

# Theoretical study on structures and stability of triplet SiC<sub>3</sub>O isomers

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**Abstract** Various levels of calculations are carried out for exploring the potential energy surface (PES) of triplet SiC<sub>3</sub>O, a molecule of potential interest in interstellar chemistry. A total of 38 isomers are located on the PES including chain-like, cyclic and cage-like structures, which are connected by 87 interconversion transition states at the DFT/B3LYP/6-311G(d) level. The structures of the most relevant isomers and transition states are further optimized at the QCISD/6-311G(d) level followed by CCSD(T)/6-311+G(2df) single-point energy calculations. At the QCISD level, the lowest lying isomer is a linear SiCCCO **1** (0.0 kcal/mol) with the  $^3\Sigma$  electronic state, which possesses great kinetic stability of 59.5 kcal/mol and predominant resonant structure  $|\text{Si}-\text{C}\equiv\text{C}-\text{C}\equiv\dot{\text{O}}|$ . In addition, the bent isomers CSiCCO **2** (68.3 kcal/mol) and OSiCCC **5** (60.1 kcal/mol) with considerable kinetic stability are also predicted to be candidates for future experimental and astrophysical detection. The bond natures and possible formation pathways in interstellar space of the three stable isomers are discussed. The predicted structures and spectroscopic properties for the relevant isomers are expected to be informative for the identification of SiC<sub>3</sub>O and even larger SiC<sub>n</sub>O species in laboratory and interstellar medium.

**Keywords** Theoretical study · Structure · Stability · Potential energy surface (PES) · SiC<sub>3</sub>O

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## 1 Introduction

Silicon and oxygen chemistry have obtained considerable attention from various fields. One particular interesting area is the possible role in astrophysical chemistry. It is well known that many silicon- or oxygen-containing molecules have been detected, such as SiC<sub>n</sub> ( $n = 1 - 4$ ), C<sub>n</sub>O ( $n = 1, 2, 3, 5$ ), NO and SO [1]. Moreover, extensive experimental and theoretical investigations have been performed on the larger SiC<sub>n</sub> [2] and C<sub>n</sub>O [3] species, which have been expected to be carriers of some interstellar bands. Here, we optimistically expect that the mixed SiC<sub>n</sub>O species may be of astronomical interest and will be detected in the interstellar medium. On the other hand, the silicon, carbon and oxygen-related chemistries have been believed to play important roles in microelectronic materials. It is well known that binary silicon carbides are used frequently in microelectronic and photoelectronic applications [4]. Oxygen is usually used as minute dopant. During O-doped SiC vaporization process, the smaller species SiC<sub>n</sub>O may be generated. Understanding the structure, bond and stability properties of SiC<sub>n</sub>O clusters may be helpful for future identification of new Si, C and O-containing species either in laboratory or in space and also for elucidation of the formation mechanism of the Si-doped C<sub>n</sub>O clusters or O-doped SiC<sub>n</sub> clusters.

Indeed, the ternary series SiC<sub>n</sub>O have attracted researchers' interest [5–8]. Weltner et al. [9] found the existence of the simplest SiCO using electron spin resonance and optical spectra. Afterwards, the SiCO system has been the subject of many studies. Recently, Sanz et al. have detected SiCCO in a supersonic expansion by a DC electric discharge of silane, acetylene and carbon monoxide in the diluted neon. They also probed it by Fourier-transform microwave spectroscopy [10]. Moreover, the chain-like SiCCO and SiC<sub>n</sub>O species are theoretically studied [11, 12]. Very recently, our theoretical

studies on the SiC<sub>2</sub>O molecule showed that linear SiCCO and cyclic O-cSiCC have considerable kinetic stability and may be observable both in laboratory and interstellar space [13].

In view of the potential importance of SiC<sub>*n*</sub>O series, in this paper, we carefully study the penta-atomic SiC<sub>3</sub>O molecule, which is the isoelectronic species of the C<sub>3</sub>P<sub>2</sub> molecule. Very recently, our theoretical studies on the C<sub>3</sub>P<sub>2</sub> molecule revealed that one triplet isomer and seven singlet isomers have considerable kinetic stability, and may be observable in laboratory [14]. Therefore, it is highly possible that there will be various kinetically stable SiC<sub>3</sub>O species of experimental and astrophysical interest. For the SiC<sub>3</sub>O molecule, to our knowledge, only the linear SiCCCO isomer has been theoretically studied [12]. Because of the rather limited knowledge of the important SiC<sub>3</sub>O molecule, we decided to perform a detailed theoretical study on its triplet potential energy surface (PES), which is very significant for prediction of the promising species to be detected. The following problems will be resolved: (1) Is the triplet chain-like SiCCCO the ground state structure of the SiC<sub>3</sub>O molecule like PCCCP? (2) Are there any other chain-like species which are kinetically stable enough to be detected in the laboratory or interstellar space? (3) Does SiC<sub>3</sub>O have cyclic or cage-like isomers which are kinetically stable? (4) What is the nature of bonding in the relevant isomers?

## 2 Theoretical computational methods

All computations are carried out using the GAUSSIAN 98 [15] and NBO 5.0 [16] program packages. The optimized geometries and harmonic vibrational frequencies of the local minima and transition states are initially obtained at the DFT/B3LYP/6-311G(d) level. To get reliable energies, the CCSD(T)/6-311G(2d) single-point energy calculations are performed based on the optimized geometries at the B3LYP/6-311G(d) level. The zero-point vibrational energies (ZPVE) at the B3LYP/6-311G(d) are also included for energy correction. The total CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE is simplified as CCSD(T)//B3LYP. To confirm the right connective relationship between the isomers or dissociated fragments and the obtained transition states, we perform the intrinsic reaction coordinate (IRC) calculations at the B3LYP/6-311G(d) level. Finally, for the relevant isomers, the structures and frequencies are refined at the QCISD/6-311G(d) level and the energies at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level [simplified as CCSD(T)//QCISD]. Note that all the computations are done with UHF-based wave functions.

## 3 Results and discussion

To include as many isomers as possible, we initially considered five types of isomers: (1) linear or chain-like and

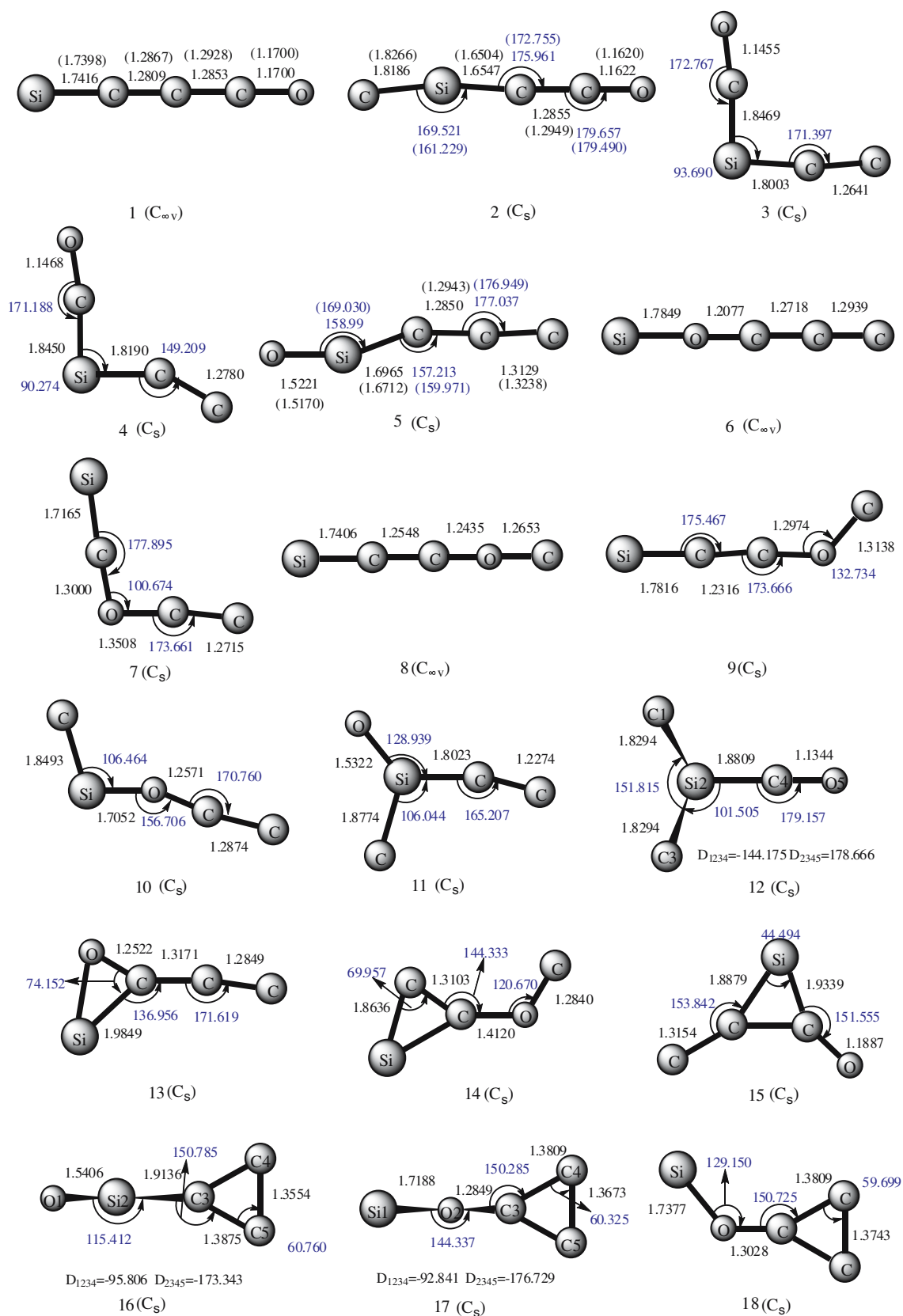
branched-chain species, (2) three-membered-ring species, (3) four-membered-ring species, (4) five-membered-ring species, and (5) cage-like species.

