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Structures and electronic properties of $Si_mN_{8-m}(0 < m < 8)$ clusters: a density functional theory study*

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The geometries, electronic structures and related properties of $Si_mN_{8-m}(0 < m < 8)$ clusters are studied using density functional theory (DFT) with hybrid functional B3LYP. The calculated results reveal several trends. For any stoichiometric clusters, the lowest energy isomers with an alteration of N and Si atoms are favourable in energy if the numbers of Si and N atoms are large enough to form ...Si–N–Si–N... alternative chains. The bond lengths of single Si–N bonds are very close to the corresponding values of the bulk and other Si–N clusters. The geometries for N-rich and Si_4N_4 clusters are planar structures, but three-dimensional structures are favourable in energy for Si-rich clusters. With the increase of m, the isotropic polarizability and average polarizability increase, the total binding energies generally decrease, the HOMO-LUMO gap and vertical ionization potential oscillate with increasing number of valence electrons, and their values with even valence electrons are larger than those with odd valence electrons. The atomic charges, IR and Raman properties are also reported.

Keywords: cluster, structure and properties, density functional theory, silicon nitride
PACC: 3640B, 3640C, 7125W

1. Introduction

The chemical and physical properties of a cluster are different from those of the component atoms/molecules or of the extended bulk materials. The size-dependent evolution of the structures and properties of clusters is an extremely active area of researches due to their importance in applied technology.[1−3] Furthermore, from a more fundamental perspective, it is interesting to study the character of phenomenon and the nature of compound clusters, to determine how the geometry, electronic structure, bonding and relative stability of clusters are affected by their size and stoichiometry.[4−7] Silicon nitride Si_3N_4 is an advanced material that has the potential to be used in various applications because of its good performance of mechanical, chemical, electrical and thermal properties.[8,9] Until now, however, the existing research works of Si–N clusters are very limited. Goldberg *et al* studied neutral, anionic and cationic Si_3N via collision experiments and high-level *ab initio* calculations.[10] Ornellas *et al* studied SiN_2,[11] Si_2N[12] and Si_2N_2[13] by means of high level *ab initio* calculations (MP2, MP4, CCSD (T)). Jackson *et al* presented a computational study of the structures, thermodynamic and chemical stabilities of Si_nN_m $(n + m = 20, m = 2, 4, 6, 8)$ clusters.[14] Jungnickel *et al*[15] reported a detailed study of the structures and energetics of Si_nN_m clusters with $n+m \leq 6$. Their calculations revealed that the linear or quasi-linear structures are predominant for N-rich clusters with strong multiple-bond character, and the Si-rich clusters favour planar or three-dimensional structures. Moreover, the possible growth pathways for the clusters were also discussed.[15] The structures and properties of Si_6N_8 and Si_3N_4 clusters were investigated by using density functional theory (DFT) in our previous work.[16,17] The results show that the three-dimensional structures of Si_6N_8 and Si_3N_4 clusters are favourable in energy, though they are all N-rich clusters, this geometrical character is different from the smaller Si_nN_m clusters $(n + m \leq 6)$ in Ref.[15].

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This induces several questions as follows: Are the planar and linear structures becoming less stable than the three-dimensional systems with increasing cluster size? What is the difference of structures and properties between the N-rich and Si-rich larger clusters (the number of atoms in the cluster is larger than 6)? How does the stoichiometry influence the geometry, electronic structure and related properties of Si-N clusters? By raising these questions, the main objective of this work is to address these questions at the level of DFT and thus to try to provide answers that can help to establish the structural parameters, and investigate electronic structures, as well as the related properties of Si_mN_{8-m} $(0 < m < 8)$ clusters.

2. Computational Methods

In the present study, the first step was using an unbiased genetic algorithm (GA) method to extensively search for and explore the potential energy surface (PES) of Si_mN_{8-m} $(0 < m < 8)$ clusters. In this procedure, the semi-empirical quantum chemical method PM3 Hamiltonian (PM3 is a modified neglect of diatomic overlap (MNDO) parametric method 3) was used to calculate the total energy of each structure. Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was applied to optimize the structure to the closest local minimum of PES. The PM3 parameters of N and Si were adopted from Ref.[18]. The details and reliability of GA combined semi-empirical quantum chemical calculations have been described in our earlier publication.[16] In addition, a number of candidate structures of Si_mN_{8-m} $(0 < m < 8)$ clusters were constructed in terms of chemical intuition in order to extend the searching range of possible isomers, in this course, the bonding topologies and distinct decorations of each topology with nitrogen and silicon atoms were systematically considered. Then the structures from the first step of searching and constructing process were further optimized using DFT method. The DFT was treated according to Becke's three-parameter gradient-corrected exchange potential and the Lee-Yang-Parr gradient-corrected correlation potential (B3LYP).[19−21] The symmetry was not constrained in DFT calculations. The basis sets were 6-31G(d) except for the computations of polarizability and hyperpolarizability. All the DFT calculations were performed using the Gaussian 03 package. Finally, the electronic structures and related properties were also calculated.

3. Results and discussions

3.1. The geometrical structures

The optimized geometries for Si_mN_{8-m} $(0 < m < 8)$ clusters are shown in Figs.1–7 with different serial numbers and relative energies, and the related geometrical parameters of the most stable isomers are listed in supplementary materials (the hindmost part of the article). The bond lengths of N–N, Si–N and Si–Si bonds for the most stable isomers of Si_mN_{8-m} $(0 < m < 8)$ clusters are listed in Table 1.

Table 1. The bond lengths of N–N, Si–N and Si–Si bonds in the most stable isomers of Si_mN_{8-m} $(0 < m < 8)$ clusters (in nm). (B3LYP/6-31G(d)).

clusters	N-N	Si-N	Si-Si
SiN_7	0.113−0.136	0.186−0.189	
Si_2N_6	0.129−0.137	0.159−0.188	
Si_3N_5	0.122−0.129	0.158-0.196	
Si_4N_4		0.158−0.171	0.218
Si_5N_3		0.169−0.189	
Si_6N_2		0.158−0.171	0.228−0.235
Si_7N		0.159−0.170	0.237−0.277

The five optimized possible isomers of SiN_7 clusters are shown in Fig.1. Isomers 1–4 are all planar structures. The lowest energy structure is isomer 1 that can be formed from the ground state N_5 planar ring bonded to the ground state SiN_2 chain (the ground state structures of Si_nN_m clusters with $n + m \leq 6$ were given in Ref.[15]). According to the reference values of bond lengths for conventional single and multiple bonds,[13] the average bond lengths of N_5 ring in isomer 1 is intermediate in length between the conventional single and double bonds, and the Si-N bonds are of single bond character. Isomers 2 and 5 could be composed of the ground state of N_3 chains and SiN dimer, but the atomic configuration is different from those of the two isomers. Isomer 5 is a three-dimensional structure, and has the highest energy among these isomers. Isomers 3 and 4 could be viewed as two pentagons with different atomic arrangements, and the Si atom is located at a corner of the pentagon. The calculated relative energies suggest that the isomer 1 with a N_5 pentagon is more stable than isomers 3 and 5 with double pentagons. This may result in a tensile force for bond bending.

