# Theoretical Study of Cycloaddition Reactions of C₆₀ on the Si(100)-2×1 Surface

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*Received February 19, 2010, Accepted April 8, 2010*

Density functional theory was adopted to study the various surface products and their reaction channels focusing on the *on-dimer* configuration which has not been suggested before. Energetic results show that the most stable *on-dimer* configuration is the 6,6-[2+2] structure which resembles the typical [2+2] cycloaddition product. The 6,6-[2+2] product is also more stable than any other possible surface structures of *inter-dimer* configuration further suggesting its existence. Potential energy surface scan along various possible initial surface reactions show that some of the possible *on-dimer* surface products require virtually no reaction barrier indicating that initial population of *on-dimer* surface products is thermodynamically determined. Various surface isomerization reaction channels exist further facilitating thermal redistribution of the initial surface products.

**Key Words**: *On-dimer*, *Inter-dimer*, Cycloaddition, SIMOMM, Isomerization

## Introduction

A great deal of efforts has been devoted to developing molecular based electronics by synthetically attaching organic molecules to the semiconductor surface. Such interfacial chemical reactions not only result in the formation of new types of surface chemical bonds but it can also introduce new functional groups to the semiconductor surface. These modifications can then be used to provide new electronic, optical as well as biological properties to the plain semiconductor.[1]

Many saturated and unsaturated organic and organometallic compounds are actively being tested for the creation of new types of interfacial chemical bonds. Interfacial Si-C bonds have been created mostly by surface cycloaddition reactions using unsaturated hydrocarbon compounds. Although [2ₛ+2ₛ] cycloadditions are formally orbital symmetry forbidden,[2] experimental[3,4] and theoretical[5,6] studies have shown that ethylene, propylene and acetylene can easily chemisorb on Si(100)-2×1 yielding [2+2] products, and are able to resist temperatures of up to 600 K. Diene systems have also been actively studied. In the case of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, theoretical and experimental studies have shown[7] that the surface dimer can act as a good dienophile yielding 'Diels-Alder' or [4+2] cycloaddition products. Subsequent experimental[8] and theoretical[9] studies indicate that there is strong competition between the [2+2] and [4+2] products. Aromatic systems, such as benzene appear to rather easily undergo addition reactions on the Si(100) surface. Such reactions create new C-Si bonds thereby removing aromatic stability.[10,11] While adsorption of simple alkenes and dienes on Si(100) is essentially irreversible due to the formation of strong C-Si bonds, benzene has been shown to adsorb reversibly[10] and even exhibit redistribution of surface products.[11]

In this regard, the C₆₀ molecule can provide unique and interesting possibilities to these synthetic efforts. Due to its aromatic stability, addition reactions of C₆₀ require rather harsh conditions. For instance, C₆₀ polymerizes *via* photo-reaction[12] or only

under high-pressure conditions.[13] C₆₀ can dimerize *via* [2+2] cycloaddition but requires catalysis[14] or again high-pressure.[15] These observations indicate that the Woodward-Hoffmann rule is still valid in the [2+2] cycloaddition of C₆₀ requiring high activation energy. At the same time, a rather different reaction behavior of C₆₀ can be expected on the highly reactive Si surface.

Since its discovery,[16] C₆₀ has attracted significant attention from the surface science community. One of the most studied semiconductor/C₆₀ system is Si(100)-2×1 surface/C₆₀ due in part to the body of knowledge regarding the chemical and electronic nature of the pristine silicon surface. Despite a number of experimental studies by scanning tunneling microscopy (STM),[17] scanning tunneling spectroscopy (STS),[18] photoelectron spectroscopy[19] and near-edge X-ray absorption fine structure (NEXAFS)[20] among other techniques, the nature of C₆₀ interaction with silicon surfaces still remains controversial. For example, Hashizume *et al*.[17b] observed that STM images show the internal structure of the individual C₆₀: three or four bright stripes run in parallel on C₆₀. From this, they concluded that the molecules are not rotating randomly on the Si(100)-2×1 surface at room temperature. However, Chen and Sarid[17c] found no internal structure of C₆₀ adsorbates. At 1.0 mL in most studies, the interaction between C₆₀ and the Si(100)-2×1 surface is reported to be van der Waals. However, at low coverage, while high-resolution electron-energy-loss (HREELS) result[21] suggests physisorbed C₆₀, photoelectron spectroscopy results[19a,22] indicate
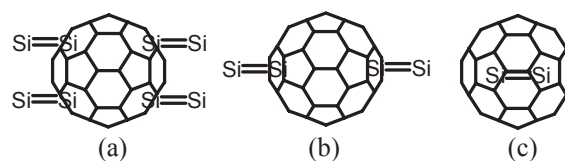


**Figure 1.** The possible surface configurations of C₆₀ on Si(100)-2×1 surface. The surface Si dimers are represented as Si=Si. (a) *on-trough*, (b) *inter-dimer* and (c) *on-dimer* configurations.

chemisorbed $C_{60}$.