After an exhaustive search, 38 triplet SiC<sub>3</sub>O minimum isomers (**m**) and 87 triplet interconversion transition states (**TSm/n**) are obtained at the B3LYP/6-311G(d) level. The optimized geometries of the SiC<sub>3</sub>O isomers, transition states governing the kinetic stability of isomers and possible dissociated fragments are shown in Figs. 1, 2 and 3, respectively. The schematic triplet potential energy surface (PES) of SiC<sub>3</sub>O and the most possible pathways of the relevant isomers are illustrated in Figs. 4 and 5, respectively. The calculated spectroscopic properties of the relevant isomers are listed in Table 1. And the relative energies of all isomers and transition states governing the kinetic stability of triplet SiC<sub>3</sub>O isomers on different levels are given in Table 2. The relative energies of various dissociated fragments of SiC<sub>3</sub>O are collected in Table 3. Finally, natural resonance structure, weight and electronic spin densities for the relevant isomers are laid out in Table 4.

### 3.1 Triplet SiC<sub>3</sub>O isomers

On the triplet PES of SiC<sub>3</sub>O, there are ten chain-like species (linear or bent) and two branched-chain-like isomers. They are SiCCCO **1** (0.0, 0.0), CSiCCO **2** (67.9, 68.3), CCSiCO **3** (44.0), CCSiCO **4** (45.2), OSiCCC **5** (60.0, 60.1), SiOCCC **6** (73.8), CCOCSi **7** (127.8), SiCCOC **8** (103.0), SiCCOC **9** (96.7), CSiOCC **10** (155.6), OSi(C)CC **11** (131.3) and CSi(C)CO **12** (149.2). Note that the first and second values in parentheses are relative energies (in kcal/mol) with reference to isomer **1** (0.0, 0.0), which are obtained at the CCSD(T)//B3LYP and CCSD(T)//QCISD levels, respectively. Among them, **1**, **6** and **8** are linear structures with <sup>3</sup>Σ electronic state. The isomers **2**, **3**, **4**, **5**, **7**, **9** and **10** are bent structures belonging to C<sub>s</sub> symmetry with <sup>3</sup>A'' electronic state, whereas the two remaining species **11** and **12** are branched-chain structures with <sup>3</sup>A'' electronic state and C<sub>s</sub> symmetry. The present B3LYP/6-311G(d) method predicts that the lowest lying isomer is the linear SiCCCO **1** (0.0, 0.0), which is similar to PCCCP, because it contains better atomic arrangement, i.e., SiCC- plus -CO combination.

There are eleven isomers that possess three-membered ring structure. Among them, CO-cCCSi **14** (96.6), CO-cCSiC **22** (94.8) and OC-cSiCC **23** (50.0) have the cSiCC three-membered ring structure, which can be viewed as adducts between CO and ring cSiCC molecules, whereas OSi-cCCC **16** (67.5), SiO-cCCC **17** (70.2) and SiO-cCCC **18** (69.2) have cCCC ring, which can be regarded as adducts between SiO and ring cCCC molecules. Isomers CSi-cCOC **19** (154.4) and CSi-cCCO **20** (154.1) have the cCCO ring structure with the exocyclic CSiC bond, **19** and **20** lie higher energy than other cyclic species with the three-membered rings cSiCC or



**Fig. 1** Optimized geometries of triplet  $\text{SiC}_3\text{O}$  isomers and the stable singlet structures at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees. The values parentheses are at the QCISD/6-311G(d) level

