

Adsorption of Acetylene on Si(100)-(2 × 1)

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A study of a single acetylene adsorbed onto the Si(100)-(2×1) surface is presented. A MCSCF+MRMP2 wave function is used to study this system, which is shown to be significantly multiconfigurational over large sections of the potential energy surface. The lowest energy isomer is shown to have the acetylene adsorbed directly above a single dimer, di-σ, where the silicon–silicon dimer bond remains intact. These results are compared with those from a previous DFT study.

I. Introduction

There is a great deal of interest in the interaction of organic molecules with the 2×1 reconstructed silicon (100) surface. The primary motivation for this interest is a desire to combine the vast amounts of knowledge about the Si(100)-(2×1) surface with the even more expansive field of organic chemistry. As the methods for manipulating and machining silicon wafers have become quite sophisticated, surface scientists are increasingly able to create micron-sized gears, engines, and many other structures from silicon.¹ The centuries old field of organic chemistry encompasses the study of an extensive collection of molecules spanning nearly every kind of functionality known to chemists. It is not difficult to understand, therefore, why there is a great deal of interest in combining these two fields. If organic molecules can be reacted with and attached to the Si(100)-(2×1) surface in such a way that they retain their functionality, the utility of silicon-based materials would be greatly expanded. Many advances have been made in this direction^{2,3} and continue to be explored.

In recent years our group has been interested in modeling the interactions of small molecules with the Si(100)-(2×1) surface. It was established early on⁴ that saturated hydrocarbons do not react with the surface; it is necessary that the hydrocarbon contain at least one multiple bond as a reaction center to react with the surface dimers. Acetylene is the simplest hydrocarbon containing a carbon–carbon triple bond. It is therefore an important prototype molecule, as well as being an interesting system in its own right.

The 2×1 reconstruction of the Si(100) surface leads to rows of surface Si–Si dimers that are trivalent. Because Si–Si π bonds are very weak, these dimers have a significant amount of diradical character. Consequently, many recent studies^{5–7} of the Si(100)-(2×1) surface and its reactions have suggested that a multireference wave function is essential for a correct description of these dimers and their reactions. This study was initiated to assess the impact of multireference calculations on the predicted results for the Si(100)/acetylene system.

Early experimental studies of the Si(100)-(2×1)/C₂H₂ system disagreed initially about whether the silicon dimer bond was broken⁸ or remained intact⁹ upon chemisorption of an acetylene molecule. It was soon resolved that upon addition of an acetylene to the dimer, a σ bond remained between the silicons. Most ab initio and DFT calculations that have been performed on this system agree that in the “di-σ” (see Figure 1), or on-

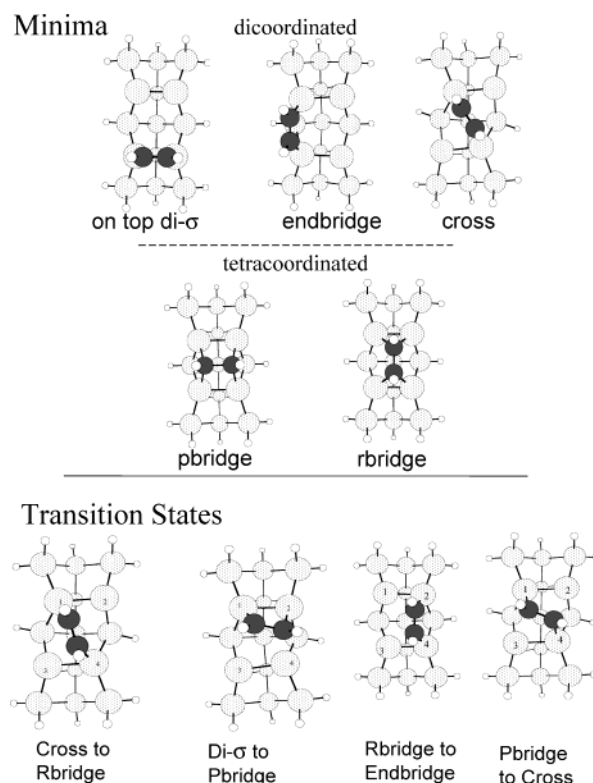


Figure 1. Stationary points.

top, configuration the dimer bond remains intact.^{10–12} Subsequent experimental studies observed two additional adsorption configurations: (1) “endbridge”, where the acetylene carbons coordinated to one silicon each on the same side of adjacent dimers, or (2) another structure that is postulated to be a tetracoordinated species, with the acetylene coordinated to adjacent dimers either perpendicular (“rbridge”) or parallel (“pbridge”) to the surface dimers^{3,13} (see Figure 1). It is universally agreed^{3,4,10,11,13,14} that the tetracoordinated species are higher in energy than either the di-σ or endbridge configurations; however, it has been suggested³ that the observed tetracoordinated species sit in adsorption sites that are more kinetically accessible. The acetylene, therefore, can presumably be trapped in such sites. It has also been suggested that the observation of so-called tetracoordinated species are actually misinterpretations of two acetylenes adsorbed in the endbridge fashion.¹⁴

