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Distorted icosahedral cage structure of Si_{60} clusters

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Using full-potential linear-muffin-tin-orbital molecular-dynamics method, we have performed calculations on the structure and the binding energy of cluster Si_{60}. It is found that the stable structure for Si_{60} cluster is a distorted truncated icosahedron, with T_h symmetry. Its fullerene cage structure remains, but it looks like a puckered ball. The lower symmetry and four distinct Si-Si bond lengths make the structure different from that with I_h symmetry and two C-C bond lengths in C_{60}.

I. INTRODUCTION

C_{60} cage (I_h symmetry) has extensively stimulated a variety of scientific studies on the structure, reactivity.[1] The structure of C_{60} is a truncated icosahedron containing 20 hexagons and 12 pentagons on its almost spherical surface. Silicon is contiguous to carbon in the periodic table. It may be expected that Si_{60} also has cage structure and interesting properties. To our knowledge, a few reports have involved Si_{60} structure, but the results are divided into following three categories: perfect fullerene cage structure,[2–7] distorted cage structure and stacked naphthalene structure (or network structure).[8,9] Nagase *et al.* have proposed that the structure of Si_{60} is still a icosahedral structure, with I_h symmetry, using a double-zeta basis set with *ab initio* effective-core potentials on silicon atoms.[5] They also have investigated the thermodynamic stability of different structures of Si_{60} using semi-empirical calculations at AM1 (Austin model one) level.[6] The results suggest that the buckminsterfullerene structure is much more favorable than a stacked naphthalene structure or a cylindrical structure. Piqueras *et al.* have made use of the AM1 method to investigate the ground-state structure of the icosahedral Si_{60} cage.[4] The result shows that this geometry (I_h symmetry) is an energy minimum with two distinct bond length, which is similar to that of C_{60}. Furthermore, Slanina *et al.* have performed harmonic vibrational analysis on the I_h and C_{2v} structures of Si_{60} by the AM1 method.[7] Their investigation confirms that the I_h structure is a minimum of the potential energy surface. Khan *et al.* have found that the icosahedral-cage-structure of Si_{60} is not stable and relaxes into a structure resembling a puckered balls using a conventional orthogonal tight-binding molecular dynamics.[8] However, by the same method, Menon *et al.* found that the perfect icosahedral cage is unstable, distorting to a lower symmetry C_{2h} structure with no change in the threefold coordination,[9] but atomic arrangement tends toward tetrahedral geometry. They compared the relative stabilities of 60 atom silicon and carbon network clusters with their caged structures. Si_{60} network is more stable than the C_{2h} symmetry Si_{60} fullerene, but C_{60} network is less favorable than the C_{60} fullerene.

Indirect experimental results also seem to support the cage structures and the stacked structure above, respectively. A saturation study of Si_{60} positive ion shows that the average number of ammonia molecular absorbed rapidly is close to 6.[10] This may imply the fullerene structure because the C_{60} buckminsterfullerene consists of six independent pyracyclene units to which the amines can be added most easily.[11] But, fragmentation analysis of Si_{60} positive ion into unstable Si_{20} units and subsequently into Si_{10} fragments seems to support the hypothesis of a stacked naphthalenelike structure.[12]

Despite these theoretical studies, however, their proposed geometries of Si_{60} are very different. The aim of the present work is to employ more sophisticated method to Si_{60} in the hope of obtaining a more accurate structure.

II. METHOD

The full-potential linear muffin-triorbital (FP-LMTO) method[13–16] is a self-consistent implementation of the Kohn-Sham equations in the local-density approximation.[17] In this method, space is divided into two parts: nonoverlapping muffin-tin (MT) spheres centered at the nuclei and the remaining interstitial region. LMTO's are augmented Hankel functions, and are augmented inside the MT spheres, but not in the interstitial region.[18–20] In LMTO method, one thing we must do is to calculate the interstitial-potential matrix elements:

$$V_{ij}^{I}=\int_{I}\phi_i(x)V_I(x)\phi_j(x)dx \tag{1}$$

where I is the interstitial region, V_I is the interstitial potential, i and j are abbreviation for νL and $\nu' L'$, respectively, ϕ_i is a LMTO envelope function centered at site ν with angular momentum L. L is abbreviation for the angular-momentum quantum numbers (l,m). In different methods, we handle V_{ij}^{I} in different ways. In FP-LMTO method for crystals, Methfessel *et al.*[15,16] used nonoverlapping MT spheres. They retained non-spherical potential terms inside the MT spheres, but expanded the interstitial potential $V_I(x)$

in a different set of atom-centered Hankel functions. The products $\phi_i^* \phi_j$ can be expanded, throughout the interstitial region, by $\chi_k(x)$.

$$\phi_i^* \phi_j = \sum_k C_k^{ij} \chi_k(x). \tag{2}$$

k is for $(\nu L \alpha)$, the index α runs over different locations, the χ_k are functions of the charge density Hankel function set. C_k^{ij} are expansion coefficients. The matrix element V_{ij}^I then reduces to a linear combination of integrals of the functions χ_k times the interstitial potential. Next, it is assumed that the interstitial potential itself is expanded in functions of the type as χ_k as mentioned above. Thus, the desired interstitial intergral has now been expressed as a linear combination of integrals of products of pairs of Hankel functions; i.e., the three-center integral has been reduced to a sum of two-center intergals. Because the products are smooth functions, the coefficients in Eq. (2) can be adjusted until the best fit of the values and slopes of the right-hand side to the values and slopes of the products is obtained on all spheres simultaneously by interpolating between the surfaces of the spheres. This method is suitable for the case that the interstitial region is not too large. For loosely-packed system, extra empty spheres are introdused so that every point in the interstitial region may lie close to one or more atomic spheres. The crystal FP-LMTO mehtod is different from LMTO-(ASA) (atomic spheres approximation) method.[21,22] Our cluster FP-LMTO program is similar to crystal FP-LMTO above. It has exactly same LMTO basis set as crystal FP-LMTO. But, there is no Blochsums for clusters. Besides, main difference to crystal program is how to get the expansion coefficients in Eq. (2). We obtain the coefficients by tabulation technique here, not interpolation technique as in crystal FP-LMTO. In the new cluster method, the expansion is first calculated for two atoms arranged along the z axis and the coefficients are tabulated as function of the interatomic distance. For arbitary geometry, the expansion is obtained by rotating the tabulated fit using the rotation matrices for the spherical harmonics. The tabulated fit is made by direct numerical intergration and can be made as accurate as desired.[14] Therefore, it is not necessary to introduce the empty spheres in our cluster FP-LMTO program. This method is different from the cluster LMTO methods used by Gunnarsson, Harris, Jones, Painter, Muller, and Springborg.[23–26,20] The force expression for FP-LMTO method can be obtained by Harris energy function.[13,14] In the past two years, some papers in our group have been published successively, using this method.[27–32] The results are in good agreement with the related experiments. In this paper, all sphere radii for Si are taken as 2.0 a.u. The LMTO basis sets include s, p, and d functions on all spheres.

III. STRUCTURE AND DISCUSSIONS

It is believed that the perfect truncated icosahedron of C_{60} is a very stable structure, in which each atom is bonded to three other atoms, thus making it a form of spherical graphite. We wondered if silicon contiguous to carbon in the periodic table would also form the stable icosahedral-cage structure. Starting with a perfect icosahedral configuration, we have performed calculation on Si_{60} cluster, by full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method. In each time step, the eigenvalue problem is solved exactly and the output density is admixed to the input density in the usual way. The nuclei are then moved according to the forces using the Verlet algorithm. We then decompose the mixed density, move each partial density along with its atom, and reoverlap at the new geometry. After many a iterations, the maximum of the forces is less than 0.001 (Ry/bohr), and the total enery stays nicely constant because the system stays close to selfconsistency (so the forces agree with the energy). The process is stopped when the self-consistent condition meets. We find the initial perfect icosahedral configuration with I_h symmetry to be unstable, distorting to lower T_h symmetry geometry with the same coordination. The final stable configuration for Si_{60} is shown in Fig. 1, its two-dimensional perspective view in Fig. 2, and its point group, bond lengths and binding energy in Table I. It is obvious that the cage has deformed seriously, like a puckered ball. It still has a high-symmetry T_h, though its symmetry is lower than I_h symmetry, which a perfect fullerene cage has. There are four bond lengths, ranging from 2.218 to 2.295 (Å). Its average bond length is 2.279 (Å). Our optimized geometric parameters for Si_{60} together with previ-

