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Theoretical study of silicon–sulfur clusters $(SiS_2)_n$ ($n = 1$–6)

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Abstract. The possible geometrical structures and relative stability of $(SiS_2)_n$ ($n = 1$–6) silicon–sulfur clusters are explored by means of density functional theory quantum chemical calculations. The effects of polarization functions and electron correlation are included in these calculations. The electronic structures and vibrational spectra of the most stable geometrical structures of $(SiS_2)_n$ are analyzed by the same method. As a result, the regularity of the $(SiS_2)_n$ cluster growth is obtained, and the calculation may used for predicting the formation mechanism of the $(SiS_2)_n$ cluster.

Key words: Silicon–sulfur clusters – Geometry – Electronic structure – Vibrational spectra

1 Introduction

Silicon is one of the most abundant elements on earth. Its importance in science and technology results from its diverse usage, ranging from glass to catalysis to silicon-based microelectronic devices and optical fiber communications. That is why silicon clusters have been the focus of a series of experimental and theoretical studies. Theoretical studies related to silicon clusters have proved to be invaluable in understanding the results of various experiments on silicon clusters. For example, the geometries and vibrational frequencies of neutral silicon clusters and anions of silicon clusters were calculated by Raghavachari and Rohlfing [1, 2]. Sulfur has the largest number of allotropes of any element. The study of the geometrical and electronic structure of sulfur is very important for investigating its properties and applications. Much attention has been paid to sulfur clusters, for example, Hohl et al. [3] and Raghavachari et al. [4] investigated the geometries and electronic structures of sulfur clusters. SiS_2 is an "isovalent" molecule of CO_2, SiO_2 and CS_2 and although there are many theoretical studies of the latter and their clusters [5–14], we do not know of any theoretical study of SiS_2 and clusters of $(SiS_2)_n$.

Recently silicon–sulfur cluster anions and cations have been produced using direct laser ablation on a solid sample containing a mixture of sulfur and silicon powder; the photodissociation of the clusters was studied with a tandem time-of-flight mass spectrometer. There are a batch of intense peaks of cluster anions and cations in the mass spectra, and the $(SiS_2)_n^{\pm}$ clusters are the most intense peaks. We have already studied the possible geometrical structures and relative stability of $(SiS_2)_n^{\pm}$ ($n = 1$–6) silicon–sulfur clusters by means of density functional theory (DFT) quantum chemical calculations. In this work we report calculations for the $(SiS_2)_n$ ($n = 1$–6) neutral clusters and predict the formation mechanism of the $(SiS_2)_n$ neutral clusters. As a result, regularity is obtained for the $(SiS_2)_n$ neutral cluster growth, and then we predict the formation mechanism of the $(SiS_2)_n$ neutral clusters.

2 Computational details

The geometrical and electronic structures of the $(SiS_2)_n$ neutral clusters and the harmonic vibrational frequencies of the most stable isomer were studied. The standard three-parameter Becke exchange function with the Lee, Yang and Parr correlation function (DFT/B3LYP)[15–17] with the polarized-function 6-31G* basis set [18–22] available in the GAUSSIAN94 package [23] was used.

3 Individual cluster

3.1 SiS_2

SiS_2 is the smallest cluster and can be regarded as the core of the $(SiS_2)_n$ clusters. The possible geometries of the SiS_2 clusters are given in Fig. 1, and these structures were optimized in order to obtain the lowest-energy structure. The total energy order is $2 > 4 > 3 > 1$. The Si–S bond lengths in structures 3 and 4 are similar and so are their vibrational spectra. So we can conclude that structures 3 and 4 are actually the same structure. The vibrational spectra indicate that there are no imaginary

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frequencies for all four structures, so they are all equilibrium structures of SiS_2, and the structure with $D_{\infty h}$ symmetry is the stable structure.

3.2 $(SiS_2)_2$

$(SiS_2)_2$ can be regarded as the dimer of SiS_2 and SiS_2 with the binding of Si–S, Si–Si, S–S. The optimized structures of $(SiS_2)_2$ are shown in Fig. 2. The total energy order is obtained as $6 > 4 > 3 > 7 > 2 > 5 > 1$, and structures 1, 2, 3 and 5 are the structures without imaginary frequency. So there are four equilibrium structures of $(SiS_2)_2$ and the most stable structure is 1, with D_{2h} symmetry; structure 5 is another stable structure, with C_{2v} symmetry.

