Ab Initio Investigation of Structures and Stability of Si_nC_m Clusters

Zhen-Yi Jiang,*[,†,‡,§] Xiao-Hong Xu,[§] Hai-Shun Wu,[§] and Zhi-Hao Jin*[,‡]

Multidisciplinary Materials Research Center, Xi'an Jiaotong University, Xi'an 710049, China, State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China, and Institute of Material Chemistry, Shanxi Normal University, Linfen 041004, China

Received: May 11, 2003; In Final Form: August 19, 2003

Various structural possibilities for Si_nC and Si_nC_2 ($n = 1-7$) neutral and anionic isomers were investigated using the second-order Møller−Plesset (MP2) approximation at the 6-311+G(d) level. The calculations predicted the existence of a number of previously unknown isomers (i.e., Si_5C_2 and Si_6C_2). We found that the basis set [6-31G(d)] with the MP2 approximation was too small to explain the photoelectron spectra of Si_nC_m clusters reasonably. Our present results agree satisfactorily with the photoelectron spectroscopy. The strong C−C bond is no longer the dominant factor in the building-up principle of mixed Si_6C_2 neutral and anionic clusters. The calculated adiabatic electron affinities in their ground states showed that Si_nC_m ($n + m = 3, 6$) clusters are more stable than any others in Si_nC and Si_nC_2 ($n = 1-7$) species, being consistent with the observed TOF signal intensities. Their stability tends to decrease with the increase in the size of these clusters.

1. Introduction

Silicon−carbon clusters have been of significant interest in the past few years since the detection of spectral features of SiC, SiC_2, and SiC_4 in circumstellar and interstellar environments.[1,2] Space, with its various conditions of density and temperature, constitutes a real laboratory for understanding the mechanism of nucleation of both small clusters and grains of SiC. To understand the building-up mechanism and the nature of chemical bonding in larger clusters, it is necessary to have a good understanding of small clusters. Many ab initio calculations mainly focused on neutral mixed silicon−carbon clusters.[3−8] Until now, the structure and electronic state of neutral Si_nC_m ($n + m < 6$) clusters have been theoretically well understood. However, there exist a number of well-known experimental procedures[9−11] for producing silicon−carbon clusters in the laboratory. In some variations of mass spectrometric techniques, the clusters were observed as anionic states. Hence, it is of interest to undertake a systematic study of the negatively charged ions of silicon−carbon clusters. It is well known that the acceptance of an electron would introduce significant distortions into the corresponding neutral clusters. The structures of neutral clusters are therefore expected to be less reliable in interpreting anionic geometries. Nakajima[11] proposed the geometries of $Si_nC_m^-$ ($n + m = 3-6$) utilizing second-order Møller−Plesset (MP2) theory without diffuse functions in the basis set. According to our previous experience, this level is too low to give reliable results, at least for the energy required to detach an electron from anions (vertical detachment energy, VDE). Hunsicker[12] performed a combination of molecular dynamics (MD) and density functional (DF) calculations on the geometric structures of Si_nC_m ($n + m < 9$) neutral and anionic species. Recently, Jiang et al.[13] obtained the ground-state structures of $Si_nC_m^-$ ($n + m = 3-8$) with density functional theory at the 6-311G(d) level. However, not all of the results[12,13] can account for similarities in the peak positions and their envelopes of photoelectron spectra[11] among Si_{n+1}^-, Si_nC^-, and $Si_{n-1}C_2^-$ clusters (i.e., Si_5^- and Si_4C^-). Hence, more accurate theoretical calculations are required to explain the photoelectron spectra.[11] In the present study, we performed calculations on Si_nC and Si_nC_2 ($n = 1-7$) neutral and anionic species with standard MP2/6-311+G(d) methods to provide more reliable ground-state geometries and relative stability. The charge-induced structural change in these clusters will be discussed. It is to be noted here that the reliability of the present calculations will be verified by a comparison of theoretical results and photoelectron spectra.

The rest of the paper is organized as follows. In section 2, we give a brief description of the computational method used in this work. Results, discussion, and stability will be presented in section 3 for silicon−carbon species. Finally, our conclusions will be summarized in section 4.

2. Computational Methods

Initial geometrical optimizations were performed at the B3LYP/6-31G(d) level without any symmetry constraints, except for those needed to maintain a particular geometry. These minimized Si_nC_m structures were further optimized using the MP2/6-311+G(d) method. The fourth-order spin-projected [MP4(SDTQ)] energy was evaluated to determine the most stable isomers. Harmonic frequencies were evaluated (at HF/6-31G(d) for $n + m > 5$ and at MP2/6-31G(d) for $n + m = 3-5$) to characterize the stationary points as minima or transition-state structures on the potential energy surfaces of corresponding clusters. All of the obtained most stable charged and neutral Si_nC_m clusters were characterized as energy minima without imaginary frequencies. Partial charges were given with Mulliken atomic charges. The first electron affinities of various clusters were calculated with the adiabatic approximation. All calculations were carried out using the Gaussian 98 program[14] on Dell Precision 650 workstations in our laboratory.

