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Structures and stabilities of small silicon clusters: *Ab initio* molecular-orbital calculations of Si₇–Si₁₁

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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 Si₇, Si₈, and Si₁₀, 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 Si₉, 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 Si₁₁ because several low-energy geometric isomers were found nearly isoenergetic. On the basis of MP2/6-311G(2*d*)/CCSD(T)/6-311G(2*d*) 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(2*d*)/CCSD(T)/6-311G(2*d*) calculation. Additionally, calculations of the binding energy and the cluster polarizability offer more insights into relatively strong stability of two magic-number clusters Si₆ and Si₁₀. © 2003 American Institute of Physics. [DOI: 10.1063/1.1535906]

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 clusters¹⁰ 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 Si₆⁺–Si₁₁⁺. Several photodissociation^{13–15} and collision-induced dissociation^{16–18} experiments have shown that Si₆ and Si₁₀ have exceptional stability, consistent with their “magic number” (particularly abundant) behavior in the mass spectra of Si clusters.¹⁹ The Raman²⁰ and infrared²¹ 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, spectro-

scopic 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 Logovinsky²⁵ were apparently the first to use all-electron molecular-orbital methods to calculate energies of small silicon clusters (Si₂–Si₆) and identify their lowest-energy geometries. Later, Raghavachari and Rohlfing^{27–30} studied larger silicon clusters, Si₇–Si₁₁. They performed geometry optimization of several low-energy geometric isomers of Si₇–Si₁₀ 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 Si₇–Si₁₀ clusters have been

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reported. In the cases of Si₁₀ and Si₁₁, more detailed study of several low-energy geometric isomers was undertaken at higher MP4 or quadratic configuration-interaction [QCISD(T)] levels.^{28–30} For Si₇–Si₁₁, other theoretical methods have also been employed to search for their lowest-energy structures.^{21,26–31,35–45} Note that for Si₁₁, 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 Si₇–Si₁₁ 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 correlation⁴⁷ can sometimes have qualitative effects on the cluster geometry as some previously obtained stable isomers at the HF level can become 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 Si₇–Si₁₁. Correlation effects of all electrons in the clusters are thus taken into account approximately. For the geometry optimization, the Berny algorithm⁵⁴ in the GAUSSIAN 98 software⁵⁵ 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 Si₇–Si₁₁ 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 unbiasedly, 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 Si₇–Si₁₁, 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 Si₂ and Si₂H₆ 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 Si₇–Si₁₁, 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 Si₇ 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 Si₇ is *7a*, a *pentagonal bipyrimid* with *D*_{5h} symmetry, in agreement with the experiment²⁰ 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 cluster²⁴ 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 Si₈, 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}(¹*A*_g) point group, is the lowest-energy structure.^{27,28,36,39,42} Raghavachari and Rohlfing²⁷ have reported seven low-energy isomers of Si₈ on the basis of the HF/6-31G(*d*) level. Among the seven, six geometric isomers, i.e., *8a*(*C*_{2h},¹*A*_g), *8b*(*C*_{2v},¹*A*₁), *8d*(*C*_{2v},¹*A*₁), *8e*(*D*_{3d},³*A*_{1g}), *8f*(*C*_{3v},³*A*₂), and *8g*(*C*_s,¹*A*[′]) 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-

