Structure and Bonding in Small Silicon Clusters

Krishnan Raghavachari and Veronika Logovinsky
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 12 August 1985)

Accurate *ab initio* molecular-orbital calculations are performed to obtain the ground-state geometries and electronic configurations of the silicon clusters Si_n for $n = 2$–7,10, and Si_n^+ for $n = 2$–6. The effects of polarization functions and electron correlation are included in these calculations. All the optimized structures are considerably reconstructed from those derived from microcrystal geometries. Ionization potentials and binding energies are calculated and used to interpret the distribution and fragmentation of small silicon cluster ions observed recently.

PACS numbers: 36.40.+d, 31.20.Tz, 31.90.+s

The study of the structures and properties of small clusters of atoms has been an increasingly active area of research in the last few years. Though much of the earlier work involved metallic systems, several groups have recently obtained considerable experimental information for semiconductor systems such as Si and Ge.[1–5] In particular, Bloomfield, Freeman, and Brown[3] have recently obtained not only the cluster-distribution patterns for positive cluster ions of Si but also the individual fragmentation patterns for each cluster ion (up to Si_{12}^+) after mass separation. In this Letter we report the first detailed *ab initio* quantum chemical investigation of the equilibrium geometries and electronic configurations for neutral (Si_n, $n = 2$–7 and $n = 10$) and ionic (Si_n^+, $n = 2$–6) clusters of Si atoms.[6] All the clusters are found to be considerably reconstructed from ideal microcrystal geometries assumed in some previous studies. We also report ionization potentials and binding energies which are useful in the interpretation of the distribution and fragmentation patterns of the ionic clusters.

Our calculations are based on accurate all-electron *ab initio* molecular-orbital techniques. Hartree-Fock (HF) theory was used with the polarized 6-31G* basis set[7] (valence double-zeta plus a set of *d*-type polarization functions on each Si) as the starting point in our calculations. This basis set has been widely used previously[7,8] in the case of second-row elements to calculate accurate molecular geometries, vibrational frequencies, and reaction energies. For each cluster under consideration, several possible geometrical arrangements and electronic configurations were considered in detail.[9] The geometries for each of these states were completely optimized by total energy minimization with use of analytical gradient techniques.[10] The optimized geometries are expected to be very accurate with errors in the computed Si-Si bond lengths of only about (1–2)%.[11] Electron correlation effects were included by means of complete fourth-order Møller-Plesset perturbation theory (MP4).[12] Such a treatment includes the effects of single, double, triple, and quadruple excitations from the reference HF determinant and has been shown to be reliable in the calculation of bond energies.[13]

We believe that absolute minima have been located in the case of neutral and ionic clusters up to Si_6. For each of these structures, the complete matrix of Cartesian force constants and the associated harmonic vibrational frequencies were evaluated by analytical second-derivative techniques.[10] All of the computed frequencies were positive, providing additional confirmation that the calculated structures were indeed minima. In the case of Si_7 and Si_{10}, the search was more limited, and only structures likely to be absolute minima (on the basis of the results of smaller calculations) were optimized fully. However, vibrational analysis showed that our best structure for Si_7 was indeed a minimum on the potential surface. Possible distortions to lower symmetries were not considered for Si_{10}. Effects of electron correlation were only estimated for Si_7 and Si_{10}.

The ground-state equilibrium structures[14] for the neutral and ionic structures of Si_2–Si_6 are displayed in Fig. 1. A detailed account of the different geometries and energies considered for all the clusters will be pub-

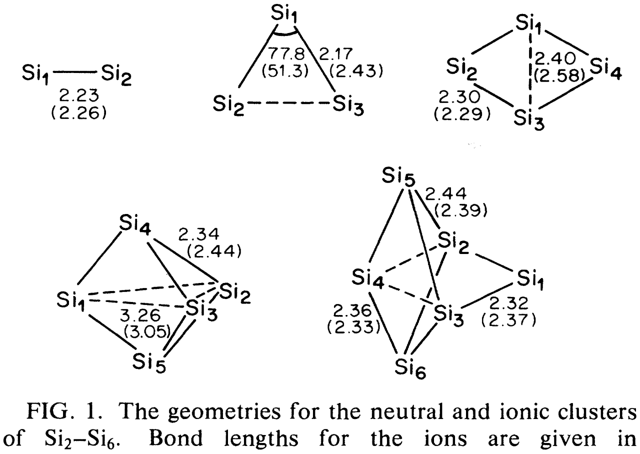

FIG. 1. The geometries for the neutral and ionic clusters of Si_2–Si_6. Bond lengths for the ions are given in parentheses. Not all the optimized geometrical parameters are listed.