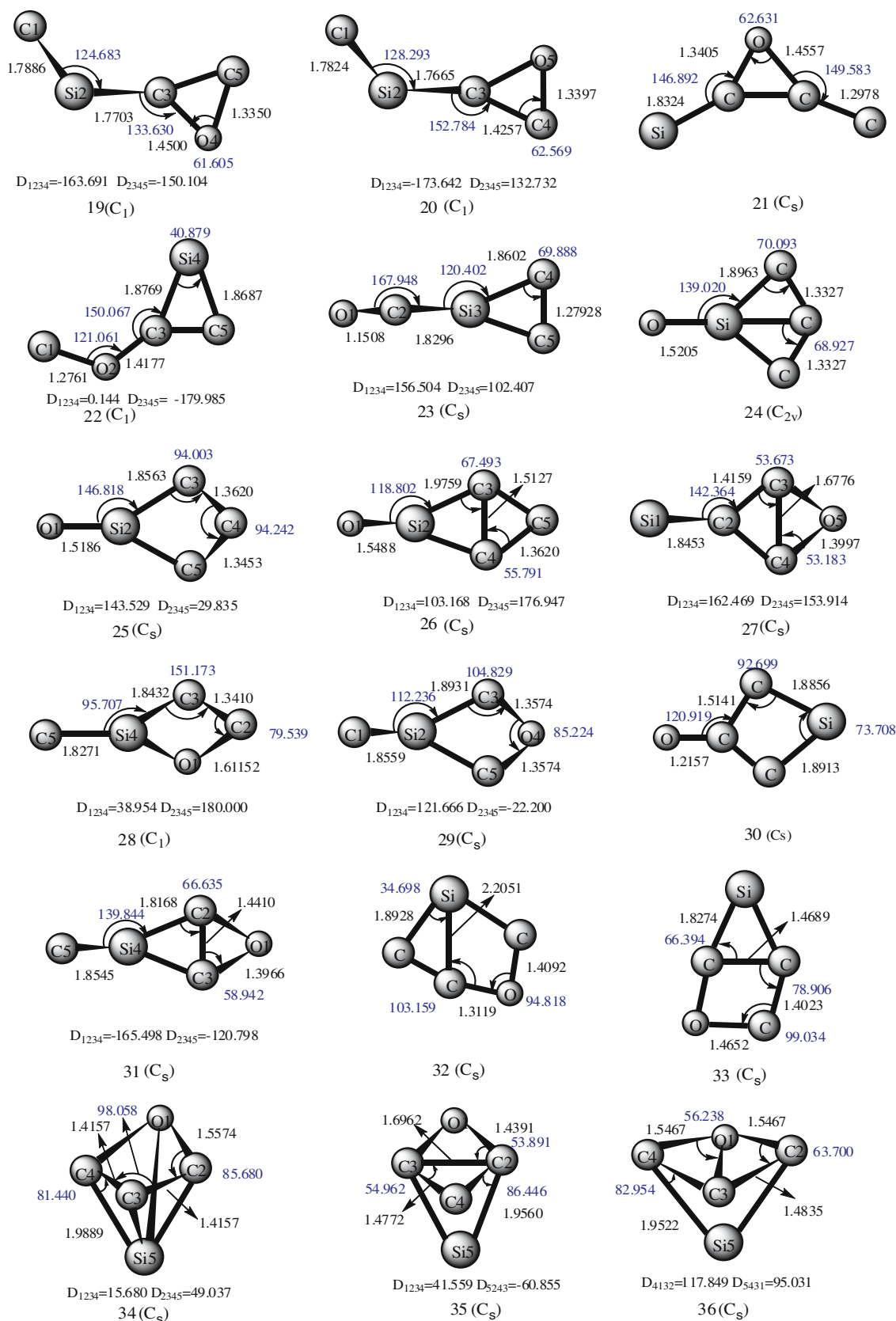


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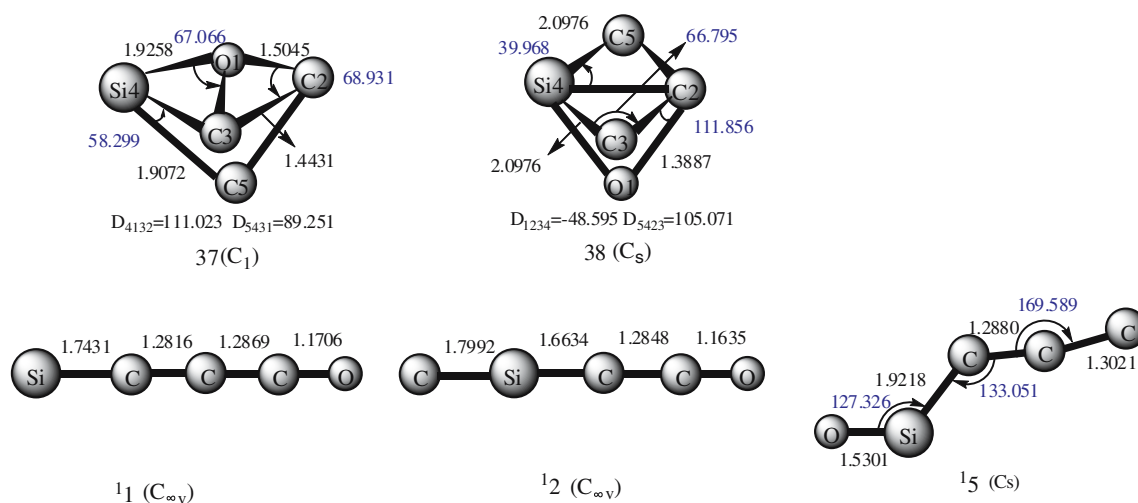


Fig. 1 continued

cCCC. Species CC-cCOSi **13** (67.6) with the COSi ring has an exocyclic CCC bond. C-cCSiC-O **15** (56.6) and Si-cCOC-C **21** (117.6) have the CSiC ring with two exocyclic CC and CO bond and COC ring with two exocyclic CSi and CC bond, respectively, as shown in Fig. 1. All of above are of  $C_s$  symmetry except **19**, **20** and **22** belonging to  $C_1$  symmetry. In the case of electronic state, **13**, **16**, **17**, **21** and **23** have  $^3A''$  state, **14**, **15** and **18** have  $^3A'$  state.

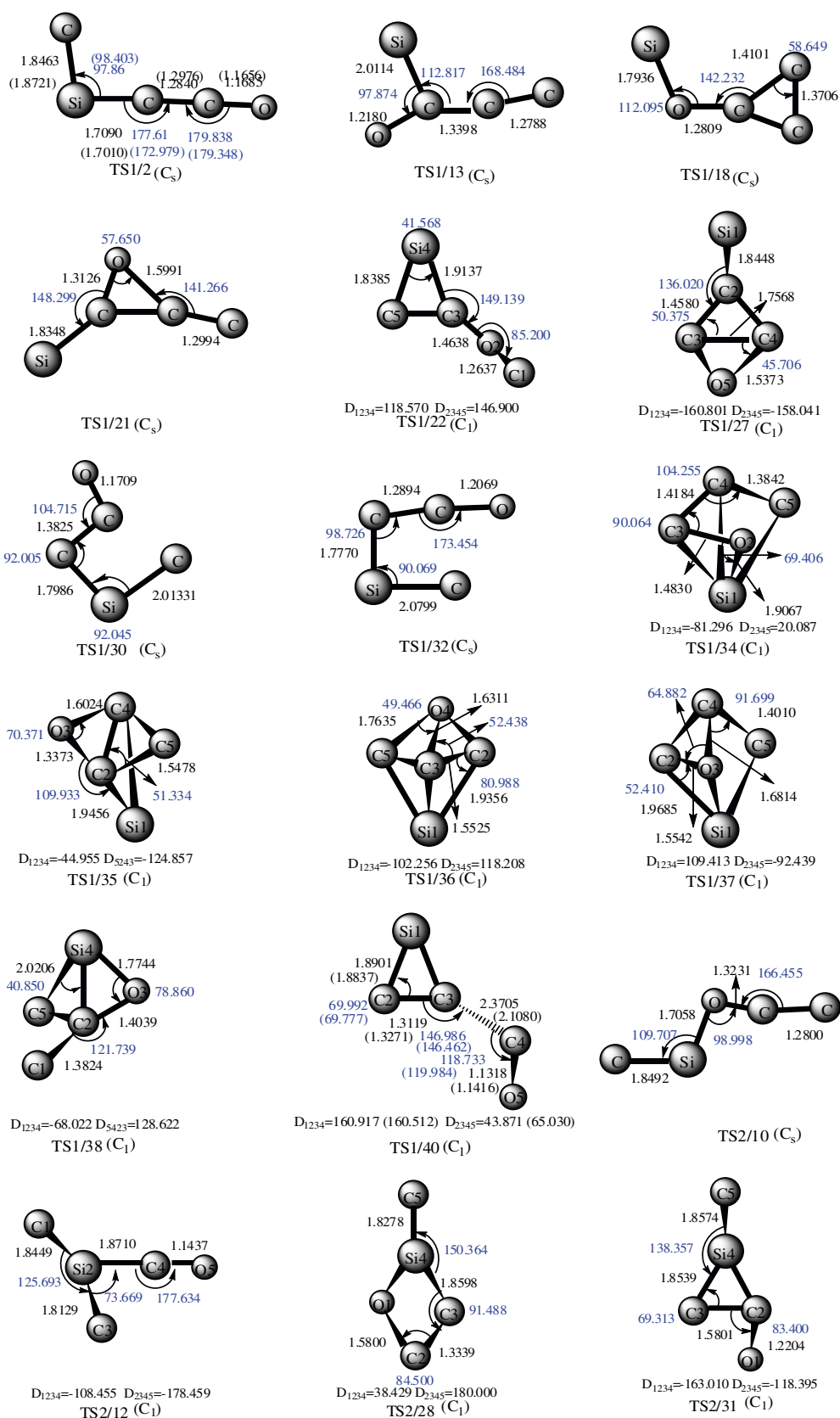
Eight isomers can be located as minima with four-membered ring structures. They are O-cSiCCC **24** (69.8), O-cSiCCC **25** (68.9), O-cSiCCC **26** (71.0), Si-cCCOC **27** (96.9), C-cSiCCO **28** (154.4), C-cSiCOC **29** (178.5), O-cCCSiC **30** (100.5) and C-cSiCOC **31** (159.5). Isomers **24**, **25** and **26** have cCCCSi four-membered ring and an exocyclic SiO bond, however, **24** and **26** possess CSi and CC crossing-bonds, respectively. Species **24** is a  $C_{2v}$  symmetry with  $^3B_1$  state, whereas **25** and **26** belong to  $C_s$  point group with the respective  $^3A''$  and  $^3A'$  states. Similar to the three isomers above, isomer **30** also has cCCCSi ring, but **30** possesses a CO exocyclic bond. Isomer **27** has cCCOC ring with the CSi exocyclic bond and CC crossing-bond. Isomer **28** with  $C_1$  symmetry only has cCCOSi ring and CSi exocyclic bond. Isomers **29** and **31** have cSiCOC ring and SiC exocyclic bond, while **31** has CC crossing-bond with  $^3A'$  electronic state.

In the five-membered ring species cSiCCOC **32** (90.3) and cSiCOCC **33** (88.2), each has a planar cSiCCOC ring with the O- and Si-atoms separated by one or two C-atoms. Isomers **32** and **33** have SiC and CC crossing-bond, respectively. Isomers **32** and **33** belong to  $C_s$  point group with  $^3A''$  electronic state, and can be regarded as adducts of CO molecule bridging to the two different sides CC and SiC of cSiCC ring, respectively.

The isomers **34** (108.3), **35** (117.3), **36** (140.9), **37** (116.5) and **38** (100.5) can be viewed as interesting cage-like species. Except for the isomer **37** belonging to  $C_1$  point group, others have  $C_s$  symmetry. The species **34**, **36**, and **38** have the  $^3A''$  electronic states except isomer **35** with  $^3A'$  state. Obviously, all of the five cage-like isomers are high-lying and kinetically unstable, which will be introduced in the following section. It is understandable that for such a small molecule, the “cage” is rather strained with the composed bond angle being very acute, and no or few multiple bonds are formed.