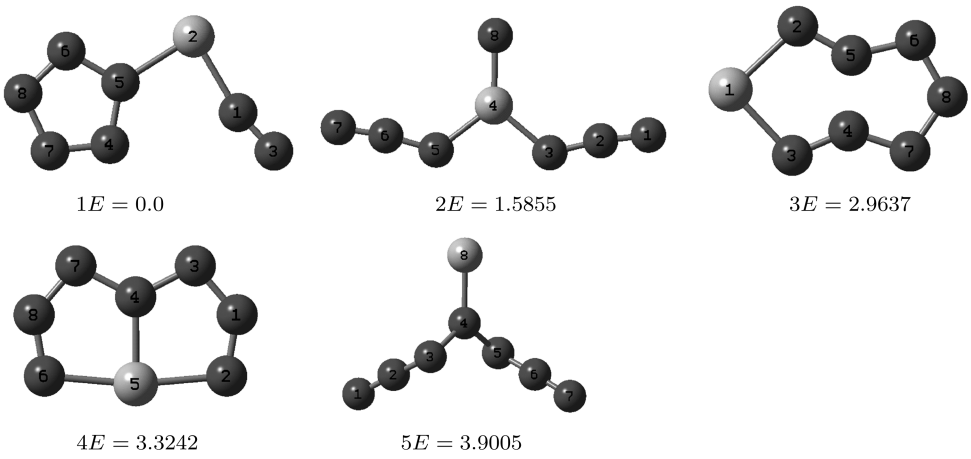


Fig.1. Optimized geometrical structures and relative energies ($E = E_i - E_1$, in eV) of five possible isomers of SiN_7 clusters with lower energies. (The larger light coloured spheres: Si atoms; the smaller dark coloured spheres: N atoms).

The seven optimized possible isomers of Si_2N_6 clusters are shown in Fig.2. Isomers 1–7 are all planar structures. The lowest energy structure of Si_2N_6 clusters is isomer 1, composed of the ground state N_5 ring and the ground state Si_2N chain, the bonds of N_5 ring are very similar to that in isomer 1 of SiN_7 cluster, but the bond N1-Si3 has a double-bond character, and the bonds Si2-N1 and Si2-N5 are single bonds. Isomers 2 and 4 could be composed of two pentagons with different atomic configurations. Isomer 3 could be formed by two ground state SiN_3 chains. Isomer 5 could consist of Si_2 cluster and two ground state N_3 chains. Other isomers have higher energies. It is worthwhile to note that isomer 1 with a N_5 pentagon is more stable than that with double pentagons. This trend is similar to that in SiN_7 clusters.

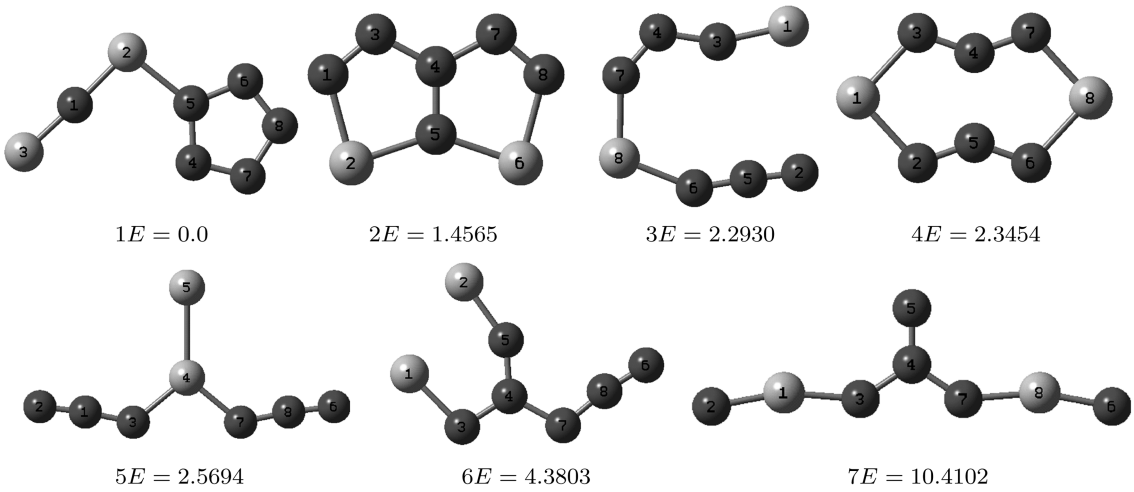


Fig.2. Optimized geometrical structures and relative energies ($E = E_i - E_1$, in eV) of seven possible isomers of Si_2N_6 clusters with lower energies. (The larger light coloured spheres: Si atoms; the smaller dark coloured spheres: N atoms).

The eight optimized possible isomers of Si_3N_5 clusters are shown in Fig.3. The lowest energy structure of Si_3N_5 clusters is isomer 1, a planar structure that is the component of the ground state of Si_2N_4 and SiN clusters. Isomer 2 has a structure very similar to that of isomer 1, but the binding fashion between the Si_2N_4 cluster and SiN is different from that of isomer 1. Isomer 3 is a three-dimensional structure, with N6 and N8 located symmetrically on the two sides of the plane which is formed by Si1–N4–Si2–Si3–N5–N7. Isomer 4 is a planar structure with a pentagon unit, while isomer 5 is also a planar structure but with double pentagons. The energies of other isomers are higher. From the geometry and relative energy of Si_3N_5 isomers, it is suggested that the order of stability is as follows: isomer with a hexagon, isomer with a pentagon, isomer with double pentagons, secund distribution of Si and N in isomers, and isomer with a quadrangle.

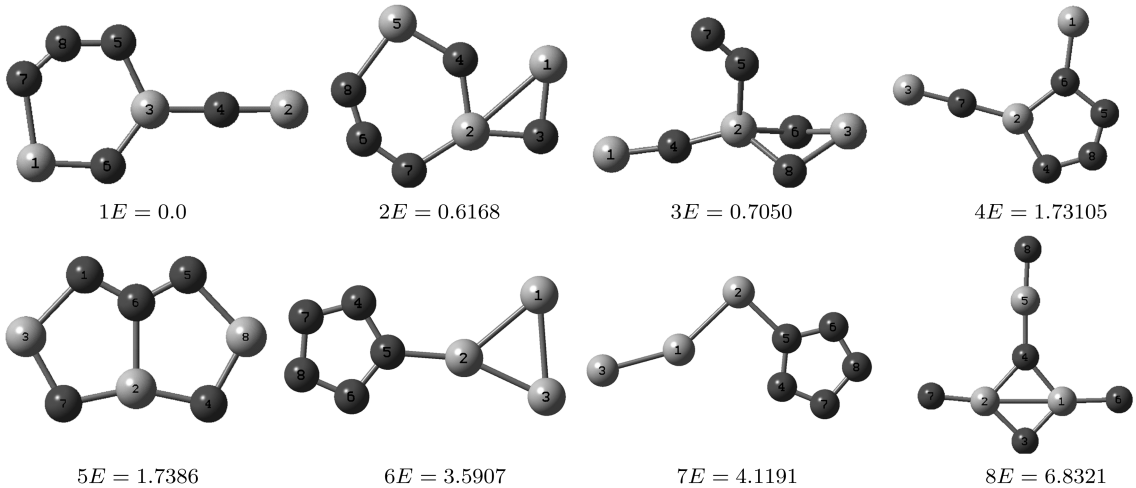


Fig.3. Optimized geometrical structures and relative energies ($E = E_i - E_1$, in eV) of eight possible isomers of Si_3N_5 clusters with lower energies. (The larger light coloured spheres: Si atoms; the smaller dark coloured spheres: N atoms).