---

* Corresponding authors. E-mail: jiang_chemphy@yahoo.com. Tel: +86-29-2665236. Fax: +86-29-2665114.

[†] Multidisciplinary Materials Research Center, Xi'an Jiaotong University.

[‡] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University.

[§] Shanxi Normal University.

10.1021/jp0352940 CCC: $25.00

TABLE 1: Distances between Two Atoms (L/Å) in Si_nC and Si_nC_2 Neutral Clusters

	symmetry	type	L		symmetry	type	
Si_2C	C_{2v}	1−2	1.708			7−8	2.284
		2−3	2.878	SiC_2	C_{2v}	1−2	1.842
Si_3C	C_{2v}	1−2	1.775			2−3	1.285
		1−4	1.938	Si_2C_2	D_{2h}	1−2	1.839
		2−4	2.412			1−3	1.466
Si_4C	C_{3v}	1−2	1.849	Si_3C_2	C_{2v}	1−2	2.562
		1−5	2.589			1−3	1.922
		2−5	2.366			2−3	1.736
Si_5C	C_{4v}	1−2	1.900			3−4	1.386
		1−6	2.270	Si_4C_2	D_{2d}	1−2	1.840
		2−6	2.455			1−3	1.829
Si_6C	C_{5v}	1−2	2.098			2−3	2.140
		1−3	2.053	Si_5C_2	C_{2v}	1−2	1.343
		2−3	2.617			1−3	2.038
Si_7C	C_s	1−3	2.045			2−6	1.762
		3−4	3.070			3−4	2.578
		1−2	1.845			3−5	2.245
		2−3	2.462			4−6	2.319
		5−6	2.575	Si_6C_2	C_{3v}	1−2	1.863
		3−6	2.431			2−4	2.525
		1−6	2.034			2−3	2.566
		3−7	2.504			3−5	1.839
		6−7	2.575			3−6	3.100
		6−8	2.461				

TABLE 2: Distances between Two Atoms (L/Å) in Si_nC^- and $Si_nC_2^-$ Anions

	symmetry	type	L		symmetry	type	
Si_2C	$D_{\infty}h$	1−2	1.705			2−3	1.776
Si_3C	C_{2v}	1−2	1.785	Si_2C_2	$D_{\infty}h$	1−2	1.314
		1−4	1.891			1−3	1.725
		2−4	2.381	Si_3C_2	C_{2v}	1−2	2.449
Si_4C	C_s	1−2	1.931			1−3	2.053
		1−3	1.856			2−3	1.767
		1−5	2.466			3−4	1.335
		2−3	2.690	Si_4C_2	C_s	1−2	1.565
		2−5	2.382			1−3	1.877
		3−4	3.242			1−4	1.819
		3−5	2.355			1−5	2.082
Si_5C	C_{2v}	1−2	1.813			3−5	2.488
		1−3	2.034			4−5	2.493
		1−6	2.685			4−6	2.570
		2−6	2.768	Si_5C_2	C_{2v}	1−2	1.358
		3−6	2.357			1−3	1.982
Si_6C	C_{5v}	1−2	1.966			2−6	1.778
		1−3	2.029			3−4	2.572
		2−3	2.688			3−5	2.212
Si_7C	C_{3v}	1−2	1.887			4−6	2.275
		2−3	3.234	Si_6C_2	C_3	1−2	1.877
		2−4	2.459			2−4	2.585
		4−5	2.669			2−3	2.472
		4−6	2.361			3−5	1.889
SiC_2	$C_{\infty}v$	1−2	1.263			3−6	3.123

3. Results and Discussion

3.1. Geometry. Geometric parameters of the lowest-energy neutral and anionic species are listed in Tables 1 and 2, respectively. Several equilibrium geometries for energetically low-lying isomers are presented in Figures 1−6, and the respective "bonds" are shown for internuclear separations of less than 2.80 Å (Si−Si), 2.40 Å (Si−C) and 2.00 Å (C−C). The larger and smaller spheres denote Si and C atoms, respectively. Total energies are reported in Table 3 for neutral and anionic clusters.

A. Si_nC Clusters. The photoelectron spectra[11] of Si_nC^- ($n = 3−7$) clusters are similar to those of pure Si_{n+1}^- clusters in the peak positions and their envelopes. This similarity indicates that the substitution of a Si atom by a C atom in Si_{n+1}^- clusters does not change either the geometrical or electronic structures substantially. This is attributed to the fact that both C and Si atoms take a similar valence structure because of the same family in the periodic table. The structures of Si_4^-, Si_5^-, Si_6^-, Si_7^-, and Si_8^- are known to be a rhombus, trigonal bipyramid, tetragonal bipyramid, pentagonal bipyramid, and deformed bicapped octahedron, respectively.[15−18] Thus, the calculated geometrical and electronic structures of Si_nC^- ($n = 3−7$) clusters should be analogous to those of pure Si_{n+1}^- clusters.

