



Ab initio investigation of structure, spectrum, aromaticity and electronic properties of C₁₀ carbon cluster



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ABSTRACT

The predicted lower energy structures of neutral carbon cluster C₁₀ are presented by using the particle swarm optimization method in combination with quantum chemistry calculation. Our results describe a wonderful diversity of C₁₀ configuration with the DFT and MP2 methods. For linear and cyclic clusters, the energy of most stable monocyclic structure with D_{5h} symmetry is lower by 1.38 kcal/mol than the transition isomers with D_{10h} symmetry at CCSD(T)/cc-pVTZ level, which is consistent with the previous theoretical results by others. All linear structures of C₁₀ cluster have been certified as the metastable states at different calculation methods in this work. Simulated infrared spectra reveals that the extensive electron localization exists in the D_{10h} configuration leading to the decreasing of the number of vibration modes compared with D_{5h} configuration. The nucleus independent chemical shift (NICS) calculations indicate that planar C₁₀ system is a stable aromatic compound and the position used to calculate the aromatic indices can be affected by the most shielding or deshielded location that we employed. The contribution of the delocalized electrons to the π-aromaticity is identical in C1_a and C1_b. By the adaptive natural density partitioning (AdNDP) and canonical molecular orbital (CMO) analysis, we know that the highly symmetric structures have more energy degenerate CMOs and 2 center-2 electron bond connection, and monocyclic C₁₀ cluster is a globally doubly (σ- and π-) aromatic compound. Topological analysis and natural bond orbital (NBO) analysis show that there isn't any electrostatic type of interactions in C₁₀ structures, and much of negative natural valence electron configuration comes from high angular momentum orbitals. According to the electron configurations, the natural hybrid orbital is mainly composed of sp hybrid in the systems. It is worth mentioning that the competition of complicated many-body effects plays a significant role in stabilizing the distorted configuration of C₁₀ cluster. We expect our work can provide more information for further experimental studies.

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1. Introduction

The successful exfoliation of monocrystalline graphitic films, which was found to be a semimetal with exhibiting a strong ambipolar electric field effect [1], has again brought about a special fascination for research on different size carbon clusters [2–5]. As the most basic framework of substance, small carbon clusters are often connected with the formations of nanotubes [6–8], fullerenes [9,10], single grapheme sheets [11] and thin solid diamond films [12], and play important roles in the interstellar chemistry [13], astrophysics [14], and combustion process [15]. Factually, the in-depth investigations of structures and properties of carbon clusters have been going on for more than 50 years in theoretical and

experimental respects [3]. The nontrivial electronic characteristics and the reduced dimensionality of carbon clusters have been promising for various practical applications in nanoscale materials and devices, like nanoelectromechanical devices, nanoelectronic components, and hydrogen storage materials [8,16]. So the exploration of the nature of carbon clusters can not only extremely deepen and broaden the understanding of their structural evolutions and behavioral characteristics at the atomic level, but also greatly contribute to the reformation and innovation of products in high-tech fields.

Historically, for the limitation of experimental techniques and theoretical models in generating and simulating the carbon clusters, researchers cannot give out accurate systemic information about all the small cluster structures [17]. Remarkable progress has been made in both theoretical interpretations and experimental explorations in recent years. Until now, the electronic

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structures, fluorescence spectra and vibrational frequencies [18–25] of some special ring and linear chain carbon isomers have been explored. For examples, Gregory and Adina [18,19] investigated the surface plasmon polariton-enhanced Raman spectra of C_n ($n = 14, 16, 18, 20$) in the range of visible light wavelengths. The strong resonance enhancement and systematic shifts of spectra peaks suggested that the four clusters have the same geometry and eliminated the existence possibility of a bowl or cage structure. Maier and co-workers [20,21] detected the electronic spectra of cyclic C_{4n+2} ($n = 2, 3, 4$) in the gas phase by a mass selective resonant two-color two-photon ionization technique coupled to a laser ablation source, and revealed that the cyclic bare carbon systems are not responsible for the stronger diffuse interstellar bands carriers. Moreover, they further drew a conclusion that the electronic spectrum of C_{10} can be used to explain the connection between the evolution of the spectral pattern and the expected structural change [21]. The infrared vibrational spectroscopy of carbon chains (up to C_{13}) have been observed via a supersonic cluster beam-diode laser spectroscopy [23,24,26], which focus on explaining the asymmetric stretching transitions and high temperature stability of small linear carbon clusters.

