CALCULATIONS ON THE STABLE STRUCTURES OF $ScGe_5$ CLUSTER ON THE POTENTIAL ENERGY SURFACE AND ITS CO ADSORPTION

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Abstract

The structures of the $ScGe_5$ cluster were investigated by a combination of the genetic algorithm (GA) with the density functional theory (DFT) calculations. The structural parameters and relative energy of isomers were reported. These doped germanium clusters were applied to study CO adsorption by calculations with PBE functional. The adsorbed structure, the adsorption energy, and the ELF graphs of CO adsorption were also presented. Results indicated that CO molecule can be adsorbed at many positions of these clusters. The positions around the Sc atom can adsorb CO molecule better than others. The Sc-CO model of adsorption is more advantageous than the Sc-OC model. Scandium doped germanium cluster can be used to produce materials that can treat CO gas by adsorption method.

Keywords: *CO, density functional theory, GA-DFT, optimization, $ScGe_5$.*

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TÍNH TOÁN CÁC CẤU TRÚC BỀN CỦA CLUSTER $ScGe_5$ TRÊN BỀ MẶT THẾ NĂNG VÀ SỰ HẤP PHỤ CO

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Tóm tắt

Các cấu trúc của cluster $ScGe_5$ được nghiên cứu bằng phương pháp kết hợp giải thuật di truyền với tính toán lý thuyết phiếm hàm mật độ. Các thông số cấu trúc, năng lượng tương đối của các đồng phân được báo cáo. Cluster $ScGe_5$ được nghiên cứu hấp phụ CO bằng tính toán toán với phiếm hàm PBE. Các cấu trúc hấp phụ, năng lượng tương đối, năng lượng hấp phụ, ảnh ELF của cấu trúc hấp phụ được trình bày. Kết quả cho thấy phân tử CO có thể được hấp phụ bởi cluster $ScGe_5$ ở nhiều vị trí. Các vị trí quanh nguyên tử Sc hấp phụ CO tốt hơn. Kiểu hấp phụ Sc-CO ưu tiên hơn kiểu hấp phụ Sc-OC. Cluster germani pha tạp scandi có thể tạo nên vật liệu hấp phụ khí CO.

Từ khóa: *CO, GA-DFT, lý thuyết phiếm hàm mật độ, $ScGe_5$, sự tối ưu hóa.*

1. Introduction

Germanium clusters are highly regarded by their wide applications in electronic, adsorption, catalyst, pharmacy fields. Clearly, germanium was used to produce LED, solar cell, lithium-ion batteries with faster charge-discharge ability, stably through many cycles (Biswas et al., 2017; Carolan, 2017; McVey et al., 2017). In addition, germanium can be used in pharmacy for its non-toxic and high biocompatibility (Abel et al., 2013; Biswas et al., 2017; Carolan, 2017; McVey et al., 2017). The optic property, electronic property, and stability of materials depend on their sizes (Carolan, 2017; Janssens et al., 2005).

The structures of germanium, and scandium were studied by the experiment and the theoretical calculations as $Ge_n^{-/0/+}$ (n=1-25) (Bandyopadhyay & Sen, 2010; Gingerich et al., 2000; Giuseppe et al., 1993; Pacchioni & Koutecký, 1986; Shvartsburg et al., 1999; Ugrinov & Sevov, 2002; Wang & Han, 2005; Wang et al., 2001), $Sc_n^{-/0/+}$ (n=2-13), and Sc_nO (Pápai & Castro, 1997; Sajjad et al., 2019; Sajjad et al., 2018; Wang et al., 2012), $ScGe_n^-$ (n=6-20) (Atobe et al., 2012; Borshch et al., 2015). The high-temperature mass spectrometric method was employed to measure the equilibrium partial pressures of Ge_3 and Ge_4 above liquid germanium contained in a graphite Knudsen cell (Gingerich et al., 2000). These results indicated that the stability and property of transition metal-doped germanium are higher than the pure germanium cluster. Since the 3d orbitals have near degeneration in energy, transition metal-doped germanium clusters can build many structures with the same stability.