Although the exact nature of the interaction between $C_{60}$ and Si(100)-2×1 surface is not clear, experimental findings suggest *on-trough* (1a) and *inter-dimer* (1b) surface configurations of adsorbed $C_{60}$ as shown in Fig. 1. Another possible surface adsorption configuration, *on-dimer* (1c), however, has not been suggested yet.

Some theoretical attempts to elucidate the electronic nature of the adsorbed $C_{60}$ have been performed. Kawazoe *et al.*[23] have calculated the electronic structure of the $C_{60}$ molecule on the Si(100)-2×1 surface by a first-principle calculation treating the Si(100) substrate as a positive charge background. Yamaguchi[24] has calculated the electronic structure of a model cluster of $C_{60}$ on Si(100)-2×1 surface by DV-Xα method. Yajima and Tsukada[25] also calculated the band structure of monolayer of $C_{60}$ using DV-Xα method. These studies assumed the experimentally suggested configurations for their calculations.

Detailed study of the initial surface reaction mechanisms and their precise surface structures in atomistic scale is essential to establish the technologies to construct the surface nano-structures. By studying the factors that govern the reactivity of these routes, precise control of these surface reactions can be possible. In this paper, theoretical study of the potential energy surface of the reaction mechanisms of $C_{60}$ on Si(100)-2×1 surface focusing on the *on-dimer* surface configurations is performed to understand the initial and subsequent surface reactions, and the possible surface structures of the relatively inert $C_{60}$ on Si(100)-2×1 surface.

### Computational Details

All electron 6-31(d)[26] basis set and SBKJC(d) effective core potential[27] basis set were used for the on-dimer and inter-dimer configurations, respectively. The minimum energy reaction paths were determined by first optimizing the geometries of the minima and transition states. Then, each stationary point was characterized by computing and diagonalizing the Hessian matrix (matrix of energy second derivatives). In order to follow the minimum energy path (MEP), the Gonzalez-Schlegel second-order method[28] was used with a step size of 0.3 amu$^{1/2}$-bohr.

Various points on the reaction path, particularly the transition states and intermediates, are often inherently multi-configurational. Therefore CASSCF (complete active space SCF)[29] wave functions would be the primary choice to properly describe these species. However, due to the computational demand, single-reference density function theory (DFT) was adopted using the B3LYP[30] exchange-correlation functional. The GAMESS (General atomic and molecular electronic structure system)[31] program was used for all of the computations.

To take into account the surface size effect for the study of *inter-dimer* configuration, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called SIMOMM (surface integrated molecular orbital molecular mechanics)[32] was used. MM3[33] parameters were chosen for the molecular mechanics optimization part of the computation. All of the computations were done without imposing symmetry unless otherwise specified.

### Results and Discussion

***On-Dimer* surface products.** We first studied the possible surface products of $C_{60}$ on the single surface Si dimer as illustrated in Fig. 1c. In order to systematically study various possible surface products, symmetry unique atoms of $C_{60}$ making interfacial bonds with the Si dimer are identified in Figure 2a. The black dotted atom position is the reference point which is shared by all possible surface structures. Depending on the position of the white dotted atom, unique surface structures are determined. It would be useful to understand that there are two types of bonds in $C_{60}$. The bond shared by the two 6-membered rings and the



| name | bond position |
|------|---------------|
| I | 1 |
| 6,5-[2+2] | 1,2 |
| 5-[4+2] | 1,3 |
| 6,6-[2+2] | 1,4 |
| 6-[3+2] | 1,5 |
| 6-[4+2] | 1,6 |

| name | bond position |
|------|---------------|
| SIMOMM : 6,6-[2+2] | 1,4 |
| SIMOMM : ID-6,6-[2+2] | 1,4,3 |
| SIMOMM : ID-6,5-[2+2] | 1,2,8 |
| SIMOMM : ID-6-[3+2] | 1,5 |
| SIMOMM : ID-6-[4+2] | 1,6 |
| SIMOMM : ID-7 | 1,7 |
| SIMOMM : ID-8 | 1,8 |
| SIMOMM : ID-9 | 1,9 |

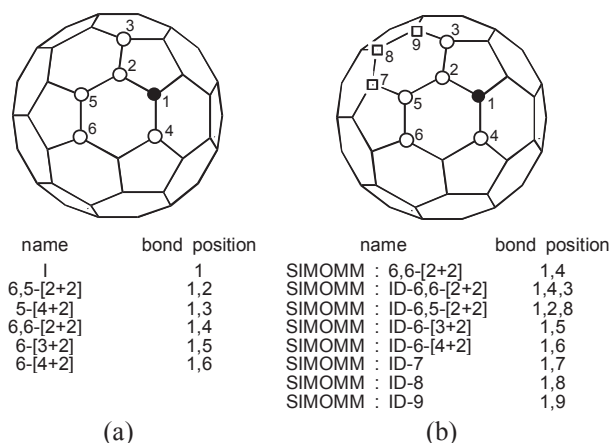(a)                                          (b)

**Figure 2.** Symmetry unique positions of the possible surface structures. The black dot is the reference position which is shared by all surface structures. Depending on the the position of the white dot, the unique surface structures are determined. The white square positions correspond to the additional structures considered for the *inter-dimer* configuration. (a) Naming of the possible structures of *on-dimer* configuration. (b) Naming of the possible structures of *inter-dimer* configurations.