3.3 $(SiS_2)_3$

We designed the structures of the trimer with the same scheme as for the dimer, i.e. the binding of Si–S is the main binding effect among the monomers. The structures are shown in Fig. 3. The total energy order is

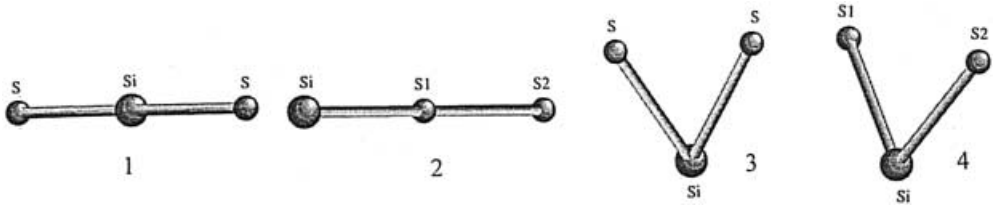

Fig. 1. The geometrical structures of the SiS_2 cluster

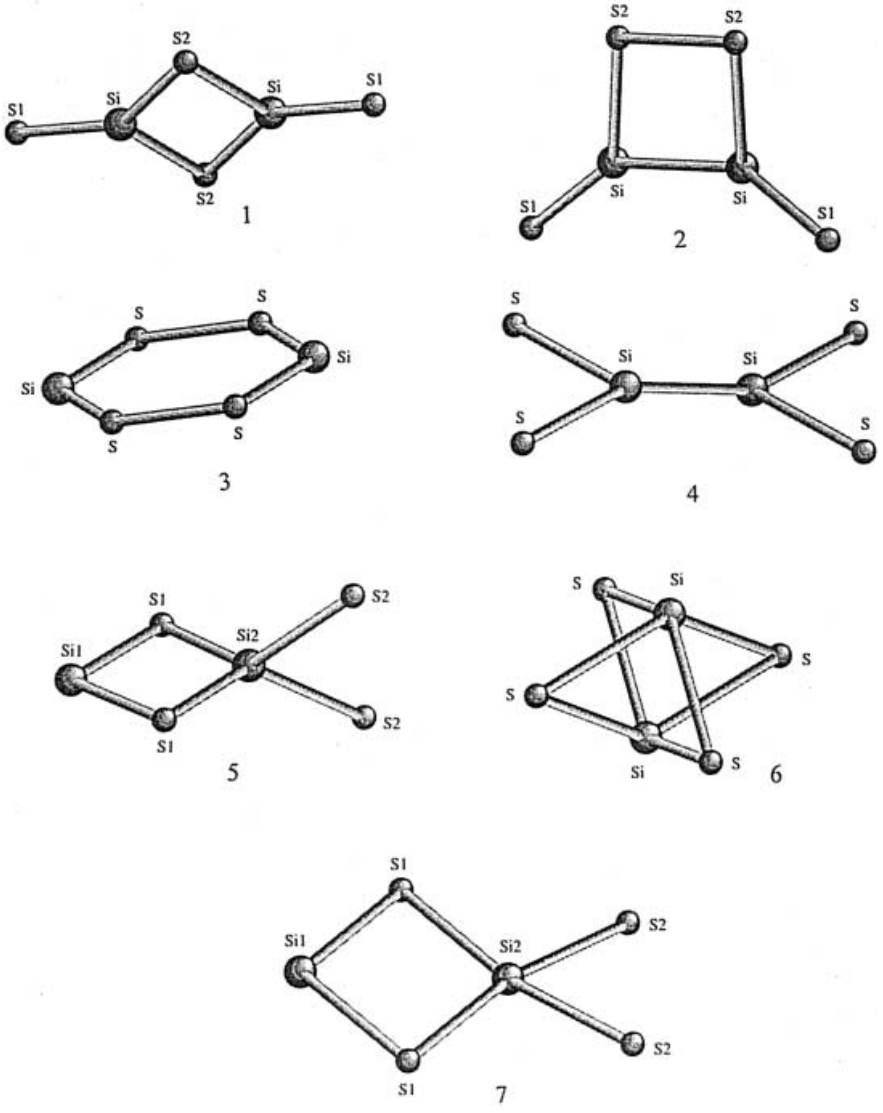

Fig. 2. The geometrical structures of the $(SiS_2)_2$ cluster

obtained as $4 > 3 > 5 > 6 > 2 > 1$. The analysis of the vibrational spectra reveals there are no imaginary frequencies of structures 1, 2 and 6, so we can conclude that there are three isomers of the $(SiS_2)_3$ cluster and that structure 1 is the most stable structure. Also as for the dimer of $(SiS_2)_2$, structure 2 is a more stable structure, with C_{2v} symmetry.

3.4 $(SiS_2)_4$

The optimized geometrical structures of $(SiS_2)_4$ are shown in Fig. 4. The total energy order is $3 > 5 > 6 > 1 > 7 > 4 > 2$. The relative vibrational frequencies reveal that structures 2 and 4 are stable structures of $(SiS_2)_4$; it is said that there are two isomers of $(SiS_2)_4$, with D_{2h} and C_{2v} symmetry.

3.5 $(SiS_2)_5$ and $(SiS_2)_6$

On the basis of the geometrical structures of $(SiS_2)_n$ ($n = 2$–4), we may conclude that the more stable structures of $(SiS_2)_n$ have D_n ($D_{\infty h}$, D_{2h}, D_{2d}) and C_{2v} symmetry, and the formation regularity is that based on the structure of SiS_2 as the core adding building block of SiS_2 through the binding of two S atoms in SiS_2 and a Si atom in SiS_2, forming tetratomic rings which are perpendicular to each other. So we designed pentamer $(SiS_2)_5$ and hexamer $(SiS_2)_6$ according to the regularity. The structures are shown in Fig. 5, and there are no imaginary frequencies, so the structures of $(SiS_2)_5$ and $(SiS_2)_6$ with D_n (D_{2h}, D_{2d}) and C_{2v} symmetry are stable structures.