The seventeen optimized isomers of Si_4N_4 clusters are shown in Fig.4, in which the lowest energy structure of Si_4N_4 clusters is isomer 1, a planar structure which can be viewed as a Si_2N_2 quadrangle-bonded to two SiN dimers. Isomer 2 is a planar structure that could be formed by a Si_3N_3 and a SiN. Isomers 3–6 can be viewed as the ground state Si_3N_3 bonded to a SiN unit at different positions. Isomers 1–5, 7, 10, 13 and 16 are all planar structures and other isomers are all three-dimensional structures. According to the relative energy and geometry of the isomers, we can find that the isomers with alteration of N and Si atoms are favourable in energy.

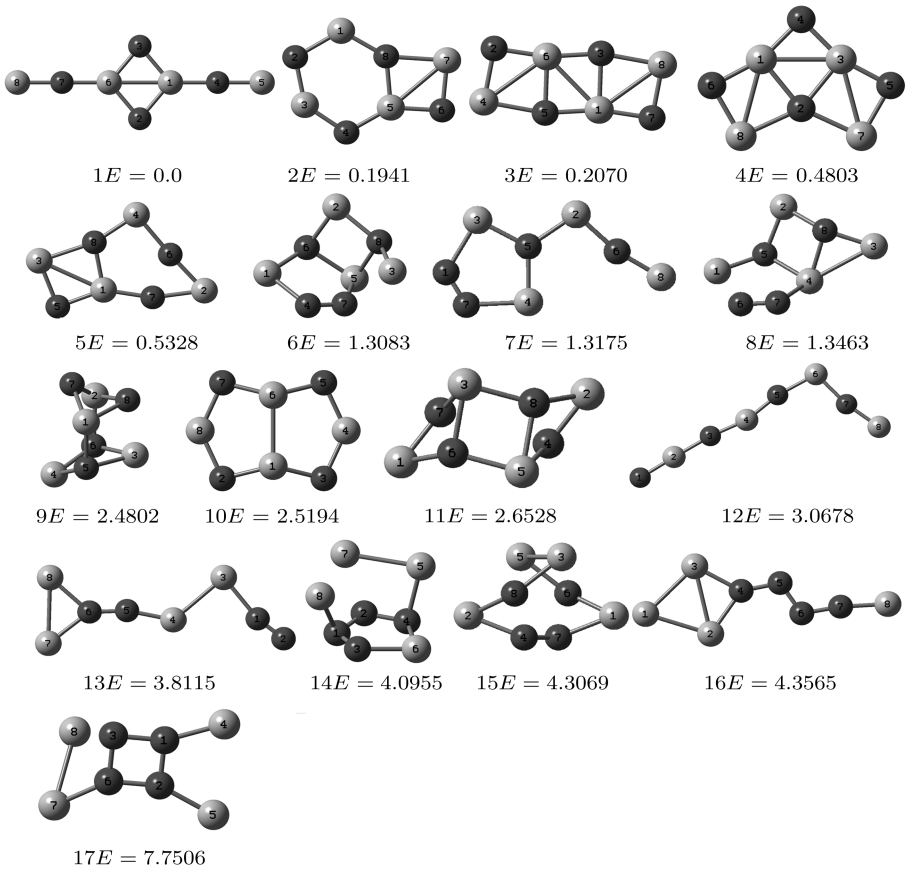


Fig.4. Optimized geometrical structures and relative energies ($E = E_i - E_1$, in eV) of seventeen possible isomers of Si_4N_4 clusters with lower energies. (The larger light coloured spheres: Si atoms; the smaller dark coloured spheres: N atoms).

The eight optimized isomers of Si_5N_3 clusters are plotted in Fig.5. The lowest energy structure of Si_5N_3 clusters is isomer 1, a boat-like structure which could be viewed as the ground state Si_3N_3 cluster bonded to two Si atoms through two strong Si-N bonds. Isomer 2 is a planar structure consisting of the ground state Si_3N_2 and Si_2N chains. Isomer 3 could be composed of a SiN and two Si_2N chains. Isomer 4 is a planar structure that could be formed by the ground state Si_3N cluster and two SiN dimers. Isomer 5 is a cube-like structure and isomers 6–8 are all three-dimensional structures with higher energies. The geometries and relative energies indicate that the isomers with alternation of Si and N atoms are favourable in energy.

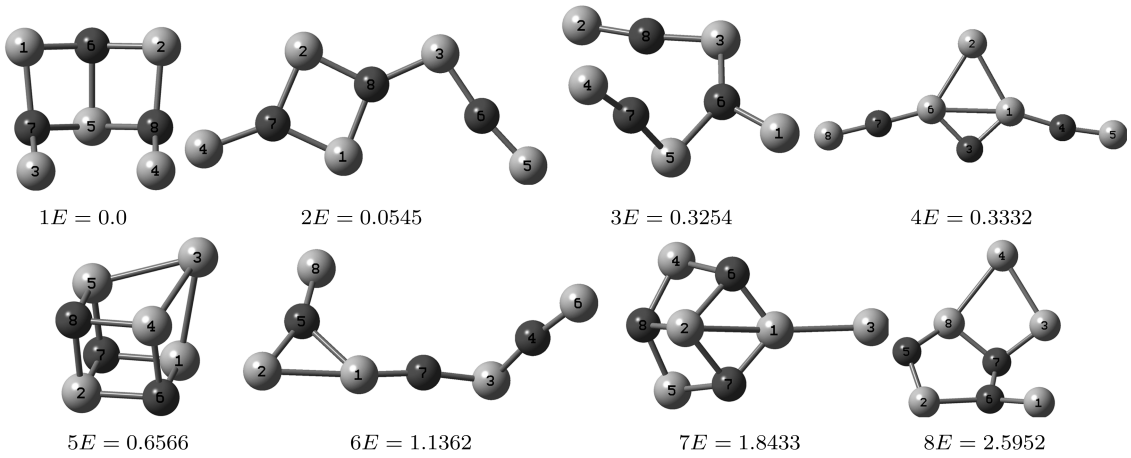


Fig.5. Optimized geometrical structures and relative energies ($E = E_i - E_1$, in eV) of eight possible isomers of Si_5N_3 clusters with lower energies. (The larger light coloured spheres: Si atoms; the smaller dark coloured spheres: N atoms).

The sixteen optimized isomers of Si_6N_2 clusters are shown in Fig.6. The lowest energy structure of Si_6N_2 clusters is isomer 1, which could be formed by two SiN units and the ground state of Si_4 cluster.[22]

