REGULAR ARTICLE

Theoretical study on the structures, isomerization and stability of SiC$_4$ isomers

Hao Sun · Hongwei Gong · Huiling Liu · Fang Wang · Xiumei Pan · Zhongmin Su · Chiachung Sun · Rongshun Wang · Xuri Huang

Abstract The structures, energetics, dipole moments, vibrational spectra, rotational constants, and isomerization of singlet SiC$_4$ isomers were explored using ab initio methods. Five types of isomers, a total of 11 minima, connected by 11 interconversion transition states, were located on the potential energy surface at the MP2/6-311G(d, p) level. More accurate energies were obtained at the G3(MP2) level. With the highest isomerization barrier, a C2v tetra-angular cone possesses the largest kinetic stability. The lowest-lying structure, linear SiCCCC is also highly kinetically stabilized. Besides, D2d bicyclic c-Si(CC)$_2$, C2v five-membered ring c-SiCCCC, another C2v tetra-angular cone isomer and C3v trigonal bipyramid isomer are also considered to be kinetically stable, because their isomerization barriers are all over 10 kcal/mol. Other isomers cannot be kinetically stabilized with considerably low isomerization barriers. Investigation on the vibrational spectra, dipole moments, and rotational constants for SiC$_4$ isomers are valuable for their detections in the interstellar space and laboratory.

Keywords SiC$_4$ · Potential energy surface · Isomer · Stability

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1 Introduction

Silicon and carbon chemistry have attracted considerable interest of experimental and theoretical chemists due to the particular properties of silicon and carbon element. Small silicon–carbon clusters have become hot issues of research, since they were identified in laboratory. SiC, the simplest Si–C cluster, was initially observed by Bemath et al. [1] with high-resolution Fourier-transform emission spectroscopy. Ground-stated SiC$_2$ was first identified as a C2v triangular structure by Michalopoulos et al. [2] using rotationally resolved resonance two-photon ionization (R2PI) spectrum technique. Based on the measured IR data, Margrave et al. [3] concluded that Si$_2$C has C2v symmetry. Graham group identified the most stable C2v rhombic Si$_2$C$_2$ and Si$_3$C, linear Si$_2$C$_3$ (SiCCCSi) and SiC$_4$ (SiCCCC), and C2v pentagonal Si$_3$C$_2$ at their respective ground states using Fourier-transform infrared technique [4–8]. In 1999, rhomboidal SiC$_3$, a planar ring with C2v symmetry was detected at centimeter wavelengths in a pulsed supersonic molecular beam with a Fourier transform microwave spectrometer by McCarthy et al. [9]. Next year, McCarthy group characterized the rotational spectra of linear silicon–carbon chains SiCn (n = 3, 5–8) by the same experimental technique [10]. Most research has been emphasized on the equilibrium geometry, spectrum and isotopic substitution of these clusters [7, 11–13].

Furthermore, many small silicon–carbon clusters, such as SiC$_4$ [14, 15], SiC [15], SiC$_2$ [15], SiC$_3$ [16, 17] and SiCN [18] have been detected in the interstellar space, and they are considered to be relevant to star evolvement and combustion process [19]. Therefore, complicated exploration on these clusters is really important for astrophysics and atmosphere chemistry [20–24].

In the present work, our research focuses on SiC$_4$ cluster. It is well known that both silicon and carbon atom may be either singly or multiply bonded to the adjacent atoms in the cluster, which results in a large number of chain and ring isomers of considerable stability. Since sometimes the observed species are not necessarily stable in interstellar space or in laboratory, theoretical investigation on the all possible isomers and their conversions of the interstellar silicon–carbon clusters (SiCn) is greatly beneficial for exploring the new silicon–carbon species in laboratory and interstellar space. A successful example is that based on the theoretical results of rotational constant and geometry, SiCnH, SiCN and SiNC were subsequently identified in the laboratory [25]. In this paper, the quantum chemistry method was used to study the structures, spectroscopies, isomerization and stability of SiC$_4$. Our computational work may provide theoretical foundation for future experimental detection of SiC$_4$, and enrich the information and property of SiCn system.

2 Computational methods

Electronic structure calculations were carried out with the Gaussian 03 program [26]. The optimized geometries, harmonic vibrational frequencies and zero-point energy (ZPE) of 11 local minima and 11 transition states were calculated at the MP2/6-311G(d, p) level of theory [27–29]. At the same level, the connections between isomers were confirmed by the intrinsic reaction coordinate calculations [30–32]. Natural bond orbital (NBO) calculations [33–35] were also performed at the same level based on the optimized geometries. The natural resonance theory analysis was further calculated using the NBO 5.0 program [36] to reveal bonding nature of isomers. In order to acquire more reliable energetics, further single-point energy calculations were performed with G3(MP2) method [37] using the MP2/6-311G(d, p) geometries. The energies discussed in the present work are at the G3(MP2)//MP2/6-311G(d, p) + ZPE level, including the values in the parentheses unless otherwise stated.

3 Results and discussion

As shown in Fig. 1, eight possible types of SiC$_4$ isomers, total 31, i.e. chain-like species (A), branched species (B),

