

Geometry and energetics of Si₆₀ isomers

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Abstract

The novel electronic, optical and super-conducting properties exhibited by C₆₀ and its assembled materials have greatly stimulated the scientists all over the world racing to study Si₆₀. In this paper we performed an extensive search from eighteen isomers including cages, wires, and stuffed structures of Si. It is found that the fullerene cage is not stable, and the tricapped-trigonal-prism unit is not the structural unit for Si₆₀. While the spherical compact structure is the most stable energetically, in agreement with experiments which suggested a transition from the elongated geometry to a more spherical one for the medium sized Si clusters [J. Chem. Phys. 111 (1999) 7865, J. Chem. Phys. 117 (2002) 3219].

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1. Introduction

Carbon and silicon are two of the most common as well as important elements on earth: carbon atoms form the basis of all living objects, while silicon plays a pivotal role in the electronics industry. However, these elements exhibit very little commonality in their chemical or physical properties. For example, oxide of carbon namely CO and CO₂ form gases, while oxides of silicon constitute common sand. Similarly the sp² and sp³ bonding characteristics of carbon give rise to novel forms starting from the well known planar graphite and tetrahedral diamond to ‘spherical’ fullerene and cylindrical nano-tube. On the other hand, silicon prefers only tetrahedral bonding due to its larger core. The discovery [1] of C₆₀ fullerene and carbon nano-tubes [2] and their large scale synthesis have added a new dimension to the study of nano-structures. The carbon based nano-materials not only display novel mechanical, electronic, optical, and super conducting properties, but also they serve as vehicles for the synthesis of new nano-structures by inserting atoms and clusters. Possibilities of new technologies have also fueled much research into study of silicon

clusters, which have great potential applications in nano-devices such as quantum dots, quantum wires, nonlinear electronic components and memory devices. Parallel to the studies of C₂₀, C₂₈, and C₆₀, it is well established that Si₂₀ has a wire-like structure composed of two Si₁₀ units [3]. Similarly, Si₂₈ also has a wire structure composed of tricapped trigonal prism (TTP) units [4]. In spite of considerable efforts in the past, the structure of Si₆₀ is still in dispute [5] due to the fact that the structures of silicon clusters are much more complicated than those of carbon. For example, the pentagon and the hexagon are the basic structural units for carbon fullerene cages. Unfortunately, for silicon clusters, such a unified picture does not exist. Many studies have been devoted to this subject and several structural models have been proposed including a fullerene cage model [5], a TTP model [3], and a stuffed fullerene model [6]. Based on these studies, we used first-principles method to study the geometrical structures and the energetics of isomers for Si₆₀.

2. Computational method

In this paper, we have used density-functional theory [7]. For the exchange-correlation functional, gradient-corrected functionals in the form of the generalized gradient

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approximation (GGA) [8] have been chosen. In order to optimize geometry effectively, a plane-wave basis set is adopted with the projector-augmented wave (PAW) method originally developed by Blöchl [9] and recently adapted by Kresse and Joubert [10]. In our calculations, the cluster is placed in a cubic cell with edge length of 30 Å, which is sufficiently large to make dispersion effects negligible. In such a big supercell only the G point can be used to represent the Brillouin zone. The plane-wave cutoff is 300 eV, which is found to be large enough to get good convergence. The structure optimization is symmetry unrestricted, and conjugate-gradient algorithm has been chosen. The optimization is terminated when all the forces acting on the atoms are less than 0.01 eV/Å.

3. Results

Knowledge of the geometrical structure of clusters is essential to understand their physical and chemical properties. However, obtaining the ground state geometry of a large cluster is not a trivial task as there are many isomers and the result may depend upon the initial geometry used for optimization. Here we made an extensive search by using many different initial structures. We first start with cage related geometries, as shown in Fig. 1. The first one is a fullerene cage (CG1); the second labeled CG2 represents three interlocking fullerene-24 cages, which was presumed as the structural unit for Si nano-wires [11]; the third one (CG3) is also an interlocking structure of three 24-cages but with 4-coordinated Si atoms in sub-units. The fourth and fifth configurations are composed of 10 and 6 rings, respectively, and each Si atom is four fold coordinated. The fullerene structure (CG1) optimized with I_h symmetry yields the average bond length to be 2.262 Å, and the diameter of Si_{60} cage is 10.65 Å, the total binding energy is 231.666 eV, and HOMO–LUMO gap is 0.593 eV. After removing the symmetry restriction, the average diameter D is 10.57 Å, the binding energy increases to 235.693 eV, and the gap is reduced a little bit. All the optimized structures

