

A Density Functional Study of the Structural and Electronic Properties of Silicon Monoxide Clusters

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By use of density functional theory, a systemic theoretical study was conducted on the structural and electronic properties of ground-state silicon monoxide clusters ((SiO)_n, where $n = 1-26$). In our calculations, the most energetically favorable geometry for each cluster size was found to undergo a structural change from one dimension (linear) to three dimensions at cluster size $n = 4$, with the buckled structure as the favorable one. The sp³ silicon containing structures are favorable for $n = 5-13$, and the Si-cored structures are energetically favorable at $n = 14$ and larger. Furthermore, for the lowest-energy structures obtained, the energy gaps between the highest occupied and lowest unoccupied molecular orbital, binding energies, ionization potentials, and electron affinities were calculated and analyzed to understand the evolutions in geometries and to identify any particularly stable species.

Introduction

Silicon monoxide clusters are useful materials for many industrial applications as well as prototypes for fundamental research. They contribute to the formation of protective layers and optical coatings,¹⁻⁵ play crucial roles in the oxide-assisted growth of silicon nanowires,⁶ and provide simple but useful modeling frameworks for understanding the structural and binding properties of bulk materials.^{3-5,7-9} Studies of silicon monoxide clusters at the molecular level are deemed critical for explaining the formation of their known structures and extending their applications to new areas. With currently available computing power, the electronic properties of small-size clusters can be accurately calculated, allowing a meaningful comparison with experimental measurements.¹⁰ Presently, a large number of experimental¹¹⁻¹⁴ and theoretical¹⁵⁻¹⁷ studies have been published, which have considerably improved our understanding of the structures and properties of silicon monoxides.¹⁸⁻²⁸ However, the detailed structures of the silicon monoxide clusters have remained the subject of controversy^{17,29-31} and need to be clarified unambiguously.

Zhang et al.^{10,27,28,32} proposed that silicon monoxide clusters facilitate the nucleation and growth of silicon nanostructures through the formation of sp³ silicon cores surrounded by silicon oxide sheaths. Reber et al.,³³ on the basis of their calculations, suggested that there is a tendency for (SiO)_n clusters to segregate into Si- and O-rich cores, particularly SiO₂. More recently, Wang et al.³⁴ proposed that medium-sized silicon suboxide clusters consist of polygonal bipyramid Si clusters with 5–7 Si atoms attached to low-energy Si₈O₁₂ or Si₁₂O₁₈ structures; but these structures, as confirmed with MD simulations by Huang et al.,³² are unlikely to exist at the temperature for synthesis of silicon nanostructures and have a higher reactivity with oxygen than Si-cored isomers. On the other hand, Huang et al.'s study³²

mainly emphasized the stability of the published Si-cored structures and did not investigate any new or larger cluster. Overall, few studies have been conducted to examine the structural and electronic properties of the series of silicon monoxide clusters. The reason could be that the large-size (SiO)_n clusters have more than one theoretically possible structure. In addition, the size of basic set functions would exponentially increase with increasing size and electron number of the silicon monoxide clusters, greatly deteriorating the ability of theoretical calculation to accurately predict the structures of large silicon monoxide clusters.

The present study was intended to systematically investigate the structural and electronic properties of (SiO)_n ($n = 1-26$) clusters, employing density functional theory (DFT) to perform both optimization and energy calculations. Subsequently, charge distributions, chemical stabilities, bonding natures, highest-occupied and lowest-unoccupied molecular orbital (HOMO–LUMO) gaps, ionization potentials, and electron affinities of the lowest-energy structures of (SiO)_n ($n = 1-26$) clusters were carefully examined.