three-membered-ring species (C), four-membered-ring species (D), five-membered-ring species (E), tetrahedron species (F), tetra-angular cone (G) and triangular cone (H) were initially designed. However, only 11 isomers and 11 transition states were theoretically located. TSX/Y denotes the transition states connecting the isomers X and Y. The optimized geometries of all the local minima and transition states are depicted in Figs. 2, 3, respectively. Table 1 lists the harmonic vibrational frequencies, the infrared intensities, dipole moments, and rotational constants of all the minima. The harmonic vibrational frequencies of transition states are listed in Table 2 and all the transition states have only one imaginary frequency. The relative energies of all isomers and transition states are summarized in Table 3. The relative energies of possible dissociation products are listed in Table 4. The optimized fragments of SiC$_4$ dissociations are shown in Fig. 4. The potential energy surface (PES) of the isomerization of SiC$_4$ species is depicted in Fig. 5.
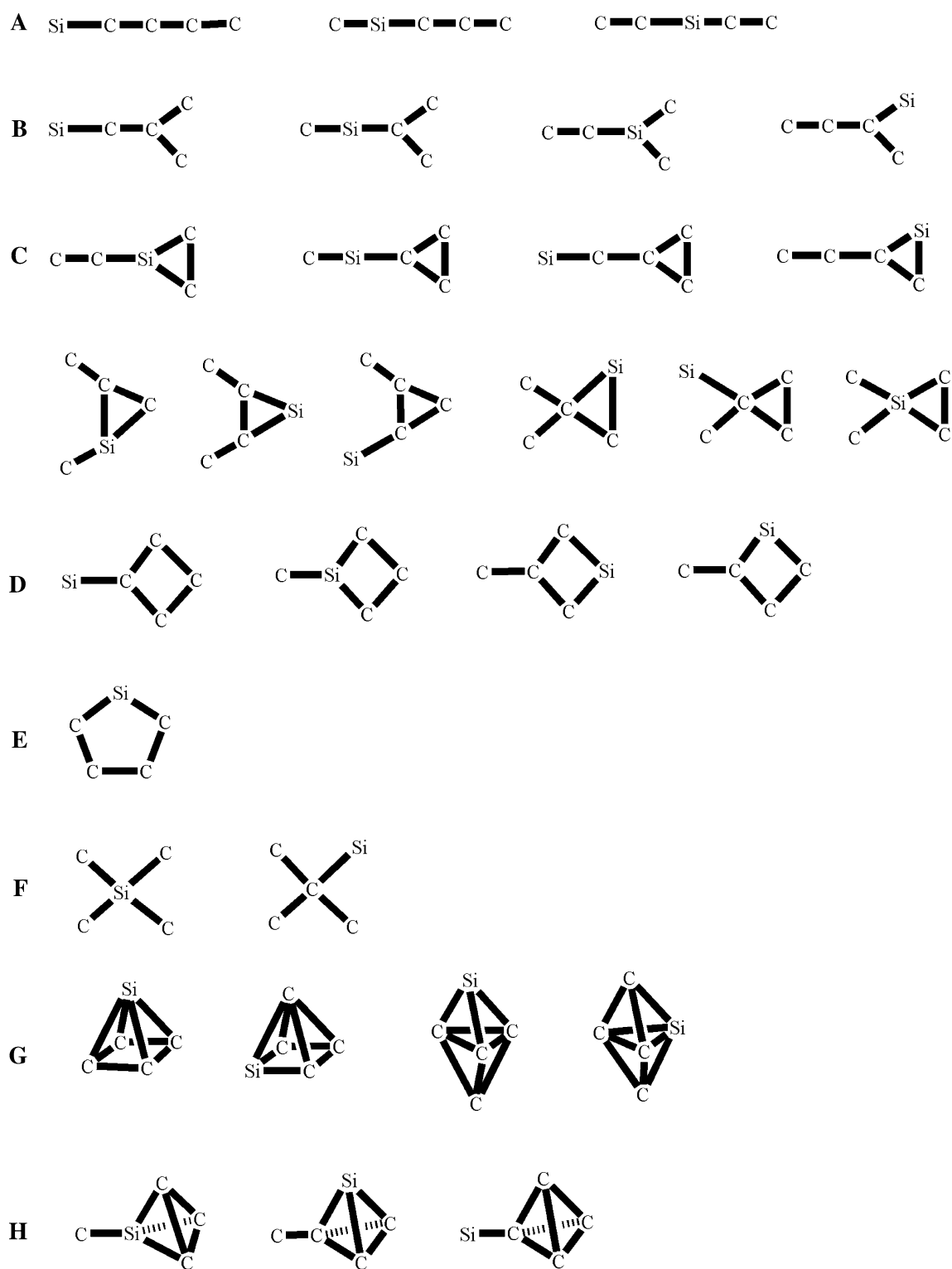
3.1 SiC$_4$ isomers

For chain-like isomers, all the three designed isomers (A1, A2 and A3) were located. But on the contrary, none of four initially designed structures with a branch (B) were found as minima. With Si atom standing at the terminal, linear A1 (0.0) lies at the lowest level of isomerization PES. The relative energies of A2 and A3 are 91.80 and 60.26 kcal/mol, respectively. Both A1 and A2 have the C$_{\infty v}$ symmetries with $^1\Sigma$ electronic state, and C$_{2v}$ A3 corresponds to the $^1A_1$ electronic state.

For three-membered-ring structure, no isomers were located as minima. However, isomer C (in Fig. 2) has a similar structure with the last one of the initially designed three-membered-ring. Isomer C (32.59 kcal/mol) has two–three-membered rings connected by Si atom, and it is in D$_{2d}$ symmetry, corresponding to the $^1A_1$ electronic state.

Among the supposed four D isomers, three four-membered-ring structures were located, labeled as D1 (50.91), D2 (140.72), and D3 (52.57). With a CCCC ring, D1, c-C(Si)CCC is the lowest-lying four-membered isomer. D2 and D3 are c-Si(C)CCC and c-C(C)CSiC structures, with C atoms bonded with Si and C of SiCCC rings, respectively. Among all the isomers, D2 has the highest relative energy. All the three planar isomers are of C$_{2v}$ symmetry with the $^1A_1$ electronic state. However, the isomer D4, with C bonded with the neighbor C atom of Si, was not found.

The C$_{2v}$ five-membered-ring, planer isomer E, is located at the energy level of 17.84 kcal/mol on SiC$_4$ isomerization PES. External and internal Si–C bonds are 2.100 and 1.975 Å. The distance between C(2) and C(3) is 1.387 Å, and C(1)–C(2) and C(3)–C(4) bonds are 1.298 Å. From

Fig. 1 All the initially designed structures for SiC$_4$ isomers structures

Table 3 and Fig. 5, isomer E has the second lowest energy of all the located isomers.

