Study of the Si fullerene cage isomers

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Abstract. We present the results of a study on the structural and electronic properties of the Si_{38} fullerene isomers, which are constructed by making all possible permutations among their pentagons and hexagons. These structures were firstly fully optimized with a tight binding molecular dynamics method and the resulting structures were further optimized with two more accurate, but more time consuming, methods, namely the generalized tight binding molecular dynamics and a DFT calculation at the B3LYP level. For comparison, the optimum structure of the Si_{20} fullerene cage is also presented, optimized with the same methods.

1. Introduction

By definition fullerenes are cage structures constructed of only pentagonal and hexagonal rings. Interest in them began with the I_h C_{60} structure, proposed by Kroto et al [1], in order to explain the abundance of the C_{60} molecule in their graphite laser vaporization experiment. It is easy to show that an N-atom fullerene structure is composed of exactly 12 pentagons and $N/2 - 10$ hexagons [2]. With permutations between these pentagons and hexagons, many isomers can be constructed, the number of which increases very rapidly with the number of atoms [2].

It was obvious that, after the discovery of the carbon fullerenes and their properties, questions about the silicon fullerenes would arise, since silicon is contiguous to carbon in the Periodic Table. Although these questions were posed very early, Si fullerenes were found to be thermodynamically unstable structures (see for example Ref. [3]). This is due to the difference in behavior between carbon and silicon in forming chemical bonds. Carbon prefers to form sp^2-like bonding and it can also form sp^1 and sp^3. On the other hand, silicon strongly prefers sp^3 bonding, forming dangling bonds rather than engaging in multiple bonds.

Nevertheless, the interest in Si fullerenes is still active. Their properties are interesting for the understanding of the Si trivalent bonding systems, as on surfaces, Si-C heterofullerenes, nanowires, nanotubes [4, 5], Si endohedral clusters [5, 6], clathrates [7] etc, which are expected to have potential application in nanotechnology.

To the best of our knowledge, the studied Si_N fullerene structures are those with N=20-32,36,44,50,60, (see for example Ref. [8]). Most of these publications are focused on the Si_{60} fullerene (see, for example, Ref. [3, 9, 10] and references therein). A recent work by Ju-Guang Han et al [11] presents a systematic theoretical study of some Si_N (N=26-36,60) fullerene-like

cages. Not all of these structures are true fullerenes, because many of them include four-valent atoms.

Early papers reported several Si fullerenes to be stable structures. More recent calculations find them to be unstable. Nevertheless, Q. Sun et al [6] reported that the Si_{60} fullerene could be stabilized by encapsulating a "magic" cluster within it, such as $Al_{12}X$ (X=Si,Ge,Sn,Pb) or $Ba@Si_{20}$.

All the previous mentioned work was focused on highly symmetrical starting structures, which were usually found to reduce to structures with lower symmetry. To date there is no systematic study of all possible structures with a given nuclearity. The only general conclusions arising from these studies are the following: (a) All the Si fullerenes are thermodynamically unstable though they represent local energy minima in their configuration space and, (b) the structures at these local minima look like "puckered" balls [9], with the Si atoms moved radially outwards and inwards [3].

In this work, a systematic study of the Si fullerene isomers, constructed by permutation of pentagons and hexagons, is presented for the first time, for the 38-atom Si fullerene. For comparison, a study of the Si_{20} with the same methods is also presented.

2. The method

To find the global optimum structures for the 17 Si_{38} fullerene isomers [2], a novel global optimization method is applied [12], which combines the algorithm of Berendsen et al. [13] and the usual damping molecular dynamics. This method was found to reproduce the first hundred Lennard-Jones clusters, as they are presented in the Cambridge Cluster Database [14].

By freezing the atoms every time an interatomic distance becomes larger than a particular cut off distance, the initial fullerene net with trivalent bonding is conserved, and the search for the global minimum is restricted to the configuration space of each particular fullerene isomer. Without this freezing, an initial fullerene net collapses to a more compact and more stable structure in some hundreds of time steps, and the search for the optimum fullerene structure will fail. To speed up the search for the global minimum, a simple orthogonal tight binding hamiltonian with a fitted repulsive pair potential (see for example Ref. [15] and references therein) is applied to describe the potential energy surface of the 17 Si_{38} fullerene isomers. Within this approach the global optimization method is orders of magnitude faster than with any ab-initio methods. The 17 optimum structures found with the orthogonal tight binding approximation were further optimized with two more accurate but more time consuming methods, namely generalized tight binding molecular dynamics [16] and a DFT calculation with the B3LYP functional, using a DZP basis set. The DFT calculation was carried out with the GAMESS-UK program [17]. On general grounds, it is to be expected that the DFT/B3LYP method will give results that are more reliable than the semi-empirical OTBMD and the GTBMD methods, but as will be shown, the structures found with all three methods differ only slightly from each other, so that all three methods give useful information on structural patterns.