### 3.2 Triplet SiC<sub>3</sub>O isomerization and dissociation stability

To discuss the kinetic stability, one needs to consider various isomerization and dissociation pathways as many as possible. The lowest isomerization or dissociation barrier governs the kinetic stability of an isomer. In general, an isomer with higher barrier could have higher kinetic stability. For simplicity, the obtained 87 transition states structural details (in Fig. 2) are not discussed here. On the PES of SiC<sub>3</sub>O, three isomers **1**, **2** and **5** attract us much interest with relatively high kinetic stability, as shown in Fig. 5. For species **1**, the lowest dissociation barrier governs its kinetic stability, however, for the isomers **2** and **5**, the lowest isomerization barrier decides their kinetic stability. Seen from the PES, the lowest lying isomer **1** possesses great kinetic stability as 53.3 (59.5) (**1**→**40**) kcal/mol. As a result, the lowest lying isomer **1** with high kinetic stability is expected to be observable in laboratory and interstellar space. Compared with the species **1**, other two bent isomers **2** and **5** have slightly lower kinetic stability 15.0 (15.3) (**2**→**1**) and 11.7 (11.1) (**5**→**24**) kcal/mol, respectively. Such kinetic stability is enough to guarantee



**Fig. 2** Optimized geometries of transition states governing the kinetic stability of triplet SiC<sub>3</sub>O isomers at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees. The values in parentheses are at the QCISD/6-311G(d) level

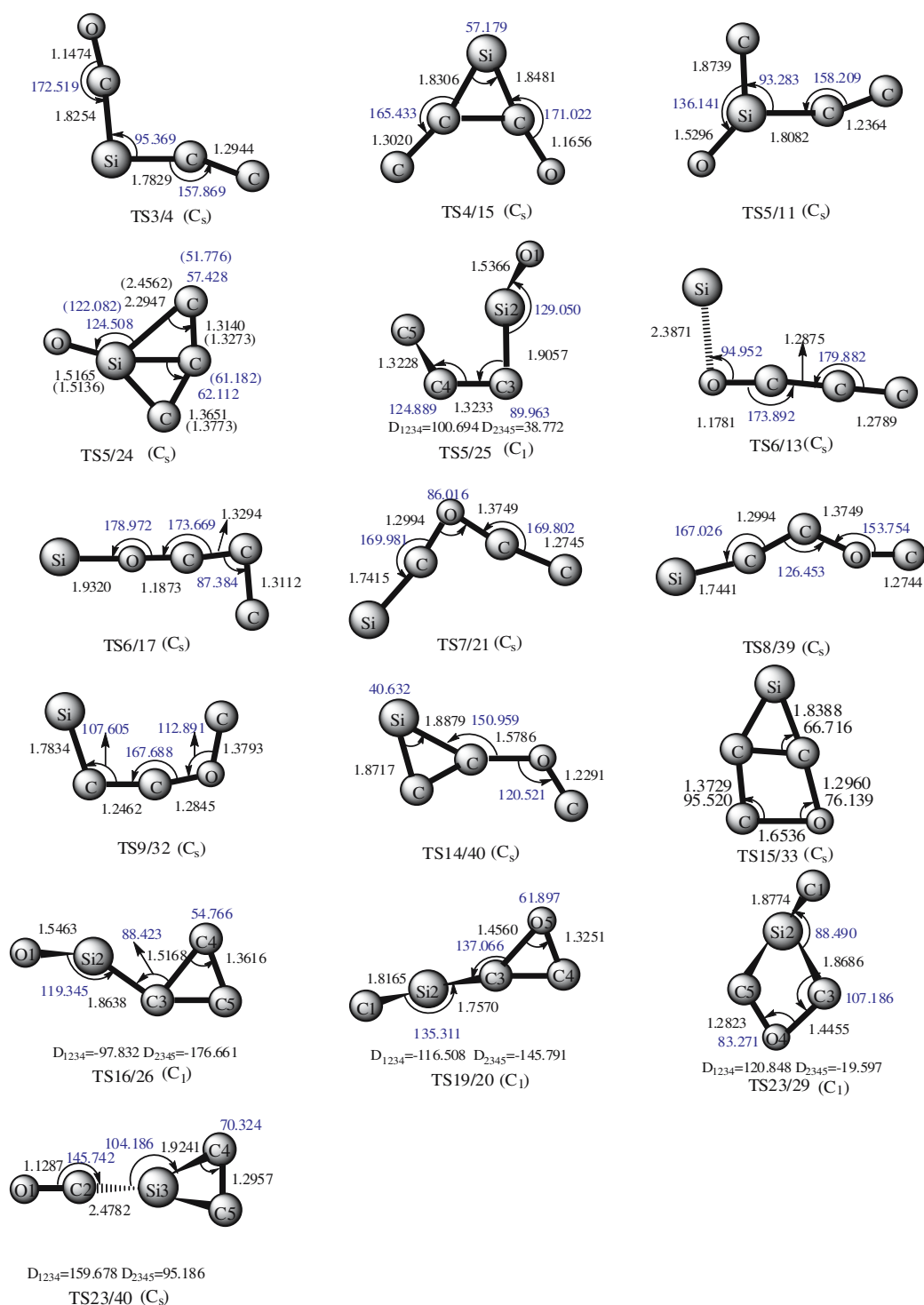
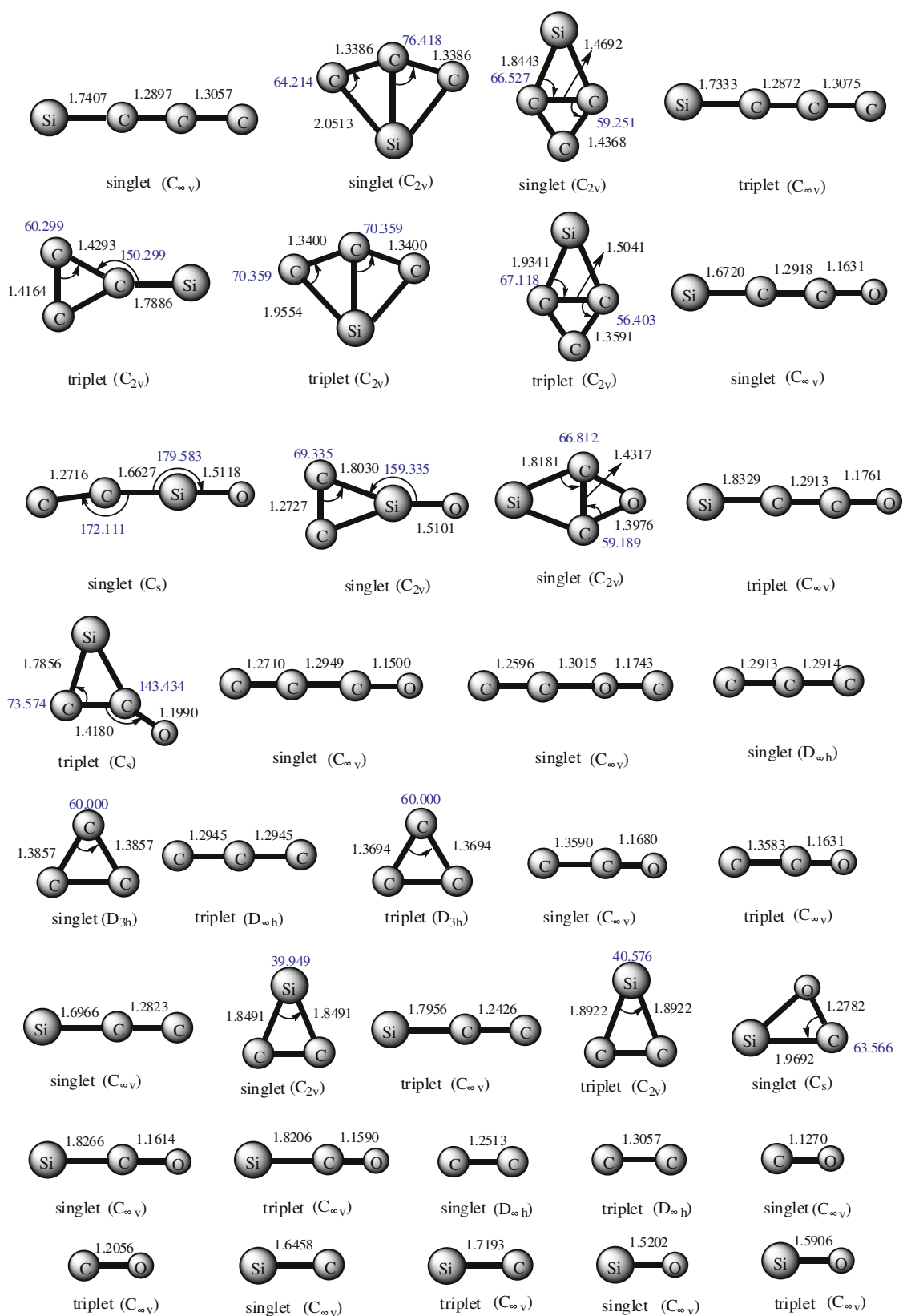


