

University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Xiao Cheng Zeng Publications

Published Research - Department of Chemistry

5-15-2004

Structures and stability of medium silicon clusters. II. Ab initio molecular orbital calculations of Si₁₂-Si₂₀

X.-L. Zhu

University of Nebraska-Lincoln

Xiao Cheng Zeng

University of Nebraska-Lincoln, xzeng1@unl.edu

Y.A. Lei

University of Nebraska-Lincoln

B. Pan

University of Science and Technology of China, Hefei, 230000, China

Follow this and additional works at: <https://digitalcommons.unl.edu/chemzeng>

 Part of the [Chemistry Commons](#)

Zhu, X.-L.; Zeng, Xiao Cheng; Lei, Y.A.; and Pan, B., "Structures and stability of medium silicon clusters. II. Ab initio molecular orbital calculations of Si₁₂-Si₂₀" (2004). *Xiao Cheng Zeng Publications*. 27.

<https://digitalcommons.unl.edu/chemzeng/27>

This Article is brought to you for free and open access by the Published Research - Department of Chemistry at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Xiao Cheng Zeng Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Structures and stability of medium silicon clusters. II. *Ab initio* molecular orbital calculations of Si₁₂–Si₂₀

X. L. Zhu, X. C. Zeng,^{a)} and Y. A. Lei

Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska 68588

B. Pan

Department of Physics, University of Science and Technology of China, Hefei, 230000, China

(Received 5 December 2003; accepted 6 February 2004)

Ab initio all-electron molecular-orbital calculations are carried out to study the structures and relative stability of low-energy silicon clusters (Si_{*n*}, *n* = 12–20). Selected geometric isomers include those predicted by Ho *et al.* [Nature (London) **392**, 582 (1998)] based on an unbiased search with tight-binding/genetic algorithm, as well as those found by Rata *et al.* [Phys. Rev. Lett. **85**, 546 (2000)] based on density-functional tight-binding/single-parent evolution algorithm. These geometric isomers are optimized at the Møller–Plesset (MP2) MP2/6-31G(*d*) level. The single-point energy at the coupled-cluster single and double substitutions (including triple excitations) [CCSD(T)] CCSD(T)/6-31G(*d*) level for several low-lying isomers are further computed. Harmonic vibrational frequency analysis at the MP2/6-31G(*d*) level of theory is also undertaken to assure that the optimized geometries are stable. For Si₁₂–Si₁₇ and Si₁₉ the isomer with the lowest-energy at the CCSD(T)/6-31G(*d*) level is the same as that predicted by Ho *et al.*, whereas for Si₁₈ and Si₂₀, the same as predicted by Rata *et al.* However, for Si₁₄ and Si₁₅, the vibrational frequency analysis indicates that the isomer with the lowest CCSD(T)/6-31G(*d*) single-point energy gives rise to imaginary frequencies. Small structural perturbation onto the Si₁₄ and Si₁₅ isomers can remove the imaginary frequencies and results in new isomers with slightly lower MP2/6-31G(*d*) energy; however the new isomers have a higher single-point energy at the CCSD(T)/6-31G(*d*) level. For most Si_{*n*} (*n* = 12–18, 20) the low-lying isomers are prolate in shape, whereas for Si₁₉ a spherical-like isomer is slightly lower in energy at the CCSD(T)/6-31G(*d*) level than low-lying prolate isomers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1690755]

I. INTRODUCTION

Over the past 15 years, medium-sized silicon clusters Si_{*n*} (*n* > 10) have attracted much attention both experimentally^{1–8} and theoretically.^{9–41} Considerable effort has been devoted to determine the ground-state geometric structures, namely, the global minima as a function of the cluster size *n*. For *n* ≤ 7, the global minima are firmly established by both *ab initio* calculations and Raman/infrared spectroscopy measurements, whereas for *n* ≤ 12 the global minima based on *ab initio* calculations^{11,16,29,30} are well accepted. For 13 ≤ *n* ≤ 24, unbiased search for the global minima has been undertaken based on either the genetic algorithm coupled with semi-empirical tight-binding (TB) technique,²³ or the single-parent evolution algorithm coupled with density-functional (DF) TB and density-functional theory (DFT) methods.^{27,38} For Si₂₅, several candidates for the lowest-energy isomers have been proposed based on *ab initio* quantum Monte Carlo²⁶ or high-level molecular orbital calculations.⁴¹ For *n* > 25, the global minima based on either semi-empirical or *ab initio* methods are largely unexplored. A recent *ab initio* investigation of the relative stability of 17 isomers of Si₃₆ has been reported.⁴⁰ It is known that as the size of cluster increases, finding the global-minimum struc-

ture becomes increasingly difficult because of the much increased complexity of the potential surface as well as the rapid increase of the number of low-energy isomers.

For silicon cation clusters Si_{*n*}⁺, ion mobility experiments have revealed a structural transition from prolate to more spherical-like geometries, which occurs in between 24 < *n* < 30.^{2,3} For neutral silicon clusters, however, photoionization experiments⁵ have shown that the prolate-to-spherical-like structural transition may occur in between 20 ≤ *n* ≤ 22. On the theoretical side, early *ab initio* calculations suggested that the critical size for the structural transition is bounded by 24 < *n* < 28.¹³ The more recent unbiased semi-empirical TB calculation in conjunction with the DFT optimization for the final structures²³ indicated that a spherical-like Si₁₉ isomer (containing an endohedral atom) becomes slightly more stable than the low-lying prolate Si₁₉ isomers.

In our previous paper (Paper I),³⁰ we reported all-electron molecular-orbital calculations of geometric structures, energies, vibrational frequencies, as well as ionization potentials for small low-lying silicon clusters (Si_{*n*}, *n* = 7–11). In this paper, we extend the all-electron molecular-orbital approach to medium-sized silicon clusters (Si_{*n*}, *n* = 12–20). Selected low-energy isomers are those predicted by Ho *et al.*²³ based on an unbiased search with TB/genetic algorithm, as well those found by Rata *et al.*²⁷ based on the unbiased search with DFTB/single-parent evolution algo-

^{a)}Electronic mail: xzeng1@unl.edu

rithm. Energies of these medium-sized clusters have been calculated only at the DF level of theory. It is thus useful and important to confirm their stability via vibrational frequency analysis and to further examine their relative stability by using high-level all-electron molecular-orbital methods.

II. COMPUTATIONAL DETAILS

As in Paper I,³⁰ we used molecular-orbital methods at the MP2/6-31G(d)//CCSD(T)/6-31G(d) level of theory, compiled in the GAUSSIAN 98 software package.⁴² The MP2/6-31G(d) level of theory is selected for geometry relaxation to approximately account for the correlation effect of all electrons to the geometric structures. Honea *et al.*⁴³ have demonstrated that the MP2/6-31G(d) level of theory is

required in order to correctly predict the tetragonal bipyramidal ground-state structure of the magic-number cluster Si_6 . The Hartree–Fock (HF) level of theory on the other hand gives rise to the ground-state structure of Si_6 to be either capped trigonal bipyramid or bicapped tetrahedron, which disagrees with the measured ground-state structure.⁴³ In previous benchmark calculations by us at the MP2/6-31G(d) level³⁰ we found that the calculated Si–Si bond lengths typically deviate from the measurements by only 0.5%. To identify the most stable isomer among nearly degenerated isomers, the CCSD(T)/6-31G(d) single-point energy calculation was performed. Moreover, for the isomer with the lowest CCSD(T)/6-31G(d) energy its stability was further examined by calculating its vibrational frequencies at the MP2/6-31G(d) level of theory. As mentioned earlier,

