Structure of Si$_{60}$. Cage versus network structures

Madhu Menon, K.R. Subbaswamy

Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506-0055, USA

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Abstract

A generalized tight-binding molecular dynamics technique which was used to obtain complete agreement with ab initio results for small silicon clusters is used to optimize the Si$_{60}$ cage without any symmetry restrictions. The perfect icosahedral cage is found to be unstable, distorting to a lower symmetry $C_{3v}$ structure with no change in the threefold coordination. The relaxed geometry shows increasing tendency for tetrahedral arrangement of atoms, and is energetically unfavorable compared to a relaxed bulk-like fragment. This is in contrast to carbon, where the cage is favored.

1. Introduction

Determination of the ground state geometry of the Si$_{60}$ cage has been the subject of some recent works [1,2]. Piqueras et al. [1] have made use of the AM1 method [3] to investigate the ground state structure of the icosahedral Si$_{60}$ cage. Based on their symmetry-restricted optimization they found this geometry ($I_h$ symmetry) to be an energy minimum with two distinct bond lengths, namely the same qualitative feature that characterizes the C$_{60}$ cage. Using a conventional orthogonal tight-binding molecular dynamics optimization scheme the authors of ref. [2] have performed a relaxation of an Si$_{60}$ icosahedral cage structure. Their results showed this icosahedral geometry to be unstable, relaxing into a structure resembling a puckered ball. While the orthogonal tight-binding molecular dynamics optimization scheme [4] has been used to obtain good agreement with ab initio [5,6] results for some small silicon clusters, no such comparisons have been reported using the AM1 method for these same clusters.

In this Letter we present our results for the symmetry-unrestricted geometry optimization for the Si$_{60}$ cage using the generalized tight-binding molecular dynamics scheme of Menon and Subbaswamy [7,8]. This approach has been applied to obtain equilibrium geometries for small silicon clusters in complete agreement with ab initio [5,6] results for the lowest energy structures of silicon clusters of size up to $N=10$ (for which ab initio results are available). This method has also been used to obtain equilibrium geometries, bond lengths, and cohesive energies for carbon clusters of arbitrary size [9]. The results obtained for small carbon clusters ($N<10$) are in complete agreement with available ab initio results [10]. The bond lengths for bulk-like diamond and graphitic structures are in excellent agreement with experiments [9]. The present scheme has also been successful in predicting the lowest energy configuration for an oxygen atom chemisorbed on a C$_{60}$ molecule [8,11]. Our prediction that this happens for the "epoxide" structure has been confirmed experimentally [12,13].
2. Theoretical methods

The details of the technique can be found elsewhere [7]. The method is a generalization of the conventional tight-binding molecular dynamics formulation [14,15] so as to apply to nontetrahedral, and multicoordinated covalent systems. The explicit inclusion of nonorthogonality of the orbitals in the scheme allows us to treat interactions between atoms without any cutoff. Hellmann–Feynman theorem is used to perform molecular dynamics optimization with no symmetry restrictions. The present scheme is an improvement over the conventional tight-binding schemes where the overlap interactions are neglected. This incorporation of nonorthogonality has yielded much improved agreement with available ab initio results for small silicon [7] and carbon [9] clusters when compared with the conventional orthogonal schemes. The most noteworthy improvement is in the area of vibrational frequencies where the orthogonal schemes have been found to be inadequate.

The method is orders of magnitude faster than ab initio or LDA techniques and, therefore, permits a much larger sampling of the configuration space to determine minimum energy structures. The tight-binding method can also be used to obtain valuable electronic structure information. The electronic tight-binding parameters (e.g., $V_{ss}$, $V_{pp}$, etc.) used here for silicon are generated using Harrison’s [16] universal parameter scheme and listed in ref. [7]. This allows us to keep the number of adjustable parameters to a minimum. The force evaluation involves only two adjustable parameters per chemical element, the coefficient of nonorthogonality and the coefficient of repulsion term. These are fitted by requiring that the correct experimental bond length and vibrational frequency for the silicon dimer be reproduced. This simple fitting procedure has shown to yield good agreement for bond lengths and frequencies for larger clusters [7].

3. Results and discussion

For a Si$_{60}$ cage we first obtained the equilibrium structure by starting from a perfect icosahedral configuration (Fig. 1, initial) and allowing all atoms to relax by removing 1% of each velocity at each time step. No symmetry restriction is imposed while the optimization is being carried out. The process is stopped when the largest velocity component of any atom falls below 54 m/s (corresponding to a temperature of about 10 K). We find the initial configuration with I$_h$ symmetry to be unstable, distorting to a lower symmetry geometry without any change in the coordination. The silicon atoms that formed planar hexagons and pentagons in the perfect icosahedral structure now move radially inward or outward, with atomic arrangement tending toward tetrahedral geometry. The relaxed structure has C$_{2h}$ symmetry (Fig. 1, final). Of the 60 vertices, 10 have the ideal tetrahedral angle. Another 36 vertices have at least one angle within 2° of the ideal tetrahedral angle. This suggests that the Jahn–Teller distortions favor displacements of atoms in the direction of increasing coordination. Several distinct bond lengths are obtained for the optimized structure, ranging from 2.34 to 2.53 Å with an average bond length of 2.40 Å. These bond lengths are in the same range as those obtained from ab initio calculations for the optimized structure for Si$_{60}$ [6].