are distorted, and the CG3 structure has the lowest energy, which suggests that the assumption [11] of fullerene 24-cage being the building unit for Si wire is not correct, which is further confirmed for longer wires of Si_n with $n = 78, 96,$ and 114 containing 4, 5, and 6 interlocking fullerene-24 cages, respectively.

Besides these cage-like isomers, we consider another important candidate as a starting configuration, namely TTP that has been identified as the building block for Si clusters [3]. Here we consider three typical stacking ways for TTP units as shown in Fig. 2: ring stacking, wire stacking, and spherical stacking.

In the ring configurations, the 6 TTP- Si_{10} units are arranged in a circle with one to four bonds between the units, labeled as TR1 to TR4, respectively.

In the wire configurations, the first three structures (TW1, TW2, and TW3) composed of three Si_{20} units connected with different bonds and orientations, which can be kept when optimized. While 6 TTP- Si_{10} units in a wire with different orientations give TW4 and TW5, both of which are seriously distorted in optimization.

In the spherical stacking, the 6 TTP- Si_{10} units construct an octahedron with two orientations, labeled as TS1 and TS2. When optimized, the skeletons of octahedral remain but the energies are higher than that of CG3.

From the 16 isomers considered above, it seems that the most stable one is CG3, in which some Si atoms are moved to the inside of the cage as required by sp^3 bonding feature and formed the elongated net-like structure. However, experimental results predicted a structural transition from the elongated geometry to more spherical one for the medium sized silicon cluster [12]. Accordingly, we consider the so called stuffed fullerene structure which can result a more spherical geometry. The well known stuffed fullerene structure for Si cluster is Si_{33} [6] in which the tetrahedral core of Si_5 is encapsulated into Si_{28} fullerene cage. For Si_{60} , here we consider Si_{20} encapsulated into Si_{40} both with fullerene structures. C_{20} is the smallest fullerene with dodecahedral geometry [13], while the stable structure for C_{40} has D_{5d} symmetry [14], which is matchable with C_{20}

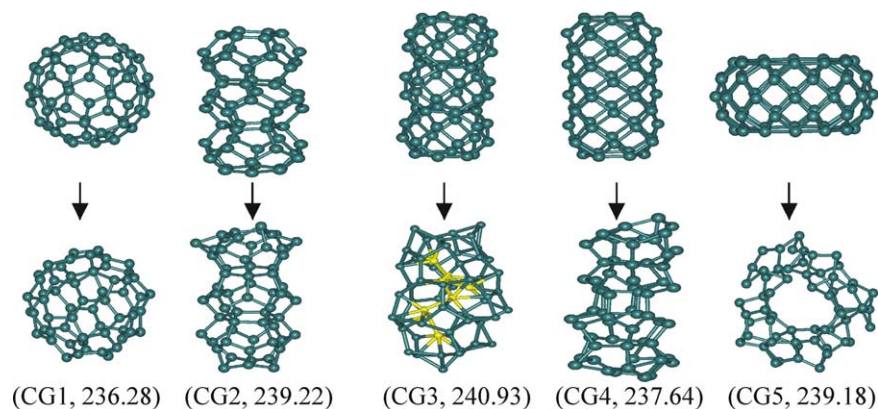


Fig. 1. The isomers of Si_{60} with cage-related structures (CG1–CG5), the numbers in brackets show the total binding energy (eV). In the case of CG3, the atoms inside the cage are in yellow color in web version for the optimized structure.