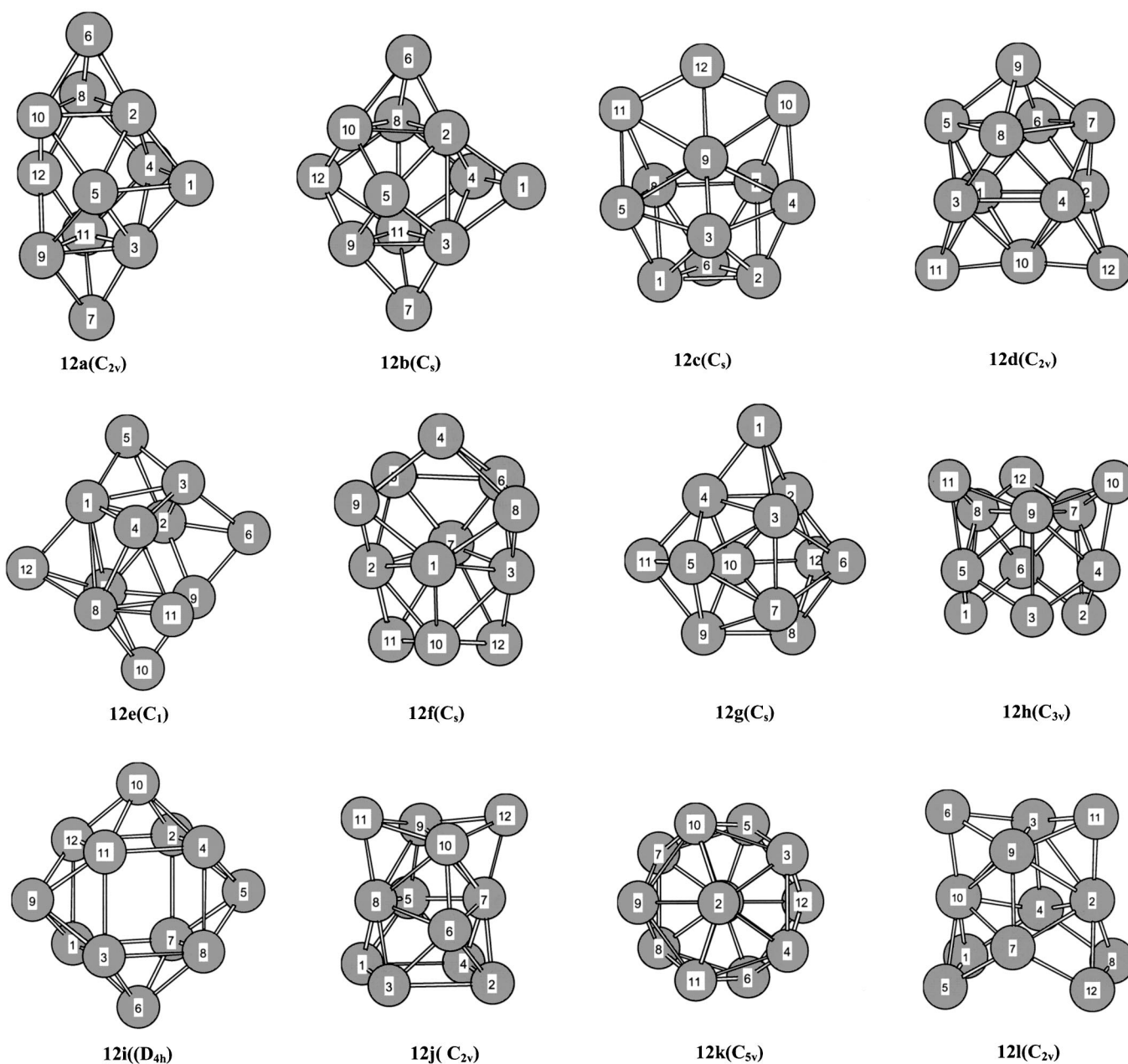


FIG. 1. Geometries of the low-energy structures of Si_{12} – Si_{20} optimized at the MP2/6-31G(d) level.

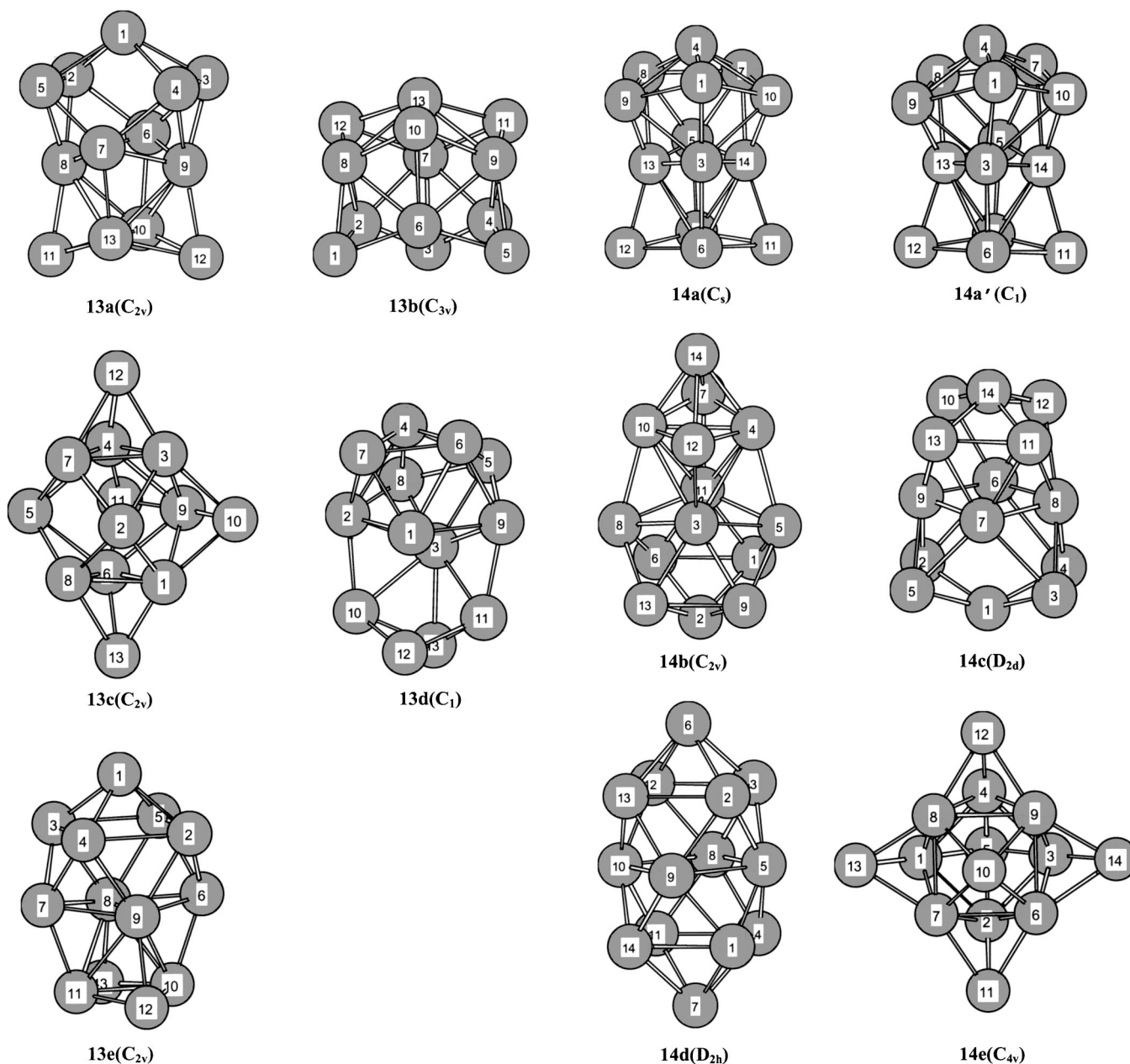


FIG. 1. (Continued.)

structures of the low-lying isomers of Si_{12} – Si_{20} have been reported in the literature,^{23,27} and some of them are possibly true global minima.