A brief history of carbon monoxide and its therapeutic origins have been reported (Hopper et al., 2021; Siracusa et al., 2021). Many studies have been performed to find out the ways to remove CO molecule or to transform CO gas into different products by the chemical process. However, the C-O bond is the strongest bond of the diatom molecule (Saha et al., 2017), so it is very difficult to perform the production process. Clusters of scandium and germanium elements are good materials to adsorb and decrease the binding of the C-O bond (Feng et al., 2020; Nagarajan & Chandiramouli, 2017; Sajjad et al., 2019; Wang et al., 2012; Zhou et al., 2019). In this study, we search the minimum structure of the $ScGe_5$ clusters by combining the genetic algorithm with DFT quantum calculation (GA-DFT) to search the minimum structures of the $ScGe_5$ cluster. The GA-DFT is one of the useful methods to find the global structure with high exact (Jennings & Johnston, 2013). The clusters' structures can be optimized cheaply and quickly by the density functional theory. The CO adsorption by the $ScGe_5$ cluster is investigated on the most stable isomer.

2. Methods

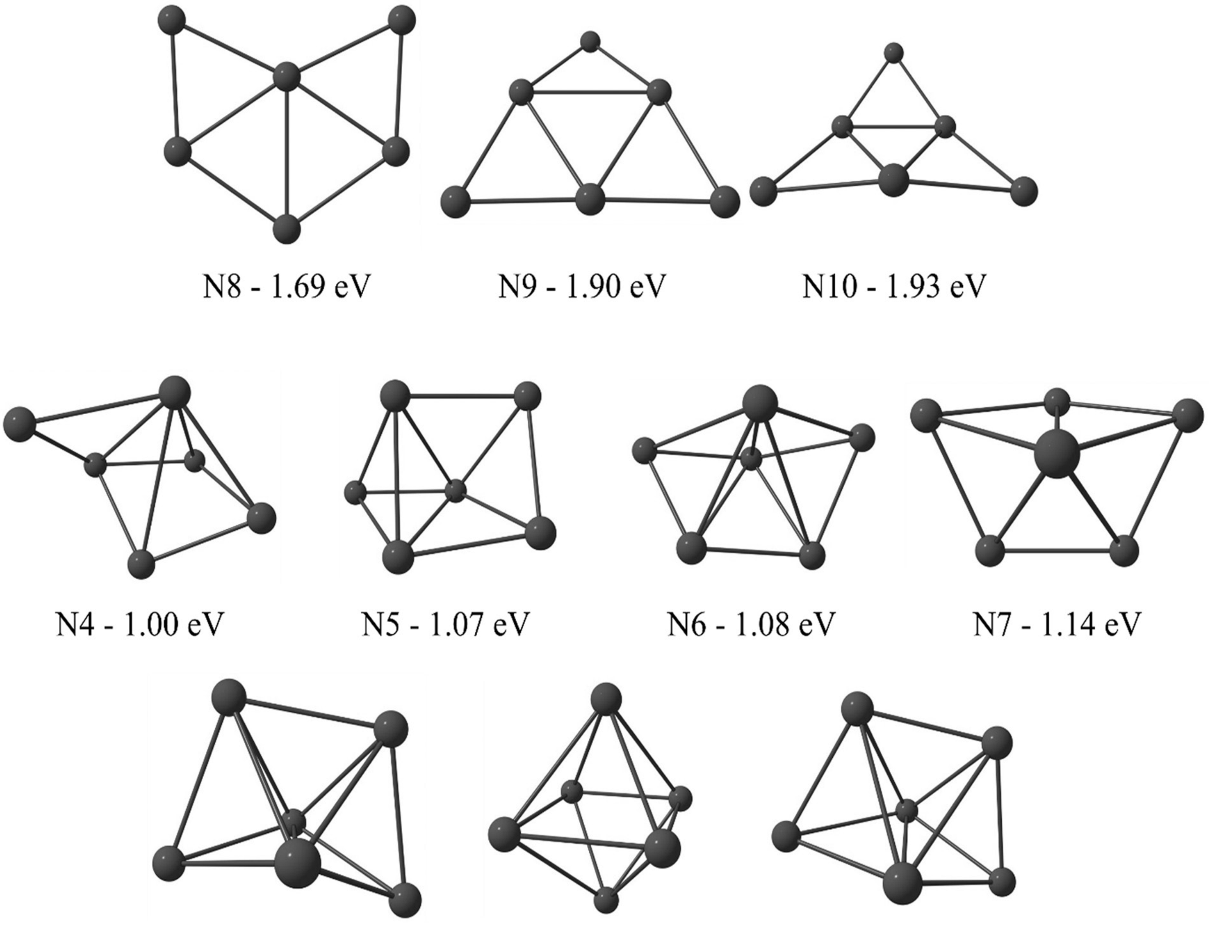
The structures of $ScGe_5$ clusters are investigated by a combination of the genetic algorithm and the density functional theory calculations with the PBE functional (Hussein & Johnston, 2019; Jennings & Johnston, 2013). Firstly, random individuals are created with specific atoms. The optimization is performed by the pwSCF code of the Quantum Espresso 6.0 package (Giannozzi et al., 2009). The low-energy structures are kept in the next generation. Some random structures, mutual structures, and crossing structures are formed and added to the pool of individuals. These GA-DFT processes have been done until the stop condition is obtained. The GA process is performed by USPEX 10.3 code (AR et al., 2011; AR & CW, 2006; Lyakhov et al., 2013).