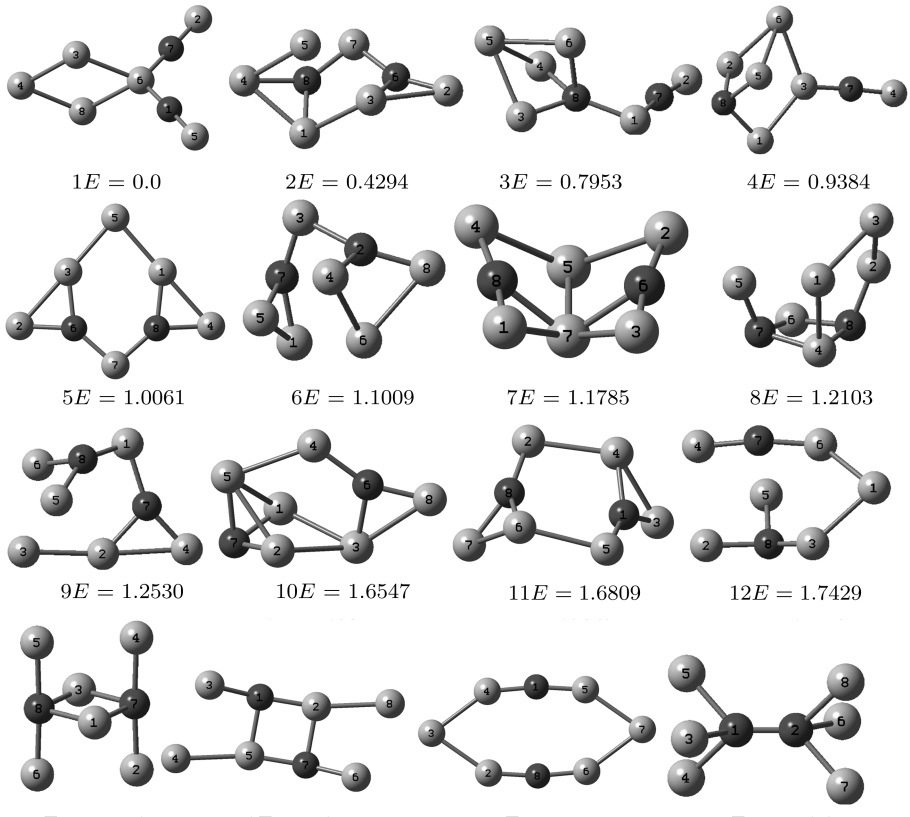


Fig.6. Optimized geometrical structures and relative energies ($E = E_i - E_1$, in eV) of sixteen possible isomers of Si_6N_2 clusters with lower energies. (The larger light coloured spheres: Si atoms; the smaller dark coloured spheres: N atoms).

In this isomer, N coordinated with Si at bridge site and the bonds of Si6 is saturated because the coordination number of this atom is 4. Isomer 2 is a three-dimensional structure. Isomer 3 could be constructed by the ground state Si_4N cluster and a Si_2N chain. In isomer 4, the positions of Si2 and Si3 are equivalent in symmetry. Isomers 5 and 7 are all butterfly-like structures. Isomers 6, 8–12 are all disordered structures without distinct geometrical character. In isomer 13, the coordination number of N is 4, the bond lengths of Si–N in rhombus are about 0.191 nm, and that of others are about 0.185 nm. Though the number of Si–N bonds and Si–Si bonds in isomer 15 is the same as that of isomer 1, the energy of isomer 15 is higher because the planar structure is not favourable in energy for Si–Si bond. The structure of isomer 16 is similar to ethane, and the energy of this isomer is higher than others for its higher symmetry and the N–N bond; this also reveals that N–N bond is not favourable in Si-rich clusters.

The six optimized isomers of Si_7N clusters are shown in Fig.7, of which the lowest energy structure is isomer 1. The ground state of Si_5 is a trigonal bipyramid.[22] Isomers 1–3 could be formed by the ground state of Si_5 cluster bonded to Si_2N chain at different sites. In isomer 1, the positions of Si6 and Si8 are equivalent in symmetry. Isomer 4 is a spade-like structure. Isomer 5 is a three-dimensional structure and isomer 6 is a pyramid-like structure. From the geometry of these isomers, we can find that the isomers, in which Si atoms are close-packed and the coordination number of N is 2, are favourable in energy, but the energy of the isomers in which N atom is coordinated with three Si atoms are higher.

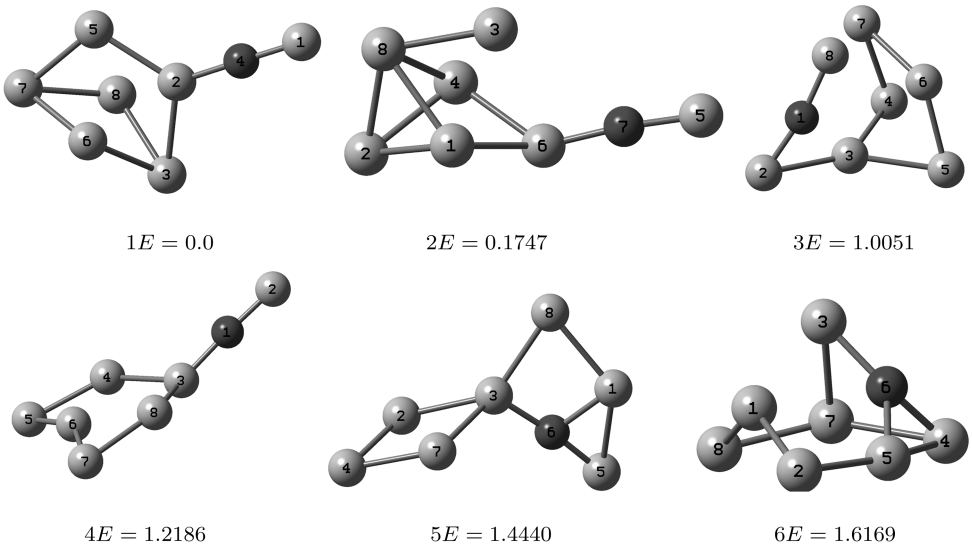


Fig.7. Optimized geometrical structures and relative energies ($E = E_i - E_1$, in eV) of six possible isomers of Si_7N clusters with lower energies. (The larger light coloured spheres: Si atoms; the smaller dark coloured spheres: N atoms).

Based on the above analyses of Si_mN_{8-m} $(0 < m < 8)$ clusters, the major geometrical tendencies for the lowest energy isomers are summarized as follows:

For any stoichiometric Si_mN_{8-m} $(0 < m < 8)$ clusters, the isomers with the alteration of N and Si atoms are favourable in energy if the number of Si and N atoms are large enough to form ... Si–N–Si–N ... alternating chain. This character of atomic configuration also appears in Si_nN_m $(n + m = 20, m = 2, 4, 6, 8)$[7] and $Si_nN_m(n + m \leq 6)$[15] clusters. The bond lengths of single Si–N bonds are very close to those of the bulk[23] and other Si–N clusters in Refs.[13–15].

The geometry of the lowest energy isomers for Si_nN_m clusters with $m \geq 4$ are planar structures, which are different from the N-rich $Si_nN_m(n + m \leq 6)$[15] clusters, in which linear or quasi-linear structures dominate, whereas there is a ring-like structure unit such as pentagon, hexagon in the N-rich clusters. The ground state structures of N_5 and Si_2N_4 clusters are pentagon and hexagon respectively,[15] and the isomers of small nitrogen clusters also have ring-

like structure unit N_5.[24−28] So at this point we can compare N-rich Si–N clusters with small nitrogen clusters.

For Si-rich clusters, three-dimensional structures are favourable in energy, Si atoms are tending to be close-packed, and one N atom is coordinated with two Si atoms at bridge site except that in the lowest energy isomer of Si_5N_3 cluster. The peculiarity of Si_5N_3 cluster could be understood from two aspects: first, the number of atoms in Si_5N_3 cluster is large enough to saturate the bonds of N; second, because there are lone pair electrons on N atoms, the geometry of Si_5N_3 cluster is favourable in a three-dimensional structure with single bond character. Moreover, the energy of Si–N bonds is more favourable in these isomers than that of N–N bonds, so that N atoms tend to be separated from each other to maximize the number of Si–N bonds. The atomic arrangement and Si–N bonds distribution are very similar to that of other Si-rich Si–N clusters.[14,15]

3.2. Charges and bonds properties

Natural Bond Orbital (NBO) theory was used to analyse the charge populations and bond properties. The atomic natural charges in order of atomic serial numbers are listed in supplementary materials (the hindmost part of the article). The results show that the electrons are transferred from Si to N, and that the closer the numbers of Si and N atoms in the cluster, the larger the charges transferred, and the larger the average value of atomic net charges, so the atomic interactions of N–Si bonds are of strong ionic bonding. Since the electronegativities of Si and N are very different, the Si–N bonds are polar bonds. For this reason, an alternating Si–N atomic arrangement is favourable in energy.