III. RESULTS AND DISCUSSIONS

The optimized geometric structures of the selected low-energy isomers Si_n ($n = 12$ – 20) are plotted in Fig. 1, where all Si–Si distances less than 2.95 Å are ascribed as Si–Si “bonds.” The single-point energies at various levels of theory are summarized in Table I. Isomers that have the lowest energy at each level of theory are listed in Table II. For the isomers with the lowest CCSD(T)/6-31G(*d*) energy their vibrational frequencies were calculated at the MP2/6-31G(*d*) level of theory. The vibrational frequency analysis confirmed that all the isomers with the lowest CCSD(T)/6-31G(*d*) energy are stable except for Si_{14} (14a)

and Si_{15} (15a). For 14a, one imaginary frequency was found while for 15a two imaginary frequencies were found, even after a tight structural optimization at the MP2/6-31G(*d*) level. To remove the imaginary frequencies, the geometry of 14a and 15a was slightly perturbed. After geometric relaxation with the perturbed structure, new isomers 14a' and 15a' were obtained, both show no imaginary frequencies. They all have slightly lower MP2/6-31G(*d*) energy but show slightly higher CCSD(T)/6-31G(*d*) energy than the original isomers (14a and 15a), respectively. The calculated vibrational frequencies for these stable isomers are listed in Table III.

A. Optimized geometric structure

1. $n = 12$

For Si_{12} cluster, the isomer with the lowest CCSD(T)/6-31G(*d*) energy, 12a, is a hexacapped trigonal

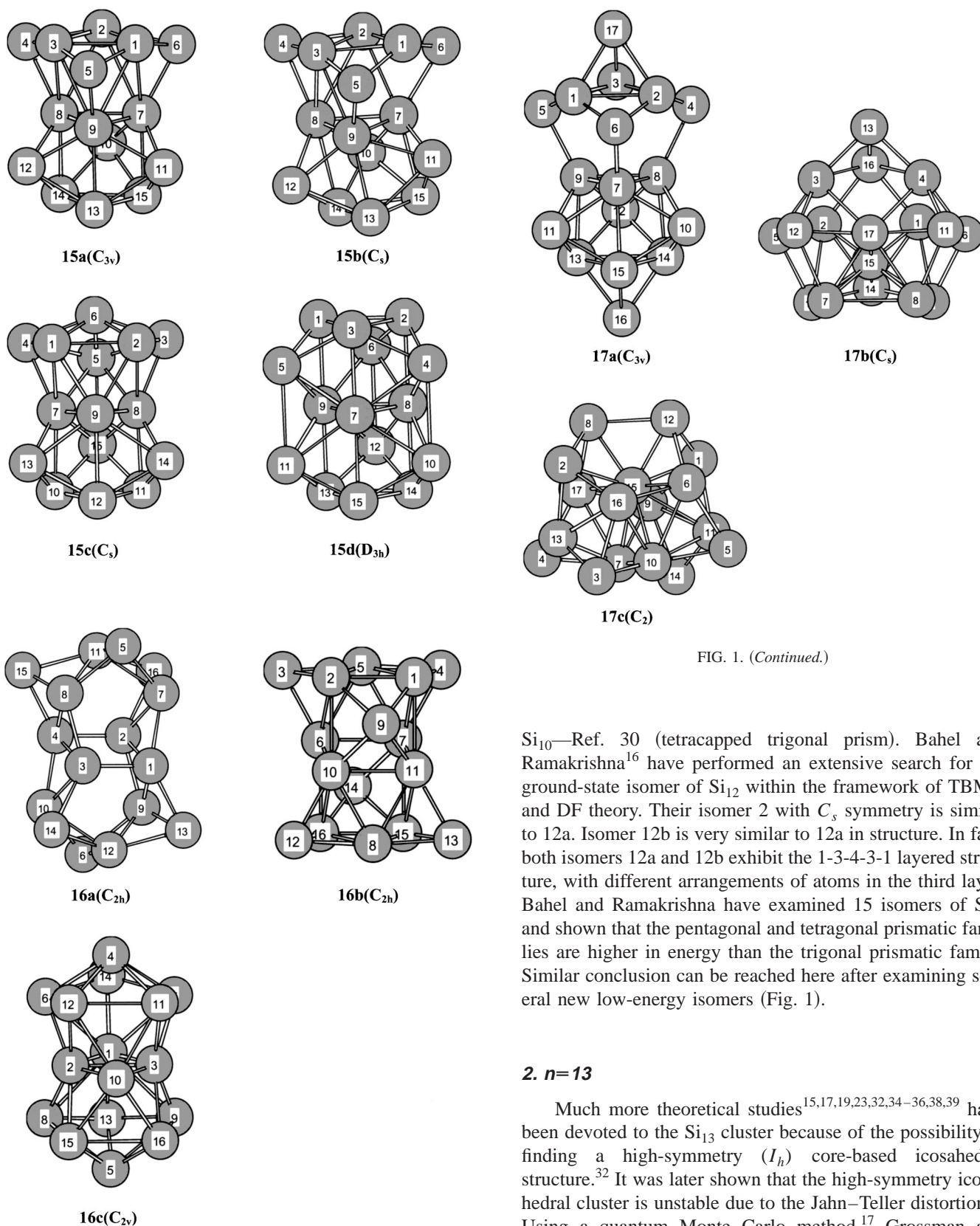


FIG. 1. (Continued.)

Si_{10} —Ref. 30 (tetracapped trigonal prism). Bahel and Ramakrishna¹⁶ have performed an extensive search for the ground-state isomer of Si_{12} within the framework of TBMD and DF theory. Their isomer 2 with C_s symmetry is similar to 12a. Isomer 12b is very similar to 12a in structure. In fact, both isomers 12a and 12b exhibit the 1-3-4-3-1 layered structure, with different arrangements of atoms in the third layer. Bahel and Ramakrishna have examined 15 isomers of Si_{12} and shown that the pentagonal and tetragonal prismatic families are higher in energy than the trigonal prismatic family. Similar conclusion can be reached here after examining several new low-energy isomers (Fig. 1).

2. $n=13$

Much more theoretical studies^{15,17,19,23,32,34–36,38,39} have been devoted to the Si_{13} cluster because of the possibility of finding a high-symmetry (I_h) core-based icosahedral structure.³² It was later shown that the high-symmetry icosahedral cluster is unstable due to the Jahn–Teller distortion.³⁵ Using a quantum Monte Carlo method,¹⁷ Grossman and Mitas investigated several isomers of Si_{13} and found that the C_{3v} trigonal antiprism isomer 13b is more stable than the core-based icosahedral $\text{Si}_{13}(I_h)$. Here we also confirmed that the core-based icosahedral Si_{13} is unstable. The most stable structure, 13a, is identical to the reported lowest-energy structure based on DF-TB calculation.¹⁹ Isomer 13a can be described as a distorted tricapped trigonal prism with an ad-

prism with C_{2v} symmetry as previously predicted via TB calculations^{16,23} as well as *ab initio* Car-Parrinello molecular dynamics simulated annealing.²⁹ 12a can be constructed by adding two capping atoms to the global-minimum of

FIG. 1. (Continued.)

