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Structures and stabilities of small silicon clusters: *Ab initio* molecular-orbital calculations of Si_7–Si_{11}

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Structures and stabilities of small silicon clusters: *Ab initio* molecular-orbital calculations of Si_7-Si_{11}

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Ab initio all-electron molecular-orbital calculations have been carried out to study the structure and relative stability of small silicon clusters (Si_n, $n=7-11$). A number of low-energy geometric isomers are optimized at the second-order Møller–Plesset (MP2) MP2/6-31G(d) level. Harmonic vibrational analysis has been performed to assure that the optimized geometries are stable. The total energies of stable isomers are computed at the coupled-cluster single and double substitutions (including triple excitations) [CCSD(T)] CCSD(T)/6-31G(d) level. The calculated binding energies per atom at both the MP2/6-31G(d) and CCSD(T)/6-31G(d) levels agree with the experiments. For Si_7, Si_8, and Si_{10}, the lowest-energy structures are the same as those predicted previously from the all-electron optimization at the Hartree–Fock (HF) HF/6-31G(d) level [Raghavachari and Rohlfing, J. Chem. Phys. **89**, 2219 (1988)]. For Si_9, the lowest-energy isomer is same as that predicted based on density-functional plane-wave pseudopotential method [Vasiliev, Ogut, and Chelikowsky, Phys. Rev. Lett. **78**, 4805 (1997)]. Particular attention has been given to Si_{11} because several low-energy geometric isomers were found nearly isoenergetic. On the basis of MP2/6-311G($2d$)//CCSD(T)/6-311G($2d$) calculation, we identified that the C_{2v} isomer, a tricapped trigonal prism with two additional caps on side trigonal faces, is most likely the global-minimum structure. However, another competitive geometric isomer for the global minimum is also found on basis of the MP2/6-311G($2d$)//CCSD(T)/6-311G($2d$) calculation. Additionally, calculations of the binding energy and the cluster polarizability offer more insights into relatively strong stability of two magic-number clusters Si_6 and Si_{10}.
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I. INTRODUCTION

Since the advent of advanced laser vaporization techniques[1–6] semiconductor atomic and nanoclusters have become an active subject of research, both experimentally and theoretically.[1–50] A great deal of understanding has been obtained on this microscopic form of matter, for example, their selectivity, stability, and reactivity, and their evolution toward the bulk matter. Silicon atomic and nanoclusters have been extensively studied because of their relevance to the development of nanoelectronics.[7–9] In particular, spectroscopic studies of atomic silicon clusters have been carried out by many groups.[10–22] Photoelectron spectroscopy of silicon anion clusters[10] indicates that silicon clusters with 4, 6, 7, and 10 atoms are closed-shell clusters. Photodissociation of silicon cation clusters[11,12] demonstrates Si_n^+ fragmentation products are mainly $Si_6^+-Si_{11}^+$. Several photodissociation[13–15] and collision-induced dissociation[16–18] experiments have shown that Si_6 and Si_{10} have exceptional stability, consistent with their "magic number" (particularly abundant) behavior in the mass spectra of Si clusters.[19] The Raman[20] and infrared[21] spectroscopy experiments have been utilized to infer the most stable structures of small silicon clusters. Mobility measurements[22,23] have also provided evidences of various stable isomers. Note that all these spectroscopic measurements provide only indirect information on the structures of small silicon clusters. Nevertheless, spectroscopic measurements have motivated considerable theoretical and computational studies on the microscopic silicon clusters.

In principle, *ab initio* molecular-orbital theory can provide direct structural information of the clusters. However, it is known that the number of stable geometric isomers of a cluster (local minima in the potential energy surface) increases exponentially with the number of atoms in the cluster.[5] As such, determination of the global-minimum structure is a challenging problem.[22,24] A series of systematic theoretical studies of small silicon clusters using all-electron molecular-orbital methods have been carried out by Raghavachari, Rohlfing, and their coworkers.[21,25–30] Quantum Monte Carlo simulation,[31] density-functional plane-wave pseudopotential methods,[22,32–34,39–42] and other quantum mechanical means[35–38,43–46] have also been employed by many groups to investigate various properties of silicon clusters and search for their global-minimum structures. Raghavachari and Logovinsky[25] were apparently the first to use all-electron molecular-orbital methods to calculate energies of small silicon clusters (Si_2-Si_6) and identify their lowest-energy geometries. Later, Raghavachari and Rohlfing[27–30] studied larger silicon clusters, Si_7-Si_{11}. They performed geometry optimization of several low-energy geometric isomers of Si_7-Si_{10} at the HF/6-31G(d) level, followed by a total-energy calibration at the second-order Møller–Plesset (MP2), MP3, and MP4 levels with the polarized 6-31G(d) basis set.[27] The structures, bonding properties, and relative stability of Si_7-Si_{10} clusters have been

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reported. In the cases of Si_{10} and Si_{11}, more detailed study of several low-energy geometric isomers was undertaken at higher MP4 or quadratic configuration-interaction [QCISD(T)] levels.[28–30] For Si_7-Si_{11}, other theoretical methods have also been employed to search for their lowest-energy structures.[21,26–31,35–45] Note that for Si_{11}, there is still some uncertainty on the global-minimum structure due to sensitivity of low-energy structures and their energies to the selected theoretical methods (e.g., levels of theory and basis sets).

The aim of this work is to reexamine a number of low-energy geometric isomers of Si_7-Si_{11} that have been reported previously at the Hartree-Fock (HF) or density-functional levels of theory. We have used all-electron molecular-orbital methods with including electron correlation effects in the determination of the cluster geometry. The geometry optimization is at the MP2/6-31G(d) level followed by the calibration of total energy at the CCSD(T)/6-31G(d) level. It is found that the electron correlation[47] can sometimes have qualitative effects on the cluster geometry as some previously obtained stable isomers at the HF level can became unstable at the MP2 level. This study also provides some additional insight into the relative stability of two magic-number clusters of silicon.

II. COMPUTATIONAL DETAILS

We used the Møller–Plesset perturbation to the second order[51–53] with a polarized 6-31G(d) basis set, i.e., the MP2/6-31G(d) level, to optimize the geometry of a number of low-energy isomers of Si_7-Si_{11}. Correlation effects of all electrons in the clusters are thus taken into account approximately. For the geometry optimization, the Berny algorithm[54] in the GAUSSIAN 98 software[55] is employed. This algorithm is designed to locate the local minimum but not the global minimum. Hence, a careful choice of initial isomeric structures of the cluster is important to seek possible candidate for the global-minimum isomer.

In this work, most geometric isomers of Si_7-Si_{11} are taken from previously obtained by other groups on basis of either the HF level of theory or plane-wave pseudopotential techniques. To obtain the local-minimum structure unbiasly, first, a full geometry optimization without constraining the cluster symmetry is undertaken at the MP2/6-31G(d) level. Second, the initial structures are optimized again with keeping the point-group symmetry of the clusters. Once the optimized structures are obtained from both approaches, the harmonic vibrational frequencies are then computed to examine possible appearance of any imaginary frequencies, that is, to examine whether the optimized structures are stable. Finally, for those stable isomers, their total energy is evaluated at the CCSD(T)/6-31G(d) level.[52,56–58]

III. RESULTS AND DISCUSSIONS

Figure 1 displays the optimized geometries of several low-energy geometric isomers of Si_7-Si_{11}, where the silicon atoms are connected with a "bond" when the Si-Si interatomic distance is less than 3.0 Å. The bond lengths are listed in Table I. In a benchmark calculation at the MP2/6-31G(d) level, the Si–Si bond length of Si_2 and Si_2H_6 are 2.26 and 2.34 Å, respectively, whereas the experimental values are 2.25 and 2.33 Å.[25] This test calculation indicates that the relative percentage error of the calculated Si–Si bond length is less than 0.5%. Table II lists the calculated harmonic vibrational frequencies, IR intensities, and zero-point energy (ZPE). No imaginary frequencies were found for most of low-energy geometric isomers of Si_7-Si_{11}, at least at the MP2/6-31G(d) level of theory. Tables III and IV present the binding energies per atom at both the MP2/6-31G(d) and CCSD(T)/6-31G(d) levels, together with the experimental values. As shown in Fig. 2, there is a good correlation between the calculated and the measured binding energies.

A. Structure

1. N=7

For Si_7 we have examined a number of low-energy geometric isomers as those studied by Raghavachari and Rohlfing.[27] No qualitative change in the geometry of these isomers is found except the capped trigonal prism, which no longer is a local minimum at the MP2/6-31G(d) level. The lowest-energy isomer of Si_7 is $7a$, a *pentagonal bipyrimid* with D_{5h} symmetry, in agreement with the experiment[20] and previous theoretical studies.[27,28,35,36,39,42] Note that the pentagonal bipyrimid (D_{5h}) is also the global minimum structure of the argon cluster[24] with seven atoms. Note also that the structures of small silicon clusters are different from the tetrahedral coordination characteristic of bulk silicon.