Fig. 2 continued

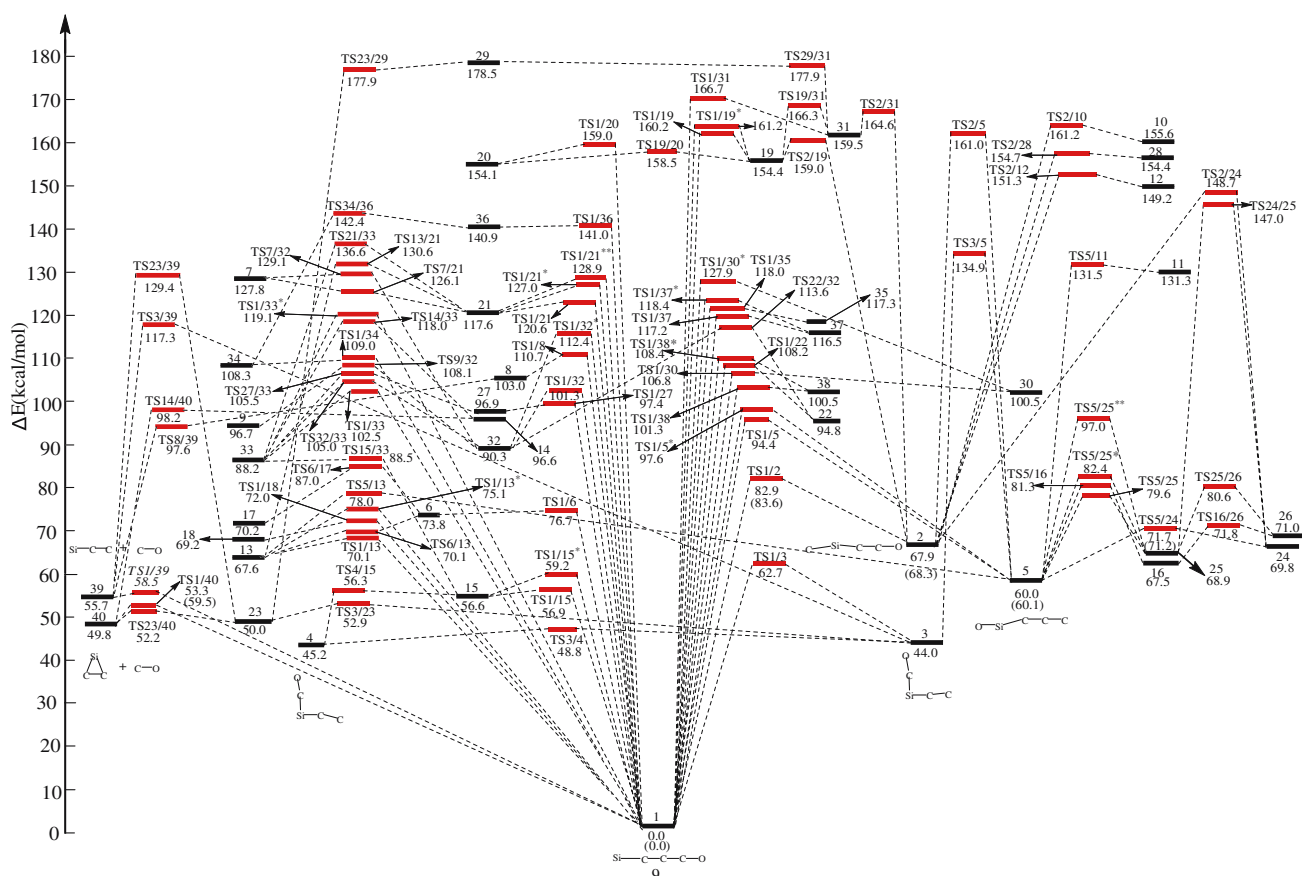
existence of isomers **2** and **5** under low temperature conditions in laboratory or interstellar space (such as in the dense interstellar clouds). Therefore, existence of our predicted

kinetically stabilized isomers **2** and **5** are also promising. The italic values in parentheses are for CCSD(T)//QCISD single-point calculations.

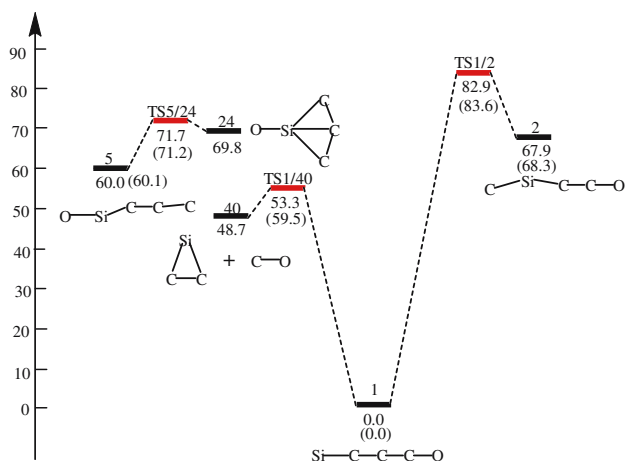


**Fig. 3** Optimized the dissociation fragments of  $\text{SiC}_3\text{O}$  at the B3LYP/6-311G(d) level. Bond lengths are in angstroms and angles in degrees





**Fig. 4** Schematic potential energy surface of triplet  $\text{SiC}_3\text{O}$  at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE level. The relative values in *italic* and parentheses are at the CCSD(T)/6-311G(2d)//MP2/6-311G(d)+ZPVE and CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level, respectively



**Fig. 5** Schematic potential energy surface of triplet  $\text{SiC}_3\text{O}$  including the most feasible pathways of the kinetically stable at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d)+ZPVE level. The relative values in *parentheses* are at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d)+ZPVE level

In addition to species **1**, **2** and **5**, the other isomers have less possibility to be detected due to their lower kinetic stability or the high-lying energies. As shown in Fig. 4, at the

CCSD(T)//B3LYP level, the least barriers of the remaining species are **3** (4.8, **3**→**4**), **4** (3.6, **4**→**3**), **6** (−3.7, **6**→**13**), **7** (−1.7, **7**→**21**), **8** (−5.4, **8**→**39**), **9** (11.4, **9**→**32**), **10** (5.6, **10**→**2**), **11** (0.2, **11**→**5**), **12** (2.1, **12**→**2**), **13** (2.5, **13**→**1**), **14** (1.6, **14**→**40**), **15** (−0.3, **15**→**4**), **16** (4.3, **16**→**26**), **17** (16.8, **17**→**6**), **18** (2.8, **18**→**1**), **19** (4.1, **19**→**20**), **20** (4.4, **20**→**19**), **21** (3.0, **21**→**1**), **22** (13.4, **22**→**1**), **23** (2.2, **23**→**40**), **24** (1.9, **24**→**5**), **25** (10.7, **25**→**5**), **26** (0.8, **26**→**16**), **27** (4.4, **27**→**1**), **28** (0.3, **28**→**2**), **29** (−0.6, **29**→**23**), **30** (5.6, **30**→**1**), **31** (5.1, **31**→**2**), **32** (11.0, **32**→**1**), **33** (0.3, **33**→**15**), **34** (0.7, **34**→**1**), **35** (0.7, **35**→**1**), **36** (0.1, **36**→**1**), **37** (0.7, **37**→**1**) and **38** (0.8, **38**→**1**) kcal/mol, respectively. For the five isomers **9**, **17**, **22**, **25** and **32**, their least barrier energies lie between 10.0 and 17.0 kcal/mol and they seem to have moderate kinetic stability. However, they may be of little interest as observable species either in laboratory or in space because of their high-lying energies (about or more than 70 kcal/mol). It should be noted that for isomers **6**, **7**, **8**, **15** and **29**, the negative values are a result of the single-point energy (CCSD(T)) and geometrical (B3LYP) calculations at different levels. We are aware that at the ZPVE-corrected B3LYP level, the isomers **6**, **7**, **8**, **15** and **29** have very small or almost zero

**Table 1** Harmonic vibrational frequencies ( $\text{cm}^{-1}$ ), infrared intensities ( $\text{km/mol}$ ) (in parentheses), dipole moment (D), rotational constants (GHz) and  $\langle S^2 \rangle$  value of the relevant triplet  $\text{SiC}_3\text{O}$  isomers at the B3LYP/6-311G(d) level

