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Structures and stability of medium silicon clusters. II. *Ab initio* molecular orbital calculations of Si$_{12}$–Si$_{20}$

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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 Si$_{12}$–Si$_{17}$ and Si$_{19}$ 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 Si$_{18}$ and Si$_{20}$, the same as predicted by Rata *et al.* However, for Si$_{14}$ and Si$_{15}$, 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 Si$_{14}$ and Si$_{15}$ 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 Si$_{19}$ 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 Si$_{25}$, several candidates for the lowest-energy isomers have been proposed based on *ab initio* quantum Monte Carlo[26] 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 Si$_{36}$ has been reported.[40] It is known that as the size of cluster increases, finding the global-minimum structure 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 experiments[5] 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 structures[23] indicated that a spherical-like Si$_{19}$ isomer (containing an endohedral atom) becomes slightly more stable than the low-lying prolate Si$_{19}$ 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-

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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) level[30] 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,
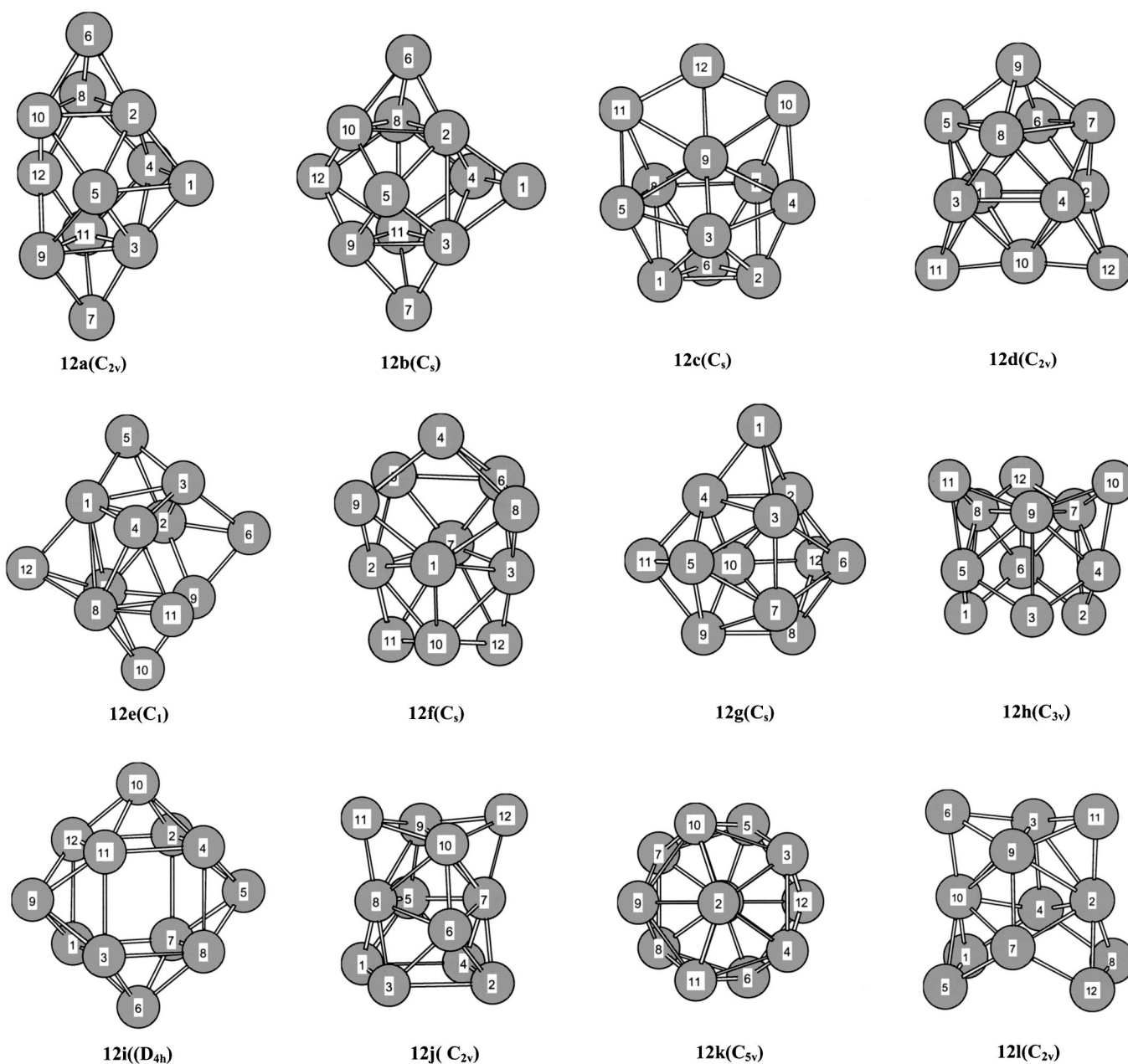