Computational Details

The semiempirical molecular orbital MNDO/d method has often been used to study the conformation of large molecular systems, especially those composed of elements in the first two rows of the periodic table. The method is efficient and able to produce reliable results. In the present study, the MNDO/d method embedded in the Spartan 04 program package³⁵ was first used to identify all the potential ground-state structures. Further geometric optimizations to identify the lowest energy structure from the structures obtained by the semiempirical calculation were carried out by means of DFT with the B3LYP (Becke-3-Lee-Yang-Par) functional and 6-31G(d) basis set for both Si and O atoms using the Gaussian 03 program package.³⁶ To examine the effects of basis sets on the computational results, a larger basis set, Aug-CC-pVTZ, in addition to 6-31G(d), was also employed to optimize the structures and calculate the electron affinities of (SiO)₅ clusters. The results (Tables S1 and

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TABLE 1: Energy Difference (Hartree) between the Lowest-Energy Configuration and Other Isomers of a Given (SiO)_n (n = 4–10) Cluster

species	(SiO) ₄	(SiO) ₅	(SiO) ₆	(SiO) ₇	(SiO) ₈	(SiO) ₉	(SiO) ₁₀
1	0	0	0	0	0	0	0
2	13.58	17.46	0.14 ^a	5.22	2.34	20.33	27.24
3	19.50	20.03	0.60	9.00	4.33	20.55	37.52
4		32.23	3.77	18.56	5.11 ^a	21.24	51.11
5		39.99	5.97	19.40	11.68	27.85	51.25
6			6.95	27.36	13.54	28.76	52.45
7				29.24	13.78	29.60	52.62
8				31.29	15.51	30.85	
9				41.40	16.34	31.81	
10					18.04	32.61	
11						32.86	
12						33.98	

^a The lowest-energy geometries identified by Zhang and Fan.²⁸

S2 of Supporting Information) indicate no meaningful difference between the two basis sets (see the Supporting Information for detailed discussions). To ensure that the optimized geometries were truly at stationary state, the optimized isomers were further examined by harmonic frequency calculations at the same level. The structural parameters, theoretical band gap width, and charge distributions were evaluated using the optimized stable ground-state structure.

In addition, to assess the energetic effects in chemical reactivity and bonding capability, vertical ionization potentials and vertical electron affinities were obtained by single-point calculations on the optimized lowest-energy geometries. Adiabatic ionization potentials and electron affinity were obtained by optimization of corresponding charged ions, which was carried out at the same theoretical level as that for geometric optimization.

Results and Discussion

Structures of Silicon Monoxide Clusters. Among the local minimal structures of small silicon monoxide (SiO)_n (n = 1–10) clusters (Figure S1 of Supporting Information), both (SiO)₂ and (SiO)₃ clusters are “planar-ring”. Similar structures have been reported by Wang et al.,³⁴ Zhang et al.,^{27,28,31} and Huang et al.³² On the other hand, the lowest-energy structures of (SiO)₄ and (SiO)₅ clusters are buckled ring (Figure S1-1-4a of Supporting Information) and a Si-cored (Figure S1-1-5a of Supporting Information), respectively, involving a 5-member and a six-member ring, which are consistent with the findings by Zhang et al.^{27,28} Two other competitive isomers of (SiO)₄ cluster are 13.58 and 19.50 kcal/mol higher in energy (less stable) than the buckled one (Figure S1 of Supporting Information and Table 1). In addition, four other less stable structures are identified for (SiO)₅ clusters, 17.46, 20.03, 32.23, and 39.99 kcal/mol higher in energy (Figure S1 of Supporting Information and Table 1), respectively, compared to the lowest energy one.

For (SiO)₆ clusters, six additional local minimal geometries are obtained (Figure S1-1-6 of Supporting Information and Table 1), with the first one containing a similar Si-cored structure with a Si–Si bond length of 2.450 Å (Table 2). The predicted Si-cored structure for (SiO)₆ clusters based on Zhang et al.’s study²⁷ lies in 0.14 kcal/mol (1.2 kcal/mol with zero-point energy correction) higher in energy than our lowest-energy one. However, this small difference requires performing statistically meaningful number of MD simulations to identify the most favorable structures. Furthermore, nine very competitive isomers of (SiO)₇ clusters are obtained, and the lowest-energetic one has a triple-ring-like structure involving the formation of two eight-member rings by two four-coordinate Si atoms with another Si atom as a bridge. On the contrary, the buckled rhombus structure reported previously³¹ are not locally minimal