Three tetra-angular cone isomers, G1, G2 and G3 are found, whose relative energies are 61.00 kcal/mol,

59.78 kcal/mol and 65.47 kcal/mol, respectively. G1 is a C$_{2v}$ tetra-angular cone, in which Si atom acts as the vertex and quasi-planar CCCC ring as the bottom. From Table 3 and Fig. 5, isomer G1 is the most kinetically stable of all
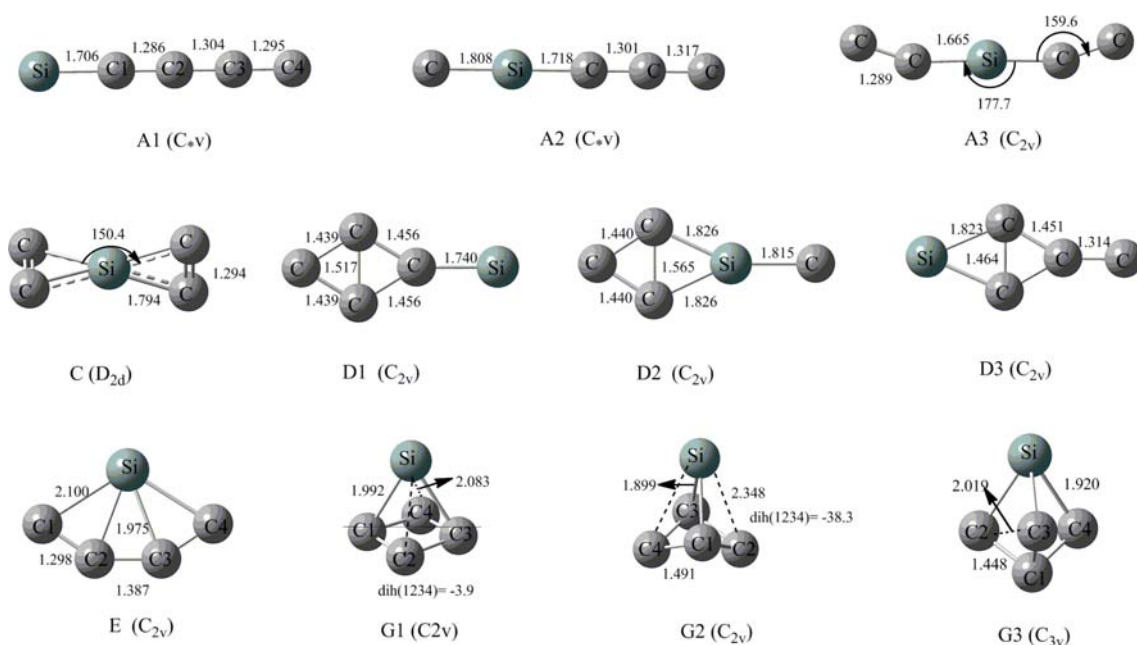
Fig. 2 Optimized geometries of SiC$_4$ isomers at the MP2/6-311G(d, p) level (Bond length unit angstrom, Bond angle unit degree)
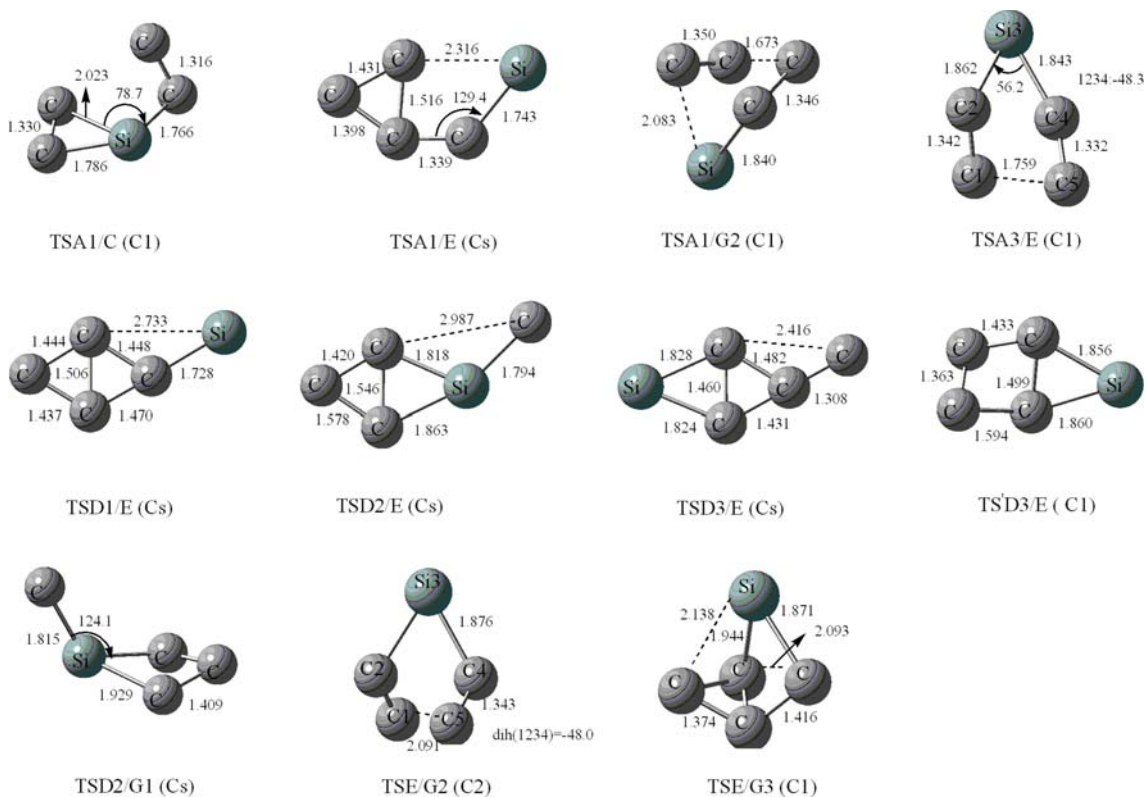
Fig. 3 Optimized geometries of SiC$_4$ transition states at the MP2/6-311G(d, p) level (Bond length unit angstrom, Bond angle unit degree)

the located isomers. G2 is also in the C$_{2v}$ symmetry with the $^1A_1$ electronic state, and it seems the bending type of G1. Dihedral angels 1234 of G1 and G2 are −3.9° and 38.3°, and the bond lengths of Si–C(1) and Si–C(2) in G1

and G2 are 1.992 Å [Si–C(1) in G1], 2.208 Å [Si–C(2) in G1], 1.899 Å [Si–C(1) in G2] and 2.348 Å [Si–C(2) in G2], respectively. Isomer G3 is more like a trigonal bipyramid, with the C$_{3v}$ symmetry.