FIG. 1. Geometries of the low-energy structures of Si_{12}–Si_{20} optimized at the MP2/6-31G(d) level.
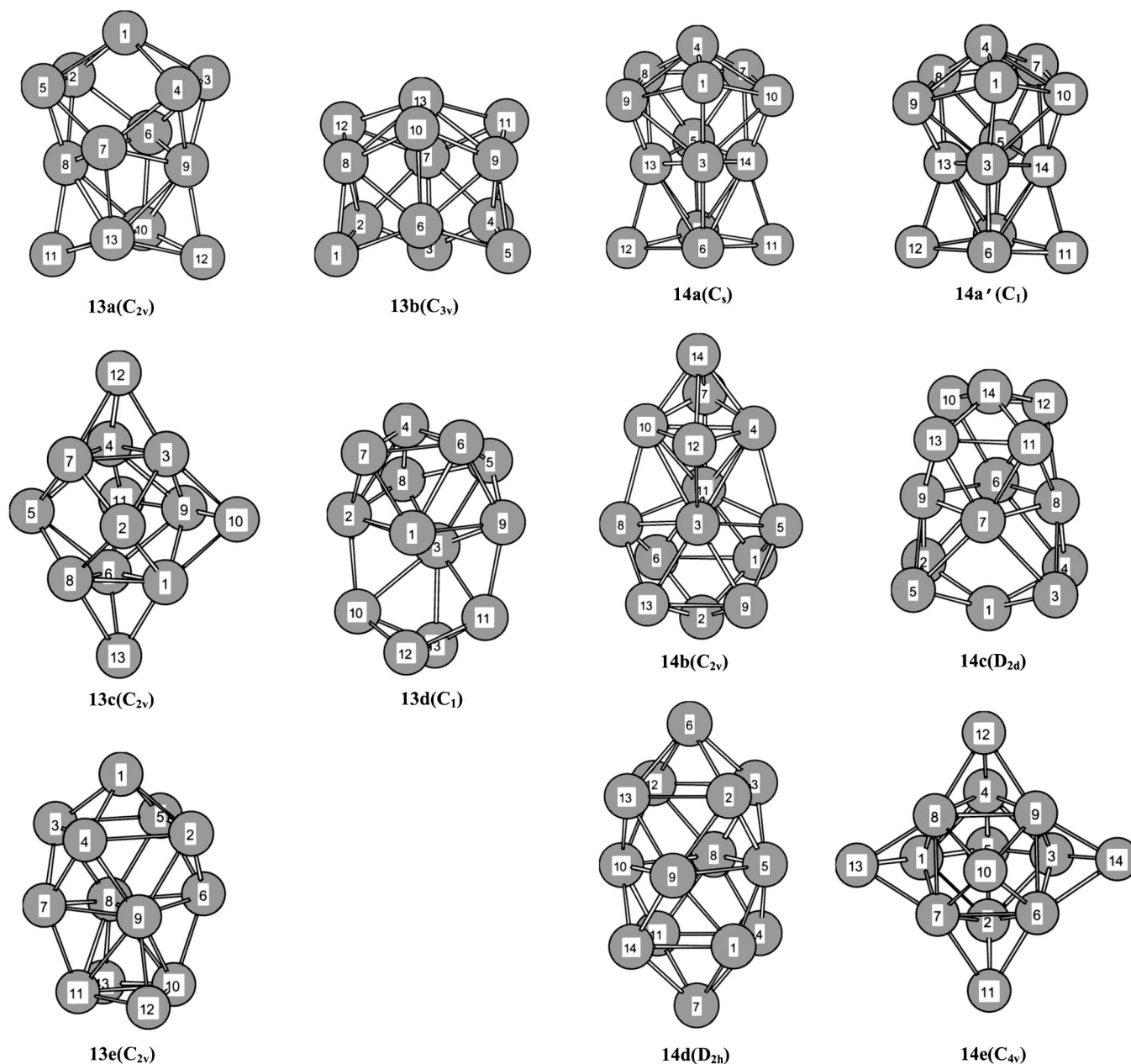
13a(C$_{2v}$)   13b(C$_{3v}$)   14a(C$_s$)   14a′(C$_1$)