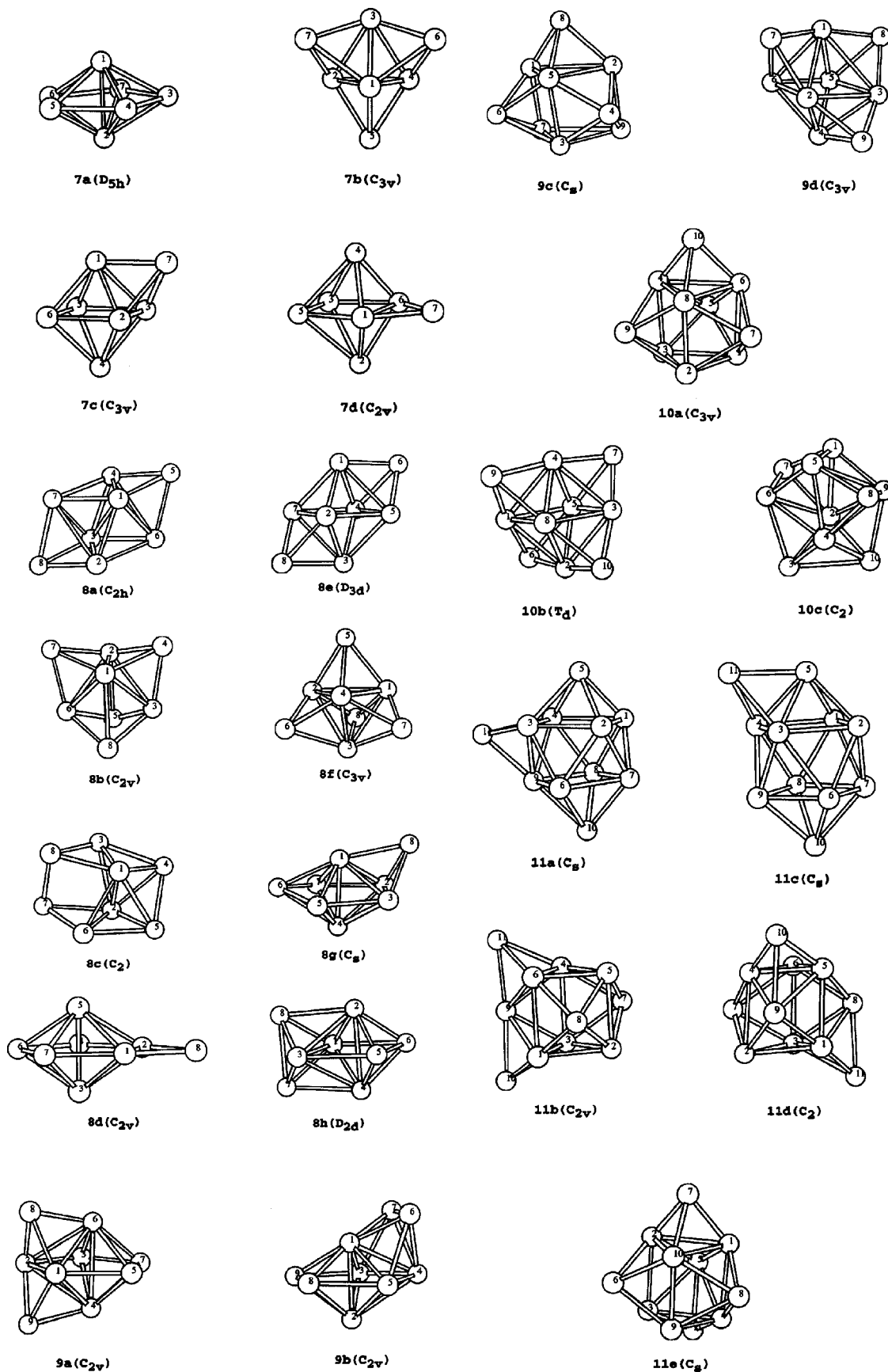


FIG. 1. Geometries of the low-energy isomer structures of Si_7 – Si_{11} at the MP2/6-31G(d) level [11e at the MP2/6-311(2d) level].

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 Si₇-Si₁₁ at the MP2/6-31G(d) level and (b) three low-energy isomers of Si₁₁ at the MP2/6-311(2d) level.

Cluster	Isomer	PG (State)	Bond length (Å)		Cluster	Isomer	PG (State)	Bond length (Å)		
(a)								Si ₂ -Si ₈	2.373	
Si ₇	7a	<i>D</i> _{5h} (¹ <i>A</i> ' ₁)	Si ₁ -Si ₄	2.458	8g	<i>C</i> _s (¹ <i>A</i> ' ₁)	Si ₃ -Si ₈	2.490		
			Si ₃ -Si ₄	2.483			Si ₁ -Si ₃	2.508		
			Si ₁ -Si ₂	2.512			Si ₁ -Si ₇	2.524		
	7b	<i>C</i> _{3v} (¹ <i>A</i> ₁)	Si ₁ -Si ₄	2.485	Si ₁ -Si ₆	2.386				
			Si ₂ -Si ₄	2.493	Si ₁ -Si ₄	2.478				
			Si ₁ -Si ₇	2.558	Si ₃ -Si ₄	2.559				
			Si ₂ -Si ₇	2.341	Si ₄ -Si ₇	2.422				
					Si ₄ -Si ₆	2.532				
	7c	<i>C</i> _{3v} (¹ <i>A</i> ₁)	Si ₁ -Si ₇	2.415	Si ₂ -Si ₃	2.897				
			Si ₁ -Si ₂	2.452	Si ₂ -Si ₇	2.485				
			Si ₁ -Si ₆	2.463	Si ₆ -Si ₇	2.440				
			Si ₄ -Si ₆	2.555	Si ₁ -Si ₈	2.470				
7d	<i>C</i> _{2v} (¹ <i>A</i> ₁)			8h	<i>D</i> _{2d} (¹ <i>A</i> ₁)	Si ₃ -Si ₈	2.403			
		Si ₁ -Si ₇	2.293			Si ₁ -Si ₇	2.343			
		Si ₁ -Si ₆	2.926			Si ₁ -Si ₂	2.619			
		Si ₁ -Si ₅	2.415			Si ₄ -Si ₇	2.926			
		Si ₁ -Si ₄	2.504			Si ₇ -Si ₈	2.636			
		Si ₃ -Si ₅	2.315			Si ₂ -Si ₄	2.894			
Si ₈	8a	<i>C</i> _{2h} (¹ <i>A</i> _g)	Si ₄ -Si ₅	2.687	Si ₉	9a	<i>C</i> _{2v} (¹ <i>A</i> ₁)	Si ₅ -Si ₇	2.401	
			Si ₁ -Si ₄	2.462				Si ₂ -Si ₃	2.552	
			Si ₄ -Si ₆	2.865				Si ₁ -Si ₂	2.547	
			Si ₁ -Si ₂	2.399				Si ₃ -Si ₆	2.529	
			Si ₂ -Si ₆	2.750				Si ₆ -Si ₇	2.391	
			Si ₁ -Si ₅	2.276				Si ₁ -Si ₆	2.757	
