The Bare and Acetylene Chemisorbed Si(001) Surface, and the Mechanism of Acetylene Chemisorption

Qiang Liu and Roald Hoffmann*

Contribution from the Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853-1301

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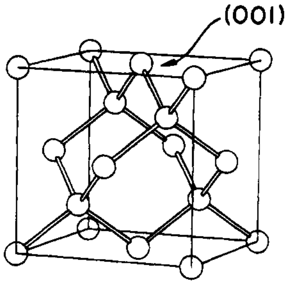
Abstract: Both cluster and extended slab models for the bare Si(001) surface and for acetylene chemisorbed on that surface were studied by various theoretical methods. Our calculations point to a buckled Si−Si dimer on the bare reconstructed surface. Acetylene adsorbs onto the dimer to form a four-member disilacyclobutene ring without breaking the Si−Si bond. Upon acetylene chemisorption, the buckled dimers become symmetric. The surface reaction is orbital symmetry-forbidden. A likely pathway for the cycloaddition, via a π-complex precursor and a biradical intermediate, is suggested.

Introduction

Silicon is at the heart of our information age. The most common form of this element has the beautiful bulk structure of diamond (**1**, a conventional unit cell), in which every Si atom is covalently bonded to four Si's.



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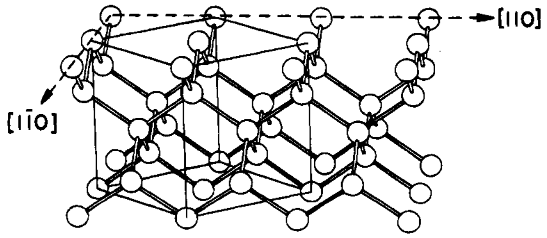
Both the bulk material and silicon surfaces are of technological importance. If a silicon crystal is cut, one of the simplest surfaces one gets, and one very well studied, is Si(001). The unreconstructed surface would expose a two-dimensional square lattice (**2**; a conventional unit cell is outlined), with each surface silicon atom bonded only to two other Si's and having (in a simple valence bond (VB) representation) two singly occupied orbitals at each surface Si. These are commonly called dangling bonds (**db**) in the literature.



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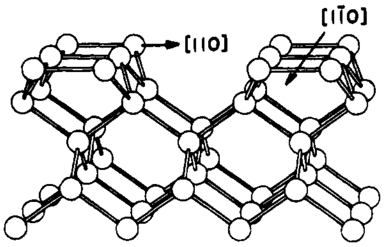
There is stabilization to be gained by bonding. So the **db**'s drive the surface—and to some extent the sub-surface layers—to undergo relaxation (normal to the surface) and reconstruction (lateral movement). We will refer to both these attempts by the surface to heal itself as reconstruction in this paper. This fascinating reconstruction phenomenon has been studied experimentally and theoretically for 35 years. It is well established that the (001) surface atoms form dimers along the [110] direction and dimer rows along [1$\bar{1}$0]; the reconstruction is shown in **3**. The unit cell of **3** is doubled relative to **2**; this is the so-called Si(001)−(2×1) reconstruction.



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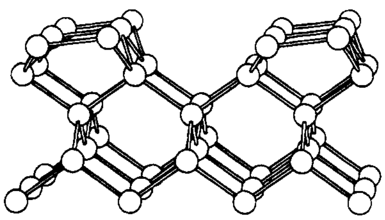

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The two Si atoms in each dimer in **3** are equivalent (or "symmetric", as they are often termed). Surface dimers could also be buckled (tilted along the surface normal). We show one such possibility, **4**, retaining the 2×1 periodicity. There are strong indications but no consensus that such a deformation might occur.[1−18]

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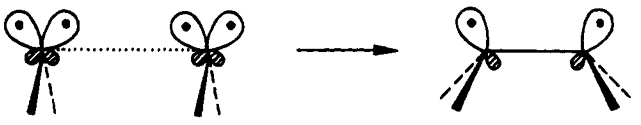
After the reconstruction, half of the surface **db**'s are still left over, as shown schematically in **5**. There may be some π-bonding in the dimer, but given the inherent instability of the Si=Si double bond[19] and the strain in the dimer, the π-bonding cannot contribute much to stability. Therefore, it is no surprise that the Si(001) surface is quite reactive. The interaction of Al,[20-22] alkali metals,[23] trimethylindium,[24] Sb_4,[25] benzene,[26] $CoSi_2$,[27] hydrogen,[28,29] ammonia,[30-32] silanes,[33,34] water,[35,36] HF,[37] and PH_3[38] with the surface has been studied. Theoretical investigations were carried out in Carter's group on fluorine etching[39-43] as well as hydrogen desorption and diffusion.[44-47] The desorption of hydrogen from the surface has also been studied theoretically by others, with a focus on the unusual first-order desorption kinetics.[28,48-5048] Yates' group has provided us with pioneering studies of the reactions of many small organic molecules with the (001) surface.[51-60] They found that acetylene,[51,53,55] ethylene,[52,54-56] and propylene[57] react readily with the (001) surface. This is very interesting, since the direct addition of a single Si=Si dimer and an acetylene molecule seems to constitute a 2_s+2_s cycloaddition, which is orbital symmetry forbidden.[61]



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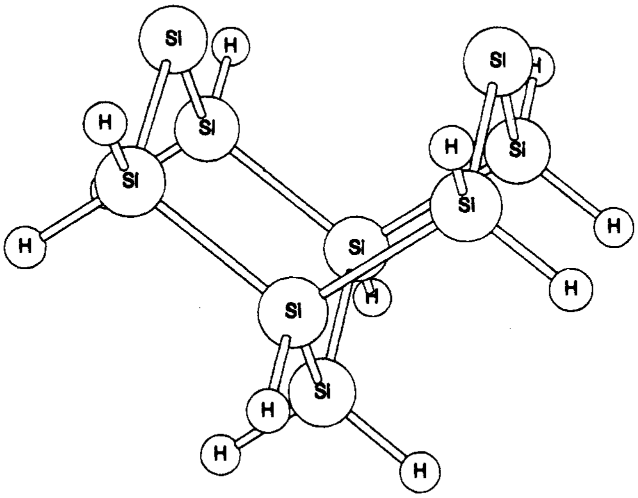
In this paper, we address some questions of the surface structure from a chemist's point of view, the structural changes upon acetylene chemisorption, and the mechanism of the acetylene chemisorption on the (001) surface.

Two Models for the Surface

Two models, **6** and **7**, were used in our studies, one a molecular model, the other an extended, two-dimensionally periodic slab. Si_9 is perhaps the smallest unit one could cut out of the unreconstructed (001) surface that might yet represent the surface reasonably realistically. In such a Si_9 model, two Si's are like the surface atoms of Si(001), while the other Si's are "bulk-like". These we "terminate" or "passivate" with hydrogens to complete a local tetrahedral environment, a modeling procedure justified by the very much localized Si bonding. The geometrical constraint imposed by the underlying bulk atoms on the two surface Si's, and the possible coupling of those atoms through the sub-surface Si's is very important, a point that will become clear later on when we discuss the



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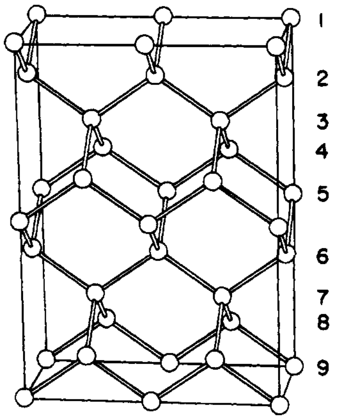
reaction pathway. **6** shows the discrete Si_9H_{12} model. This model was used before by others.[16,29,42,46]

Going to another extreme, **7** is a nine-layer two-dimensionally infinite slab of the silicon crystal, in which the bottom surface is passivated by hydrogens (not shown). Two unit cells for the unreconstructed surface are shown. This is another kind of model for the extended (001) surface. Comparing in our computations **7** with the bulk Si crystal, we found the 5th and 6th layers of the slab (counted from the surface) reproduce the bulk electronic structure (as measured by the density of states (DOS) and charges) very well. Furthermore, the H's at the bottom do not interfere with that part of the electronic structure (the levels a few electronvolts around the Fermi energy) we are most interested in.



