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Parity alternation of linear ground-state hydrogenated cationic carbon clusters HC_nSi^+ ($n = 1–10$)

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ABSTRACT

Making use of molecular graphics software, we have designed numerous models of HC_nSi^+ ($n = 1–10$), and by means of the B3LYP density functional method, performed geometry optimization and calculation on vibrational frequency. The ground-state isomers of HC_nSi^+ ($n = 1–10$) are found to be linear with the Si and H atom located at the ends of the C_n chain. When n is even, the C_n chain is polyacetylene-like whereas when n is odd, the C_n chain displays a structure that fades into a cumulenic-like arrangement towards the Si end. According to the results of mass spectrometric investigation available in the literature, the intensities of even-n HC_nSi^+ are more intense than those of odd-n HC_nSi^+, implying that the former are more stable than the latter. We detect trends of odd/even alternation in electronic configuration, the highest vibrational frequency, ionization potential, incremental binding energy as well as in certain bond length and certain atomic charge of the linear ground-state structures of the HC_nSi^+ ($n = 1–10$) clusters. The calculation results reveal that the even-n cationic clusters are more stable than the odd-n ones.

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1. Introduction

The research on the structures and properties of small carbon clusters has a long history [1]. In the last decade, carbon clusters doped with heteroatom(s) have attracted immense attention. It is of fundamental significance to compare the reactivity of carbon clusters with that of the doped counterparts. Carbon chains doped with heteroatom(s) are also important in astrophysics. A variety of carbon clusters bonded to heteroatom(s) such as O, N, S, and Si have been observed in interstellar clouds. The UMIST database for astrochemistry stores thousands of gas-phase reactions that are important in astrophysical environments, and the species involved in their hundreds [2]. As described by Millar, species belong to the polyynes series have been detected in circumstellar environment of late-type carbon-rich stars (such as star IRC +10216), and in dense and dark interstellar molecular clouds (such as TMC-1) as well as in hot molecular cores [3]. In recent years, carbon chains and rings which are of astrophysical interest have been identified in supersonic molecular beams by means of Fourier-transform microwave and laser cavity ring down spectroscopy [4,5]. Silicon is a major constituent of interstellar dust, and silicon-doped carbon clusters are fairly abundant in certain interstellar and circumstellar sources [6]. In laser ablation of graphite targets and arcing across graphite electrodes in ammonia, compounds belonging to the polyynes series were generated [7]. Using a mixture of silicon carbide and polycyclic aromatic compounds as a target for laser ablation, Huang et al. generated clusters ions composed of carbon and silicon atoms and a single hydrogen atom [8].

Despite the intriguing findings, theoretical investigations on hetero-carbon triatomic clusters are not that many. Using a large-scale coupled cluster method, Botschwina et al. conducted investigations on HC_5N, HC_5NH, HC_4NC, HC_5NC, HC_6NC, and HC_9NH^+ [9–12]. High-level coupled cluster calculations on theoretical structures of the carbine HC_4N and NC_nS ($n = 1–7$) were carried out by McCarthy et al. [13,14]. Scemama et al. examined the structures and properties of polyynes $HC_{2n}H$ ($n = 1–8$) and cyanopolyynes $HC_{2n-1}N$ ($n = 1–7$) by density functional calculations [15]. Using the B3LYP density functional method, Allamandola et al. investigated the geometries and harmonic frequencies of hydrogenated cyanopolyyne $HC_{2n+1}N$, ($n = 0–5$) species [16]. By means of ab initio calculations, Liu et al. examined structures of HC_nS^+ ($n = 3–13$) and HC_nS^- ($n = 4–18$) [17] while Flores studied the electronic spectra of SC_nH radicals ($n = 2–4$) [18].

The time-of-flight mass spectra of $HSiC_n^+$ clusters show an abundance pattern of odd/even alternation: the even-n clusters are more prominent than the odd-n ones [8]. To the best of our knowledge, there are no systematic theoretical studies on

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small $HSiC_n^+$ clusters. To explore the experimental observation theoretically, we designed a huge number of structural models of HC_nSi^+ ($n = 1–10$), and performed geometry optimizations and calculations on vibrational frequencies by means of the B3LYP density functional method in this study. The geometry structure, bonding character, atomic charge, electronic configuration, the highest vibrational frequency, ionization potentials, incremental binding energy, and dissociation channels of the linear ground-state clusters were examined. Based on the results, we provide explanation on why the even-*n* HC_nSi^+ ($n = 1–10$) isomers are more stable than the odd-*n* ones. The outcomes can serve as a guideline for the synthesis of similar kind of materials as well as for future theoretical studies on heteroatom(s)-doped carbon clusters which are so commonly found in circumstellar environments.