	8b	<i>C</i> _{2v} (¹ <i>A</i> ₁)	Si ₅ -Si ₆	2.454			Si ₂ -Si ₈	2.345		
			Si ₁ -Si ₃	2.802			Si ₄ -Si ₉	2.386		
					9b	<i>C</i> _{2v} (¹ <i>A</i> ₁)	Si ₄ -Si ₆	2.976		
			Si ₁ -Si ₆	2.647			Si ₁ -Si ₄	2.644		
			Si ₁ -Si ₂	2.480			Si ₁ -Si ₃	2.541		
	Si ₆ -Si ₇	2.359	Si ₁ -Si ₇	2.370						
	Si ₁ -Si ₇	2.384	Si ₁ -Si ₂	2.644						
	8c	<i>C</i> ₂ (¹ <i>A</i>)	Si ₆ -Si ₈	2.376			Si ₂ -Si ₄	2.751		
			Si ₁ -Si ₈	2.656			Si ₄ -Si ₅	2.583		
					9c	<i>C</i> _s (¹ <i>A</i> ' ₁)	Si ₄ -Si ₆	2.525		
			Si ₄ -Si ₅	2.536			Si ₁ -Si ₉	2.370		
			Si ₅ -Si ₆	2.516			Si ₈ -Si ₉	2.404		
Si ₂ -Si ₄			2.503	Si ₃ -Si ₇			2.458			
Si ₁ -Si ₄			2.326	Si ₃ -Si ₆			2.379			
Si ₂ -Si ₃			2.487	Si ₆ -Si ₇			2.656			
Si ₁ -Si ₃			2.511	Si ₅ -Si ₆			2.398			
Si ₁ -Si ₂			2.649	Si ₁ -Si ₆			2.441			
Si ₂ -Si ₇			2.491	Si ₁ -Si ₅			2.567			
Si ₃ -Si ₈			2.483	Si ₁ -Si ₈			2.376			
Si ₇ -Si ₈	2.356	Si ₅ -Si ₈	2.283							
8d	<i>C</i> _{2v} (¹ <i>A</i> ₁)	Si ₁ -Si ₅	2.535					Si ₇ -Si ₉	2.972	
		Si ₄ -Si ₅	2.482			Si ₁ -Si ₇	2.344			
		Si ₅ -Si ₆	2.425			Si ₃ -Si ₅	2.464			
		Si ₃ -Si ₅	2.695	9d	<i>C</i> _{3v} (³ <i>A</i> ₂)	Si ₁ -Si ₅	2.493			
		Si ₁ -Si ₂	2.380			Si ₁ -Si ₈	2.334			
		Si ₂ -Si ₄	2.483			Si ₁ -Si ₃	2.953			
		Si ₄ -Si ₆	2.482			Si ₅ -Si ₆	2.454			
		Si ₁ -Si ₈	2.320							
						Si ₁₀	10a	<i>C</i> _{3v} (¹ <i>A</i> ₁)	Si ₄ -Si ₈	2.760
		Si ₁ -Si ₄	2.574						Si ₃ -Si ₄	2.491
Si ₁ -Si ₇	2.495	Si ₂ -Si ₃	2.547							
Si ₁ -Si ₆	2.368	Si ₄ -Si ₁₀	2.318							
		Si ₄ -Si ₉	2.460							
		Si ₃ -Si ₉	2.434							
8e	<i>D</i> _{3d} (³ <i>A</i> _{1g})									
8f	<i>C</i> _{3v} (³ <i>A</i> ₂)	Si ₂ -Si ₄	2.674							
		Si ₂ -Si ₃	2.536							
		Si ₂ -Si ₅	2.469							