lished separately.[15] All the neutral clusters considered in this study have singlet ground electronic states except Si_2 ($^3\Sigma_g^-$ ground state). The best calculated structures for Si_3–Si_7 correspond to an isosceles triangle, a planar rhombus, a flattened trigonal bipyramid (with the trigonal atoms not bonded to each other and the apex atoms only 2.78 Å apart), an edge-capped trigonal bipyramid, and a tricapped tetrahedron, respectively. The best calculated structure for Si_{10} corresponds to a tetracapped octahedral arrangement (alternate faces capped to yield a structure with T_d symmetry). The qualitative aspects of the smaller clusters are somewhat similar to those obtained previously on Ge clusters.[16]

Consideration of the structures of Si_3–Si_7 reveals that each cluster Si_n can be built from a smaller cluster Si_{n-1} by addition of a Si atom at an appropriate edge- or face-capped bonding site. Though edge-capped structures are favored in the case of the smaller clusters, face-capped structures become comparable in energy for the intermediate clusters. For example, the rhombus structure of Si_4 can be considered as an edge-capped triangular form and is considerably more stable than the face-capped structure (tetrahedron) by $\simeq 2.6$ eV. The ground-state structure for Si_5 can be formed by edge-capping of the short diagonal of the rhombus and twisting to make the three caps equivalent. In this case, there is a triplet state corresponding to a face-capped tetrahedral structure which is $\simeq 0.9$ eV higher in energy. For Si_6, an edge-capped trigonal bipyramidal structure (ground state) is only slightly ($\simeq 0.1$ eV) lower in energy than a face-capped structure (a bicapped tetrahedron which, however, is not a minimum on the Si_6 surface).

The larger clusters, though not considered in detail, appear to be similar. The best structure for Si_7 (not shown) is a tricapped tetrahedron, which can also be considered as a capped octahedron where the face being capped has enlarged considerably. Si_8 and Si_9, though not considered explicitly, are likely to be derived from bicapped and tricapped octahedral structures. Si_{10} is a tetracapped octahedron, though the bond length within the octahedron (2.65 Å) indicates only partial "bond" formation. The four cap atoms, however, are bound strongly (bond length $\simeq 2.37$ Å) to the atoms forming the respective faces of the octahedron, yielding a structure with overall T_d symmetry.

It can be immediately seen that all the calculated structures are considerably different from those derived from microcrystal geometries which have been suggested in some previous studies.[2,3] These include the pyramidal form for Si_4, the tetrahedral form for Si_5, the hexagonal "chair" form for Si_6, and the "adamantane"-type structure (symmetric crystalline subunit containing four fused six-membered chair rings)[3] for Si_{10}. In all cases, our calculated structures are more stable than the microcrystal structures by $\simeq 3$–6 eV. In particular, our compact structure calculated for Si_6 is about 5.5 eV more stable than the hexagonal chair form. It is interesting to note that our calculated structure for Si_{10} has the same framework symmetry (T_d) as the adamantane-type crystal fragment. However, the nature of the bonding is very different. For example, the divalent atoms in the adamantane crystal fragment (second-nearest neighbors, 3.8 Å apart) have moved considerably closer in our structure (only 2.65 Å apart) and form the partially bonded octahedron.

Though all our calculated structures are more compact than the microcrystal geometries, compactness (i.e., high coordination) is not the only criterion which determines the geometries of these structures. In general, structures such as a tetragonal pyramidal form for Si_5 or an octahedral (or tetragonal bipyramidal) form for Si_6 are unstable. These structures have the apex atoms in an unfavorable arrangement (forming four primary "bonds" all oriented on one side of a plane) and they rearrange to other structures which formally have fewer "bonds" but are more stable energetically.