4 Results and discussion

From the study of the individual clusters of the $(SiS_2)_n$ structures, we can predict that there are two methods for $(SiS_2)_n$ cluster formation: one is that a S and the Si atom of one SiS_2 molecule bind to the S and Si atoms of another SiS_2 molecule and form a tetratomic ring with S atoms binding to two Si atoms as a bridge; the other is a Si atom of one SiS_2 molecule binding to two S atoms of the other SiS_2 molecule and forming a tetratomic ring. As n increases, the tetratomic rings of the $(SiS_2)_n$ cluster become perpendicular to each other. The symmetry is D_n ($D_{\infty h}$, D_{2h}, D_{2d}) and C_{2v}, respectively.

In the structures with D_n ($D_{\infty h}$, D_{2h}, D_{2d}) symmetry, $S_{(t)}$ denotes the S atoms which bind to a Si atom, and the Si atoms are denoted as $Si_{(t)}$. In the structures with C_{2v} symmetry, we denote S atoms which bind to a Si atom as $S_{(t)}$, and the Si atoms which bind to two S atoms as $Si_{(t)}$. We present the bond lengths and the Mulliken charges on the equilibrium geometries of $(SiS_2)_n$ ($n = 1$–6) clusters with D_n ($D_{\infty h}$, D_{2h}, D_{2d}) symmetry in Table 1. SiS_2 is the core of $(SiS_2)_n$ and there is negative charge on the S atoms and positive charge on the Si atom, so when forming the dimer, the reaction probably happens on the S atoms and the Si atom of SiS_2. The regularity of the formation of the other clusters is also like this. This conclusion can also be drawn from the net charge distribution of $(SiS_2)_n$. For all the clusters, in the structures with D_n ($D_{\infty h}$, D_{2h}, D_{2d}) symmetry, the net charge on the terminal $S_{(t)}$ atoms is negative and on $Si_{(t)}$ it is positive. With the cluster chain growth, the net charge on $S_{(t)}$ increases monotonically with increasing n; when $n = 2$ the net charge on $S_{(t)}$ is –0.1935, $Si_{(t)}$ is 0.3448, when

