

Comparative study on the structure and properties of small C_n and NaC_n clusters

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Abstract. The structures, binding energies, and electronic properties of C_n and NaC_n ($n = 2-12$) clusters have been systematically investigated using density functional theory (DFT). A number of previously undiscovered isomers of NaC_n clusters are reported, including fan-like, linear and three-dimensional structures. Moreover, NaC_n clusters with even n are found to be more stable than those with odd n , in contrast with the case of C_n clusters.

PACS. 31.15.Ew Density-functional theory – 36.40.-c Atomic and molecular clusters

1 Introduction

Pure carbon clusters have been extensively studied both experimentally and theoretically since the discovery of the highly stable C_{60} cluster [1–11]. Bai and colleagues employed finite-difference pseudopotential density-functional theory in real space along with Langevin molecular dynamics annealing to study the structure and properties of small carbon clusters C_n ($n = 2-8$) [7]. Shlyakhter et al. have systematically studied the energetics of carbon clusters C_8 and C_{10} in several configurations by all-electron quantum Monte Carlo calculations [8]. Jones et al. investigated many isomers of neutral carbon clusters C_n ($4 \leq n \leq 32$, $n = \text{even}$) using density functional calculations. Their results show that double rings are less stable than monocyclic rings in all cases [9]. The structure, stability and fragmentation of C_n ($n = 2-10$) have been researched in great detail by Raghavachari and Binkley [10]. A series of annular structures of C_n ($n = 3-31$) have been optimized with density function theory (DFT) methods by Xu and co-workers [11]. These papers present the interesting result that an even-odd parity effect in the incremental binding energies is observed for these small carbon clusters. Odd-numbered clusters are found to be more stable than the adjacent, even-numbered clusters. Moreover, odd atom structures easily form linear structures, whereas even atom structures adopt a ring as their optimum configuration.

Compared with pure carbon clusters, most investigations on heteroatom-doped carbon clusters mainly focus on differently sized nonmetallic binary clusters. Recently, along with extensive investigation of pure carbon clusters and nonmetal-doped carbon clusters, some theoretical

studies on small, metal-doped carbon clusters have also been reported, including NaC_n , CaC_n , MgC_n and AlC_n clusters [12–20]. For Na-doped carbon clusters, previous works have only studied NaC_n , ($n \leq 8$) open-chain and cyclic isomers. It is therefore unknown whether other isomers exist which are more stable than those open-chain and cyclic structures. In addition, in order to explore the effects of impurity atoms on pure clusters, it is very illustrative to compare the structures and properties of NaC_n with those of C_n . To the best of our knowledge, no comparative studies of Na-doped carbon clusters have been performed. A series of computational investigations has therefore been performed on the geometry and stability of NaC_n and C_n ($n = 2-12$) clusters.

The paper is arranged as follows: computational methods are described in Section 2; results and discussion are presented in Section 3, and our final conclusions are given in Section 4.

2 Computational methods

Firstly in this paper, the equilibrium geometries of C_n clusters are generated. On the basis of the optimized C_n cluster geometries, different evolution patterns for determining the differently sized NaC_n isomers (i.e., Na-capped, Na-substituted, and C-capped patterns) are taken into account. The geometrical optimizations of C_n and NaC_n ($n = 2-12$) are studied at the B3LYP/6-31G(d) level of theory, where B3LYP is a DFT (density-functional theory) method using Becke's three-parameter nonlocal exchange functional [21] with the nonlocal correlation of Lee et al. [22]. The 6-31G(d) is a split-valence double- ζ plus polarization basis set. Vibrational frequencies, calculated at the same level of theory, are used to determine

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the nature of the stationary points. Local stable structures are characterized without imaginary frequencies, transition states with one imaginary frequency, and higher-order saddle points with multiple imaginary frequencies. In order to test the reliability of our calculation, the triplet C_2 dimer is calculated and discussed first. Theoretical results indicate that the C-C bond length (1.311 Å), vibrational frequency (1703 cm^{-1}) and binding energy (3.07 eV) obtained by using 6-31G(d) basis sets are in good agreement with the experiment values of 1.243 Å, 1828 cm^{-1} , and 3.10 eV [23], respectively. All theoretical calculations are performed with the GAUSSIAN-03 program package [24].

3 Results and discussion

3.1 Growth behavior of differently sized Na-doped carbon clusters

Using the computational method described in Section 2, we have explored a number of low-lying isomers and determined the lowest-energy structures for NaC_n clusters up to $n = 12$. The obtained ground state structures and some low-lying metastable isomers are shown in Figure 1. The lowest energy structures for pure C_n clusters are also plotted in Figure 1 for the purpose of comparison.

Possible NaC_2 geometries, such as two linear isomers and a triangular structure, are considered; the lowest-energy structure C_{2v} [2a in Fig. 1], with a total energy of -238.33486 Hartree, two Na-C bonds of 2.375 Å, and one C-C bond of 1.271 Å, can be obtained by directly capping one Na atom to a pure C_2 cluster [Fig. 1, -75.91838 Hartree]. The linear chain ($C_{\infty v}$ or C_{2v}) isomers [2b, 2c in Fig. 1] are higher in energy than the lowest-energy structure by 0.701 eV and 8.932 eV, respectively.