The obtained structures are reoptimized by PBE functional (Perdew et al., 1996). In addition, some local minimum structures are built from other references to reduce the loss of minimum structures. To save calculation time, the geometrical structures are optimized by a small basis set def2-SVP. Then, re-optimization was done by a larger basis set def2-TZVPP. The most stable structures are used to survey the CO adsorption on the surface. The relative energies are computed with the correctness of the zero-point energy (ZPE) value. The relative energy and frequency values of optimized structures are obtained. The DFT calculations are performed by ORCA 4.2.1 code (Neese, 2012).

3. Results and discussion

3.1. The structures of $ScGe_5$ cluster

The structure, symmetry, electronic state, relative energy, and harmonic vibrational frequencies of the isomers of the $ScGe_5$ cluster are presented in Figure 1 and Table 1. The N1 isomer is the global minimum structure of the $ScGe_5$ cluster based on the calculations at the PBE/def2-TZVPP level. The N1 isomer has the structure of the trigonal bipyramid with one Sc top capped by a Ge atom on the ScGeGe surface. The isomer N3 has the same structure as the isomer N1, but the capping happens at the GeGeGe surface. The isomer N3 is less stable in energy than the global structure N1 by 0.25 eV at the PBE/def2-TZVPP level. The two isomers of N2 and N3 with the C_s point group symmetry are different about 0.05 eV. The isomer N2 is a tetragonal bipyramid with a Sc top containing a C_{2v} point group symmetry. The structure of the isomers N1 and N3 can be formed by replacing one Ge atom with the Sc atom in the edge-capped trigonal bipyramid structure of the Ge_6 cluster, while the isomer N2 can be created from the tetragonal bipyramid form of the Ge_6 cluster (Giuseppe et al., 1993).



N8 - 1.69 eV
N9 - 1.90 eV
N10 - 1.93 eV

N4 - 1.00 eV
N5 - 1.07 eV
N6 - 1.08 eV
N7 - 1.14 eV

N1 - 0.00 eV
N2 - 0.20 eV
N3 - 0.25 eV

Figure 2. The structure, symmetry, electronic state, and relative energy of the isomers of the $ScGe_5$ cluster

The relative energies of four isomers N4, N5, N6, and N7 are 1.00, 1.07, 1.08, and 1.14 eV, respectively. The point group symmetry of these isomers is also C_1, while the N7 structure belongs to the C_s symmetry. The isomer N8 is less stable than the isomer N1 by 1.69 eV. The geometrical structure of the isomer N8 is C_{2v} point group symmetry with the $^2B_2$ state. Two isomers with the equivalent energy are both the C_s symmetry. The electronic state of the isomer N9 is the $^2A'$ state and the electronic state of the isomer N10 is the $^2A''$ state. The above results show that the structures of the isomer of the $ScGe_5$ cluster also have a low spin multiplicity of 2.