**Table 1.** Energetics (kcal/mol) of products, intermediates, and transition states as obtained with B3LYP/6-31G(d)

|  |  | $\Delta E^a$ |
|------|------|------|
| Reactant | **3a** | 0 |
| I | **3b** | 0 |
| 6,6-[2+2] | **3c** | −34 |
| 6-[4+2] | **3d** | −22 |
| 6,5-[2+2] | **3e** | −14 |
| 5-[4+2] | **3f** | 1 |
| $TS_{I \leftrightarrow 6,5-[2+2]}$ | **3g** | 2 |
| $TS_{I \leftrightarrow 5-[4+2]}$ | **3h** | 7 |
| $TS_{I \leftrightarrow 6-[3+2]}$ | **3i** | 9 |
| $TS_{6,5-[2+2] \leftrightarrow 5-[4+2]}$ | **3j** | 8 |
| $TS_{6,5-[2+2] \leftrightarrow 6-[3+2]}$ | **3k** | 3 |
| $TS_{6-[4+2] \leftrightarrow 6-[3+2]}$ | **3l** | 2 |
| Open-6,6-[2+2] | **3m** | 44 |
| Open-6,5-[2+2] | **3n** | 46 |

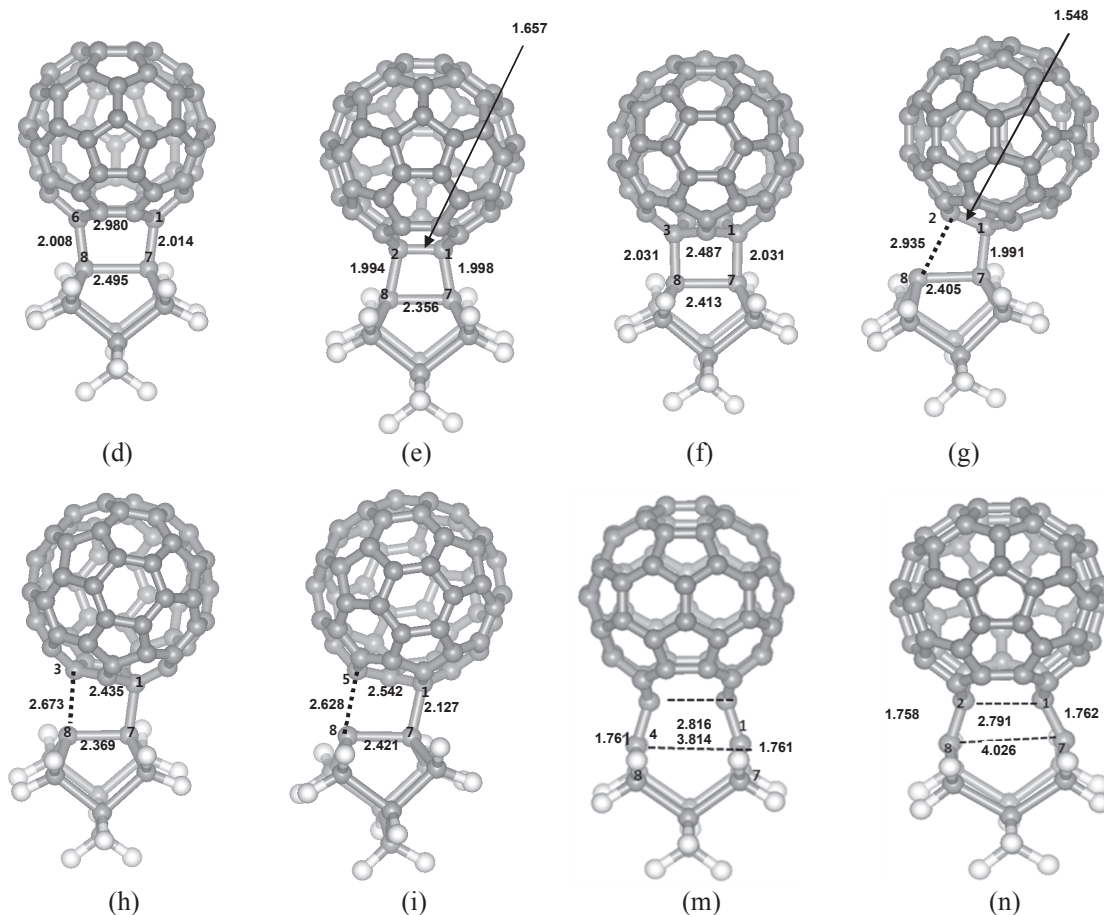$^a$Values represent the relative energies with respect to reactant.