Species	Frequencies (infrared intensity)	Dipole moment	Rotational constant			$\langle S^2 \rangle$ value for UHF
SiCCCO <b>1</b>	336 (2), 506 (13), 506 (13), 529 (7), 1119 (22), 1868 (37), 2275 (2105)	1.1000	1.381422			2.014344
SiCCCO <b>1</b> <sup>a</sup>	94(14), 229(12), 500(12), 534(20), 1122(13), 1882(12), 2273(3163)	0.7991	1.374661			2.149745
CSiCCO <b>2</b>	44(20), 98(2), 102(5), 555(20), 604(30), 842(0), 1574(19), 2247 (1908)	0.7004	1223.05284	1.57115	1.56914	2.015667
CSiCCO <b>2</b> <sup>a</sup>	75(1), 82(5), 181(36), 557(3), 613(38), 615(38), 829(5), 1582(46), 2228(2223)	1.1710	18.39650	0.07586	0.07555	2.072944
CCCSiO <b>5</b>	93 (30), 112 (26), 1543(24), 363(6), 380(15), 573 (4), 1215(32), 1366(147), 1956(133)	1.7514	331.61153	1.67081	1.66244	2.022532
CCCSiO <b>5</b> <sup>a</sup>	107(10), 145(50), 161(53), 338(5), 381(14), 602(1), 1218(11), 1404(212), 1991(4)	2.5282	490.20495	1.66107	1.65546	2.13494

For the relevant isomers the QCISD/6-311G(d) value is also included

<sup>a</sup> At the QCISD/6-311G(d) level

kinetic stability (6.6, 0.0, 1.0, 1.9 and 0.7 kcal/mol for **6**→**13**, **7**→**21**, **8**→**39**, **15**→**4** and **29**→**23** conversions, respectively) (see Table 2) and are of little practical interest. Thus, higher level energy calculations at higher level geometries are not performed further.

### 3.3 Properties and implications of the of stable $\text{SiC}_3\text{O}$ isomers

From what have discussed above, we know that three isomers **1**, **2** and **5** have higher kinetic stability relative to other isomers and more possibilities to be detected in laboratory or interstellar space. In this section, we analyze their structural and bonding properties with the NBO 5.0 analysis programs [16], mainly based on the B3LYP results.

For the lowest lying species SiCCCO **1**, at the B3LYP/6-311G(d) level, its calculated SiC bond length (1.7416 Å) lies between the typical Si=C double bond (1.7068 Å in  $\text{H}_2\text{C}=\text{SiH}_2$ ) and Si-C single bond (1.8853 Å in  $\text{H}_3\text{C}-\text{SiH}_3$ ). Similarly, the calculated two CC (1.2809 and 1.2853 Å) and one CO (1.1700 Å) bond values also lie between their corresponding triple bond (1.1981 Å in  $\text{HC}\equiv\text{CH}$  and 1.1269 Å in  $\text{C}\equiv\text{O}$ ) and double bond (1.3269 Å in  $\text{H}_2\text{C}=\text{CH}_2$  and 1.1999 Å in  $\text{H}_2\text{C}=\text{O}$ ), respectively. It should be mentioned that on the basis of (R)CCSD(T) with the cc-pVTZ and cc-pVQZ basis set, Botschwina recommends the bond lengths of SiC, two internal CC and CO of the isomer **1** are 1.7349, 1.2799, 1.2865 and 1.1670 Å, respectively [12]. Obviously, our calculated results are consistent with the Botschwina's results. The spin density distribution is 0.867, 0.348, 0.291, 0.198 and 0.295e for Si, C, C, C and O, respectively. In order to confirm the structure of isomer SiCCCO **1**, we perform the NRT (Natural Resonance Theory) [17] calculation using NBO 5.0 analysis programs. At the B3LYP/6-311G(d) level, NRT calculates a set of 14 candidates, of which only the leading three are listed in Table 4. The structure of the highest weight is the conjugated structure  $|\text{Si}-\text{C}\equiv\text{C}-\text{C}\equiv\text{O}|$

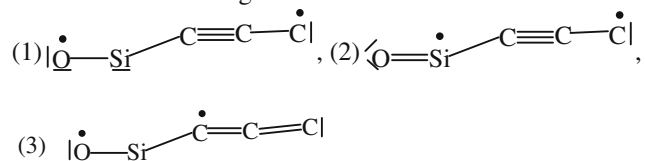
(72.39 %), followed by the forms  $|\text{Si}-\text{C}=\text{C}=\text{C}=\text{O}|$  (16.53 %) and  $|\text{Si}=\text{C}=\text{C}-\text{C}\equiv\text{O}|$  (5.04 %). The symbols “•” and “|” represent the single electron and lone-pair electrons, respectively. From the analysis above, the conjugated structure  $|\text{Si}-\text{C}\equiv\text{C}-\text{C}\equiv\text{O}|$  should be view as the main form of the resonance structure and contributes a lot to the stability of species **1**. Seen from the dissociation fragments and transition states (**TS1/39** and **TS1/40**), the isomer **1** can be regard as direct addition between singlet CO and triplet SiCC (SiCC or cSiCC form) molecules.

As to the bent isomer **2**, the spin density distribution is 1.463, 0.188, 0.199, 0.037 and 0.113e for the C, Si, C, C and O, respectively. Similar to the isomer **1**, combined with the bond lengths (in Fig. 1) and the weight (in Table 4), isomers **2** can be viewed as resonating between the following two forms:



The NRT calculations of the NBO 5.0 programs show that the weight of conjugated triple bonding structure (1) (38.91%) is higher than that of the conjugated double bonding form (2) (29.65 %), so the conjugated structure  $|\text{C}-\text{Si}\equiv\text{C}-\text{C}\equiv\text{O}|$  may be viewed as the main form of the resonance structure of the species **2**.

For the bent OSiCCC **5**, the spin density distribution (0.170, 0.394, 0.526, 0.101 and 0.809e for O, Si, C, C and C, respectively), on the basis of the bond lengths (in Fig. 1) and the weight (in Table 4), the species **5** can be regarded as the following three resonance structures:



The NRT calculation results indicate that the weight of three forms gradually decreases from (1) to (3), as shown in

**Table 2** Relative energies (kcal/mol) of triplet SiC<sub>3</sub>O isomers and transition states governing the kinetic stability of isomers at the B3LYP/6-311G(d) and single-point CCSD(T)/6-311G(2d) levels

Species	State	B3LYP <sup>b</sup>	□ZPVE B3LYP <sup>b</sup>	CCSD(T) <sup>c</sup> //B3LYP <sup>b</sup>	Total 1	QCISD <sup>b</sup>	□ZPVE QCISD <sup>b</sup>	CCSD(T) <sup>d</sup> //QCISD <sup>b</sup>	Total 2
SiCCCO 1 <sup>a</sup>	<sup>3</sup> Σ	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CSiCCO 2	<sup>3</sup> A''	76.1	-1.5	69.4	67.9	69.5	-1.0	69.3	68.3
CCSiCO 3	<sup>3</sup> A''	59.2	-2.2	46.2	44.0				
CCSiCO 4	<sup>3</sup> A''	61.6	-2.5	47.7	45.2				
CCCSiO 5	<sup>3</sup> A''	70.4	-2.1	62.1	60.0	65.5	-1.6	61.7	60.1
CCCOsi 6	<sup>3</sup> Σ	74.1	-1.8	75.6	73.8				
CCOCSi 7	<sup>3</sup> A''	135.2	-2.5	130.3	127.8				
SiCCOC 8	<sup>3</sup> Σ	106.2	-2.6	105.6	103.0				
SiCCOC 9	<sup>3</sup> A''	107.5	-2.6	99.3	96.7				
CSiOCC 10	<sup>3</sup> A''	164.2	-3.5	159.1	155.6				
OSi(C)CC 11	<sup>3</sup> A''	154.3	-3.4	134.7	131.3				
CSi(C)CO 12	<sup>3</sup> A''	167.2	-3.7	152.9	149.2				
CC-cOSi 13	<sup>3</sup> A''	76.2	-2.0	69.6	67.6				
CO-cCCSi 14	<sup>3</sup> A'	112.2	-2.3	98.9	96.6				
C-cSiC-O 15	<sup>3</sup> A'	66.4	-2.4	59.0	56.6				
OSi-cCCC 16	<sup>3</sup> A''	82.8	-2.9	70.4	67.5				
SiO-cCCC 17	<sup>3</sup> A''	79.8	-1.7	71.9	70.2				
SiO-cCCC 18	<sup>3</sup> A'	80.6	-1.4	70.6	69.2				
CSi-cCOC 19		171.4	-3.9	158.3	154.4				
CSi-cCOC 20		171.7	-3.9	158.0	154.1				
Si-cCOC-C 21	<sup>3</sup> A''	128.3	-2.4	120.0	117.6				
CO-cCSiC 22		110.4	-2.2	97.0	94.8				
OC-cSiCC 23	<sup>3</sup> A''	66.0	-2.1	52.1	50.0				
O-cSiCCC 24	<sup>3</sup> B <sub>1</sub>	89.3	-1.9	71.7	69.8				
O-cSiCCC 25	<sup>3</sup> A''	89.1	-2.0	70.9	68.9				
O-cSiCCC 26	<sup>3</sup> A'	87.7	-1.8	72.8	71.0				
Si-cCCOC 27	<sup>3</sup> A''	112.0	-2.4	99.3	96.9				
C-cSiCCO 28		179.2	-4.1	158.5	154.4				
C-cSiCOC 29	<sup>3</sup> A'	195.2	-3.9	182.4	178.5				
C-cCCSiC 30	<sup>3</sup> A'	113.6	-0.8	101.3	100.5				
C-cSiCOC 31	<sup>3</sup> A''	178.6	-4.0	163.5	159.5				
cSiCOCC 32	<sup>3</sup> A''	105.8	-1.8	92.1	90.3				
cSiCOCC 33	<sup>3</sup> A''	100.9	-1.5	89.7	88.2				
cageSiCCOC 34	<sup>3</sup> A''	127.1	-2.1	110.4	108.3				
cageSiCCCO 35	<sup>3</sup> A'	134.5	-2.7	120.0	117.3				
cageSiCOCC36	<sup>3</sup> A''	158.9	-3.3	144.2	140.9				
cageCSiCCO 37		136.3	-2.9	119.4	116.5				
cageCSiOCC 38	<sup>3</sup> A''	119.8	-2.5	103.0	100.5				
SiCC+CO 39 <sup>e</sup>		74.8	-3.6	53.4	49.8				
cSiCC +CO 40 <sup>e</sup>		81.2	-3.9	59.6	55.7				
TS1/2	<sup>3</sup> A''	87.8	-1.8	84.7	82.9	83.3	-1.6	85.2	83.6
TS1/13	<sup>3</sup> A''	78.3	-1.8	71.9	70.1				
TS1/18	<sup>3</sup> A''	83.9	-1.7	73.8	72.1				
TS1/21	<sup>3</sup> A''	129.1	-3.2	123.8	120.7				
TS1/22		122.8	-2.8	111.0	108.2				
TS1/27		111.6	-2.9	100.3	97.4				
TS1/30	<sup>3</sup> A''	122.9	-2.4	108.5	106.1				

