

Structure of the  $\text{Si}_{12}$  cluster

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Tight-binding molecular-dynamic simulations have revealed that  $\text{Si}_{12}$  is an icosahedron with all atoms on the surface of an approximately 5 Å diameter sphere. This is the most spherical cage structure for silicon clusters in the 2–13 atom size range.

The chemical reactions of silicon clusters with various reagents have puzzled both experimentalists and theoreticians.<sup>1–10</sup> Experimentally,  $\text{Si}_N$  clusters containing  $N = 2$ –50 atoms have exhibited strong oscillations in reactivities as a function of cluster size.<sup>1,2</sup> Theoreticians have attempted to explain this phenomenon either through the determination of cluster structures or through educated speculations.<sup>3–10</sup> Despite these efforts, a consistent view of the cluster structures and reactivities has not emerged.

Recently, we started to investigate this problem by calculating the structures of small silicon clusters using the tight-binding molecular-dynamics (TB-MD) method developed by Menon and co-workers.<sup>11–14</sup> This all-valence-electron method is equivalent to the extended Hückel method well known in theoretical chemistry.<sup>15</sup> This method has yielded structures in excellent agreement with *ab initio* electronic-structure calculations for both carbon and silicon clusters.<sup>11–14,16</sup> The particular Hamiltonian we employ consists of Harrison's universal tight-binding parameters,<sup>17</sup> supplemented with two additional parameters that are fit to the bond length and vibrational frequency of  $\text{Si}_2$ .<sup>14</sup> Full details of this method are described elsewhere.<sup>14</sup> Using this method in combination with classical molecular dynamics<sup>18</sup> and a slow annealing schedule, we optimized the structures of silicon clusters up to  $N = 13$ . The cluster structures thus derived for sizes up to  $N = 10$  are in complete agreement with the *ab initio* calculations of Raghavachari and co-workers.<sup>19,20</sup> This is remarkable considering that the parameters in this tight-binding Hamiltonian are not fit to any of the cluster structures.<sup>14</sup> This test verifies the reliability and predictability of our TB-MD method for the study of the structures of larger silicon clusters.

We now focus our attention on  $N = 11$ –13 clusters because experiments with ethylene show the most dramatic variations in reactivities in this size range, with  $\text{Si}_{12}$  being most reactive and  $\text{Si}_{13}$  being least reactive, even though all these clusters are equally abundant.<sup>2</sup> We found that  $\text{Si}_{11}$  is a tetragonal antiprism with one cap at the bottom and two caps at the top. Rohlifing and Raghavachari found this structure to be one of two possible candidates for the ground-state structure of  $\text{Si}_{11}$ .<sup>20</sup> The structure of  $\text{Si}_{13}$  may be described either as a 1-5-6-1 layered structure or as a capped trigonal antiprism, similar to that obtained by Röthlisberger and co-workers,<sup>21</sup> but unlike the atom-centered icosahedron proposed by Chelikowsky *et al.*<sup>22</sup> Even though these two structures are interesting

in themselves, neither of them are unique in their geometry.

The TB-MD simulated annealing calculations also revealed that the lowest energy structure of  $\text{Si}_{12}$  is an icosahedron with a diameter of  $\approx 5$  Å (see Fig. 1). Distortion from the ideal icosahedral geometry is small. Such a highly spherical cage structure for this cluster had not been anticipated before. The cohesive energy of this structure is  $-3.75$  eV/atom, its band gap is 1.8 eV, and its average coordination number is 5.0. Small distortions away from the ideal structure do not significantly change the cohesive energy. The ground-state is a singlet in all cases, but the perfect icosahedron has a smaller band gap (0.26 eV) compared to its distorted form (1.8 eV). We have also investigated several other geometries for this cluster and found that they are about 0.4–0.7 eV higher in energy than the icosahedron. Hence, several structural isomers of  $\text{Si}_{12}$  are possible, with the icosahedron being the ground state structure. The local coordination of atoms in the icosahedral form of  $\text{Si}_{12}$  is similar to that of the axial atoms in the pentagonal bipyramidal ground state of  $\text{Si}_7$ .