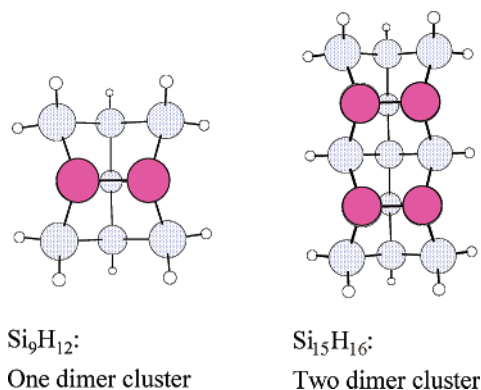


Figure 2. One and two dimer clusters.

II. Computational Details

When studying surface chemistry using quantum mechanics, one must develop a model of the surface that is able to capture both the local properties of the surface and the bulk behavior. Eliminating edge effects is important, but it must be feasible to perform the calculations using available computational resources. To study surface chemistry in this manner, it must be possible to construct a model cluster of reasonable size that captures the essential features of the surface. In the case of Si(100)-(2 × 1), the cluster must accurately represent the dimerized structure of the surface. The smallest reasonable one and two dimer clusters are Si_9H_{12} and $\text{Si}_{15}\text{H}_{16}$, respectively (see Figure 2). These clusters model the behavior of the surface well, yet are small enough to study with a reasonably high level of theory. A more sophisticated approach is to use an embedded cluster model, in which the quantum mechanics (QM) cluster is embedded into a larger bulk region represented by a lower level of theory. This approach diminishes edge effects while allowing the "action region" to be described by the highest levels of theory. In the present study, a $\text{Si}_{15}\text{H}_{16}$ QM cluster is surrounded by a larger molecular mechanics (MM) cluster, to adequately treat several isomers in which the acetylene molecule is interacting with two dimers in the same dimer row. The details of this model are as follows.

Bulk Model. Bulk effects are taken into account using the hybrid quantum mechanics/molecular mechanics (QM/MM) approach called surface integrated molecular orbital/molecular mechanics (SIMOMM).¹⁵ This method, implemented in the quantum chemistry package GAMESS¹⁶ (General and Atomic Molecular Electronic Structure System), employs MM3¹⁷ parameters in the Tinker program.¹⁸ Tinker is linked to GAMESS to perform the MM portion of the calculation. The interface between the QM and MM regions is handled by terminating the severed Si—Si bonds with hydrogens as link atoms. The bulk model includes 333 atoms, comprising five layers of silicon. The surface includes 18 dimers, being 3 dimer rows wide by 6 dimers long (Figure 3).

Ab Initio Region. The atomic basis set employs a mixture of all electron and effective core potential (ECP) basis functions. Each silicon atom has the Hay-Wadt¹⁹ ECP supplemented with the d function from the 6-31G(d) basis set,²⁰ giving each silicon a double- ζ plus polarization basis in the valence. Carbons and hydrogens have the 6-31G(d)²¹ all-electron basis set. This basis set will henceforth be referred to as Mixed HW(d),6-31G(d).

It has been established that the bare Si(100)-(2 × 1) surface has considerable multireference character and therefore should be studied using a multireference method.^{6,7} Often, when the surface has been saturated with adsorbates, it acquires more

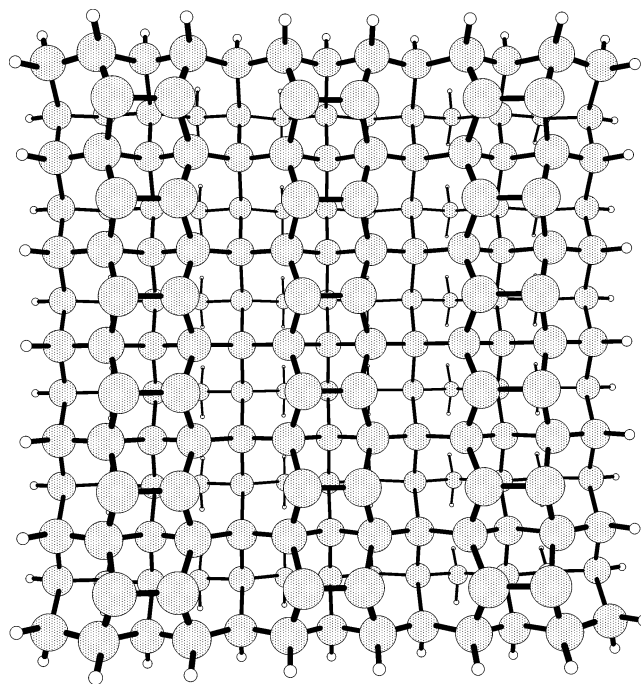


Figure 3. Bulk model.

