuse functions (6-31+G*) are also used. At the levels of calculations employed, the bicapped tetragonal antiprism structure with D_{4d} symmetry is found to be most stable. Compared with the small fragments $[\text{Co} + \text{Ge}_{10}(D_{4d})]$, this structure is 97.7 kcal/mol more stable at the B3LYP/LanL2DZ level. Other low-energy structures have also been optimized on the potential energy surface of the endohedral CoGe_{10}^- cluster anion. © 2002 Published by Elsevier Science B.V.

1. Introduction

The materials consisting of transition metal and germanium element have been widely investigated in material science because germanium element can form alloys with many metal and nonmetal elements and transition metal germanides act as potential materials in solid state electronic devices. Binary M/Ge and ternary M/Ge/Si alloys (where M is a transition metal) are currently receiving much attention as promising candidates for low-resistivity interconnect lines and contacts to silicon sub-

strates in Si-based semiconductor devices [1]. These binary and ternary germanides possess low room-temperature resistivity, high thermal stability and good adherence to silicon substrates. Thus, we studied the clustering behaviors of germanium element and transition metal produced by laser ablation and analyzed by a Tandem TOF mass spectrometer. In the experiments on Co/Ge binary clusters, a remarkably strong signal was presented in the mass spectrum, which was assigned to the cluster anion consisting of 10 germanium atoms and one cobalt atom, CoGe_{10}^- . Our experimental results indicated that a transition metal atom (Co) might be trapped in a semiconductor cage (Ge_{10}) [2].

The fact that an atom or a group of atoms can be trapped in a fullerene cage has been generally recognized since 1991 [3,4], when techniques to produce metallofullerene were developed [5,6] and

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the samples were produced in bulk. This provided the conditions to directly study the characteristics of a metallofullerene [6], and consequently the numerous experimental explorations of endohedral fullerenes were conducted. Theoretical studies on the structures and the formation mechanism of the new complexes were also developed [7,8]. But for almost a decade, most of the species with endohedral structures produced and studied mainly had carbon fullerene cages [9–15]. Recently, metal-encapsulated caged clusters of silicon were reported for WSi_{12} [16], M@Si_{14} ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) and M@Si_{16} ($\text{M} = \text{Hf}, \text{Zr}$) [17]. In this Letter, theoretical calculations were carried out to predict the possible structures of the endohedral CoGe_{10}^- cluster anion.

2. Theoretical methods

Geometries of the endohedral CoGe_{10}^- cluster anion were optimized using ab initio and density functional theory (DFT) methods at the Hartree–Fock (HF) and B3LYP levels of theory, where B3LYP was a DFT method using Becke’s three-parameter nonlocal exchange functional [18] with the nonlocal correlation of Lee, Yang, and Parr [19]. The effective core potentials (ECPs) and basis sets developed by Hay and Wadt [20] were used for both Co and Ge atoms, which retained the outer $3s^2 3p^6 3d^7 4s^2$ shells of the Co atom and $4s^2 4p^2$ shells of the Ge atom, explicitly replacing the remaining chemically inert core electrons with ECPs. The contraction schemes used for the basis sets were (5s5p5d)/[3s3p2d] for Co and (3s3p)/[2s2p] for Ge. This type of basis sets was referred as LanL2DZ in the GAUSSIAN program. The LanL2DZ* basis sets were constructed from the standard LanL2DZ ECPs basis sets by adding a set of d-type polarization functions [21] to each Ge atom. For some important structures, all-electron basis sets, which employed split-valence polarization basis sets 6-31G* [22] augmented with diffuse functions, labeled as 6-31+G*, were also used. Note that the spin-restricted wave functions were used for all closed shell systems, and the spin-unrestricted references were employed for the open-shell species.

All calculations were carried out with the GAUSSIAN 98 program suite [23]. The default integration grid (75, 302) of GAUSSIAN 98 was applied.