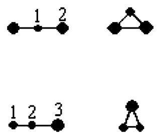

Figure 1. Low-lying isomers of (a, b) Si_2C^- and (c, d) SiC_2^- anions.

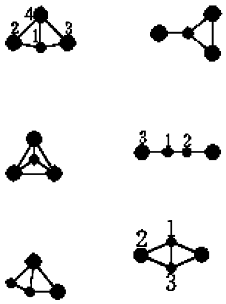

Figure 2. Low-lying isomers of (a, b, c) Si_3C^- and (d, e, f) $Si_2C_2^-$ anions.

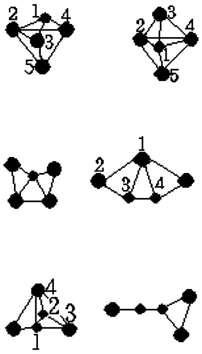

Figure 3. Low-lying isomers of (a, b, c) Si_4C^- and (d, e, f) $Si_3C_2^-$ anions.

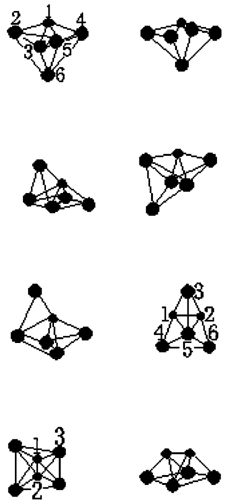

Figure 4. Low-lying isomers of (a, b, c) Si_5C^- anions, (d, e) Si_5C neutral, (f, g) $Si_4C_2^-$ anions, and (h) Si_4C_2 neutral.

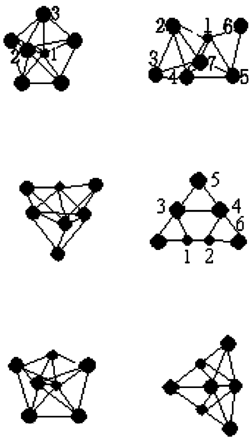

Figure 5. Low-lying isomers of (a, b, c) Si_6C^- and (d, e, f) $Si_5C_2^-$ anions.

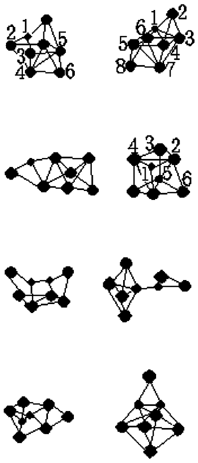

Figure 6. Low-lying isomers of (a, b, c) Si_7C^-, (d, e, f) $Si_6C_2^-$ anions, and (g, h) Si_6C_2 neutral clusters.

TABLE 3: Total Energy (au/MP2) for Neutral and Anionic Clusters

neutral	symmetry	energy	anion	symmetry	energy
Si_2C	C_{2v}	615.9210	Si_2C^-	$C_{\infty v}$	615.9326
Si_3C	C_{2v}	904.9530	Si_3C^-	C_{2v}	904.9908
Si_4C	C_{3v}	1193.9585	Si_4C^-	C_s	1194.0133
Si_5C	C_{4v}	1483.0419	Si_5C^-	C_{2v}	1483.0648
Si_6C	C_{5v}	1772.0532	Si_6C^-	C_{5v}	1772.0911
Si_7C	C_s	2061.0593	Si_7C^-	C_{3v}	2061.1175
SiC_2	C_{2v}	364.8454	SiC_2^-	$D_{\infty}h$	364.8817
Si_2C_2	D_{2h}	653.8868	$Si_2C_2^-$	$D_{\infty}h$	653.9280
Si_3C_2	C_{2v}	942.9227	$Si_3C^-{}_2$	C_{2v}	942.9711
Si_4C_2	D_{2d}	1231.9796	$Si_4C_2^-$	C_s	1232.0047
Si_5C_2	C_{2v}	1520.9780	$Si_5C_2^-$	C_{2v}	1521.0037
Si_6C_2	C_{3v}	1809.9858	$Si_6C^-{}_2$	C_3	1810.0437

TABLE 4: Lowest Vibrational Frequencies (cm^{-1}) for Neutral and Anionic Ground-State Clusters[a]

neutral	symmetry	n	anion	symmetry	ν
Si_2C	C_{2v}	121.8	Si_2C^-	$D_{\infty}h$	151.3
Si_3C	C_{2v}	202.3	Si_3C^-	C_{2v}	295.5
Si_4C	C_{3v}	239.0	Si_4C^-	C_s	221.2
Si_5C	C_s	43.2	Si_5C^-	C_{2v}	138.1
Si_6C	C_{5v}	61.1	Si_6C^-	C_s	83.2
Si_7C	C_s	137.8	Si_7C^-	C_{3v}	142.3
SiC_2	C_{2v}	157.3	SiC_2^-	$C_{\infty}\nu$	182.9
Si_2C_2	D_{2h}	220.1	$Si_2C_2^-$	$D_{\infty}h$	136.5
Si_3C_2	C_{2v}	143.5	$Si_3C_2^-$	C_{2v}	113.9
Si_4C_2	D_{2d}	181.5	$Si_4C_2^-$	C_s	181.2
Si_5C_2	C_{2v}	100.4	$Si_5C_2^-$	C_{2v}	50.2
Si_6C_2	C_{3v}	113.1	$Si_6C_2^-$	C_{3v}	103.1