For NaC_3 , the lowest-energy state (-276.39889 Hartree) was found to be a (C_{2v}) fan-like structure [3a in Fig. 1]. This is followed by a planar isomer (C_{2v}) [3b in Fig. 1], which is located only 0.057 eV higher in energy than the fan-like structure, and both structures have C_{2v} symmetry. However, the bond angle between C-Na-C atoms (38.27°) in 3b of Figure 1 obviously differs from the bond angle (61.57°) between C-Na-C atoms in 3a of Figure 1. Hence, they are different in structure and coexist experimentally. The lowest-energy state can be viewed as the ground state of the C_3 cluster [Fig. 1, $r_{1C-2C} = r_{2C-3C} = 1.297$ Å] capped by a Na atom, whereas, the fan-like structure can be understood as a substitution of a C atom by a Na atom in a rhombic-formed C_4 [Fig. 1] cluster. The two other low-lying isomers [3c and 3d in Fig. 1] can also be obtained by adding one Na atom into the linear form of C_3 , but these configurations are 0.129 eV and 6.664 eV higher in total energy than the lowest-energy one.

The lowest-energy structure for C_4 , which has two kinds of bond lengths (1.4970 and 1.4495 Å), is a planar rhombus [Fig. 1] with a total energy of -152.07018 Hartree, and its four bond lengths in the ring are 1.4495 Å. Adding one Na atom on a C_4 rhombus cluster, a low-lying isomer [4c in Fig. 1] of NaC_4 via obtained

with C_s symmetry and at 0.947 eV higher than the lowest-energy structure. On the basis of the ground state of C_5 [see Fig. 1], as Na replaces different C atoms, energetically different NaC_4 [4a and 4d] isomers can be produced. The isomer 4a is the lowest-energy structure with $C_{\infty v}$ symmetry and -314.48909 Hartree in total energy.

For NaC_5 clusters, we have identified four different minima, namely, one structure with $C_{\infty v}$ symmetry, two structures with C_{2v} symmetry, and another structure with C_s symmetry [see Fig. 1]. Among these, the linear structure 5a, with $C_{\infty v}$ symmetry and -352.56701 Hartree in ${}^2A''$ state, is the lowest in energy at the B3LYP/6-31(d) level of theory, in agreement with the result obtained by Li et al. [12]. This form can be obtained by adding one Na atom on the side of the ground-state C_5 which has $D_{\infty h}$ symmetry and is at -190.20477 Hartree in total energy [5a in Fig. 1]. The rest [5b, 5c and 5d] are all characterized as local minima, which have all real vibrational frequencies. They are predicted to be 0.150, 0.290 and 0.564 eV, respectively, higher in energy than structure 5a.

The shield form of C_6 [Fig. 1, C_{3h} symmetry], which has two alternating bond lengths of 1.328 Å and 1.327 Å, is more stable than the other structures. For NaC_6 , four kinds of isomers can be generated as the energetic minima. The two stable NaC_6 clusters can be viewed as being derived from the C_6 [Fig. 1] cluster. One [6c in Fig. 1, C_{2v} symmetry] is obtained from adding a Na atom at the side of a C_6 cluster. When adding a Na atom on the top of the C_6 structure, another different 6d isomer is yielded with a shortest distance $r_{3\text{Na}-7C} = 2.544$ Å and C_1 symmetry. In addition, an analogous fan-like 6b structure can also be generated, and is described as a C atom in the C_7 cyclic isomer being substituted by sodium. However, this isomer is not also the lowest-energy NaC_n isomer. The lowest-energy NaC_6 6a structure, with -390.65525 Hartree and ${}^2A'$ state, is formed when the carbon atom at end of the C_7 [Fig. 1] structure is substituted by sodium.

For C_7 , we obtain a linear structure with $D_{\infty h}$ symmetry [see Fig. 1], in agreement with the result obtained by Agrawal et al. [25]. Placing a Na atom at the end of C_7 cluster, the lowest-energy structure for AlB_7 can be obtained with -428.73265 Hartree and $C_{\infty v}$ symmetry [7a in Fig. 1]. The shortest Na-C bond length occurs at 1C-8Na and with 2.232 Å. The bond distance at 1B-2B is shortest among B-B bonds at 1.255 Å. Several other isomers were considered, including two plane structures and three, 3D structures [7b, 7c, 7d, 7e, 7f in Fig. 1]. Their total energies are 0.659 eV, 1.642 eV, 2.262 eV, 2.527 eV and 7.348 eV higher than the lowest-energy state, respectively.