2. N=8

In the case of Si_8, full geometry optimizations at the MP2/6-31G(d) level followed by the total-energy calculation at the CCSD(T)/6-31G(d) level suggest that the isomer $8a$, a *distorted bicapped octahedron* (capping two opposite faces) with $C_{2h}(^1A_g)$ point group, is the lowest-energy structure.[27,28,36,39,42] Raghavachari and Rohlfing[27] have reported seven low-energy isomers of Si_8 on the basis of the HF/6-31G(d) level. Among the seven, six geometric isomers, i.e., $8a(C_{2h}, {}^1A_g)$, $8b(C_{2v}, {}^1A_1)$, $8d(C_{2v}, {}^1A_1)$, $8e(D_{3d}, {}^3A_{1g})$, $8f(C_{3v}, {}^3A_2)$, and $8g(C_s, {}^1A')$ have the same structure as ours despite of some differences in energy ordering and geometric parameters due to different levels of theory. However, the bicapped-trigonal-prism C_{2v} isomer shown in Ref. 27 is no longer a local minimum due to the appearance of several imaginary frequencies at the MP2/6-31G(d) level. Indeed, the full geometry optimization of the bicapped-trigonal-prism isomer yielded a new local-minimum structure ($8c$, with C_2 symmetry). The isomer $8c$ could be viewed as a distorted $8a$. Like the global-minimum isomer $8a$, the isomer $8h$ with D_{2d} symmetry is also a *distorted bicapped octahedron* but the caps are on adjacent faces. Our calculation indicates that $8h$ is a relatively high- energy local minimum at the MP2/6-31G(d) level. $8h$ was previously thought to be the global minimum based on a semiempirical method.[43] The isomer $8g$, a singly-

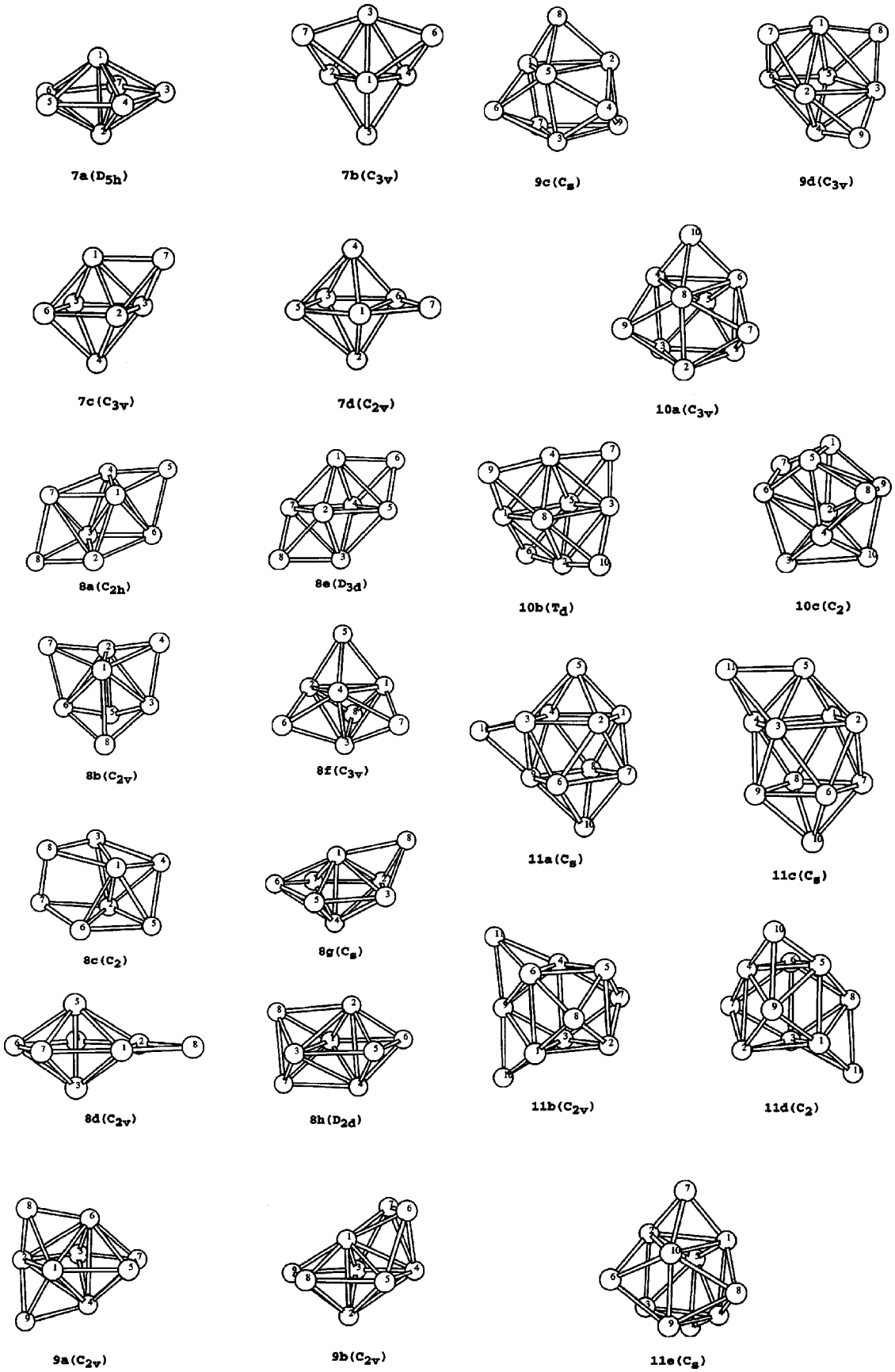

FIG. 1. Geometries of the low-energy isomer structures of Si_7-Si_{11} at the MP2/6-31G(d) level [11e at the MP2/6-311(2d) level].

capped pentagonal bipyramid, was also previously thought to be the global minimum based on the tight-binding molecular dynamics calculation.[35]

3. $N=9$

For Si_9, the global-minimum isomer appears to be the $9a(C_{2v}, {}^1A_1)$, whose structure has been viewed as *two*

TABLE I. Optimized geometry parameters for (a) low-energy geometric isomers of Si_7-Si_{11} at the MP2/6-31G(d) level and (b) three low-energy isomers of Si_{11} at the MP2/6-311($2d$) level.

Cluster	Isomer	PG (State)	Bond length (Å)	
(a)				
Si_7	7a	$D_{5h}(^1A_1')$		
			Si_1-Si_4	2.458
			Si_3-Si_4	2.483
			Si_1-Si_2	2.512
	7b	$C_{3v}(^1A_1)$		
			Si_1-Si_4	2.485
			Si_2-Si_4	2.493
			Si_1-Si_7	2.558
			Si_2-Si_7	2.341
	7c	$C_{3v}(^1A_1)$		
			Si_1-Si_7	2.415
			Si_1-Si_2	2.452
			Si_1-Si_6	2.463
			Si_4-Si_6	2.555
	7d	$C_{2v}(^1A_1)$		
			Si_1-Si_7	2.293
			Si_1-Si_6	2.926
			Si_1-Si_5	2.415
			Si_1-Si_4	2.504
			Si_3-Si_5	2.315
			Si_4-Si_5	2.687
Si_8	8a	$C_{2h}(^1A_g)$		
			Si_1-Si_4	2.462
			Si_4-Si_6	2.865
			Si_1-Si_2	2.399
			Si_2-Si_6	2.750
			Si_1-Si_5	2.276
			Si_5-Si_6	2.454
			Si_1-Si_3	2.802
	8b	$C_{2v}(^1A_1)$		
			Si_1-Si_6	2.647
			Si_1-Si_2	2.480
			Si_6-Si_7	2.359
			Si_1-Si_7	2.384
			Si_6-Si_8	2.376
			Si_1-Si_8	2.656
	8c	$C_2(^1A)$		
			Si_4-Si_5	2.536
			Si_5-Si_6	2.516
			Si_2-Si_4	2.503
			Si_1-Si_4	2.326
			Si_2-Si_3	2.487
			Si_1-Si_3	2.511
			Si_1-Si_2	2.649
			Si_2-Si_7	2.491
			Si_3-Si_8	2.483
			Si_7-Si_8	2.356
	8d	$C_{2v}(^1A_1)$		
			Si_1-Si_5	2.535
			Si_4-Si_5	2.482
			Si_5-Si_6	2.425
			Si_3-Si_5	2.695
			Si_1-Si_2	2.380
			Si_2-Si_4	2.483
			Si_4-Si_6	2.482
			Si_1-Si_8	2.320
	8e	$D_{3d}(^3A_{1g})$		
			Si_1-Si_4	2.574
			Si_1-Si_7	2.495
			Si_1-Si_6	2.368
	8f	$C_{3v}(^3A_2)$		
			Si_2-Si_4	2.674
			Si_2-Si_3	2.536
			Si_2-Si_5	2.469
			Si_2-Si_8	2.373
			Si_3-Si_8	2.490
	8g	$C_s(^1A')$		
			Si_1-Si_3	2.508
			Si_1-Si_7	2.524
			Si_1-Si_6	2.386
			Si_1-Si_4	2.478
			Si_3-Si_4	2.559
			Si_4-Si_7	2.422
			Si_4-Si_6	2.532
			Si_2-Si_3	2.897
			Si_2-Si_7	2.485
			Si_6-Si_7	2.440
			Si_1-Si_8	2.470
			Si_3-Si_8	2.403
	8h	$D_{2d}(^1A_1)$		
			Si_1-Si_7	2.343
			Si_1-Si_2	2.619
			Si_4-Si_7	2.926
			Si_7-Si_8	2.636
			Si_2-Si_4	2.894
Si_9	9a	$C_{2v}(^1A_1)$		
			Si_5-Si_7	2.401
			Si_2-Si_3	2.552
			Si_1-Si_2	2.547
			Si_3-Si_6	2.529
			Si_6-Si_7	2.391
			Si_1-Si_6	2.757
			Si_2-Si_8	2.345
			Si_4-Si_9	2.386
			Si_4-Si_6	2.976
	9b	$C_{2v}(^1A_1)$		
			Si_1-Si_4	2.644
			Si_1-Si_3	2.541
			Si_1-Si_7	2.370
			Si_1-Si_2	2.644
			Si_2-Si_4	2.751
			Si_4-Si_5	2.583
			Si_4-Si_6	2.525
			Si_1-Si_9	2.370
			Si_8-Si_9	2.404
	9c	$C_s(^1A\prime)$		
			Si_3-Si_7	2.458
			Si_3-Si_6	2.379
			Si_6-Si_7	2.656
			Si_5-Si_6	2.398
			Si_1-Si_6	2.441
			Si_1-Si_5	2.567
			Si_1-Si_8	2.376
			Si_5-Si_8	2.283
			Si_7-Si_9	2.972
			Si_1-Si_7	2.344
			Si_3-Si_5	2.464
	9d	$C_{3v}(^3A_2)$		
			Si_1-Si_5	2.493
			Si_1-Si_8	2.334
			Si_1-Si_3	2.953
			Si_5-Si_6	2.454
Si_{10}	10a	$C_{3v}(^1A_1)$		
			Si_4-Si_8	2.760
			Si_3-Si_4	2.491
			Si_2-Si_3	2.547
			Si_4-Si_{10}	2.318
			Si_4-Si_9	2.460
			Si_3-Si_9	2.434