[a] HF/6-31G(d) for $n + m > 5$ and MP2/6-31G(d) for $n + m = 3-5$.

a. Si_2C. The neutral Si_2C can adopt C_{2v} and $D_{\infty h}$ structures with comparable energy, the C_{2v} ($^1A_1$) isomer being 0.05 eV more stable than the linear ($^1\Sigma_g^+$). Their energy difference and ordering is similar to those of previous calculations[12] on neutral molecules. The linear molecule with an imaginary bending-mode frequency shows the tendency of the carbon atom to vibrate along the radial direction into the triangle, 1(b).

Their energy ordering is preserved in the anion. The C_{2v} ($^2A_1$) configuration is more stable than the linear configuration by only 0.04 eV. Their energy ordering differs from that of the reference.[12] To interpret the above-mentioned discrepancy, fourth-order [MP4(SDTQ)] point energy was evaluated at the 6-311+G(d) level. The linear configuration is favorable by 0.08 eV.

A comparison between neutral and anionic triangular species shows a reduction of 23.3% in the Si−C−Si bond angle. This may be ascribed to the decrease in electrostatic force between Si atoms because the net charge of Si atoms is reduced significantly upon charging.

b. Si_3C. Rittby[6] investigated six different neutral isomers using a Hartree−Fock (HF) calculation. We support their predictions that the energetically most favorable isomer is the rhomboidal (C_{2v}, $^1A_1$) structure 2(a). This geometrical structure can be obtained by substituting a Si atom by a C atom in the Si_4^- anion. The next structure in the energetic ordering is a spatial C_s ($^1A'$) isomer, which is an out-of-plane distortion in the planar (C_{2v}, $^1A_1$) form 2(b). It has an imaginary bending-mode frequency, which is located 1.14 eV above the rhombus 2(a). The planar 2(b) also has an imaginary bending-mode frequency that is 1.16 eV higher in energy.

The energy ordering of the anion is partially changed. Structure 2(a) (C_{2v}, $^2A_2$) is also energetically favorable. Isomer 2(b) ($^2B_1$) lies 0.74 eV higher in energy, which is also a transition state. Its bending-mode frequency shows the tendency of trying to fold the three silicon atoms into the circular 2(a) in both neutral and anionic species 2(b). Only the third most stable isomer is a new configuration (C_{3v}, $^4A_1$) 2(c) in the anion, which is located 1.98 eV higher in energy. It can be derived from the substitution of a Si atom by a C atom in an energetically low-lying cagelike Si_4 structure with T_d symmetry.

The addition of an electron to neutral molecule 2(a) yields an increase of 2.4% in the Si−Si−Si (2, 4, 3) bond angle. This results from the antibonding nature of the highest occupied orbital (HOMO), which is localized between the Si2 and Si3 atoms because of the additional electron.

c. Si_4C. Calculations[4] on the Si_4C cluster indicate that the most stable neutral isomer is a trigonal (C_{3v}) bipyramid [quite similar to the C_s structure 3(a)] with the C atom at the apex. The present calculation leads to the same conclusion. The distorted pentagonal (C_2, ^1A) ring 3(c) lies 0.12 eV higher in energy than the trigonal (C_{3v}, $^1A_1$) bipyramid and only 0.09 eV below the (C_{2v}, $^1A_1$) isomer 3(b). Both species 3(b) and 3(a) are related to the ground-state geometry of the Si_5^- cluster, which is D_{3h} trigonal bipyramidal.[18] Structure 3(b) is derived from this trigonal bipyramid by substituting a Si atom in transverse equatorial positions by one carbon atom. Isomer 3(a) represents the corresponding trigonal bipyramid with C in the apical position.

The energy ordering of anionic states is partially changed. The energetically most stable structure is the distorted trigonal bipyramid (C_s, $^2A''$) 3(a). There is a symmetry lowering ($C_{3v} \rightarrow C_s$) upon charging. This is followed by the distorted trigonal (C_{2v}, $^2B_2$) bipyramid 3(b) that lies 0.22 eV above the 3(a). The next minimum is 0.33 eV higher and corresponds to the C_2 (^2A) form 3(c).