Table 1. The symmetry, electronic state, relative energy (RE), and harmonic vibrational frequency of the isomers of $ScGe_5$ cluster

Isomer	Sym.	State	RE (eV)	Harmonic vibrational frequency (cm^{-1})
N1	${}_{C}$s	$^2A'$	0.00	67.83; 85.73; 136.31; 146.41; 169.48; 175.11; 183.24; 205.14; 206.95; 244.18; 259.67; 296.74
N2	C_{2v}	$^2B_1$	0.20	69.87; 87.94; 95.29; 137.85; 163.19; 175.14; 178.73; 198.77; 204.08; 220.98; 244.38; 285.10
N3	C_s	$^2A'$	0.25	58.79; 64.16; 113.67; 122.05; 157.63; 161.13; 170.43; 200.84; 216.23; 234.27; 249.82; 292.00
N4	C1	^2A	1.00	22.39; 47.62; 85.31; 111.83; 139.14; 168.91; 184.92; 206.21; 219.44; 241.22; 255.65; 282.01
N5	C1	^4A	1.07	46.89; 75.76; 92.42; 117.11; 138.77; 156.00; 163.17; 201.66; 205.10; 223.19; 246.89; 258.82
N6	C1	^2A	1.08	23.27; 62.45; 88.30; 106.60; 139.46; 147.68; 175.96; 186.71; 219.63; 228.96; 257.15; 269.61
N7	C_s	$^2A''$	1.14	32.69; 67.21; 75.45; 114.83; 118.34; 150.32; 169.59; 175.57; 198.95; 219.33; 239.78; 274.38
N8	C_{2v}	$^2B_2$	1.69	15.63; 50.59; 57.20; 92.13; 123.01; 148.72; 182.72; 188.43; 240.16; 250.71; 274.86; 291.24
N9	Cs	$^2A'$	1.90	35.32; 40.81; 47.09; 71.11; 135.07; 139.14; 174.18; 180.82; 226.42; 250.32; 303.43; 306.66
N10	Cs	$^2A''$	1.93	31.07; 38.46; 61.15; 102.48; 133.25; 143.56; 155.95; 200.34; 234.17; 241.32; 281.87; 313.08

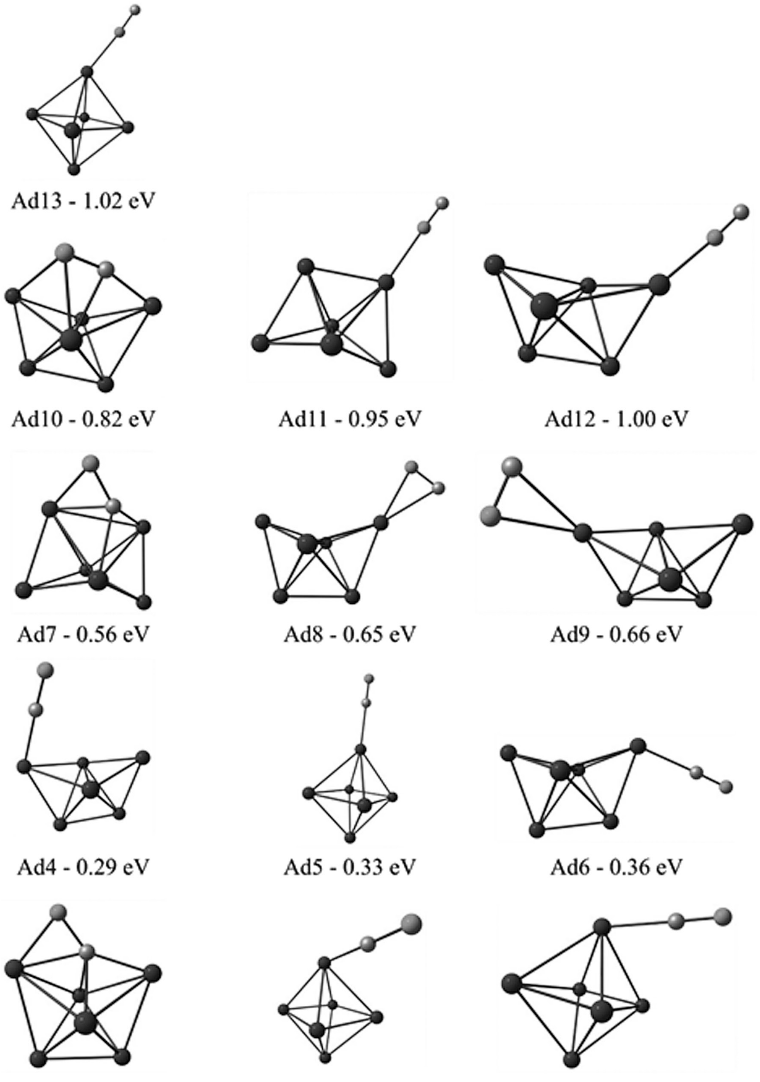
3.2. Studying the CO adsorption by the most stable isomers of the $ScGe_5$ cluster