single reference character.²² This is not surprising, since the unpaired electrons (or dangling bonds) from which the multi-reference character arises have bonded with the substrate on the surface. Thus, when beginning a study of the acetylene on Si(100)-(2 × 1) system, it is necessary to determine the extent to which multireference wave functions are a necessary zeroth-order description.

Preliminary fully optimized reaction space (FORS)-MCSCF calculations revealed natural orbital occupation numbers (NOONs) for some isomers that deviate significantly from the Hartree–Fock values of 2.0 and 0.0 for occupied and virtual orbitals, respectively. As expected, the most significant deviation occurs when the surface dimers are not fully saturated. Although some isomers, particularly the tetracoordinated species, are well-described by single-reference wave functions, our intention to study a significant portion of the surface in a continuous manner precludes any possibility of using single reference methods to study some isomers and multireference methods for others.

Due to these considerations, the QM region is represented by a FORS-MCSCF²³ wave function with an eight electrons in eight orbitals active space. Active orbitals include both π bonds on acetylene, the π bond on each Si—Si dimer, and the four corresponding antibonds (see Figure 4).

Geometry Optimizations. Geometries are fully optimized in both the QM and MM regions.¹⁵ Minima and transition states are characterized by the calculation and diagonalization of the energy second derivative matrix (Hessian). A positive definite Hessian indicates that a local minimum has been found, and one negative eigenvalue indicates that the stationary point is a transition state (first-order saddle point). No higher order saddle points were encountered in this study.

Minimum energy paths²⁴ are performed to connect minima and transition states, using the second-order Gonzalez–Schlegel (GS2) method,²⁵ employing a step size of 0.15 (amu)^{1/2}·bohr.

Multireference second-order perturbation theory²⁶ (MRMP2) calculations are performed at all stationary points to provide accurate relative energies and reaction barriers.

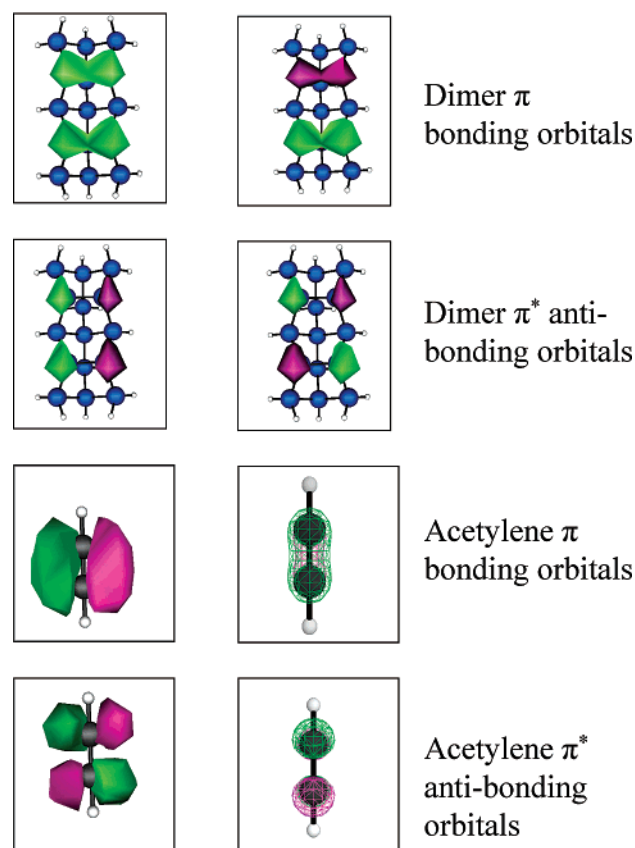


Figure 4. Active space.

III. Ground-State Potential Energy Surface

To include all surface minima that may be relevant to the interpretation of experimental data on the acetylene on Si(100)-(2 \times 1) surface, five minima have been examined, the di- σ (also called on-top dimerized), endbridge, pbridge, rbridge, and cross configurations (see Figure 1). Other possible adsorption configurations are not included, since previous studies have suggested that they are much higher in energy.¹⁰

A. Relative Energies and Adsorption Energies. The energies discussed in this section have been obtained at the MRMP2//FORS(8,8)/Mixed HW(d),6-31G(d) level of theory. Adsorption energies are defined as $E_{\text{ads}} = E(\text{surface+acetylene}) - E(\text{complex})$. $E(\text{surface+acetylene})$ is obtained by doing a calculation on the supermolecule, consisting of the surface and acetylene separated by >100 Å at their optimized geometries. $E(\text{complex})$ is the MRMP2 energy of the isomer in question. Thus, although MRMP2 is not size extensive, in this study, the size consistency errors²⁷ have been corrected for. At the FORS level, the NOONs are exactly the same for the separated species and for the supermolecule. The energies are the same to 10⁻⁵ hartree. Thus, the FORS part of the calculation is size consistent, as expected for fully variational methods.

