Theoretical study on structures and stability of triplet SiC\textsubscript{3}O isomers

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Abstract Various levels of calculations are carried out for exploring the potential energy surface (PES) of triplet SiC\textsubscript{3}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\textsubscript{1} (0.0 kcal/mol) with the \textit{3}\sum\textsuperscript{1} electronic state, which possesses great kinetic stability of 59.5 kcal/mol and predominant resonant structure \textsuperscript{3}\textsuperscript{1}SiC\textsuperscript{1}O\textsuperscript{1}CC. In addition, the bent isomers CSiCCCO\textsubscript{2} (68.3 kcal/mol) and OSiCCC\textsubscript{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\textsubscript{3}O and even larger SiC\textsubscript{n}O species in laboratory and interstellar medium.

Keywords Theoretical study · Structure · Stability · Potential energy surface (PES) · SiC\textsubscript{3}O

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\textsubscript{n}(n = 1 – 4), C\textsubscript{n}O (n = 1, 2, 3, 5), NO and SO [1]. Moreover, extensive experimental and theoretical investigations have been performed on the larger SiC\textsubscript{n} [2] and C\textsubscript{n}O [3] species, which have been expected to be carriers of some interstellar bands. Here, we optimistically expect that the mixed SiC\textsubscript{n}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\textsubscript{n}O may be generated. Understanding the structure, bond and stability properties of SiC\textsubscript{n}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\textsubscript{n}O clusters or O-doped SiC\textsubscript{n} clusters.

Indeed, the ternary series SiC\textsubscript{n}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\textsubscript{n}O species are theoretically studied [11,12]. Very recently, our theoretical
studies on the SiC₂O 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 SiC₆O series, in this paper, we carefully study the penta-atomic SiC₃O molecule, which is the iso-electronic species of the C₃P₂ molecule. Very recently, our theoretical studies on the C₃P₂ 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 SiC₃O species of experimental and astrophysical interest. For the SiC₃O molecule, to our knowledge, only the linear SiCCCO isomer has been theoretically studied [12]. Because of the rather limited knowledge of the important SiC₃O 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 SiC₃O 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 SiC₃O 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) level 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)//CCISD/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 SiC₃O 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 SiC₃O 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 SiC₃O 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 SiC₃O isomers on different levels are given in Table 2. The relative energies of various dissociated fragments of SiC₃O 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 SiC₃O isomers

On the triplet PES of SiC₃O, 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), CSSiCO 3 (44.0), CCSI CO 4 (45.2), OSiCC 5 (60.0, 60.1), SiOCCC 6 (73.8), COCSi 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 \( \sum_{\text{electronic state}} \) electronic state. The isomers 2, 3, 4, 5, 7, 9 and 10 are bent structures belonging to \( C_2 \) symmetry with \( 3\alpha' \) electronic state, whereas the two remaining species 11 and 12 are branched-chain structures with \( 3\alpha'' \) electronic state and \( C_2 \) 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., SiC⁺ plus -CO combination.

There are eleven isomers that possess three-membered ring structure. Among them, CO-cCSCI 14 (96.6), CO-cSiC 22 (94.8) and OC-cSiC 23 (50.0) have the cCSCI 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 (152.4) and Csi-cCO 20 (154.1) have the cCCO ring structure with the exocyclic CISC bond, 19 and 20 lie higher energy than other cyclic species with the three-membered rings cSiCC or