3. Results and discussion

The structures of the Ge_{10} and Ge_{10}^- clusters are investigated firstly. The optimized geometries and their relative energies are respectively given in Tables 1 and 2. It has been reported [24,25] that for the Ge_{10}^- cage a bicapped tetragonal antiprism structure (**1aa**, Fig. 1) has lowest energy while the tetracapped trigonal prism structure (**1ab**) is slightly higher in energy, and for the Ge_{10} cage a tetracapped trigonal prism structure (**1nb**) has the lowest energy while the bicapped tetragonal antiprism structure (**1na**) and tetracapped octahedral structure (**1nc**) are 16.1 kcal/mol (0.7 eV) and 20.8 kcal/mol (0.9 eV) higher, respectively. Our calculations on the Ge_{10} and Ge_{10}^- clusters fall into the same energy orders, i.e., $E_{1aa} < E_{1ab} < E_{1ac}$ for Ge_{10}^- and $E_{1nb} < E_{1na} < E_{1nc}$ for Ge_{10} at the B3LYP/LanL2DZ level, as shown in Table 2. The bicapped tetragonal antiprism structures with D_{4d} -symmetry (**1aa-1** and **1na-1**) have a larger imaginary vibrational frequency for both Ge_{10} (108.3i cm^{-1} , b_2) and Ge_{10}^- (103.8i cm^{-1} , b_2), indicating that they are unstable at their potential energy surfaces (PES). Following the eigenvectors for the imaginary frequencies leads to C_{4v} -symmetry bicapped tetragonal antiprism structures (**1aa-2** and **1na-2**). However, the neutral structure **1na-2** still has imaginary vibrational frequencies (45.0i cm^{-1} , e_1) at the B3LYP/LanL2DZ level. It should be noted that the low magnitude imaginary vibrational frequencies may be artificial with all currently available DFT methods, because the numerical integration procedures used in existing DFT methods (such as the integration grid (75, 302) of the GAUSSIAN 98 default) may not have enough accuracy. Thus, when we see an imaginary vibrational frequency with the magnitude less than 100i cm^{-1} , the sober conclusion should be that there is a genuine minimum of energy identical to or very close to the stationary point in question [26,27]. Accordingly, we do not follow the small

Table 1
Optimized bond distances (in Å) for possible structures of the Ge₁₀/Ge₁₀⁻ species

	Structure	Symmetry	Coordinate ^a	HF/LanL2DZ	B3LYP/LanL2DZ	B3LYP/LanL2DZ*
Ge ₁₀	1na-1	D _{4d}	<i>R</i> ₁₂	2.620	2.639	2.555
			<i>R</i> ₂₇	2.762	2.731	2.634
			<i>R</i> ₂₃	3.204	3.203	3.082
	1na-2	C _{4v}	<i>R</i> ₁₂	2.800	2.772	2.670
			<i>R</i> ₂₇	2.745	2.742	2.646
			<i>R</i> ₆₇	2.643	2.632	2.538
			<i>R</i> ₂₃	3.010	2.975	2.836
			<i>R</i> ₇₈	3.570	3.523	3.417
	1nb	C _{3v}	<i>R</i> ₁₂	2.630	2.628	2.547
			<i>R</i> ₂₈	2.688	2.726	2.652
			<i>R</i> ₅₆	2.838	2.854	2.750
			<i>R</i> ₅₈	2.940	2.863	2.725
			<i>R</i> ₂₅	2.893	2.850	2.727
	1nc	T _d	<i>R</i> ₂₃	3.175	3.180	3.007
			<i>R</i> ₁₇	2.590	2.583	2.501
<i>R</i> ₁₂			3.165	3.219	2.965	
Ge ₁₀ ⁻	1aa-1	D _{4d}	<i>R</i> ₁₂	2.689	2.700	2.611
			<i>R</i> ₂₇	2.718	2.717	2.627
			<i>R</i> ₂₃	3.113	3.117	2.990
	1aa-2	C _{4v}	<i>R</i> ₁₂	2.781	2.758	2.659
			<i>R</i> ₂₇	2.703	2.711	2.624
			<i>R</i> ₆₇	2.682	2.691	2.604
			<i>R</i> ₂₃	3.009	2.999	2.870
			<i>R</i> ₇₈	3.278	3.248	3.128
	1ab	C _{3v}	<i>R</i> ₁₂	2.683	2.676	2.591
			<i>R</i> ₂₈	2.641	2.686	2.621
			<i>R</i> ₅₆	2.760	2.797	2.705
			<i>R</i> ₅₈	2.933	2.863	2.731
			<i>R</i> ₂₅	3.073	3.007	2.873
	1ac^b	C _{2v}	<i>R</i> ₂₃	3.094	3.089	2.910
			<i>R</i> ₁₇	2.613	2.639	2.581
			<i>R</i> ₅₇	2.580	2.572	2.531
			<i>R</i> ₅₈	2.516	2.653	2.601
			<i>R</i> ₆₈	2.721	2.465	2.399
<i>R</i> ₁₂			3.519	3.334	3.114	
<i>R</i> ₂₃			3.858	3.900	3.785	
<i>R</i> ₂₆			3.824	3.257	3.016	
		<i>R</i> ₃₄	3.318	3.206	2.994	

^a Atom numbering is shown in Fig. 1. The longer distances are listed in italics.