Analysing the hybridization of molecular orbitals can help us to understand the properties of chemical bonds in a system. In fact, structure, bonds and hybridizations of molecular orbitals may affect and restrict each other, so that different structures have different bonds and hybridizations. It is worth to note that the traditional orbital hybridization is associated with the atom, but in NBO theory, the natural hybridization is corresponding to orbitals. A good reference about natural hybrid orbitals is the work of Foster and Wienhold.[29] The bond properties of Si_4N_4 cluster (as an example of Si_mN_{8-m} $(0 < m < 8)$ clusters) are analysed as follows:

For the lowest energy isomer of Si_4N_4, the hybridization of Si1–N2, Si1–N3, Si6–N2 and Si6–N3 bonds is $sp^{1.79}$ for Si and $sp^{3.27}$ for N. The hybridization of Si1–N4 and Si6–N7 is $sp^{2.32}$ for Si and $sp^{1.12}$ for N. There are three bond orbitals in N4–Si5 and N7–Si8 bonds, two of which are formed by p orbital of Si and N atoms, and the hybridization of other orbitals is $sp^{0.89}$ for N and $sp^{5.73}$ for Si. There exist lone pair electrons in Si1, N2, N3, Si5, Si6 and Si8 atoms. These hybridized models ensure the atomic orbitals of Si and N overlapped well, and we can conclude that this structure is the most stable isomer in Si_4N_4 clusters. This may also be confirmed by binding energy and average Si–N bond length of isomer 1. The total bond number of isomer 1 for Si_4N_4 cluster is not the maximum of the isomers mentioned above, but for isomer 1, the binding energy is the largest and the average Si–N bond length is the shortest. The results also show that the same atom in different bonds has different hybridizations, for example, the hybridization of N2 in N2–Si1 bond is $sp^{3.27}$, and that in its lone pair orbital is $sp^{0.89}$.

3.3. IR and Raman frequencies

The vibrational frequencies calculations and normal mode analysis were performed with the lowest energy isomers of Si_mN_{8-m} $(0 < m < 8)$ clusters in order to confirm that they are true minima on the cluster potential energy surface (PES) and to study the IR and Raman properties. The frequencies, IR intensities and Raman activities are listed in supplementary materials (the hindmost part of the article). Calculated results show that there is no imaginary frequency, implying that the structures are located at minimum position of PES.

Based on the analysis of vibrational properties, the strongest IR and Raman vibrational frequencies is independent of the stoichiometry of Si_mN_{8-m} $(0 < m < 8)$ clusters. The vibrational modes of the strongest IR and Raman peaks correspond to the stretch movement of Si–N bonds except that of SiN_7 and Si_4N_4 clusters. The vibrational frequency of the strongest IR absorption of Si_5N_3 cluster is lower than that of other clusters. This may be attributed to the average Si–N bond energy in Si_5N_3 cluster, where N atoms are three-coordinated with Si, and this average bond energy is less than that in other isomers with N atoms coordinated with two Si atoms.

3.4. Polarizabilities and hyperpolarizabilities

Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field.[30] They determine not only the strength of molecular interactions (such as the long-range intermolecular induction, dispersion forces, etc.) as well as the cross-sections of different scattering and collision processes,[31,32] but also the nonlinear optical properties of the system.[33−36]

In principle, one should use a large sized basis sets for the calculation of the polarizability and hyperpolarizability in order to describe the polarized effects. However, the use of such a basis set for these clusters is very expensive. Furthermore, our aim is to study the evolution of the polarizabilities with cluster stoichiometry, rather than to evaluate the quantities accurately. So we have used the 6-31+G(d) basis sets to calculate polarizabilities and hyperpolarizabities for the 6-31G(d) geometries. The definitions of the isotropic polarizability, the polarizability anisotropy invariant and the average hyperpolarizability were presented in Refs.[31,32].

The values of the polarizabilities and hyperpolarizabilities of Si_mN_{8-m} $(0 < m < 8)$ clusters are listed in supplementary materials (the hindmost part of the article). In addition to the individual tensor components of the polarizabilities and the hyperpolarizabilities, the calculated isotropic polarizability, average polarizability, polarizability anisotropy invariant and hyperpolarizability are α = 84.9378, 89.4878, 124.7595, 138.7192, 180.3487, 220.1279, 239.0337; α/n = 10.6172, 11.1860, 15.5949, 17.3399, 22.5436, 27.5160, 29.8792; $\Delta\alpha$ = 55.0354, 66.0438, 97.6594, 146.3094, 56.2112, 86.2673, 125.9472 and $\beta_{||} = -1.9727$, 6.5769, 238.8090, –0.2407, –995.0883, –105.8167, 0.0871, with the increase of m respectively, with all the values given in atomic units.

The calculated results show that isotropic polarizability α and average polarizability α/n of Si_mN_{8-m} $(0 < m < 8)$ clusters increase with increasing m. This may be achieved as follows: the interaction of N–N and Si–Si bonds are strong covalent interactions, and the average charges per atom transferred from Si to N increase with the increase of m until $m = 4$; the bond properties show mixed character, so the localization of bonds are weakened and delocalization of bonds are enhanced.

The polarizability anisotropy invariant $\Delta\alpha$ of clusters is determined in two aspects. One approach is to use the bond properties; and the other involves the distribution of atoms and bonds in the cluster. The $\Delta\alpha$ of Si_mN_{8-m} $(0 < m < 8)$ clusters increases with increasing m for m from 1 to 4, and the geometries of the Si_mN_{8-m} $(0 < m < 5)$ clusters are all planar structure, reflecting the bond properties of clusters. For Si_mN_{8-m} $(0 < m < 8)$ clusters $\Delta\alpha$ decreases abruptly at m between 4 and 5, and at this point the clusters geometry changes from planar to three-dimensional, so the isotropic degree of atoms and the bonds distribution are increased. Then, with increasing m from 5 to 8, the number of Si–Si bonds increases, because Si atoms are more polarizable than N atoms, and as a result $\Delta\alpha$ of Si_mN_{8-m} clusters increases.

3.5. Thermodynamic stability and electronic dynamic stability

The total energies, total binding energies (TBEs), HOMO-LUMO gap and vertical ionization potential (VIP) of Si_mN_{8-m} $(0 < m < 8)$ clusters are listed in Table 2. The TBEs of Si_mN_{8-m} $(0 < m < 8)$ clusters generally decrease with increasing m, but increase slightly at $m = 4$. The trend of TBE change is very similar to that of isotropic polarizability α and average polarizability α/n. This change also can reflect the number and strength of bonds in clusters, whereas the HOMO–LUMO gap and VIP of Si_mN_{8-m} $(0 < m < 8)$ clusters show oscillating character with increasing m, and the values of these quantities for odd m are smaller than that for even m. The oscillation of HOMO-LUMO gap and VIP is similar to the change of valence electrons in clusters.