**Figure 3.** DFT optimized surface structures and transition states of *on- dimer* configuration. (a) Reactant which is composed of isolated C$_{60}$ and bare surface. (b) **I**. (c) 6,6-[2+2]. (d) 6-[4+2]. (e) 6,5-[2+2]. (f) 5- [4+2]. (g) TS$_{I<->6,5-[2+2]}$. (h) TS$_{I<->5-[4+2]}$. (i) TS$_{I<->6-[3+2]}$. (j) TS$_{6,5-[2+2]<->5-[4+2]}$. (k) TS$_{6,5-[2+2]<->6-[3+2]}$. (l) TS$_{6-[4+2]<->6-[3+2]}$. (m) open-6,6-[2+2]. (n) open-6,5-[2+2]. Bond lengths are in angstrom.

bond shared by the 6- and 5-membered rings. The two bond lengths were determined to be 1.388 and 1.432 Å respectively by X-ray data.[34] Although the bond lengths of the two bonds are close to the aromatic C-C bond lengths, the two types of bonds shall be called double and single bonds in the following discussion.

Full geometry optimizations were performed with density functional theories, and the results are presented in Table 1 and Figure 3. Although six possible structures were studied, only five minima were located. Among these, 6,6-[2+2], **3c** is calculated to be the most stable structure with the relative stability of 33.7 kcal/mol as compared to the reactant, **3a**. Since 6,6-[2+2] is the reaction product of the C$_{60}$ double bond and surface dimer, it resembles a typical [2+2] cycloaddition product, which is an orbital-symmetry forbidden reaction. 6-[4+2], **3d**, and 6,5-[2+2], **3e**, are the next most stable structures with the relative stability of 21.7 and 14.3 kcal/mol. The 6-[4+2] structure may be considered as the product of diene (in the 6-membered ring of C$_{60}$) and dienophile (the surface Si dimer). In the ordinary organic chemistry, the [4+2] cycloaddition product is more stable than the [2+2] product. However, in our particular case, the relative stability is reversed. The 6,5-[2+2] product can be considered as the reaction product of the C$_{60}$ single bond and surface Si dimer. Since the C$_{60}$ single bond still has some double

bond character due to the conjugations, it may also be considered as a typical [2+2] cycloaddition reaction. 5-[4+2], **3f**, is also a minimum but it is 0.7 kcal/mol less stable than the reference point, **3a**. This structure can be formally considered as the reaction product of diene (5-membered ring of C$_{60}$) and dienophile (the surface dimer). The instability of 5-[4+2] may be attributed to the fact that all bonds of the 5-membered ring of C$_{60}$ are single bonds. As a result, the [4+2] cycloaddition *via* C$_{60}$ 5-membered ring would not yield a stable surface product. Singly bonded structure **I** (**3b**) also turned out to be a minimum and is 0.1 kcal/mol less stable than the reference point. Although this structure is not thermodynamically interesting, it plays a major role in the initial surface reactions as discussed in the following section. In our preliminary studies, 6-[3+2] product was found to be minimum with HF/STO-3G theory. However, B3LYP/6-31G(d) theory does not find 6-[3+2] to be a minimum indicating that the potential surface near 6-[3+2] product is extremely flat. According to Fig. 2a, 6-[3+2] structure may yield a radical species which prevents it from being a minimum.

It is interesting to note that all Si-C bond lengths of the structures mentioned above are near 2.0 Å with vary little variations indicating that all structures have strong interfacial single bond (s) regardless of the surface structures. However, **3b** and **3f** are less stable than the reference point suggesting that the relative

stabilities are not only determined by the number of interfacial bonds but also other factors such as ring strain, reduction of aromaticity $C_{60}$ moiety and van der Waals repulsions.

Although 6,6-[2+2], 6-[4+2] and 6,5-[2+2] products turned out to be thermodynamically stable, in order for these species to exist on the surface, kinetic stability as well as kinetic accessibility are required. In the following sections, the potential energy surfaces along possible routes to these surface species are explored.

**Reaction mechanism to 6,6-[2+2]cycloaddition product.** According to our potential energy surface search, **I** is formed without any reaction barrier. This is a surprising result, since the pristine $C_{60}$ is rather inert toward addition reactions due in part to the fact that such [2+2] cycloaddition disrupts the aromatic network of $C_{60}$. Internal rotation along the $Si_7$-$C_1$ bond requires virtually no activation energy. Since the relative energy of **I** is almost identical to the reference point, it is possible that the experimentally found physisorbed species may correspond to **I** which can easily desorb with mild thermal energy. By connecting $C_4$-$Si_8$, **I** becomes the most stable 6,6-[2+2] product *via* the step-wise radical mechanism. According to our potential energy search, this initial reaction occurs without reaction barrier indicating that **I** can be considered as a metastable species with extremely flat potential surfaces around it. The potential energy surface search shows that, among possible *on-dimer* species, 6,6-[2+2] is not only thermodynamically the most stable but also kinetically highly accessible product.