TABLE I. (*Continued.*)

Cluster	Isomer	PG (State)	Bond length (Å)	
	10*b*	$T_d(^1A_1)$		
			Si_4-Si_5	2.581
			Si_4-Si_8	2.354
	10*c*	$C_2(^1A)$		
			Si_4-Si_6	2.722
			Si_4-Si_9	2.708
			Si_2-Si_7	2.358
			Si_1-Si_2	2.508
			Si_1-Si_7	2.353
			Si_5-Si_6	2.420
			Si_3-Si_6	2.522
			Si_3-Si_{10}	2.695
			Si_3-Si_4	2.311
			Si_4-Si_{10}	2.473
			Si_1-Si_6	2.791
			Si_1-Si_5	2.366
Si_{11}	11*a*	$C_s(^1A')$		
			Si_1-Si_2	2.698
			Si_2-Si_3	2.531
			Si_3-Si_4	2.598
			Si_1-Si_5	2.450
			Si_3-Si_5	2.555
			Si_3-Si_6	2.412
			Si_1-Si_7	2.347
			Si_1-Si_8	2.419
			Si_3-Si_9	2.390
			Si_3-Si_{11}	2.483
			Si_6-Si_7	2.671
			Si_6-Si_9	2.481
			Si_6-Si_{10}	2.612
			Si_7-Si_{10}	2.369
			Si_9-Si_{10}	2.468
			Si_9-Si_{11}	2.365
	11*b*	$C_{2v}(^1A_1)$		
			Si_2-Si_7	2.501
			Si_3-Si_7	2.416
			Si_2-Si_5	2.566
			Si_3-Si_4	2.660
			Si_1-Si_3	2.479
			Si_1-Si_9	2.433
			Si_1-Si_{10}	2.414
			Si_9-Si_{10}	2.442
			Si_1-Si_2	2.475
	11*c*	$C_s(^1A')$		
			Si_2-Si_3	2.690
			Si_3-Si_4	2.515
			Si_1-Si_5	2.369
			Si_3-Si_5	2.522
			Si_2-Si_6	2.333
			Si_3-Si_6	2.382
			Si_1-Si_7	2.372
			Si_1-Si_8	2.333
			Si_4-Si_8	2.382
			Si_3-Si_9	2.401
			Si_3-Si_{11}	2.455
			Si_5-Si_{11}	2.376
			Si_6-Si_7	2.673
			Si_6-Si_9	2.661
			Si_6-Si_{10}	2.447
			Si_7-Si_{10}	2.480
			Si_9-Si_{10}	2.674
	11*d*	$C_2(^1A)$		
			Si_1-Si_2	2.558
			Si_1-Si_3	2.441
			Si_2-Si_3	2.456
			Si_1-Si_5	2.601
			Si_3-Si_6	2.700
			Si_3-Si_7	2.385
			Si_1-Si_8	2.590
			Si_3-Si_8	2.459
			Si_1-Si_9	2.340
			Si_4-Si_{10}	2.428
			Si_5-Si_{10}	2.369
			Si_9-Si_{10}	2.504
(b)				
Si_{11}	11*a*′	$C_s(^1A')$		
			Si_1-Si_2	2.648
			Si_2-Si_3	2.504
			Si_3-Si_4	2.778
			Si_1-Si_5	2.468
			Si_3-Si_5	2.591
			Si_3-Si_6	2.405
			Si_1-Si_7	2.399
			Si_1-Si_8	2.442
			Si_3-Si_9	2.440
			Si_3-Si_{11}	2.493
			Si_6-Si_7	2.686
			Si_6-Si_9	2.519
			Si_6-Si_{10}	2.582
			Si_7-Si_{10}	2.416
			Si_9-Si_{10}	2.499
			Si_9-Si_{11}	2.391
	11*b*′	$C_{2v}(^1A_1)$		
			Si_2-Si_7	2.511
			Si_3-Si_7	2.434
			Si_2-Si_5	2.594
			Si_3-Si_4	2.677
			Si_1-Si_3	2.524
			Si_1-Si_9	2.463
			Si_1-Si_{10}	2.442
			Si_9-Si_{10}	2.470
			Si_1-Si_2	2.506
	11*e*	$C_s(^1A')$		
			Si_7-Si_{10}	2.459
			Si_1-Si_7	2.354
			Si_1-Si_2	2.603
			Si_2-Si_{10}	2.932
			Si_1-Si_7	2.502
			Si_6-Si_{10}	2.495
			Si_1-Si_5	2.429
			Si_4-Si_5	2.667
			Si_3-Si_6	2.458
			Si_4-Si_9	2.480
			Si_4-Si_{11}	2.451
			Si_3-Si_4	2.503
			Si_1-Si_4	2.576
			Si_9-Si_{10}	2.558
			Si_5-Si_{11}	2.478
			Si_6-Si_9	2.467

stacked distorted rhombi with an additional atom capped on top.[22,45] It can be also viewed as a *bicapped pentagonal bipyramid*. This lowest-energy structure was predicted by Vasiliev, Ogut, and Chelikowsky[42] and later by other groups.[38,45] The isomer $9b(C_{2v}, {}^1A_1)$, also a *bicapped pentagonal bipyramid* (but the two caps are on the same side of the pyramid), is a local minimum. $9b$ can be obtained via a full geometry optimization starting from the $(D_{3h}, {}^1A_1)$ *tri-*

TABLE II. Vibrational frequencies (cm^{-1}), IR intensities, and zero-point energies of low-energy geometric isomers of Si_7-Si_{11}.