A comparison between our anionic results and previous calculations[11] shows a discrepancy. According to their level[11] [MP2/6-31G(d) level], we performed a structural optimization, and a conclusion can be reached that 3(b) is 0.56 eV more stable than 3(a), which is in agreement with the reference.[11] However, the calculations optimized at the MP2/6-311G(d) level predict 3(a) to be favorable over 3(b) by 0.27 eV. However, the calculated geometrical structure of the Si_4C^- anion should be analogous to those of neutral Si_4C clusters because the sharp envelope of the photoelectron spectroscopy[11] indicates the similarity between the anionic and neutral Si_4C structures. The structure of neutral Si_4C molecule is the 3(a) configuration;[4] hence the stability of the 3(a) anion over the 3(b) can be predicted.

The addition of an electron to the lowest-energy C_{3v} isomer results in an increase of the separation between atoms 3−4 by about 14.9% in the anionic isomer 3(a). An additional electron occupies the HOMO localized respectively between atoms 2−3 and atoms 2−4 in the anion. The bonding character of the HOMO in the anion interprets the respective reduction of separation between atoms 2−3 and atoms 2−4. This reduction results in an increase of the separation between atoms 3−4.

d. Si_5C. Nakajima et al.[11] and Hunsicker et al.[12] predicted that the lowest-energy Si_5C structure is a (C_{2v}, $^1A_1$) octahedron 4(a). The present calculation concludes that the C_{4v} ($^1A_1$) octahedron [quite similar to 4(a)] is the energetically most favorable isomer, which is obtained by substituting a Si atom by a C atom in the Si_6^- cluster. We performed geometric optimization with C_{2v} structure 4(a) as the initial geometry for comparison. The energy of the optimized isomer is equal to our most favorable C_{4v} ($^1A_1$) isomer, and the optimized structure finally becomes the C_{4v} octahedron. Two C_s ($^1A'$) isomers 4(d) and 4(e) lie 0.62 and 0.97 eV above the ground state, respectively. They are built by capping a Si atom over atoms (2, 4, 5) and atoms (1, 5) in anion 3(b), respectively.

The energy ordering is partially changed in the anion. C_{2v} ($^2A_1$) octahedron 4(a) in the anion is the energetically most favorable isomer. The symmetry of the neutral structure (C_{4v}) is lowered to C_{2v} symmetry upon charging. C_{2v} ($^2A_1$) structure 4(b) is only 0.04 eV higher in energy than isomer 4(a) and 0.41 eV below C_s ($^2A'$) isomer 4(c). Because the sharp envelop of the photoelectron spectroscopy[11] indicates the similar structure between the anionic and neutral Si_5C clusters, the neutral and anionic Si_5C species having an analogous geometrical structure should be reasonable.

The addition of an electron to the neutral C_{4v} isomer results in symmetry lowering. This results from the change in electrostatic force between C−Si atoms because two Si atoms in equatorial positions reverse the sign of their charge upon charging.

e. Si_6C. Hunsicker and co-worker[12] gave three lower isomers and found the C_{2v} structure to be the most stable both for the anionic and neutral species. This C_{2v} structure can be obtained by replacing a Si atom in a transverse equatorial position with a C atom in the structure of Si_7 (a pentagonal D_{5h} bipyramid[16]). We performed geometric optimization with their (C_{2v}, $^1A_1$) structure as the initial geometry for comparison. The energy of the optimized isomer is 0.94 eV less stable above the most favorable C_{5v} ($^1A_1$) isomer 5(a). Structure 5(c) (C_s, $^1A'$) can be considered to cap a Si atom over atoms (1, 2, 3) and (1, 2, 4) in configuration 3(a), respectively. It lies 0.69 eV higher in energy. Structure 5(b) (C_s, $^1A'$) lies 0.92 eV higher in energy, which can be derived from isomer 3(b) by capping a Si atom over atoms (1, 3) and atoms (1, 5), respectively.

The energy ordering of anionic states is partially changed. The (C_{5v}, $^2A_1$) structure 5(a) is the most favorable configuration. It is obtained by replacing a Si atom in an apical position with a C atom in structure of Si_7 (a pentagonal D_{5h} bipyramid[16]). It lies 1.31 eV below the above-mentioned C_{2v} isomer. Two C_s isomers 5(b) and 5(c) lie 0.15 and 0.64 eV above the 5(a) isomer, respectively.

The addition of an electron to the neutral C_{5v} isomer results in an increase in the separation among atoms Si−Si and a reduction in the separation among atoms Si−C in the anion. This may be linked to the different change of electrostatic force among Si−Si atoms and C−Si atoms because transverse equatorial Si atoms reverse the sign of their charge upon charging.

The existence of a broad envelop in the photoelectron spectroscopy[11] of the Si_6C anion indicates significant geometrical reorganization in the neutral. However, this has not yet been theoretically obtained for this cluster.

f. Si_7C. Hunsicker et al.[12] performed a calculation on the three geometric structures of Si_7C and obtained the lowest-energy isomer to be C_s structure 6(b). Our present results support their predictions that the (C_s, $^1A'$) structure as the ground state of the Si_7C molecule, which is derived from the substitution of a Si atom by a C atom in a deformed bicapped octahedron.[17] The next structure in the energy ordering is (C_{3v}, $^1A_1$) isomer 6(a) built from the substitution of a Si atom by a C atom in cagelike Si_8 structure[19] lying 0.22 eV above the ground state. Another low-lying isomer is C_1 structure 6(c) at 0.39 eV.