The ring isomer, with two kinds of bond lengths ($r_{1C-2C} = 1.262$ Å and $r_{1C-5C} = 1.382$ Å) and C_{4h} symmetry, is by far the most stable of C_8 structures. Earlier works [9, 25] have also found the cyclic structure to be stable. Five isomers identified for NaC_8 are shown in Figures 1(8a-8e). Structure 8a is the lowest-energy structure and can be obtained as for 7a. The shortest Na-C bond length is at 1C-2Na and is 2.234 Å. Fan-like structure 8b is 0.958 eV higher in energy, and can be acquired when one C atom in the cyclic C_9 (the low-lying structure of C_9)

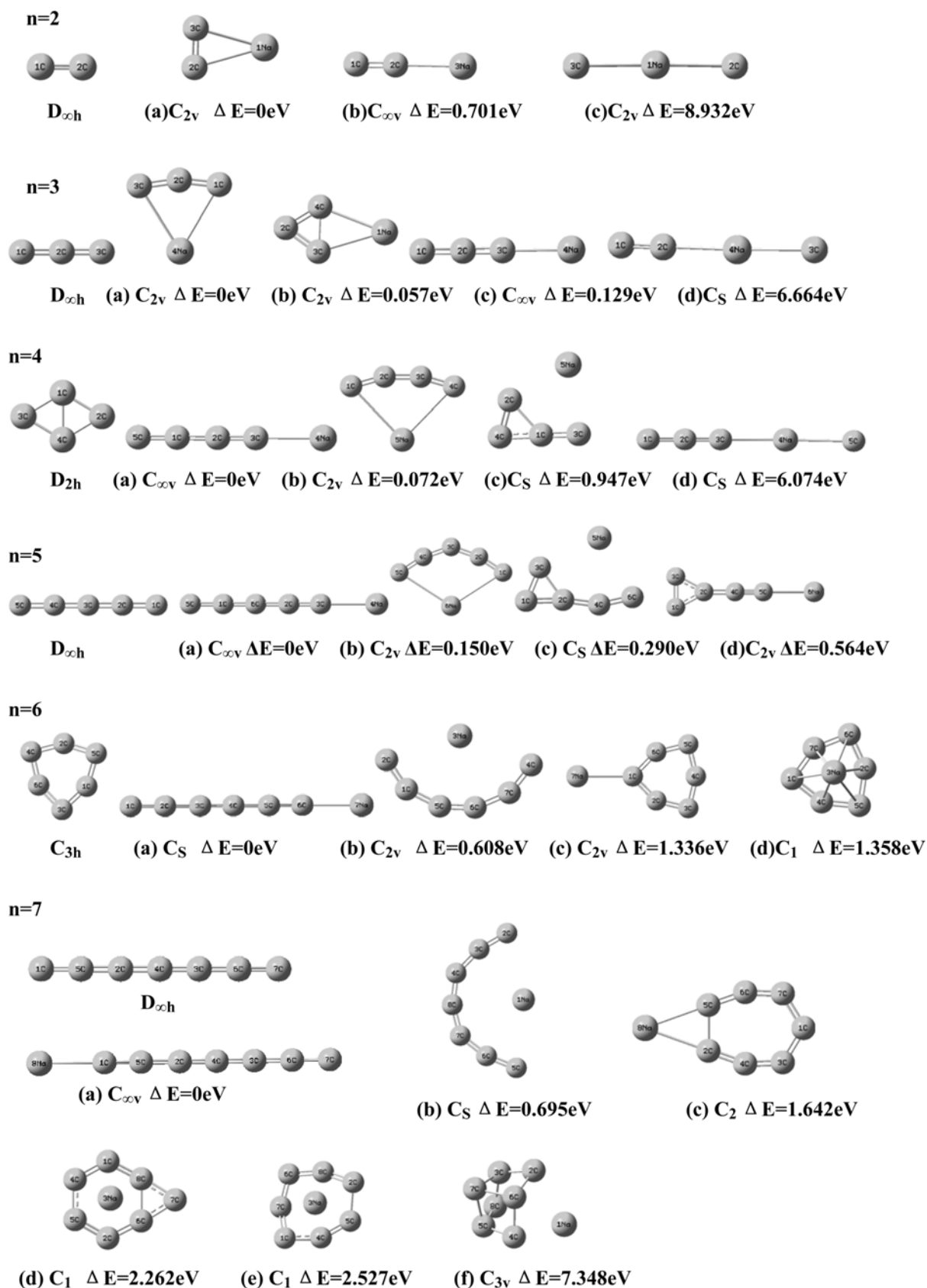
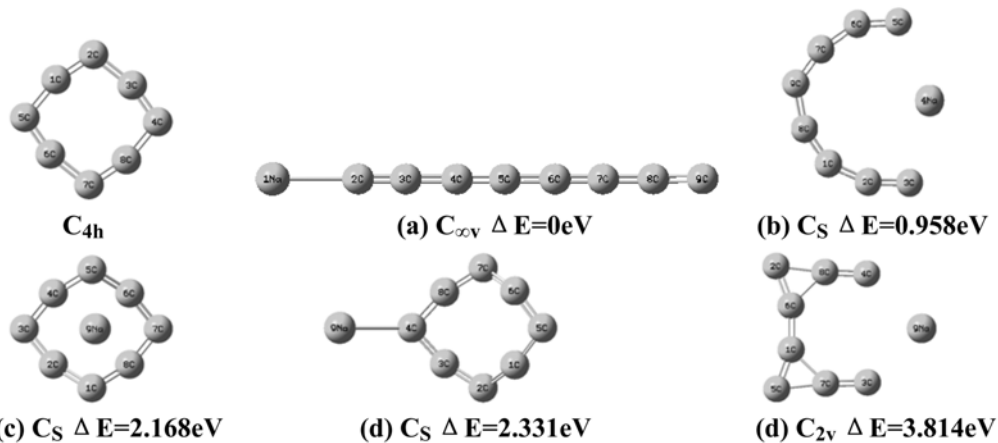
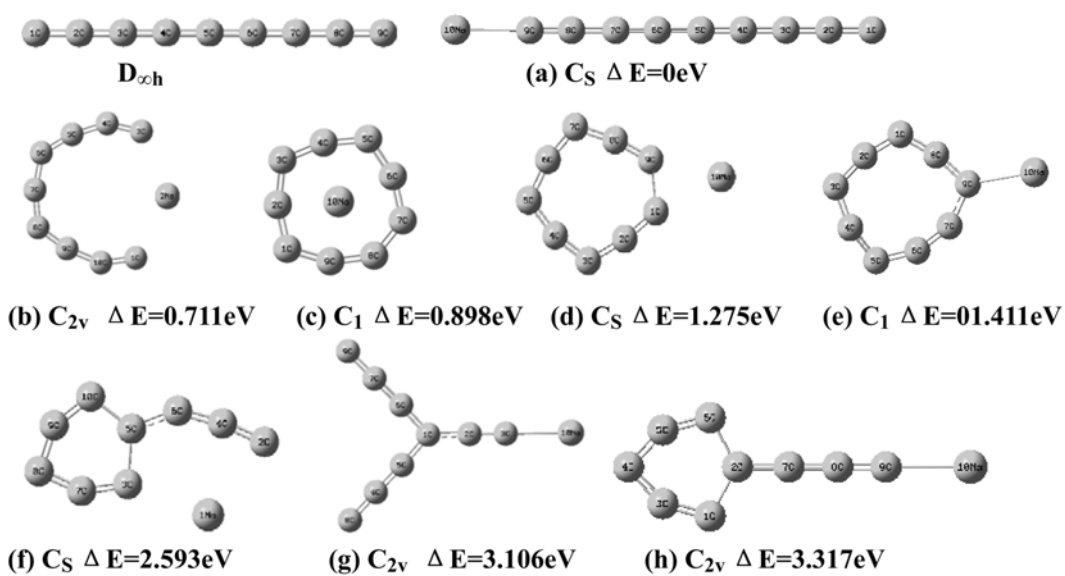