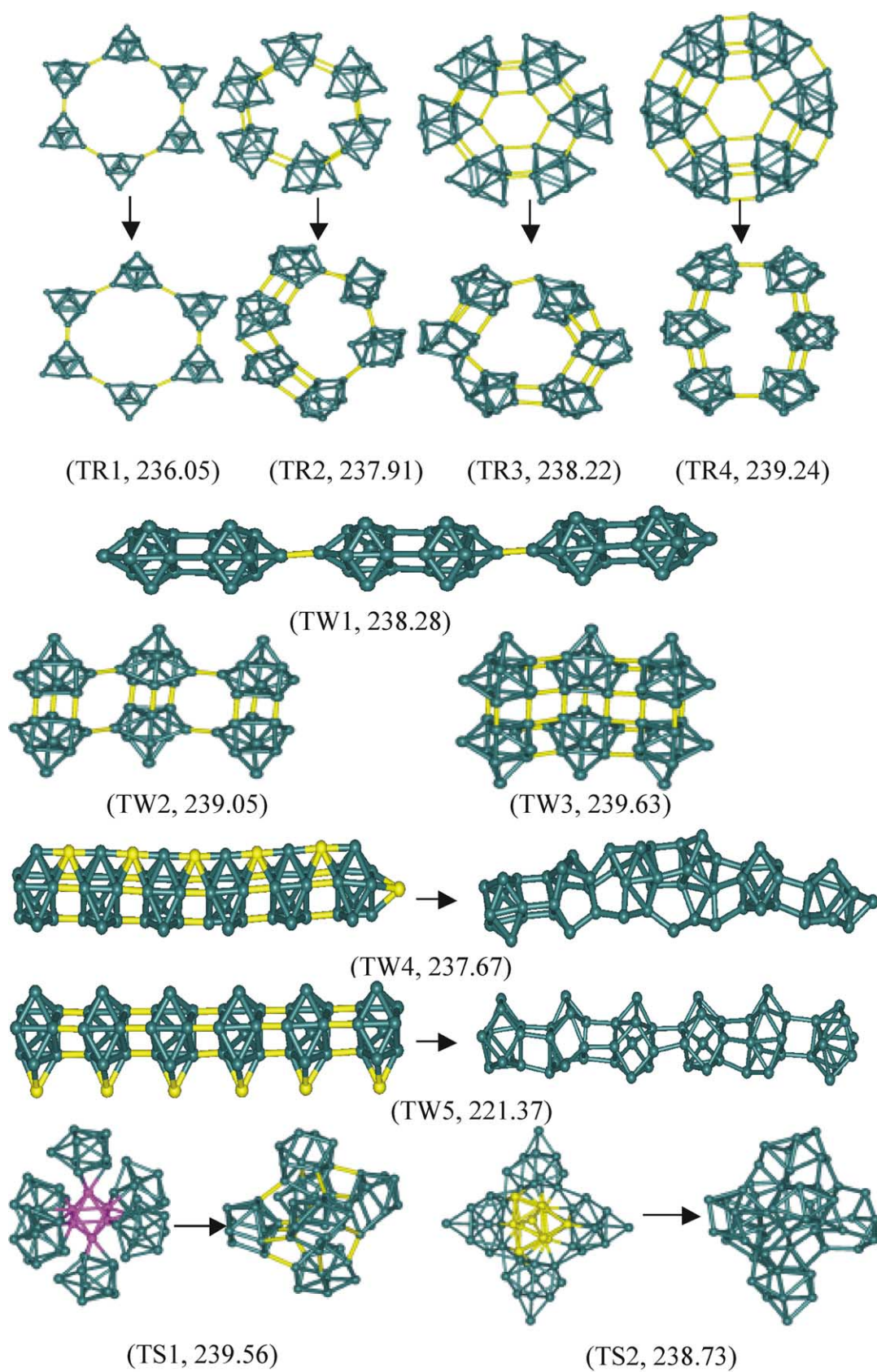


Fig. 2. Ring stacking, wire stacking, and spherical stacking of TTP units for Si_{60} , the numbers in brackets show the total binding energy (eV). In TW4 and TW5, the capping atoms are in yellow in web version. In TS1, six Si_{10} units are arranged in an octahedron as shown in red color in web version. In TS2, the yellow color in web version presents the two Si_{10} units are in the out of the plane.