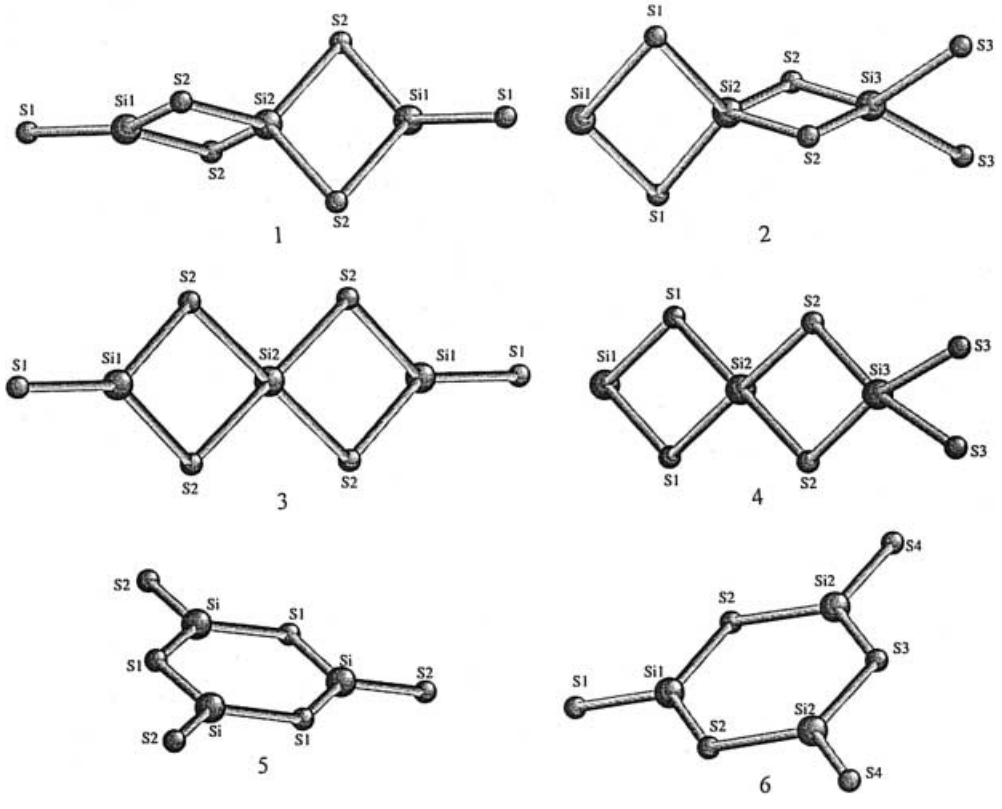

Fig. 3. The geometrical structures of the $(SiS_2)_3$ cluster

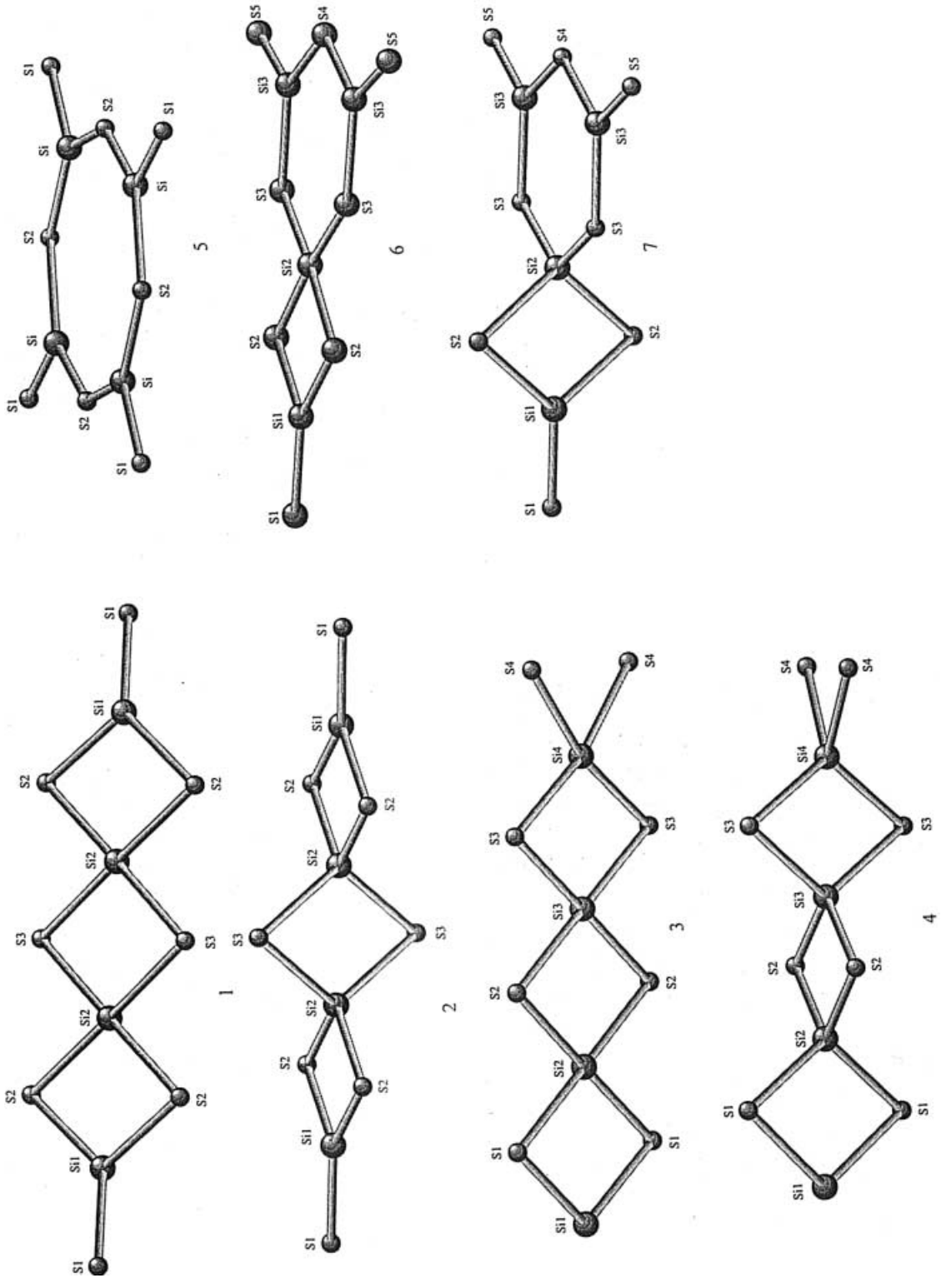

Fig. 4. The geometrical structures of the $(SiS_2)_4$ cluster

$n = 6$, the net charge on $S_{(t)}$ is –0.2117, $Si_{(t)}$ is 0.3510. The net charge distribution in the cluster chain also changes slightly. From the result of the charge distribution, we can conclude that the polarity in $Si_{(t)}$–$S_{(t)}$ is greater than in Si–S between the cluster chain. The $Si_{(t)}$–$S_{(t)}$ bonds change slightly, the length of $Si_{(t)}$–$S_{(t)}$ is from 1.948 to 1.950 Å, and the lengths of $Si_{(t)}$–S decrease monotonically from 2.149 to 2.139 Å with increasing n. From the overlap population, we can predict that the binding between $Si_{(t)}$ and $S_{(t)}$ is nearly twice that of the Si–S among cluster chains.