Cluster	Isomer	PG (state)	Vibrational frequency (IR intensities)			ZPE (eV)
Si_7	7*a*	$D_{5h}(^1A_1')$				
			232.54(0.21)	261.75(0.15)	443.38(10.52)	0.31
	7*b*	$C_{3v}(^1A_1)$				
			131.68(0.03)	186.23(0.02)	242.02(3.25)	0.28
			300.72(2.84)	332.40(0.23)	364.05(0.05)	
			365.61(0.003)	459.62(3.40)	531.29(12.68)	
	7*c*	$C_{3v}(^1A_1)$				
			137.84(1.44)	181.66(0.54)	283.53(0.93)	0.31
			301.88(3.01)	332.30(0.91)	368.55(3.93)	
			407.06(10.69)	426.94(3.91)	491.86(25.05)	
	7*d*	$C_{2v}(^1A_1)$				
			38.97(0.02)	100.69(0.33)	109.02(1.13)	0.26
			189.99(0.24)	247.14(1.88)	253.24(0.26)	
					355.39(21.04)	
			329.29(2.76)	335.69(8.44)	376.51(0.14)	
			449.01(13.54)	469.22(0.73)	501.24(2.28)	
Si_8	8*a*	$C_{2h}(^1A_g)$				
			75.32(0.09)	150.67(0.70)	174.11(0.88)	0.34
			255.47(0.54)	318.59(4.63)	385.50(0.59)	
			317.05(2.07)			
			409.01(8.52)	544.93(8.35)		
	8*b*	$C_{2v}(^1A_1)$				
			132.26(4.49)	179.77(3.97)	214.29(0.19)	0.35
			222.47(5.60)	254.85(2.00)	261.10(1.42)	
			292.59(0.35)	303.69(0.01)	319.27(3.02)	
			370.52(0.33)	407.71(7.94)	428.76(0.04)	
			445.17(0.2)	477.61(0.50)	498.07(0.38)	
	8*c*	$C_2(^1A)$				
			90.04(1.39)	123.25(0.02)	172.61(0.21)	0.32
			177.92(0.48)	186.86(1.19)	201.84(0.19)	
			210.49(1.15)	289.20(0.05)	301.71(0.61)	
			325.50(4.87)	330.55(0.54)	338.80(0.001)	
			372.49(5.19)	376.38(0.03)	424.67(10.23)	
			461.55(6.35)	488.39(6.84)		
	8*d*	$C_{2v}(^1A_1)$				
			92.60(0.35)	145.75(0.001)	162.03(0.97)	0.33
			162.42(0.08)	194.11(2.27)	260.71(1.40)	
			274.41(0.52)	284.94(0.51)	310.04(0.31)	
			340.26(4.13)	362.84(1.39)	385.43(7.05)	
			408.50(0.06)	420.07(7.49)	439.13(9.88)	
			524.54(24.89)			
	8*e*	$D_{3d}(^3A_{1g})$				
			135.79(0.53)	308.90(8.10)	323.85(0.02)	0.63
			412.11(4.70)	482.84(3.58)		
	8*f*	$C_{3v}(^3A_2)$				
			140.58(0.26)	230.19(0.05)	230.65(0.06)	0.34
			248.87(0.004)	251.79(4.51)	268.42(2.16)	
			322.38(1.66)	345.73(0.55)	386.96(4.96)	
			437.36(4.17)	463.54(5.78)		
	8*g*	$C_s(^1A')$				
			127.07(1.19)	128.32(1.15)	170.27(1.80)	0.34
			185.39(0.44)	221.53(0.04)	221.75(0.47)	
			252.09(1.69)	261.79(1.89)	295.76(0.66)	
			316.11(0.46)	329.26(0.02)	334.85(1.05)	
			357.38(1.64)	399.79(0.12)	425.12(2.62)	
			426.16(1.58)	463.86(0.05)	482.58(4.86)	
	8*h*	$D_{2d}(^1A_1)$	145.56(1.59)			
			276.74(4.34)	316.27(0.01)	326.41(1.03)	0.38
			468.87(0.53)	496.35(0.001)	616.34(18.34)	
Si_9	9*a*	$C_{2v}(^1A_1)$				
			91.92(2.29)	119.14(3.33)	172.73(0.96)	0.39
			203.75(4.54)	216.59(1.70)	248.10(0.01)	
			270.59(1.37)	280.11(0.07)	299.67(3.97)	
			305.60(1.57)	323.10(2.83)	338.33(1.50)	
			356.02(1.35)	423.99(1.25)	430.69(0.002)	
			452.31(1.47)	488.95(1.96)	498.22(1.76)	
	9*b*	$C_{2v}(^1A_1)$				
			134.13(0.13)	165.82(0.001)	173.83(1.22)	0.37
			181.72(0.27)	233.35(0.83)	257.63(0.001)	

TABLE II. (*Continued.*)

Cluster	Isomer	PG (state)	Vibrational frequency (IR intensities)			ZPE (eV)
			265.31(2.49)	267.56(0.87)	296.65(0.85)	
			308.31(1.44)	317.82(1.48)	331.62(0.09)	
			367.38(2.02)	369.82(2.65)	408.56(0.004)	
			440.17(6.94)	552.78(1.39)		
	9*c*	$C_s(^1A')$				
			70.55(1.38)	107.13(0.22)	162.90(0.15)	0.38
			166.91(1.95)	205.91(0.25)	238.60(3.57)	
			252.71(5.60)	263.56(1.22)	287.39(1.92)	
			295.07(2.84)	304.44(1.97)	308.15(1.37)	
			347.10(0.70)	354.96(0.28)	369.99(1.36)	
			405.09(0.35)	452.67(3.80)	460.95(6.73)	
			487.42(0.13)	514.49(0.16)		
	9*d*	$C_{3v}(^3A_2)$				
			100.30(6.84)	113.54(2.35)	179.23(9.29)	0.45
			208.35(0.64)	283.20(1.64)	324.14(0.60)	
			341.40(0.06)	350.19(3.98)	397.04(0.87)	
			431.64(3.79)	503.95(10.61)	801.40(523.22)	
Si_{10}	10*a*	$C_{3v}(^1A_1)$				
			110.51(1.90)	189.31(0.16)	228.24(1.35)	0.46
			243.64(0.14)	270.09(0.27)	305.10(1.49)	
			316.02(1.06)	318.51(0.18)	341.12(2.00)	
			351.17(4.99)	387.62(0.42)	426.80(0.20)	
			459.25(0.02)	510.07(0.32)		
	10*b*	$T_d(^1A_1)$				
			98.10(8.03)	203.50(1.91)	299.79(3.46)	0.42
			546.14(22.05)			
	10*c*	$C_2(^1A)$				
			101.52(0.01)	103.27(0.15)	116.33(1.78)	0.45
			133.66(0.02)	210.44(1.42)	212.20(0.87)	
			221.85(0.42)	229.57(3.29)	259.72(0.45)	
			264.72(0.26)	286.64(1.55)	295.28(2.08)	
			300.78(0.40)	309.33(0.19)	325.89(0.12)	
			344.38(4.21)	348.26(1.31)	373.22(0.67)	
			383.12(0.39)	395.78(0.50)	440.76(3.84)	
			475.49(0.61)	524.86(1.32)	533.19(1.12)	
Si_{11}	11*a*	$C_s(^1A')$				
			69.40(0.26)	97.15(6.49)	119.32(0.17)	0.48
			124.63(0.54)	140.27(0.83)	177.48(0.11)	
			215.03(1.35)	229.82(0.07)	240.20(7.61)	
			244.78(1.82)	259.02(0.59)	261.36(0.15)	
			280.38(2.71)	289.11(0.59)	295.83(1.67)	
			316.73(4.63)	325.23(1.15)	328.26(0.10)	
			358.32(0.85)	367.64(0.28)	378.00(1.25)	
			392.65(0.002)	412.75(10.72)	429.90(5.09)	
			432.35(1.94)	470.02(4.49)	517.23(9.70)	
	11*b*	$C_{2v}(^1A_1)$				
			104.53(1.17)	134.20(2.19)	136.35(3.31)	0.48
			153.96(4.23)	164.43(0.73)	177.84(0.87)	
			222.28(0.78)	229.28(0.15)	259.98(1.50)	
			270.32(2.25)	291.92(0.48)	304.56(7.21)	
			320.46(0.05)	335.13(0.01)	336.64(0.82)	
			344.59(8.56)	374.74(0.03)	388.99(0.39)	
			432.26(0.37)	432.74(0.01)	472.00(6.56)	
			496.16(18.95)	519.60(22.37)		
	11*c*	$C_s(^1A')$				
			51.32(2.61)	69.05(0.61)	106.88(0.17)	0.47
			114.82(2.59)	129.32(2.43)	163.01(0.50)	
			164.29(0.54)	201.17(0.87)	225.80(0.06)	
			228.96(0.69)	238.83(1.73)	241.71(1.10)	
			262.43(2.53)	285.86(0.15)	287.24(0.23)	
			304.84(0.74)	341.84(0.03)	364.25(0.09)	
			368.26(5.43)	386.66(2.20)	390.20(0.002)	
			401.69(11.69)	427.14(0.29)	431.83(6.47)	
			446.87(2.88)	483.25(2.27)	504.03(12.67)	
	11*d*	$C_2(^1A)$				
			68.90(0.82)	88.65(0.47)	109.24(0.53)	0.47
			127.18(2.26)	139.19(2.17)	194.75(0.64)	

TABLE II. (*Continued.*)

Cluster	Isomer	PG (state)	Vibrational frequency (IR intensities)			ZPE (eV)
			219.95(0.05)	228.05(0.05)	252.04(0.91)	
			252.39(1.46)	260.18(0.85)	262.62(4.36)	
			279.70(1.57)	284.32(2.10)	305.01(1.14)	
			310.71(0.12)	314.60(0.32)	329.07(1.33)	
			335.36(0.98)	348.85(0.08)	368.54(0.27)	
			380.61(3.94)	463.57(11.86)	483.36(9.54)	
			524.65(30.37)	527.53(4.02)		

capped trigonal prism (TTP). Previously, Lee, Chang, and Lee[35] and also Luo, Zhao, and Wang[43] reported that the isomer $9b(C_{2v}, {}^1A_1)$ was a possible global minimum based on semiempirical methods.