Since all the neutral clusters are unsaturated, we can expect that the positive ions may be formed by removing an electron from one of the high-lying orbitals which is principally "lone pair" (nonbonding) in character. The primary bonding aspects of the neutral clusters would be retained in such cases and, indeed, all the ionic clusters (except Si_5^+, where there is a Jahn-Teller distortion) have the same framework symmetries as the parent neutral clusters. In all cases except Si_3^+ (where the neutral cluster has very low-lying excited states),[17,18] the orbital configurations of the ionic clusters correlate directly with those of the neutral states, as expected. Detailed analysis of the charge distributions in the ionic clusters shows that the positive charge resides primarily on the most "divalent" atoms (e.g., atoms 2 and 4 in Si_4 or atom 1 in Si_6), consistent with the electron being removed from the most "lone-pair"-like orbital.

Our results can be compared to those obtained from recent experiments on cluster distribution and fragmentation. In the experimental work,[3-5] Si_6^+ and Si_{10}^+ were found to be the prominent clusters. In addition, these clusters along with Si_4^+ were found to have small photofragmentation cross sections, indicating that 4, 6, and 10 are the "magic numbers" for the silicon cluster ions.

We have computed ionization potentials and binding energies for all the clusters at the MP4/6-31G* level (Table I). Comparison of the calculated binding energies of Si_2 and Si_3 with the corresponding experimental values[19,20] suggests that (80–85)% of the binding energy is obtained at this level of theory. Hence, all the

TABLE I. Binding energies and ionization potentials calculated for neutral and ionic clusters.

	Neutral cluster binding energy (eV)				Ionization potential (eV)		Ionic cluster binding energy (eV)
Molecule	HF	MP4	Scaled MP4	Expt.	MP4	Expt.	Best estimate
Si	· · ·	· · ·	· · ·	· · ·	8.0[a]	8.15[b]	· · ·
Si$_2$	1.51	2.64	3.17	3.21[c]	7.5[a]	7.4 ± 0.3[d]	3.7
Si$_3$	3.04	6.42	7.70	7.7 ± 0.2[e]	7.9	· · ·	7.8
Si$_4$	6.04	10.71	12.85	· · ·	7.6	· · ·	13.2
Si$_5$	7.42	13.92	16.70	· · ·	7.8[f]	· · ·	16.9
Si$_6$	10.13	18.26	21.91	· · ·	7.5[g]	· · ·	22.4
Si$_7$	11.69	(21.9)[h]	(26.3)	· · ·	· · ·	· · ·	(26.3)[i]
Si$_{10}$	18.11	(32.6)[j]	(39.2)	· · ·	· · ·	· · ·	(39.2)[i]

[a] Calculated with a $6s, 5p, 2d$ basis set.

[b] Reference 21.

[c] Reference 19.

[d] J. Drowart, G. De Maria, and M. K. Inghram, J. Chem. Phys. **29**, 1015 (1958).

[e] Reference 20.

[f] A correction due to spin contamination has been included in this value.

[g] Calculated at the MP4 level excluding triple excitations.

[h] Estimated under the assumption that the correlation effect was parallel to that of Si$_5$.

[i] The small effects due to ionization were not included in these estimates.

[j] Estimated under the assumption that the correlation effect was parallel to that of Si$_6$.

computed values are scaled by a factor of 1.2 to account for this systematic underestimation (Table I). The scaled binding energies of Si$_2$ and Si$_3$ (3.17 and 7.70 eV) are in excellent agreement with the experimentally derived values (3.21 eV[19] and 7.7 ± 0.2 eV[20]). The computed ionization potentials were then used to derive the binding energies of the ionic clusters. The binding energies per atom for Si$_n^+$ are plotted against the number of atoms n in Fig. 2. The plot indicates that Si$_4^+$ and Si$_6^+$ are more stable than suggested by the smoothly increasing background.