We present the bond lengths and the Mulliken charges on the equilibrium geometries of $(SiS_2)_n$ (n = 1–

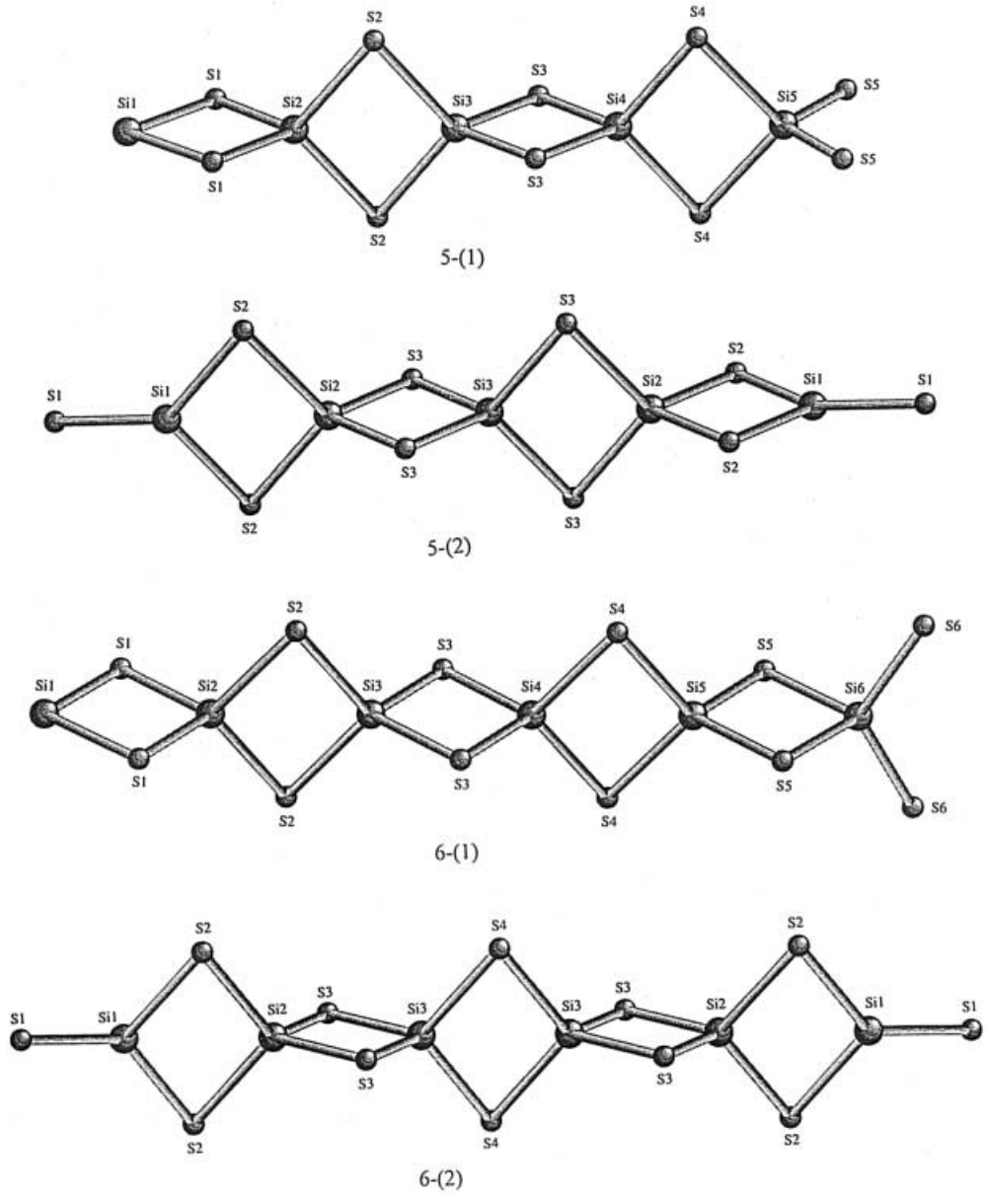

Fig. 5. The geometrical structures of the $(SiS_2)_5$ and $(SiS_2)_6$ clusters

6) clusters with C_{2v} symmetry in Table 2. With the cluster chain growth, the net charge on the top Si_1 atoms changes slightly: on Si_1 it is from 0.3698 to 0.3802 ($n = 2$–6); when $n = 1$–4, the net charges on $Si_{(t)}$ and $S_{(t)}$ change slightly with the cluster chain growth, $Si_{(t)}$ is from 0.3562 to 0.3936, S(t) is from –0.1223 to –0.1292; however, when $n = 5$ or 6, the charges on $Si_{(t)}$ and $S_{(t)}$ change greatly from $n = 1$–4, $Si_{(t)}$ is from 0.0985 to 0.0972 and the charge on the $S_{(t)}$ atoms is from –0.0660 to –0.0646, the charge on the S atoms which bind to $Si_{(t)}$ is from –0.0872 to –0.0854, quite different from the others. We can conclude that the bonds between the $Si_{(t)}$ atoms and S and the $S_{(t)}$ atoms in the $(SiS_2)_5$ and $(SiS_2)_6$ clusters are stronger covalent bonds and that the polarity becomes weaker as the cluster chains grow. The Si_1–S bond lengths change slightly from 2.210 to 2.208 Å, the regularity of the bond change of $Si_{(t)}$–$S_{(t)}$ coincides with the charge. For $n = 2$–4, the $Si_{(t)}$–$S_{(t)}$ bond lengths are from 2.110 to 2.107 Å in $(SiS_2)_5$ and $(SiS_2)_6$ clusters and the $Si_{(t)}$–$S_{(t)}$ bond lengths are 2.072 and 2.073 Å, respectively. The Si–S bond length in the cluster chain changes slightly with increasing n.