The adsorption energies presented in this study are all positive and indicate stable structures (see Table 1). In the di- σ , endbridge, and cross species, the acetylene is dicoordinated, while the acetylene is tetracoordinated in the rbridge and pbridge species. The di- σ (dimerized) species is the most stable configuration for one acetylene molecule on the Si(100)-(2 \times 1) surface (see Table 2), with an adsorption energy of 51.2 kcal mol⁻¹. The endbridge is a very low energy isomer, only 4.5 kcal mol⁻¹ less stable than the di- σ species. The cross species is quite high in energy, 40.6 kcal mol⁻¹ above di- σ . The energy

TABLE 1: Adsorption Energies (kcal mol⁻¹)

isomer	MRMP/FORS(8,8)	DFT ^a
di- σ	51.2	62.2
endbridge	46.7	60.1
pbridge	11.2	30
rbridge	20.8	49.3
cross ^b	10.6	38.1 ^b

^a DFT adsorption energies are taken from Sorescu and Jordan, ref 5, at a coverage of 0.25 monolayers, except. ^b Cross for which the 0.5 ML coverage adsorption energy is used, because that for 0.25 ML is not available.

TABLE 2: Relative Energies (kcal mol⁻¹) for MRMP/Mixed//FORS(8,8)/Mixed

minima		transition states	
di- σ	0.0	di- σ to pbridge	59.2
endbridge	4.5	endbridge to rbridge	35.5
pbridge	40.4	pbridge to cross	52.9
rbridge	30.3	cross to rbridge	39.2
cross	40.6		

of pbridge relative to the di- σ isomer is 40.4 kcal mol⁻¹, while that of rbridge is 30.3 kcal mol⁻¹.

B. Local Minima. *Di- σ .* In the di- σ configuration the acetylene is situated directly above a silicon dimer. Each carbon is σ bonded to the corresponding silicon of the surface dimer. In the adsorbed acetylene unit, there is double bonding between the carbons and a bond length of 1.36 Å, just slightly longer than the ethylene carbon-carbon bond length, 1.33 Å. Because the acetylene is directly above the dimer, there is no strain between dimers in the row. Comparing the geometric parameters of the clean surface with those of the di- σ configuration, it is clear that there is very little perturbation of the remainder of the surface by the acetylene molecule. The interdimer distances are virtually identical, 3.84 Å in the bare surface and 3.83 Å in di- σ . Similarly, the unsaturated silicon-silicon dimer bond distances are 2.25 Å in both the clean surface and the di- σ structure. There is only a slight elongation of the Si-Si bond distance in the saturated dimer relative to the unsaturated dimer, 2.32 Å and 2.25 Å, respectively. Some elongation is expected, since the dimer partial π bond has been broken. Examining the NOONs (see Figure 5b) it is easy to see that there is very little interaction between the dimers in the same row. The π and π^* orbitals on the unsaturated dimer and their NOONs are almost identical to those on the clean surface (Figure 5a). This implies that there would be little advantage to adsorbing two acetylenes on adjacent dimers in the dimerized di- σ configuration relative to acetylenes being on dimers separated by a great distance. Adjacent dimers can be considered to be essentially noninteracting,⁷ and placing an acetylene on one of these dimers does not change that situation.

Endbridge. In the endbridge isomer (see Figure 1), the acetylene is again dicoordinated, but now it is bridging two adjacent dimers, perpendicular to the dimer row. This leaves one silicon unsaturated on each dimer. This configuration is essentially a pure singlet diradical (see Figure 5c), with HOMO and LUMO NOONs of 1.05 and 0.95, respectively. This isomer is therefore the most multireferential of all isomers studied. Relative to the clean surface, in the endbridge species the intradimer Si-Si distance is lengthened by 0.12 Å (2.37 Å vs 2.25 Å). The angle between the Si-C bond and the dimer bond ($\angle\text{C-Si-Si}$) is 113°, 23° off normal. Each dimer partial π bond has been broken, and in addition, the unpaired electrons on the unsaturated surface silicon and the π electrons on the acetylene are expected to repel each other. The interdimer Si-Si distances are shortened by 0.51 and 0.21 Å for the saturated and