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In our calculations, the Si−Si and Si−H bond lengths, if not stated otherwise, are set at 2.352[62] and 1.480 Å,[63] respectively. The former is the value experimentally determined for a bulk silicon crystal, and the latter comes from SiH_4. All relevant bond angles around Si's are fixed at 109.5°, unless they have to be different as required by local geometry. Our theoretical work utilized a variety of procedures: extended Hückel (EH)[64] calculations (both for molecules and extended structures), restricted Hartree−Fock (RHF)[65] and unrestricted HF (UHF)[66] computations with Gaussian basis sets for molecules, and a density-functional theory (DFT)[67] method for extended structures. Details of those are given in the Appendix.

The Molecular Model: Dimerization and Buckling

To an organic chemist, a single Si atom of the unreconstructed Si(001) surface seems to be quite analogous to a silylene, SiR_2. And this in turn would be analogous to the archetypical carbene, CH_2. It is known that CH_2 has a triplet ground state, while SiH_2 has a singlet.[68] If we really had isolated singlet silylenes, a dimerization (through a least-motion path) leading to a low-spin $H_2Si{=}SiH_2$ would be symmetry-forbidden.[69] However, these surface "silylenes" cannot be treated separately, as we will show. Furthermore, the geometry constraint imposed on the "silylenes" makes an otherwise forbidden reaction proceed without a barrier.

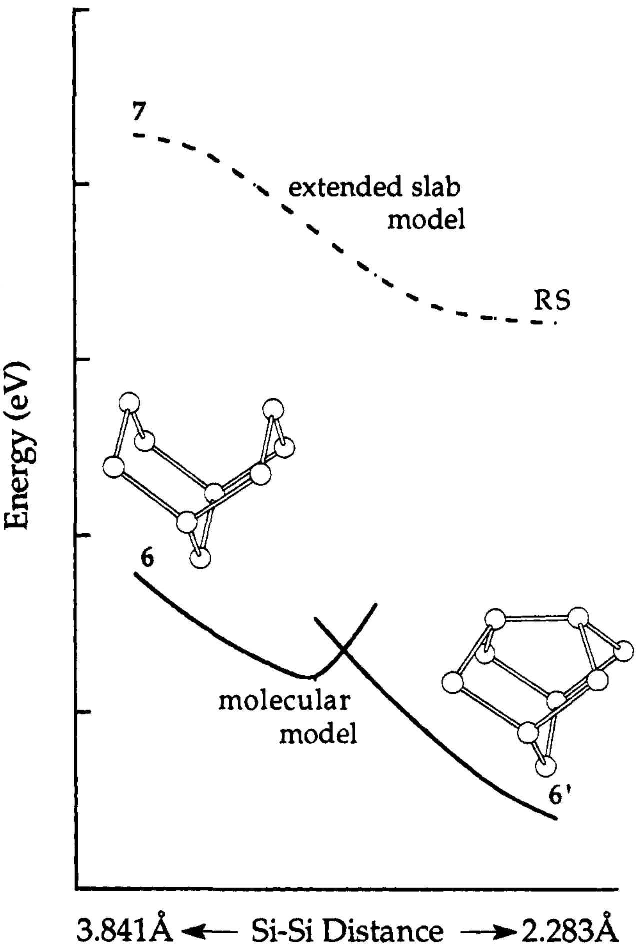
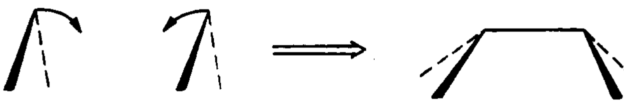


Figure 1. The potential energy surfaces (PES) for the dimerization of the molecular model **6** (solid curve; the hydrogen atoms are omitted for clarity) and the extended model **7** (dashed curve) displayed in the same plot for convenience; the relative position of two curves is arbitrary.

Let us take a look at the computational results. Figure 1 shows the potential energy surfaces (PES) for the dimerization in molecular model **6** (solid curve) and extended slab **7** (dashed), computed by the EH method. The assumed reaction coordinate here corresponds to a change of the surface or "silylene" Si−Si distance symmetrically and continuously from 3.841 (**6** and **7**) to 2.283 Å (**6′** and RS; this latter distance was chosen to be between a reasonable experimental Si−Si single bond distance in the crystal, 2.352 Å, and a double bond 2.116 Å[70]), while keeping other distances fixed. Another way to describe this reaction coordinate is to say that two surface Si units swing continuously on an arc, toward each other (see arrows in **8**).



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The energies decrease for both cases. For the dimerization of molecular model **6** there is a small hump, which on closer

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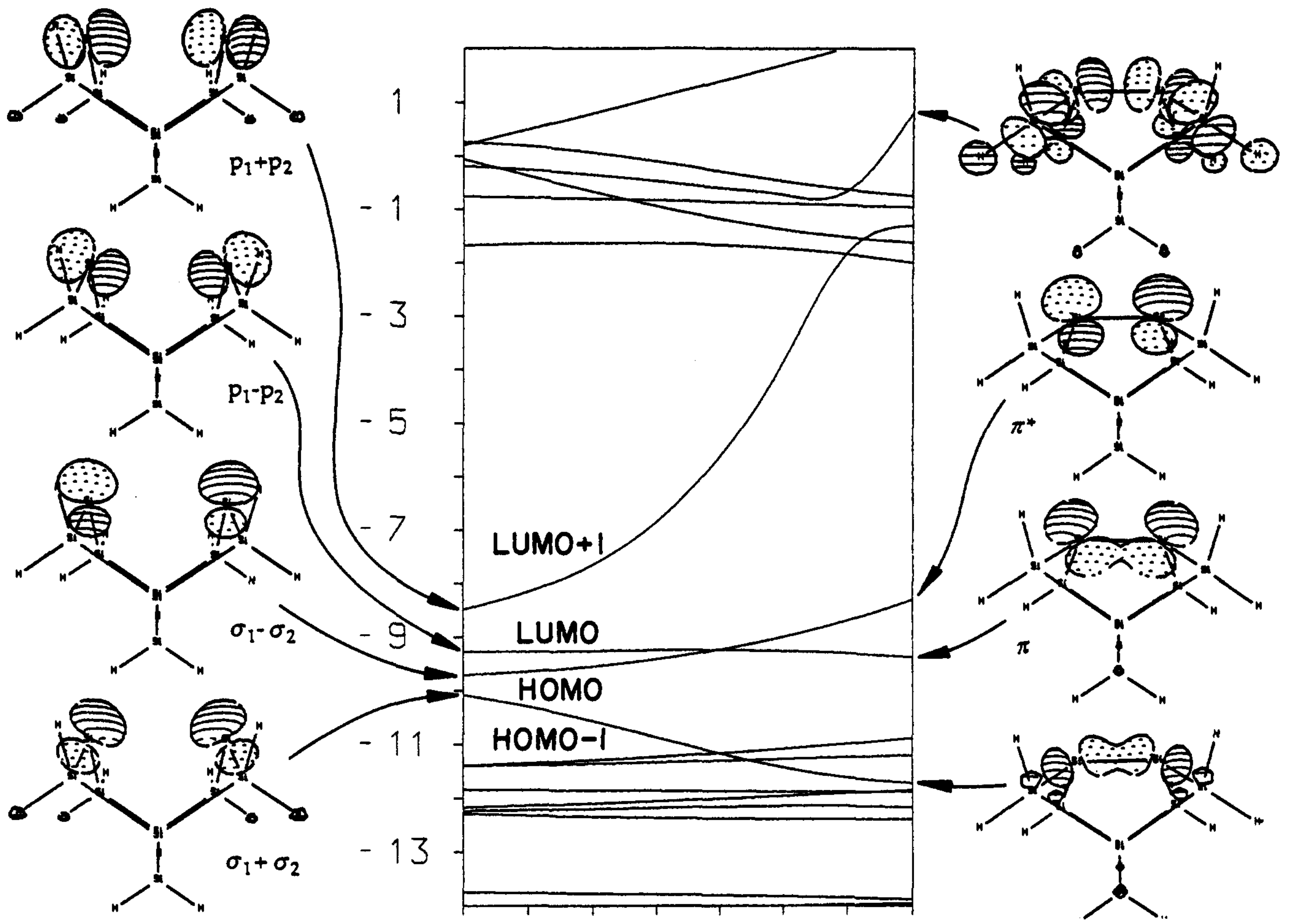