Fig. 1. The lowest-energy and low-lying structures of NaC_n ($n = 2-12$) clusters and lowest-energy structures of pure C_n ($n = 2-12$) clusters.

n=8



n=9



n=10

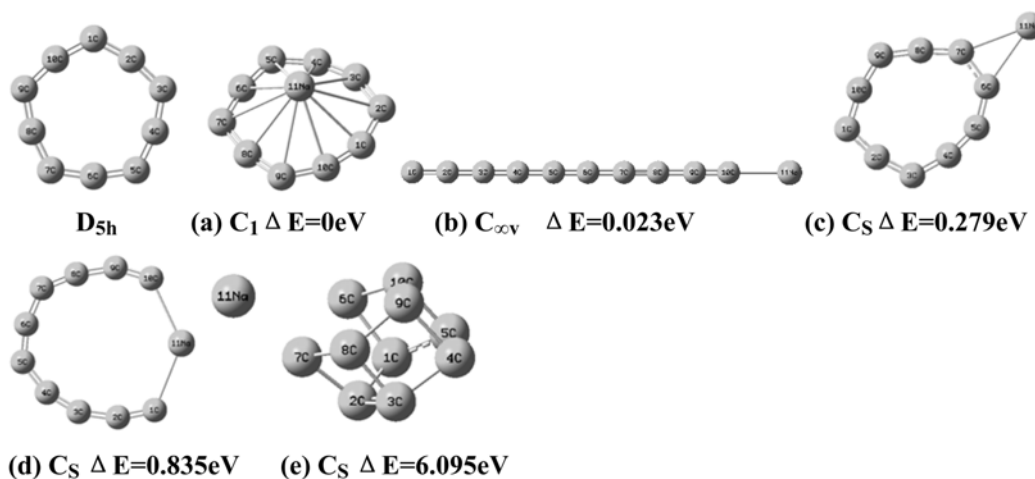
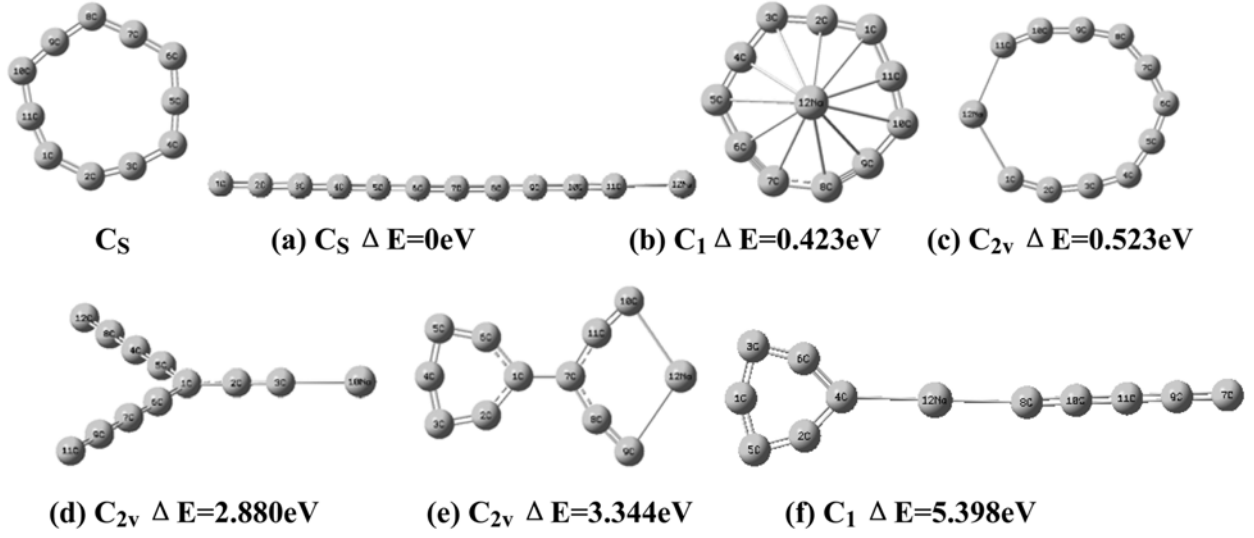
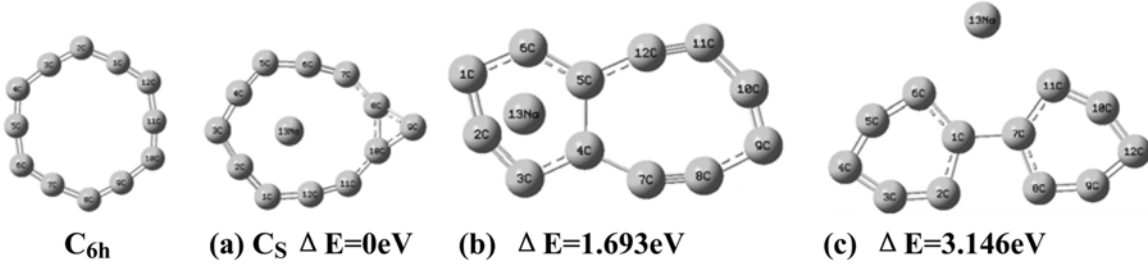