^b For Ge₁₀⁻, the tetracapped octahedron structure with T_d-symmetry cannot converge for the Jahn–Teller effect. Noted that the T_d-symmetry tetracapped octahedral structure of Ge₁₀ has two degenerate lowest unoccupied molecular orbitals (LUMO).

imaginary eigenvector to search a stationary point with no imaginary vibrational frequencies. The distances between the opposite two Ge atoms are *R*₁₆ = 4.821, *R*₂₅ = 4.529, *R*₂₉ = 4.687 Å for **1na-1**; *R*₂₉ = 4.744 Å for **1nb**; *R*₁₆ = 4.552 Å for **1nc**; *R*₁₆ = 5.247, *R*₂₅ = 4.408, *R*₂₉ = 4.596 Å for **1aa-1**; *R*₂₉ = 4.625 Å for **1ab** and *R*₁₆ = 5.088 Å for **1ac** (see Fig. 1 for the atom numbering). Since the

covalent radii of the Co and Ge atoms are 1.16 and 1.223 Å [28], respectively, the anion cages are more suitable to encage a Co atom in their interior.

Putting the Co atom into the Ge₁₀⁻ cages gives three possible structures of the endohedral CoGe₁₀⁻ cluster anion, i.e., (**2aa**) bicapped tetragonal antiprism, (**2ab**) tetracapped trigonal prism, and (**2ae**) tetracapped octahedron, as shown in Fig. 2.

Table 2

The relative energies^a E_{rel} , in kcal/mol) and the imaginary vibrational frequencies (Freq_{ima} , in cm^{-1}) for the possible structures of Ge_{10} and Ge_{10}^-

	Structure	Symmetry	HF/LanL2DZ		B3LYP/LanL2DZ		B3LYP/LanL2DZ*	
			E_{rel}	Freq_{ima}	E_{rel}	Freq_{ima}	E_{rel}	Freq_{ima}
Ge_{10}	1na-1	D_{4d}	27.1	172.3i (b_2)	14.6	108.3i (b_2)	19.2	116.4i (b_2)
	1na-2	C_{4v}	4.5	53.6i (e)	4.2	45.0i (e)	6.6	54.0i (e)
	1nb	C_{3v}	0.0	None	0.0	None	0.0	None
	1nc	T_d	0.1	24.4i (t_2)	9.6	None	15.8	None
Ge_{10}^-	1aa-1	D_{4d}	9.0	None	1.4	103.8i (b_2)	1.3	99.0i (b_2)
	1aa-2	C_{4v}	0.0	18.9i (e)	0.0	None	0.0	None
	1ab	C_{3v}	9.5	109.3i (e)	6.5	59.3i (e)	2.5	30.1i (e)
	1ac	C_{2v}	28.2	38.1i (b_2)	40.6	58.0i (a_2) 35.6i (b_2)	46.8	76.0i (a_2) 46.1i (b_2)

^a The total energies are -36.33612 , -37.77743 , -37.91947 a.u. for structure **1nb** and -36.43005 , -37.87595 , -37.99577 a.u. for structure **1aa-2** at the HF/LANL2DZ, B3LYP/LANL2DZ and B3LYP/LANL2DZ* levels, respectively.

Furthermore, other four structures of CoGe_{10}^- are also optimized: (**2ac**) tetracapped trigonal antiprism, (**2ad**) pentagonal prism, (**2af**) pentagonal antiprism, and (**2ag**) bicapped tetragonal prism. Table 3 shows the optimized geometries while their relative energies are given in Table 4. At both HF/LanL2DZ and B3LYP/LanL2DZ levels of calculations, the bicapped tetragonal antiprism structure (**2aa**) has the lowest energy on the potential energy surface (PES) of the endohedral CoGe_{10}^- cluster anion. Structure **2aa** has the D_{4d} symmetry. When we start with the C_{4v} symmetry bicapped tetragonal antiprism structure of CoGe_{10}^- , it also goes back to the D_{4d} symmetry structure (**2aa**). Structure **2aa** is a genuine minimum predicted by the HF/LanL2DZ method, while the B3LYP/LanL2DZ approach gives two very small degenerate imaginary vibrational frequencies ($10.8i \text{ cm}^{-1}$, e_1). We interpret these small imaginary vibrational frequencies as due to numerical error from the DFT method. The Co–Ge and Ge–Ge bond lengths in **2aa** are $R[\text{Co1–Ge2}] = 2.509$, $R[\text{Co1–Ge3}] = 2.497$, $R[\text{Ge2–Ge3}] = 2.706$ and $R[\text{Ge3–Ge8}] = 2.708 \text{ \AA}$, respectively, at the B3LYP/LanL2DZ level. Compared with the D_{4d} symmetry Ge_{10}^- anion (**1aa-1**), the distance between the two cap Ge atoms in structure **2aa** shortened ($R[\text{Ge2–Ge7}] = 5.018 \text{ \AA}$, contrasted to that of 5.247 \AA in **1aa-1**), while the distances between the eight vertexes Ge atoms lengthened ($R[\text{Ge3–$