The oscillation of HOMO–LUMO gap and VIP was also described in many experimental and theoretical results of alkali and noble metal clusters.[32] In order to interpret the oscillation of HOMO-LUMO gap and VIP, the jellium model, ellipsoidal shell model and mean effective coordination number model etc. were proposed.[37] But these models are not appropriate to describe those clusters with highly localized bonds. The oscillations of VIP and HOMO-LUMO gap in different clusters may result from the same cause because the VIP as well as HOMO-LUMO gap of a cluster is related to an excited procedure of a quantum many-body system (electrons and nucleus). This oscillation may be brought about by the effects of closing the electronic shell, which implies that it is more difficult to

remove or excite an electron from a closed-shell system than from an open-shell system.[5,14,38] The VIP and HOMO–LUMO gap may be also affected by electron–phonon coupling (EPC) though it is not included in the present theoretical background.

Usually, the TBE, average polarizability α/n, HOMO-LUMO gap and VIP are used to describe the relative stability of clusters. But from the calculated data, the trend of TBE change versus stoichiometry (N atoms in the clusters) is different from that of HOMO-LUMO gap and VIP, and this difference is also revealed in Ga-P clusters.[3] So it is necessary to distinguish two kinds of stability in order to investigate the details of the relative stability of clusters. The first is the thermaldynamic stability related with dissociation processes, and it could be described by TBE. The other is the electronic dynamic stability related to the dynamic process such as excitation etc., and it could be described by HOMO-LUMO gap and VIP. According to the above analysis, SiN_7 cluster has the highest thermaldynamic stability, and Si_2N_6 cluster has the highest dynamic stability.

Table 2. The total energies E_t, total binding energies E_{bt}, HOMO-LUMO gap and VIP of Si_mN_{8-m} $(0 < m < 8)$ clusters ($E_{bt} = E_t - m \cdot E_{Si} - (8-m) \cdot E_N$).

cluster	E_t/a.u.	E_t/a.u. (including ZPE*)	E_{bt}/eV (including ZPE*)	HOMO-LUMO gap/eV	VIP/eV (including ZPE*)
SiN_7	–672.6345	–672.6035	31.0308	2.2803	7.5873
Si_2N_6	–907.4173	–907.3879	30.9536	3.8169	8.5164
Si_3N_5	–1142.1891	–1142.1646	30.6650	2.2615	6.5660
Si_4N_4	–1376.9762	–1376.9541	30.7258	2.4868	6.5797
Si_5N_3	–1611.7219	–1611.7034	29.6941	1.7410	6.3076
Si_6N_2	–1846.4572	–1846.4404	28.3256	3.4885	7.7091
Si_7N	–2081.1576	–2081.1436	26.0391	1.5736	6.5363

*ZPE is zero point energy.

4. Conclusions

In this paper, a systematic DFT study has been performed on the geometries, electronic structures and related properties of Si_mN_{8-m} $(0 < m < 8)$ clusters. The results can be summarized as follows:

(1) The alteration of N and Si atoms in the lowest energy isomers for different stoichiometries of Si_mN_{8-m} $(0 < m < 8)$ clusters is favourable in energy if the number of Si and N atoms is large enough to form ... Si–N–Si–N ... chains, and all the bond lengths of single Si–N bonds are very close to those of the bulk and other Si–N clusters. The geometrical trends of the lowest energy isomers for N-rich and Si_4N_4 clusters are planar structures. Three-dimensional structures are favourable in energy for Si-rich clusters, Si atoms tend to be close-packed, and one N atom is coordinated with two Si atoms at bridge site except that in the lowest energy isomer of Si_5N_3 cluster. Moreover, the energy of Si–N bonds is more favourable in these isomers than that of N–N bonds, so that N atoms tend to be separated from each other to maximize the number of Si–N bonds.

(2) The NBO charges suggest that the atomic interaction in Si–N bonds is of strongly ionic bonding.

(3) The strongest IR and Raman vibrational frequencies is independent of the stoichiometry of Si_mN_{8-m} $(0 < m < 8)$ clusters.

(4) With increasing m, the total binding energies of Si_mN_{8-m} $(0 < m < 8)$ clusters generally decrease, but increase slightly at $m = 4$; also the isotropic polarizability α and average polarizability α/n increase. The HOMO–LUMO gap and VIP oscillate with increasing number of valence electrons, and the values of them with odd valence electrons are smaller than that with even valence electrons.

(5) The necessity for distinguishing the thermaldynamic stability and the electronic dynamic stability are proposed, and the possible criterions for describing these two kinds of stabilities may be the total binding energy, HOMO–LUMO gap and VIP respectively.

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Supplementary materials

Table 1. Bond lengths (in nm) and bond angles (in degree) of the isomer 1 of SiN_7 cluster (B3LYP/6-31G(d)).

Definition	Values	Definition	Values	Definition	Values
N1–Si2	0.189	N7–N8	0.136	A(2,5,4)	131.7
N1–N3	0.113	A(2,1,3)	167.4	A(2,5,6)	118.2
Si2–N5	0.186	A(1,2,5)	88.4	A(4,5,6)	110.1
N4–N5	0.134	A(1,3,4)	44.7	A(5,6,8)	106.0
N4–N7	0.129	A(3,4,5)	82.6	A(4,7,8)	109.2
N5–N6	0.134	A(3,4,7)	171.5	A(6,8,7)	108.8
N6–N8	0.130	A(5,4,7)	105.8		

Table 2. Bond lengths (in nm) and bond angles (in degree) of the isomer 1 of Si_2N_6 cluster (B3LYP/6-31G(d)).

Definition	Values	Definition	Values	Definition	Values
N1–Si2	0.170	N6–N8	0.129	A(2,5,6)	119.8
N1–Si3	0.159	N7–N8	0.137	A(4,5,6)	109.7
Si2–N5	0.188	A(2,1,3)	177.4	A(5,6,8)	106.4
N4–N5	0.134	A(1,2,5)	96.9	A(4,7,8)	109.1
N4–N7	0.129	A(5,4,7)	106.1	A(6,8,7)	108.6
N5–N6	0.134	A(2,5,4)	130.5		

Table 3. Bond lengths (in nm) and bond angles (in degree) of the isomer 1 of Si_3N_5 cluster (B3LYP/6-31G(d)).

Definition	Values	Definition	Values	Definition	Values
Si1–N6	0.168	N5–N8	0.129	A(3,5,8)	114.6
Si1–N7	0.196	N7–N8	0.122	A(1,6,3)	124.5
Si2–N4	0.158	A(6,1,7)	101.0	A(1,7,8)	123.0
Si3–N4	0.167	A(4,3,5)	116.0	A(5,8,7)	139.8
Si3–N5	0.172	A(4,3,6)	126.9		
Si3–N6	0.164	A(5,3,6)	117.1		

Table 4. Bond lengths (in nm) and bond angles (in degree) of the isomer 1 of Si_4N_4 cluster (B3LYP/6-31G(d)).

Definition	Values	Definition	Values	Definition	Values
Si1–N2	0.171	N3–Si6	0.171	A(2,1,4)	129.4
Si1–N3	0.171	N4–Si5	0.158	A(3,1,4)	129.4
Si1–N4	0.168	Si6-N7	0.168	A(2,6,3)	101.2
Si1–Si6	0.218	N7-Si8	0.158	A(2,6,7)	129.4
N2–Si6	0.171	A(2,1,3)	101.2	A(3,6,7)	129.4

Table 5. Bond lengths (in nm) and bond angles (in degree) of the isomer 1 of Si_5N_3 cluster (B3LYP/6-31G(d)).