At the MP2/6-31G(d) level, the vibrational frequency analysis indicates that the distorted TTP $(C_{2v}, {}^1A_1)$ (Ref. 22) is unstable. However, it has been shown that the distorted TTP (C_{2v}) isomer, although unstable at the MP2/6-31G(d) level, can be a favorable structural motif in some larger silicon clusters.[22] The distorted tricapped octahedron $(C_s, {}^1A')$ (Refs. 27, 28, and 31) is also found unstable at the MP2/6-31G(d) level as it transforms into $9c(C_s, {}^1A')$, another form of *distorted tricapped trigonal prism* (TTP), in a full geometry optimization. To our knowledge, the distorted TTP $(C_s, {}^1A')$ isomer has not been reported in the literatures. The tricapped octahedron in triplet state, $9d(C_{3v}, {}^3A_2)$, is a relatively high-energy local minimum, as predicted by Raghavachari and Kohlfing.[27]

4. N=10

Si_{10} is a magic-number cluster which has been extensively studied theoretically.[27,28,30,31,35,36,38–40,43,45] Our calculation confirms that the isomer $10a(C_{3v}, {}^1A_1)$, a *tetracapped trigonal prism*, is the global minimum, as already predicted by many other groups.[28,31,36,38,40] The isomer $10b(T_d, {}^1A_1)$, a tetracapped octahedron, is a low-energy local minimum as shown by Raghavachari and Kohlfing.[27] The isomer $10c(C_2, {}^1A)$, obtained via a full geometry optimization from the geometric isomer $10k(C_s)$ in Ref. 40, is a new low-energy isomer that not has been reported in the literatures. Its energy is close to that of the isomer $10b$.

TABLE III. The energy separations for low-energy isomers of Si_7-Si_{11}.

Cluster	Isomer	PG (state)	MP2/6-31G(d) (eV)	CCSD(T)/6-31G(d) (eV)	MP2/6-311(2d) (eV)	CCSD(T)/6-311(2d) (eV)
Si_7						
	$7a$	$D_{5h}(^1A_1')$	0.00	0.00		
	$7b$	$C_{3v}(^1A_1)$	0.93	0.67		
	$7c$	$C_{3v}(^1A_1)$	2.17	1.71		
	$7d$	$C_{2v}(^1A_1)$	2.63	2.21		
Si_8						
	$8a$	$C_{2h}(^1A_g)$	0.00	0.00		
	$8b$	$C_{2v}(^1A_1)$	0.31	0.19		
	$8c$	$C_2(^1A)$	0.58	0.52		
	$8d$	$C_{2v}(^1A_1)$	0.41	0.55		
	$8e$	$D_{3d}(^3A_{1g})$	0.68	0.58		
	$8f$	$C_{3v}(^3A_2)$	0.95	0.60		
	$8g$	$C_s(^1A')$	0.52	0.62		
	$8h$	$D_{2d}(^1A_1)$	1.00	1.73		
Si_9						
	$9a$	$C_{2v}(^1A_1)$	0.00	0.00		
	$9b$	$C_{2v}(^1A_1)$	0.60	0.74		
	$9c$	$C_s(^1A')$	1.28	1.24		
	$9d$	$C_{3v}(^3A_2)$	2.07	1.60		
Si_{10}						
	$10a$	$C_{3v}(^1A_1)$	0.00	0.00		
	$10b$	$T_d(^1A_1)$	1.99	0.75		
	$10c$	$C_2(^1A)$	1.27	0.81		
Si_{11}						
	$11a$	$C_s(^1A')$	0.00	0.00	0.00($11a'$)	0.09($11a'$)
	$11b$	$C_{2v}(^1A_1)$	0.53	0.02	0.40($11b'$)	0.00($11b'$)
	$11c$	$C_s(^1A')$	0.21	0.22		
	$11d$	$C_2(^1A)$	0.87	0.53		
	$11e$	$C_s(^1A')$			0.00	0.03

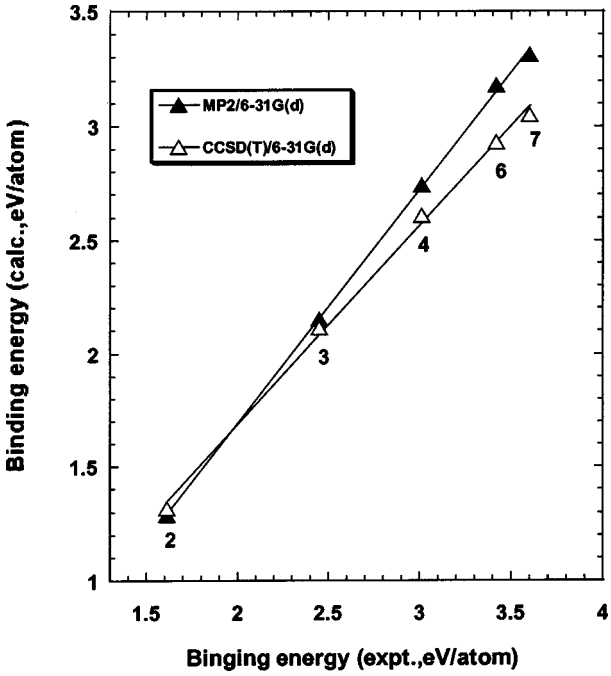

FIG. 2. Correlation of the calculated binding energies per atom and measured values for the low-energy isomers of Si_n ($n=2-4,6-7$).

5. $N=11$

Si_{11} deserves more discussion because the global-minimum structure of Si_{11} was not fully conclusive due to the existence of multiple nearly degenerate low-energy isomers.[28,35,38,39,45] In fact, Si_{11} can be a good model system for testing theoretical methods. At the MP2/6-31G(d) level we found that the D_{3h} pentacapped trigonal prism is unstable, although it is a stable structure when calculated at the HF/6-31G(d) level.[28] Table III lists the total energy of three nearly isoenergetic geometric isomers calculated at the MP2/6-31G(d)//CCSD(T)/6-31G(d) level, $11a(C_s, {}^1A')$, a *distorted tricapped tetragonal antiprism* or a *distorted pentacapped trigonal prism*, $11b(C_{2v}, {}^1A_1)$, a *tricapped trigonal prism* with two additional caps on side trigonal faces, and $11c(C_s, {}^1A')$, a *bicapped tetragonal antiprism* with an additional cap on one upper trigonal face. Among the three isomers, $11a(C_s, {}^1A')$ was proposed by Lee, Chang, and Lee[35] and also later by Sieck *et al.*;[45] $11b(C_{2v}, {}^1A_1)$ and $11c(C_s, {}^1A')$ were predicted by Rohlfing and Raghavachari[28] based on the HF/6-31G(d)//MP4SDQ/6-31G(d) calculation. The isomer $11b(C_{2v}, {}^1A_1)$ was also predicted to be a possible global minimum by Ho and coworkers[39] using a density-functional pseudopotential theory within both local density and generalized gradient approximations; $11a(C_s, {}^1A')$ [Cs(II) in Ref. 39] was predicted to be a local minimum. Ho and co-workers[39] recently used Car–Parrinello molecular dynamics combined with the simulated annealing method to search for the global-minimum structure of Si_{11}. They found again that 11b is most likely the global minimum. At the MP2/6-31G(d)//CCSD(T)/6-31G(d) level, we found that both isomers 11a and 11b are the possible global minimum while 11c is only about 0.2 eV higher in energy than 11a and 11b. The isomer $11d(C_2, {}^1A)$, another capped trigonal prism, is a new low-energy isomer whose energy is 0.53 eV higher than that of 11a.