TABLE 2: Bond Lengths (Å), Bond Angles (deg), and Mulliken Charge Distributions (au.) for the Lowest-Energy Structures of (SiO)_n Clusters (n = 1–6) Using the B3LYP/6-31G(d) Method

species	R _{Si–Si}	R _{Si–O}	∠SiOSi	∠OSiO	q _{Si}	q _O
(SiO) ₁		1.524			0.472	−0.472
		1.54 ^a			0.47 ^a	
(SiO) ₂		1.714	93.0	87.0	0.640	−0.640
		1.683 ^d		85.7 ^d		
		1.70 ^e	140 ^e	100 ^e		
(SiO) ₃		1.689	138.2	101.8	0.640	−0.640
		1.689 ^b	138.3 ^b	101.7 ^b	0.853 ^b	−0.853 ^b
		1.63 ^c	134 ^c	102 ^c		
(SiO) ₄		1.677	∠152:160.4	∠518:102.8	0.614	−0.614
		1.676 ^b	∠263:157.7	∠523:102.8	0.648 ^b	−0.648 ^b
		1.65 ^c	∠374:160.4	∠637:102.8		
			∠184:157.8	∠847:102.8		
			165.58 ^b	104.42 ^b		
			127 ^c	104 ^c		
		1.70 ^e	140 ^e	100 ^e		
(SiO) ₅	2.450	1–5:1.691	∠163:123.2	∠637:100.3	(1) 0.814	(3) −0.633
		1–3:1.674	∠273:131.2	∠273:131.2	(2) 0.376	(4) −0.633
		1–4:1.673	∠184:134.6	∠8410:101.9	(7) 0.684	(5) −0.624
		2–6:1.690	∠195:134.6	∠9410:102.0	(8) 0.652	(6) −0.644
		8–9:1.688	∠4105:139.6	∠819:106.9	(10) 0.651	(9) −0.644
		1.65 ^c	122 ^c 104 ^c	0.645/0.650/0.630 ^b	−0.681/−0.639/−0.630 ^b	
(SiO) ₆	2.446	1–8:1.682	∠1810:134.3	∠918:106.9	(1) 0.833	(2) −0.611
		1–9:1.673	∠125:145.5	∠257:103.1	(3) 0.378	(4) −0.610
		1–2:1.673	∠346:158.8	∠91120:101.9	(5) 0.629	(7) −0.618
		3–4:1.675	∠1911:134.8	∠467:102.1	(6) 0.645	(8) −0.654
		8–10:1.682		(10) 0.638	(9) −0.632	
		2–5:1.669		(11) 0.648	(12) −0.645	

^a Calculated values using B3LYP/6-311G** method by Nayak.¹⁸ ^b Calculated values obtained with B3LYP/6-31G* by Zhang and Fan.²⁸

^c Calculated values obtained using LDA method by Chelikowsky.¹⁷ ^d Calculated values obtained with HF/6-31G* by Snyder.⁷ ^e Experimental values obtained by Anderson.³⁰