Figure 2. An orbital correlation diagram for the molecular model. The starting point (left) is **6**, and the final point (right) is **6′**. The energy scale is in eV.

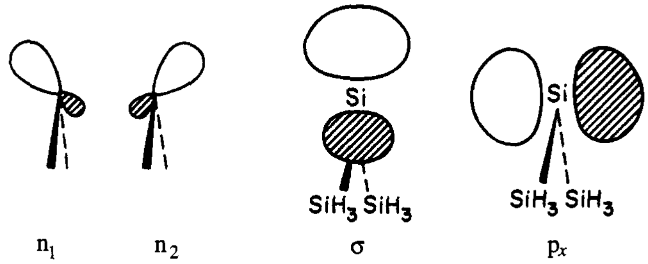
examination turns out to be a level-crossing. That discontinuity is absent in the upper curve, probably washed out by the extended surface structure.

The deformation studied induces some strain and Si(surface)−Si(sub-surface) bond weakening; nevertheless, the energies are lowered by 1.28 and 1.07 eV along this reaction path for **6** and **7**, respectively. It turns out that for **6** the Si(surface)−Si(sub-surface) bond is weakened a little (the relevant Mulliken overlap population (OP) changes from 0.769 to 0.708). At the same time the OP between the surface Si's changes from essentially non-bonding (0.054) to quite strongly bonding (1.036). This is the driving force for the dimerization. Extended model **7** gives almost the same results.

We also studied the same reaction using quite different computational techniques. The energy falls by 0.94 eV in the dimerization of **6**, using now the RHF method with a 6-31G** basis set.[71−73] A DFT computation for an extended Si(001) surface structure (see Appendix for details) yields 1.35 eV for the surface dimerization energy.

The orbital correlation diagram for the surface Si−Si dimerization process in molecular model **6** is displayed in Figure 2. Let us focus on the evolution of the frontier orbitals, which, at the starting point (surface Si−Si distance 3.841 Å), are the highest occupied molecular orbital (HOMO), HOMO-1, the lowest unoccupied molecular orbital (LUMO), and LUMO+1. Those four orbitals are mainly the symmetry-adapted linear combinations of the four **db**'s of the two unreconstructed surface atoms, and we take some space to construct these.

The **db**'s are traditionally represented as at left in **9**, two sp^3 hybrids (n_1, n_2) in a VB representation. However, the molecular orbital (MO) description forces us to take the linear combinations $n_1 \pm n_2$, which may be called σ (this orbital is mainly p_z (z is normal to the surface), with some s character) and p_x (the dimer is aligned along x). These orbitals are shown at the right in **9** (taken from an actual calculation on a model $Si(SiH_3)_2$).



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The σ and p orbitals of a single silyl substituted silylene, $Si(SiH_3)_2$, are split by 0.71 eV. This is a substantial energy, likely to ensure a singlet ground state for such a species. Such a preference is in fact calculated for molecular silylenes (for SiH_2, the singlet is calculated to be 18 kcal/mol lower in energy than the triplet[68]).

In the unreconstructed surface model **6** one has two such silylene units. The resulting $\sigma_1 \pm \sigma_2$ and $p_1 \pm p_2$ combinations are shown on the left side of Figure 2. The small tilts evident

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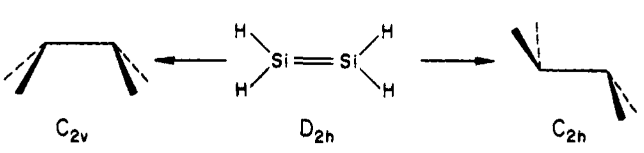
in these are the result of further orbital mixing. Even though there is some $\langle p_1|p_2\rangle$ overlap, the level ordering is dominated by the s character in σ, i.e. both $\sigma_1 \pm \sigma_2$ are below $p_1 \pm p_2$.

At the right (Figure 2) we clearly see the π- and π^*-orbitals, alternatively to be viewed as remaining **db** in- and out-of-phase combinations. Given the level ordering at left and right, one clearly has a level crossing along this reaction coordinate. But the "forbiddenness" of the reaction is not great, since the $\sigma_1-\sigma_2/p_1-p_2$ gap is not big. The energetics of the product being more stable, due to new Si–Si σ-bond formation, determines the calculated PES of Figure 1.

The surface dimer clearly has a fairly strong σ-bond. However the π-bonding seems to be quite weak (a $\pi-\pi^*$ gap of only 1.07 eV). For small molecules with a planar Si=Si double bond, a gap of about 3 eV was determined experimentally.[19] The π-type interaction between Si's is intrinsically weak, for the π-type overlap is small at typical equilibrium Si–Si separations. Other theoretical methods have provided an estimate of ~15 kcal/mol as the bond strength increment due to π-bonding.[74,75] The "pinned-back" or *cis*-bent C_{2v} geometry constraint on the surface dimer weakens the π-bonds even more. $H_2Si{=}SiH_2$ (**10**) was found to have a *trans*-bent C_{2h} geometry, the D_{2h} modification slightly higher in energy.[70,76,77] These calculations do not report a C_{2v} geometry, but we found that it is quite unstable. It was pointed out that substitutions at Si in disilene, especially by π-donors, can lead to greater preferences for a *trans*-bent C_{2h} structure.[77] Therefore, a biradical picture for the surface dimer (implied by many workers) is not too bad.



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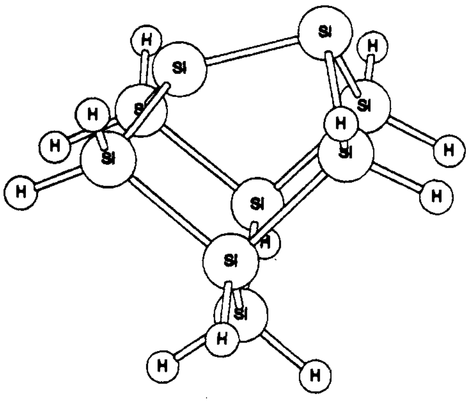
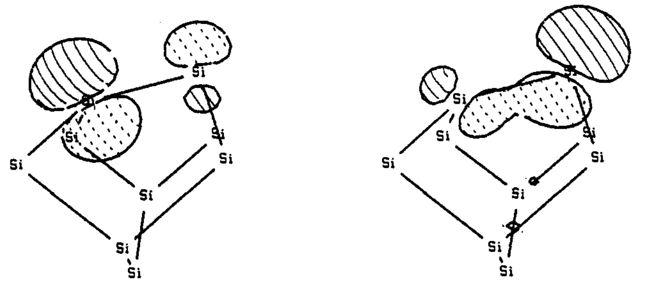
When we optimized the geometry of the C_{2v} product of dimerization in an RHF/STO-3G[78-80] singlet configuration, we found that this structure is not an absolute minimum but has a single negative vibration frequency. Slightly lower in energy (by only 0.08 eV) is **11a**, a stable "buckled" dimer.