The energy ordering is partially changed in the anion. The (C_{3v}, $^2A_2$) structure 6(a) is the most favorable form in the anionic isomers. The C_s ($^2A'$) isomer 6(b) is only 0.08 eV higher in energy than the 6(a) and 0.75 eV below the C_1 (^2A) 6(c). In fact, isomer 6(a) is quite similar to isomer 6(b), and they are the same topological isomers. The sharp envelop of the photoelectron spectroscopy[11] indicates the similar structure between the anionic and neutral Si_7C clusters; our calculated results are consistent with such experimental observations.

B. Si_nC_2 Clusters. a. SiC_2. The present calculations predict a C_{2v} ($^1A_1$) ground state with a bond angle of $\alpha_{CSiC} = 40.8°$ for SiC_2 molecule. A bent chain (C_s, $^1A'$) similar to 1(c) is 0.19 eV less stable. The linear $C_{\infty v}$ with an imaginary bending-mode frequency shows the tendency of the vibrating middle carbon atom along the radial direction into the above-mentioned C_s isomer. Our calculated bond angle agrees well with the measured value of 40−41°.[20]

The C_{2v} ($^2B_2$) anionic conformer 1(d) is also an energetically most favorable configuration, which is only 0.03 eV more stable than $C_{\infty v}$ isomer 1(c). A comparison of the triangle shows that the bonds in the anion are longer than those in the neutral isomer by about 3.0%, but the bond angles remain the same. This may be linked to the increase in electrostatic repulsive force between C and C atoms because an additional electron makes the net charge of the Si atom zero in the anion.

As shown in ref 11, the spectrum of SiC_2^- indicates a broad feature, which suggests the large geometry change from the anion to the corresponding neutral by photoelectron detachment. To interpret the discrepancy between experimental observation and theoretical prediction, the fourth-order [MP4(SDTQ)] point energy was evaluated at the 6-311+G(d) level. The linear anion is energetically favorable by 0.10 eV, hence it can account for the observed broad band.

b. Si_2C_2. Hunsicker et al.[12] studied three isomers and predicted that the ground state is the D_{2h} rhombus 2(f). Our calculations support their predictions. The energy of (C_s, $^1A'$) trapezoid 2(e) is 0.49 eV above (D_{2h}, ^1A_g) rhombus 2(f) and 0.31 eV below $D_{\infty h}$ linear 2(d).

The energy ordering of the anions differs from that of the neutral cluster. An additional electron makes linear 2(d) stable. Two low-lying isomers are the C_s ($^2A''$) form 2(e) and D_{2h} ($^2B_{2g}$) rhombus 2(f), located 0.05 and 0.20 eV above the linear, respectively.

A noticeable point is that the charge is equally distributed along the linear (0.3e per silicon and −0.3e per carbon) in a neutral molecule whereas a C atom bears a −0.4e charge in the linear anion. A comparison between neutral and anionic linear species shows an increase of 1.9% in the C−C bond length. This may be linked to the increase in electrostatic repulsive force between C and C atoms upon charging.

Because the existence of a sharp peak among the broad peaks in the photoelectron spectroscopy[11] indicates the coexistence of several isomers in the neutral cluster, the small energy difference in 2(d) and 2(e) anionic isomers is compatible with the observed complicated spectrum.

c. Si_3C_2. Froudakis et al.[7] investigated five Si_3C_2 neutral isomers. We support their results that the most stable configuration is the planar C_{2v} ($^1A_1$) form 3(d). Next in the energy ordering, located 0.71 eV above the 3(d), is a D_{3h} ($^1A'_1$) bipyramid [quite similar to 3(e)]. The third is a C_{2v} isomer with an imaginary frequency, which is located 1.13 eV above the ground state.

The additional electron has little effect on the relative stability of the anionic isomers. The planar C_{2v} ($^2B_1$) pentagon 3(d) is also the energetically most favorable form, which agrees well with the calculations.[12] The distorted bipyramid (C_{2v}, $^2B_1$) 3(e) built from replacing two Si atoms in apical positions by a C atom is located 0.61 eV above the ground state and 0.15 eV below C_s ($^2A'$) structure 3(f).

A comparison between neutral and anionic pentagons 3(d) shows an increase in the separation of atoms 1−3 by about 6.8%, which is linked to the inverse of electrostatic force between atoms 1−3 upon charging.

d. Si_4C_2. Among the four different isomers of Si_4C_2 investigated by Froudakis et al.,[3] C_{2v} structure 4(h) was found to be a stable minimum. However, our present calculation suggests that D_{2d} ($^1A_1$) octahedron 4(g) is the energetically most favorable isomer, which is obtained by the substitution of two apical Si atoms by a C atom in the Si_6^- cluster. Their difference in energy is 0.16 eV. Another octahedron (D_{4h}, $^1A_{1g}$) [quite similar to 4(g)] is 0.18 eV less stable.