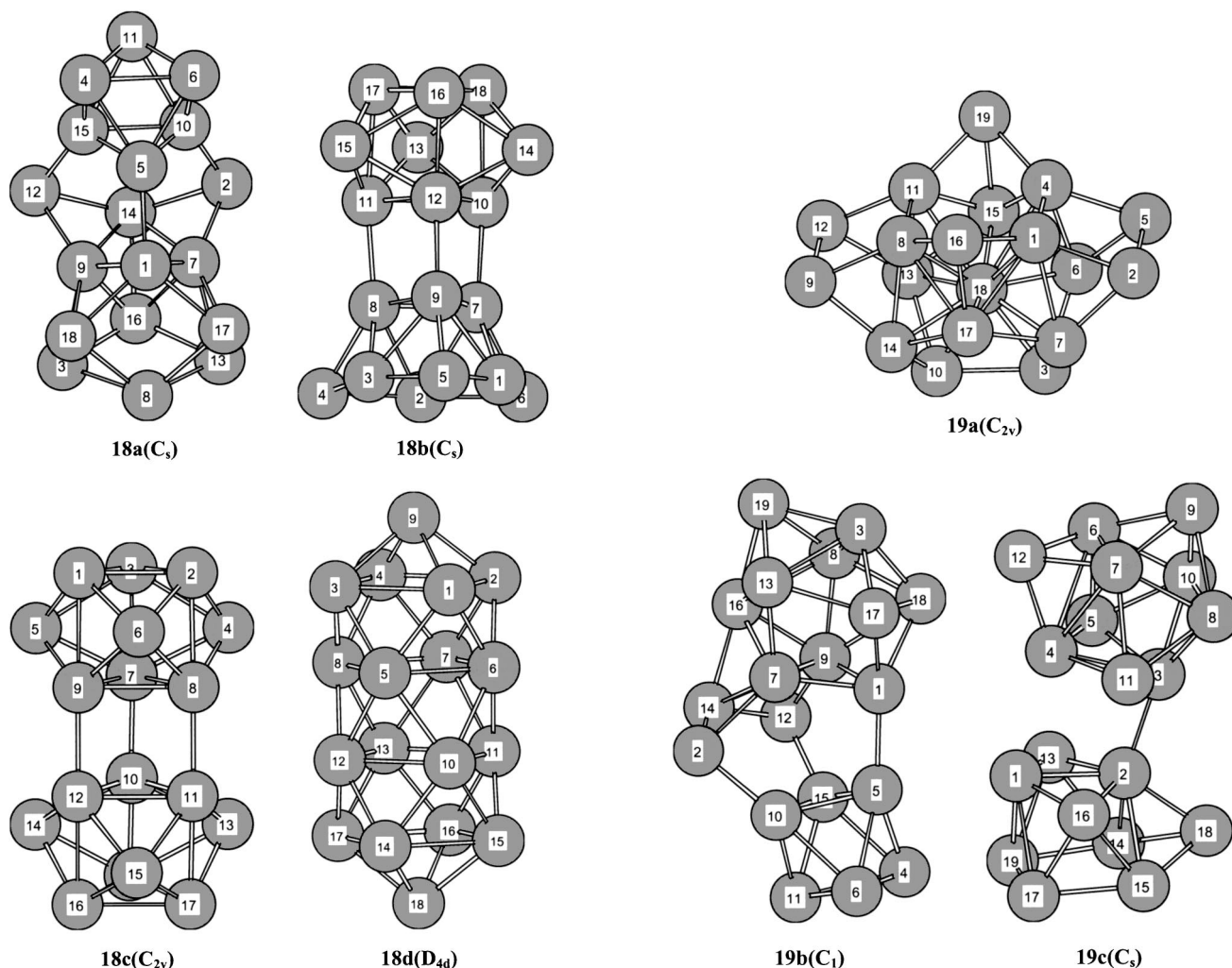


FIG. 1. (Continued.)

ditional rhombus capped on one edge of the prism. Ho *et al.*^{23,29} have found that the lowest-energy isomer of Si_{13} has C_s symmetry, which can be viewed as a slightly distorted $13a(C_{2v})$. The C_{3v} capped trigonal antiprism,¹⁷ $13b$, is slightly higher in energy than $13a$ [0.16 eV at the CCSD(T)/6-31G(*d*) level]. Isomers based on capped trigonal prism motif ($13c$ and $13d$) are also very close in energy to $13a$. Like $13a$, isomer $13e$ has a stacking sequence of three rhombi with a capped atom but $13e$ is higher in energy than $13a$.

3. $n=14$

For Si_{14} cluster, a number of low-lying isomers have been reported in the literature.^{15,19,23,38,39} General consensus was that the isomer $14a(C_s)$ found by Sieck *et al.*¹⁹ is possibly the global minimum. $14a$ has two stacked rhombi with distortion and one fivefold ring capped with an atom. As mentioned earlier, it is found that at the MP2/6-31G(*d*) level of theory, the vibrational frequency analysis indicates isomer $14a$ has one imaginary frequency. A structural perturbation followed by geometry relaxation gives isomer $14a'(C_1)$ which is very close in structure to $14a$. $14a'$ also exhibits a stacking sequence of two distorted rhombi, one fivefold ring,

and an atom on top. Isomers $14b$, $14c$, and $14d$ all exhibit a stacking sequence of three (distorted) rhombi with one atom on top and one at the bottom. Their energy is much higher than $14a$ and $14a'$. Isomer $14e$ has a capped trigonal-prism unit and is also much higher in energy than $14a$ and $14a'$.

4. $n=15$

For Si_{15} cluster, the low-lying clusters ($15a$ – $15d$) all contain the capped trigonal-prism unit, as revealed from the unbiased TB search.²³ The isomer having the lowest energy at the CCSD(T)/6-31G(*d*) level is $15a(C_{3v})$ whose geometry is a tricapped trigonal prism fused with a tricapped trigonal antiprism. It has been reported that the calculated mobility of isomer $15a$ agreed with the mobility measurements.²³ However, vibrational frequency analysis at the MP2/6-31G(*d*) level shows that $15a$ has two imaginary frequencies. Thus, isomer $15a(C_{3v})$ may not be a stable structure but a transition-state structure at the MP2/6-31G(*d*) level of theory. As mentioned earlier a structural perturbation to $15a$ followed by geometry relaxation gives rise to isomer $15a'$ with C_s symmetry. $15a'$ shows no imaginary frequency and its MP2 energy is 0.025 eV lower than that of $15a$ but its CCSD(T) energy becomes 0.19 eV higher than that of $15a$.

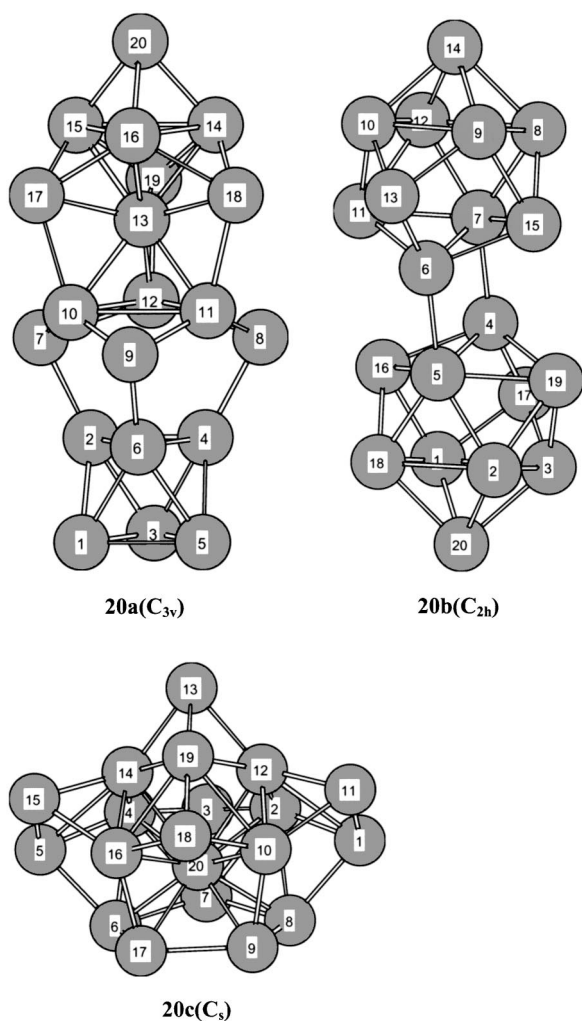


FIG. 1. (Continued.)