The UHF/STO-3G optimizations we did gave almost the same results. At room temperature the dimer should tilt dynamically up and down, like a see-saw, and might appear on the average symmetrical to many experimental techniques. This may be the reason for the experimental (and theoretical, because of the very small amount of energy involved) ambiguity about the true nature of the reconstructed surface.[15,17,18]

The buckling may appear surprising to a chemist, but then the geometry of group IV double bonded species has its special features.[70,81-83] One way to think about this within a VB framework is that buckling gives one orbital (on the buckled-*up* atom) more s character and lowers its energy, while it pushes the other one (on the buckled-*down* atom) toward a pure p orbital and a higher energy. This results in a bigger HOMO–LUMO gap and a lower total energy for the dimer. Some would call this a second-order Jahn–Teller driven distortion.[84]



11a



LUMO **HUMO**

11b

The buckling, while governed by only a small energetic preference, has substantial effects on the charge distribution and electronic structure of the surface. [It may be that the calculated buckling of silicon dimers is an artifact of the HF theory (see ref 16 of this paper). However, we think that the buckling phenomenon is real and provides us with a consistent picture of what happens on the Si(001) surface. A recent STM experimental result supports our point of view.[85]] With the deformation we expect partial electron transfer to the buckled-*up* Si, making it a nucleophilic site. The buckled-*down* atom should be electrophilic. Our simple EH calculations confirm this trend; the net charge on the *up* Si is −0.77, while on the *down* one it is 0.55. The frontier orbitals polarize accordingly; the shapes of the LUMO and HOMO are shown in **11b**.

The Extended Slab Model: Dimerization and Buckling

We proceed to a calculation of the band structure of the surface, using the nine-layer slab model **7**. The result for the unreconstructed surface is at the left of Figure 3. A density of states (DOS)[86] plot for **7** is at right (Figure 3); the contribution of the surface atoms is projected out in the shaded area. As can be seen, the DOS contribution (and thus the bands) around the Fermi energy ϵ_F is dominated by the surface Si's, a situation reminiscent of the molecular model, **6**. Four bands, marked 37, 38, 39, and 40 (numbered from the lowest energy band), are responsible for most of these surface states. Since the ϵ_F cuts through several bands, **7** should, in principle, be metallic.

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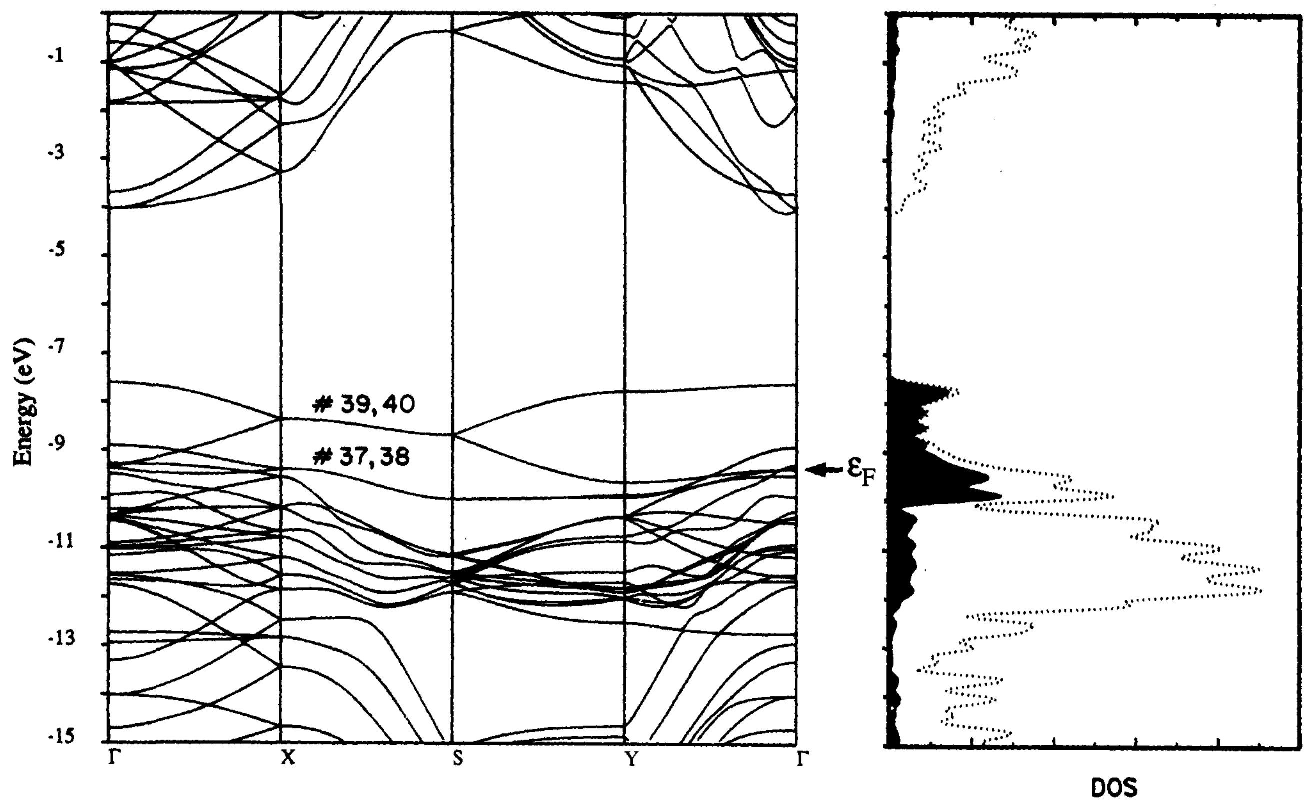

Figure 3. The band structure (left) and density of states (DOS) plot (right) for the unreconstructed Si(001)−(2×1) surface, model **7**. The shaded area in the right panel is the contribution of the surface Si atoms.

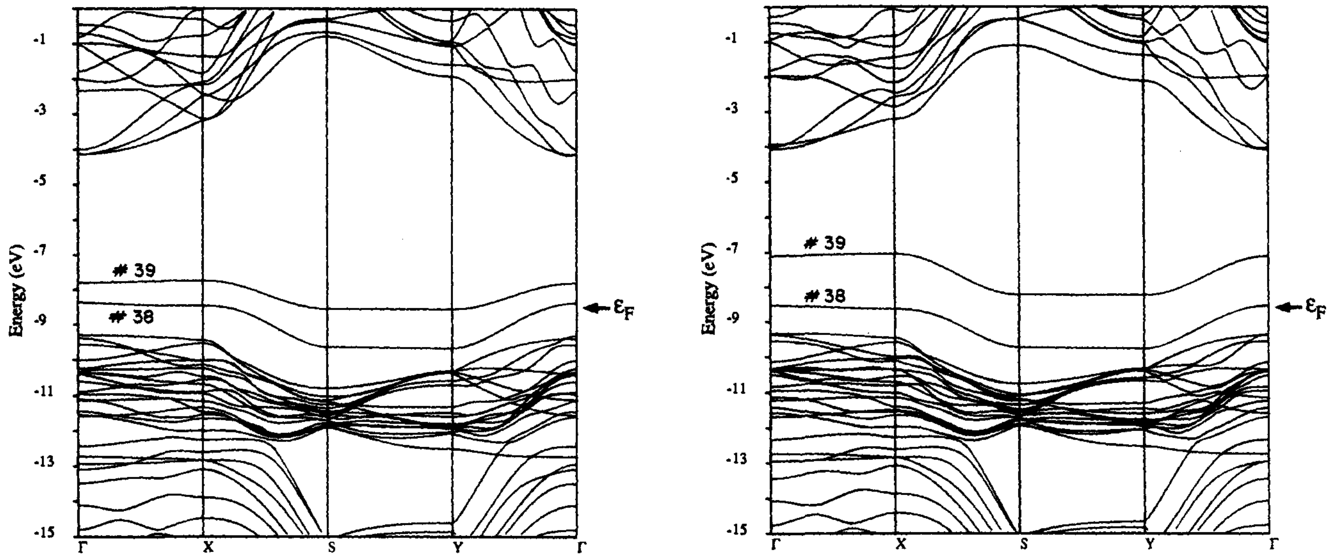

Figure 4. The band structures for two different reconstructed Si(001)−(2×1) surfaces: left for RS; right for the geometry reported in ref 11.