Table 1 Harmonic vibrational frequencies (cm^{-1}), infrared intensities (km/mol) (in parentheses), dipole moment (D) and rotational constants (GHz) of SiC$_4$ isomers at the MP2/6-311G(d, p) level

Isomers	Frequencies (infrared intensity)	Dipole moment	Rotational constant
A1	66(0), 66(0), 223(11), 223(11), 331(5), 331(5), 566(15), 1,161(50), 1,831(0), 2,220(1,801)	6.6314	1.50546
A2	81(23), 81(23), 277(8), 277(8), 459(158), 459(158), 492(3), 852(15), 1,332(98), 2,057(13)	0.5608	1.63248
A3	14(11), 37(0), 38(4), 234(57), 242(57), 652(1), 1,029(66), 1,920(15), 1,938(1,383)	0.3836	184.40434, 1.90106, 1.88166
C	142(0), 244(56), 244(56), 495(32), 495(32), 657(0), 1,055(429), 1,679(0), 1,692(18)	0.0016	25.16033, 3.49982, 3.49947
D1	78(3), 181(0), 546(16), 558(12), 617(41), 927(11), 977(1), 1,364(75), 1,493(11)	5.1001	36.59301, 2.61593, 2.44140
D2	70(10), 72(27), 358(3), 526(50), 566(31), 704(14), 985(12), 1,091(26), 1,403(124)	1.4797	34.41116, 3.02385, 2.77959
D3	51(9), 177(0), 433(4), 455(71), 577(70), 989(0), 1,019(2), 1,122(90), 1,797(339)	3.7316	39.28037, 2.87313, 2.67730
E	191(19), 239(46), 389(25), 449(0), 564(46), 622(5), 1,010(2), 1,654(10), 1,842(22)	1.0780	11.13086, 5.81924, 3.82140
G1	508(27), 539(35), 571(17), 1,092(750, 1,153(244), 1,165(0), 1,367(17), 2,347(0), 3,631(0)	0.3020	9.64018, 6.47833, 6.11402
G2	338(6), 353(0), 528(80), 609(20), 728(7), 837(1), 935(5), 937(13), 1,205(2)	3.3188	10.76533, 5.71668, 5.66701
G3	340(22), 340(22), 585(1), 633(44), 633(44), 807(13), 1,182(167), 1,281(3), 1,281(3)	0.8507	10.32816, 5.97262, 5.97262

Table 2 Harmonic vibrational frequencies (cm^{-1}) of all the transition states on the isomerization PES at the MP2/6-311G(d, p) level

TSs	Frequencies
TSA1/C	295i, 198, 233, 312, 567, 808, 929, 1,475, 1,634
TSA1/E	428i, 185, 186, 538, 785, 811, 1,098, 1,320, 1,611
TSA1/G2	443i, 124, 396, 445, 493, 584, 766, 1,439, 1,469
TSA3/E	209i, 225, 388, 501, 539, 573, 800, 1,461, 1,597
TSD1/E	96i, 187, 520, 536, 679, 886, 1,009, 1,357, 1,486
TSD2/E	111i, 140, 355, 431, 589, 767, 984, 1,081, 1,404
TSD2/G1	305i, 241, 309, 363, 547, 572, 944, 1,204, 1,288
TSD3/E	128i, 189, 410, 430, 595, 941, 1,030, 1,172, 1,830
TS'D3/E	567i, 270, 377, 562, 665, 870, 932, 1,183, 1,363
TSE/G2	397i, 177, 373, 380, 529, 577, 791, 1,523, 1,532
TSE/G3	966i, 275, 501, 583, 712, 839, 1,129, 1,395, 1,669

Besides, there is a point needed to note that no tetrahedron species (F) or triangular cone (H) isomer was located in spite of numerous searches.

As the energies of triplet isomers are generally much higher than those of singlet ones [for example, the lowest-lying triplet state A1(^{3}A) was found to lie more than 64.63 kcal/mol above A1($^1\Sigma$)], it is reasonable to deduce that SiC$_4$ molecule isomerizes mainly on singlet PES. Figures in supporting information described the optimized geometries of isomers, transition states and isomerization PES on triplet, and the details about triplet species and higher spin states were not further discussed in the work.

Table 3 Relative energies (kcal/mol) of all the isomers and transition states at various levels

Species	ΔZPVE (MP2)	Er (MP2 + ZPE)	Er (G3MP2 + ZPE)
A1 ($^1\Sigma$)	10.03	0.00	0.00
A2 ($^1\Sigma$)	9.10	102.51	91.80
A3 (^{1}A$_1$)	8.73	58.69	60.26
C (^{1}A$_1$)	9.58	30.72	32.59
D1 (^{1}A$_1$)	9.63	43.66	50.91
D2 (^{1}A$_1$)	8.26	139.93	140.72
D3 (^{1}A$_1$)	9.46	48.62	52.57
E (^{1}A$_1$)	9.95	16.57	17.84
G1 (^{1}A$_1$)	31.98	70.20	61.00
G2 (^{1}A$_1$)	9.25	63.01	59.78
G3 (^{1}A$_1$)	10.13	72.87	65.47
TSA1/C (^{1}A)	8.80	92.09	86.51
TSA1/E (^{1}A$_1$)	9.34	47.89	51.32
TSA1/G2 (^{1}A)	8.17	74.03	76.06
TSA3/E (^{1}A)	8.70	60.92	65.24
TSD1/E (^{1}A')	9.52	44.01	51.86
TSD2/E (^{1}A')	8.22	141.14	142.98
TSD2/G1 (^{1}A')	7.82	172.02	155.80
TSD3/E (^{1}A')	8.89	50.51	54.00
TS'D3/E (^{1}A)	8.89	65.06	69.28
TSE/G2 (^{1}A)	8.41	75.71	79.62
TSE/G3 (^{1}A)	10.15	97.44	91.54

The symbols in parentheses denote the electronic states

Table 4 Relative energies (kcal/mol) of dissociation fragments of SiC$_4$ at various levels