3. Results and discussion

Optimizing the 17 isomers of the Si_{38} fullerene with the three methods mentioned above, it was found that the isomer which initially belongs to the D_3 point group symmetry (isomer 38:9 in the spiral numbering system [2], p. 185) is the optimum one. Although the 17 isomers considered as graphs embedded on the sphere have various maximum point group symmetries, $D_{3h}(1)$, $C_{3v}(1)$, $D_3(1)$, $C_{2v}(1)$, $C_2(5)$, $C_1(7)$ [2], on optimization all distort to C_1 symmetry. As mentioned in the introduction, Si_{20} fullerene is also studied here for comparison. The single isomer of the Si_{20} fullerene is the well known dodecahedron with topologically maximum I_h symmetry. However, its symmetry is reduced to C_2 in the OTBMD optimization, and, on GTBMD and DFT further

| Compound | OTBMD | GTBMD | DFT/B3LYP |

Si_{38}
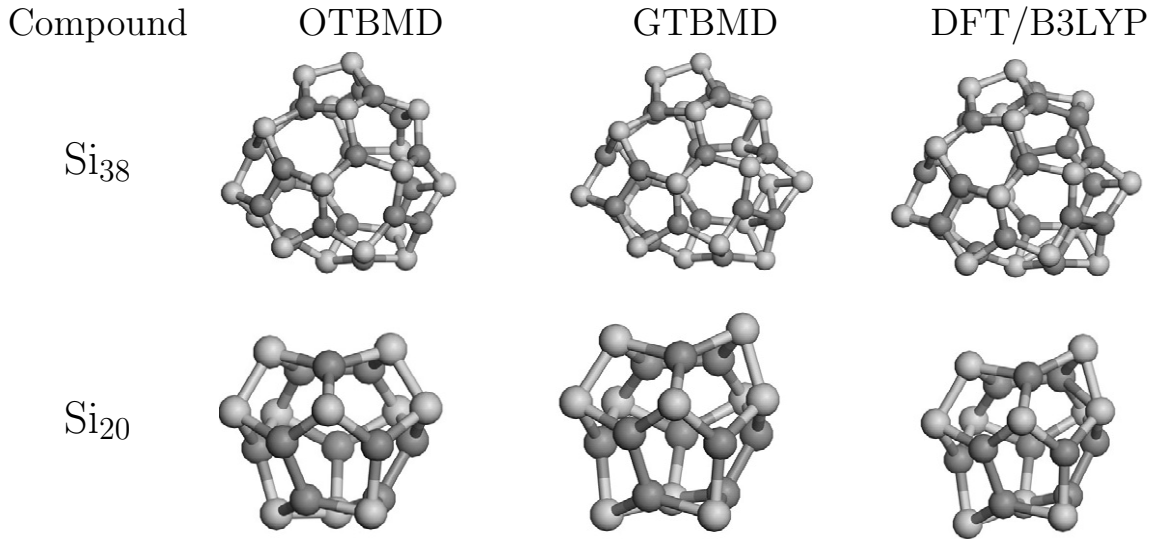
Si_{20}

Figure 1. Optimum structures

optimization, it is reduced to C_1 symmetry. Bao-xing Li and Pei-lin Cao [8], using a full-potential linear-muffin-tin-orbital molecular dynamics method, reported that the relaxed Si_{20} fullerene belongs to the I_h point group. In view of the electron count, which implies a Jahn - Teller distortion for the neutral cluster in I_h symmetry, this reported retention of symmetry is difficult to rationalize. In Fig. 1 the optimum structures of Si_{38} (isomer no 9) and Si_{20} fullerenes obtained with the three methods are presented. As one can see, the structures obtained by the three methods are essentially similar. In these figures, atoms that move outwards are light coloured, and atoms which move inwards are dark coloured.