The fact that Si_{11} has at least three possible candidates for the global-minimum structure on the basis of MP2/6-31G(d)//CCSD(T)/6-31G(d) calculation prompts us to further examine the relative stability of these three geometric isomers with a larger basis set. We chose MP2/6-311G(2d)//CCSD(T)/6-311G(2d) levels for which our current computer facility can afford. The full geometry optimization at the MP2/6-311G(2d) level reveals that the previously optimized structure of 11a and 11b remains nearly unchanged [the newly optimized structures, called $11a'(C_s, {}^1A_1)$ and $11b'(C_{2v}, {}^1A_1)$, are given in Table I(b)]. However, significant structural change occurred for the isomer $11c(C_s, {}^1A')$. The newly optimized structure starting from 11c is hereafter called $11e(C_s, {}^1A')$, which is also a capped trigonal prism. The structural data of 11e is shown in Table I(b). The calculated single-point energies for 11a', 11b', and 11e at both the MP2/6-311G(2d) and CCSD(T)/6-311G(2d) levels are listed in Table III. At the MP2/6-311G(2d) level, now both $11a'(C_s, {}^1A')$ and $11e(C_s, {}^1A')$ are the two lowest-energy structures, whereas at the CCSD(T)/6-311G(2d) level $11b'(C_{2v}, {}^1A_1)$ becomes the global minimum but $11e(C_s, {}^1A')$ is merely 0.03 eV higher in energy than 11b'. It can be also seen from Table III that the use of the larger basis set at the MP2 level [6-311G(2d)] results in a smaller energy difference between 11b' and 11a', compared to that between 11b and 11a at the MP2/6-31G(d) level, while at the CCSD(T)/6-311G(2d) level 11b' becomes the global minimum. From this trend, it appears that the isomer 11b' would be more energetically favorable if an even larger basis set [e.g., 6-311(3df)] were used. Note that the difference in the zero-point vibrational energy for the three geometric isomers is less than 0.01 eV (see Table II). Therefore, including zero-point vibrational energy in the total energy will not qualitatively affect the energy ordering among the three nearly isoenergetic isomers. Note also that the structure of newly obtained $11e(C_s, {}^1A')$ does not resemble that of Cs(I) isomer reported in Ref. 39, which was predicted to be another possible global minimum of Si_{11} [the Cs(I)'s geometric structure resembles that of C_{2v} 11b].[59]

To summarize, our calculations at both the MP2 and

TABLE IV. Binding energies per atom calculated at the MP2/6-31G(d) and CCSD(T)/6-31G(d) levels compared with available experimental data.

Cluster (isomer)	Point group	Binding energy (eV/atom)		
		MP2/6-31G(d)	CCSD(T)/6-31G(d)	Expt.[a]
Si_2	$D_{\infty h}$	1.29	1.32	1.61
Si_3	C_{2v}	2.15	2.11	2.45
Si_4	D_{2h}	2.74	2.61	3.01
Si_6	D_{4h}	3.18	2.93	3.42
Si_7(7a)	D_{5h}	3.31	3.05	3.60
Si_8(8a)	C_{2h}	3.20	2.95	
Si_9(9a)	C_{2v}	3.33	3.04	
Si_{10}(10a)	C_{3v}	3.50	3.14	
Si_{11}(11a)	C_s	3.40	3.08	

[a]Reference 31.

CCSD(T) levels consistently reproduce all the global-minimum structures of Si_7-Si_{10} reported in the literature.[27,39,45] For Si_{11}, however, the predicted global-minimum structure is different on the basis of the MP2 level and the CCSD(T) level. The CCSD(T)/6-311G(2d) calculation indicates that the isomer $11b'(C_{2v}, {}^1A_1)$ is the global minimum, but also shows that $11e(C_s, {}^1A')$ is a very competitive candidate for the global minimum.

B. Cluster growth feature

As shown in Fig. 1, the pentagonal bipyrimid, tetrahedron, distorted octahedron, and tricapped trigonal prism (TTP) all could be viewed as motifs for low-energy structures of Si_7-Si_{11}. For example, the isomer $7a(D_{5h}, {}^1A_1')$ appears to be such a motif due to its high stability. Low-energy clusters such as $8d$, $8g$, $9a$, and $9b$ can be constructed via capping $7a$ on edges or faces. The distorted octahedron is the global minimum of Si_6.[20,25] When capped on edges or faces, it becomes clusters $7c$, $7d$, $8e$, $8h$, $9d$, or $10b$. Although the tetrahedron (Si_4) is not a stable structure itself due to large strain energy,[27] it can also be viewed as a building block for some low-energy structures (e.g., $7b$ and $8f$) when its faces are properly capped. Moreover, the TTP in triplet state is a local minimum of Si_9, but it has a higher energy compared to many other low-energy isomers. Nevertheless, it can be viewed as a motif for some low-energy structures of Si_{11} ($11a-11e$) and even some larger Si_n ($n=12-26$) clusters[21] as well.

A common feature in small silicon clusters Si_7-Si_{11} is that the lowest-energy structures are all spherical-like. The spherical-like shape minimizes the surface area and reduces the number of dangling bonds.[46] The low-energy structures of Si_7, for example, deviate gradually from spherical-like shape, as the energy increases from isomer $7a$ to $7d$ (see Table III), indicating that the more spherical-like isomer $7a$ is more energetically favorable. This deviation from spherical-like shape ($7a$ to $7d$) is also manifested in their dipole moments (see Table V). As shown in Fig. 3, the binding energy per atom for the lowest-energy structure of Si_n ($n=2-11$) increases with $n^{-1/3}$, supporting the spherical-like cluster growth.[24] For nonspherical-like (prolate) cluster growth, the binding energy per atom would be nearly independent of the size of cluster.

In most cases, if clusters favor spherical-like shape the lowest-energy structures of the clusters tend to have high degree of symmetry. However, high symmetrical clusters with incomplete electronic shells can be even more stabilized through a geometry deformation which results in a lower degree of symmetry.[24] As an example, the lowest-energy structure of Si_8 does not exhibit cubic symmetry with the O_h point group. Rather, it exhibits C_{2h} symmetry due to Jahn–Teller distortion, similar to the cases of Si_4 (Ref. 27) and Si_6 (Ref. 20). For Si_9, the global minimum is $9a$ with C_{2v} symmetry; it can be derived from the distortion of tricapped octahedron (C_{3v}) in singlet state.

TABLE V. Dipole moments of low-energy isomers of Si_7-Si_{11} at the MP2/6-31G(d) level.

Cluster	Isomer	PG (state)	μ(D)
Si_7	$7a$	$D_{5h}({}^1A_1')$	0.000
	$7b$	$C_{3v}({}^1A_1)$	1.518
	$7c$	$C_{3v}({}^1A_1)$	1.602
	$7d$	$C_{2v}({}^1A_1)$	1.639
Si_8	$8a$	$C_{2h}({}^1A_g)$	0.000
	$8b$	$C_{2v}({}^1A_1)$	0.611
	$8c$	$C_2({}^1A)$	1.360
	$8d$	$C_{2v}({}^1A_1)$	1.929
	$8e$	$D_{3d}({}^3A_{1g})$	0.000
	$8f$	$C_{3v}({}^3A_2)$	0.324
	$8g$	$C_s({}^1A')$	0.880
	$8h$	$D_{2d}({}^1A_1)$	0.000
Si_9	$9a$	$C_{2v}({}^1A_1)$	0.430
	$9b$	$C_{2v}({}^1A_1)$	1.216
	$9c$	$C_s({}^1A')$	1.235
	$9d$	$C_{3v}({}^3A_2)$	0.897
Si_{10}	$10a$	$C_{3v}({}^1A_1)$	1.101
	$10b$	$T_d({}^1A_1)$	0.000
	$10c$	$C_2({}^1A)$	1.148
Si_{11}	$11a$	$C_s({}^1A')$	1.258
	$11b$	$C_{2v}({}^1A_1)$	2.098
	$11c$	$C_s({}^1A')$	2.288
	$11d$	$C_2({}^1A)$	1.215

C. Energy and stability

It can be seen from Table III that the lowest-energy structures of Si_7-Si_{11} all have *closed-shell* structures. It is known that the CCSD(T) level of theory[52,56–58] is more accurate in estimating electron correlation than the MP2 level. In many cases, the CCSD(T) level yields only small quantitative changes in the relative energy of geometric isomers. For instance, isomers $7b$ and $7c$ of Si_7 are higher in energy

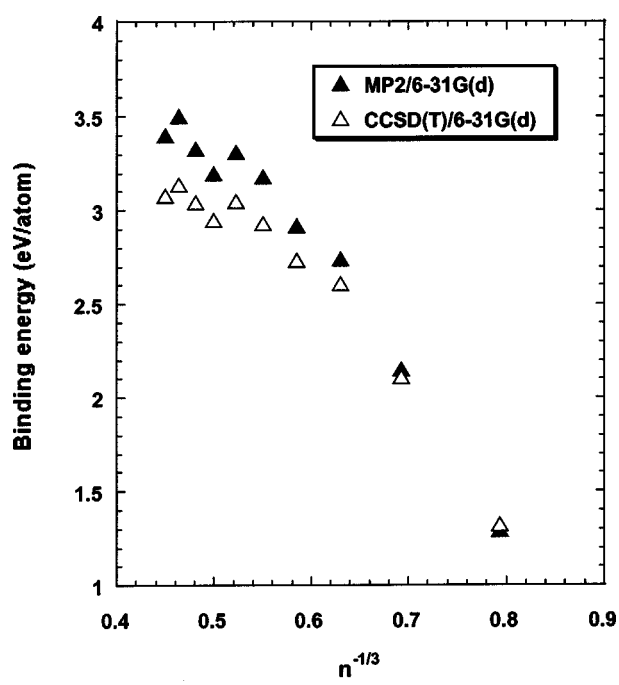

FIG. 3. Correlation of binding energy per atom and $n^{-1/3}$ for the low-energy isomers of Si_2-Si_{11}.

than 7*a* by 0.93 and 2.17 eV at the MP2/6-31G(*d*) level, but at the CCSD(T)/6-31G(*d*) level, 7*b* and 7*c* are 0.67 and 1.71 eV higher than 7*a*. However, for some isomers of Si_7-Si_{11} the CCSD(T) level can qualitatively affect the relative energy, that is, the MP2/6-31G(*d*) energy ordering can be different from the CCSD(T)/6-31G(*d*) one. This shows the importance of having accurate electron-correlation energy in the determination of the relative stability for geometric isomers with very close energy, for example, the three nearly isoenergetic isomers of Si_{11}.