TABLE I. (Continued.)

Cluster	Isomer	PG (State)	Bond length (Å)		Cluster	Isomer	PG (State)	Bond length (Å)	
	10b	$T_d(^1A_1)$	Si ₄ -Si ₅	2.581		11d	$C_2(^1A)$	Si ₉ -Si ₁₀	2.674
	10c	$C_2(^1A)$	Si ₄ -Si ₈	2.354				Si ₁ -Si ₂	2.558
			Si ₄ -Si ₆	2.722				Si ₁ -Si ₃	2.441
			Si ₄ -Si ₉	2.708				Si ₂ -Si ₃	2.456
			Si ₂ -Si ₇	2.358				Si ₁ -Si ₅	2.601
			Si ₁ -Si ₂	2.508				Si ₃ -Si ₆	2.700
			Si ₁ -Si ₇	2.353				Si ₃ -Si ₇	2.385
			Si ₅ -Si ₆	2.420				Si ₁ -Si ₈	2.590
			Si ₃ -Si ₆	2.522				Si ₃ -Si ₈	2.459
			Si ₃ -Si ₁₀	2.695				Si ₁ -Si ₉	2.340
			Si ₃ -Si ₄	2.311				Si ₄ -Si ₁₀	2.428
			Si ₄ -Si ₁₀	2.473				Si ₅ -Si ₁₀	2.369
			Si ₁ -Si ₆	2.791				Si ₉ -Si ₁₀	2.504
			Si ₁ -Si ₅	2.366	(b)				
Si ₁₁	11a	$C_s(^1A')$	Si ₁ -Si ₂	2.698	Si ₁₁	11a'	$C_s(^1A')$	Si ₁ -Si ₂	2.648
			Si ₂ -Si ₃	2.531				Si ₂ -Si ₃	2.504
			Si ₃ -Si ₄	2.598				Si ₃ -Si ₄	2.778
			Si ₁ -Si ₅	2.450				Si ₁ -Si ₅	2.468
			Si ₃ -Si ₅	2.555				Si ₃ -Si ₅	2.591
			Si ₃ -Si ₆	2.412				Si ₃ -Si ₆	2.405
			Si ₁ -Si ₇	2.347				Si ₁ -Si ₇	2.399
			Si ₁ -Si ₈	2.419				Si ₁ -Si ₈	2.442
			Si ₃ -Si ₉	2.390				Si ₃ -Si ₉	2.440
			Si ₃ -Si ₁₁	2.483				Si ₃ -Si ₁₁	2.493
			Si ₆ -Si ₇	2.671				Si ₆ -Si ₇	2.686
			Si ₆ -Si ₉	2.481				Si ₆ -Si ₉	2.519
			Si ₆ -Si ₁₀	2.612				Si ₆ -Si ₁₀	2.582
			Si ₇ -Si ₁₀	2.369				Si ₇ -Si ₁₀	2.416
			Si ₉ -Si ₁₀	2.468				Si ₉ -Si ₁₀	2.499
			Si ₉ -Si ₁₁	2.365				Si ₉ -Si ₁₁	2.391
	11b	$C_{2v}(^1A_1)$	Si ₂ -Si ₇	2.501		11b'	$C_{2v}(^1A_1)$	Si ₂ -Si ₇	2.511
			Si ₃ -Si ₇	2.416				Si ₃ -Si ₇	2.434
			Si ₂ -Si ₅	2.566				Si ₂ -Si ₅	2.594
			Si ₃ -Si ₄	2.660				Si ₃ -Si ₄	2.677
			Si ₁ -Si ₃	2.479				Si ₁ -Si ₃	2.524
			Si ₁ -Si ₉	2.433				Si ₁ -Si ₉	2.463
			Si ₁ -Si ₁₀	2.414				Si ₁ -Si ₁₀	2.442
			Si ₉ -Si ₁₀	2.442				Si ₉ -Si ₁₀	2.470
			Si ₁ -Si ₂	2.475				Si ₁ -Si ₂	2.506
	11c	$C_s(^1A')$	Si ₂ -Si ₃	2.690		11e	$C_s(^1A')$	Si ₇ -Si ₁₀	2.459
			Si ₃ -Si ₄	2.515				Si ₁ -Si ₇	2.354
			Si ₁ -Si ₅	2.369				Si ₁ -Si ₂	2.603
			Si ₃ -Si ₅	2.522				Si ₂ -Si ₁₀	2.932
			Si ₂ -Si ₆	2.333				Si ₁ -Si ₇	2.502
			Si ₃ -Si ₆	2.382				Si ₆ -Si ₁₀	2.495
			Si ₁ -Si ₇	2.372				Si ₁ -Si ₅	2.429
			Si ₁ -Si ₈	2.333				Si ₄ -Si ₅	2.667
			Si ₄ -Si ₈	2.382				Si ₃ -Si ₆	2.458
			Si ₃ -Si ₉	2.401				Si ₄ -Si ₉	2.480
			Si ₃ -Si ₁₁	2.455				Si ₄ -Si ₁₁	2.451
			Si ₅ -Si ₁₁	2.376				Si ₃ -Si ₄	2.503
			Si ₆ -Si ₇	2.673				Si ₁ -Si ₄	2.576
			Si ₆ -Si ₉	2.661				Si ₉ -Si ₁₀	2.558
			Si ₆ -Si ₁₀	2.447				Si ₅ -Si ₁₁	2.478
			Si ₇ -Si ₁₀	2.480				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 Chelikowsky⁴² 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 Si₇-Si₁₁.

Cluster	Isomer	PG (state)	Vibrational frequency (IR intensities)			ZPE (eV)	
Si ₇	7a	<i>D</i> _{5h} (¹ <i>A</i> ' ₁)	232.54(0.21)	261.75(0.15)	443.38(10.52)	0.31	
			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)		
	7c	<i>C</i> _{3v} (¹ <i>A</i> ₁)	365.61(0.003)	459.62(3.40)	531.29(12.68)	0.31	
			137.84(1.44)	181.66(0.54)	283.53(0.93)		
			301.88(3.01)	332.30(0.91)	368.55(3.93)		
	7d	<i>C</i> _{2v} (¹ <i>A</i> ₁)	407.06(10.69)	426.94(3.91)	491.86(25.05)	0.26	
			38.97(0.02)	100.69(0.33)	109.02(1.13)		
			189.99(0.24)	247.14(1.88)	253.24(0.26)		
	Si ₈	8a	<i>C</i> _{2h} (¹ <i>A</i> _g)	329.29(2.76)	335.69(8.44)	376.51(0.14)	0.34
				449.01(13.54)	469.22(0.73)	501.24(2.28)	
				75.32(0.09)	150.67(0.70)	174.11(0.88)	
8b		<i>C</i> _{2v} (¹ <i>A</i> ₁)	255.47(0.54)	318.59(4.63)	385.50(0.59)	0.35	
			317.05(2.07)	544.93(8.35)			
			409.01(8.52)				
8c		<i>C</i> ₂ (¹ <i>A</i>)	132.26(4.49)	179.77(3.97)	214.29(0.19)	0.32	
			222.47(5.60)	254.85(2.00)	261.10(1.42)		
			292.59(0.35)	303.69(0.01)	319.27(3.02)		
8d		<i>C</i> _{2v} (¹ <i>A</i> ₁)	370.52(0.33)	407.71(7.94)	428.76(0.04)	0.33	
			445.17(0.2)	477.61(0.50)	498.07(0.38)		
			90.04(1.39)	123.25(0.02)	172.61(0.21)		
8e	<i>D</i> _{3d} (³ <i>A</i> _{1g})	177.92(0.48)	186.86(1.19)	201.84(0.19)	0.63		
		210.49(1.15)	289.20(0.05)	301.71(0.61)			
		325.50(4.87)	330.55(0.54)	338.80(0.001)			
8f	<i>C</i> _{3v} (³ <i>A</i> ₂)	372.49(5.19)	376.38(0.03)	424.67(10.23)	0.34		
		461.55(6.35)	488.39(6.84)				
		92.60(0.35)	145.75(0.001)	162.03(0.97)			
8g	<i>C</i> _s (¹ <i>A</i> ' ₁)	162.42(0.08)	194.11(2.27)	260.71(1.40)	0.34		
		274.41(0.52)	284.94(0.51)	310.04(0.31)			
		340.26(4.13)	362.84(1.39)	385.43(7.05)			
8h	<i>D</i> _{2d} (¹ <i>A</i> ₁)	408.50(0.06)	420.07(7.49)	439.13(9.88)	0.38		
		524.54(24.89)					
		135.79(0.53)	308.90(8.10)	323.85(0.02)			
Si ₉	9a	<i>C</i> _{2v} (¹ <i>A</i> ₁)	412.11(4.70)	482.84(3.58)		0.39	
			140.58(0.26)	230.19(0.05)	230.65(0.06)		
			248.87(0.004)	251.79(4.51)	268.42(2.16)		
	9b	<i>C</i> _{2v} (¹ <i>A</i> ₁)	322.38(1.66)	345.73(0.55)	386.96(4.96)	0.37	
			437.36(4.17)	463.54(5.78)			
			91.92(2.29)	119.14(3.33)	172.73(0.96)		
	9b	<i>C</i> _{2v} (¹ <i>A</i> ₁)	203.75(4.54)	216.59(1.70)	248.10(0.01)	0.39	
			270.59(1.37)	280.11(0.07)	299.67(3.97)		
			305.60(1.57)	323.10(2.83)	338.33(1.50)		
	9b	<i>C</i> _{2v} (¹ <i>A</i> ₁)	356.02(1.35)	423.99(1.25)	430.69(0.002)	0.37	
			452.31(1.47)	488.95(1.96)	498.22(1.76)		
			134.13(0.13)	165.82(0.001)	173.83(1.22)		
9b	<i>C</i> _{2v} (¹ <i>A</i> ₁)	181.72(0.27)	233.35(0.83)	257.63(0.001)	0.37		