Fig. 1. Continued.

n=11**n=12**Fig. 1. *Continued.*

is substituted by Na. Like 6c and 6d, 8b and 8c can be viewed as being generated from the C_8 cluster by adding a Na atom at different sites. Their total energies are obviously higher than the ground state.

A linear form was obtained for pure C_9 . The lowest energy structure of NaC_9 (9a), with -504.89598 Hartree in energy and $C_{\infty v}$ symmetry, can be viewed as the ground-state structure of pure C_9 with an appended C atom at one side or a C atom substituted into the linear form of C_{10} (the low-lying structure of C_{10}). The fan-like structure 9b was also obtained as a metastable structure which is only 0.711 eV higher in energy. Another low-lying isomer should be mentioned [9c in Fig. 1], as it is 0.898 eV higher in total energy than the lowest-energy structure.

For C_{10} , our calculations favor the ring structure [Fig. 1, D_{5h} , $r = 1.298$ Å]. This structure is in agreement with the theoretical calculation by Jones [9]. Differing from the above Na-doped clusters — although the linear NaC_{10} structure is still the most stable structure — it is no longer the lowest-energy state because of its higher total energy as compared to the umbrella-like isomer. In such-sized clusters, two different three-dimensional structures are considered. One is the typical capped structure

with C_1 symmetry [10a in Fig. 1]. The other structure 10e may be described as adding a Na atom at the flank of a C_{10} isomer. In analogy to other NaC_n , the linear structure 10b can be obtained by appending a Na atom to the linear C_{10} structure. However, the stability of the 10b isomer is lower than the umbrella-like structure 10a due to its slightly higher total energy. The two other isomers are also shown in Figure 1 [10c and 10d] and their total energies are also higher than that of the umbrella-like structure.

Energetically, the most stable structure among all of the C_{11} isomers is the ring structure with C_s symmetry and with a shortest bond length $r_{1C-11C} = 1.251$ Å. Six different stable NaC_{11} isomers are predicted using the same level of theory. The lowest-energy structure for NaC_{11} can be obtained with C_s symmetry [11a in Fig. 1]. The distance of $11C-12Na$ is 2.237 Å and the shortest C-C bond length occurs at $8C-9C$ and is 1.249 Å. Moreover, the three-dimensional structure 11b is strongly competitive as the lowest-energy structure, being only 0.423 eV higher compared to 11a. The fan-like structure [11c] also can be obtained, and is 0.523 eV higher in total energy. The other three isomers are shown in Figure 1 [11d, 11e

and 11f in Fig. 1], and there is a much greater difference (at least 2.880 eV) between 11a and the other isomers.