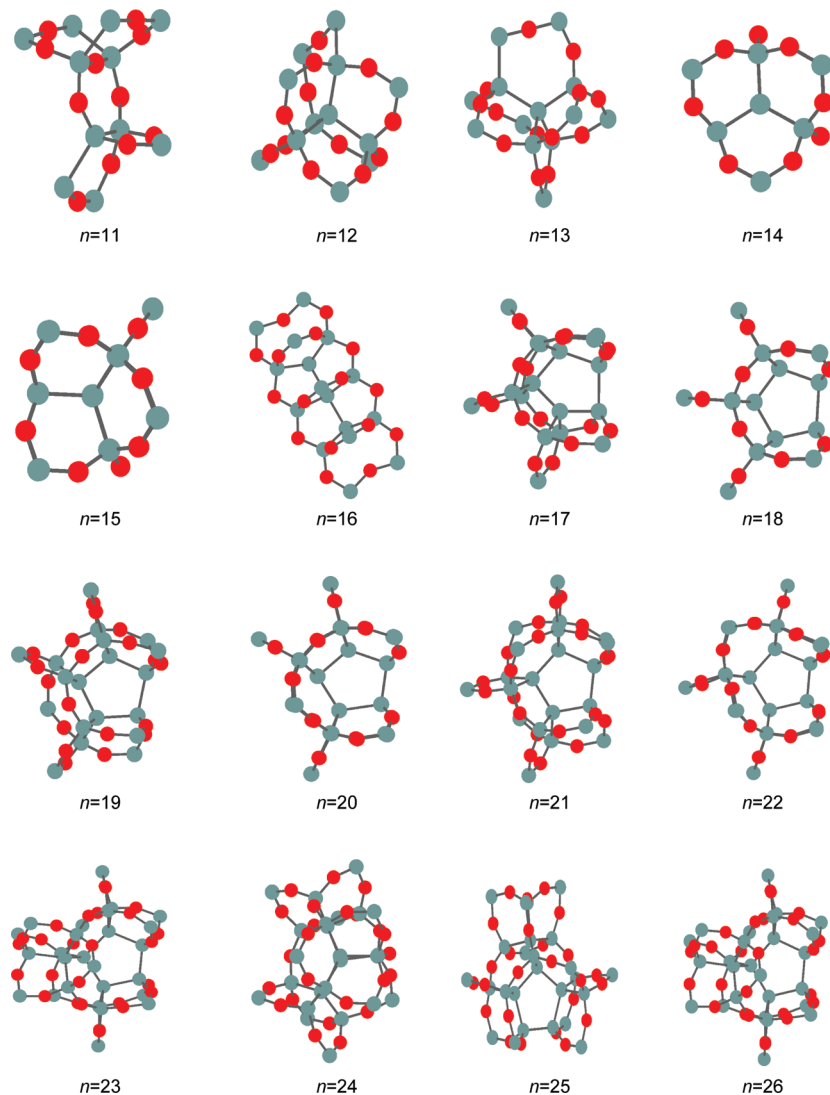


Figure 1. The lowest-energy geometries of the $(\text{SiO})_n$ clusters ($n = 11\text{--}26$) at the B3LYP/6-31G(d) level.

based on the results from the present study. A new lowest-energy Si-cored structure (Figure S1-1-8a of Supporting Information) for $(\text{SiO})_8$ clusters with nine proposed isomers (Figure S1-1-8 of Supporting Information) was obtained in the present study, which is different from the lowest-energy structure (Figure S1-1-8c of Supporting Information) predicted by Zhang et al.²⁷ For $(\text{SiO})_9$ clusters; in addition to the structure previously identified,^{27,28} another 11 isomers were obtained in the present study. It is noted that most Si–O bond lengths range from 1.520 to 1.714 Å (Table 2). The values presented herein are closer to the experimental data³⁰ than previous reported calculated values.^{10,17} In addition, weak Si–Si bonds with bond lengths of approximately 2.450 Å (Table 2) are found in the double-ring-like structures. The coordination number is 2 for most oxygen atoms except for SiO and 2 or 4 for silicon atoms in the clusters, and structural complexity increases with increasing cluster size.

On the basis of the above results, we can draw a few stepwise conclusions: (1) the fixed “planar-ring” structure, which is one of the initially designed structures, is not at a local minimum in energy but tends to revert to a “buckled-ring” structure relaxing the degree of freedom from the planar structure and resulting in sp^3 hybridization for the bonding between Si and O atoms (it should be noted that this conclusion is partly

consistent with previous findings;¹⁰ (2) a real Si–O ring should have less than eight atoms, or else it is simply hypothetical; (3) the main cause for the instability of four-member rings is due to a bond angle of Si–O–Si and O–Si–O close to 90° which deviates substantially from the value in silicon crystals; (4) Si and O atoms prefer to form five- or six-member heterogeneous rings. Moreover, the six-member ring is the most stable structure. It is obvious that the interaction between Si and Si atoms, which is inevitable in a five-member ring, is much weaker than that between Si and O atoms (the binding enthalpy values for Si–O and Si–Si bonds are 191.12 and 78.84 kcal/mol, respectively³⁷), leading to the instability of the five-member ring.