In Figure 4 (left), we show the band structure for the reconstructed surface. We will term this RS, for the Reconstructed Surface. This is the symmetrical dimer geometry corresponding to the end point of the PES for reconstruction of **7** in Figure 1; it is very much like structure **3**. Several significant changes take place. Whereas we see two bands (#39 and #40) degenerate between Brillouin-zone points X and S[87] for **7** (Figure 3, left), we find for RS instead two bands (#38 and #39) almost parallel. Band #40 of the unreconstructed surface is pushed so high up that we can no longer locate it easily (remember LUMO+1 of **6**, which became a Si−Si σ^*). RS should also be a metallic conductor, since bands #38 and #39 overlap "indirectly", i.e. at different *k*-points in the Brillouin zone.

In an extended system reaction (such as **7** → RS), it is not easy to draw a correlation diagram such as we did for the molecular reaction **6** → **6′** in Figure 2. In principle, there is an infinity of such diagrams, one for each point in the Brillouin zone. Later on we are going to construct such diagrams for the Si(001) surface reacting with acetylene. Here we only point out that these two types of correlation diagrams (for molecular and extended systems) are very similar.

The (001) surface was found experimentally to be semiconducting.[88] How can we reconcile this with our calculations? Perhaps the simple reconstruction we have studied is inadequate. A pseudopotential total energy DFT calculation[11] found reconstruction reaching down as deep as 5 layers and a buckled (2×1) structure a little bit more stable than a symmetrical one. Using

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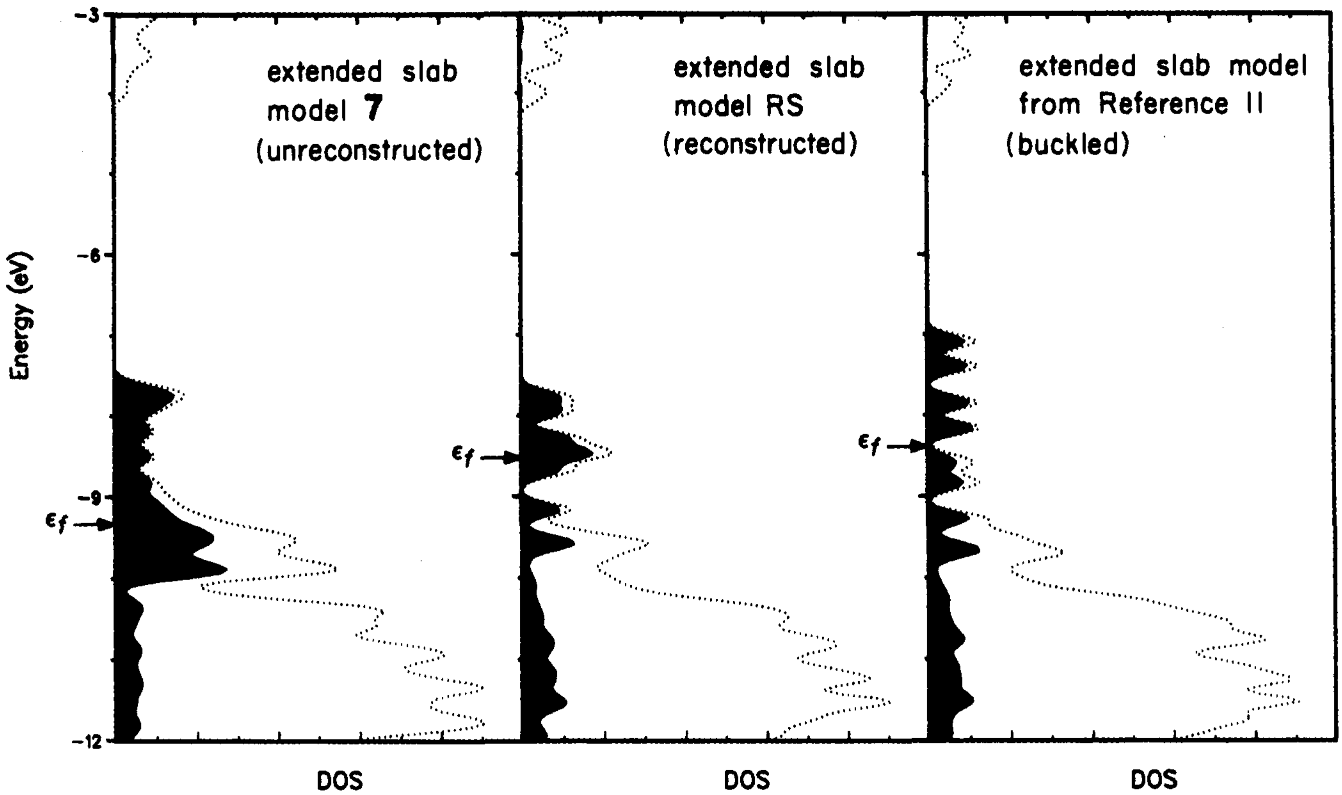

Figure 5. The contributions of the surface Si atoms to the DOS (shaded areas) in the unreconstructed model **7** (left), the symmetrical (2×1) RS (middle), and a buckled (2×1) reconstruction (right). The small gap seen in the band structure for the buckled surface (Figure 4, right) is buried here by the broadening effect of Gaussian functions used to plot the DOS curve (right).

that fully optimized geometry for the buckled (2×1) surface, we obtained its EH band structure (Figure 4, right). Clearly an overall bigger gap between bands #38 and #39 results, compared with that of RS (Figure 4, left). This is what would be expected by the same argument we applied to the buckling of the dimer in model **6** in the previous section. The energy is lowered by 0.44 eV from RS. Now there is a small indirect gap between bands #38 and #39 (about 0.5 eV, close to another calculated result[6]).

Consistent with the buckling we detect partial electron transfer—the net charges are +0.30 on the buckled-*down* and −0.64 on the *up* silicon.

It is instructive here to step back and look at the evolution of the DOS as the surface reconstructs. In Figure 5 we show the contribution of the Si surface atoms to the total DOS in the unreconstructed surface model **7** (left), the symmetrical (2×1) reconstruction RS (middle), and the buckled (2×1) surface (from ref 11). The movement of states out of the region near the Fermi energy is obvious—it is clear that the surface heals itself by rebonding. An inner layer, say the bulk-like fifth one, shows essentially no change during the same sequence, nor is it different from that of the bulk silicon.

It should be noted that the Si(001) surface might also reconstruct to p(2×2),[11] c(4×2),[6,89] and other periodicity structures. Defects (missing dimers or impurities) and steps may also render even the symmetric dimer semiconducting (Anderson transition[90]). The semiconducting behavior of the surface with symmetric dimers could also be explained by an antiferromagnetic ordering model.[91,92] We are not, however, in a position to study those more complicated situations.