It is illustrative to compare the calculated binding energies of these clusters to that of the cohesive energy of a silicon atom in a crystal (4.63 eV).[21] The computed binding energy per atom for Si$_6$ (3.65 eV) corresponds to 79% of the cohesive energy. This is consistent with crude considerations of the clusters as compact forms where all the atoms are on the surface. Then we might expect to recover $\frac{3}{4}$ of the binding energy in the crystal, assuming an average of three effective "bonds" per atom. The estimated binding energy per atom for Si$_{10}$ (3.9 eV) is significantly higher than that of Si$_6$ (perhaps indicative of the stability of Si$_{10}$ whose ion is a prominent cluster) and represents 84% of the cohesive energy in the crystal. The effective number of "bonds" per atom (assuming four bonds per atom in the crystal) in this structure is $\simeq 3.4$. This value is considerably higher than that for the microcrystal forms of Si$_6$ and Si$_{10}$ which have an average coordination of only 2.0 and 2.4, respectively, again indicating the instability of such geometries.

In order to compare our results with the experimental fragmentation behavior, we have calculated the smallest energy necessary to fragment the clusters into smaller pieces. In all cases except Si$_{10}$, this corresponds to the process Si$_n \rightarrow$ Si$_{n-1}$ + Si. This is not surprising since earlier analysis showed that the clusters can be considered as being built from smaller clusters by addition of Si atoms. This is also consistent with the experimental results[3] for Si$_n^+$, $n = 2$–8, where the most prominent fragmentation process corresponds to the formation of Si$_{n-1}^+$. The calculated fragmentation energies for Si$_n^+$, $n = 2$–7, are plotted against n in Fig. 3. Si$_4^+$ and Si$_6^+$ show clear peaks, con-

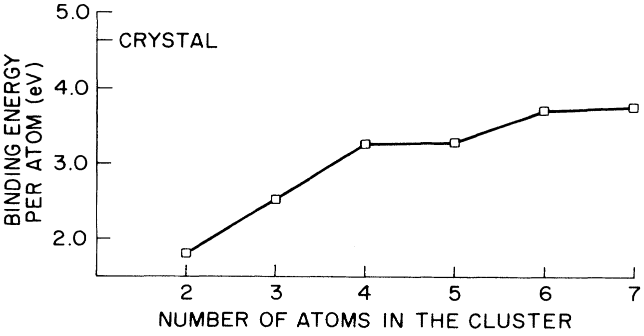

FIG. 2. Binding energy per atom (eV) vs the number of atoms in Si$_2^+$–Si$_7^+$.

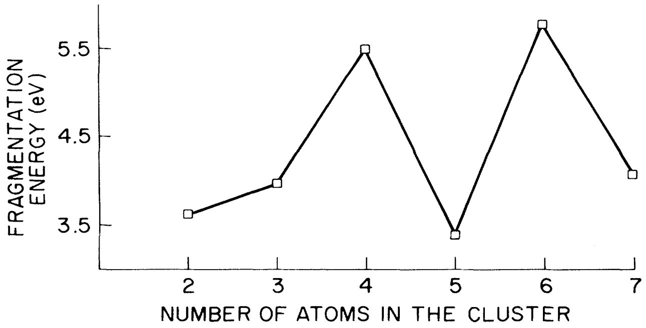

FIG. 3. Fragmentation energy (eV) for the reaction $Si_n^+ \rightarrow Si_{n-1}^+ + Si$ vs the number of atoms n for Si_2^+–Si_7^+.

sistent with the small observed photofragmentation cross sections for these clusters.[3]

The situation for Si_{10}^+ is more complicated. Firstly, the ground state of the ion will be Jahn-Teller distorted since the highest occupied orbital of Si_{10} is triply degenerate. Secondly, the fragmentation process involving the lowest energy appears to be $Si_6^+ + Si_4$ and not $Si_9^+ + Si$ (with the assumption of reasonable values for the binding energy of Si_9^+). This is entirely consistent with the observed fragmentation pattern[3] for Si_{10}^+ where the prominent fragment was indeed Si_6^+. However, it is not obvious in this case if such a process is viable without the requirement of additional bond breaking. In contrast to the simple fragmentation mechanisms for Si_2^+–Si_7^+, Si_{10}^+ may require a more complicated process involving simultaneous bond breaking and rearrangement.

We are indebted to F. H. Stillinger and M. Schlüter for some interesting discussions.

---

[1] R. E. Honig, J. Chem. Phys. **22**, 1610 (1954).

[2] T. T. Tsong, Appl. Phys. Lett. **45**, 1149 (1984), and Phys. Rev. B **30**, 4946 (1984).