$\text{Ge4}] = 3.212$, $R[\text{Ge3–Ge6}] = 4.542$, $R[\text{Ge3–Ge10}] = 4.682 \text{ \AA}$, contrasted to those of 3.203 , 4.408 , 4.596 \AA in **1aa-1**), i.e., the Ge_{10} -cage in structure **2aa** become ‘shorter’ and ‘thicker’. Structure **2aa** is more stable than the fragments $[\text{Co} + \text{Ge}_{10}(\text{D}_{4d})]$ and $[\text{Co}^- + \text{Ge}_{10}(\text{D}_{4d})]$ systems by 97.7 and 159.0 kcal/mol , respectively, at the B3LYP/LanL2DZ level. The large energy gap of 57.4 kcal/mol (2.49 eV) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) also indicates that structure **2aa** is very stable.

On the PES of the endohedral CoGe_{10}^- cluster anion, another energetically lower lying structure is the tetracapped trigonal prism structure with C_{3v} symmetry (**2ab**). Structure **2ab** is 41.6 kcal/mol higher in energy than the D_{4d} structure (**2aa**) at the HF/LanL2DZ level, but the B3LYP/LanL2DZ method predicts **2ab** and **2aa** are almost energetically degenerate, with the former being only 0.2 kcal/mol higher. Since the HF method is lack of electron correlation effect, in the following discussions, we will mainly use the B3LYP results unless indicated. Structure **2ab** has all real vibrational frequencies with the HF/LanL2DZ method but two very small degenerate imaginary vibrational frequencies ($12.2i \text{ cm}^{-1}$, e) at the B3LYP/LanL2DZ level, indicating that this structure is either a minimum or very close energetically to a minimum. The C_{3v} symmetry tetracapped trigonal

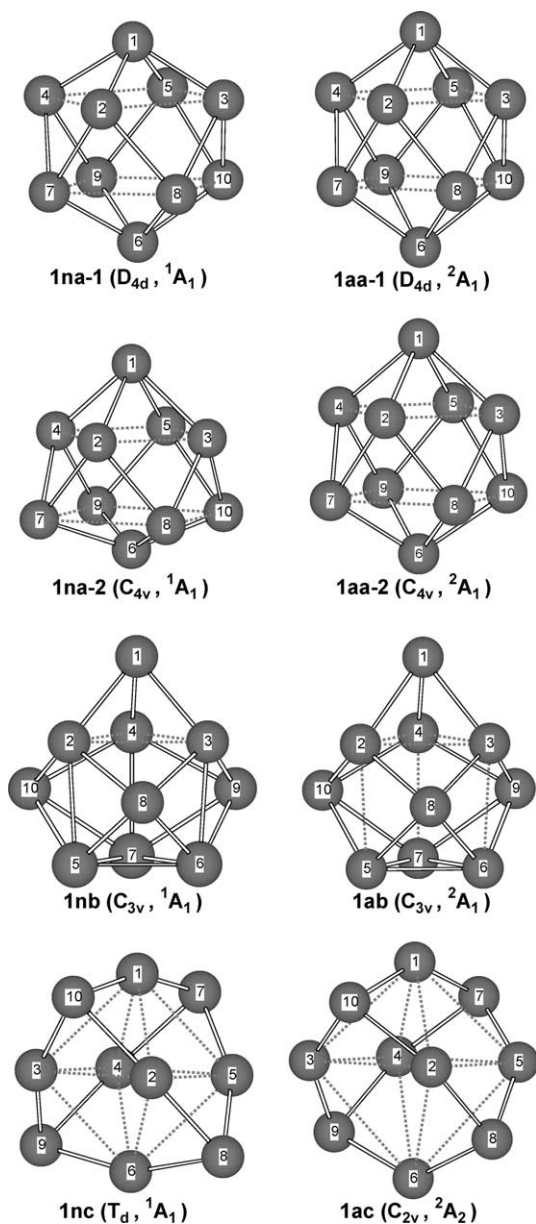


Fig. 1. The optimized structures for the Ge_{10}/Ge_{10}^- clusters: **1na-1nc** for Ge_{10} and **1aa-1ac** for Ge_{10}^- .

antiprism structure (**2ac**) is also a low-energy structure of the endohedral $CoGe_{10}^-$ cluster anion, with its energy only 14.9 kcal/mol higher than the D_{4d} structure (**2aa**) at the B3LYP/LanL2DZ level. Harmonic vibrational frequency calculations predict that structure **2ac** has a single low imaginary

frequency at both HF ($39.7i$ cm^{-1} , a_2) and B3LYP ($20.5i$ cm^{-1} , a_2) methods with LanL2DZ basis sets.