For C_{12} , the ring structure, with -456.78779 Hartree in total energy and C_{6h} symmetry, is the lowest-energy structure. Our ring structure agrees with the theoretical predictions by Jones [9] and Xu et al. [11]. Three isomers for NaC_{12} are obtained and are shown in Figure 1 [12a, 12b and 12c]. The three-dimensional structure 12a is the lowest-energy one, with C_s symmetry and -619.10087 Hartree. The shortest Na-C bond length occurs at 6C-13Na and 12C-13Na and is 2.569 Å. The distance of 1.262 Å at 6C-7C and 11C-12C is the shortest among C-C bond lengths. The remaining isomers, due to higher total energy, are less stable than the three-dimensional structure 12a.

It is well-accepted that the lowest-energy structures of C_n ($n \leq 12$) small clusters favor non-three-dimensional configurations, and a parity alternation phenomena can be observed; odd-numbered atomic clusters easily form linear structures and even-numbered ones adopt a ring as their optimum. However, the situation is changed when adding one Na atom to carbon clusters. In brief, three different kinds of configurations are obtained for the lowest-energy structures of NaC_n clusters ($n = 2-12$), i.e., fan-like, linear and three-dimensional. For NaC_2 and NaC_3 clusters, the lowest-energy structures favor fan-like configurations. From $n = 4$ to $n = 9$, the lowest-energy structures of NaC_n clusters favor linear forms, and can be viewed as a Na atom being added at the side of the linear C_n clusters or substituting a C atom at the side of the linear C_{n+1} . With increasing cluster size n , the lowest-energy structures, to the exclusion of NaC_{11} , prefer three-dimension forms to planar ones. According to this trend, we can predict that the lowest-energy structures of NaC_n clusters will prefer more complex three-dimension forms when $n > 12$.

3.2 Relative stability and electronic properties

3.2.1 Relative stability

The relative stability of the differently sized clusters can be predicted by calculating the average binding energy and fragmentation energy. The average binding energy for the C_n , and NaC_n clusters can be defined as follows: $E_b(n) = [nE_T(C) - E_T(C_n)]/n$, $E'_b(n) = [nE_T(C) + E_T(Na) - E_T(NaC_n)]/n + 1$, where $E_T(C)$, $E_T(Na)$, $E_T(NaC_n)$, and $E_T(C_n)$ represent the total energies of the most stable C, Na, NaC_n , and C_n clusters, respectively.

From Figure 2, it can be seen that the binding energy generally increases with cluster size. Thus, the clusters can continue to gain energy during the growth process. Furthermore, it is interesting to note that the C_n curves reveal an even-odd parity effect in the incremental binding energies, with enhanced stability at $n = 3, 5$ and 7 . The obtained results are agreement with experiment [23,26,27]. [See C_n (Exp) in Fig. 2] However, the parity phenomenon

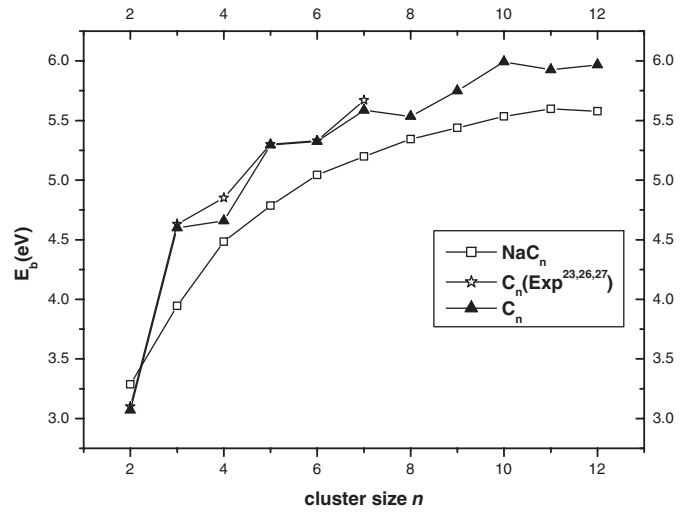


Fig. 2. Size dependence of the binding energy per atom of NaC_n and C_n clusters.

disappears and the binding energy increases smoothly for Na-doped carbon clusters.

In addition to the binding energies of C_n and NaC_n clusters have also been investigated. Fragmentation energy can be defined as the following: $E_F(n) = E_T(C) + E_T(C_{n-1}) - E_T(C_n)$, $E'_F(n) = E_T(NaC_{n-1}) + E_T(C) - E_T(NaC_n)$, where $E_T(C)$, $E_T(C_{n-1})$, $E_T(NaC_{n-1})$, $E_T(Na)$, $E_T(NaC_n)$ and $E_T(C_n)$ represent the total energies of the most stable C, C_{n-1} , NaC_{n-1} , $E_T(Na)$, $E_T(NaC_n)$ and $E_T(C_n)$ clusters, respectively.