TABLE II. (Continued.)

Cluster	Isomer	PG (state)	Vibrational frequency (IR intensities)			ZPE (eV)			
Si ₁₀	9c	C _s (¹ A')	265.31(2.49)	267.56(0.87)	296.65(0.85)	0.38			
			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)					
			70.55(1.38)	107.13(0.22)	162.90(0.15)				
			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)				
	9d	C _{3v} (³ A ₂)	347.10(0.70)	354.96(0.28)	369.99(1.36)	0.45			
			405.09(0.35)	452.67(3.80)	460.95(6.73)				
			487.42(0.13)	514.49(0.16)					
			100.30(6.84)	113.54(2.35)	179.23(9.29)				
			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)				
	10a	C _{3v} (¹ A 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)					
			10b	T _d (¹ A ₁)	98.10(8.03)		203.50(1.91)	299.79(3.46)	0.42
					546.14(22.05)				
10c	C ₂ (¹ A)	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	11a	C _s (¹ A')		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)				
11b	C _{2v} (¹ A 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)					
			11c	C _s (¹ A')	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)							
11d	C ₂ (¹ A)	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 Lee³⁵ and also Luo, Zhao, and Wang⁴³ 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

Si₁₀ 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 *tetra-capped 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 Si₇–Si₁₁.

Cluster	Isomer	PG (state)	MP2/6-31G(<i>d</i>) (eV)	CCSD(T)/6-31G(<i>d</i>) (eV)	MP2/6-311(2 <i>d</i>) (eV)	CCSD(T)/6-311(2 <i>d</i>) (eV)
Si ₇	<i>7a</i>	$D_{5h}(^1A'_1)$	0.00	0.00		
	<i>7b</i>	$C_{3v}(^1A_1)$	0.93	0.67		
	<i>7c</i>	$C_{3v}(^1A_1)$	2.17	1.71		
	<i>7d</i>	$C_{2v}(^1A_1)$	2.63	2.21		
Si ₈	<i>8a</i>	$C_{2h}(^1A_g)$	0.00	0.00		
	<i>8b</i>	$C_{2v}(^1A_1)$	0.31	0.19		
	<i>8c</i>	$C_2(^1A)$	0.58	0.52		
	<i>8d</i>	$C_{2v}(^1A_1)$	0.41	0.55		
	<i>8e</i>	$D_{3d}(^3A_{1g})$	0.68	0.58		
	<i>8f</i>	$C_{3v}(^3A_2)$	0.95	0.60		
	<i>8g</i>	$C_s(^1A')$	0.52	0.62		
	<i>8h</i>	$D_{2d}(^1A_1)$	1.00	1.73		
Si ₉	<i>9a</i>	$C_{2v}(^1A_1)$	0.00	0.00		
	<i>9b</i>	$C_{2v}(^1A_1)$	0.60	0.74		
	<i>9c</i>	$C_s(^1A')$	1.28	1.24		
	<i>9d</i>	$C_{3v}(^3A_2)$	2.07	1.60		
Si ₁₀	<i>10a</i>	$C_{3v}(^1A_1)$	0.00	0.00		
	<i>10b</i>	$T_d(^1A_1)$	1.99	0.75		
	<i>10c</i>	$C_2(^1A)$	1.27	0.81		
Si ₁₁	<i>11a</i>	$C_s(^1A')$	0.00	0.00	0.00(11 <i>a'</i>)	0.09(11 <i>a'</i>)
	<i>11b</i>	$C_{2v}(^1A_1)$	0.53	0.02	0.40(11 <i>b'</i>)	0.00(11 <i>b'</i>)
	<i>11c</i>	$C_s(^1A')$	0.21	0.22		
	<i>11d</i>	$C_2(^1A)$	0.87	0.53		
	<i>11e</i>	$C_s(^1A')$			0.00	0.03