5. $n=16$ and 17

For Si₁₆ cluster, it is found that 16a with C_{2h} symmetry gives the lowest energy at the CCSD(T)/6-31G(d) level, similar to the prediction by Ho *et al.*²³ 16a can be described as two fused pentagonal prisms. Its structure is unique in the sense that it is neither based on the tricapped trigonal-prism motif (as 16b) nor based on a stacking sequence of fourfold and fivefold rings with capping atoms (as 16c). On the other hand, for Si₁₇ cluster, 17a with C_{3v} symmetry is possibly the lowest-energy structure as predicted by Ho *et al.*²³ and it does contain a tricapped-trigonal-prism (TTP) unit and a *hexagonal-chair* unit. The six-atom hexagonal-chair unit can be viewed as a fragment in bulk diamond silicon.⁹ It is interesting to note that the more spherical-like Si₁₇ isomer, 17c, is very competitive in stability compared to the prolate-shaped isomer 17a.

6. $n=18$

For Si₁₈ cluster, four low-lying isomers considered are shown in Fig. 1. The elongated 18a has the lowest-energy at the CCSD(T)/6-31G(d) level. 18a has the structure similar to the ground-state structure of Si₁₈⁺, predicted-by Rata *et al.*²⁷ It contains a magic-number-cluster Si₆ unit and a hexagonal-

chair unit. Another previously predicted lowest-energy isomer of Si₁₈ with C_{3v} symmetry gives imaginary frequencies at the MP2/6-31G(d) level. Again, a slight structural perturbation to this C_{3v} isomer followed by geometry relaxation gives isomer 18b with C_s symmetry. Both 18b and 18c contain tricapped-trigonal-prism unit and both are very competitive in stability compared to 18a. 18d is a new isomer with high symmetry but relatively high energy. It is composed of two capped tetragonal antiprisms.

7. $n=19$

For Si₁₉ cluster, a spherical-like isomer 19a was found by Ho *et al.*²³ The isomer 19b which contains a tetra-capped-trigonal-prism unit and a magic-number-cluster Si₆ unit is very competitive in stability compared with 19a. 19b was found based on a novel single-parent evolution algorithm coupled with DFTB/DFT methods. Isomer 19c²³ is composed of a TTP unit and a Si₁₀ (bicapped tetrahedral antiprism) unit. Its energy is slightly higher than both 19a and 19b.

8. $n=20$

Finally, for Si₂₀ cluster, the lowest-energy isomer appears to be 20a, as predicted by Rata *et al.*²⁷ from the unbiased DFTB search. 20a is composed of three units: a magic-number cluster Si₆ unit, a hexagonal-chair unit in the middle, and a low-energy isomer of Si₈ unit (see isomer 8f in Ref. 30). 20b is another low-lying isomer which is composed of two Si₁₀ (bicapped tetrahedral antiprism) units. 20b was first predicted by Mitas *et al.*²⁶ on the basis of quantum Monte Carlo calculation. Isomer 20c²³ exhibits compact spherical-like structure and its energy is slightly higher than both prolate-shaped isomer 20a and 20b.

B. Relative stability, binding energy, and ionization potential

As shown in Tables I and II, unequivocal determination of the lowest-energy cluster can be very tricky sometimes if only low-level *ab initio* calculation of the single-point energies is considered. Taking Si₁₃ as an example, one can see from Tables I and II that the HF energies indicate 13c has the lowest energy, but MP2 energies indicated 13d has the lowest energy, and MP3 energies show 13c has the lowest energy. However, MP4, CCSD, and CCSD(T) energies can lead to consistent prediction, that is, 13a has the lowest energy. This example demonstrates the sensitivity of low-lying structures to the electron correlation effect. It is known that MP2 and MP3 levels of theory can only partially account for the correlation effects whereas CCSD(T) calculation provides much more reliable prediction to the relative stability among low-lying isomers. It is interesting to note from Table II that there exists some systematic correlation between HF, MP3, CCSD, and DFT energies,^{23,27} particularly for larger clusters. Namely, the isomer (optimized at the MP2 level) with the lowest HF energy is likely to have lowest MP3, CCSD, and DFT energies.

One can also see from Table II that the spherical-like compact isomers (for $n > 13$), such as 14e, 17b, 17c, and 20c, are generally higher in energy than the prolate-shaped

TABLE I. Energies of low-energy isomers of Si₁₂–Si₂₀ (optimized at the MP2/6-31G* level).

Cluster	Isomer (PG)	Energy (hartrees)					
		HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4(SDQ)/6-31G*	CCSD/6-31G*	CCSD(T)/6-31G*
Si ₁₂	12a(C _{2v})	-3466.755 12	-3467.975 20	-3467.873 03	-3467.967 18	-3467.925 73	-3468.039 85
	12b(C _s)	-3466.722 41	-3467.963 59	-3467.840 17	-3467.947 30	-3467.900 60	-3468.020 69
	12c(C _s)	-3466.685 83	-3467.947 08				
	12d(C _{2v})	-3466.729 86	-3467.940 23				
	12e(C ₁)	-3466.748 50	-3467.939 46				
	12f(C _s)	-3466.681 04	-3467.921 39				
	12g(C _s)	-3466.718 23	-3467.914 83				
	12h(C _{3v})	-3466.679 83	-3467.911 27				
	12i(D _{4h})	-3466.560 63	-3467.909 96				
	12j(C _{2v})	-3466.691 96	-3467.908 72				
	12k(C _{5v})	-3466.638 61	-3467.907 09				
	12l(C _{2v})	-3466.685 52	-3467.890 61				
Si ₁₃	13a(C _{2v})	-3755.630 03	-3756.969 13	-3756.843 36	-3756.961 60	-3756.908 11	-3757.036 72
	13b(C _{3v})	-3755.613 27	-3756.977 66	-3756.824 69	-3756.955 55	-3756.896 45	-3757.030 83
	13c(C _{2v})	-3755.649 18	-3756.930 09	-3756.854 41	-3756.943 09	-3756.904 97	-3757.022 06
	13d(C ₁)	-3755.565 51	-3756.980 07	-3756.781 47	-3756.955 25	-3756.873 12	-3757.014 30
	13e(C _{2v})	-3755.613 19	-3756.947 00				
Si ₁₄	14a(C _s)	-4044.550 49	-4046.001 55	-4045.850 63	-4045.996 09	-4045.929 42	-4046.067 46
	14a'(C ₁)	-4044.549 18	-4046.001 86	-4045.849 48	-4045.995 11	-4045.928 43	-4046.066 82
	14b(C _{2v})	-4044.466 78	-4045.975 63				
	14c(D _{2d})	-4044.365 01	-4045.944 39				
	14d(D _{2h})	-4044.425 21	-4045.917 31				
	14e(C _{4v})	-4044.503 95	-4045.888 55				
Si ₁₅	15a(C _{3v})	-4333.464 12	-4335.016 53	-4334.848 31	-4335.016 94	-4334.939 23	-4335.086 44
	15a'(C _s)	-4333.444 66	-4335.017 45	-4334.830 50	-4335.013 83	-4334.928 46	-4335.079 36
	15b(C _s)	-4333.402 89	-4335.027 13	-4334.794 94	-4335.016 22	-4334.908 69	-4335.066 69
	15c(C _s)	-4333.396 23	-4335.030 09	-4334.785 67	-4335.017 92	-4334.904 74	-4335.064 65
	15d(D _{3h})	-4333.389 59	-4335.012 06	-4334.773 87	-4335.003 14	-4334.891 48	-4335.050 33
Si ₁₆	16a(C _{2h})	-4622.409 70	-4623.982 20	-4623.892 15	-4623.989 11	-4623.947 98	-4624.094 66
	16b(C _{2h})	-4622.328 90	-4624.003 51	-4623.802 57	-4623.990 84	-4623.904 56	-4624.065 19
	16c(C _{2v})	-4622.308 09	-4623.991 82				
Si ₁₇	17a(C _{3v})	-4911.262 79	-4913.021 83	-4912.843 92	-4913.015 17	-4912.938 19	-4913.109 87
	17b(C _s)	-4911.085 31	-4913.017 72				
	17c(C ₂)	-4911.272 45	-4912.988 60	-4912.842 80	-4913.003 12	-4912.930 85	-4913.097 69
Si ₁₈	18a(C _s)	-5200.198 16	-5202.012 29	-5201.870 16	-5202.022 00	-5201.951 84	-5202.120 28
	18b(C _s)	-5200.170 90	-5202.010 44	-5201.841 68	-5202.012 37	-5201.933 47	-5202.105 80
	18c(C _{2v})	-5200.119 61	-5202.022 97	-5201.798 54	-5202.007 00	-5201.909 60	-5202.092 00
	18d(D _{4d})	-5199.976 08	-5201.983 73				
Si ₁₉	19a(C _{2v})	-5489.093 55	-5491.036 04	-5490.844 01	-5491.043 98	-5490.950 71	-5491.139 59
	19b(C ₁)	-5489.087 92	-5491.015 05	-5490.850 28	-5491.022 91	-5490.943 26	-5491.124 99
	19c(C _s)	-5488.942 44	-5490.992 57	-5490.714 92	-5490.975 24	-5490.849 03	
Si ₂₀	20a(C _{3v})	-5778.056 91	-5780.033 42	-5779.906 77	-5780.049 79	-5779.986 42	-5780.167 09
	20b(C _{2h})	-5777.975 42	-5780.062 29	-5779.839 27	-5780.057 63	-5779.953 16	-5780.150 34
	20c(C _s)	-5777.964 21	-5780.061 31	-5779.811 13	-5780.057 83	-5779.939 69	