Species	ΔZPVE (MP2)	E0r (MP2 + ZPE)	E0r (G3MP2 + ZPE)
C$_4$($^1\Pi_g$) + Si(^{1}D)	8.01	195.18	208.88
C$_4$($^1\Pi_g$) + Si(^{3}P)	8.01	162.54	185.74
C$_4$($^3\Sigma_g$) + Si(^{1}D)	8.18	186.84	197.00
C$_4$($^3\Sigma_g$) + Si(^{3}P)	8.18	154.20	173.86
c-C$_4$(^{1}A$_g$) + Si(^{1}D)	8.14	171.55	187.93
c-C$_4$(^{1}A$_g$) + Si(^{3}P)	8.14	138.91	164.79
c-C$_4$(^{3}B$_{3u}$) + Si(^{1}D)	9.34	191.11	205.24
c-C$_4$(^{3}B$_{3u}$) + Si(^{3}P)	9.34	158.48	182.09
C$_3$($^1\Sigma_g$) + CSi($^1\Sigma$)	6.69	185.46	193.48
C$_3$($^1\Sigma_g$) + CSi($^3\Pi$)	6.55	175.59	187.77
C$_3$($^1\Pi_g$) + CSi($^1\Sigma$)	8.39	239.33	233.80
C$_3$($^1\Pi_g$) + CSi($^3\Pi$)	8.25	229.46	228.10
c-C$_3$(^{3}A$_1'$) + CSi($^1\Sigma$)	28.40	220.09	228.39
c-C$_3$(^{3}A$_1'$) + CSi($^3\Pi$)	28.26	210.22	222.68
C$_2$($^1\Sigma_g$) + CCSi(^{1}A$'$)	6.53	139.12	270.10
C$_2$($^1\Sigma_g$) + CCSi($^3\Pi$)	7.82	201.55	195.83
C$_2$($^3\Pi_u$) + CCSi(^{1}A$'$)	6.21	144.54	285.97
C$_2$($^3\Pi_u$) + CCSi($^3\Pi$)	7.45	206.96	211.70
C$_2$($^1\Sigma_g$) + CSiC($^1\Sigma$)	6.05	263.44	269.63
C$_2$($^1\Sigma_g$) + CSiC($^3\Pi$)	6.38	320.32	300.85
C$_2$($^3\Pi_u$) + CSiC($^1\Sigma$)	5.73	268.85	285.50
C$_2$($^3\Pi_u$) + CSiC($^3\Pi$)	6.06	325.74	316.71
C(^{1}D) + C$_3$Si($^1\Pi$)	6.90	230.66	244.29
C(^{1}D) + C$_3$Si($^3\Sigma$)	7.08	223.33	239.42
C(^{3}P) + C$_3$Si($^1\Pi$)	6.90	183.15	207.27
C(^{3}P) + C$_3$Si($^3\Sigma$)	7.08	175.82	202.40
C(^{1}D) + C$_2$SiC($^1\Pi$)	5.38	318.17	325.29
C(^{3}P) + C$_2$SiC($^1\Pi$)	5.38	270.65	288.27

The symbols in parentheses denote the electronic states

3.2 SiC$_4$ isomerization and isomer stability

Both feasible isomerization and dissociation of SiC$_4$ isomers are considered to evaluate the kinetic stabilities in this section. Table 4 lists the relative energies of all the theoretically possible dissociation products. The optimization were performed at the MP2/6-311G(d, p) level, and the isomer A1 was also set to zero on the PES for comparison. As shown in Table 4, the relative energies of all the optimized dissociation products were so high that we did not put effort to investigate the transition states in the dissociation. Therefore, the kinetic stability of SiC$_4$ isomers is primarily controlled by the isomerization barriers.

From Fig. 5, we can see that A1, C, E, G1, G2 and G3 have relatively higher kinetic stability. At the G3(MP2)//MP2/6-311G(d, p) level, isomer G1 has a largest kinetic stability of 94.8 kcal/mol (G1 → D3). The lowest-lying

isomer, linear A1, and D$_{2d}$ isomer C also have considerable kinetic stability of 51.32 (A1 → E) and 53.92 kcal/mol (C → A1). The discovery is different from our previous conclusion of similar system that linear SiCCCH is the most kinetically stable SiC$_3$H isomer [38]. The lowest energy barrier for isomerizations of the five-membered-ring isomer E is 33.48 kcal/mol during E→A1, while the isomerizations to other isomers, A3, D1, D2, D3, G2 and G3 are 47.40, 34.02, 125.14, 36.16 (or 51.44), 61.78 and 73.70 kcal/mol, respectively. Besides, G2 and G3 have the kinetic stabilities of 16.28 (G2 → A1) and 26.07 kcal/mol (G3 → E), respectively. These isomers may have high enough kinetic stability to exist under low temperature conditions, such as in dense interstellar clouds.

The transition states of A2 isomerizations have not been located in spite of numerous searches. Other isomers, A3, D1, D2 and D3 are less kinetically stable. The isomerization barriers of these species are 4.98 (A3 → E), 0.95 (D1 → E), 2.25 (D2 → E) and 1.43 kcal/mol (D3 → E), respectively.

3.3 Properties of the stable SiC$_4$ isomers

Another important and interesting issue is the bonding properties of the kinetically stable isomers. For comparison, CH$_3$SiH$_3$, CH$_2$SiH$_2$, CHSiH, CH$_3$CH$_3$, CH$_2$CH$_2$ and C$_2$H$_2$ were also optimized at the same level, MP2/6-311G(d,p). The calculated C–C, C=C and C≡C bond lengths are 1.529, 1.337 and 1.215 Å, and corresponding experimental values are 1.536, 1.339 and 1.203 Å [39], respectively. The calculated lengths of Si–C, Si=C and Si≡C bonds are 1.875, 1.711 and 1.608 Å, and only experimental value for Si–C bond length is available, 1.869 Å [40].