In summary, using two different models (molecular **6** and extended **7**), and from two different approaches (the equilibrium geometry and the semiconducting nature of the surface), we reach the same conclusion: the (001) surface dimer is likely to be buckled, but not by much.

The Structure of the Acetylene Chemisorbed (001) Surface

Acetylene chemisorbs onto the Si(001) surface at a coverage of one C_2H_2 per Si dimer.[51,53] It is difficult to determine the structure of the C_2H_2 chemisorbed surface. By thermochemical arguments the Yates group reasoned that acetylene binds to the dimer by two σ-bonds, with the Si−Si dimer bond cleaved, **12**. The same conclusion was reached by the Weinberg group.[93] A EH type calculation for C_2H_2 adsorption,[94] however, assumed a structure with the Si−Si dimer bond unbroken, **13**. This is also the structure proposed by a different group.[95]

We constructed geometries for **12** and **13** by "adding" a C_2H_2 unit onto **6** and **6′** (the distances are set at 1.90 Å for Si−C (close to a single bond length in small molecules[70]), 1.34 Å for C−C (a double bond length), and 1.10 Å for C−H and the H−C−C angle is fixed at 120°). A single point computation using RHF/6-31G** showed that such a model for **13** is 3.66 eV lower in energy than its counterpart **12**. For the extended structure (see the Appendix) with a monolayer coverage of C_2H_2, the DFT calculation gave the unbroken Si−Si dimer bond structure an edge of 1.13 eV over the dimer "cleaved" one. EH results also favor the same structures.

Without geometry optimization and better calculations, a rigorous theoretical conclusion cannot be reached. We believe,

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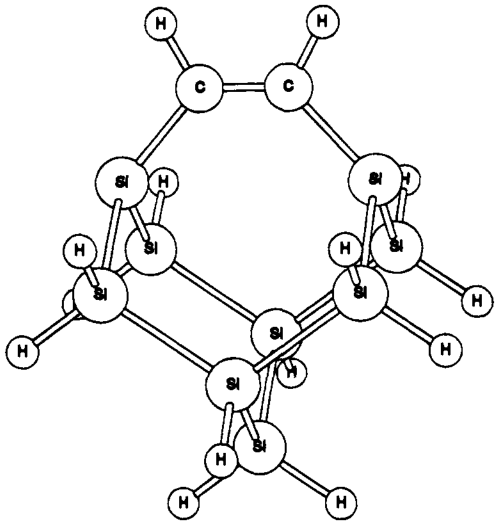

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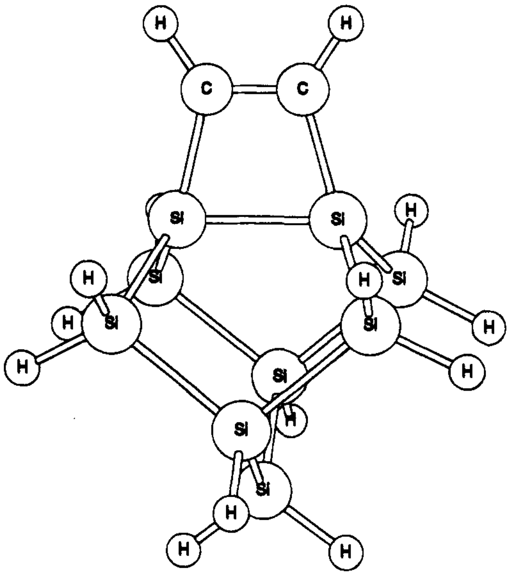

13

however, that an optimization would probably not change the situation drastically, since all the bond lengths/angles (except the 75.63° of C−Si−Si, constrained by symmetry) seem to be reasonable. In fact, a full geometry optimization (using RHF/STO-3G), starting from an asymmetrical analogue of **13**, ended up with a stable (no negative frequency) C_{2v} structure, yielding the bond lengths 1.33 Å for C−C, 1.87 Å for C−Si, and 2.23 Å for the dimer Si−Si. Very recently the first crystal structure of a disilacyclobutene was reported, giving the bond lengths 1.357 (C−C), 1.881 (C−Si), and 2.359 Å (Si−Si).[96]

Why does the surface retain Si−Si bonding upon acetylene addition? Breaking the dimer bond would cost at least 1 eV (see the previous section). This action would create two new Si **db**'s in an orientation where they are orthogonal to, and so unable to overlap with the remaining C_2H_2 π system. In **13** all the valence electrons/orbitals are used in bonding. Ring strain is less important in silahydrocarbons than in the hydrocarbon systems.

Note that the acetylene-added surface Si−Si dimer is not buckled; such buckling would now introduce substantial strain. Also, except for the on-top site we studied above, we found that all the other conceivable acetylene adsorption sites on the Si(001) surface were unfavorable energetically.

To summarize, we favor an acetylene adduct with an unbroken Si−Si dimer bond, essentially a disilacyclobutene structure. We suggest the same is true for ethylene, propylene, and some other alkene adducts; the product would be a disilacyclobutane. In this case a different conclusion was reached recently again by the Weinberg group.[97]

The Mechanism of Acetylene Chemisorption

The small molecule analogue of the surface dimer is a deformed disilene, $R^1R^2Si{=}SiR^3R^4$. These ethylene analogues are generally not stable kinetically and have to be stabilized by bulky substitutes.[70] Disilenes are reactive and undergo many bimolecular reactions, of which the cycloadditions of phenylacetylene and (trimethylsilyl)acetylene[98] are particularly interesting to us. This reaction is quite selective; apparently it does not occur for acetylene, propyne, and 1-hexyne. Furthermore, it seems that alkenes do not easily undergo cycloaddition with disilenes.[99] Clearly, disilenes behave very differently from the reconstructed Si(001) surface.[51−57] One reason for this may be the geometrical constraint in the surface case, which must remain close to a local *cis*-bent C_{2v} dimer geometry, whereas a disilene (for example $H_2Si{=}SiH_2$) generally prefers a *trans*-bent C_{2h}.

We begin our study of the surface reaction by constructing a hypothetical $[2_s+2_s]$ concerted path for the molecular model and show the corresponding EH orbital correlation diagram in Figure 6. The starting geometry in this "linear transit" corresponds to acetylene and **6′** placed 4.00 Å apart (measured from C−C center to Si−Si center). The final point in the hypothetical reaction path is **13**. C_{2v} geometry is maintained throughout. The relevant frontier orbitals are the π- and π^*-orbitals of the Si=Si double bond and the π- and π^*-orbitals of acetylene. Figure 6 shows clearly that a level-crossing occurs between the HOMO and LUMO of the reactants (actually the π- and π^*-orbitals of the Si=Si double bond); the reaction is symmetry-forbidden.

We move on to the extended surface. From a similar calculation for RS and a monolayer acetylene we constructed correlation diagrams (Figure 7) for the Γ point ($k_x = k_y = 0$) and a general k-point G ($k_x = k_y = 0.25$). For Γ (Figure 7, left), the level pattern is extremely close to that of the molecular model **6′** plus acetylene (Figure 6). A level crossing between the "HOMO" and "LUMO" is again evident. The similarity is not an accident, since in both cases the same symmetry elements (of the C_{2v} point group) are present. No levels may cross at G (Figure 7, right), for the G point only has the identity as its symmetry element. Even at G, however, a high barrier for the reaction still exists, because the underlying crossings are just avoided by the lack of symmetry. Orbital symmetry rules are, therefore, also applicable to surface reactions.