Definition	Values	Definition	Values	Definition	Values
Si1-N6	0.176	Si5-N7	0.187	A(6,5,7)	84.3
Si1–N7	0.187	Si5–N8	0.187	A(6,5,8)	84.3
Si2–N6	0.176	A(6,1,7)	88.0	A(7,5,8)	99.5
Si2–N8	0.187	A(6,2,8)	88.0	A(1,6,2)	128.9
Si3–N7	0.169	A(1,5,2)	73.4	A(1,7,3)	129.4
Si4–N8	0.169	A(1,5,8)	101.6	A(3,7,5)	121.0
Si5–N6	0.189	A(2,5,7)	101.6	A(2,8,4)	129.4

Table 6. Bond lengths (in nm) and bond angles (in degree) of the isomer 1 of Si_6N_2 cluster (B3LYP/6-31G(d)).

Definition	Values	Definition	Values	Definition	Values
N1–Si5	0.158	Si3–Si4	0.228	A(3,6,8)	64.7
N1–Si6	0.171	Si4–Si8	0.228	A(4,3,6)	114.1
Si2–N7	0.158	A(5,1,6)	178.4	A(4,8,6)	114.1
Si6–N7	0.171	A(2,7,6)	178.3	A(3,4,6)	64.1
Si3–Si6	0.235	A(7,6,8)	118.4		
Si6–Si8	0.235	A(1,6,3)	118.4		

Table 7. Bond lengths (in nm) and bond angles (in degree) of the isomer 1 of Si_7N cluster (B3LYP/6-31G(d)).

Definition	Values	Definition	Values	Definition	Values
Si1–N4	0.159	Si6–Si7	0.237	A(2,5,7)	104. 8
Si2–N4	0.170	Si7–Si8	0.237	A(2,6,7)	99.5
Si2–Si3	0.244	A(3,2,4)	120.7	A(3,6,5)	103.2
Si2–Si5	0.277	A(3,2,5)	114.1	A(3,6,7)	108.9
Si3–Si6	0.241	A(4,2,5)	125.2	A(2,8,7)	99.5
Si3–Si8	0.241	A(4,2,6)	147.1	A(3,8,5)	103.3
Si5–Si7	0.242	A(4,2,8)	147.1	A(3,8,7)	109.0

Table 8. Atomic natural charges of Si_mN_{8-m} ($0 < m < 8$) clusters with the order of atomic labels of serial number (B3LYP/6-31G*).

cluster	Natural Charge
SiN_7	–0.31315,0.87502,0.14720,–0.06586,–0.42744,–0.06110,–0.07530,–0.07936
Si_2N_6	–1.68766,1.25774, 1.13509, –0.05366, –0.42762, –0.05252, –0.08426, –0.08712
Si_3N_5	1.10929, 1.14940, 2.05244, –1.65272, –0.75973, –1.56970, –0.49217, 0.16319
Si_4N_4	1.99650, –1.48827, –1.48753, –1.63956, 1.13098, 1.99638, –1.63954, 1.13103
Si_5N_3	1.17589, 1.17589, 0.78213, 0.78213, 1.28991, –1.73601, –1.73497, –1.73497
Si_6N_2	–1.59975, 1.05429, –0.08518, –0.00967, 1.05427, 1.27108, –1.59976, –0.08528
Si_7N	1.07462, 0.59580, 0.05517, –1.60510, 0.00956, –0.06332, 0.05777, –0.12449

Table 9. All the vibration frequencies, IR intensity and Raman activity of Si_mN_{8-m} ($0 < m < 8$) clusters (B3LYP/6-31G*).

cluster	vibration frequencies(cm^{-1})/IR intensity(km/mol)/Raman activity($Å^4$/amu) (1Å=0.1 nm)
SiN_7	37.72/0.18/0.27, 99.85/0.40/7.95, 159.41/0.27/1.84, 216.09/0.33/2.24, 270.42/0.02/0.01, 323.48/14.14/6.66, 377.40/0.60/4.34, 452.61/79.31/13.19, 729.11/0.16/0.04, 749.18/0.04/0.07, 930.28/68.38/44.15, 1043.49/4.92/0.37, 1099.82/4.11/4.28, 1122.14/6.35/15.37, 1202.69/77.26/49.18, 1282.10/1.53/36.51, 1370.91/6.25/0.35, 2120.52/511.55/198.48
Si_2N_6	50.06/0.00/0.00, 63.90/1.81/7.15, 145.44/1.19/3.03, 184.98/4.03/0.66, 210.34/1.50/3.86, 301.38/18.28/1.87, 442.60/158.49/7.27, 604.36/48.85/41.49, 731.87/0.23/0.01, 755.72/0.21/0.05, 896.87/81.07/43.99, 1045.51/8.64/4.88, 1103.64/4.47/2.63, 1120.24/17.88/7.65, 1191.10/190.55/3.51, 1302.54/2.01/10.18, 1348.56/503.43/133.47, 1393.34/9.42/0.64
Si_3N_5	67.84/0.64/0.29, 80.37/2.29/4.87, 172.11/2.03/1.07, 176.90/0.06/1.64, 273.29/39.87/29.06, 298.51/0.20/5.42, 310.10/35.54/3.84, 339.56/21.61/4.80, 393.32/67.11/11.82, 452.79/17.90/0.68, 548.39/33.87/15.67, 714.24/36.02/68.38, 768.81/26.29/35.23, 821.11/126.55/20.62, 1115.01/68.53/13.48, 1202.58/285.47/110.18, 1401.54/771.25/748.83, 1606.77/388.11/70.43
Si_4N_4	38.38/4.64/0.00, 58.78/7.16/0.00, 107.51/0.00/5.93, 115.28/0.00/2.09, 198.76/6.96/0.00, 300.41/23.20/0.00, 321.23/0.00/6.18, 323.01/0.00/61.53, 338.34/0.00/0.14, 424.24/77.42/0.00, 517.74/0.02/0.00, 646.07/0.02/13.40, 773.54/0.01/62.11, 851.20/704.86/0.00, 932.49/175.28/0.43, 943.61/0.77/81.09, 1387.64/1661.47/0.29, 1415.05/0.49/950.68

Table 9 (*continued*)

Si_5N_3	98.17/0.11/8.01, 136.25/2.55/17.50, 189.07/2.03/23.82, 190.17/0.00/8.98, 212.17/1.86/11.90, 243.26/2.87/0.78, 319.43/17.87/7.78, 372.20/16.76/4.33, 402.26/3.83/111.87, 458.33/7.78/5.28, 464.26/10.28/3.07, 507.86/58.37/35.44, 525.62/19.16/1.90, 602.32/116.48/77.11, 623.03/24.74/37.15, 814.24/52.30/12.06, 969.29/203.03/336.81, 998.33/171.17/5.54
Si_6N_2	54.69/0.37/20.41, 65.89/0.89/14.61, 80.26/0.00/29.92, 86.38/2.12/2.27, 147.64/0.20/0.36, 224.51/0.00/0.01, 234.07/1.65/1.40, 241.76/20.42/0.10, 259.04/5.55/39.50, 43.87/25.39/29.60, 354.14/12.24/0.01, 376.96/12.36/40.82, 422.06/0.12/10.38, 507.94/5.24/99.34, 618.47/227.71/31.48, 640.95/105.48/5.91, 1359.14/648.19/573.38, 1366.29/402.09/844.41
Si_7N	65.81/0.21/5.30, 72.02/0.24/3.63, 73.21/0.55/6.83, 112.85/1.07/0.18, 127.11/0.00/0.59, 231.10/8.33/0.69, 242.31/0.47/55.09, 243.37/6.98/1.65, 314.48/0.00/8.59, 326.36/4.84/7.43, 353.54/0.64/24.09, 367.80/0.01/40.15, 369.73/0.02/4.26, 403.95/6.82/2.42, 409.81/9.61/104.04, 450.66/0.02/4.00, 653.63/69.89/24.85, 1352.69/648.37/1173.53

Table 10. Polarizability (α)of the Si_mN_{8-m} $(0 < m < 8)$ clusters calculated by using B3LYP/6-31+G*(in a.u.).