In A1, Si–C(1) bond length is 1.706 Å, almost equal to the typical Si–C double bond length. The lengths of C(1)–C(2), C(2)–C(3) and C(3)–C(4) bonds are 1.286, 1.304 and 1.295 Å, and all of them are close to the typical C–C double bond length. NBO results show that both Si and C(4) have a lone pair electron, and bond orders of Si–C(1), C(1)–C(2), C(2)–C(3) and C(3)–C(4) are 1.670, 2.114, 1.421, 2.451, respectively. Combining the bond lengths with NBO results, we deduce that the isomer A1 can be considered as the following structure (the symbol "|" denote the lone pair electrons):

$$|\text{Si}=\!=\text{C1}=\!=\text{C2}=\!=\text{C3}=\!=\text{C4}|$$
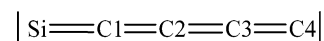
For the isomer C, the lengths of four Si–C bonds are all 1.794 Å, between the normal Si–C single bond and double bond. The two C–C bonds are 1.294 Å, between normal C–C double bond and C–C triple bond length. NBO results show that the orders of Si–C and C–C bonds are 1.032 and 2.699, respectively. Therefore, combining the geometry
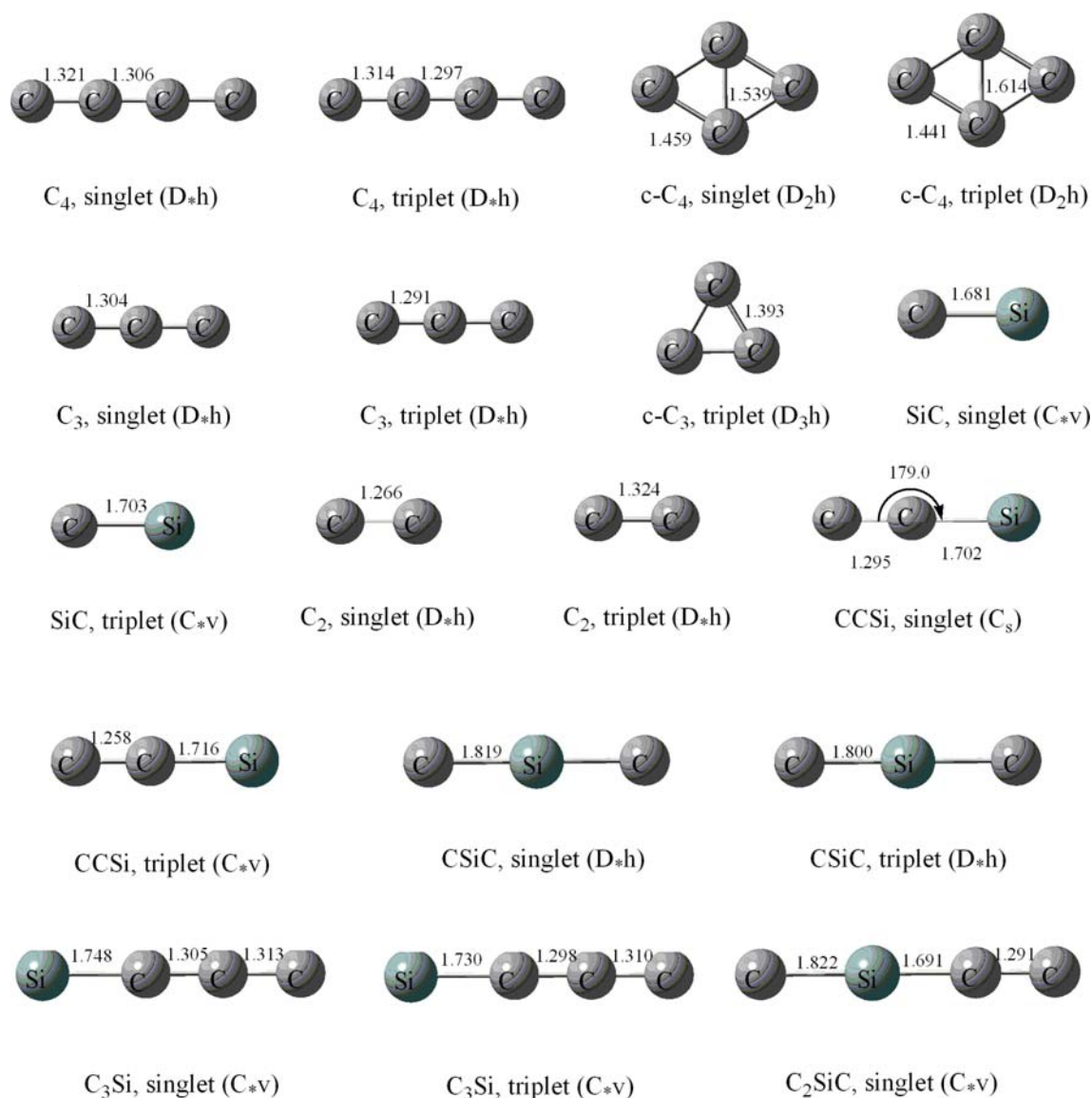
Fig. 4 Optimized fragments of the dissociations of SiC$_4$ at the MP2/6-311G(d, p) level (Bond length unit angstrom, Bond angle unit degree)

with NBO results, we can deduce that the following resonant structure has the most weight for isomer C.
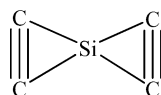
For the ring isomer E, Si–C(1) and Si–C(4) bonds are 2.100 Å and internal Si–C bonds in the ring are 1.975 Å. The four Si–C bonds are all a little longer than typical Si–C single bond in H$_3$SiCH$_3$. The C(1)–C(2) and C(3)–C(4) bonds are 1.298 Å, between typical C–C double and triple bond. The C(2)–C(3) bond is 1.387 Å, between C–C single bond and double bond. The orders of Si–C(1) or Si–C(4) bonds and Si–C(2) or Si–C(3) bonds are 0.360 and 0.397,