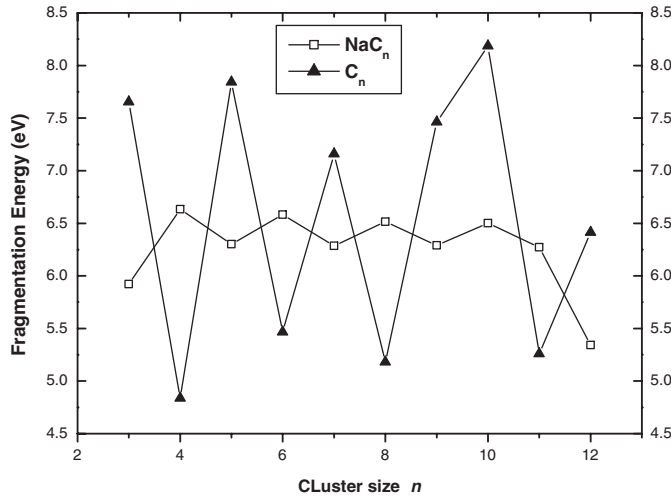
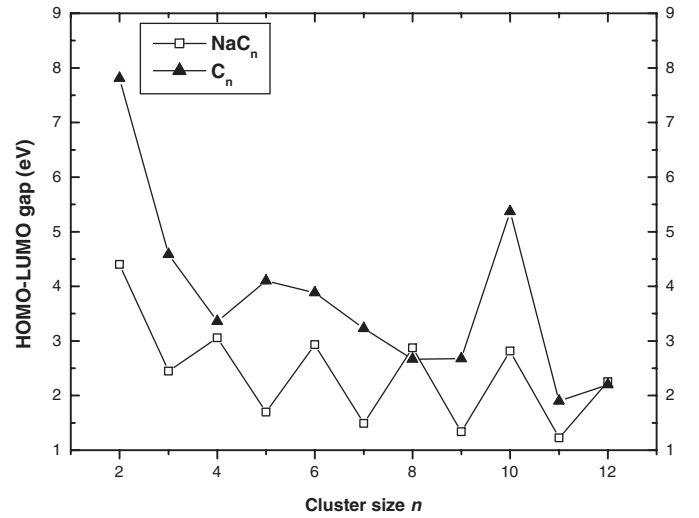
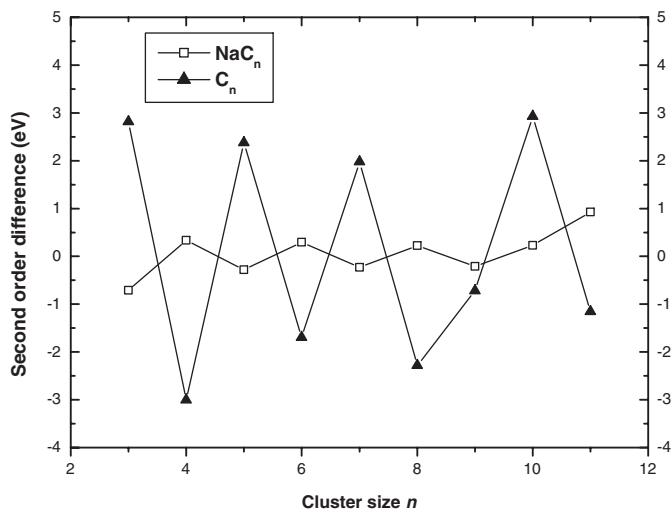
As shown in Figure 3, the lowest fragmentation energies of the C_n clusters appear at $n = 4, 6$ and 8 . This indicates that C_4 , C_6 and C_8 clusters are less stable than their neighbors, which is clearly in agreement with the result of Figure 2. However, when Na is doped in the C_n clusters, this situation greatly changes. As can be seen from Figure 3, the local maxima of $E'_F(n)$ appear at the even sizes of 4, 6, 8 and 10, contrary to the result for small carbon clusters.

In cluster physics, the second-order difference of cluster energies, $\Delta_2 E(n) = E(n+1) + E(n-1) - 2E(n)$, is a sensitive quantity that reflects the relative stability of clusters [28]. Figure 4 shows the second-order difference of cluster energies, $\Delta_2 E(n)$, as a function of the cluster size. For carbon clusters, maxima are found at $n = 3, 5, 7$ and 10 , indicating that these clusters possess higher stability. On the other hand, the more stable of the NaC_n clusters are located at $n = 2, 4, 6, 8$ and 10 , which is perfectly consistent with the trend of fragmentation energies as shown in Figure 3.

As shown in Figure 5, the HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gaps of NaC_n are usually smaller than those of C_n clusters, except for $n = 8$ and 12 . As far as the NaC_n cluster curve is concerned, even structures have higher HOMO-LUMO gaps than odd structures. Thus,

Table 1. Total energy, shortest Na-C and C-C distance, and electronic state of NaC_n and C_n clusters for the lowest-energy structures.

Cluster	TE (Hartree)	R_{Na-C} (Å)	R_{C-C} (Å)	State	Cluster	TE (Hartree)	R_{C-C} (Å)	State
NaC_2	238.3348646	2.35671	1.27079	$^2A'$	C_2	75.91838433	1.31070	
NaC_3	276.3988929	2.34950	1.31130	2A	C_3	114.0460636	1.29687	$^1\Sigma$
NaC_4	314.4890913	2.22621	1.25995	$^2A'$	C_4	152.0701849	1.44988	$^1A'$
NaC_5	352.5670060	2.22802	1.26124	$^2A''$	C_5	190.2047724	1.28683	$^1A'$
NaC_6	390.6552516	2.22802	1.26124	$^2A'$	C_6	228.2519778	1.32734	$^1A'$
NaC_7	428.7326529	2.23232	1.25453	2A	C_7	266.3614824	1.27675	1A
NaC_8	466.8184434	2.23377	1.24853	2A	C_8	304.3982166	1.26208	1A
NaC_9	504.8959833	2.23556	1.25091	2A	C_9	342.5188734	1.27513	1A
NaC_{10}	542.9812814	2.55350	1.26803	2A	C_{10}	380.6661028	1.29805	1A
NaC_{11}	581.0581565	2.23689	1.24918	1A	C_{11}	418.7057475	1.25137	$^1A'$
NaC_{12}	619.1008699	2.56890	1.26175	2A	C_{12}	456.7877897	1.25144	1A