13c(C$_{2v}$)   13d(C$_1$)   14b(C$_{2v}$)   14c(D$_{2d}$)

13e(C$_{2v}$)   14d(D$_{2h}$)   14e(C$_{4v}$)

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

15a(C$_{3v}$)

15b(C$_s$)

15c(C$_s$)

15d(D$_{3h}$)

16a(C$_{2h}$)

16b(C$_{2h}$)

16c(C$_{2v}$)

FIG. 1. (*Continued.*)
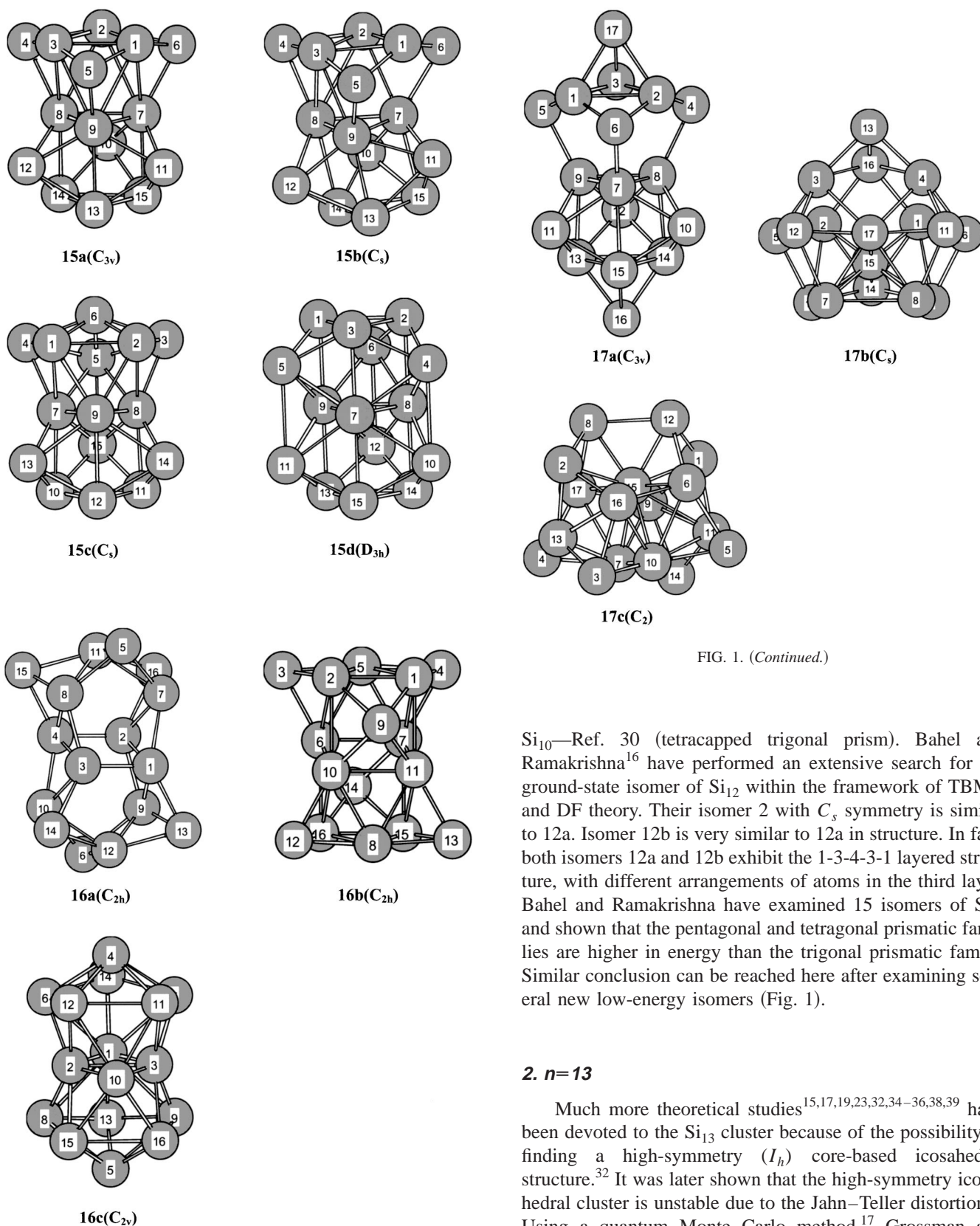
17a(C$_{3v}$)