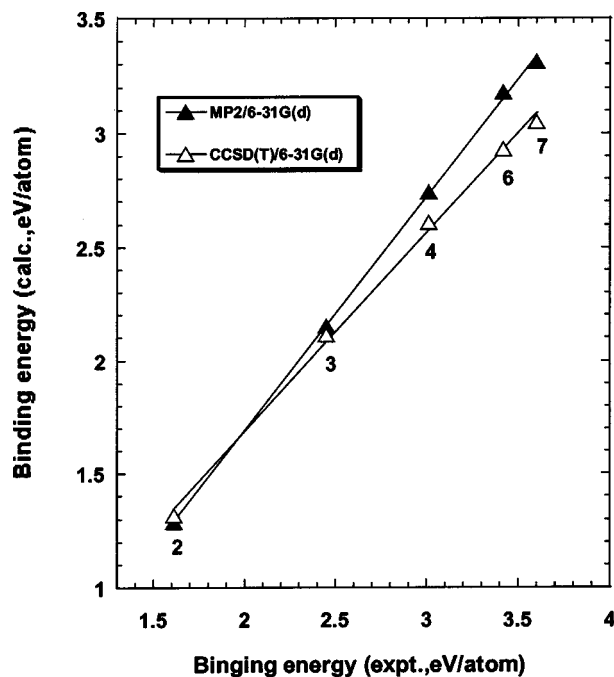


FIG. 2. Correlation of the calculated binding energies per atom and measured values for the low-energy isomers of Si_n ($n=2-4,6-7$).

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 Lee³⁵ and also later by Sieck *et al.*,⁴⁵

$11b(C_{2v}, ^1A_1)$ and $11c(C_s, ^1A')$ were predicted by Rohlfing and Raghavachari²⁸ 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 coworkers³⁹ using a density-functional pseudo-potential 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-workers³⁹ 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(2*d*)/CCSD(T)/6-311G(2*d*) levels for which our current computer facility can afford. The full geometry optimization at the MP2/6-311G(2*d*) 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(2*d*) and CCSD(T)/6-311G(2*d*) levels are listed in Table III. At the MP2/6-311G(2*d*) 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(2*d*) 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(2*d*)] 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(2*d*) 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(3*df*)] 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(<i>d</i>)	CCSD(T)/6-31G(<i>d</i>)	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
$\text{Si}_7(7a)$	D_{5h}	3.31	3.05	3.60
$\text{Si}_8(8a)$	C_{2h}	3.20	2.95	
$\text{Si}_9(9a)$	C_{2v}	3.33	3.04	
$\text{Si}_{10}(10a)$	C_{3v}	3.50	3.14	
$\text{Si}_{11}(11a)$	C_s	3.40	3.08	

^aReference 31.

CCSD(T) levels consistently reproduce all the global-minimum structures of Si₇–Si₁₀ reported in the literature.^{27,39,45} For Si₁₁, 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}, ¹A₁) 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 Si₇–Si₁₁. 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 Si₆.^{20,25} When capped on edges or faces, it becomes clusters 7c, 7d, 8e, 8h, 9d, or 10b. Although the tetrahedron (Si₄) 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 Si₉, 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 Si₁₁ (11a–11e) and even some larger Si_n (n = 12–26) clusters²¹ as well.

A common feature in small silicon clusters Si₇–Si₁₁ 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 Si₇, 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 Si₈ 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 Si₄ (Ref. 27) and Si₆ (Ref. 20). For Si₉, 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 Si₇–Si₁₁ at the MP2/6-31G(d) level.

Cluster	Isomer	PG (state)	μ(D)
Si ₇	7a	D _{5h} (¹ A' ₁)	0.000
	7b	C _{3v} (¹ A ₁)	1.518
	7c	C _{3v} (¹ A ₁)	1.602
	7d	C _{2v} (¹ A ₁)	1.639
Si ₈	8a	C _{2h} (¹ A _g)	0.000
	8b	C _{2v} (¹ A ₁)	0.611
	8c	C ₂ (¹ A)	1.360
	8d	C _{2v} (¹ A ₁)	1.929
	8e	D _{3d} (³ A _{1g})	0.000
	8f	C _{3v} (³ A ₂)	0.324
	8g	C _s (¹ A')	0.880
	8h	D _{2d} (¹ A ₁)	0.000
Si ₉	9a	C _{2v} (¹ A ₁)	0.430
	9b	C _{2v} (¹ A ₁)	1.216
	9c	C _s (¹ A')	1.235
	9d	C _{3v} (³ A ₂)	0.897
Si ₁₀	10a	C _{3v} (¹ A ₁)	1.101
	10b	T _d (¹ A ₁)	0.000
	10c	C ₂ (¹ A)	1.148
Si ₁₁	11a	C _s (¹ A')	1.258
	11b	C _{2v} (¹ A ₁)	2.098
	11c	C _s (¹ A')	2.288
	11d	C ₂ (¹ A)	1.215

C. Energy and stability

It can be seen from Table III that the lowest-energy structures of Si₇–Si₁₁ 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 Si₇ are higher in energy