Of course, this reaction does not happen by the simultaneous approach of a monolayer of acetylenes toward the Si surface. Much more likely is the addition of an acetylene here and there randomly on the surface, acetylenes in succession approaching the reactive dimer sites. The flat Si(001) surface state bands (#38 and #39 in Figure 3 and 4) imply quite localized π- and π^*-bands. This in turn makes it likely that if a smaller number of acetylenes (i.e. a lower coverage of the surface) approaches, one would still get a correlation diagram with the characteristics of a forbidden reaction. This would be true even in the limit

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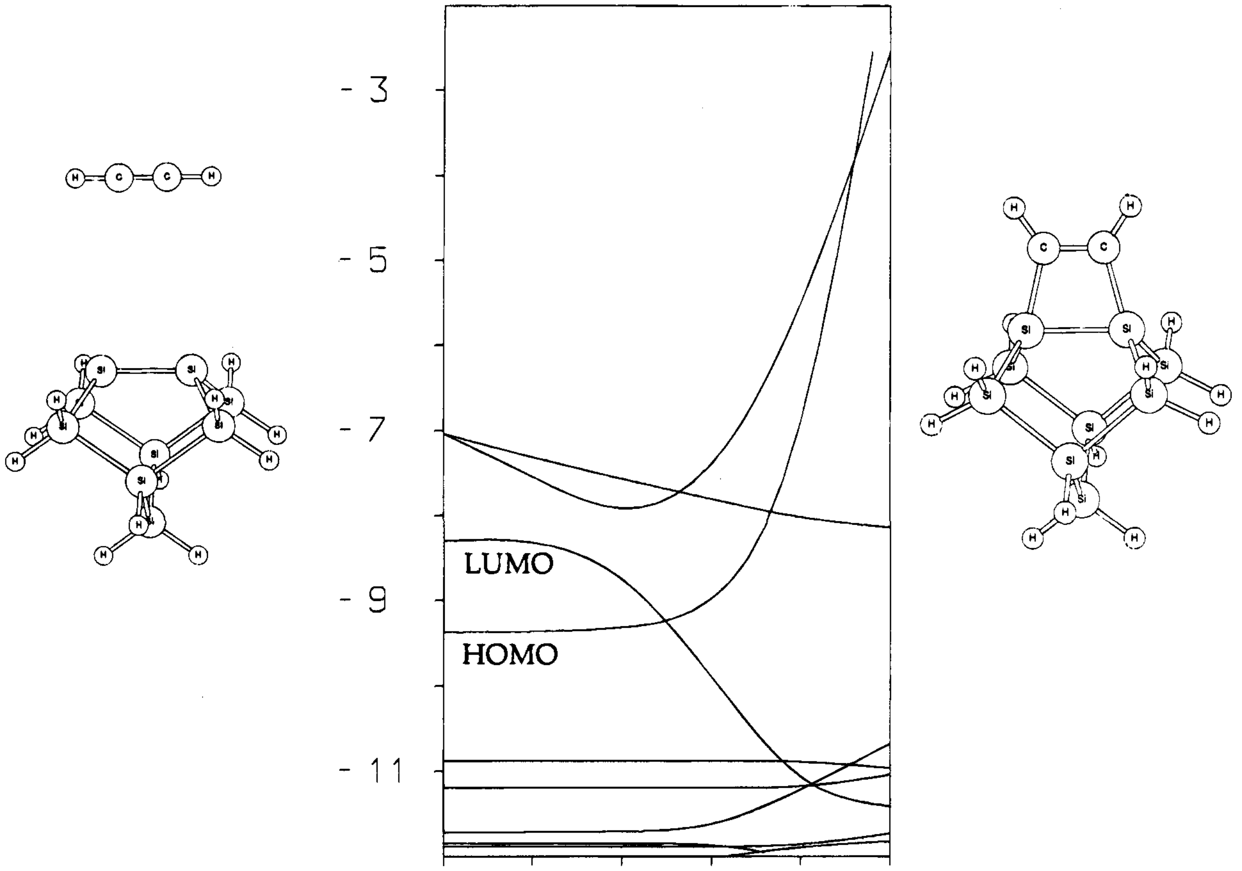


Figure 6. An orbital correlation diagram for the concerted 2_s+2_s reaction path of acetylene adding to model **6′**. At left are the reactants and at right the product.

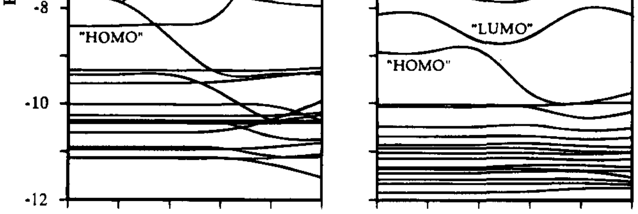


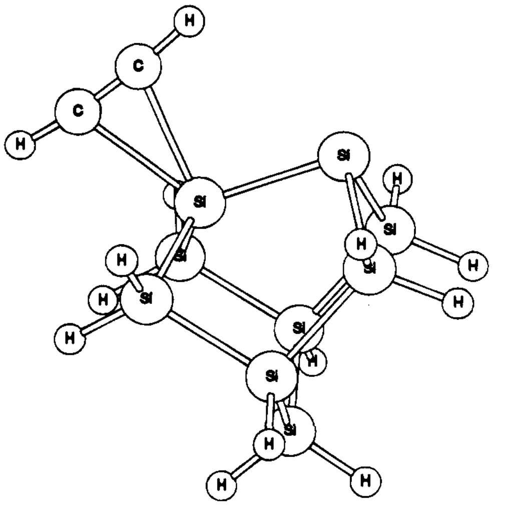
Figure 7. Orbital correlation diagrams at the *k*-points Γ (left) and G (right) for an acetylene monolayer approaching the Si(001) surface, RS, in a way as described for the case shown in Figure 6.

of zero coverage, an isolated acetylene approaching a bare surface. And it is also likely for acetylenes approaching surfaces partially reacted to disilacyclobutanes.

Other concerted paths are unfavorable as well, as our EH computations showed. For example, the $[2_s+2_a]$ path with the acetylene approaching the dimer orthogonally (the C−C axis in the previous path rotated 90° around the surface normal) gives a purely repulsive PES. Returning to the "parallel" approach, if we start out with the dimers buckled, the level crossing disappears due to the lower symmetry. But an avoided crossing still occurs, resulting again in a PES with a high barrier.

We have to find some other channel for this surface [2+2] cycloaddition. It is known that [2+2] cycloadditions occur for small molecules via either a zwitterionic[100] or a biradical intermediate.[101−105] The cycloaddition of disilene and acetylene was postulated to occur via a biradical intermediate,[98] $SiR^1R^2{-}SiR^3R^4{-}CR^5{=}CR^6$. Our EH result for the molecular model **6′** seems to give a path with a biradical intermediate and two small barriers on the PES. That is encouraging. Unfortunately, the EH method has its limitations here, in that it is not reliable when distances are varied. We felt that a further study was needed.

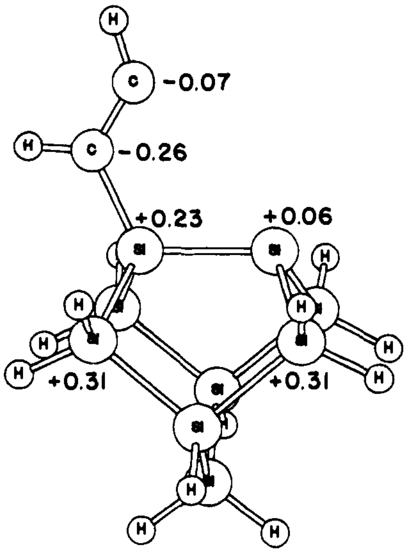
At first, we searched for an "intermediate" using a UHF/STO-3G geometry optimization. Surprisingly, what we got is a π-complex, **14**, instead of the "biradical" we were looking



14

for. **14** has an energy 0.25 eV lower than the sum of the geometry-optimized energies of acetylene and **6′**; perhaps it is the mobile precursor indicated by experiments.[53] The result makes perfect sense, since the buckled dimer has a partially positive site (the buckled-down Si, electrophilic), which acts as an electron-acceptor toward the donor acetylene π-bond.