**Table 2** continued

Species	State	B3LYP <sup>b</sup>	□ZPVE B3LYP <sup>b</sup>	CCSD(T) <sup>c</sup> //B3LYP <sup>b</sup>	Total 1	QCISD <sup>b</sup>	□ZPVE QCISD <sup>b</sup>	CCSD(T) <sup>d</sup> //QCISD <sup>b</sup>	Total 2
TS1/32	<sup>3</sup> A''	117.3	−2.7	104.0	101.3				
TS1/34		127.8	−2.8	111.8	109.0				
TS1/35		134.5	−3.3	121.3	118.0				
TS1/36		158.8	−3.7	144.7	141.0				
TS1/37		136.5	−3.6	120.9	117.2				
TS1/38		120.0	−2.8	104.1	101.3				
TS1/40		75.7	−3.3	56.6	53.3	56.5	−2.9	62.4	59.5
TS2/10	<sup>3</sup> A''	174.8	−3.8	165.0	161.2				
TS2/12		168.3	−4.0	155.3	151.3				
TS2/28		178.7	−4.4	159.1	154.7				
TS2/31		185.2	−4.6	169.3	164.7				
TS3/4	<sup>3</sup> A''	62.0	−2.6	51.4	48.8				
TS4/15	<sup>3</sup> A''	68.6	−2.7	59.0	56.3				
TS5/11	<sup>3</sup> A''	154.1	−3.7	135.2	131.5				
TS5/24	<sup>3</sup> A''	90.7	−2.2	73.9	71.7	72.4	−1.8	73.0	71.2
TS5/25		99.3	−3.0	82.6	79.6				
TS6/13	<sup>3</sup> A''	80.7	−1.8	71.9	70.1				
TS6/17	<sup>3</sup> A''	96.0	−2.6	89.6	87.0				
TS7/21	<sup>3</sup> A''	135.7	−3.0	129.1	126.1				
TS8/39	<sup>3</sup> A''	108.3	−3.7	101.3	97.6				
TS9/32	<sup>3</sup> A''	118.8	−2.7	110.8	108.1				
TS14/40	<sup>3</sup> A''	113.3	−3.5	101.7	98.2				
TS15/33	<sup>3</sup> A''	102.0	−2.5	91.0	88.5				
TS16/26		88.7	−2.3	74.1	71.8				
TS19/20		172.1	−4.0	162.5	158.5				
TS23/29		196.5	−4.5	182.4	177.9				
TS23/40	<sup>3</sup> A''	74.5	−3.2	55.4	52.2				

For the relevant isomers the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) values are also included

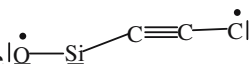
<sup>a</sup> The total energies of reference isomer **1** at the B3LYP/6-311G(d) level is −478.96874070 au, at the CCSD(T)/6-311G(2d)//B3LYP/6-311G(d) level is −478.03887170 au, at the QCISD/6-311G(d) level is −477.9578353 au, at the CCSD(T)/6-311+G(2df)//QCISD/6-311G(d) level is −478.1181016 au. The ZPVE at the B3LYP and QCISD levels are 11.01145 and 10.66241 kcal/mol, respectively

<sup>b</sup> The basis set is 6-311G(d) for B3LYP and QCISD

<sup>c</sup> The basis set is 6-311G(2d) for CCSD(T)//B3LYP

<sup>d</sup> The basis set is 6-311+G(2df) for CCSD(T)//QCISD

<sup>e</sup> **39** and **40** are the dissociation fragments of SiCC(<sup>3</sup>Π) + CO(<sup>1</sup>Σ) and cSiCC(<sup>3</sup>B<sub>2</sub>) + CO(<sup>1</sup>Σ), respectively

Table 4. In consequence, the structure  can be viewed as the leading form of the resonance structure of the species **5**.

### 3.4 Interstellar and laboratory implications

On the PES of triplet SiC<sub>3</sub>O, two sets of dissociated fragments **39**(SiCC(<sup>3</sup>Π) + CO(<sup>1</sup>Σ)) and **40** (cSiCC(<sup>3</sup>B<sub>2</sub>) + CO(<sup>1</sup>Σ)) attract us much attention. It is well known that SiC<sub>2</sub> has long been of astrophysical importance. Its electronic

absorption spectrum was first observed by Merrill [18] and Sanford [19] in the atmospheres of carbon-rich stars. The CO molecule is also a famous molecule popularly existing in interstellar medium [1,20]. So the association reaction between SiC<sub>2</sub> and CO molecules is expected to form the SiC<sub>3</sub>O isomers in the laboratory and interstellar space. From the PES of triplet SiC<sub>3</sub>O, at the CCSD(T)//MP2 level, the fragments SiCC + CO are connected to form SiCCCO **1** with a small barrier (1.3 kcal/mol) via transition state **TS1/39**. Therefore, the formation of SiCCCO **1** may occur easily via such an association reaction under laboratory

**Table 3** Relative (kcal/mol) energies of dissociation fragments of the SiC<sub>3</sub>O isomers at the B3LYP/6-311G(d) and single-point CCSD(T)/6-311G(2d) levels