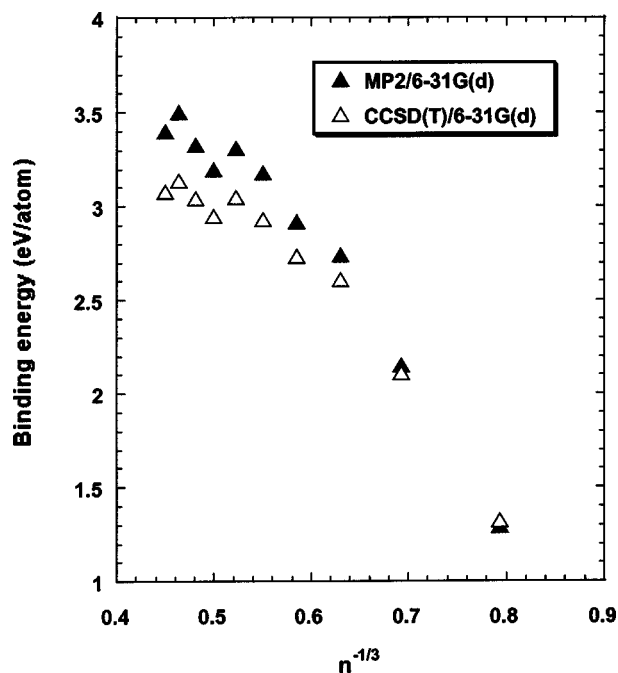


FIG. 3. Correlation of binding energy per atom and n^{-1/3} for the low-energy isomers of Si₂–Si₁₁.

than $7a$ by 0.93 and 2.17 eV at the MP2/6-31G(*d*) level, but at the CCSD(T)/6-31G(*d*) level, $7b$ and $7c$ are 0.67 and 1.71 eV higher than $7a$. 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 values⁴⁸ 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” clusters³² 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 Wang⁴³ 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

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	$7a$	$D_{5h}(^1A'_1)$	7.86	~7.90
Si_8	$8a$	$C_{2h}(^1A_g)$	7.16	7.46–7.87
Si_9	$9a$	$C_{2v}(^1A_1)$	7.53	7.46–7.87
Si_{10}	$10a$	$C_{3v}(^1A_1)$	7.95	~7.90
Si_{11}	$11a$	$C_s(^1A')$	7.03	7.46–7.87

^aReference 50.

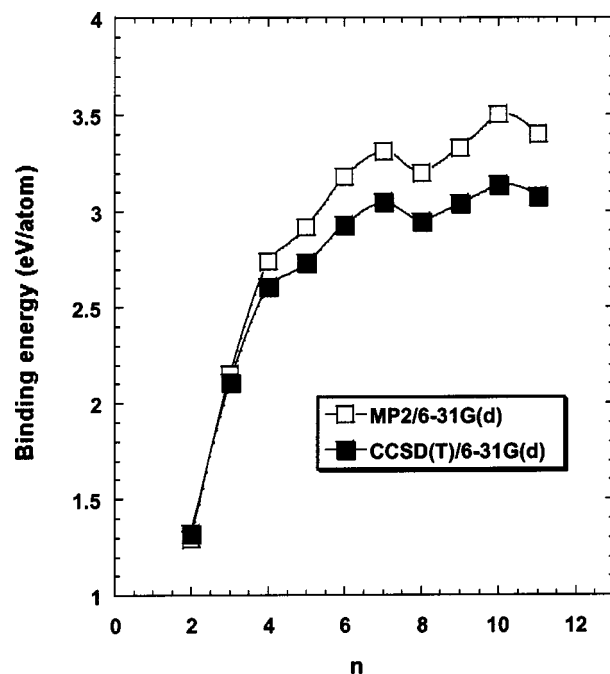


FIG. 4. Binding energy per atom of the lowest-energy structures of Si_2 – Si_{11} vs cluster size n .

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

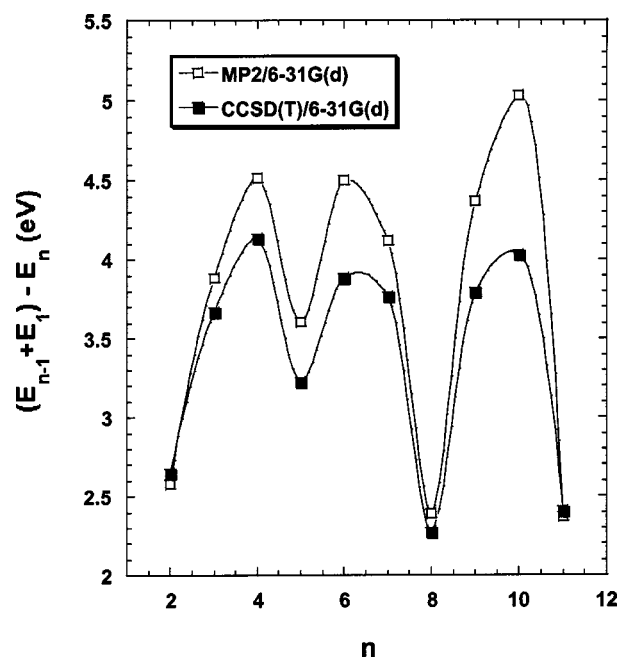


FIG. 5. Incremental binding energy of Si_2 – Si_{11} clusters vs cluster size n .