α	XX	XY	YY	XZ	YZ	ZZ
SiN_7	113.0329334	–12.3552951	91.3263188	0.167325	–0.4399543	50.454224
Si_2N_6	85.8985563	9.7398656	129.2858553	0.2926053	–2.0067222	53.2788682
Si_3N_5	187.9060854	5.8392331	107.6793499	–24.8848235	–1.2728085	78.693026
Si_4N_4	235.7308784	–0.0023935	98.9901089	0.0135418	0.0000038	81.4366796
Si_5N_3	201.015225	0.000024	197.0876452	11.9326854	–0.0000256	142.9432572
Si_6N_2	288.5311474	0.3929982	195.9022239	0.0452976	–0.190402	175.9482863
Si_7N	317.5019366	–9.5402679	225.6764926	–0.0247878	0.0024626	173.9225874

Table 11. Hyperpolarizability (β) of the Si_mN_{8-m} $(0 < m < 8)$ clusters calculated by using B3LYP/6-31+G*(in a.u.).

β	XXX	XXY	XYY	YYY	XXZ	XYZ	YYZ	XZZ	YZZ	ZZZ
SiN_7	–14.3679	–127.9287	231.8666	139.0727	2.8900	–5.2956	2.6366	–11.5331	145.4974	–8.8144
Si_2N_6	–346.9469	–192.6628	–205.2909	–528.0192	–0.0762	2.2799	10.9157	–13.7776	–9.5676	0.1220
Si_3N_5	–1682.5262	–543.0917	–135.6877	–90.2109	398.1351	98.5052	29.4453	–14.5473	–110.9108	–29.5654
Si_4N_4	–2.6864	–1.7671	–0.0092	–0.0746	–0.3861	0.0001	–0.0017	0.0128	0.0051	–0.0133
Si_5N_3	–1144.1228	0.0011	–338.0508	0.0022997	–705.6465	0.0007	–532.3276	–163.4279	0. 0003	–420.5062
Si_6N_2	704.0369	–6.4989	1107.9187	13.8129	0.7115	–0.7963	0.7843	–176.8371	–0.7156	–0.2536
Si_7N	–2922.8549	–596.0697	55.4049	–13.1874383	0.6977	0.0630	–0.6496	226.3200	90.6622	0.0971

References

[1] Jensen P 1999 *Rev. Mod. Phys.* **71** 1695

[2] Bai Y L, Chen X R, Cheng X H and Yang X D 2007 *Chin. Phys.* **16** 700

[3] Zhang C R, Chen H S, Song Y and Xu G J 2007 *Chin. Phys.* **16** 2394

[4] Baletto F and Ferrando R 2005 *Rev. Mod. Phys.* **77** 371

[5] Yang P, Ge J H and Jiang Z Y 2007 *Chin. Phys.* **16** 1014

[6] Wang H Y, Li X B, Tang Y J, Bruce R K and Henry F S 2007 *Chin. Phys.* **16** 1660

[7] Wang Q L, Ge G X, Zhao W J, Lei X L, Yan Y L, Yang Z and Luo Y H 2007 *Acta Phys. Sin.* **56** 3219

[8] He J L, Guo L C, Yu D L, Liu R P, Tian Y J and Wang H T 2004 *Appl. Phys. Lett.* **85** 5571

[9] Wei Y L, Yoshio B, Zhu Y C and Li Y B 2003 *Appl. Phys. Lett.* **83** 3584

[10] Goldberg N, Iraqi M, Schwarz H, Boldyrev A and Simons J 1994 *J. Chem. Phys.* **101** 2871

[11] Ornellas F R, Ueno L T and Iwata S 1997 *J. Chem. Phys.* **106** 151

[12] Ornellas F R and Iwata S 1996 *J. Phys. Chem.* **100** 10919

[13] Ornellas F R and Iwata S 1996 *J. Phys. Chem.* **100** 16155

[14] Jackson K, Jungnickel G and Frauenheim T 1998 *Chem. Phys. Lett.* **292** 235

[15] Jungnickel G, Frauenheim T and Jackson K A 2000 *J. Chem. Phys.* **112** 1295

[16] Zhang C R, Chen H S, Xu G J, Chen Y H and Zhang H L 2007 *J. Mol Struct.* (THEOCHEM) **805** 161
[17] Zhang C R, Zhang B X, Chen Y H, Li W X and Xu G J 2006 *J. At. Mol. Phys.* **23** 171
[18] Stewart J J P 1989 *J. Comp. Chem.* **10** 209
[19] Lee C, Yang W and Parr R G 1988 *Phys. Rev.* B **37** 785
[20] Miehlich B, Savin A, Stoll H and Preuss H 1989 *Chem. Phys. Lett.* **157** 200
[21] Becke A D 1993 *J. Chem. Phys.* **98** 5648
[22] Yang J C, Xu W G and Xiao W S 2005 *J. Mol. Struct.* (THEOCHEM) **719** 89
[23] Vashishta P, Kalia R K and Ebbsjö I 1995 *Phys. Rev. Lett.* **75** 858
[24] Wang X, Tian A M, Wong N B, Law C K and Li W K 2001 *Chem. Phys. Lett.* **338** 367
[25] Li Q S, Hu X G and Xu W G 1998 *Chem. Phys. Lett.* **287** 94
[26] Zhao J F and Li Q S 2003 *Chem. Phys. Lett.* **368** 12
[27] Wang X, Ren Y, Shuai M B, Wong N B, Li W K and Tian A M 2000 *J. Mol. Struct.* (THEOCHEM) **538** 145
[28] Wang L J, Xu G W and Li Q S 2000 *J. Mol. Struct.* (THEOCHEM) **531** 135
[29] Foster J P and Wienhold F 1980 *J. Am. Chem. Soc.* **102** 7211
[30] Zhang C R, Chen H S and Wang G H 2004 *Chem. Res. Chinese U.* **20** 640
[31] Sun Y, Chen X, Sun L, Guo X and Lu W 2003 *Chem. Phys. Lett.* **381** 397
[32] Christiansen O, Gauss J and Stanton J F 1999 *Chem. Phys. Lett.* **305** 147
[33] Cheng H, Feng J, Ren A and Liu J 2002 *Acta Chim. Sin.* **60** 830
[34] Cheng H, Feng J and Ren A 2004 *Acta Chim. Sin.* **62** 362
[35] Sa R, Wu K, Lin C, Chen X, Liu P, Mang C and Zhuang B 2003 *Chin. J. Struct. Chem.* **22** 481
[36] Cheng H, Feng J, Ren A and Liu J 2003 *Acta Chim. Sin.* **61** 541
[37] Wang G H 2003 *Cluster Physics* (Shanghai: Shanghai Scientific and Technological Publishing House) p116
[38] Wang S, Liu Z P, Lu J and Fan K N 2007 *Acta Chim. Sin.* **65** 1831