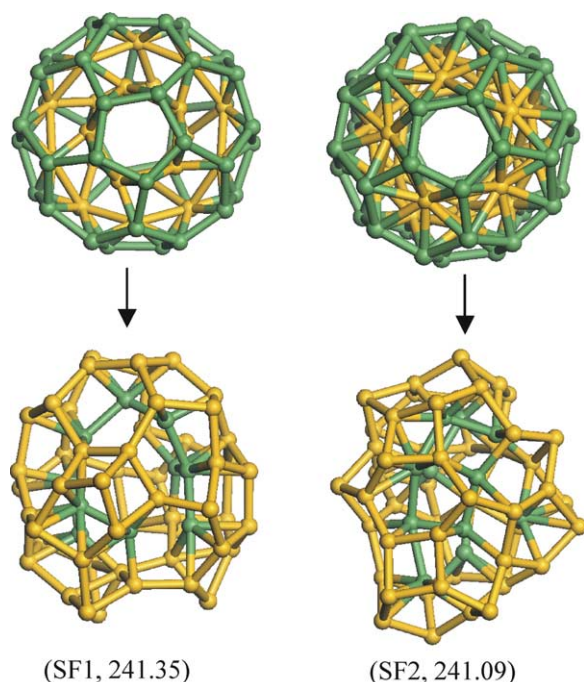


Fig. 3. The initial and optimized stuffed fullerene structures of $\text{Si}_{20}@\text{Si}_{40}$ with two orientations (SF1 and SF2), the numbers in brackets show the total binding energy (eV). The atoms inside the cage are presented in different colors in web version.

cage. The different relative orientations give two higher symmetric structures with symmetry of C_5 and S_{10} for $\text{Si}_{20}@\text{Si}_{40}$ as shown in Fig. 3, labeled as SF1 and SF2, respectively. When fully optimized, the geometries are distorted, SF1 is more spherical in shape and more stable in energy than SF2.

Among the 18 isomers for Si_{60} considered, SF1 has the lowest energy. SF1 is 0.425 eV lower in energy than CG3, while SF2 is just 0.161 eV lower in energy than CG3, i.e. these two are almost degenerate. From these results we can get following conclusions: (1) Si_{60} with fullerene cage structure is not stable energetically, different from the previous results [5]; TTP is not the building unit for Si_{60} . For the medium sized Si cluster, spherical structure is more stable, confirmed the experimental predictions [12]. In fact, this kind of structural transition already begins at Si_{36} cluster [15]; (2) Si_{24} with fullerene cage is not the structure unit for Si nano-wire, different from the expectations [11].

4. Discussions

Although Si and C are in the same group of periodic table, the structures of nano Si are much more complicated and different from those of nano-carbon system, Si_{60} is such an example. However, the recent realization that the chemical and physical properties of elements can be fundamentally altered at the nano-scale has led to considerable efforts to see if nano Si can be made to behave

like nano C. There are currently two main directions in this search for new nano Si structures: (1) to design a Si cluster with a fullerene cage structure; (2) to create a one-dimensional Si structure such as nano-wire or nano-tube. It has been found that Si_{20} fullerene cage can be stabilized by one metal atom such as Ba, Sr, Ca, Zr, and Pb. [16]. However, it has been found recently that C_{60} cannot be used to stabilize Si_{60} , while the magic clusters with 40 electrons such as Al_{12}X ($\text{X} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) will do [17], because the magic cluster can be used as a superatom [18]. As for the one-dimensional Si structure, we found that the tube-like Si_{12}W cluster cannot be used as the building block for the construction of 1D Si nano-structure [19], while encapsulating Si clusters into carbon nano-tube can fabricate one-dimensional Si structure, and change effectively the electronic and optical properties of the system [20]. Therefore, the structure of Si can be tuned at nano-scale, and this new freedom provides flexible ways to design novel structures with exotic properties for the applications in physics, chemistry, materials science, and in microelectronics.

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