The energy ordering differs in the anion. The lowest-energy state is found to be 3D C_s ($^2A'$) structure 4(f). Two octahedrons D_{2d} ($^2B_2$) 4(g) and D_{4h} ($^2A_{2u}$) are 0.23 and 0.64 eV less stable relative to 4(d), respectively. C_{2v} isomer 4(h) is 0.89 eV higher in energy.

A comparison of spectral features in the series Si_6^-, Si_5C^-, and $Si_4C_2^-$[11] shows the apparent similarity, which leads to the similarity in the electronic and geometric feature in these clusters. As mentioned above, the structures of Si_6^- and Si_5C^- are calculated to be tetragonal bipyramidal. Then, the spectral similarity among Si_6^-, Si_5C^-, and $Si_4C_2^-$ anions reasonably indicates that the geometry of $Si_4C_2^-$ is similar to tetragonal bipyramidal. Hence, the octahedron (D_{2d}, $^2B_2$) anion can account for the observed similarity.

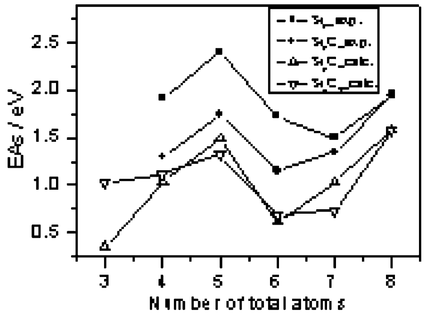

Figure 7. EAs of Si_nC_m clusters against the number of total atoms.

e. Si_5C_2. The lowest-energy Si_5C_2 isomer is 3D C_s ($^1A'$) structure 5(e), which can be derived from the minimum-energy structure of Si_6C [5(a)] by replacing a basal-plane Si atom with a C atom. Next in the energy ordering is triangular planar (C_{2v}, $^1A_1$) isomer 5(d), located only 0.02 eV above the ground state. Their energies should be evaluated with MP4(SDTQ) because of their near degeneracy. It is found that 5(d) is 0.05 eV more stable than 5(e), which is in agreement with the density functional calculation.[13] The third is C_s ($^1A'$) isomer 5(f), which is 0.20 eV higher in energy. It is derived from capping a C atom over atoms (1, 3, 4) and atoms (2, 3, 4) in anion 3(e).

The additional electron has no effect on the relative stability of the anionic isomers. Planar triangular C_{2v} anion 5(d) lies only 0.05 eV above isomer 5(e) and 0.41 eV below the 5(f) isomer. We found that 5(d) is 0.08 eV more stable than 5(e) at the MP4-(SDTQ) level, which is also in agreement with the density functional calculation.[13] A low-lying (D_{5h}, $^2A''_2$) isomer at 0.48 eV should be pointed out, which is obtained by replacing two Si atoms in apical positions with the C atom in the pentagonal D_{5h} bipyramid[16].

f. Si_6C_2. The ground state of the Si_6C_2 molecule is found to be the (C_{3v}, $^1A_1$) isomer, which is quite similar to 6(d) built from the substitution of two Si atoms by two C atoms in cagelike Si_8 structure.[19] This is followed by C_s ($^1A'$) isomer 6(g), lying 0.05 eV above the 6(d). It is built from bridging two basal-plane Si atoms by a Si atom in 5(e). Another low-lying isomer is C_{2v} ($^1A_1$) structure 6(h), which is 0.41 eV less stable.

The energy ordering is partially changed in the anion. The (C_3, ^2A) form 6(d) is energetically favored in the anion. There is symmetry lowering ($C_{3v} \rightarrow C_3$) upon charging for this isomer. Next in energy ordering is C_2 (^2B) form 6(e), lying 0.15 eV above the 6(d). This is followed by C_s ($^2A'$) isomer 6(f), lying 0.16 eV above the 6(d). We can very roughly decompose this structure into two interacting entities: structure 3(b) and 1(b) are bridged with a C−C bond. Froudakis et al.[3] put forward a building-up principle of carbon−silicon clusters in which strong C−C bonds are favored over C−Si bonds and Si−Si bindings are of lesser importance to the geometrical arrangement of the mixed clusters. However, this principle is not valid for the Si_6C_2 cluster. The structures derived from substituting C for Si atoms in Si_n cluster are stable in various Si_6C_2 isomers. The higher symmetry compensates for the opening in the C−C bond in these substitution isomers and makes isomer 6(d) the lowest in energy.

No photoelectron measurements are available for this cluster at present. However, the structural similarity among Si_8^-, Si_7C^-, and isomer 6(d) indicates that the lowest-state 6(d) anion should be reasonable.