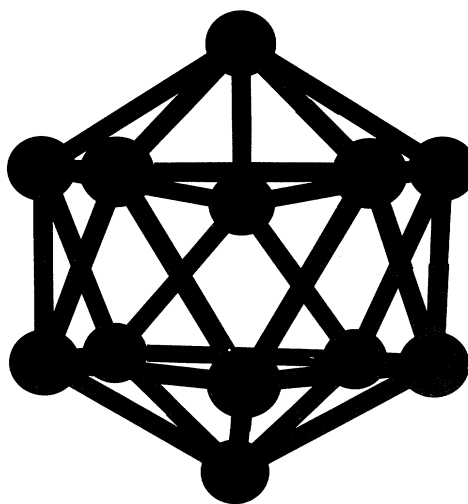


FIG. 1. The lowest energy structure of the  $\text{Si}_{12}$  cluster. It is a bicapped pentagonal antiprism, called an icosahedron. This geometry is also describable as a 1-5-5-1 layered structure. Experiments have shown this cluster to be highly reactive (Ref. 2).

Our calculations also show that the cohesive energies of  $\text{Si}_{12}$  and  $\text{Si}_{13}$  are nearly the same, indicative that reactivity differences between these two clusters are not related to their structural stabilities. However,  $\text{Si}_{11}$  and  $\text{Si}_{13}$  are either prolate or asymmetric tops, whereas  $\text{Si}_{12}$  is a spherical top. This finding is consistent with the observation of Jarrold and Bower that spherical clusters are at least an order of magnitude more reactive than the nonspherical clusters.<sup>23</sup> This is probably because the spherical surface provides the maximum number of nearest-neighbor pairs of silicon atoms that are needed to bind the ethylene molecule.

Since  $\text{Si}_{12}$  is highly reactive it has not aroused as much theoretical interest as the inert clusters. Consequently, until now the structure of  $\text{Si}_{12}$  has not been investigated through accurate calculations. The few calculations<sup>24,25</sup> that do exist on  $\text{Si}_{12}$  obtained structures consisting of four- and five-membered rings that are very different from ours. However, these calculations employed the Stillinger-Weber<sup>26</sup> or other empirical potentials that almost always yielded incorrect cluster structures, because these potentials were derived by fitting to the properties of bulk Si. Our tight-binding method does not suffer from this limitation because all the valence electrons are explicitly included in the calculation of the electronic energy.<sup>11-14,16</sup>

The icosahedral geometry with an atom at the center gives the closest packing of 13 hard spheres. The atoms interacting through two-body pair potentials typ-

ically form clusters with this structural pattern. For example,  $\text{Ar}_{13}$  is an atom-centered icosahedron.<sup>27</sup> However,  $\text{Ar}_{12}$  is not an icosahedron with an empty cage.<sup>27</sup> The metal clusters also prefer compact structures and do not allow empty cages.<sup>21,28</sup> Thus, the icosahedral cage structure is unique only for  $\text{Si}_{12}$  among elemental clusters. The compound clusters boranes and carboranes are the only other clusters that form icosahedral cage structures.

If two-body interaction is dominant in our tight-binding Hamiltonian, then we would expect to obtain an atom-centered icosahedron for  $\text{Si}_{13}$ . However, our calculations show such a structure to be about 2 eV higher in energy compared to the lowest energy structure. Furthermore, the structures of other  $\text{Si}_N$  clusters in the 3-11 size range are also not similar to those of  $\text{Ar}_N$  clusters. These two observations indicate that our tight-binding Hamiltonian includes the necessary many-body interactions required to describe the silicon cluster structures correctly.

In summary, our tight-binding molecular-dynamic simulations predict an icosahedral cage structure for  $\text{Si}_{12}$ . To our knowledge, such a highly symmetric noncrystalline cage structure has not been discovered previously for any other 12-atom elemental cluster.