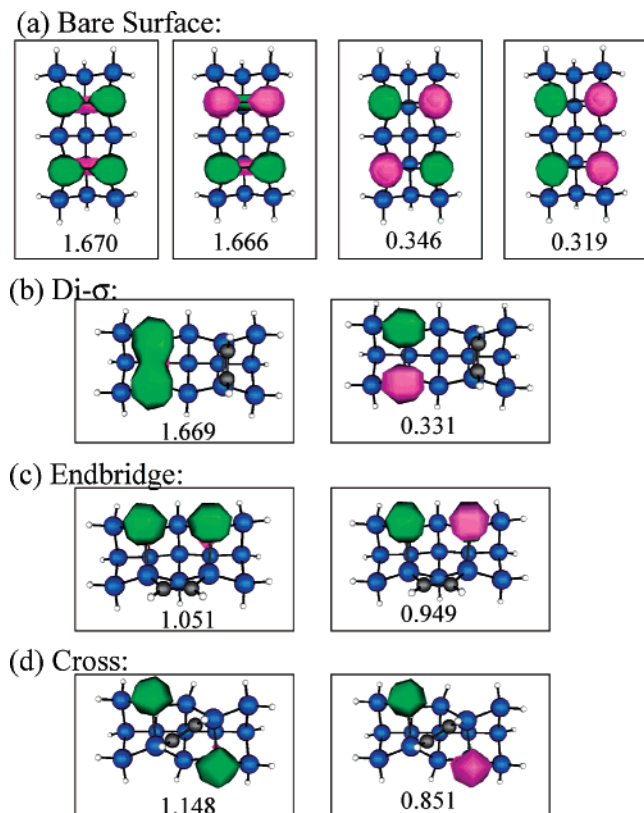


Figure 5. Orbitals.

unsaturated silicons, respectively (3.33 Å and 3.63 vs 3.84 Å), having been pulled together due to the adsorption of the acetylene group directly above. The saturated distance undergoes a larger change, since these silicons are directly attached to the acetylene carbons.

Although the endbridge isomer is only slightly higher in energy than the di- σ species, the impact on the surface is quite different. As discussed above, in the di- σ isomer the addition of an acetylene molecule perturbs the rest of the surface very little, while the endbridge isomer has a significant effect on the geometry of the surface. Since the endbridge isomer is only slightly higher in energy than the di- σ isomer, the favorable interaction of the acetylene with the surface must nearly cancel the effect of disrupting the structure of the surface.

Cross. In the cross configuration (Figure 1, 5d) the acetylene is again dicoordinated; however, the acetylene bridges opposite silicons in two adjacent dimers. This is an intermediate structure along the pathway that rotates the acetylene from the rbridge to the pbridge configuration (see following section). The cross isomer is also highly multiconfigurational, with NOONs of 1.148 and 0.851 for the HOMO and LUMO orbitals (Figure 5d). Each dimer bond in this isomer is lengthened by 0.08 Å from 2.25 Å in the clean surface to 2.33 Å. Because the acetylene bonds across two dimers, it pulls in the two adjacent dimers to give a shortened interdimer Si–Si distance of 3.56 Å, 0.28 Å shorter than the clean surface distance of 3.84 Å. The orbitals and C–C bond length of 1.37 Å indicate the presence of a C–C double bond. The C–Si bonds are single bonds, with bond lengths of 1.98 Å.

Rbridge and Pbridge. The rbridge and pbridge isomers each contain a tetracoordinated acetylene molecule, with the acetylene perpendicular and parallel to the silicon dimer bond, respectively. These are both higher energy isomers, due in part to the strain caused by coordinating to all four silicon atoms of the two dimers. The dimer–dimer distance is significantly reduced