2. Computational method

During the investigation, devices for molecular graphics, molecular mechanics, and quantum chemistry were used. To start, a three-dimensional model of a cluster was designed using HyperChem for Windows [19] and Desktop Molecular Modeller [20] on a PC computer. The model was optimized by MM+ molecular mechanics and semi-empirical PM3 quantum chemistry. Then, geometry optimization and calculation of vibrational frequencies were conducted using the B3LYP density functional method of Gaussian 03 package [21] with 6–311G** basis sets, i.e., Becke's 3-parameter nonlocal exchange functional with the correlation functional of Lee–Yang–Parr [22,23]. It has been pointed out that geometries computed with more expensive basis sets do not necessarily lead to more accurate final results [24]. The single point energy calculations following the optimizations were performed using the larger 6–311+G** basis set (i.e., B3LYP/6–311 + G**//B3LYP/6–311G**). Because the change of zero point energy (ZPE) could only be affected slightly by the quality of the employed method, all energies were calculated with ZPE correction at the B3LYP/6–311G** level. The optimized models were again displayed using HyperChem for Windows. The data of partial charges and bond orders were explored with Gaussian natural bond orbital (NBO). All of the calculations were carried out on the servers of SGI.

3. Results and discussion

3.1. Geometry configuration

Because there are so many possible structures of the clusters, the identification of the ground-state isomers is important. For a particular family of molecules, the basic structure with the lowest energy affects the "building" of larger molecules. The ground-state isomers of heteroatom(s)-doped carbon clusters may adopt different configurations. The linear configurations terminated by the heteroatom(s) are rather popular among the most stable isomers, e.g., C_nN^- ($n = 1–7$) [25]. For the boron-doped carbon clusters C_nB ($n = 4–10$) [26] and beryllium-doped carbon dianion clusters C_nBe^{2-} ($n = 4–14$) [27], the linear configuration with the boron and beryllium atoms located inside the carbon chain are the most stable isomers. For C_nH^- ($n \leq 10$) clusters, the configurations with a bent C_n chain terminated by the hydrogen atom are the most favorable in energy [28]. In the cases of CsC_7^-, CsC_9^-, and $TiC_n^{+/-}$ ($n = 1–6$) clusters isomers with a "lightly embracing" or "fan" structure have been suggested to be the most stable [29,30].

At the beginning of our investigation, nothing was known other than the HC_nSi^+ formula. The assumption of a reasonable geometrical structure was the initial step. Unfortunately, there is no experimental technique that can provide direct information on cluster geometry. The only method that enables the determination of cluster geometries at present is based on comparing the total energy after theoretical calculations. In order to locate the global minimum on an energy surface, it is necessary to investigate a large number of models; otherwise the structure with the lowest energy may be missed. In order to reduce the chance of having the ground-state structures wrongly determined, we examined a huge number of models which are reasonable in chemical understandings. After geometry optimization, the total energies were compared for the identification of ground-state isomers. For models with imaginary vibrational frequencies and/or of higher energies, they were discarded.

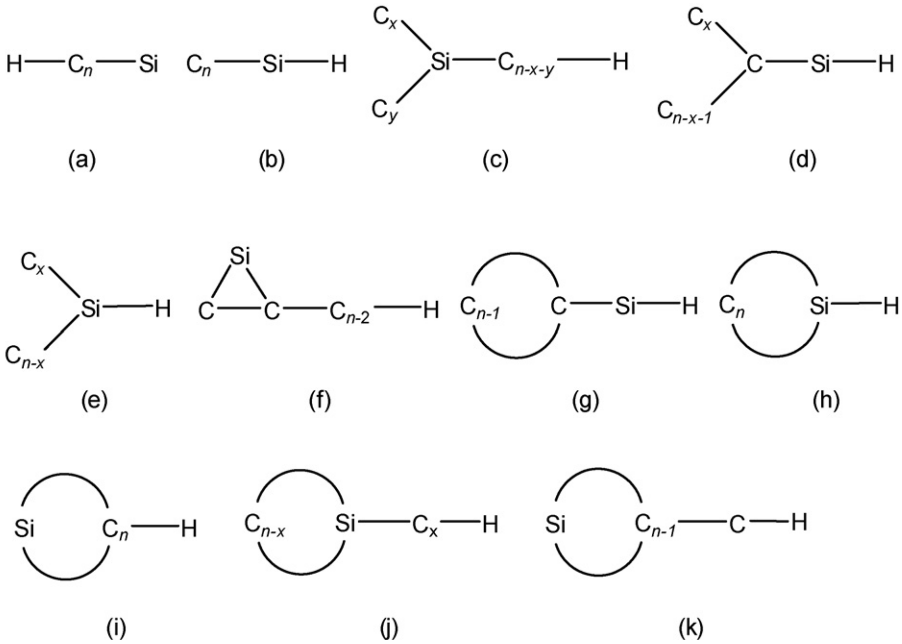

Fig. 1. Eleven main categories of HC_nSi^+ ($n = 1–10$) structures (*x*, *y* denote numbers of carbon atom(s)).

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