respectively. The C(1)–C(2) and C(3)–C(4) bonds have the bond order of 2.315, and the bond order between C(2) and C(3) is 1.161. Isomer E can be viewed as the followed resonance structure:
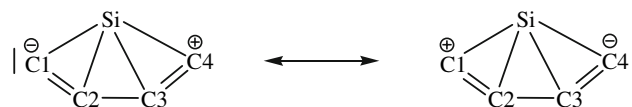
In tetra-angular cone G1, Si–C(1) and Si–C(3) bonds are 1.992 Å, the distance between Si and C(2) or C(4) is 2.083 Å, and C–C bonds are 1.467 Å. The four Si–C bonds are all a bit longer than Si–C single bond, and C–C bonds are between C–C single and double bond. The bond orders
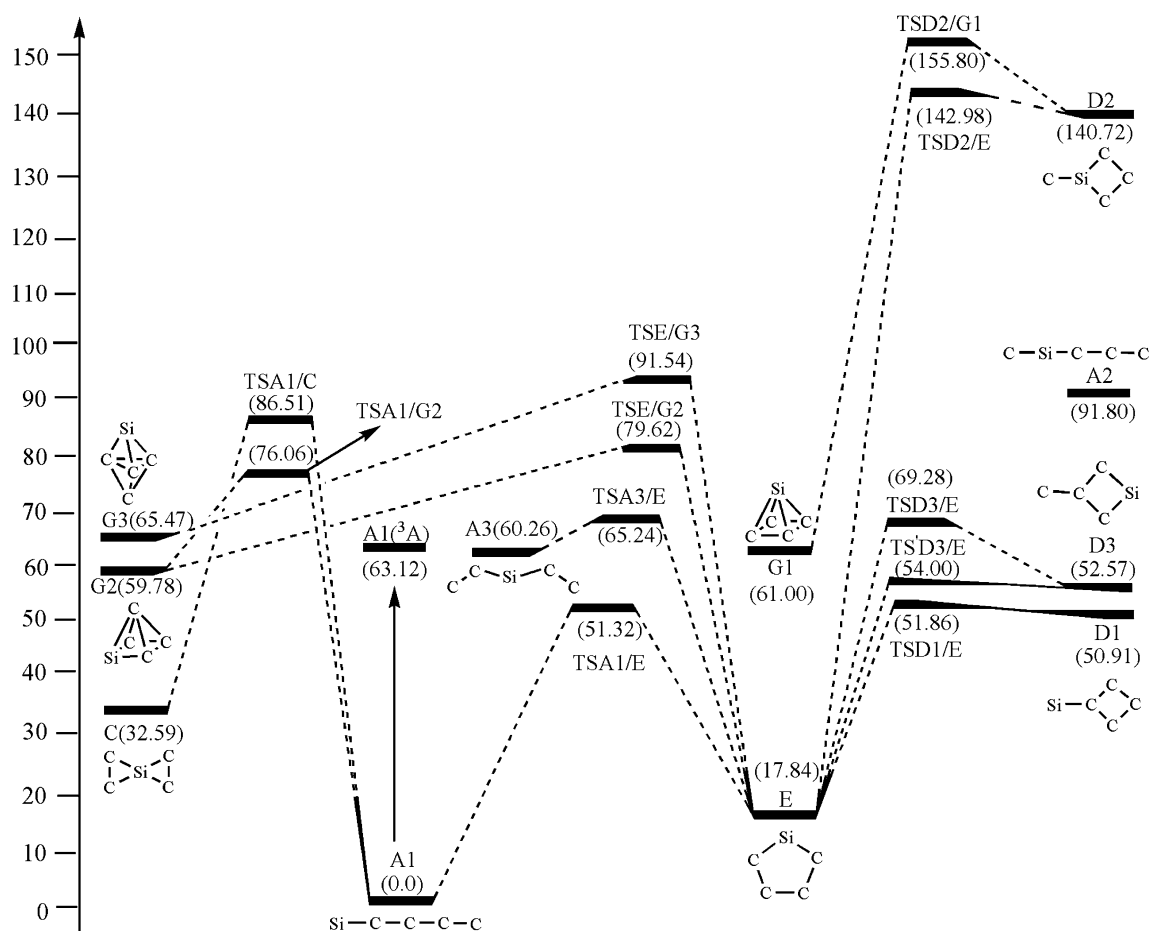
Fig. 5 Schematic potential energy surface of SiC$_4$ isomerizations at the G3(MP2)//MP2/6-311G(d, p) level. The values in the parentheses are at the G3(MP2)//MP2/6-311G(d, p) + ZPE levels, respectively

of Si–C(1) or Si–C(3), SiC(2) or Si–C(4) and C–C bonds are 0.830, 0.470 and 1.371, respectively. Combining geometry and NBO analysis, we deduced that isomer G1 may resonate between the following two structures:
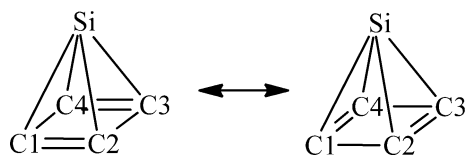
Similar with isomer G1, Si–C(1) and Si–C(3) bonds are 1.899 Å in isomer G2, almost equal to Si–C single bond. The distance between Si and C(2) or C(4) is 2.208 Å, rather longer than typical Si–C single bond. The bond orders of Si–C(1) and Si–C(3) are 0.936, and those of C(1)–C(2), C(2)–C(3), C(3)–C(4) and C(1)–C(4) bonds are 1.035, respectively. Although the distance between C1 and C3 atom is 1.941 Å, NBO result showed that C(1)–C(2) bond order is 0.791. Hence, the resonance structure of G2 can be described as:
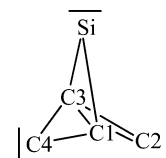
For isomer G3, three identical Si–C bonds are 1.920 Å, a little longer than typical Si–C single bond and three C–C bonds are 1.448 Å, a bit longer than C–C single bond. Si–C and C–C bonds have the bond orders of 0.678 and 1.197, respectively. The long distance (2.384 Å) between Si and C(1) and small bond order datum (0.373) implies a rather weak bond between the two atoms. From the geometry and NBO results, the dominant resonance structure of G3 can be viewed as follows:
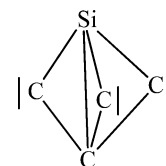
In order to understand small silicon–carbon clusters more systemically, we also summarized the bonding properties of the most stable structures of other Si_xC_y ($x + y \leq 5$) including SiC, SiC_2, Si_2C, SiC_3, Si_3C, Si_2C_2, Si_2C_3, Si_2C_3 and Si_4C in this section. These structures were confirmed by referring available reports [1–10], and the optimization and NBO calculations were also performed at the MP2/6-311G(d, p) level. From the bond lengths and NBO analysis, the most stable isomers can be considered as the following resonance structure:

3.4 Interstellar and laboratory implications

In this section, we mainly focus our interest on the kinetically stable isomers, A1, C, E, G1, G2 and G3. Table 1 lists the dipole moments and rotational constants for SiC_4 isomers at the MP2/6-311G(d, p) level. As seen from Table 1, C, G1 and G3 have rather small dipole moments (0.0016, 0.3020 and 0.8507 D, respectively) and their characterization may be identified by infrared spectrum; A1, E and G2 have considerably large dipole