It is very unlikely that a barrier exists for π-complex formation. Combining the transition state search and the geometry optimization using the UHF/STO-3G method, we found an intermediate, **15**, and two transition states, TS1 and TS2 **16**, preceding and following it. With those we could draw a tentative "PES", as in Figure 8.



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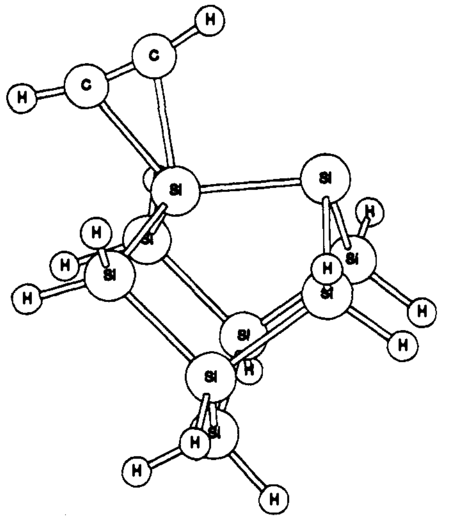
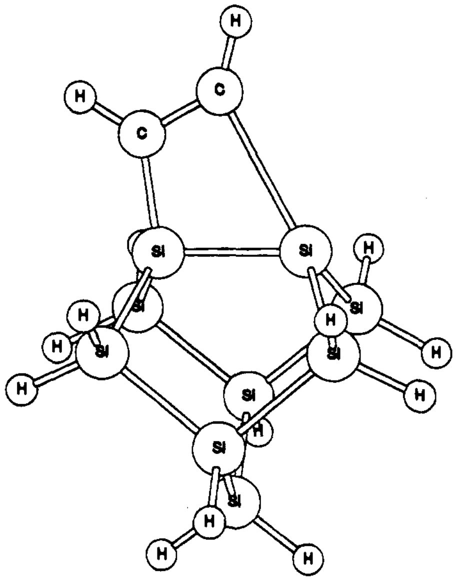
TS1 is only about 0.007 eV above **14**, the π-complex. The structure of TS1 is very close to that of **14**, only with shorter C−Si distances (2.19 and 2.20 Å for TS1, compared with 2.35 and 2.36 Å for **14**).



TS1
16



TS2
16

As the acetylene moves further in toward the silicon atom, one carbon atom swings back and the other forms a pretty full C−Si bond (bond length 1.86 Å). That gives us **15**, an intermediate, which is substantially stabilized (by 3.61 eV, relative to **14**). Is this intermediate a zwitterion or a biradical? We think it is the latter, since **15** has a dipole moment of only 0.722 D and a quite symmetric Si dimer. The relevant Mulliken charges, shown in **15**, indicate that not much charge disparity has developed. Furthermore, the 131.90° H−C(−0.07)−C(−0.26) angle is very close to the 130.85° we found for the equivalence in the vinyl radical by using UHF/STO-3G optimization. Notice we have a "*cis*" C−C−Si−Si structure here. It is possible that a "*trans*" intermediate, rotated 180° around the C−Si axis, also forms. We did not, however, search for it.

In the next stage of the reaction, the second C−Si bond closes to form the product, disilacyclobutene, via a second transition state, TS2. From **15** to TS2, there is a small energy barrier of 0.20 eV. Therefore, in our calculations a stepwise reaction could proceed smoothly, without encountering substantial barriers.

It should be said that the Hartree−Fock instability may preclude our reaching a definite conclusion based on this "PES", since we must deal with real or potential biradicals here.[106] However, we cannot at present afford more sophisticated computations with a better treatment of electron correlation. Nor is it yet possible to do the same kinds of calculations for extended systems. Nevertheless, we think that molecule **6** should be a reasonably good model for studying reactions on the Si(001) surface and that its study has given us some insight on the reaction mechanism.

Conclusion

The structures of the Si(001) surface with and without chemisorbed acetylene molecules have been studied using EH, HF, and DFT methods. Also investigated by EH and HF methods was the mechanism of the acetylene chemisorption. We find the following:

1. The Si(001) surface dimers are probably buckled, energetically, by just a little. Great polarization of the weak double bond accompanies that buckling.

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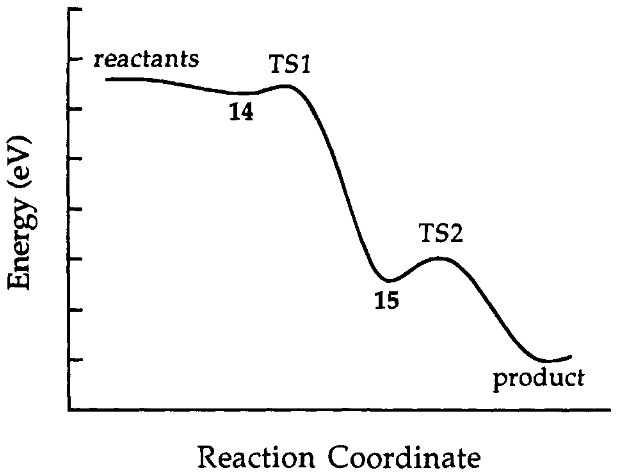

Figure 8. A schematic "potential energy surface" for the cycloaddition of acetylene and molecular model **11**, the buckled dimer. The reactants are at the far left and the product are at the far right. Only six points, corresponding to maxima and minima, were calculated using the UHF/STO-3G method.

2. Acetylene adsorbs on the Si(001) surface to form "disilacyclobutenes", without breaking the dimer Si−Si bond. The acetylene chemisorbed Si−Si dimers are symmetrical, not buckled.

3. The chemisorption of acetylene onto the Si surface dimer is symmetry-forbidden. The reaction probably proceeds through an initial π-complex precursor, then a biradical intermediate, which collapses with a low computed barrier to the product.

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Appendix

Table 1. EH Parameters

atom	orbital	H_{ii} (eV)	ζ_{ii}
H	1s	−13.60	1.30
C	2s	−21.40	1.63
	2p	−11.40	1.63
Si	3s	−17.30	1.53
	3p	−9.20	1.53

1. Table 1 shows the extended Hückel parameters used in our calculations. For H and C, values are taken from earlier work.[64] The Si parameters[107] were slightly adjusted so as to give a reasonable dimer bond length on the Si(001) surface. The CACAO program[108] was used for computations on small molecules.

In computing the surface structure, a 16 *k*-point set for the 2-dimensional tetragonal unit cell was used to calculate averaged properties. The band structures were calculated using Chong Zheng's ZNEW3 program (a version of our EH tight-binding program, available from C. Zheng of Northern Illinois University).

2. Ab initio calculations were carried out on an IBM RISC System/6000 (donated by IBM) using the Spartan code (versions 3.0 and 3.1) provided generously by WaveFunction, Inc. In all cases singlet ground or transition states were assumed. The basis set superposition error (BSSE) was not taken into consideration.

3. A repeated 3-layer Si(001)−(2×1) slab with one side terminated by hydrogens was chosen in the DFT computation, using the Corning code written by Douglas C. Allan. This is a pseudopotential LDA method with a planewave basis.[109] Slabs (without acetylene) are separated by a 10 Å vacuum gap. Nine *k*-points were used in the calculation. The kinetic energy cutoff is 6.0 atomic units. The exchange and correlation is approximated by Mike Teter's superior parametrization of Ceperly-Alder electron gas data. We are grateful to M. P. Teter for making this program available to us.

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