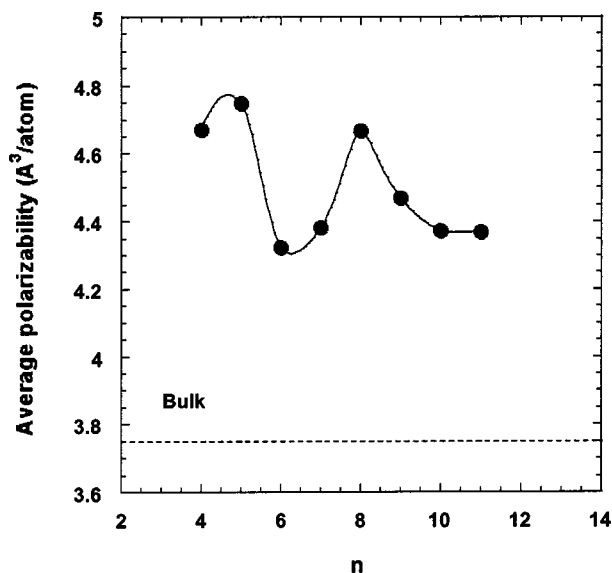


FIG. 6. Average polarizability for the lowest-energy structures of Si₄-Si₁₁ as a function of cluster size n .

MP2/6-31G(*d*) and CCSD(T)/6-31G(*d*) levels. Clearly, the local maximum in the incremental binding energy corresponds to the cluster Si₄, Si₆, and Si₁₀. For the latter, the marked local stability together with the fact that Si₁₀ has the highest binding energy compared to other small silicon clusters provide reasonable explanation why Si₁₀ 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 Si₇-Si₁₁, 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 Si₄-Si₁₁. The relatively strong stability of the magic-number cluster Si₆ and Si₁₀ 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 Si₇-Si₁₁ at the MP2/6-31G(*d*) level and their energy at the CCSD(T)/6-31G(*d*) level. For Si₁₁, a larger basis set with both levels of theory, MP2/6-311G(2*d*) and CCSD(T)/6-311G(2*d*), 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 Si₁₁. The calculated binding energies and vertical ionization potentials for the lowest-energy structures of Si₇-Si₁₁ 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 Si₁₁ 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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- T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smalley, *J. Chem. Phys.* **74**, 6511 (1981).
- M. D. Morse, J. B. Hopkins, P. R. R. Langridge-Smith, and R. E. Smalley, *J. Chem. Phys.* **79**, 5316 (1983).
- J. L. Gole, J. H. English, and V. E. Bondybey, *J. Phys. Chem.* **86**, 2560 (1982).
- V. E. Bondybey and J. H. English, *J. Chem. Phys.* **80**, 568 (1984).
- D. J. Trevor, R. L. Whetten, D. M. Cox, and A. Kaldor, *J. Am. Chem. Soc.* **107**, 5181 (1985).
- S. J. Riley, E. K. Parks, G. C. Nieman, L. G. Pobo, and S. Wexler, *J. Chem. Phys.* **80**, 1360 (1984).
- M. F. Jarrold, *Science* **252**, 1085 (1991).
- W. L. Brown, R. R. Freeman, K. Raghavachari, and M. Schluter, *Science* **235**, 860 (1987).
- S. Hayashi, Y. Kanzawa, M. Kataoka, T. Nagarede, and K. Yamamoto, *Z. Phys. D: At., Mol. Clusters* **26**, 144 (1993).
- O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu, and R. E. Smalley, *Chem. Phys. Lett.* **138**, 119 (1987).
- 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).
- Q. L. Zhang, Y. Liu, R. F. Curl, F. K. Tittel, and R. E. Smalley, *J. Chem. Phys.* **88**, 1670 (1988).
- L. A. Bloomfield, R. R. Freeman, and W. L. Brown, *Phys. Rev. Lett.* **54**, 2246 (1985).
- L. A. Bloomfield, M. E. Guesic, R. R. Freeman, and W. L. Brown, *Chem. Phys. Lett.* **121**, 33 (1985).
- K. D. Rinnen and M. L. Mandich, *Phys. Rev. Lett.* **69**, 1823 (1992).
- W. Begemann, K. H. Meiwes-Broer, and H. O. Lutz, *Phys. Rev. Lett.* **73**, 2248 (1986).
- M. F. Jarrold and E. C. Honea, *J. Phys. Chem.* **95**, 9181 (1991).
- J. M. Hunter, J. L. Fye, M. F. Jarrold, and J. E. Bower, *Phys. Rev. Lett.* **73**, 2063 (1994).
- T. P. Martin and H. Schaber, *J. Chem. Phys.* **83**, 855 (1985).
- 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).
- S. Li, R. J. Van Zee, W. Weltner, and K. Raghavachari, Jr., *Chem. Phys. Lett.* **243**, 275 (1995).
- 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).
- 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).
- H. Haberland, *Clusters of Atoms and Molecules: Theory, Experiment, and Clusters of Atoms* (Springer Verlag, New York, 1994).
- K. Raghavachari and V. Logovinsky, *Phys. Rev. Lett.* **55**, 2853 (1985).
- K. Raghavachari, *J. Chem. Phys.* **84**, 5672 (1986).
- K. Raghavachari and C. M. Rohlfing, *J. Chem. Phys.* **89**, 2219 (1988).
- C. M. Rohlfing and K. Raghavachari, *Chem. Phys. Lett.* **167**, 559 (1990); *J. Chem. Phys.* **96**, 2114 (1992).
- K. Raghavachari and C. M. Rohlfing, *Chem. Phys. Lett.* **94**, 3670 (1991).
- K. Raghavachari and C. M. Rohlfing, *Chem. Phys. Lett.* **198**, 521 (1992).
- 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).
- 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).

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