We also present total energies, binding energies and average binding energies of $(SiS_2)_n$ ($n = 1$–6) in Tables 1 and 2. The binding energy is defined as

$$E_B = E[(SiS_2)_n] - nE(Si) - 2nE(S),$$

where E is the total energy of the cluster or atom as indicated. The average binding energy is indicated as the binding energy per unit in the different $(SiS_2)_n$ clusters. We plot average binding energy as a function of n (Fig. 6) and as n increases, the average binding energy increases monotonically when the symmetry is D_n ($D_{\infty h}$, D_{2h}, D_{2d}). When the symmetry is C_{2v}, the average binding energy increases while $n = 1$–4, whereas when $n = 5$ and 6, the average binding energy becomes lower

Table 1. Bond length, overlap population, Mulliken charge, total energy (E_T), binding energy (E_B) and average binding energy ($\langle E_B \rangle$) of $(SiS_2)_n$ ($n = 1$–6) with D_n ($D_{\infty h}$, D_{2h}, D_{2d}) symmetry

Structure	Symmetry	State	Bond length/nm	Overlap population	Mulliken charge	E_T/au	E_B/eV	$\langle E_B \rangle$/eV
1–1	$D_{\infty h}$	$^1\sum_g$	Si–S 0.1942	0.5035	Si 0.3961 S –0.1981	−1085.91222	13.49	13.49
2–1	D_{2h}	^1A_g	Si–S1 0.1948 Si–S2 0.2149	0.5884 0.2055	Si 0.3448 S1 –0.1935 S2 –0.1513	−2171.89958	29.02	14.51
3–1	D_{2d}	$^1A_1$	Si1–S1 0.1949 Si1–S2 0.2142 Si2–S2 0.2160	0.5974 0.2133 0.2422	Si1 0.3522 Si2 0.2142 S1 –0.2038 S2 –0.1278	−3257.89644	44.81	14.94
4–2	D_{2h}	^1A_g	Si1–S1 0.1949 Si1–S2 0.2141 Si2–S2 0.2164 Si2–S3 0.2155	0.5976 0.2144 0.2584 0.2457	Si1 0.3509 Si2 0.2462 S1 –0.2080 S2 –0.1337 S3 –0.1217	−4343.89079	60.53	15.13
5–2	D_{2d}	$^1A_1$	Si1–S1 0.1950 Si1–S2 0.2140 Si2–S2 0.2165 Si2–S3 0.2154 Si3–S3 0.2159	0.5976 0.2152 0.2577 0.2466 0.2624	Si1 0.3512 Si2 0.2454 Si3 0.2779 S1 –0.2102 S2 –0.1357 S3 –0.1269	−5429.885176	76.26	15.25
6–2	D_{2h}	^1A_g	Si1–S1 0.1950 Si1–S2 0.2139 Si2–S2 0.2165 Si2–S3 0.2152 Si3–S3 0.2160 Si3–S4 0.2157	0.5975 0.2157 0.2572 0.2477 0.2615 0.2632	Si1 0.3510 Si2 0.2460 Si3 0.2767 S1 –0.2117 S2 –0.1366 S3 –0.1286 S4 –0.1316	−6515.87948	91.98	15.33

than for $n = 4$. From the result, we can infer that the cluster stability increases when $n = 1$–4 and then decreases slightly and then basically remains unchanged.

The relative stability of these clusters can be better understood by calculating the energy gained by adding successive SiS_2 units to the $(SiS_2)_n$ clusters. We define $\Delta E(n)$, the energy gain in adding a SiS_2 monomer to a $(SiS_2)_n$ cluster, as

$$\Delta E(n) = -E(n+1) + E(n),\ n \geq 1.$$

We plot $\Delta E(n)$ as a function of n in Fig. 7. Note that there is a great discrepancy between the D_n and C_{2v} symmetries. When the symmetry is D_n ($D_{\infty h}$, D_{2h}, D_{2d}), the energy changes slightly on adding a SiS_2 to a $(SiS_2)_n$ cluster; however, when the symmetry is C_{2v}, $\Delta E(n)$ also changes slightly, but when $n = 4$, there is a great decrease, which means that the stability of $(SiS_2)_5$ is less than that of the smaller $(SiS_2)_n$ ($n = 1$–4) cluster. The conclusion coincides with the analysis of the average binding energy of $(SiS_2)_n$ clusters.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies and the HOMO–LUMO gap of $(SiS_2)_n$ are shown in Table 3. The HOMO energies are rather low and decrease monotonically, which may indicate that the electron on the HOMO of $(SiS_2)_n$ is not easily lost. The HOMO–LUMO gaps are, in general, unchanged with the size of the clusters, but there is a special case when $n = 5$ and 6 with the symmetry of C_{2v}: the gaps is much less than the others. This may indict that the $(SiS_2)_5$ and $(SiS_2)_6$ clusters are more active in chemical reaction than the other clusters.