**Reaction mechanism to 6-[4+2]cycloaddition product.** By connecting $C_6$-$Si_8$, **I** becomes the second most stable 6-[4+2] product, **3d**. No reaction barrier is associated with this bond formation. Although thermodynamically less stable than 6,6-[2+2], **3d** is kinetically highly accessible. It is interesting to note that although the typical [4+2] cycloaddition reaction occurs *via* concerted mechanism, 6-[4+2] is formed *via* step-wise radical mechanism.

**Reaction mechanism to 6,5-[2+2]cycloaddition product.** $TS_{I<>6,5-[2+2]}$, **3g** connects the **I** and 6,5-[2+2], **3e** with the overall forward activation energy of 2.4 kcal/mol which is negligibly small. Thus, **3g** is also kinetically highly accessible. Since the backward activation energy of 16.7 kcal/mol can be overcome with large thermal energies, thermal redistribution to more stable surface structures is possible. Therefore, **3e** is considered to be kinetically unstable.

**Reaction mechanism to 5-[4+2]cycloaddition product.** $TS_{I<>5-[4+2]}$, **3h** connects the **I** and 5-[4+2], **3f** with the forward and overall activation energies of 6.9 and 7.0 kcal/mol respectively, which is somewhat higher than for the previous surface structures. In addition, the backward activation energy of 6.3 kcal/mol is not big enough for this species to exist on the surface. Therefore, 5-[4+2] species is not only thermodynamically but also kinetically the least stable suggesting that 5-[4+2] has much less chance to exist on the Si(100)-2×1 surface.

**Reaction mechanism to 6-[3+2]cycloaddition product.** As discussed above, 6-[3+2] is not a minimum with B3LYP/6-31G (d) level of theory. However, a transition state, $TS_{I<>6-[3+2]}$, **3i** that appears to connect **I** and 6-[3+2] was located with the overall activation energy of 9.0 kcal/mol. Although IRC run initially leads to the region of 6-[3+2] configuration, due to the extreme-

ly flat potential near the 6-[3+2], it eventually yields 6,6-[2+2] indicating that there is no reaction barrier between 6-[3+2] and 6,6[2+2]. The structure 6,6-[2+2] can be formed from 6-[3+2] by shifting the bond position from 1 to 2 in Fig. 2a. Therefore, the transition state $TS_{I<>6-[3+2]}$ connects **I** and the most stable 6,6-[2+2] product. Consequently, even if this channel is activated, only the most stable 6,6-[2+2] would be formed.

**Surface isomerization reactions among *On-Dimer* structures.** Since **I** is the initial surface structure that is connected to all the possible *on-dimer* surface structures, surface isomerization can occur *via* this metastable species. It is also possible that there are various direct surface isomerizations among the surface products. Of these, the 1,2-shift type reactions were considered in this study, since these reactions can occur within one surface dimer and require only one bond shift. One example, the isomerization between 6-[3+2] and 6,6-[2+2] has been given in the previous section.

According to Fig. 2a, the reaction channel between 6,5-[2+2] and 5-[4+2] can occur by 1,2-shift of $C_2$ and $C_3$ atom positions. The transition state **3j** connects 6,5-[2+2] and 5-[4+2] with the forward and backward activation energies of 22.0 kcal/mol and 7.0 kcal/mol, respectively. It is noted that the activation energy of the isomerization from 5-[4+2] to **I** is 6.3 kcal/mol. Due to the similar activation energies, the last two reaction channels will be competing with each other. Therefore, if the 5-[4+2] surface product is initially formed, it will soon be converted to either **I** or 6,5-[2+2].

The transition state $TS_{6,5-[2+2]<>6-[3+2]}$, **3k** connects 6,5-[2+2]
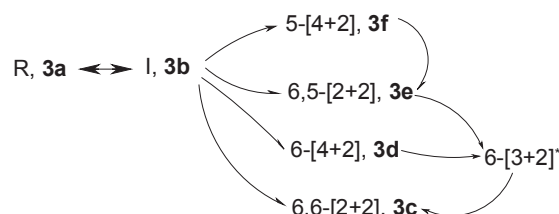


**Figure 4.** Illustration of the reaction channels of various possible surface structures found. The starred species, 6-[3+2]* is not a minimum with B3LYP/6-31G(d) level of theory. However, it appears in the reaction channels.
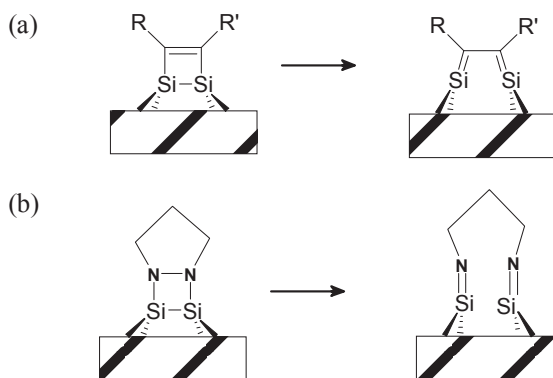