The ionization potentials (IPs) can also be used to evaluate the relative stability of isomers. In principle, cluster IP should decrease gradually towards the work function of bulk phase as the size of clusters increase. In the case of metal clusters,[47] the classical conducting spherical droplet (CSD) model suggests a linear IP versus $n^{-1/3}$ relationship, which can reproduce many experimental IPs quite well. However, the experimental IPs of Si_n ($n=2-200$) deviate notably from the CSD model.[47] We cannot offer a theoretical explanation for this deviation because of the limited size range of Si_n ($n=7-11$) considered here. But we have found an agreement between the calculated vertical ionization potentials (VIP) and measured values[48] for Si_2-Si_{11}, as shown in Table VI. It is interesting to note that there is a large gap between $n=20$ and $n=22$ in the photoionization threshold measurements of Si_n ($n=2-400$),[49] which might imply a possible structural transition in this size range of silicon clusters. An *ab initio* molecular-orbital study for this size range of Si clusters is under way.

It is known that some simple-metal clusters are "magic-number" clusters[32] when the number of valence electrons in the clusters is 8, 20, 40, or 58 etc. The magic-number clusters can be understood on the basis of particle-in-box model or jellium model.[50] The "magic-number" behavior of small silicon clusters has been correlated with the trend of binding energy per atom as a function of cluster size.[27] Luo, Zhao, and Wang[43] pointed out that two factors can play major role in the cluster stability, one is the electronic configuration of an atom and another is the number of atoms in the cluster. Here, the binding energies of the lowest-energy structures of Si_2-Si_{11} are calculated at the MP2/6-31G(*d*) and CCSD(T)/6-31G(*d*) level, as shown in Table IV. Figure 4 plots the binding energies per atom versus the number of Si atoms *n*. A notable decrease in the slope of the curve can be seen at the cluster size of Si_4, Si_7, and Si_{10}.

As pointed out by Raghavachari and Rohlfing,[27] a better way to show the relative local stability of small silicon clusters is through the use of the incremental binding energy as a function of cluster size. The incremental binding energy can be defined as $(E_{n-1}+E_1)-E_n$, where E_n is the single-point total energy of cluster Si_n. Figure 5 shows the calculated incremental binding energy versus cluster size *n* at both

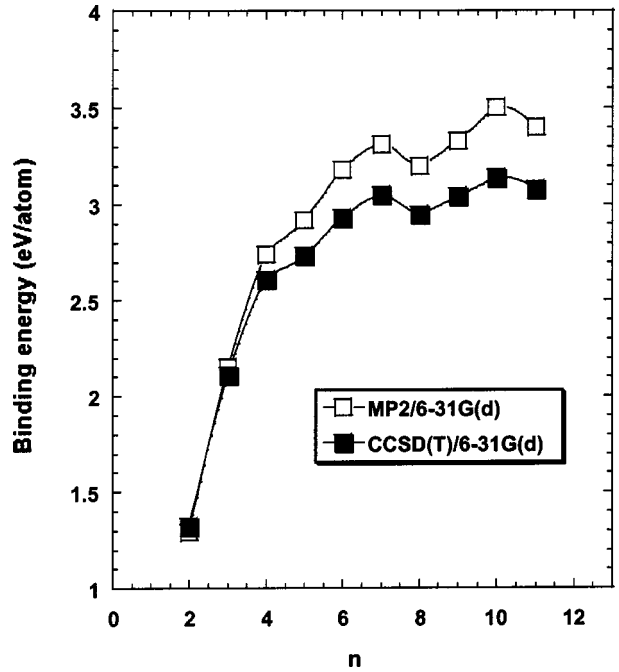

FIG. 4. Binding energy per atom of the lowest-energy structures of Si_2-Si_{11} vs cluster size *n*.

TABLE VI. Vertical ionization potentials of the lowest-energy isomer of Si_7-Si_{11}.

Cluster	Isomer	PG (state)	IP (calc.) (eV)	IP (expt.)[a] (eV)
Si_2		$D_{\infty h}$	7.87	>8.49
Si_3		C_{2v}	7.88	>8.49
Si_4		D_{2h}	8.09	7.97–8.49
Si_5		D_{3h}	8.02	7.97–8.49
Si_6		D_{4h}	7.84	7.97–8.49
Si_7	7*a*	$D_{5h}(^1A_1')$	7.86	~7.90
Si_8	8*a*	$C_{2h}(^1A_g)$	7.16	7.46–7.87
Si_9	9*a*	$C_{2v}(^1A_1)$	7.53	7.46–7.87
Si_{10}	10*a*	$C_{3v}(^1A_1)$	7.95	~7.90
Si_{11}	11*a*	$C_s(^1A')$	7.03	7.46–7.87

[a]Reference 50.

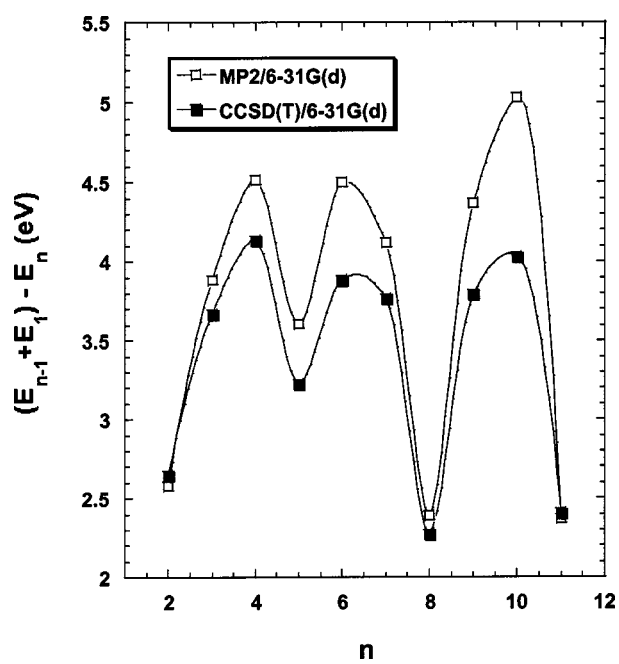

FIG. 5. Incremental binding energy of Si_2-Si_{11} clusters vs cluster size *n*.

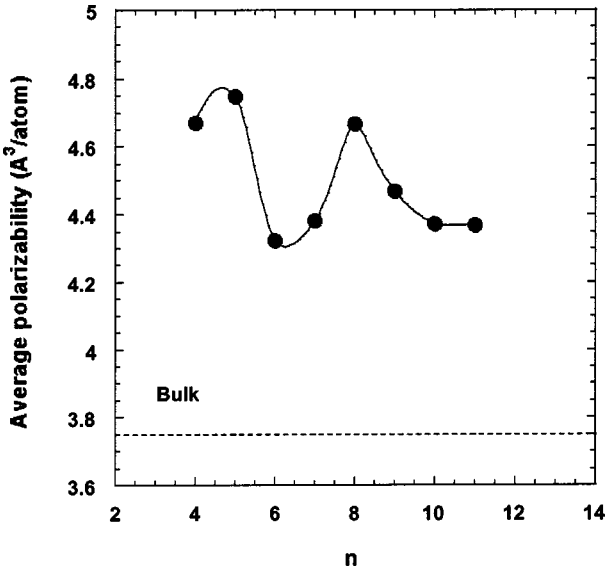

FIG. 6. Average polarizability for the lowest-energy structures of Si_4-Si_{11} as a function of cluster size *n*.

MP2/6-31G(d) and CCSD(T)/6-31G(d) levels. Clearly, the local maximum in the incremental binding energy corresponds to the cluster Si_4, Si_6, and Si_{10}. For the latter, the marked local stability together with the fact that Si_{10} has the highest binding energy compared to other small silicon clusters provide reasonable explanation why Si_{10} is a magic-number cluster with exceptional stability.

The cluster polarizability stems mainly from the surface electron density of the cluster.[42] As mentioned above, smaller clusters have a larger surface/interior atom ratio. For Si_7-Si_{11}, nearly all atoms are on the surface of the clusters. Thus, the polarizability of these clusters is expected to be larger than that of the bulk. In addition, the unsaturated bonds at the cluster surface will make polarizabilities even larger. In Fig. 6, results are shown for the size dependence of mean polarizability for Si_4-Si_{11}. The relatively strong stability of the magic-number cluster Si_6 and Si_{10} seems to correlate well with the local minimum in the cluster polarizability versus *n*.