For pentagonal prism structure, when D_{5h} symmetry is constrained, structure **2ad-1** cannot converge with both HF and B3LYP methods. Reducing the point group symmetry to C_{2v} gives structure **2ad-2**. Structure **2ad-2** is 21.9 kcal/mol less stable than the D_{4d} structure (**2aa**) and has an imaginary vibrational frequency ($26.4i$ cm^{-1} , a_2) at the B3LYP/LanL2DZ level. Since HF method predicts this structure has large imaginary vibrational frequencies ($226.0i$ cm^{-1} , a_2 ; $139.6i$ cm^{-1} , b_2), further calculations are carried out following the eigenvector for the larger imaginary frequency, which leads to a pentagonal prism structure with C_2 symmetry (**2ad-3**). The energy of structure **2ad-3** is almost equal to that of structure **2ad-2**, but has no imaginary vibrational frequencies with B3LYP/LanL2DZ method.

The T_d symmetry tetrapped octahedral structure (**2ae-1**) is 48.7 kcal/mol less stable in energy than the D_{4d} structure (**2aa**) at the B3LYP/LanL2DZ level. It has large imaginary vibrational frequencies, indicating it is unstable on the PES of the endohedral $CoGe_{10}^-$ cluster anion. Following the eigenvectors for these imaginary frequencies leads to the D_{2d} symmetry structure (**2ae-2**) and the C_{2v} symmetry structure (**2ae-3**). Structure **2ae-2** is 8.2 kcal/mol more stable than structure **2ae-1** at the HF/LanL2DZ level, but it falls back to **2ae-1** with the B3LYP/LanL2DZ method. Structure **2ae-3** has all real vibrational frequencies, corresponding to a minimum on the PES of the $CoGe_{10}^-$ cluster anion, with its energy 36.8 kcal/mol higher than that of the D_{4d} structure (**2aa**) at the B3LYP/LanL2DZ level.

The pentagonal antiprism structure with D_{5d} symmetry (**2af-1**) is also unstable on the PES of the $CoGe_{10}^-$ cluster anion for its large imaginary vibrational frequencies with both HF and B3LYP methods (see Table 4). Reducing the point group symmetry to C_{2h} gives structure **2af-2**. Structure **2af-2** is 33.3 kcal/mol more stable than structure **2af-1** at the B3LYP/LanL2DZ level, but it still has large imaginary vibrational frequencies. When following the normal modes related to the imaginary frequencies, structure **2af-2** falls into the C_s