**Figure 5.** (a) Possible surface pericyclic reaction of adsorbed acetylene. (b) Possible surface pericyclic reaction of adsorbed 1-pyrazoline.
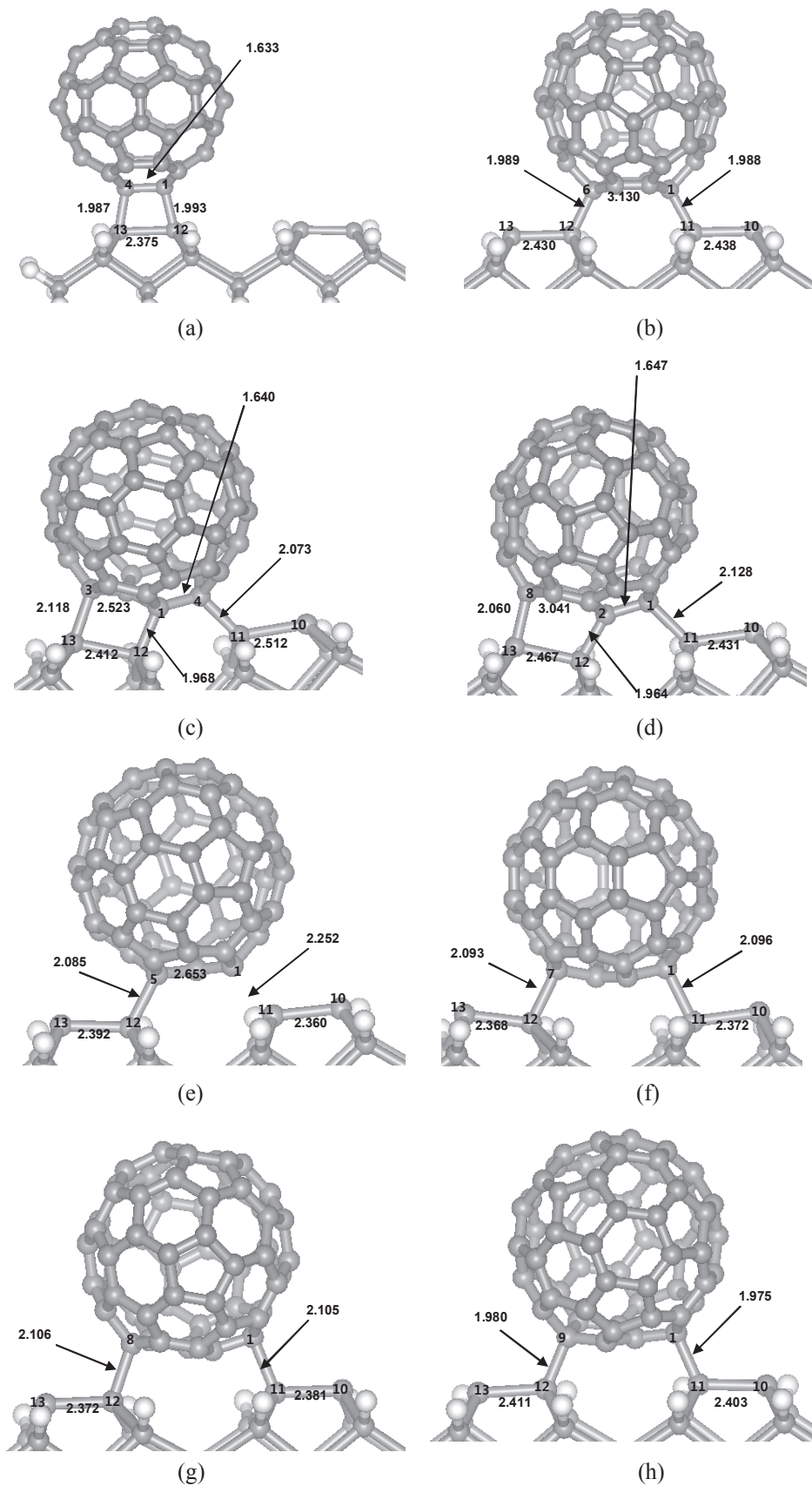
**Figure 6.** DFT optimized surface structures and transition states of *inter-dimer* configuration. (a) SIMOMM:6,6-[4+2], the reference point. (b) SIMOMM:ID-6-[4+2]. (c) SIMOMM:ID-6,6-[2+2]. (d) SIMOMM:ID-6,5-[2+2]. (e) SIMOMM:ID-6-[3+2]. (f) SIMOMM:ID-7. (g) SIMOMM: ID-8. (h) SIMOMM:ID-9. Bond lengths are in angstrom.