The electronic level structure near the Fermi level for the undistorted and distorted Si$_{60}$ cages is shown in Fig. 2. The degeneracies, where they exist, are also noted. The arrow denotes the Fermi level. The perfect icosahedron (our starting configuration) has metallic character with a partially filled fivefold degenerate HOMO level. In the relaxed structure the degeneracies are completely removed by a symmetry lowering Jahn–Teller distortion and a HOMO–LUMO gap of 0.42 eV opens up. Although this value is less than half the gap found in bulk crystalline sili-
Fig. 2. The electronic level structure near the Fermi level for the (left) unrelaxed and (right) relaxed cages. Degeneracies are shown on the left. The Fermi levels are denoted by arrows. In the unrelaxed structure the Fermi level is partially occupied.

...tron, the tendency toward semiconducting character is clear.

This result for $Si_{60}$ is in striking contrast to that for $C_{60}$ which has a perfect icosahedral symmetry. This difference must be understood on general grounds by a consideration of the special chemistry of the C–C bond. Although Si and C are both isovalent, their behavior in forming chemical bonds is quite different. The smaller covalent radius of the carbon atom can generate sufficient strain energy to offset any energy gain by forming more closed packed structures for carbon clusters. This explains the persistence of linear and ring structures with low coordination for small carbon clusters with $N \leq 10$. As is well known, the threefold coordinates graphitic structure is nearly isoenergetic with the fourfold coordinated diamond. Silicon, on the other hand, readily forms multicordinated (coordination in excess of four) structures for $N \leq 10$ [5–7]. It should perhaps be not surprising that a threefold coordinated silicon cage, when allowed to relax, distorts to more tetrahedral-type geometry.

In order to investigate the differences further, we compare the relative stabilities of 60 atom silicon and carbon network (building blocks for bulk diamond structure) clusters with their caged structures. Although the fullerene forms benefit from lowering of energy due to cage closure, the network clusters have larger coordination even for a 60-atom cluster. The chemistry of the bonding largely determines which tendency predominates. Fig. 3 shows the fully optimized $Si_{60}$ and $C_{60}$ network clusters. As seen in Fig. 3, the equilibrium configuration shows considerable relaxation and reconstruction, particularly for the surface atoms. The relaxed structures also show the formation of surface dimers, namely, the well known $2 \times 1$ reconstruction of the $(001)$ surface [9]. In Table 1 we list the relative energies with respect to the fullerene cages formed by the respective elements. Also included in Table 1 are the average coordination for the atoms.

Interestingly, even though both silicon and carbon network clusters have larger coordination per atom than their fullerene counterparts, the binding energies show qualitatively different ordering. As seen in Table 1 the $Si_{60}$ network is more stable than the $C_{6n}$ symmetry $Si_{60}$ fullerene (by 0.31 eV/atom). By contrast, the $C_{60}$ fullerene is more favorable than the $C_{60}$ network cluster by a substantial energy difference (1.22 eV/atom).

4. Conclusion

Using the AM1 method with symmetry-restricted optimization, Piqueras et al. [1] have predicted the $Si_{60}$ cage to be stable. We have applied a generalized tight-binding molecular dynamics optimization scheme to study equilibrium geometries of 60-atom silicon cage and find the fullerene cage to be unstable on relaxation, distorting to a lower symmetry $C_{6n}$ geometry. The distortions of the relaxed cage are reminiscent of tetrahedral bonding geometry. Even with such high symmetry lowering distortions, the gain in...
Table 1
Relative total energies of C\textsubscript{60} and Si\textsubscript{60} isomers

<table>
<thead>
<tr>
<th>Structure</th>
<th>Silicon</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>average</td>
<td>average</td>
</tr>
<tr>
<td></td>
<td>coordination</td>
<td>coordination</td>
</tr>
<tr>
<td>fullerene</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>network</td>
<td>3.13</td>
<td>3.15</td>
</tr>
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energy is not sufficient to offset the energy gain by forming larger coordinated structures such as the network cluster. The 60-atom carbon cage, on the other hand, while retaining the Ih symmetry on relaxation, is considerably lower in energy when compared to the higher coordinated network cluster. This leads us to conclude that among the group IV elements the perfect icosahedral symmetry is unique to carbon whose smaller covalent radius generates sufficient strain to overcome any gain in energy by forming structures with larger coordination.

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References

[16] W. Harrison, Electronic structure and the properties of solids (Freeman, San Francisco, 1980).