Inspired by the above conclusions, DFT calculations on several much larger $(\text{SiO})_n$ ($n = 11\text{--}26$) clusters were conducted to obtain the ground-state structures of the $(\text{SiO})_n$ clusters (Figure 1) and to assess the variability in the structural and electronic properties as the cluster size grows. From these exercises, additional conclusions can be deduced: (1) Si-cored structures are energetically favorable starting at $n = 14$ as the cluster size increases; (2) the lowest-energy structures possess a high degree of symmetry; (3) the structural characteristics of silicon monoxides are similar to those of crystalline silicon (a face-centered cubic structure with a lattice spacing of 5.431 Å³⁸),

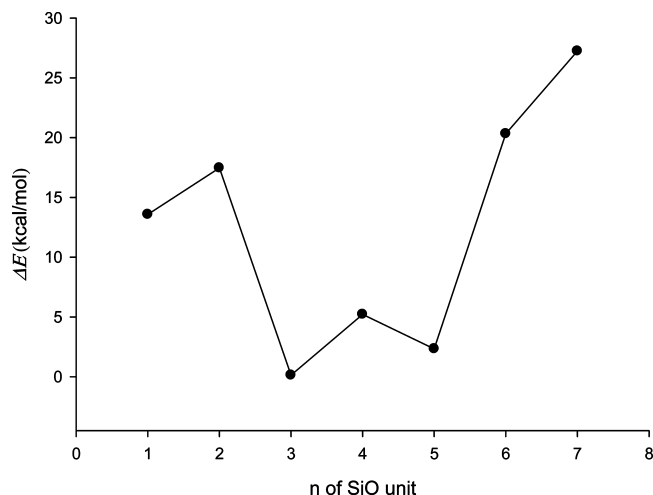


Figure 2. Differences in total energies between the substable and lowest-energy structures for the $(\text{SiO})_n$ clusters ($n = 4-10$) obtained with B3LYP/6-31G(d).

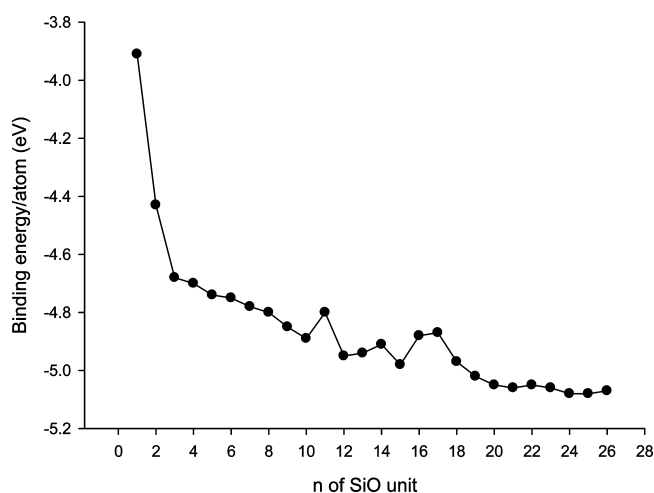


Figure 3. Binding energy for the lowest-energy structures of the $(\text{SiO})_n$ clusters ($n = 1-26$) at the B3LYP/6-31G(d) level.

with four-coordinated Si atoms at the internal part surrounded by silicon oxide sheaths at outer shell, which agree well with the results of Zhang et al.²⁷ and (4) the most energetically favorable geometries of $(\text{SiO})_n$ ($n = 1-26$) clusters obtained in the present study contain oxygen and silicon atoms of sp^3 hybridization.

Chemical Stability and Electronic Properties of Silicon Monoxides ($n = 1-26$). The binding energies, band gaps, ionization potentials, and electron affinities of the $(\text{SiO})_n$ ($n = 1-26$) clusters are expressed as the functions of cluster size n (Table S3 of Supporting Information) and plotted in Figures 2–6. Detailed discussions of these parameters are presented below.