The characteristic vibrational modes and vibrational frequencies of the most stable structures of the $(SiS_2)_n$ clusters with C_{2v} symmetry are presented in Table 4. From the analysis of the vibrational spectra of the clusters, the conclusion may be obtained that there are three characteristic vibrational spectral lines and that the more intense IR vibrations are all A_1 symmetry. In the IR vibrational spectra, there are vibration spectral lines at 462–460 cm^{-1}, which are the modes of the Si_1 atom stretching vibration along the molecular axis. The most intense vibrations are the n-1 Si atoms in the cluster chain stretching vibration along the molecular axis, with spectral lines at 581–536 cm^{-1} ($n = 3$–6). There is another intense IR stretching vibration of terminal Si atoms along the molecular axis, with spectral lines at 682–690 cm^{-1} when $n = 2$–4 and at 513 or 512 cm^{-1} when $n = 5$ and 6.

We also present the characteristic vibrational modes and vibrational frequencies of the stable structure of $(SiS_2)_n$ clusters with D_n ($D_{\infty h}$, D_{2h}, D_{2d}) symmetry. There are three characteristic vibrational spectral lines: at 387–436 cm^{-1}, the vibrational mode is the vibration of S atoms perpendicular to the molecular axis; there are vibrations of $Si_{(t)}$ at 767–781 cm^{-1}; and, in general, the most intense vibration is the Si atoms which are in the chain of $(SiS_2)_n$ ($n = 3$–6) clusters is at 583–531 cm^{-1}.

Table 2. Bond length, overlap population, Mulliken charge, E_T, E_B and $\langle E_B \rangle$ of $(SiS_2)_n$ ($n = 1$–6) with C_{2v} symmetry

Structure	Symmetry	State	Bond length/nm	Overlap population	Mulliken charge	E_T/au	E_B/eV	$\langle E_B \rangle$/eV
1—3	C_{2v}	$^1A_1$	Si–S 0.2143	0.1621	Si 0.3552 S –0.1776	−1085.88093	12.64	12.64
2–5	C_{2v}	$^1A_1$	Si1–S1 0.2210 Si2–S1 0.2133 Si2–S2 0.2110	0.1577 0.2645 0.1606	Si1 0.3689 Si2 0.3562 S1 –0.2403 S2 –0.1223	−2171.86371	28.04	14.02
3–2	C_{2v}	$^1A_1$	Si1–S1 0.2208 Si2–S1 0.2143 Si2–S2 0.2166 Si3–S2 0.2142 Si3–S3 0.2108	0.1537 0.2748 0.2236 0.2612 0.2040	Si1 0.3794 Si2 0.2362 Si3 0.3990 S1 –0.2321 S2 –0.1454 S3 –0.1299	−3257.85767	43.76	14.59
4–4	C_{2v}	$^1A_1$	Si1–S1 0.2208 Si2–S1 0.2143 Si2–S2 0.2163 Si3–S2 0.2152 Si3–S3 0.2166 Si4–S3 0.2142 Si4–S4 0.2107	0.1541 0.2841 0.2246 0.2707 0.2564 0.2500 0.2088	Si1 0.3793 Si2 0.2545 Si3 0.2673 Si4 0.3936 S1 –0.2339 S2 –0.1430 S3 –0.1413 S4 –0.1292	−4343.85180	59.47	14.87
5–1	C_{2v}	$^1A_1$	Si1–S1 0.2209 Si2–S1 0.2142 Si2–S2 0.2164 Si3–S2 0.2151 Si3–S3 0.2164 Si4–S3 0.2152 Si4–S4 0.2154 Si5–S4 0.2199 Si5–S5 0.2072	0.1535 0.2847 0.2230 0.2783 0.2563 0.2580 0.2828 0.1629 0.3898	Si1 0.3820 Si2 0.2513 Si3 0.2796 Si4 0.2846 Si5 0.0985 S1 –0.2317 S2 –0.1399 S3 –0.1232 S4 –0.0872 S5 –0.0660	−5429.77090	73.15	14.63
6–1	C_{2v}	$^1A_1$	Si1–S1 0.2208 Si2–S1 0.2143 Si2–S2 0.2163 Si3–S2 0.2152 Si3–S3 0.2162 Si4–S3 0.2153 Si4–S4 0.2162 Si5–S4 0.2153 Si5–S5 0.2153 Si6–S5 0.2198 Si6–S6 0.2073	0.1540 0.2847 0.2240 0.2806 0.2561 0.2664 0.2578 0.2570 0.2835 0.1624 0.3900	Si1 0.3804 Si2 0.2537 Si3 0.2836 Si4 0.2708 Si5 0.2852 Si6 0.0972 S1 –0.2337 S2 –0.1430 S3 –0.1359 S4 –0.1229 S5 –0.0854 S6 –0.0646	−6515.76510	88.87	14.81