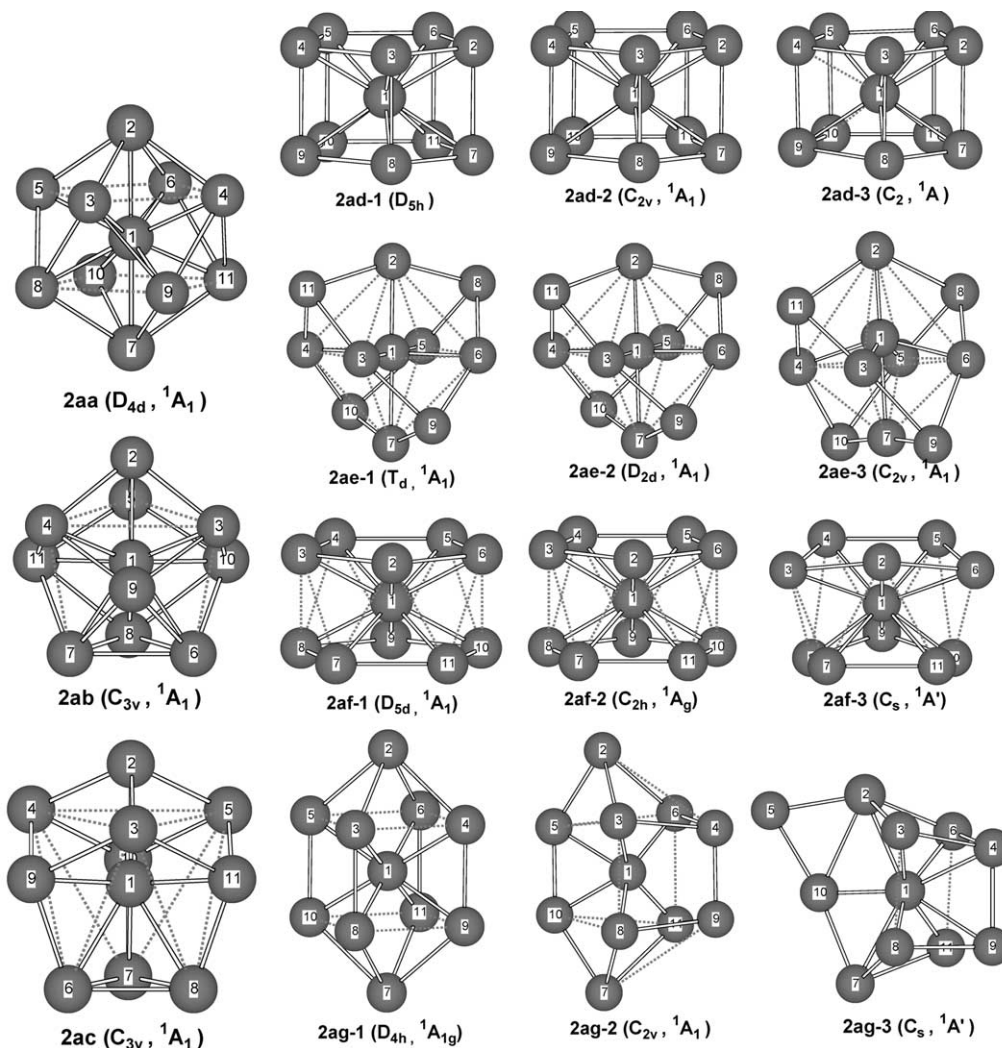


Fig. 2. The possible structures of the endohedral CoGe_{10}^- cluster anion (1 is Co atom and the others are Ge atoms).

symmetry structure (**2af-3**). Structure **2af-3** has small imaginary vibrational frequencies (HF: $38.5i \text{ cm}^{-1}$, a'' ; B3LYP: $44.4i \text{ cm}^{-1}$, a'' , $26.9i \text{ cm}^{-1}$, a''). Compared with the energetically most stable structure (**2aa**), structure **2af-3** is 41.6 kcal/mol less stable at the B3LYP/LanL2DZ level.

Among the structures of the CoGe_{10}^- cluster anion investigated here, the D_{4h} symmetry bicapped tetragonal prism structure (**2ag-1**) has the highest energy. It is higher than structure **2aa** by 117.8 kcal/mol at the B3LYP/LanL2DZ level.

Structure **2ag-1** has seven or eight imaginary frequencies with HF and B3LYP methods, as shown in Table 4. Following the eigenvector for the largest imaginary frequency leads to a C_{2v} -symmetry structure (**2ag-2**) with its energy 45.9 kcal/mol lower than that of structure **2ag-1**. Since structure **2ag-2** also has large imaginary vibrational frequencies, further calculations are performed, leading to a C_s -symmetry structure (**2ag-3**). Structure **2ag-3** is 76.5 kcal/mol energetically more stable than structure **2ag-1**, but one of its Ge atoms, i.e., Ge5 in Fig. **2ag-3**, is far away

Table 3
Optimized bond distances (in Å) for possible structures of the endohedral Co Ge₁₀⁻ cluster anion

Structure	Symmetry	Coordinate ^a	HF/LANL2DZ	B3LYP/ LANL2DZ	B3LYP/ LANL2DZ*	B3LYP/6-31+G*
2aa	D _{4d}	<i>R</i> ₁₂	2.804	2.509	2.476	2.400
		<i>R</i> ₁₃	2.522	2.497	2.459	2.398
		<i>R</i> ₂₃	2.860	2.706	2.666	2.587
		<i>R</i> ₃₈	2.774	2.708	2.669	2.608
		<i>R</i> ₃₄	3.224	3.212	3.162	3.080
2ab	C _{3v}	<i>R</i> ₁₂	2.244	2.423	2.393	2.394
		<i>R</i> ₁₃	2.453	2.489	2.449	2.385
		<i>R</i> ₁₆	2.728	2.558	2.517	2.397
		<i>R</i> ₁₉	2.497	2.483	2.454	2.385
		<i>R</i> ₂₃	2.733	2.646	2.627	2.501
		<i>R</i> ₃₉	2.689	2.669	2.639	2.550
		<i>R</i> ₆₈	2.771	2.798	2.736	2.682
		<i>R</i> ₆₉	2.802	2.833	2.778	2.723
		<i>R</i> ₃₄	4.017	3.913	3.866	3.684
		<i>R</i> ₃₆	3.093	3.096	3.039	2.965
2ac	C _{3v}	<i>R</i> ₁₂	2.461	2.497	2.475	
		<i>R</i> ₁₃	2.369	2.740	2.706	
		<i>R</i> ₁₆	2.646	2.598	2.558	
		<i>R</i> ₁₉	2.646	2.422	2.401	
		<i>R</i> ₂₃	2.660	2.600	2.555	
		<i>R</i> ₃₉	2.636	2.665	2.615	
		<i>R</i> ₆₈	2.509	2.603	2.561	
		<i>R</i> ₆₉	2.471	2.519	2.513	
		<i>R</i> ₃₄	3.770	4.082	4.013	
		<i>R</i> ₃₆	3.686	4.079	4.034	
2ad-2^b	C _{2v}	<i>R</i> ₁₂	2.570	2.571	2.543	
		<i>R</i> ₁₃	2.559	2.550	2.524	
		<i>R</i> ₁₅	2.516	2.562	2.535	
		<i>R</i> ₂₃	2.448	2.495	2.478	
		<i>R</i> ₄₅	2.583	2.605	2.581	
		<i>R</i> ₅₆	2.712	2.735	2.705	
		<i>R</i> ₂₇	2.654	2.649	2.602	
		<i>R</i> ₃₈	2.604	2.642	2.600	
		<i>R</i> _{5,10}	2.661	2.602	2.562	
2ae-1	T _d	<i>R</i> ₁₂	2.491	2.427	2.396	
		<i>R</i> ₂₈	2.569	2.579	2.543	
		<i>R</i> ₁₈	3.008	3.052	3.008	
2af-1	D _{5d}	<i>R</i> ₁₂	2.651	2.626	2.579	
		<i>R</i> ₂₃	2.671	2.657	2.628	
		<i>R</i> ₂₇	3.071	3.017	2.920	
2ag-1	D _{4h}	<i>R</i> ₁₃	2.435	2.463	2.451	
		<i>R</i> ₂₃	2.741	2.757	2.679	
		<i>R</i> ₃₈	2.546	2.575	2.550	
		<i>R</i> ₁₂	3.062	3.075	2.947	
		<i>R</i> ₃₄	2.936	2.969	2.960	