3.2. Stability. The adiabatic electron affinities (EAs) of Si_nC and Si_nC_2 ($n = 1-7$) are shown in Figure 7. We found that the tendency is consistent with the measured EAs.[11] A comparison between theoretical and experimental EA values shows an underestimation of the EAs at an MP2 approximation that is relative to experimental data. The EA values corresponding to 3 and 6 in cluster size are smaller values, which correspond to relatively stable neutral state. In secondary-ion mass spectrometry,[21] the intensities of Si_2C and Si_5C clusters are relatively higher than those of the neighboring clusters, which suggests that Si_2C and Si_5C clusters more stable. These results agree well with our calculation. In photoelectron spectroscopy,[11] SiC_2^-, $Si_2C_2^-$, and $Si_4C_2^-$ anionic species have been found, and the final states after the photoelectron ejection are the electronic states of the neutral. This suggests that they are more stable states, being in reasonable agreement with our results. EA values tend to increase with increases in the size of these clusters, which indicates that their stability should show an opposite tendency. Hence this may be the reason that the larger Si_nC and Si_nC_2 clusters have not been observed until now.

4. Summary

In this work, the structural properties and stability of the Si_nC and Si_nC_2 ($n = 1-7$) neutral and anionic clusters were studied and compared with experimental photoelectron spectra in the literature. We found that the basis set [6-31G(d)] with the MP2 approximation is too small to interpret the photoelectron spectra of Si_nC_m clusters satisfactorily. Our results account satisfactorily for recent photoelectron detachment measurements on the anions. The strong C−C bond is no longer the dominant factor in the building-up principle of mixed Si_6C_2 neutral and anionic clusters. This is different from the building-up principle put forward by Froudakis et al.[3] In different Si_nC and Si_nC_2 ($n = 1-7$) species, Si_nC_m ($n + m = 3, 6$) clusters are predicted to be of high stability. Their stability tends to decrease with increases in the size of these clusters.

Acknowledgment. This work was supported by funds from the education ministry of China and by the Youth Science and Technology Foundation of the Shanxi Province, China. we are grateful to Professor Xiao-Bing Ren (National Institute of Materials Science, Tsukuba 305-0047, Japan) for his revision of and advice on this paper.

References and Notes

(1) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Thaddeus, P.; Vrtilek, J. M. *Astrophys. J.* **1989**, *341*, L25.

(2) Priscilla-Márquez, J. D.; Gay, S. C.; Rittby, C. M. L.; Graham, W. R. M. *J. Chem. Phys*. **1995**, *102*, 6354.

(3) Froudakis, G.; Zdetsis, A.; Mühlhäuser, M.; Engels, B.; Peyerimhoff, S. D. *J. Chem. Phys*. **1994**, *101*, 6790.

(4) Zdetsis, A. D.; Froudakis, G.; Mühlhäuser, M.; Thümnel, H. *J. Chem. Phys*. **1996**, *104*, 2566.

(5) Erkoc, S.; Türker, L. *Physica E* **2000**, *8*, 50.

(6) Rittby, C. M. L. *J. Chem. Phys*. **1992**, *96*, 6768.

(7) Presilla-Márquez, J. D.; Rittby, C. M. L.; Graham, W. R. M. *J. Chem. Phys*. **1996**, *104*, 2818.

(8) Jiang, Z. Y.; Xu, X. H.; Wu, H. S.; Zhang, F. Q.; Jin, Z. H. *J. Mol. Struct.: THEOCHEM* **2003**, *621*, 279.

(9) Gnaser, H. *Phys. Rev. A* **1999**, *60*, R2646.

(10) Gnaser, H. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2000**, *164−165*, 705.

(11) Nakajima, A.; Taguwa, T.; Nakao, K.; Gomei, M.; Kishi, R.; Iwata, S.; Kaya, K. *J. Chem. Phys*. **1995**, *103*, 2050.

(12) Hunsicker, S.; Jones, R. O. *J. Chem. Phys*. **1996**, *105*, 5048.

(13) Jiang, Z. Y.; Xu, X. H.; Wu, H. S.; Zhang, F. Q.; Jin, Z. H. *Chem. Phys*. **2003**, *290*, 223.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) Raghavachari, K.; Rohlfing, C. M. *J. Chem. Phys*. **1988**, *89*, 2219.

(16) Li, S.; Van Zee, R. J.; Weltner, W., Jr.; Raghavachari, K. *Chem. Phys. Lett*. **1995**, *243*, 275.

(17) Meloni, G.; Gingerich, K. A. *J. Chem. Phys*. **2001**, *115*, 5470.

(18) Zhao, C. Y.; Balasubramanian, K. *J. Chem. Phys*. **2002**, *116*, 3690.

(19) Hagelberg, F.; Leszczynski, J.; Murashov, V. *J. Mol. Struct.: THEOCHEM* **1998**, *454*, 209.

(20) Shepherd, R. A.; Graham, W. R. M. *J. Chem. Phys*. **1985**, *82*, 4788.

(21) Yamamoto, H.; Asaoka, H. *Appl. Sur. Sci*. **2001**, *169−170*, 305.