Binding Energies and Second Difference in Energy. The relative stability of the clusters is ranked by an energetic criterion. For those isomers that have the same numbers of Si and O atoms, the total energies obtained from the calculations can be compared directly to determine the relative stability. Figure 2 clearly shows that the difference between the total energies of the substable and lowest-energy structures of small silicon monoxide clusters ($n = 4-10$) is independent of the cluster size. For clusters having different structural units, the binding energy (E_b) per atom as defined below is used to rank

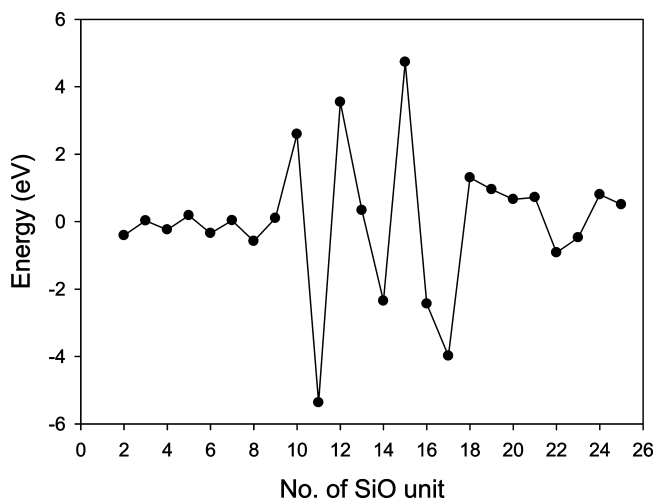


Figure 4. Second difference in energy for the $(\text{SiO})_n$ clusters ($n = 2-25$) at the B3LYP/6-31G(d) level.

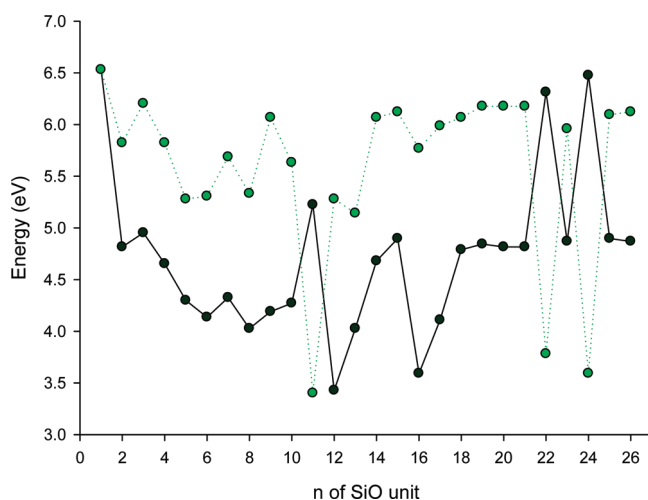


Figure 5. Energy gaps between the HOMO of the lowest-energy $(\text{SiO})_n$ clusters ($n = 1-26$) and the LUMO of SiO (in black) and between the LUMO of the lowest-energy $(\text{SiO})_n$ clusters ($n = 1-26$) and the HOMO of SiO (in green) at the B3LYP/6-31G(d) level.

the relative stability of the lowest-energy structures of $(\text{SiO})_n$ ($n = 1-26$) clusters

$$E_b[(\text{SiO})_n] = (E[(\text{SiO})_n] - nE[\text{Si}] - nE[\text{O}])/2n \quad (1)$$

where $E[(\text{SiO})_n]$ and $E[\text{Si}]$ and $E[\text{O}]$ are the total energy of a specific cluster corresponding to n and the energies of isolated spin-polarized Si and O atoms. The binding energy per atom of $(\text{SiO})_n$ ($n = 1-26$) clusters decreases dramatically from -3.91 to -5.08 eV (Table S3 of Supporting Information) with cluster size rising from 1 to 26 and especially drops to the lowest value at $n = 25$ (Figure 3). Thus, the structure at $n = 25$ may represent a significant point on the binding energy curve. The fact that the binding energy evolves slowly with cluster size starting from $n = 14$ indicates that these Si-cored structures can act as seeds for further growth motif of silicon monoxide clusters.