^a Atom numbering is shown in Fig. 2. The longer distances are listed in italics.

^b Pentagonal prism structure with D_{5h} symmetry cannot converge with both HF and B3LYP methods.

Table 4
Relative energies^a (in kcal/mol) and the imaginary vibrational frequencies (Freq_{ima}, in cm⁻¹) for possible structures of the endohedral CoGe₁₀⁻ cluster anion

Structure	Symmetry	HF/LanL2DZ		B3LYP/LanL2DZ		B3LYP/LanL2DZ*		B3LYP/6-31+G*	
		<i>E</i> _{rel}	Freq _{ima}	<i>E</i> _{rel}	Freq _{ima}	<i>E</i> _{rel}	Freq _{ima}	<i>E</i> _{rel}	Freq _{ima}
2aa	D _{4d}	0.0	None	0.0	10.8i (e ₁)	0.0	20.5i (e ₁)	0.0	None
2ab	C _{3v}	41.6	None	0.2	12.2i (e)	-0.6	None	2.7	31.2i (e)
2ac	C _{3v}	60.2	39.7i (a ₂)	14.9	20.5i (e)	15.5	11.5i (e)		
2ad-1^b	D _{5h}	–	–	–	–	–	–		
2ad-2	C _{2v}	57.9	226.0i (a ₂) 139.6i (a ₂)	21.9	26.4i (e)	25.6	None		
2ad-3	C ₂	27.6	65.8i (b)	21.9	None	25.6	None		
2ae-1	T _d	70.6	283.6i (e) 80.1i (t ₂)	48.7	105.1i (t ₂) 48.3i (t ₁)	52.2	103.5i (t ₂) 47.4i (t ₁)		
2ae-2	D _{2d}	62.4	153.0i (b ₂) 63.6i (e) 3.9i (a ₂) 3.8i (a ₂)	48.7	106.8i (e) 105.6i (b ₂) 48.8i (a ₂) 48.8i (a ₂) 48.5i (a ₂)	52.2	105.2i (e) 104.0i (b ₂) 48.2i (e) 47.9i (a ₂)		
2ae-3	C _{2v}	39.3	47.9i (b ₁) 26.7i (b ₂)	36.8	None	37.6	None		
2af-1	D _{5d}	60.4	184.9i (e) 133.8i (a) 95.1i (e) 32.1i (e)	83.5	217.5i 91.9i	85.9	430.2i 91.8i		
2af-2	C _{2h}	92.8	172.5i (b _u) 134.9i (a _u) 102.9i	50.2	97.1i (b _u) 90.3i (a _u) 79.5i (a _u) 8.6i	48.6	87.6i (b _u) 82.5i (a _u) 70.5i (a _u) 19.8i (b _g)		
2af-3	C _s	72.2	38.5i (a'')	41.6	44.4i (a'') 26.9i (a'')	42.4	44.1i (a'') 36.5i (a'')		
2ag-1	D _{4h}	160.2	276.7i (e _u) 109.1i (e _g) 79.4i (a _{2u}) 11.7i (e _u)	117.8	232.1i (e _u) 142.6i (a _{2u}) 121.0i (e _u) 97.4i (e _g) 46.9i (b _{2u})	117.0	188.6i (e _u) 139.6i (a _{2u}) 130.8i (e _u) 100.2i (e _g)		