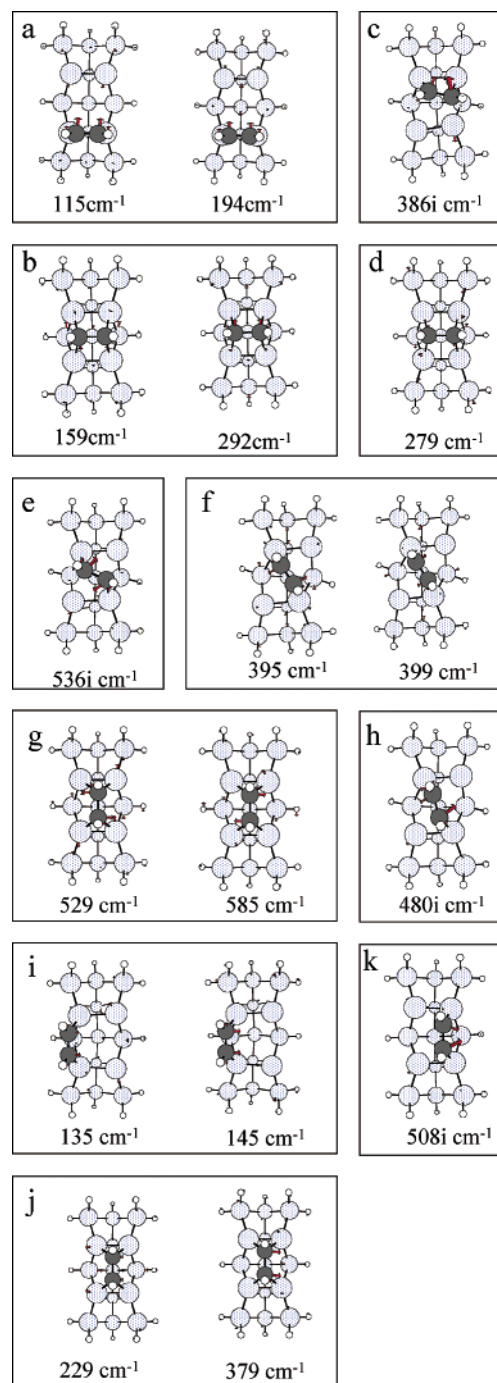


Figure 6. Normal modes.

in both the rbridge and pbridge isomers. The Si–Si distance between two dimers in the same row is 3.84 Å on the bare surface, while for rbridge and pbridge it is 3.37 and 3.01 Å, respectively, a significant perturbation.

C. Pathways Connecting Isomers. Now, consider the pathways by which the acetylene can move from one configuration to another on the surface. In the following discussion, the vibrational frequencies that are quoted should be used as a qualitative guide to the motions that occur in the cluster. Due to the large number of atoms present and the significant amount of coupling between modes, there can be significant delocalization of the normal modes throughout the molecule. See Table S1 in Supporting Information for a selection of important vibrational frequencies. Schematics of the transition state structures are given in Figure 1.

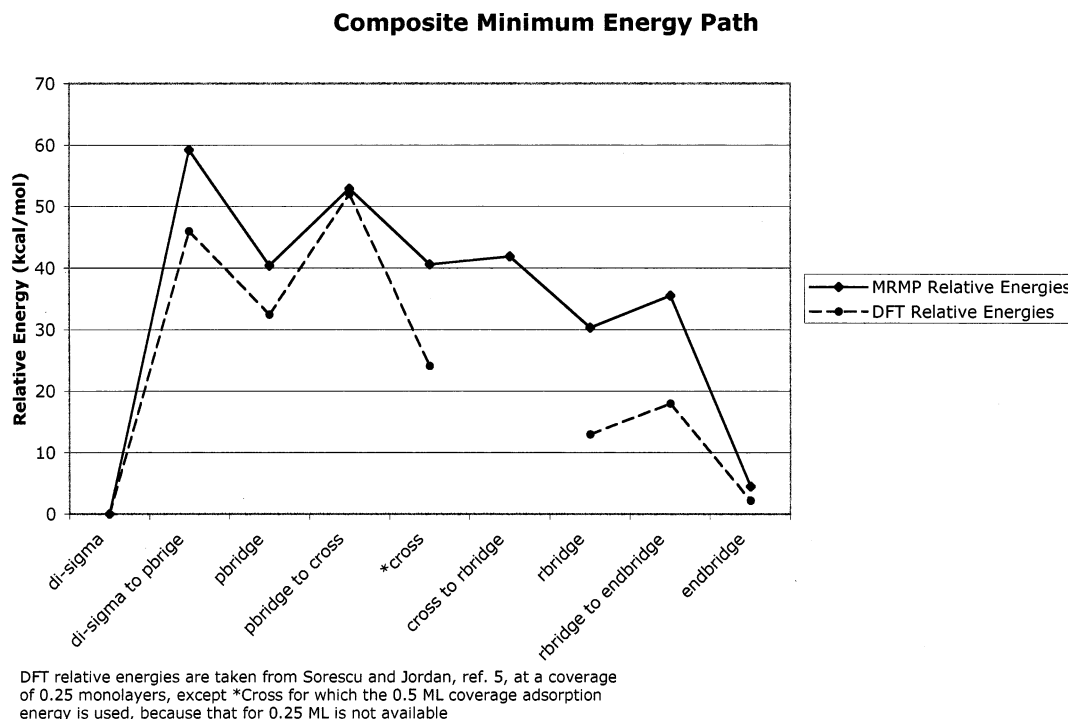


Figure 7. Composite minimum energy path.