Besides, the second difference of cluster energy in cluster physics is a sensitive quantity that reflects the relative stability of corresponding clusters, and can be directly compared with the measured relative abundances of the clusters. In the present

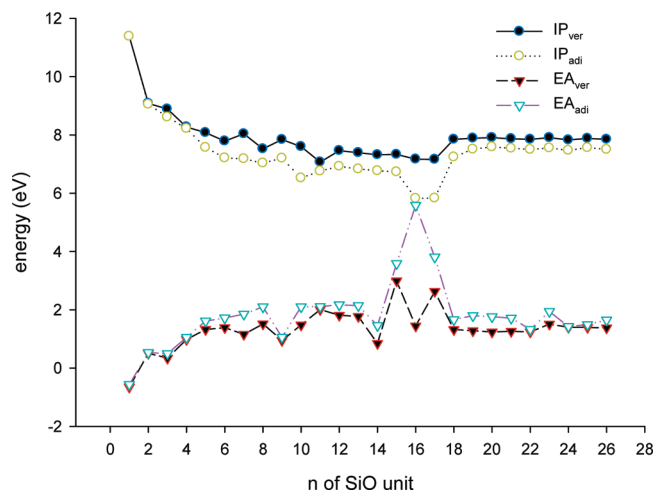


Figure 6. Vertical and adiabatic ionization potentials and vertical and adiabatic electron affinity for the lowest-energy structures of the $(\text{SiO})_n$ clusters ($n = 1-26$) at the B3LYP/6-31G(d) level.

study, it is more instructive to analyze the second difference of energy ($\Delta_2 E$) defined as

$$\Delta_2 E[(\text{SiO})_n] = E[(\text{SiO})_{n+1}] + E[(\text{SiO})_{n-1}] - 2E[(\text{SiO})_n] \quad (2)$$

where E is the total energy of a specific cluster. From the definition of $\Delta_2 E$, clusters with larger $\Delta_2 E$ values are obviously more stable. Therefore, the largest value of $\Delta_2 E$ at $n = 15$ indicates that this is the most stable cluster among the $(\text{SiO})_n$ ($n = 2-25$) clusters under investigation in the present study and that the $(\text{SiO})_{14}$ and $(\text{SiO})_{16}$ clusters are relatively unstable. In the range of $n = 18-25$, i.e., the relatively flat portion on the curve (Figure 4), a relatively high value can be identified at $n = 25$, which suggests that silicon monoxide clusters prefer to occur in the form of the $(\text{SiO})_{25}$. The value of $\Delta_2 E$ is the smallest at $n = 11$, at which the structure contains two three-coordinated Si atoms at the center and two eight-member rings.

Band Gap. A small energy gap between the HOMO of electron donor and the LUMO of electron acceptor has been known to indicate the most favorable site in a chemical reaction system. Both the gaps between the HOMO of the lowest-energy $(\text{SiO})_n$ ($n = 1-26$) clusters and LUMO of SiO (black) and between the LUMO of lowest-energy $(\text{SiO})_n$ ($n = 1-26$) clusters and HOMO of SiO (green) are not clearly correlated with the number of SiO units (Figure 5). It is obvious from the energy differences (Figure 5) that $(\text{SiO})_n$ clusters ($n > 1$) prefer to be electron donors except for $(\text{SiO})_{11}$, $(\text{SiO})_{22}$, and $(\text{SiO})_{24}$. Interestingly, the SiO cluster has the largest HOMO–LUMO gap among the clusters under investigation. The $(\text{SiO})_{11}$ cluster with the smallest band gap with SiO at 3.40 eV (Table S3 of Supporting Information) is expected to be the chemically most reactive as an electron acceptor. Besides, the $(\text{SiO})_{12}$ cluster with the smallest band gap with SiO at 3.43 eV (Table S3 of Supporting Information) is expected to be the chemically most reactive as an electron donor. Moreover, the band gaps for the $(\text{SiO})_{18-26}$ clusters except for $(\text{SiO})_{22}$ and $(\text{SiO})_{24}$ indicate that they remain chemically stable, while the $(\text{SiO})_{25}$ cluster appears to be the most stable one with the largest gap of 4.90 eV (Figure 5). This observation is consistent with the results from binding energy calculations (Figures 3 and 4 and Table 1).