Firstly, the CO molecule is optimized at the PBE/def2-TZVPP level. As a result, the length of the C-O bond is obtained by 1.136 Å. This result is the same as the one at the DKH3-R/UCCSD(T)/VTZ level of theory (Feng et al., 2020). The calculated frequency of the C-O bond by the PBE/def2-TZVPP is 2124.90 cm^{-1}, in good accordance with previous reports (Elsila et al., 1997; Ricks et al., 2010; Saha et al., 2017).

Table 2. The bond length and vibrational frequency of the CO molecule

The CO molecule	PBE/def2-TZVPP	Reference
The bond length (Å)	1.136	1.136 (Feng et al., 2020) 1.117 (Wang et al., 2012)
Harmonic vibrational frequency (cm^{-1})	2124.90	2140 (Elsila et al., 1997) 2143 (Ricks et al., 2010) 2156 (Saha et al., 2017) 2334 (Wang et al., 2012)

The bond length and vibrational frequency of the C-O bond from Wang and his coworkers are 1.117 Å and 2334 cm^{-1} (Wang et al., 2012). These results show that the calculations at the PBE/def2-TZVPP level can give a good guest of the CO adsorption on the $ScGe_5$ cluster. The adsorbed structures are presented in Figure 3. These structures are at the minima position on the potential energy surface because all vibrational frequency values are not negative values.



Ad13 - 1.02 eV

Ad10 - 0.82 eV Ad11 - 0.95 eV Ad12 - 1.00 eV

Ad7 - 0.56 eV Ad8 - 0.65 eV Ad9 - 0.66 eV

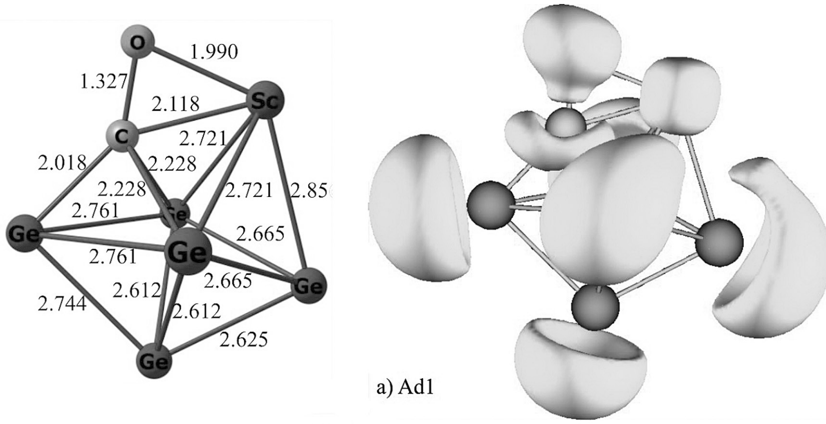
Ad4 - 0.29 eV Ad5 - 0.33 eV Ad6 - 0.36 eV