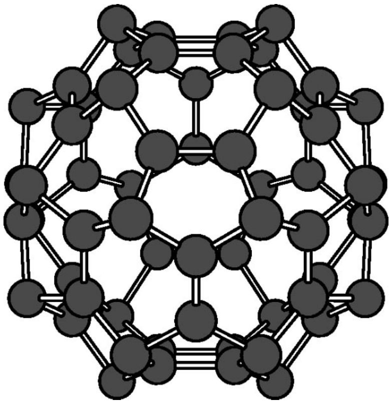

FIG. 1. Final configuration of molecular dynamics optimization for Si_{60}. The distorted structure has a T_h symmetry.

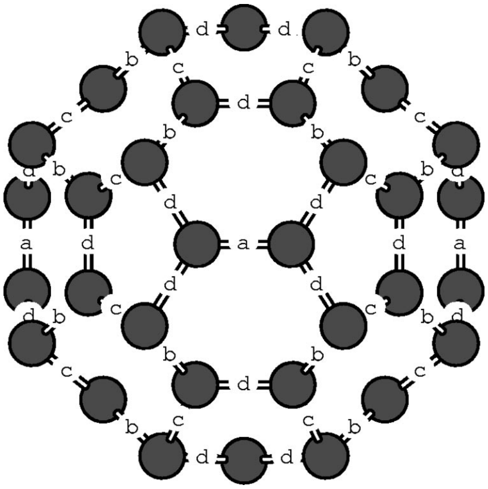

FIG. 2. Two-dimensional perspective view of Si_{60}. a, b, c, and d represent four different bond lengths.

TABLE I. Point group, bond length(Å), and binding energy (eV/atom) for cluster Si_{60}.

Point group	Bond name	Bond length	Binding energy
T_h	a	2.218	4.899
	b	2.271	
	c	2.280	
	d	2.295	

TABLE II. Our optimized geometric parameters for Si_{60} together with previously reported theoretical data. X_{max} refers to the longest Si-Si bond, X_{min} the shortest Si-Si bond, X_{av} their average value, n the number of different bond lengths. ‘‘-’’ means that corresponding datum is not presented in original reference. All bond lengths are given in (Å).

Method	Group point	n	X_{max}	X_{min}	X_{av}	Ref.
AM1	I_h	2	2.30	2.09	2.16	4
dz+ECP	I_h	2	2.27	2.19	2.22	4
TB-MD	C_{2h}		2.34	2.53	2.40	9
TB-MD		1	2.37	2.37	2.37	8
FP-LMTO-MD	T_h	4	2.30	2.22	2.28	This work

ously reported theoretical data are given in Table II. Reference 8 suggests that cluster Si_{60} is not stable and relaxes into the structure, which looks like a puckered ball. Our calculations confirm this result, but all the bonds in final structure do not become approximately 2.37 (Å) as in Ref. 8. Reference 9 shows that the initial configuration with I_h symmetry is unstable, distorted to a lower C_{2h} symmetry geometry without any change in the coordination. We find that the initial I_h symmetry becomes T_h symmetry, its distortion is not so serious as that in Ref. 9. According to our calculations, cluster Si_{60} still has the fullerene cage structure, but its symmetry becomes low. Therefore, it may be expected that Si_{60} displays some similar physical and chemical properties to C_{60}.

IV. SUMMARY

Using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO MD) method, we have performed calculations on the structure and energies of large silicon cluster Si_{60}. Calculated results suggest that the stable structure of cluster Si_{60} is a distorted icosahedral cage resembling a puckered ball, with T_h symmetry, in which there are four different bond lengths.

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