17b(C$_s$)

17c(C$_2$)

FIG. 1. (*Continued.*)

Si$_{10}$—Ref. 30 (tetracapped trigonal prism). Bahel and Ramakrishna[16] 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 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

18a(C$_s$)   18b(C$_s$)   19a(C$_{2v}$)

18c(C$_{2v}$)   18d(D$_{4d}$)   19b(C$_1$)   19c(C$_s$)
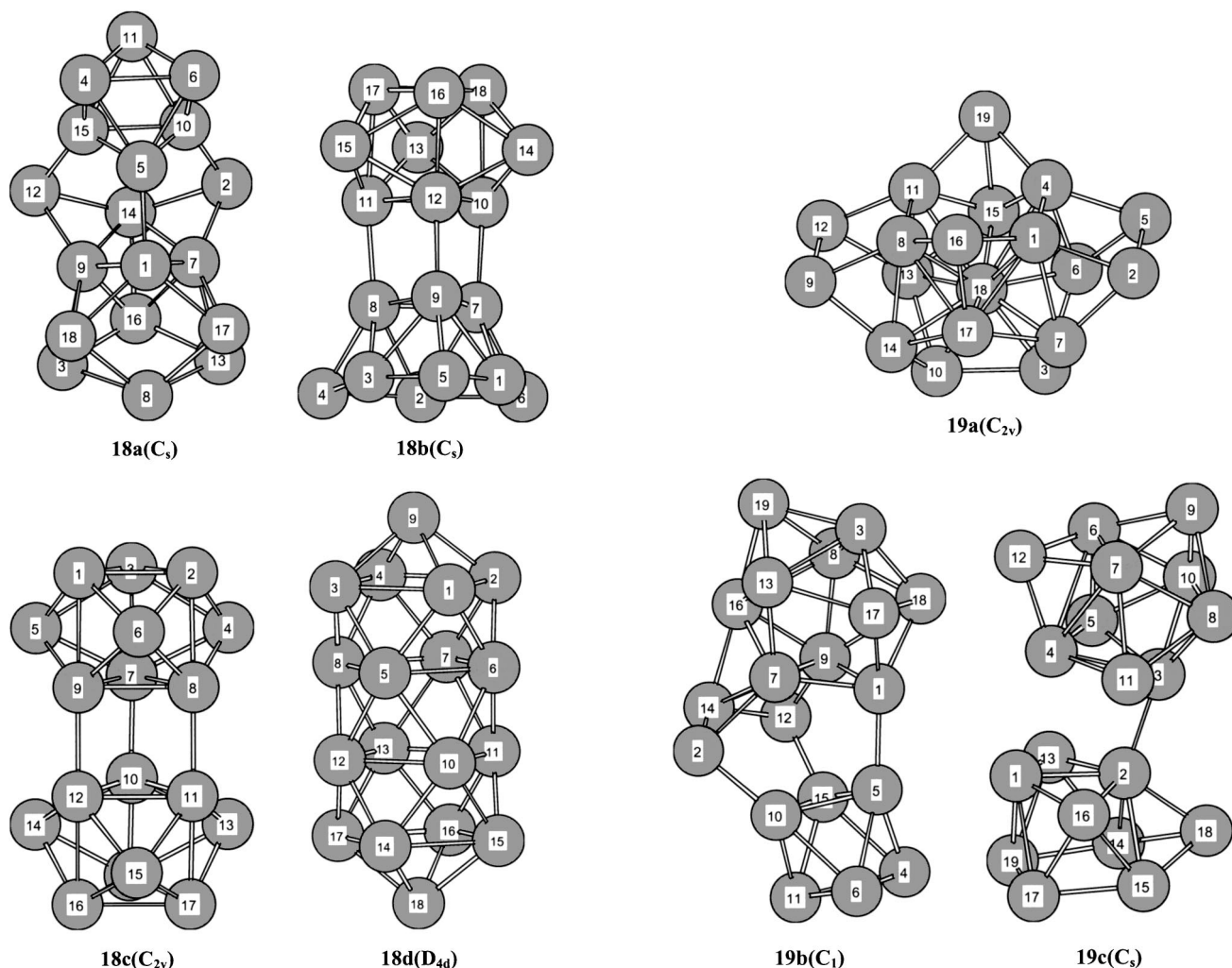
FIG. 1. (*Continued.*)