Ad1 - 0.00 eV Ad2 - 0.11 eV Ad3 - 0.16 eV

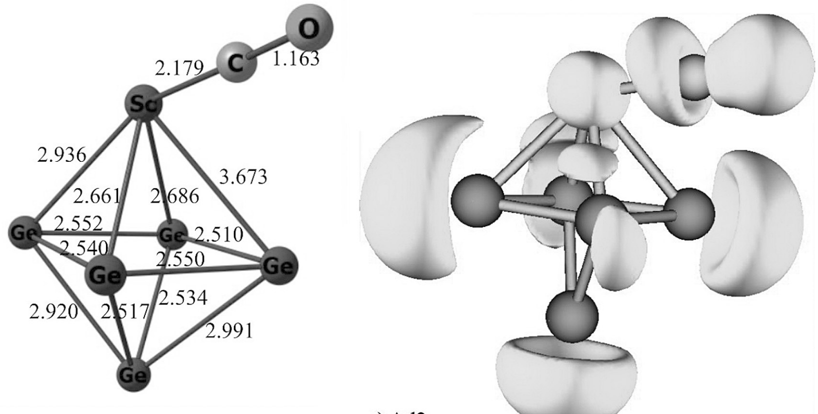
Figure 3. The relative energy of the adsorbed structures between the $ScGe_5$ cluster and CO molecule at the PBE/def2-TZVPP level

The most stable adsorbed structure is Ad1. In this structure, the CO molecule creates many bonds with the N3 isomer of the $ScGe_5$ cluster. The Sc atom connects with both C and O atoms. The C atom of the CO molecule binds with three Ge atoms and the Sc atom. Many bonds between the N3 isomer of the $ScGe_5$ cluster are considered as the reason to stabilise the adsorbed structure. The adsorbed structures Ad4, Ad6, Ad8, Ad9, and Ad12 are also created from the N3 isomer of the $ScGe_5$ cluster with CO molecule. The relative energies of these isomers are 0.29, 0.36, 0.65, 0.66, and 1.00 eV, respectively.

The structures of Ad2, Ad3, Ad5, and Ad13 are higher than the structure Ad1 by 0.11, 0.16, 0.33, and 1.02 eV, respectively. These structures are created from the isomer N2 of the $ScGe_5$ cluster and CO molecule. Two structures Ad7 and Ad11 are formed by the adsorbing CO molecule on the isomer N1 of the $ScGe_5$ cluster. Their relative energies comparing the structure Ad1 are 0.56 eV and 0.95 eV, respectively. The structure Ad10 is a combination of the isomer N6 of the $ScGe_5$ cluster with the CO molecule. From the adsorbed structures and their relative energies, the CO molecule can be adsorbed around the Sc atom in different positions. This indicates that the scandium-doped germanium cluster has high activity than the pure germanium cluster.



a) Ad1



a) Ad2

Figure 4. The structures and the ELF images (isosurface value = 0.70) of the adsorbed structures Ad1 and Ad2

In the above structures, the C atom of CO molecule can have more advantage adsorbed into $ScGe_5$ cluster than the O atom. The electronegative of the C element is smaller than the C element, so the non-bond pair electronic of the C atom can bind easily than the O atom. The bond length of the C-O bond in Ad1 and Ad2 are 1.327 Å and 1.163 Å. This value in the CO molecule is 1.136 Å, indicating that the C-O bond is decreased by the $ScGe_5$ cluster. The bond length and the ELF images of two structures Ad1 and Ad2 as in Figure 4. The ELF images are simulated by the Multiwfn_3.8_dev package (Lu & Chen, 2012).

4. Conclusion

The genetic algorithm combined with the density functional theory is an effective method for searching the global minimum and the local minimum structures. The structures and relative energies of the stable isomers were reported. The $ScGe_5$ cluster can be formed by substituting a Ge atom in the Ge_6 cluster with the Sc atom. The $ScGe_5$ cluster can be formed by adding a Ge atom around the surface of the $ScGe_5$ cluster. The stable isomers can absorb the CO molecule. The positions around the Sc atom can adsorb CO molecule better than others. The Sc-CO model of adsorption is more advantageous than the Sc-OC model. The best adsorption structures are those interacting much with the CO molecule. Scandium doped germanium cluster can be used to produce materials that can treat CO gas by adsorption method. The C-O bond is decreased when it interacts with the scandium doped germanium cluster to perform the chemical process.

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