2ag-2	C _{2v}	119.5	199.5i (a ₂) 152.6i (b ₂) 114.6i (b ₁) 91.6i (b ₂)	71.9	161.1i (b ₂) 87.3i (b ₂) 73.8i (a ₂) 48.5i (b ₁) 45.9i (a ₂) 9.0i (b ₂) 66.2i (a'')	76.1	180.7i (b ₂) 10305i (b ₂) 68.7i (a ₂) 55.5i (b ₁) 44.6i (a ₂)
2ag-3	C _s	88.9	136.8i (a'')	41.3	66.2i (a'')	45.1	66.6i (a'')
Co + Ge ₁₀ ⁻ (C _{4v})		-21.1		96.3		80.3	
Co + Ge ₁₀ ⁻ (D _{4d})		-12.1		97.7		81.6	
Co ⁻ + Ge ₁₀ ⁻ (C _{3v})		55.3		144.3		144.4	
Co ⁻ + Ge ₁₀ ⁻ (D _{4d})		82.4		159.0		136.6	

^aThe total energy of the structure **2aa** is -180.47964, -183.04685, -183.14124 and -22133.38588 a.u. at the HF/LanL2DZ, B3LYP/LanL2DZ, B3LYP/LanL2DZ* and B3LYP/6-31+G* levels, respectively.

^bThe D_{5h} symmetry pentagonal prism structure cannot converge with both HF and B3LYP methods.

from the Co atom. The distance between the Ge5 atom and Co atom is 4.199 Å.

We also try to optimize these endohedral structures in their triple states, but no significant result was obtained.

To check the effect of d-type polarization function on the structures and energies, the computations with LanL2DZ* basis sets are also performed. As shown in Table 1–4, although the optimized bond lengths obtained with LanL2DZ* basis sets are shorter than those yielded with LanL2DZ basis sets, the two basis sets calculations give similar relative energies for Ge₁₀, Ge₁₀⁻ and CoGe₁₀⁻, at the B3LYP level of theory. Since the B3LYP/LanL2DZ* calculations predict structure **2ab** being 0.6 kcal/mol lower in energy than structure **2aa**, to further characterize the energies of structure **2aa** and **2ab**, we also study these two structures with larger 6-31+G* basis sets, which lead to 987 primitive gaussians and 389 contracted basis functions for the CoGe₁₀⁻ anion. At the B3LYP/6-31+G* level, structure **2aa** is 2.7 kcal/mol more stable than structure **2ab**.

For the linear structures of the CoGe₁₀⁻ cluster anion, with the Co atom lying in the different sites of the Ge₁₀ chain, they all have several imaginary vibrational frequencies in their single and triple states. Because they all have very high energies, lying more than 250 kcal/mol above the **2aa** structure at the B3LYP/LanL2DZ* level, we do not consider this kind of structures further. We also studied some ring-like planar structures of the CoGe₁₀⁻ cluster anion, such as the 11-numbered ring structure, the cobalt atom inside or outside 10 germanium-numbered ring structures, etc. The optimized results indicate that these ring-like structures are high-lying energetically and prefer to collapse to three-dimension structures.

4. Conclusion

The possible endohedral structures of the CoGe₁₀⁻ cluster anion have been studied by ab initio and density functional theory methods at the HF and B3LYP levels with LanL2DZ, LanL2DZ* and 6-31+G* basis sets. Among the structures investigated, the D_{4d} symmetry bicapped tetragonal

antiprism structure (**2aa**) has the lowest energy. Although the B3LYP/LanL2DZ calculation shows structure **2aa** having two very small degenerate imaginary vibrational frequencies ($10.8i \text{ cm}^{-1}$, e_1), both HF/LanL2DZ and B3LYP/6-31+G* methods predict this structure to be a genuine minimum with all real vibrational frequencies. Compared with the small fragments [$\text{Co} + \text{Ge}_{10}^- (\text{D}_{4d})$], structure **2aa** is 97.7 kcal/mol energetically more stable at the B3LYP/LanL2DZ level of theory. The large energy gap of 57.4 kcal/mol (2.49 eV) between HOMO and LUMO also indicates that structure **2aa** is very stable. The tetracapped trigonal prism structure with C_{3v} symmetry (**2ab**) is either a genuine minimum or very close energetically to a genuine minimum, with its energy higher than that of structure **2aa** by only 0.2 and 2.7 kcal/mol at the B3LYP/LanL2DZ and B3LYP/6-31+G* levels, respectively. All of the other structures with high symmetry (**2ac**, **2ad**, **2ae**, **2af** and **2ag**) have higher energies and one or more larger imaginary vibrational frequencies, indicating that they all are unstable on the potential energy surface of the endohedral CoGe_{10}^- cluster anion.

Acknowledgements

We thank our colleagues in the State Key Laboratory of Molecular Reaction Dynamic for helpful discussions. This research was supported by the National Natural Science Foundation of China.

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