IV. CONCLUSIONS

We have obtained optimized geometries of a number of low-energy geometric isomers of Si_7-Si_{11} at the MP2/6-31G(d) level and their energy at the CCSD(T)/6-31G(d) level. For Si_{11}, a larger basis set with both levels of theory, MP2/6-311G($2d$) and CCSD(T)/6-311G($2d$), were also employed. In most cases the electron-correlation effects on geometries of clusters are only quantitative, compared to geometries obtained at the HF/6-31G(d) level. In some cases, the electron-correlation effects can be qualitative. This is particularly important for Si_{11}. The calculated binding energies and vertical ionization potentials for the lowest-energy structures of Si_7-Si_{11} are in agreement with experimental values. The binding energy per atom has an $n^{-1/3}$ dependence, suggesting that small silicon clusters favors spherical-like cluster growth. A few new low-energy geometric isomers are found for these silicon clusters. Among them, a new candidate for the global minimum of Si_{11} is identified. The relatively strong stability of magic-number clusters Si_n ($n=6$ and 10) appears to correlate well with their relatively higher binding energy per atom, their local-maximum feature in the incremental binding energy and their local-minimum feature in the cluster polarizability vs the cluster size *n*.

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[1] T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smally, J. Chem. Phys. **74**, 6511 (1981).
[2] M. D. Morse, J. B. Hopkins, P. R. R. Langridge-Smith, and R. E. Smalley, J. Chem. Phys. **79**, 5316 (1983).
[3] J. L. Gole, J. H. English, and V. E. Bondybey, J. Phys. Chem. **86**, 2560 (1982).
[4] V. E. Bondybey and J. H. English, J. Chem. Phys. **80**, 568 (1984).
[5] D. J. Trevor, R. L. Whetten, D. M. Cox, and A. Kaldor, J. Am. Chem. Soc. **107**, 5181 (1985).
[6] S. J. Riley, E. K. Parks, G. C. Nieman, L. G. Pobo, and S. Wexler, J. Chem. Phys. **80**, 1360 (1984).
[7] M. F. Jarrold, Science **252**, 1085 (1991).
[8] W. L. Brown, R. R. Freeman, K. Raghavachari, and M. Schluter, Science **235**, 860 (1987).
[9] S. Hayashi, Y. Kanzawa, M. Kataoka, T. Nagarede, and K. Yamamoto, Z. Phys. D: At., Mol. Clusters **26**, 144 (1993).
[10] O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu, and R. E. Smalley, Chem. Phys. Lett. **138**, 119 (1987).
[11] J. R. Heath, Y. Liu, S. C. O'Brien, Q. Zhang, R. F. Curl, F. K. Tittel, and R. E. Smalley, J. Chem. Phys. **83**, 5520 (1985).
[12] Q. L. Zhang, Y. Liu, R. F. Curl, F. K. Tiittel, and R. E. Smalley, J. Chem. Phys. **88**, 1670 (1988).
[13] L. A. Bloomfield, R. R. Freeman, and W. L. Brown, Phys. Rev. Lett. **54**, 2246 (1985).
[14] L. A. Bloomfield, M. E. Guesic, R. R. Freeman, and W. L. Brown, Chem. Phys. Lett. **121**, 33 (1985).
[15] K. D. Rinnen and M. L. Mandich, Phys. Rev. Lett. **69**, 1823 (1992).
[16] W. Begemann, K. H. Meiwes-Broer, and H. O. Lutz, Phys. Rev. Lett. **73**, 2248 (1986).
[17] M. F. Jarrold and E. C. Honea, J. Phys. Chem. **95**, 9181 (1991).
[18] J. M. Hunter, J. L. Fye, M. F. Jarrold, and J. E. Bower, Phys. Rev. Lett. **73**, 2063 (1994).
[19] T. P. Martin and H. Schaber, J. Chem. Phys. **83**, 855 (1985).
[20] E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, Nature (London) **366**, 42 (1993).
[21] S. Li, R. J. Van Zee, W. Weltner, and K. Raghavachari, Jr., Chem. Phys. Lett. **243**, 275 (1995).
[22] K. 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).
[23] M. F. Jarrold and V. A. Constant, Phys. Rev. Lett. **67**, 2994 (1991); M. F. Jarrold and J. E. Bower, J. Phys. Chem. **96**, 9180 (1992); M. F. Jarrold, J. Phys. Chem. **99**, 11 (1995).
[24] H. Haberland, *Clusters of Atoms and Molecules: Theory, Experiment, and Clusters of Atoms* (Springer Verlag, New York, 1994).
[25] K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985).
[26] K. Raghavachari, J. Chem. Phys. **84**, 5672 (1986).
[27] K. Raghavachari and C. M. Rohlfing, J. Chem. Phys. **89**, 2219 (1988).
[28] C. M. Rohlfing and K. Raghavachari, Chem. Phys. Lett. **167**, 559 (1990); J. Chem. Phys. **96**, 2114 (1992).
[29] K. Raghavachari and C. M. Rohlfing, Chem. Phys. Lett. **94**, 3670 (1991).
[30] K. Raghavachari and C. M. Rohlfing, Chem. Phys. Lett. **198**, 521 (1992).
[31] J. C. Grossman and L. Mitas, Phys. Rev. Lett. **74**, 1323 (1995); L. Mitas, J. C. Grossman, I. Stich, and J. Tobik, Phys. Rev. Lett. **84**, 1479 (2000).
[32] W. D. Knight, K. Clemenger, W. A. de Heer, W. A. Saunders, M. Y. Chou, and M. L. Cohen, Phys. Rev. Lett. **52**, 2141 (1984).

[33] P. Ballone, W. Audreoni, R. Car, and M. Parrinello, Phys. Rev. Lett. **60**, 271 (1988).
[34] U. Rothlisberger, W. Andreoni, and P. Giannozzi, J. Chem. Phys. **96**, 1248 (1992).
[35] I. H. Lee, K. J. Chang, and Y. H. Lee, J. Phys.: Condens. Matter **6**, 741 (1994).
[36] P. Ordejon, D. Lebedenko, and M. Menon, Phys. Rev. B **50**, 5645 (1994).
[37] T. Fruuenheim, F. Weich, T. Kohler, S. Uhlmann, D. Porezag, and G. Seifert, Phys. Rev. B **52**, 11492 (1995).
[38] D. J. Wales, Phys. Rev. A **49**, 2195 (1994).
[39] 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); Z. Y. Lu, C. Z. Wang, and K. M. Ho, Phys. Rev. B **61**, 2329 (2000).
[40] B. X. Li, P. L. Cao, and M. Jiang, Phys. Status Solidi B **218**, 399 (2000); B. X. Li and P. L. Cao, Phys. Rev. A **62**, 023201 (2000); B. X. Li and P. L. Cao, J. Phys.: Condens. Matter **13**, 1 (2001).
[41] S. Wei, B. N. Barnett, and U. Landman, Phys. Rev. B **55**, 7935 (1997).
[42] I. Vasiliev, S. Ogut, and J. R. Chelikowsky, Phys. Rev. Lett. **78**, 4805 (1997).
[43] Y. Luo, J. Zhao, and G. H. Wang, Phys. Rev. B **60**, 10703 (1999).
[44] G. Pacchioni and J. Koutecky, J. Chem. Phys. **84**, 3301 (1986).
[45] A. Sieck, D. Porezag, Th. Frauenheim, M. R. Pederson, and K. Jackson, Phys. Rev. A **56**, 4890 (1997).
[46] E. Kaxiras, Phys. Rev. Lett. **64**, 551 (1990); E. Kaxiras and K. Jackson, Phys. Rev. Lett. **71**, 727 (1993).
[47] C. Sebenne, D. Bolmont, G. Guichar, and M. Balkanski, Phys. Rev. B **12**, 3280 (1975).
[48] M. M. Kappes, Chem. Rev. **88**, 1271 (1988).
[49] K. Fuke, K. Tsukamoto, F. Misaizu, and M. Sanekata, J. Chem. Phys. **99**, 7807 (1993).
[50] W. A. de Heer, W. D. Knight, M. Y. Chou, and M. L. Cohen, *Solid State Phys*. Vol. 40, edited by H. Ehrenreich, D. Turnbull (Academic, San Diego, 1987).
[51] M. Haser, J. AlmLof, and G. E. Scuseria, Chem. Phys. Lett. **181**, 497 (1991).
[52] C. Moller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[53] W. J. Hehre, L. Radom, P. Von R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1985).
[54] C. Peng, P. Y. Ayala, H. B. Schelgel, and M. J. Frisch, J. Comput. Chem. **17**, 49 (1996).
[55] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A9, Gaussian, Inc., Pittsburgh, PA, 1998.
[56] J. A. Pople and M. Head-Gordon, J. Chem. Phys. **87**, 5968 (1987).
[57] R. J. Bartlett, Annu. Rev. Phys. Chem. **32**, 359 (1981).
[58] P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993).
[59] B. Pan (private communication).