^{3}SiC ^{1}SiC$_2$ ^{1}Si$_2$C ^{1}SiC$_3$ ^{3}Si$_3$C

^{1}Si$_2$C$_2$ ^{3}Si$_3$C$_2$ ^{1}Si$_2$C$_3$ ^{1}Si$_4$C
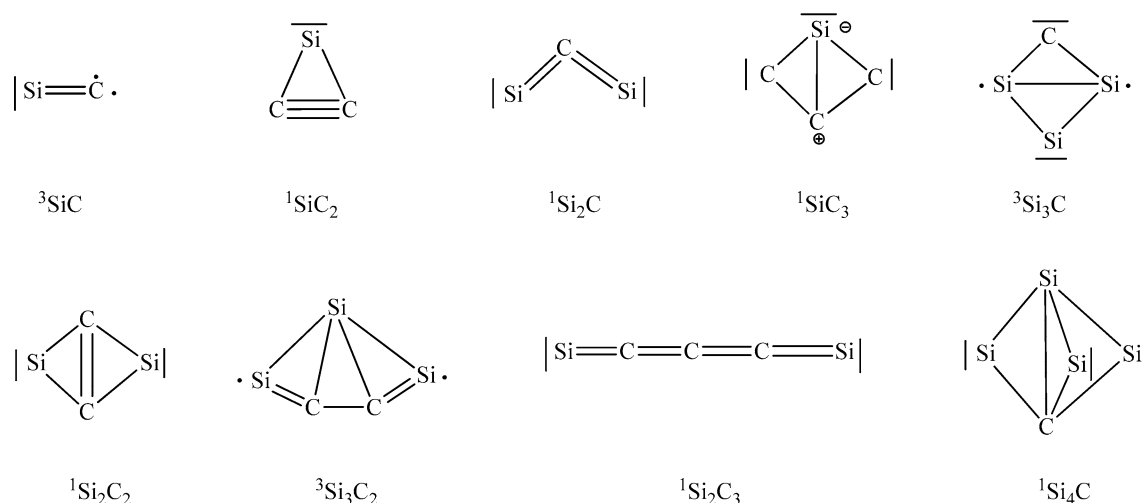
From the above scheme, the following conclusion can be deduced:

1. Singlet states are generally more stable than triplet states;
2. Chemical bonds are essentially single and double bonds, and triple bond is rarely formed in kinetically stable Si_xC_y clusters;
3. When the most stable structure is chain-like, Si atom tends to stand on the side, with long pair electrons;
4. For the stable cyclic or cage-like silicon-carbon molecules, Si atoms are apt to be far away from each other.

Si_4C and larger silicon-carbon clusters ($x + y = 6$) are under our present study, and detailed results will be reported later to improve our speculation.

moments as 6.6314, 1.0780 and 3.3188 D, respectively, making them promising for microwave detection. In fact, linear SiC_4 has been identified by laboratory microwave spectroscopy, agreeing with the above theoretical results [14]. We hope our computations will provide valuable information for further experimental research on SiC_4 molecules.

SiC_3 species has been detected in the interstellar space [15] and in the laboratory [22] as well, with the promising forms of rhombus [15, 22] and linetype [37] (see the scheme below). Michalopoulos et al. [2] established that SiC_2 radical exists as a ring on its ground state. SiC radical has also been detected in the interstellar space and laboratory (see the scheme below). Besides, C_4 species in both linear and cyclic forms have been characterized in laboratory [41].
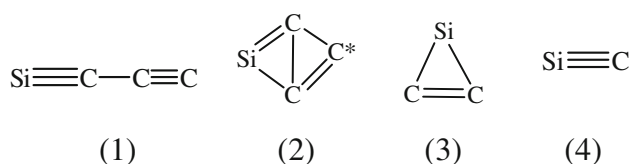
Isomer A1 can be formed by adding C atom to the terminal C of chain-like SiC_3 (1) (shown in the above scheme). Besides, the addition between C_3 and SiC may also produce A1. A further feasible formation mechanism of A1 is the addition between linear C_4 and Si atom, and simultaneously, isomer E can be produced, since cyclic SiC_2 (3) can be produced by laser vaporization of a SiC (4) target rod. C_2 species binding with Si atom of cyclic SiC_2 (3) may form the structure of isomer C. Dissociative Si atom binding with the four C atoms in cyclic C_4 can lead to the generation of tetra-angular-coned isomers G. In addition, G isomers can be produced via C addition with bending rhomboidal SiC_3 (2).

Since sometimes the observed species are not necessarily stable in interstellar space or in laboratory, the formation mechanism of less stable isomers A2, A3, D1, D2 and D3 are also analyzed in this section. Isomer A2 can be formed via the fragment combinations of SiC + C_3 and C + SiCCC. Direct addition between C_2 and SiC_2 may leads to isomer A3. It is feasible to produce isomer D1 by adding dissociate Si atom to cyclic C_4. The generation of isomers D2 and D3 can be viewed as the direct additions between C atom and rhomboidal SiC_3 (2). It should be noted that the above schemes are only theoretically possible to form stable S_iC4 isomers, and their viability in laboratory or space is not further discussed in the paper.

From Table 1, chain-like isomer A2 and A3 have small dipole moments (0.5608 and 0.3836 D, respectively) and they may be identified by infrared spectrum. With larger dipole moments of 5.1001, 1.4797 and 3.7316 D, isomers D1, D2 and D3 may be detected by microwave spectroscopy technique.

4 Conclusions

Ab initio methods were employed to investigate the structures, energies, dipole moments, rotational constants, and isomerization of the SiC_4 molecule. A total of 11 minima, including chain-like species (A), three-membered-ring species (C), four-membered-ring species (D), five-membered-ring species (E) and tetra-angular cone (G), and 11 transition states as well on the isomerization PES were located at the G3(MP2)//MP2/6-311G(d, p) level. The C2v tetra-angular cone isomer G1 has the largest kinetic stability. In addition, lowest-lying linear SiCCCC (A1),

D2d bicyclic c-Si(CC)$_2$ (C), C2v five-membered ring c-SiCCCC (E), C2v tetra-angular cone G2 and C3v trigonal bipyramid isomer (G3) also have considerably high kinetic stability. Other high-energy isomers, A3, D1, D2, and D3 are less kinetically stable. Among the stable isomers of interest, A1, E and G2 are promising for microwave detection with larger dipole moments. Due to the small dipole moments, C, G1 and G3 can be identified by infrared spectrum.

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