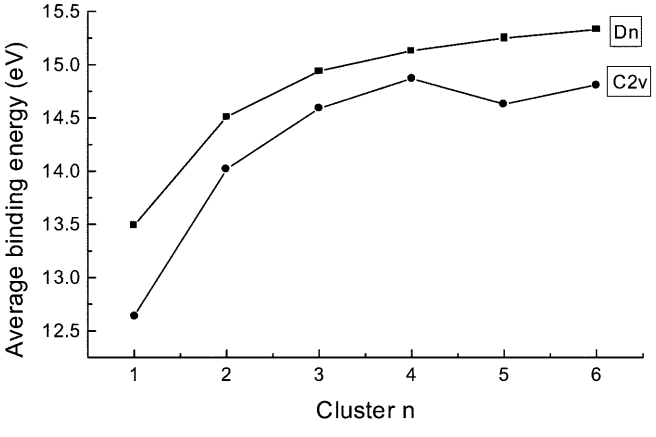

Fig. 6. Plot of average binding energy as a function of the cluster size (n)

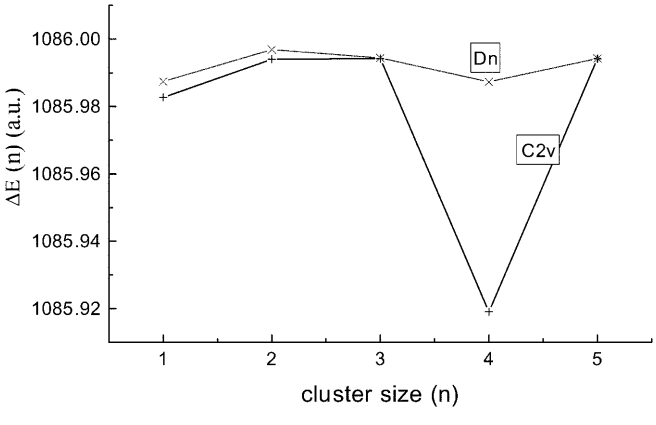

Fig. 7. Plot energy difference, $\Delta E(n)$, as a function of the cluster size (n)

Table 3. The energy of the highest occupied molecular orbital (*HOMO*) and the lowest unoccupied molecular orbital (*LUMO*) and the HOMO–LUMO energy gap (E_G)of $(SiS_2)_n$ clusters

Cluster	C_{2v}			D_n ($D_{\infty h}$, D_{2h}, D_{2d})		
	HOMO/eV	LUMO/eV	E_G/eV	HOMO/eV	LUMO/eV	E_G/eV
1	−6.36 (a_2)	−2.95 (b_1)	3.41	−7.82 (π_g)	−2.72 (σ_g)	5.10
2	−6.46 (a_2)	−3.23 (b_1)	3.23	−7.46 (b_{3g})	−3.02 (b_{2g})	5.44
3	−6.52 (a_2)	−3.22 (b_1)	3.30	−7.53 (e)	−2.62 (a_1)	4.91
4	−6.56 (a_2)	−3.21 (b_1)	3.35	−7.44 (b_{2u})	−2.61 (a_g)	4.83
5	−6.99 (b_2)	−6.35 (a_2)	0.64	−7.45 (e)	−2.39 (b_2)	5.06
6	−7.01 (b_1)	−6.37 (a_2)	0.64	−7.42 (b_{1g})	−2.57 (b_{3u})	4.85

Table 4. The characteristic vibrational mode of $(SiS_2)_n$ ($n = 1$–6) clusters

n	C_{2v}			D_n ($D_{\infty h}$, D_{2h}, D_{2d})		
1	593/48 (a_1)			90/158 (σ_u)		
2	462/73 (a_1)	682/192 (a_1)		387/47 (b_{1u})	598/93 (b_{2u})	767/417 (b_{1u})
3	462/138 (a_1)	581/379 (a_1)	689/169 (a_1)	426/87 (b_2)	583/433 (b_2)	780/401 (b_2)
4	461/201 (a_1)	558/830 (a_1)	690/172 (a_1)	433/113 (b_{3u})	557/949 (b_{3u})	780/421 (b_{2u})
5	460/304 (a_1)	546/946 (a_1)	513/138 (a_1)	435/141 (b_2)	542/1531 (b_2)	780/430 (b_2)
6	460/368 (a_1)	536/1449 (a_1)	512/299 (a_1)	436/170 (b_{3u})	531/2169 (b_{3u})	781/436 (b_{3u})

5 Conclusions

In summary, we have calculated the equilibrium geometries, energies and electronic structures and vibrational spectra of $(SiS_2)_n$ ($n = 1$–6) clusters using density function theory (DFT/B3LYP). The results calculated suggest two methods of $(SiS_2)_n$ cluster formation, i.e. along D_n ($D_{\infty h}$, D_{2h}, D_{2d}) and C_{2v} symmetries. From the analysis of the total energy and the HOMO–LUMO properties, the stabilities of the $(SiS_2)_n$ clusters are revealed. We also calculated the vibrational spectra of $(SiS_2)_n$ clusters and predicted that the most intense characteristic IR absorption should be the stretching vibration of Si atoms along the molecular chain.

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