Species	B3LYP <sup>a</sup>	ΔZPVE B3LYP <sup>a</sup>	CCSD(T) <sup>b</sup> //B3LYP <sup>a</sup>	Total
CCCO( <sup>1</sup> Σ) + Si( <sup>3</sup> P)	80.5	−1.8	67.5	65.7
CCCO( <sup>1</sup> Σ) + Si( <sup>3</sup> P)	187.8	−3.2	171.7	168.5
SiCCO( <sup>3</sup> Π) + C( <sup>3</sup> P)	176.5	−3.5	162.9	159.3
O − <sub>c</sub> CCSi( <sup>3</sup> A′) + C( <sup>3</sup> P)	193.4	−4.0	176.7	172.6
SiCCO( <sup>1</sup> Σ) + C( <sup>3</sup> P)	117.6	−2.5	101.4	98.9
CCSiO( <sup>1</sup> A′) + C( <sup>3</sup> P)	182.1	−4.3	156.8	152.5
O − <sub>c</sub> SiCC( <sup>1</sup> A <sub>1</sub> ) + C( <sup>3</sup> P)	171.8	−3.9	142.9	138.9
− <sub>c</sub> SiCOC( <sup>1</sup> A′) + C( <sup>3</sup> P)	208.7	−4.7	185.8	181.1
SiCCC( <sup>3</sup> Σ) + O( <sup>3</sup> P)	165.7	−4.1	154.1	149.9
− <sub>c</sub> CSiCC( <sup>3</sup> B <sub>1</sub> ) + O( <sup>3</sup> P)	185.3	−4.2	164.6	160.4
− <sub>c</sub> SiCCC( <sup>3</sup> B <sub>1</sub> ) + O( <sup>3</sup> P)	191.6	−4.4	173.7	169.3
Si − <sub>c</sub> CCC( <sup>3</sup> B <sub>1</sub> ) + O( <sup>3</sup> P)	212.9	−2.8	197.4	194.6
SiCCC( <sup>1</sup> Π) + O( <sup>3</sup> P)	180.7	−4.2	162.0	157.9
− <sub>c</sub> CSiCC( <sup>1</sup> A <sub>1</sub> ) + O( <sup>3</sup> P)	178.7	−4.2	156.3	152.1
− <sub>c</sub> SiCCC( <sup>1</sup> A <sub>1</sub> ) + O( <sup>3</sup> P)	173.7	−4.0	151.3	147.3
− <sub>c</sub> SiCC( <sup>3</sup> B <sub>2</sub> ) + CO( <sup>1</sup> Σ)	74.8	−3.6	53.4	49.8
SiCC( <sup>3</sup> Π) + CO( <sup>1</sup> Σ)	81.2	−3.8	59.6	55.7
SiCO( <sup>3</sup> A′′) + CC( <sup>1</sup> Σ <sub>g</sub> )	169.8	−4.1	126.6	122.5
SiCO( <sup>3</sup> A′′) + CC( <sup>3</sup> Π <sub>u</sub> )	147.2	−4.3	128.8	124.5
SiCO( <sup>1</sup> Π) + CC( <sup>1</sup> Σ <sub>g</sub> )	188.1	−4.1	143.2	139.1
− <sub>c</sub> SiCO( <sup>1</sup> A′) + CC( <sup>1</sup> Σ <sub>g</sub> )	208.5	−4.5	160.8	156.2
SiCO( <sup>1</sup> Π) + CC( <sup>3</sup> Π <sub>u</sub> )	165.5	−4.4	145.4	141.1
− <sub>c</sub> SiCO( <sup>1</sup> A′) + CC( <sup>3</sup> Π <sub>u</sub> )	185.8	−4.8	163.0	158.2
CCO( <sup>3</sup> Σ) + SiC( <sup>1</sup> Σ)	191.7	−4.2	182.2	178.0
CCO( <sup>3</sup> Σ) + SiC( <sup>3</sup> Π)	165.0	−4.4	217.8	213.4
CCO( <sup>1</sup> Π) + SiC( <sup>1</sup> Σ)	190.1	−4.3	202.5	198.2
CCO( <sup>1</sup> Π) + SiC( <sup>3</sup> Π)	202.5	−4.5	171.3	166.9
CCC( <sup>3</sup> Π <sub>u</sub> ) + SiO( <sup>1</sup> Σ)	131.3	−5.5	108.8	103.3
− <sub>c</sub> CCC( <sup>3</sup> A′ <sub>1</sub> ) + SiO( <sup>1</sup> Σ)	100.2	−3.4	81.1	77.7
CCC( <sup>1</sup> Σ) + SiO( <sup>1</sup> Σ)	81.1	−3.9	58.7	54.8
− <sub>c</sub> CCC( <sup>1</sup> Π <sub>u</sub> ) + SiO( <sup>1</sup> Σ)	130.6	−1.1	102.8	101.6

The isomer **1** is the reference species for the dissociation fragments energies, and the total energy of isomer **1** at CCSD(T)//B3LYP level is listed in Table 2. The symbols in parentheses of the column denote electronic states

<sup>a</sup> The basis set is 6-311G(d) for B3LYP

<sup>b</sup> The basis set is 6-311G(2d) for CCSD(T)

and interstellar conditions. Note that **TS1/39** is located at MP2/6-311G(d) level, since it cannot be obtained at the B3LYP level. Alternatively, the fragments cSiCC + CO can also be associated to form SiCCCO **1** with a small barrier (3.5 kcal/mol) through transition state **TS1/40**. Therefore, the observation of isomer SiCCCO **1** in the interstellar space is promising.

Up to now, a lot of interstellar molecules with chain-like or cyclic structure have actually been reported [1]. However, the chain-like silicon-containing species SiC<sub>n</sub>O (*n* ≥ 3) have

not been detected in interstellar space. So we expect that three chain-like species **1**, **2** and **5** could give good examples for experimental and interstellar detection. It is well known that the isomerism is particularly important in interstellar space where the temperature is very low so that the species with high kinetic stability can have long lifetime once formed. In fact, various isomeric species with higher energy yet considerable kinetic stability are already known in space, e.g., HNC, HCCNC and HNCCC (high-energy isomers of HCN and HCCCN, respectively), etc. Of particular

**Table 4** Natural resonance structures, weight and electronic spin densities ( $e$ ) for isomers **1**, **2** and **5**

Species	structure	Weight	Spin densities				
SiCCCO <b>1</b>		72.39%	Si	C	C	C	O
		16.53%	0.867	0.348	0.291	0.198	0.295
		5.04%					
CSiCCO <b>2</b>		38.91%	C	Si	C	C	O
		29.65%	1.463	0.188	0.199	0.037	0.113
OSiCCC <b>5</b>		56.38%	O	Si	C	C	C
		17.46%	0.170	0.394	0.526	0.101	0.809
		15.46%					

interest is that HNCCC [21] lies very high (50.9 kcal/mol) above HCCCN. Therefore, existence of our predicted kinetically stabilized isomers **1**, **2** and **5** is promising. In order to identify the isomers of SiC<sub>3</sub>O better in laboratory, the computational vibrational frequencies, dipole moments and rotational constants for the three relevant isomers **1**, **2** and **5** are shown in Table 1. At the QCISD/6-311G(d) level, the dominant frequencies of three isomers **1**, **2** and **5** are 2273, 2228 and 1404 cm<sup>-1</sup>, with the corresponding infrared intensities 3163, 2223 and 212 km/mol, respectively. They are very helpful for spectrum research of SiC<sub>3</sub>O molecule. Moreover, the isomer **5** has large dipole moment of 2.5282 D, which are also helpful to future microwave detection. Finally, it is worth to mention that for the three isomers (**1**, **2**, **5**) and relevant transition states (TS1/40, TS1/2, TS5/24), their calculated results at the B3LYP/6-311G(d) generally accord with those at higher QCISD/6-311G(d) level, as shown in Figs. 1 and 2 and Tables 1 and 2. The calculated relative energies, structures and spectroscopic properties of the three species are close to the CCSD(T)//B3LYP and CCSD(T)//QCISD results. In addition, we also investigated the singlet species **1**<sup>1</sup>, **2**<sup>1</sup> and **5**<sup>1</sup> (number **1** means singlet state) corresponding to the stable triplet isomers **1**, **2** and **5**, respectively. The geometrical structures of obtained singlet isomers are shown in Fig. 1. The computed results showed that singlet isomers **1**<sup>1</sup> (13.0 kcal/mol), **2**<sup>1</sup> (98.8 kcal/mol) and **5**<sup>1</sup> (71.3 kcal/mol) are higher in energy than the corresponding triplet species with singlet–triplet energy gap of 13.0, 22.7 and 0.9 kcal/mol, respectively, at the B3LYP level. Thus the singlet SiC<sub>3</sub>O isomers were not considered further.

Finally, we consider the spin contamination of the wave functions here. It is known that the DFT- and QCI (or CC)-

based wave functions are subject to little spin contaminations. In fact, as shown in Table 1, both  $\langle S^2 \rangle$  values (criteria for the spin contamination) at the B3LYP/6-311G(d) level and  $\langle S^2 \rangle$  values of the referenced Hartree–Fock wavefunctions in the QCISD calculations are very close to the expected value 2.0 for a pure triplet state, indicative of negligible spin contamination.

#### 4 Summary

At the CCSD(T)//B3LYP and CCSD(T)//QCISD level, the triplet potential energy surface (PES) of SiC<sub>3</sub>O molecule is established, including 38 minimum isomers and 87 interconversion transition states. At the CCSD(T)//QCISD level, the linear SiCCCO **1** (0.0) has a great kinetic stability (more than 50.0 kcal/mol). Additionally, both slight bent CSiCCO **2** (68.3) and bent OSiCCC **5** (60.1) also have considerable kinetic stability. All the three isomers may be produced under certain laboratory and interstellar conditions. The present study is expected to be helpful for the identification of SiC<sub>3</sub>O molecule in the laboratory and the interstellar space.

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