Di- σ to Pbridge. In the di- σ to pbridge reaction path, the acetylene is moving parallel to the dimer row, from being dicoordinated with one dimer to being tetracoordinated with two dimers in the same dimer row. The vibrational frequencies of the di- σ normal modes (Figure 6a) that correspond to this motion from di- σ to pbridge are 115 and 194 cm^{-1} . Starting from the other end, the analogous pbridge frequencies (Figure 6b) that lead from pbridge to di- σ are 159 and 292 cm^{-1} . The forward barrier for the process is 59.2 $\text{kcal}\cdot\text{mol}^{-1}$, while the reverse barrier is 18.8 $\text{kcal}\cdot\text{mol}^{-1}$. The imaginary mode corresponding to the motion toward minima on the potential energy surface has a vibrational frequency of 386.0i cm^{-1} (Figure 6c).

Pbridge to Cross to Rbridge. In addition to moving along the dimer row, the acetylene can also rotate with respect to the dimer rows. It is this motion that connects the pbridge, cross, and rbridge configurations. The path from pbridge to rbridge will take the acetylene through a rotation of a full 90° in a plane roughly parallel to the plane of the surface. The acetylene begins parallel to the surface dimers and ends perpendicular to the dimers. The forward barrier going from pbridge to cross is 12.5 $\text{kcal}\cdot\text{mol}^{-1}$, while the reverse barrier is 12.3 $\text{kcal}\cdot\text{mol}^{-1}$. The vibrational frequency of the normal mode (Figure 6d) at the pbridge minimum geometry corresponding to this motion is 279.7 cm^{-1} . The normal mode (Figure 6e) at the transition state corresponding to motion toward reactants has a frequency of 535.8i cm^{-1} . At the cross species the twisting motion is spread over two normal modes (Figure 6f) with frequencies of 395 and 399 cm^{-1} .

Completing the rotation, the acetylene goes from the cross intermediate through a second transition state to rbridge. The normal modes corresponding to rotation of the acetylene parallel to the surface in rbridge, going back to cross, a range from 433.2 to 584.4 cm^{-1} (Figure 6g). The cross to rbridge pathway has a 15.7 $\text{kcal}\cdot\text{mol}^{-1}$ barrier in the forward direction and an 18.2 $\text{kcal}\cdot\text{mol}^{-1}$ barrier in the reverse direction at the FORS(8,8) level. At the MRMP2 level, however, the forward barrier nearly goes to zero. Single-point MRMP2 calculations were done at several points along the FORS(8,8) reaction path to locate the

upper limit to the energy of the transition state. These single point calculations reveal an upper limit to the forward barrier of 1.3 $\text{kcal}\cdot\text{mol}^{-1}$ and to the reverse barrier of 11.6 $\text{kcal}\cdot\text{mol}^{-1}$. The normal mode corresponding to motion toward the minima is at 480.35i cm^{-1} (Figure 6h).

Rbridge to Endbridge. The motion from rbridge to endbridge involves the acetylene moving perpendicular to the dimer row from a position in which it is coordinated to each of the four silicons in two dimers in the same row to one in which it is coordinated to one silicon per dimer, on the same side of the dimer row. The barrier in the forward direction is 5.2 $\text{kcal}\cdot\text{mol}^{-1}$, while in the reverse direction, going from the more stable endbridge isomer to the rbridge, it is 31.1 $\text{kcal}\cdot\text{mol}^{-1}$. The main endbridge vibrational frequencies going toward rbridge are 134.6 and 145.0 cm^{-1} (Figure 6i). The rbridge vibrational frequencies corresponding to motion toward endbridge are 229.0 and 378.8 cm^{-1} (Figure 6j). The imaginary normal mode corresponding to motion toward reactants is 508.10 cm^{-1} (Figure 6k).

D. Comparison with Density Functional Theory Calculations. Now compare the MRMP2/FORS(8,8)/Mixed HW(d),6-31G(d) results with previous (spin polarized) density functional theory (DFT) results obtained by Sorescu and Jordan,¹⁰ employing the PW91 functional, plane wave basis sets, and slab models (including eight Si atoms per layer, allowing a $c(4\times 2)$ arrangement of the dimers) with periodic boundary conditions. While the comparison is with their results at 0.25 monolayer coverage (except for cross, which is at 0.5 ML coverage), the trends hold for all low coverages in their study. Figure 7 presents a schematic of the potential energy surface with results from both studies, while the geometries are compared in Table 3. Consider, first, the two lowest energy species. Both theoretical approaches indicate that for one acetylene adsorbed on the Si(100)-(2 \times 1) surface, the di- σ species is the most stable, while the endbridge species is only slightly less stable. Relative to di- σ , the two methods give rather significant differences in the energies of some of the less stable isomers, over 17 $\text{kcal}\cdot\text{mol}^{-1}$ in some cases. While these are significant quantitative differences, it is important to note that the qualitative nature