TABLE II. Lowest-energy isomers predicted based on various levels of theory.

Cluster	HF	MP2	MP3	MP4(SDQ)	CCSD	CCSD(T)	DFT ^{a,b}
Si ₁₂	12a	12a	12a	12a	12a	12a	12a
Si ₁₃	13c	13d	13c	13a	13a	13a	13a
Si ₁₄	14a	14a'	14a	14a	14a	14a	14a
Si ₁₅	15a	15c	15a	15c	15a	15a	15a
Si ₁₆	16a	16b	16a	16b	16a	16a	16a
Si ₁₇	17c	17a	17a	17a	17a	17a	17a
Si ₁₈	18a	18c	18a	18a	18a	18a	18a
Si ₁₉	19a	19a	19b	19a	19a	19a	19b
Si ₂₀	20a	20b	20a	20c	20a	20a	20a

^aReference 23.^bReference 27.

TABLE III. Vibrational frequencies (cm^{-1}), IR intensities, and zero-point energies (ZPEs) of the stable isomers with the lowest CCSD(T)/6-31G* energy.

Cluster	Isomer (PG)	Vibrational frequencies (IR intensities)			ZPE (eV)
Si ₁₂	12a(C _{2v})	98.3(0.29)	136.9(0.01)	138.0(0.05)	0.55
		150.7(0.77)	180.3(4.42)	220.1(0.02)	
		229.1(0.70)	254.5(0.18)	260.1(1.22)	
		275.9(0.54)	287.0(0.01)	291.4(5.39)	
		310.1(1.35)	310.6(1.30)	324.5(0.06)	
		353.2(2.66)	357.3(3.23)	362.2(0.02)	
		363.5(0.39)	364.5(0.35)	408.7(0.89)	
		420.5(2.51)	505.3(0.04)	550.0(2.98)	
		555.0(3.76)			
		Si ₁₃	13a(C _{2v})	38.6(0.01)	
154.4(1.46)	167.7(0.16)			212.6(3.72)	
228.3(0.92)	230.7(0.05)			240.9(1.46)	
279.2(0.60)	297.3(2.11)			310.4(7.38)	
322.9(3.57)	326.0(3.33)			334.4(0.31)	
355.7(5.70)	384.4(0.01)			392.5(0.93)	
394.4(0.02)	430.8(5.86)			437.1(3.32)	
501.2(0.01)	505.4(1.79)				
Si ₁₄	14a'(C ₁)	46.2(0.11)	81.1(2.10)	86.2(0.85)	0.63
		103.4(1.02)	146.3(0.57)	156.7(0.48)	
		164.4(0.51)	185.3(0.42)	187.8(1.47)	
		195.3(0.22)	207.5(0.87)	213.4(1.03)	
		225.3(0.24)	233.7(10.55)	246.1(2.04)	
		258.6(0.96)	271.3(0.10)	279.6(1.48)	
		283.6(0.67)	293.8(1.94)	300.6(0.07)	
		315.6(11.51)	328.1(2.06)	333.7(1.12)	
		349.3(3.07)	358.2(1.64)	359.7(10.67)	
		375.2(1.39)	394.9(0.32)	403.4(3.59)	
		428.5(0.99)	437.5(1.63)	443.1(2.42)	
		455.1(2.62)	470.3(1.57)	479.5(1.00)	
Si ₁₅	15a'(C _s)	44.9(4.13)	50.8(0.12)	81.5(0.14)	0.69
		112.8(0.22)	125.3(0.15)	136.7(0.09)	
		170.2(3.72)	179.6(0.09)	187.3(2.38)	
		191.6(2.62)	198.6(0.77)	200.3(0.87)	
		204.7(4.25)	210.6(0.34)	230.2(2.77)	
		233.8(1.60)	252.2(0.27)	261.6(2.90)	
		272.4(2.25)	283.0(0.29)	286.2(0.38)	
		292.9(6.54)	295.8(5.84)	318.6(0.91)	
		331.8(20.16)	335.2(3.88)	342.4(9.92)	
		368.2(17.14)	373.0(3.42)	387.1(0.18)	
		400.9(6.66)	410.8(37.00)	430.5(2.23)	
		445.5(95.47)	463.1(3.06)	473.7(1.33)	
		480.7(0.80)	525.1(2.35)	537.8(6.19)	
Si ₁₆	16a(C _{2h})	80.1(0.14)	81.0(0.12)	101.6(0.11)	0.77
		152.5(0.76)	162.6(1.77)	167.9(1.15)	
		220.5(0.18)	229.5(1.31)	267.2(3.87)	
		270.1(1.08)	277.0(1.10)	283.3(6.66)	
		350.3(3.68)	355.5(0.12)	366.2(0.11)	
		417.3(1.03)	418.2(6.19)	433.8(1.32)	
		462.3(0.06)	495.5(2.62)	521.3(1.00)	
Si ₁₇	17a(C _{3v})	64.3(0.04)	93.7(0.45)	105.0(204.35)	0.78
		150.3(0.03)	153.6(0.10)	175.3(55.71)	
		208.0(0.37)	209.8(0.37)	218.8(1.78)	
		227.9(37.24)	246.0(2.86)	264.6(1.05)	
		269.2(1.38)	282.8(0.43)	284.8(6.04)	
		330.4(1.14)	354.3(6.26)	362.5(1.33)	
		372.3(0.52)	375.3(7.66)	406.6(0.27)	

TABLE III. (Continued.)