[3] L. A. Bloomfield, R. R. Freeman, and W. L. Brown, Phys. Rev. Lett. **54**, 2246 (1985).

[4] T. P. Martin and H. Schaber, J. Chem. Phys. **83**, 855 (1985).

[5] J. R. Heath, Y. Lin, S. C. O'Brien, Q.-L. Zhang, R. F. Curl, R. E. Smalley, and F. K. Tittel, to be published.

[6] For a similarly motivated work on sodium clusters, see J. L. Martins, J. Buttet, and R. Car, Phys. Rev. Lett. **53**, 655 (1984).

[7] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, J. Chem. Phys. **77**, 3654 (1982). In the 6-31G* basis set the inner-shell orbitals ($1s, 2s, 2p$) are each represented by a linear combination of six Gaussian functions. The valence orbitals ($3s, 3p$) have a double-zeta representation with an inner function (three Gaussians) and an outer function (one Gaussian). The basis set also includes a set of six *d*-type second-order Gaussians as polarization functions.

[8] K. Raghavachari, J. Chandrasekhar, M. S. Gordon, and K. J. Dykema, J. Am. Chem. Soc. **106**, 5853 (1984).

[9] In the case of Si_2–Si_6, a large number of possible geometrical arrangements were considered in a fairly exhaustive attempt to locate the global minima on the respective potential energy surfaces. For each geometrical arrangement, several possible electronic states (singlets, triplets, etc.) were also considered in detail. As an example, the structures considered for Si_4 included the square (D_{4h}), rhombus (D_{2h}), rectangle (D_{2h}), tetrahedron (T_d), pyramidal (C_{3v}), linear ($D_{\infty h}$), and several other symmetry structures (D_{2d}, C_{2v}, etc.). In each case, complete geometry optimization and vibrational analysis were carried out to characterize the structures carefully. Detailed account of all the structures and energetics will be published separately (K. Raghavachari, to be published).

[10] J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem., Quantum Chem. Symp. **13**, 255 (1979).

[11] The calculated Si-Si bond lengths in Si_2 and Si_2H_6, 2.23 and 2.35 Å, are within 1% of the experimental values of 2.25 and 2.33 Å. For Si_3, the HF/6-31G* bond length (2.17 Å) is again in excellent agreement with the results from calculations including correlation effects (2.16–2.20 Å) [K. Raghavachari, J. Chem. Phys. **82**, 3520 (1985); G. H. F. Diercksen, N. E. Gruner, J. Oddershede, and J. R. Sabin, Chem. Phys. Lett. **117**, 29 (1985); R. S. Grev and H. F. Schaefer, Chem. Phys. Lett. **119**, 111 (1985)].

[12] R. Krishnan, M. J. Frisch, and J. A. Pople. J. Chem. Phys. **72**, 4244 (1980), and references therein.

[13] J. S. Binkley and M. J. Frisch, Int. J. Quantum Chem., Quantum Chem. Symp. **17**, 331 (1983), and references therein.

[14] Low-lying triplet electronic states (<0.2 eV above the ground state) were found for Si_2 and Si_3. In the case of Si_4–Si_6, the lowest excited states were found to be considerably higher ($\simeq$ 10 eV above the ground state).

[15] Raghavachari, Ref. 9.

[16] G. Pacchioni and J. Koutecky, Ber. Bunsenges. Phys. Chem. **88**, 242 (1984).

[17] For recent papers on Si_3, see Raghavachari, Ref. 11; Diercksen *et al.*, Ref. 11; and Grev and Schaefer, Ref. 11.

[18] In the case of Si_3^+, there are two Jahn-Teller distorted states (isosceles triangles with apex angles 51° and 71°) which are almost isoenergetic. In all other cases, there is a clear ground state, which is represented in Fig. 1.

[19] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).

[20] C. Chatillon, M. Allibert, and A. Pattoret, C.R. Hebd. Seances Acad. Sci. Ser. C **280**, 1505 (1975).

[21] C. E. Moore, *Atomic Energy Levels*, U.S. National Bureau of Standards, National Standard Reference Data Series—35 (U.S. GPO, Washington, D.C., 1969).