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- <sup>1</sup> J. L. Elkind, J. M. Alford, F. D. Weiss, R. T. Laaksonen, and R. E. Smalley, *J. Chem. Phys.* **87**, 2397 (1987); S. Maruyama, L. R. Anderson, and R. E. Smalley, *ibid.* **93**, 5349 (1990); J. M. Alford, R. T. Laaksonen, and R. E. Smalley, *ibid.* **94**, 2618 (1991); L. R. Anderson, S. Maruyama, and R. E. Smalley, *Chem. Phys. Lett.* **176**, 348 (1991).
- <sup>2</sup> M. F. Jarrold, J. E. Bower, and K. M. Creegan, *J. Chem. Phys.* **90**, 3615 (1989); K. M. Creegan and M. F. Jarrold, *J. Am. Chem. Soc.* **112**, 3768 (1990); M. F. Jarrold, U. Ray, and K. M. Creegan, *J. Chem. Phys.* **93**, 224 (1990); U. Ray and M. F. Jarrold, *ibid.* **94**, 2631 (1991).
- <sup>3</sup> J. C. Phillips, *J. Chem. Phys.* **88**, 2090 (1988).
- <sup>4</sup> D. A. Jelski, Z. C. Wu, and T. F. George, *Chem. Phys. Lett.* **150**, 447 (1988).
- <sup>5</sup> E. Kaxiras, *Chem. Phys. Lett.* **163**, 323 (1989); *Phys. Rev. Lett.* **64**, 551 (1990).
- <sup>6</sup> B. C. Bolding and H. C. Andersen, *Phys. Rev. B* **41**, 10 568 (1990).
- <sup>7</sup> C. H. Patterson and R. P. Messmer, *Phys. Rev. B* **42**, 7530 (1990).
- <sup>8</sup> B. L. Swift, D. A. Jelski, D. S. Higgs, T. T. Rantala, and T. F. George, *Phys. Rev. Lett.* **66**, 2686 (1991); D. A. Jelski, B. L. Swift, T. T. Rantala, X. Xia, and T. F. George, *J. Chem. Phys.* **95**, 8552 (1991).
- <sup>9</sup> U. Röthlisberger, W. Andreoni, and M. Parrinello, *Phys. Rev. Lett.* **72**, 665 (1994).
- <sup>10</sup> Mushti V. Ramakrishna and J. Pan, *J. Chem. Phys.* **101**, 8108 (1994); J. Pan and Mushti V. Ramakrishna, *Phys. Rev. B* **50**, 15 431 (1994).
- <sup>11</sup> M. Menon and K. R. Subbaswamy, *Phys. Rev. Lett.* **67**, 3487 (1991); *Int. J. Mod. Phys. B* **6**, 3839 (1992).
- <sup>12</sup> M. Menon, K. R. Subbaswamy, and M. Sawtarie, *Phys. Rev. B* **48**, 8398 (1993); **49**, 13 966 (1994).
- <sup>13</sup> M. Menon and K. R. Subbaswamy, *Phys. Rev. B* **47**, 12 754 (1993); *Chem. Phys. Lett.* **219**, 219 (1994).
- <sup>14</sup> P. Ordejón, D. Lebedenko, and M. Menon, *Phys. Rev. B* **50**, 5645 (1994). We use the first set of parameters with  $a = 0.08$  and  $b = -1.4$  described in this paper.
- <sup>15</sup> J. P. Lowe, *Quantum Chemistry* (Academic Press, New York, 1978).
- <sup>16</sup> D. Tomañek and M. Schlüter, *Phys. Rev. Lett.* **56**, 1055 (1986); *Phys. Rev. B* **36**, 1208 (1987); *Phys. Rev. Lett.* **67**, 2331 (1991).
- <sup>17</sup> W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
- <sup>18</sup> M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Oxford University Press, New York, 1987).
- <sup>19</sup> K. Raghavachari and V. Logovinsky, *Phys. Rev. Lett.* **55**, 2853 (1985); K. Raghavachari, *J. Chem. Phys.* **83**, 3520 (1985); **84**, 5672 (1986); K. Raghavachari and C. M. Rohlfing, *Chem. Phys. Lett.* **143**, 428 (1988); *J. Chem. Phys.* **89**, 2219 (1988).
- <sup>20</sup> C. M. Rohlfing and K. Raghavachari, *Chem. Phys. Lett.* **167**, 559 (1990).
- <sup>21</sup> U. Röthlisberger, W. Andreoni, and P. Giannozzi, *J. Chem. Phys.* **96**, 1248 (1992).
- <sup>22</sup> J. R. Chelikowsky, J. C. Phillips, M. Kamal, and M.

- Strauss, Phys. Rev. Lett. **62**, 292 (1989); J. R. Chelikowsky, K. M. Glassford, and J. C. Phillips, Phys. Rev. B **44**, 1538 (1991).
- <sup>23</sup> M. F. Jarrold and J. E. Bower, J. Chem. Phys. **96**, 9180 (1992).
- <sup>24</sup> E. Blaisten-Barojas and D. Levesque, Phys. Rev. B **34**, 3910 (1986).
- <sup>25</sup> B. P. Feuston, R. K. Kalia, and P. Vashishta, Phys. Rev. B **35**, 6222 (1987); **37**, 6297 (1988).
- <sup>26</sup> F. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
- <sup>27</sup> S. Liu, Z. Bačić, J. W. Moskowitz, and K. E. Schmidt, J. Chem. Phys. **100**, 7166 (1994).
- <sup>28</sup> U. Röthlisberger and W. Andreoni, J. Chem. Phys. **94**, 8129 (1991).