Ionization Potential and Electron Affinity. Ionization potential (IP), defined as the energy needed to remove an

electron from the neutral cluster, refers to either adiabatic ionization energy (IP_{ada}) or vertical ionization energy (IP_{ver}), which can be used to characterize the electronic structures of small clusters and obtained by

$$\text{IP}_{\text{ada}} = E_{\text{cation}}(\text{optimized cation}) - E_{\text{neutral}}(\text{optimized neutral})$$

$$\text{IP}_{\text{ver}} = E_{\text{cation}}(\text{optimized neutral}) - E_{\text{neutral}}(\text{optimized neutral})$$

It is well-known that a larger IP_{ver} value means a bigger HOMO energy level and lower reactivity (or higher chemical stability). It is interesting to note that the largest IP value locates at $n = 1$ (Figure 6). In addition, the IP values gradually reach a plateau with increasing cluster size. These results show that the $(\text{SiO})_n$ clusters maintain stable chemical reactivity with increasing cluster size. Therefore, Si-cored structures are apparently the optimal structures for large $(\text{SiO})_n$ clusters.

Electron affinity (EA) is a measure of the energy change when an electron is added to a neutral atom to form a negative ion. Adiabatic (EA_{ada}) and vertical (EA_{ver}) electron affinities can be obtained by

$$\text{EA}_{\text{ada}} = E_{\text{neutral}}(\text{optimized neutral}) - E_{\text{anion}}(\text{optimized anion})$$

$$\text{EA}_{\text{ver}} = E_{\text{neutral}}(\text{optimized neutral}) - E_{\text{anion}}(\text{optimized neutral})$$

As a result of geometry change, the value of EA_{ver} is usually larger than that of EA_{ada} . The values of EA_{ver} and EA_{ada} can be obtained from experimental photoelectron spectroscopy; however, no data of EAs for the $(\text{SiO})_n$ clusters are available in the literature. Therefore, the results from the present study can be used for comparison with future measurements. It should be noted that the calculated EAs are cohesively correlated with the calculated IPs. First, the $(\text{SiO})_1$ cluster has negative EA (Figure 6), which means it is unlikely to accept electron in chemical reaction. Second, the calculated EA_{ver} and EA_{ada} vary similarly with the number of SiO clusters from $n = 1-26$, i.e., gradually increase from $n = 2-16$ and remain practically unchanged after $n = 18$, with the exception at $n = 16$ where the contribution from the added electron results in a markedly energetic change indicating a large geometric change between the optimized and neutral clusters. Finally, the EA values for silicon monoxides also gradually reach a plateau with increasing cluster size.

The above results indicate that the Si-cored structure is probably the most stable form for each medium-size cluster, and the $(\text{SiO})_{25}$ cluster with a Si-cored structure appears to be the most possible geometry for $(\text{SiO})_n$ clusters that occur naturally.

Conclusions

Comparison of multiple possible geometries for the $(\text{SiO})_n$ clusters with the same cluster number (n) indicates that the energetically more favorable configurations of small-sized $(\text{SiO})_n$ clusters ($n = 1-5$, 18, and 21) found in the present study are identical to those determined by previous studies.^{10,28,31} For $n = 6, 8, 9, 11$, and 15, the cluster structures obtained in the

present study are energetically more favorable than those reported in a previous publication.²⁷ In addition, the lowest-energy cluster structures at $n = 7, 10, 12-14, 16, 17, 19, 20$, and $22-26$, which have not been reported previously, were obtained for the first time in the present study. Moreover, the Si-cored silicon monoxide with high structural stability and low chemical reactivity can act as a nucleation seed for further growth of silicon nanostructures. Besides, the silicon monoxide cluster at $n = 25$ was found to be the most stable among the medium-size clusters. Finally, the methodology demonstrated seems to be able to obtain the reasonable structures and energies of medium-size clusters, although further enhancement of the models used in the present study is needed to be able to identify the real structures of silicon monoxide clusters.

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Supporting Information Available: Discussion of the comparison of aug-CC-pVTZ and 6-31G(d) methods, tables comparing total energy and CPU time of calculations, electron affinity and CPU time, and total binding energies and electronic properties of some of the compounds, and a figure depicting the geometries of (SiO)₁ to (SiO)₁₀ clusters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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