The cohesive energies of the optimum 17 Si_{38} fullerene isomers are concentrated in a range of less than 60 meV. On average, the difference in cohesive energy between the optimum Si_{38} fullerene isomer and the other 16 optimized isomers is about 20 meV. The differences between successive members of the 16 isomers fall in a narrow range of 2 - 3 meV, on the average. The conclusion is that all the 17 isomers are almost isoenergetic, i.e. permutation between the pentagonal and the hexagonal faces does not affect greatly their cohesive energy or consequently their stability. Comparing the cohesive energy values for the Si_{38} isomers with those obtained for Si_{20} it is found that Si_{20} fullerene is less stable than Si_{38}. The cohesive energy difference is estimated to be 0.1171 eV (OTBMD), 0.0385 eV (GTBMD), 0.0809 eV (DFT/B3LYP). Consequently, our results are at odds with the assumptions of Marsen and Sattler [4], according to which (a) the smallest Si fullerenes are the most stable and (b) for Si a fused pentagon rule can replace the isolated pentagon rule of carbon fullerenes. Si_{20} is the smallest possible fullerene, with the maximum possible number of fused pentagons, but it is less stable than Si_{38} fullerene.

The distributions of bond lengths, obtained by the three methods, are shown in Fig. 2, for the Si_{38} optimum fullerene isomer and the Si_{20} fullerene. The figure identifies 57 (i.e. $3/2 \times 38$) and 30 (i.e. $3/2 \times 20$) nearest neighbour bonds for Si_{38} and Si_{20}, respectively. The fullerene net is still conserved although the geometries are distorted. The bond lengths fall between 2.23Å and 2.53Å in the DFT/B3LYP calculation. For GTBMD and OTBMD, this range is even smaller. An important feature of these structures is that exactly half of the atoms move radially outwards creating sharp corners. The angles between neighbouring bonds have values between 90° and 100°. This indicates that the bonding is not sp^3 like. The rest of the atoms move radially inwards and are almost co-planar with their nearest neighbours, indicating sp^2-like bonding. This can be seen in Fig. 3, where is shown the distribution of the sum of the three
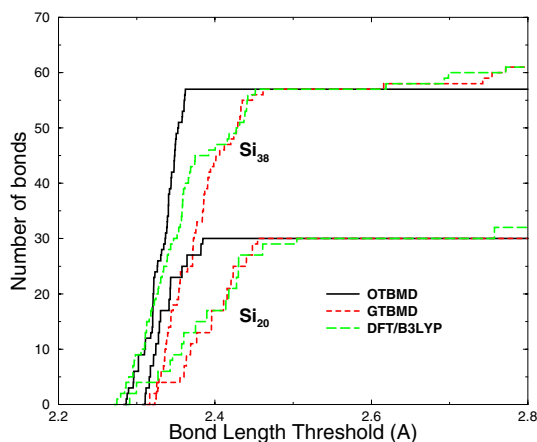
Figure 2. Number of bonds with bond length less than threshold for the optimum Si_{38} fullerene isomer and for the Si_{20} fullerene.
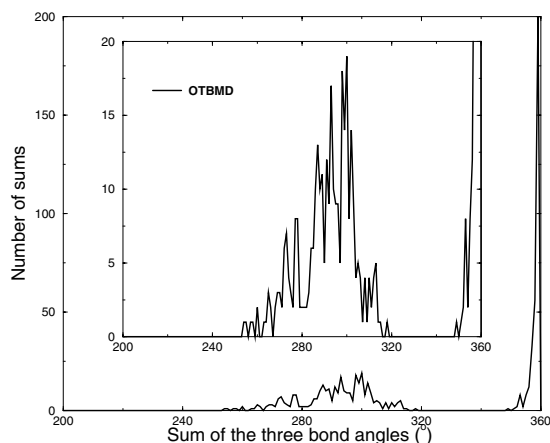
Figure 3. Distribution of the valence angle sum for all atoms of the 17 Si_{38} fullerene isomers, obtained in the OTBMD calculation. Same graph in the inset magnified.

bond associated angles with each atom. If the sum is 360° the structure is locally flat (around the particular atom). This is how the atoms that move inwards behave. On the other hand, the sums for the other half of the atoms, those which move radially outwards, are between 250° and 320°, with a mean value of approximately 290°. This means that they are not arranged in an sp^3 like geometry for which the sum should be about 328°. As shown in the figure, these two kind of sums are separated by a gap of approximately 32°, although this gap becomes less pronounced in the GTBMD and the DFT calculations.

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