Cluster	Isomer (PG)	Vibrational frequencies (IR intensities)			ZPE (eV)
Si ₁₈	18a(C _s)	421.1(5.67)	451.2(19.99)	451.7(0.91)	0.85
		488.5(5.46)	499.4(1.34)		
		35.7(0.06)	87.9(0.06)	92.5(0.18)	
		116.3(0.12)	120.3(3.53)	124.5(0.14)	
		135.0(5.88)	156.6(0.09)	164.2(1.23)	
		173.6(0.02)	181.8(0.87)	186.8(0.33)	
		191.8(1.11)	213.8(6.07)	214.5(0.31)	
		218.7(0.18)	230.7(0.05)	241.5(2.61)	
		253.4(0.68)	257.3(0.28)	258.7(2.26)	
		263.0(0.99)	281.6(0.03)	282.4(2.67)	
		292.9(3.91)	296.7(0.08)	323.2(8.60)	
		337.1(3.17)	344.2(0.18)	348.2(3.76)	
		356.7(11.05)	362.6(3.83)	366.4(2.24)	
		370.9(2.78)	379.8(0.01)	390.8(3.29)	
396.6(0.49)	404.1(4.65)	412.9(3.19)			
426.3(7.13)	429.0(0.73)	430.6(4.28)			
458.2(3.23)	462.3(0.31)	491.1(1.28)			
503.7(5.03)	550.2(11.05)				
Si ₁₉	19a(C _{2v})	28.5(0.79)	76.4(0.11)	129.7(0.01)	0.89
		143.8(0.23)	156.4(0.04)	162.9(0.97)	
		169.6(0.13)	187.0(0.18)	192.1(2.41)	
		212.5(0.05)	212.8(0.01)	219.8(0.13)	
		233.2(5.02)	233.9(0.46)	244.5(1.26)	
		245.9(0.05)	253.6(1.60)	281.6(3.72)	
		289.0(4.33)	294.7(2.77)	298.3(0.01)	
		313.5(1.94)	316.8(0.20)	345.7(0.02)	
		362.4(0.26)	381.1(0.72)	385.5(0.27)	
		390.1(1.23)	418.0(3.55)	418.3(4.21)	
		420.5(3.50)	430.7(5.62)	445.5(5.65)	
		445.8(12.03)	467.1(0.46)	475.2(3.89)	
		483.9(1.88)	505.2(0.47)		
		Si ₂₀	20a(C _{3v})	60.5(0.11)	
147.8(0.17)	189.6(0.05)			199.55(0.31)	
218.4(0.10)	219.6(0.34)			228.6(0.05)	
246.8(0.98)	265.5(0.62)			274.1(0.96)	
279.3(3.09)	307.2(3.93)			308.5(1.45)	
335.0(2.00)	338.8(19.11)			349.1(4.66)	
353.7(14.56)	360.1(0.54)			380.9(1.68)	
385.7(3.00)	413.4(6.03)			435.6(2.69)	
457.4(1.59)	464.2(0.74)			548.5(25.78)	

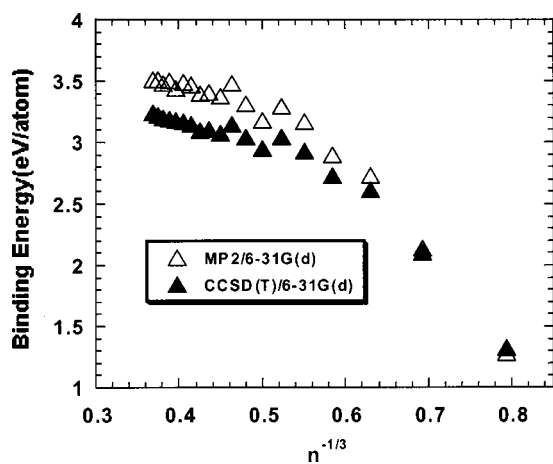


FIG. 2. Correlation of the binding energy per atom with $n^{-1/3}$ for the isomer of Si_n ($n = 12-20$) with lowest energy at the CCSD(T)/6-31G(d) level.

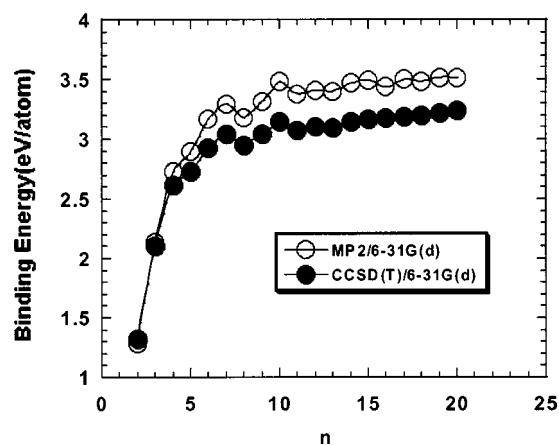


FIG. 3. Binding energy per atom of the isomer of Si_n ($n = 12-20$) with the lowest energy at the CCSD(T)/6-31G(d) level vs cluster size n .

TABLE IV. Vertical ionization potentials (IP_v) of the isomer of Si_{12} – Si_{20} with the lowest CCSD(T)/6-31G* energy.

Cluster	Isomer	PG (state)	IP_v (Calc.) (eV)	IP (Expt.) ^a (eV)
Si_{12}	12a	C_{2v}	7.247	7.17–7.46
Si_{13}	13a	C_{2v}	7.523	7.17–7.46
Si_{14}	14a'	C_1	7.487	7.17–7.46
Si_{15}	15a'	C_s	7.224	7.17–7.46
Si_{16}	16a	C_{2h}	6.589	6.80–6.94
Si_{17}	17a	C_{3v}	7.182	7.46–7.53
Si_{18}	18a	C_s	7.012	6.80–6.94
Si_{19}	19a	C_{2v}	6.463	6.80–6.94
Si_{20}	20a	C_{3v}	7.392	7.46–7.53

^aReference 5

isomers. One exception is the isomer 19a of Si_{19} . In Fig. 2 we plot the binding energies of the lowest-energy isomers of Si_{12} – Si_{20} as a function of $n^{-1/3}$ where n is the cluster size. The deviation from the linear behavior for the binding-energy versus $n^{-1/3}$ curve suggests the growth pattern of the low-lying medium-sized (Si_{12} – Si_{20}) clusters deviates from the spherical growth pattern.⁴⁴ Indeed, ion mobility measurements^{2,3} for Si_n^+ indicate that the appearance of spherical-like compact clusters only occurs for $n > 23$. In Fig. 3 we plot the binding energy per atom as a function of the cluster size n . Two “bumps” can be seen at $n = 6, 7$, and 10, corresponding to the magic-number clusters Si_6 , Si_7 , and Si_{10} . For $n > 10$, the binding energy per atom increases rather smoothly as a function of the cluster size n .

Finally, in Table IV, we present the calculated vertical ionization potential (IP) at the MP2/6-31G(*d*) level for isomers with the lowest CCSD(T)/6-31G(*d*) energy. Measurement of the IPs has been reported by Fuke *et al.*⁵ The measured IPs show an appreciable gap in between $n = 20$ and 22, suggesting certain structural transition may occur for the neutral silicon clusters within this size range. The calculated vertical ionization potentials appear to correlate with the measured values reasonably well. For example, the vertical IP of the cluster 16a, 18a, and 19a is appreciably lower in value than the IP of their neighbor clusters, consistent with the measurement.

IV. CONCLUSIONS

We have studied low-energy structures of Si_{12} – Si_{20} at the MP2/6-31G(*d*) level and their energies at the CCSD(T)/6-31G(*d*) level. The vibrational frequency analysis has been used to affirm the stability of the lowest-energy structures of Si_{12} – Si_{20} . The calculated vertical IP for the lowest-energy isomer of Si_{12} – Si_{20} is mostly in good agreement with the measurement. The binding energy per atom as a function of $n^{-1/3}$ indicates that the low-lying Si_{12} – Si_{20} clusters follow a nonspherical growth pattern.

We note that the lowest-energy structures of Si_{12} – Si_{15} and Si_{17} all contain the TTP Si_9 unit. Although the TTP Si_9 unit is not a stand-alone local minimum, it appears to be a favorable building block²³ for medium-sized clusters Si_{12} – Si_{18} . On the other hand, beginning with Si_{18} inclusion of the magic-number-cluster Si_6 unit as well as the

hexagonal-chair unit appears to be energetically favorable over the inclusion of the TTP Si_9 unit. The fact that a spherical-like Si_{19} isomer can be lower in energy at the CCSD(T)/6-31G(*d*) level of theory than low-lying prolate-shaped isomers requires further investigation with larger basis sets. Another finding that may require further study is that some isomers (14a and 15a) with the lowest energy at CCSD(T)/6-31G(*d*) level can give imaginary vibrational frequencies, i.e., they could be transition-state structure. Slight structural distortion can remove the imaginary frequencies and lower the MP2 energy but can result in slightly higher CCSD(T) energy.