**Table 2.** Energetics (kcal/mol) of Products and Intermediates as obtained with SIMOMM:B3LYP/SBK(d)

|                        |        | $\Delta E^a$ |
| ---------------------- | ------ | ------------ |
| SIMOMM:6,6-[2+2]       | **6a** | 0            |
| SIMOMM:ID-6-[4+2]      | **6b** | 16           |
| SIMOMM:ID-6,6-[2+2]    | **6c** | 43           |
| SIMOMM:ID-6,5-[2+2]    | **6d** | 34           |
| SIMOMM:ID-6-[3+2]      | **6e** | 43           |
| ID-7                   | **6f** | 33           |
| ID-8                   | **6g** | 45           |
| ID-9                   | **6h** | 30           |

$^a$Values represent the relative energies with respect to SIMOMM:6,6-[2+2].

and 6-[3+2] by the 1,2-shift of $C_2$ and $C_5$ atom with the forward and overall activation energies of 17.1 and 2.8 kcal/mol, respectively. As discussed earlier, the 6-[3+2] is soon converted to 6,6-[2+2] without reaction barrier.

The transition state $TS_{6-[4+2]<->6-[3+2]}$, **3l** can occur by 1,2-shift of $C_6$ and $C_5$ atom positions. Again, 6-[3+2] is converted to 6,6-[2+2] without reaction barrier. Therefore, these last two transition states connect 6,5-[2+2] and 6-[4+2] with 6,6-[2+2] product showing additional channels to the most stable 6,6-[2+2] product. Other than the direct isomerizations discussed above, there is no direct 1,2-shift path among surface products.

The overall reaction channels discussed above are illustrated in Fig. 4. It is clearly seen that all surface products have isomerization channels eventually leading to the most stable *on-dimer* structure, 6,6-[2+2], **3c**. Large activation energies of the reserve reactions from 6,6-[2+2] to other surface structures imply that 6,6-[2+2] is kinetically stable.

**Surface pericyclic reactions of 6,6-[2+2] and 6,5-[2+2] products.** Fig. 5a illustrates surface pericyclic reaction of acetylene [2+2] products on Si(100)-2×1. Acetylene has one C-C π bond left after chemisorption. The remaining Si-Si σ bond and the C-C π bond may undergo further pericyclic reaction releasing 4-membered ring strain energy and making two new Si=C double bonds. This reaction resembles the electrocyclic ring opening reaction, in which cyclobutene, on heating gives 1,3-butadiene.

Theoretical[35,36] and experimental[37,38] studies on this system suggest $sp^2$ hybridization of carbon atoms. Using Auger spectroscopy and temperature-programmed desorption (TPD), Taylor *et al.*[37c] proposed that the Si-Si dimer bond is cleaved when the acetylene molecule adsorbs on top of a dimer. The structure with this complete cleavage of the Si-Si dimer bond was subsequently confirmed[37] by scanning tunneling microscopy (STM) to be the major product. However, independent experimental studies concluded that no direct evidence regarding the structure of the Si-Si σ bond was observed.[39] Except for early studies,[40] the majority of theoretical studies support the unbroken Si-Si dimer structure.[35,36,41] The most recent slab model DFT study by Sorescu and Jordan[42] showed that the broken Si-Si dimer structure is about 30 kcal/mol less stable than the unbroken structure. A $Si_9H_{12}$ cluster study of the same system[43] predicts that the Si-Si cleaved structure is not a minimum on the potential energy surface.

It appears that the product of surface pericyclic reactions

which has Si=C interfacial bonds may not be a minimum, and even if it is, it may not be kinetically stable.

However, in a recent theoretical study[44] of 1-pyrazoline surface reaction with Si(100)-2×1 as shown in Fig. 5b, the surface isomerization reaction product which has two Si=N double bonds as a result of breakage of both the surface Si-Si σ bond and N-N σ bond, was found to be thermodynamically as well as kinetically stable, suggesting a possible route to a multiple interfacial Si=X bond.

The possibility of surface pericyclic reactions is only relevant to the [2+2] surface products, which are 6,6-[2+2] and 6,5-[2+2] products in the current study. By breaking $C_1$-$C_4$ and $Si_7$-$Si_8$ σ bonds of **3c**, the open-6,6-[2+2] structure, **3m** can be formed. In the same way, the open-6,5-[2+2], **3n** can be formed. According to our theoretical calculations, both open structures were found to be minima with the relative energies of 43.5 and 46.5 kcal/mol as compared with the reference point, **3a**. Even though they are minima on the potential energy surface, their high energies prevent them from being major isomers on the surface. Although the pericyclic reactions can release the ring strain energies of four membered rings, breaking C-C bond of $C_{60}$ moiety can strongly disrupt π-conjugation network of $C_{60}$ making the species much less stable. As a result, the adsorbed $C_{60}$ mostly retains its spherical geometry unless very large thermal energies are supplied.