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 that that of 15a but its CCSD(T) energy becomes 0.19 eV higher than that of 15a.
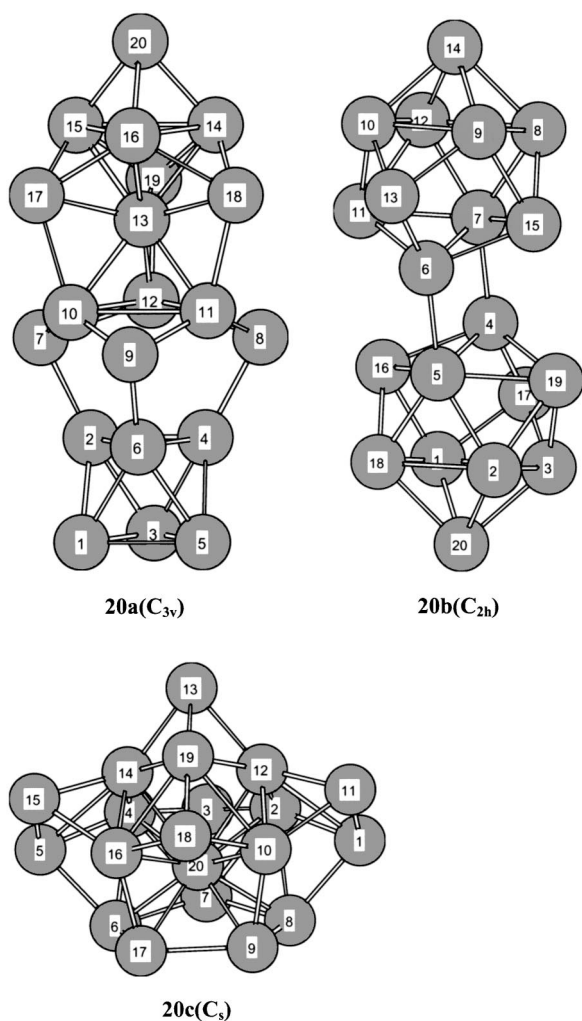
20a(C_{3v})   20b(C_{2h})

20c(C_s)

FIG. 1. (*Continued.*)

5. n=16 and 17

For Si_{16} 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 Si_{17} 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 Si_{17} isomer, 17c, is very competitive in stability compared to the prolate-shaped isomer 17a.