**Fig. 3.** Size dependence of the fragmentation energy of NaC_n and C_n clusters.**Fig. 5.** Size dependence of the HOMO-LUMO of NaC_n and C_n clusters.**Fig. 4.** The second-order energy differences of neutral NaC_n and C_n clusters.

one can roughly predict that even structures have good stability. The result reveals a strong correlation between the HOMO-LUMO gaps and the energetic stability of the clusters.

3.2.2 Electronic properties

The ionization potential (IP) is an important parameter to understand stability against the ejection of one electron from the HOMO energy level to the continuum. Usually, there are three types of IP: Koopmans IP, vertical IP and adiabatic IP. Koopmans IP is the HOMO energy, vertical IP is the energy difference between the neutral and ionic clusters at the neutral equilibrium geometry, and adiabatic IP is the energy difference between the neutral and ionic clusters at their respective equilibrium geometry. In this work, the adiabatic IP of NaC_n and C_n clusters for their lowest-energy structures are calculated and shown in Figure 6. The C_n clusters with even n were found to

Table 2. Binding energy (BE), Fragmentation energy (FE), Adiabatic Ionization potential (IP), and HOMO-LUMO gap, for the lowest-energy structures.

Cluster	BE (eV)	FE (eV)	IP (eV)	Gap (eV)
NaC ₂	3.286		9.414	4.402
NaC ₃	3.945	5.923	7.039	2.447
NaC ₄	4.483	6.635	8.224	3.059
NaC ₅	4.786	6.300	6.341	1.698
NaC ₆	5.042	6.581	7.718	2.933
NaC ₇	5.198	6.286	6.307	1.488
NaC ₈	5.344	6.515	7.387	2.874
NaC ₉	5.439	6.290	6.259	1.337
NaC ₁₀	5.535	6.501	5.761	2.814
NaC ₁₁	5.597	6.272	6.209	1.223
NaC ₁₂	5.577	5.343	5.728	2.253

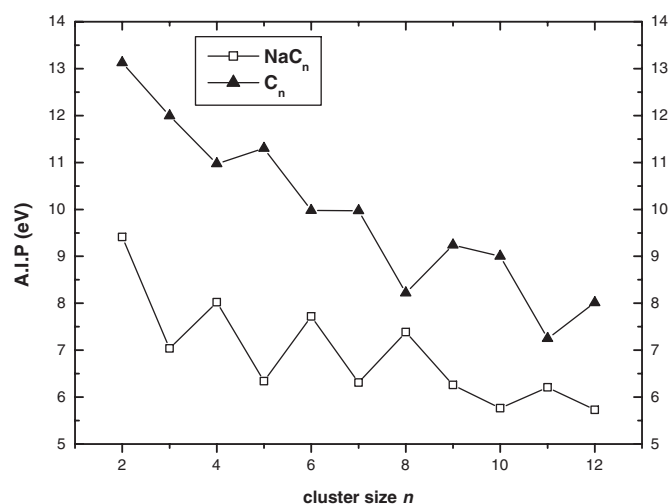


Fig. 6. Comparison of the adiabatic ionization potentials of NaC_n and C_n clusters.

have larger adiabatic ionization potentials. However, for NaC_n clusters, NaC₄, NaC₆ and NaC₈ have larger adiabatic ionization potentials, corresponding to their higher stabilities. A distinct phenomena for NaC_n clusters is that all even n (except $n = 10$) have a higher adiabatic ionization potential than odd n . In addition, there is a trend for NaC_n and C_n that the ionization potential (IP) generally decreases with cluster size.

4 Conclusion

We have conducted a systemic DFT study on NaC_n clusters with sizes of $n = 2$ – 12 , and compared these with pure C_n clusters. Three kinds of different lowest-energy structures are obtained for NaC_n clusters. For NaC₂ and NaC₃ clusters, the lowest-energy structures are fan-like. From $n = 4$ to $n = 9$, the lowest-energy structures of NaC_n clusters are linear, and can be viewed as a Na atom being added at the side of a linear C_n cluster, or as a substi-

tuted C atom at the side of a linear C_{n+1} cluster. With increasing cluster size n , the lowest-energy structures prefer three-dimensional forms to planar ones. Furthermore, the stabilities of NaC_n clusters present an obvious even/odd phenomenon, which is completely different from the case of C_n clusters. NaC_n clusters with even n are more stable than those with odd n . The trend of parity alternation can be illuminated considering the computational results in fragmentation energy, second-order energy difference, HOMO-LUMO gaps, and ionization potentials.

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