**Possible surface products of *Inter-Dimer* configuration.** In this section, possible structures of the *inter-dimer* configuration as shown in Fig 1b are explored and compared with the ones of *on-dimer* configurations found above. *Inter-dimer* configuration was suggested by most of earlier studies. Therefore, comparative study between the *inter-dimer* and *on-dimer* configurations is necessary in order to verify the relative importance of our theoretical structures of *on-dimer* configurations suggested above.

Again, in order to be systematic, symmetry unique atoms are identified in Fig. 2b. In addition to the six possible structures as explored in the previous sections, three more symmetry unique possible structures indicated as blank-squares in Fig. 2b. are studied. They were considered, since unlike *on-dimer* configuration, *inter-dimer* configuration can form distant interfacial bonds. In this part of study, B3LYP theories with SBKJC(d) effective core potential and SIMOMM models were used for full geometry optimizations. The results are presented in Fig. 6 and Table 2. The most stable *on-dimer* SIMOMM:6,6-[2+2] structure, **6a** is used as a reference energy point for all the *inter-dimer* configurations.

The most stable *inter-dimer* structure was calculated to be SIMOMM:ID-6-[4+2], **6b**. However, it is 15.8 kcal/mol less stable than the reference **6a** indicating that all of the *inter-dimer* structures considered are less stable than the most stable *on-dimer* 6,6-[2+2] structure. The two interfacial Si-C bond lengths of **6b** are calculated to be the typical single bond length of 1.90 Å. SIMOMM:ID-6,6-[2+2], **6c** and SIMOMM:ID-6,5-[2+2], **6d** the [2+2] cycloaddition analogies of *inter-dimer* configurations are found to have unexpected three interfacial bonds with the relative energies of 43.6 and 33.7 kcal/mol, respectively, indicating that they are highly thermodynamically unstable. SIMOMM:ID-6-[3+2] structure, **6e** is also found to be a minimum with 42.6 kcal/mol relative energy. The SIMOMM:ID-1,7, SIMO-

MM:ID-1,8 and SIMOMM:ID-1,9 are all found to be minimum with the relative energies of 33.4, 45.4 and 30.3 kcal/mol. Therefore, although eight different structures of *inter-dimer* configuration are possible, they are not thermodynamically as stable as the *on-dimer* 6,6-[2+2] structures further suggesting the existence of *on-dimer* configurations.

## Conclusions

Density functional theory was adopted to study potential energy surface along the possible surface reaction mechanisms of C_60 on Si(100)-2×1 surface. The overall reactions occur *via* stepwise radical mechanisms. According to the computed potential energy surfaces, initially, a Si-C singly bonded product is formed with no appreciable reaction barrier. The result is interesting since C_60 has been known to be rather inert toward addition reactions. Energetic study showed that the singly bonded surface structure turned out to be an extremely weakly bound state. Therefore, it can be considered as an experimentally suggested physisorbed species.

All the other surface products of *on-dimer* configuration are formed from this singly bonded species. Without any measurable activation barrier, the most stable 6,6-[2+2] cycloaddition product of *on-dimer* configuration is formed with the stabilization energy of 33.7 kcal/mol. The next most stable structures are 6-[4+2] and 6,5-[2+2] products with the stabilization energies of 21.7 and 14.3 kcal/mol. These two species require no or negligible activation barriers. Therefore, it is expected that the surface product population of these three species are determined thermodynamically.

Another *on-dimer* surface product, 5-[4+2] turned out to be unstable requiring 6.9 kcal/mol overall activation energy. It was found that there is a surface isomerization channel to the more stable 6,5-[2+2] with 6.3 kcal/mol activation energy. Therefore, even if 5-[4+2] is formed, it would be converted to a more stable species by thermal redistribution of surface products. Two other 1,2-shift type surface isomerization channels were found to eventually lead to the most stable 6,6-[2+2] structure of *on-dimer* configuration indicating that various surface direct channels exist which can facilitate surface thermal redistribution of surface products.

Surface pericyclic reactions which can lead to open-6,6-[2+2] and open-6,5[2+2] structures were found to be unlikely, since these species are thermodynamically unstable as compared to the reference point, **3a**.

*Inter-dimer* species were also considered. The most stable *inter-dimer* structure, SIMOMM:DI-6-[4+2] is 15.8 kcal/mol less stable than the most stable *on-dimer* structure, SIMOMM: 6,6-[2+2] further suggesting the existence of *on-dimer* 6,6-[2+2] species. SIMOMM:DI-6,6-[2+2] and SIMOMM:DI-6,5-[2+2], the two [2+2] product analogies of *inter-dimer* configuration have unusual three interfacial bondings. Five more *inter-dimer* structures were found but they are not thermodynamically interesting species.

According to our experience, DFT relative energy results are off by 3 ~ 10 kcal/mol as compared to MRMP2 values. It is due to the single configurational nature of DFT that cannot properly describe the relatively more multi-configurational Si bare-sur-face. Therefore, for more accurate results, MRMP2 theory is recommended. However, the possibility of the existence of *on-dimer* surface products as discussed in this paper would remain the same.

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