6. n=18

For Si_{18} 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 Si_{18}^{+}, predicted-by Rata *et al.*[27] It contains a magic-number-cluster Si_6 unit and a hexagonal-

chair unit. Another previously predicted lowest-energy isomer of Si_{18} 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 Si_{19} 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 Si_6 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 19c[23] is composed of a TTP unit and a Si_{10} (bicapped tetrahedral antiprism) unit. Its energy is slightly higher than both 19a and 19b.

8. n=20

Finally, for Si_{20} 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 Si_6 unit, a hexagonal-chair unit in the middle, and a low-energy isomer of Si_8 unit (see isomer 8f in Ref. 30). 20b is another low-lying isomer which is composed of two Si_{10} (bicapped tetrahedral antiprism) units. 20b was first predicted by Mitas *et al.*[26] on the basis of quantum Monte Carlo calculation. Isomer 20c[23] 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 Si_{13} 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 Si_{12}–Si_{20} (optimized at the MP2/6-31G* level).

Cluster	Isomer (PG)	HF/6-31G*	MP2/6-31G*	MP3/6-31G*	MP4(SDQ)/6-316*	CCSD/6-31G*	CCSD(T)/6-31G*
				Energy (hartrees)			
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	−4435.050 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

[a]Reference 23.
[b]Reference 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)	128.0(0.69)	145.3(0.77)	0.59
		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)
		421.1(5.67)	451.2(19.99)	451.7(0.91)	
		488.5(5.46)	499.4(1.34)		
Si_{18}	18a(C_s)				
		35.7(0.06)	87.9(0.06)	92.5(0.18)	0.85
		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)	121.5(0.08)	138.4(1.05)	0.96
		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)	
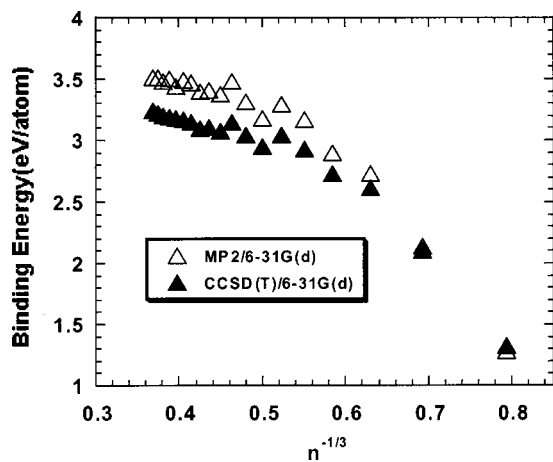
FIG. 2. Correlation of the binding energy per atom with $n^{-1/3}$ for the isomer of Si_n ($n = 12$–20) with lowest energy at the CCSD(T)/6-31G(d) level.
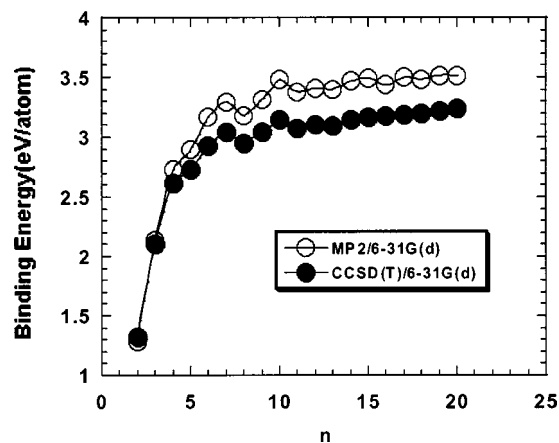
FIG. 3. Binding energy per atom of the isomer of Si_n ($n = 12$–20) with the lowest energy at the CCSD(T)/6-31G(d) level vs cluster size n.

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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

[a]Reference 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 block[23] 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 energically 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.

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