On the theoretical side, it was generally accepted that the electronic ground state of odd-numbered linear clusters are $^1\Sigma_g^+$, whereas the even-numbered clusters have $^3\Sigma_g^-$ electronic state. So far, most calculation simulations are mainly relying on ab initio techniques [27–31], empirical interatomic potentials [32–34], genetic algorithms [35] and simulated annealing [36] to obtain the possible stable structures of low dimensional carbon clusters. On the one hand, previous theoretical researches [3–5,17,37–39] focused on the structural evolution of odd-even oscillation of carbon clusters and demonstrated that the odd-numbered clusters have a linear structure and the even-numbered clusters prefer an irregular cyclic structure. On the other hand, the competitive coexistence of electron delocalization, Peierls instability [40] and second-order Jahn-Teller effect in $4n+2$ closed-shell monocyclic systems have attracted a large amount of attention to their aromaticity and antiaromaticity [41–44]. It is true that the study of those effects in the pure-carbon π -systems are important for understanding how electronic structures of finite systems approach those of infinite periodic ones [21]. In these aspects, Zhang and Xu [37] combined the genetic algorithm and simulated annealing method on the Brenner bond-order potential energy surface to discuss the structure evolution regularity of C_n ($n = 2–30$) clusters. They have arrived at some conclusions of the distribution interval of linear, single ring, double ring and multi-ring structures. Cai and Shao [17] developed a global optimization algorithm based on the parallel fast annealing evolutionary algorithm to obtain the lower energy structure of carbon clusters C_n ($n = 2–71$). The evolution process of carbon configurations from linear to mono-ring to fullerene-like to fullerene structures have been discussed in details. In order to more appropriately and accurately describe the structural evolution process and the even-odd oscillations problem, Kosimov and co-workers [3,4] employed the energy minimization technique with the conjugate gradient method to study the lower-energy configurations of carbon clusters from 2 to 55. In addition, Kassae et al. [39] confirmed that the C_{4n+2} clusters have aromatic characters. Their AIM analyses further indicated that molecular vibrations may change the topological network of small antiaromatic ring, like C_4 and C_8 . Natural bond orbital analysis suggested that aromatic clusters C_{4n+2} isomers have two big delocalized π -bonding, whereas C_{4n} clusters only have one big delocalized π -bonding [41].

To the best of our knowledge, in spite of the structures' configuration and related electrical properties of the different size carbon clusters have been widely explored, the characteristics information

about a particular size cluster are scarce. Because earlier works were chiefly focused on the ground state or few stable configurations, the actual application is limited. Simultaneously systems often don't reach their ground state (may get stuck in the metastable state) when they are formed under natural condition [3]. Moreover, the conclusions drawn by different method in previous researches didn't always fit in well with each other. Here we will go beyond such approaches and concentrate on a representative fixed-size system, C_{10} , to systematically study their related properties of the stable and metastable structures. The reasons why we choose C_{10} can be list as follows. Firstly, the earlier theoretical studies [12,45,46] deemed that aromatic ring C_{10} is the watershed of topological transition from linear structure to mono-ring structure in the moderate size carbon clusters. However, there are some considerable controversies in the theoretical study of C_{10} configuration about what the ground state is. Next, the sp^2 hybridization [47] of C_{10} have a larger energy gap when compared with its both side structures [41], and the C_{10} isomer is the first stable carbon cluster which has twin aromaticity and $D_{(2n+1)h}$ symmetry [46]. More importantly, the symmetry of the ground state C_{10} structure (the D_{5h} or D_{10h} symmetries) has always been a contentious issue [12,45,48]. Finally, the study of the sp -hybridized carbon clusters manifested the high abundance and superior stability of C_{10} at temperature 2000 K, and revealed that the cyclic C_{10} may be the major constituent units of larger clusters and fullerenes [49]. According to all above, the C_{10} may be seen as the original seed to understand the formation mechanism of sub-monolayer grapheme.

In this work, we shall carry out a systematic and quantitative investigation of the lowest energy structures of C_{10} by the particle-swarm optimization algorithm with quantum chemistry calculation. The stable structure, infrared spectrum, aromaticity and electronic structure of C_{10} are expressed with the accuracy of the calculations assessed through comparison with DFT and MP2 based employment. This paper is organized as follows. In Section 2, the computational procedures and methodology, as well as the theoretical overview of correlation properties are briefly introduced. The geometry structures and related characters of the most possible C_{10} clusters are compared with the available data obtained by others in Section 3. In Section 4, the results of the present study are summarized.

2. Computational procedures and methodology

Different from other structure prediction methods, the crystal structure analysis by particle swarm optimization (CALYPSO) [50,51] code is used to construct and search the initial low-energy configuration of the neutral carbon cluster C_{10} . Based on the evolutionary scheme of particle swarm optimization (PSO) algorithm, this method can effectively obtain a best minimization or the best local minimum position of free-energy surfaces in the hyperspace. At the beginning, the initial structures are randomly generated with the constraints of symmetries and the chemical compositions for a given compound. Then, the bond characterization matrix and the local structural optimization are applied to eliminate the repetitive structures and noise on the energy surfaces, driving systems move to a local minimum. Whether or not the ultimate local optimized structure can be accepted is dependent upon the check of Metropolis criterion [52]. Finally, those putative reasonable parental structures are picked up to produce offspring isomers in the same qualifications and algorithm checking. The procedure stops until the predetermine number of convergence iterations is reached. High rationality and superior search efficiency of this evolutionary methodology have been demonstrated by successful prediction of many various known clusters

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