ACKNOWLEDGMENTS

We are very grateful for valuable discussions with Dr. Alex Shvartsburg, Dr. C.-Z. Wang, Professor K.-M. Ho, Professor Jin-Yan Zeng, and Soohaeng Yoo. This work is supported by the National Science Foundation and by the Research Computing Facility at the University of Nebraska–Lincoln.

- ¹Y. Liu, Q.-L. Zhang, F. K. Tittel, R. F. Curl, and R. E. Smalley, *J. Chem. Phys.* **85**, 7434 (1986); J. L. Elkind, J. M. Alford, F. D. Weiss, R. T. Laaksonene, and R. E. Smalley, *ibid.* **87**, 2397 (1987); Q. L. Zhang, Y. Liu, R. F. Curl, F. K. Tittel, and R. E. Smalley, *ibid.* **88**, 1670 (1988).
- ²M. F. Jarrold, *Science* **252**, 1085 (1991); M. F. Jarrold and V. A. Constant, *Phys. Rev. Lett.* **67**, 2994 (1991); M. F. Jarrold and J. E. Bower, *J. Chem. Phys.* **96**, 9180 (1992).
- ³R. R. Hudgins, M. Imai, M. F. Jarrold, and P. Dugourd, *J. Chem. Phys.* **111**, 7865 (1999); A. A. Shvartsburg, R. R. Hudgins, P. Dugourd, and M. F. Jarrold, *Chem. Soc. Rev.* **30**, 36 (2001).
- ⁴K.-D. Rinnen and M. L. Mandich, *Phys. Rev. Lett.* **69**, 1823 (1992).
- ⁵K. Fuke, K. Tsukamoto, F. Misaizu, and M. Sanekata, *J. Chem. Phys.* **99**, 7807 (1993).
- ⁶S. Li, R. J. Van Zee, W. Weltner, Jr., and K. Raghavachari, *Chem. Phys. Lett.* **243**, 275 (1995).
- ⁷B. Marsen, M. Lonfat, P. Scheier, and K. Sattler, *Phys. Rev. B* **62**, 6892 (2000).
- ⁸D. E. Bergeron and A. W. Castleman, Jr., *J. Chem. Phys.* **117**, 3219 (2002).
- ⁹D. Tomanek and M. A. Schluter, *Phys. Rev. Lett.* **56**, 1055 (1986); *Phys. Rev. B* **36**, 1208 (1987).
- ¹⁰E. Kaxiras, *Phys. Rev. Lett.* **64**, 551 (1990).
- ¹¹C. M. Rohlfing and K. Raghavachari, *Chem. Phys. Lett.* **198**, 521 (1990); *ibid.* **198**, 521 (1992).
- ¹²B. C. Bolding and H. C. Andersen, *Phys. Rev. B* **41**, 10568 (1990).
- ¹³E. Kaxiras and K. Jackson, *Phys. Rev. Lett.* **71**, 727 (1993).
- ¹⁴P. Ordej, D. Lebedenko, and M. Menon, *Phys. Rev. B* **50**, 5645 (1994).
- ¹⁵I. H. Lee, K. J. Chang, and Y. H. Lee, *J. Phys.: Condens. Matter* **6**, 741 (1994).
- ¹⁶A. Bahel and M. V. Ramakrishna, *Phys. Rev. B* **51**, 13849 (1995); M. V. Ramakrishna and A. Bahel, *J. Chem. Phys.* **104**, 9833 (1996).
- ¹⁷J. C. Grossman and L. Mitos, *Phys. Rev. Lett.* **95**, 1323 (1995).
- ¹⁸M. R. Pederson, K. Jackson, D. V. Porezag, Z. Hajnal, and Th. Frauenheim, *Phys. Rev. B* **54**, 2863 (1996).
- ¹⁹A. Sieck, D. Porezag, Th. Frauenheim, M. R. Pederson, and K. Jackson, *Phys. Rev. A* **56**, 4890 (1997).
- ²⁰M. Menon and K. R. Subbaswamy, *Phys. Rev. B* **51**, 17952 (1995).
- ²¹J. Song, S. E. Ulloa, and D. A. Drabold, *Phys. Rev. B* **53**, 8042 (1996).
- ²²I. Vasiliev, S. Ogut, and J. R. Chelikowsky, *Phys. Rev. Lett.* **78**, 4805 (1997).
- ²³K.-M. Ho, A. A. Shvartsburg, B. Pan, Z.-Y. Lu, C.-Z. Wang, J. G. Wacker, J. L. Fye, and M. F. Jarrold, *Nature (London)* **392**, 582 (1998); B. Liu, Z.-Y. Lu, B. Pan, C.-Z. Wang, K.-M. Ho, A. A. Shvartsburg, and M. F. Jarrold, *J. Chem. Phys.* **109**, 9401 (1998).
- ²⁴A. A. Shvartsburg, M. F. Jarrold, B. Liu, Z.-Y. Lu, C.-Z. Wang, and K.-M. Ho, *Phys. Rev. Lett.* **81**, 4616 (1998).
- ²⁵U. Rothlisberger, W. Andreoni, and M. Parrinello, *Phys. Rev. Lett.* **72**, 665 (1994).

- ²⁶L. Mitas, J. C. Grossman, I. Stich, and J. Tobik, *Phys. Rev. Lett.* **84**, 1479 (2000).
- ²⁷I. Rata, A. A. Shvartsburg, M. Horoi, Th. Frauenheim, K. W. M. Siu, and K. A. Jackson, *Phys. Rev. Lett.* **85**, 546 (2000).
- ²⁸B. X. Li and P. L. Cao, *Phys. Rev. A* **62**, 023201 (2000).
- ²⁹Z.-Y. Lu, C.-Z. Wang, and K.-M. Ho, *Phys. Rev. B* **61**, 2329 (2001).
- ³⁰X. Zhu and X. C. Zeng, *J. Chem. Phys.* **118**, 3558 (2003).
- ³¹J. R. Chelikowsky, *Phys. Rev. Lett.* **60**, 2669 (1988).
- ³²J. R. Chelikowsky and J. C. Philips, *Phys. Rev. Lett.* **63**, 1653 (1989).
- ³³K. Raghavachari, *Phase Transitions* **24-26**, 61 (1990).
- ³⁴U. Rothlisberger, W. Andreoni, and P. Giannozzi, *J. Chem. Phys.* **96**, 1248 (1992).
- ³⁵B.-L. Gu, Z.-Q. Li, and J.-L. Zhu, *J. Phys.: Condens. Matter* **5**, 5255 (1993).
- ³⁶B. C. Pan, C. Z. Wang, D. E. Turner, and K.-M. Ho, *Chem. Phys. Lett.* **292**, 75 (1998).
- ³⁷K. Jackson, M. Pederson, C.-Z. Wang, and K.-M. Ho, *Phys. Rev. A* **59**, 3685 (1999).
- ³⁸B.-X. Li, P.-L. Cao, and S.-C. Zhan, *Phys. Lett. A* **316**, 252 (2003).
- ³⁹S. N. Behera, B. K. Panda, S. Mukherjee, and P. Entel, *Phase Transitions* **75**, 41 (2002).
- ⁴⁰Q. Sun, Q. Wang, P. Jena, S. Waterman, and Y. Kawazoe, *Phys. Rev. A* **67**, 063201 (2003).
- ⁴¹S. Yoo, X. C. Zeng, X. Zhu, and J. Bai, *J. Am. Chem. Soc.* **125**, 13316 (2003).
- ⁴²M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.11, Gaussian, Inc., Pittsburgh, PA, 2002.
- ⁴³E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, *Nature (London)* **366**, 42 (1993).
- ⁴⁴H. Haberland, *Clusters of Atoms and Molecules: Theory, Experiment, and Clusters of Atoms* (Springer, New York, 1994).