TABLE 3: Important Geometrical Parameters—Minimum Bond Length (Å)

	bare surface	free acetylene	dimerized		endbridge		pbridge		rbridge		cross
			FORS	DFT ^a	FORS	DFT ^a	FORS	DFT ^a	FORS	DFT ^a	FORS
Si–Si unsaturated	2.25		2.25		—		—		—		
Si–Si saturated	—		2.32	2.36	2.37	2.39	2.30	2.36	2.27	2.29	2.33
						2.46		2.36		2.29	
Si–Si interdimer	—		3.83		—		—		—		3.56
Si–Si interdimer saturated	—		—		3.33		3.01		3.37		
Si–Si interdimer unsaturated	3.84		—		3.63		—		—		
C–C	—	1.21	1.36	1.35	1.36	1.36	1.60	1.56	1.57	1.51	1.37
C–Si	—		1.93	1.90	1.94	1.92	2.05	2.06	2.00	2.00	1.98
				1.92		1.92		2.06		2.01	
<hr/>											
		di→p ^b	p→cross ^b		cross→r ^b		end→r ^b				
Si1–Si2		2.31	2.32		2.27		2.27				
Si3–Si4		2.36	2.32		2.26		2.26				
interdimer Si1–Si3		3.41	3.25		3.48		3.56				
interdimer Si2–Si4		3.10	3.25		3.52		3.40				
C–C		1.49	1.47		1.44		1.47				
C–Si1		1.95	1.99		1.96		2.65				
C–Si2		2.01	2.67		2.73		1.95				
C–Si3		3.15	2.66		2.41		2.35				
C–Si4		2.28	1.99		1.97		1.95				

^a DFT geometries are taken from Sorescu and Jordan.⁵ ^b Transition states: di→p, di-σ to pbridge; p→cross, pbridge to cross; cross→r, cross to rbridge; end→r, endbridge to rbridge.

of the surface is the same in both studies. Except for the two highest energy isomers, pbridge and cross, the energetic ordering of the isomers is the same in both studies.

IV. Conclusions

The multireference results presented here predict that the lowest energy arrangement for acetylene adsorbed on the Si(100)-(2×1) surface is the di-σ on-top dimerized configuration. The endbridge arrangement is only slightly higher in energy than the di-σ species.

The calculations in this study confirm that when studying the Si(100)-(2×1) surface the PES will be quite multiconfigurational where there are unsaturated dimers present, but when dimers are fully saturated, there is generally just one important configuration. In the latter cases, single-configuration methods are likely to be reliable.

Comparing the spin-polarized DFT and MRMP2 results for this system, the same trends are predicted. Both studies agree that the di-σ arrangement is the global minimum for adsorption of acetylene on the surface at low coverage. While DFT and MCSCF predict buckled and symmetric dimers, respectively, for the clean surface, the geometries of the saturated species in this study are quite similar for both methods. However, as discussed above, this system has a significant amount of multireference character. The parametrization of DFT makes difficult a detailed analysis of the origin of the differences in results that do exist. Because there are regions of the PES that are so clearly multireference, it is our assertion that when discrepancies occur between DFT and MRMP2, the MRMP2 results should be considered more reliable. It is likely that spin-restricted (e.g., RHF-like) DFT calculations on this system would be in much worse agreement with the multireference results.

The evidence in this paper does not support the theory that one of the tetracoordinated sites is more accessible and traps an acetylene there, but it also does not definitively rule it out. Both tetracoordinated species involve a significant perturbation of the surface structure and the formation of four bonds to the surface. Forming the pbridge structure must involve pulling the dimers 0.83 Å closer together than in the clean surface; forming

rbridge pulls them 0.47 Å closer than the clean surface. Without mapping out a pathway by which an acetylene reaches each of these sites, it is not possible to quantitatively describe how easy or difficult to access they are. Their structure indicates that they are not likely to be easy to access. In addition to those considerations, neither of these minima is trapped by large barriers from getting to a lower energy species. Pbridge must get over a maximum barrier of 12.3 kcal·mol⁻¹ to get to a lower energy species and eventually to endbridge. Rbridge is separated from endbridge by a barrier of only 5.2 kcal mol⁻¹. Only at very low temperatures would those barriers be sufficient to trap an acetylene in a tetracoordinated minimum.

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Supporting Information Available: Table containing the vibrations and frequencies of acetylene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Qin, D.; Xia, Y. N.; Rogers, J. A.; Jackman, R. J.; Zhao, X. M.; Whitesides, G. M. *Microsystem Technol. Chem. Life Sci.* **1998**, *194*, 1. Maboudian, R. *Surf. Sci. Rep.* **1998**, *30* (6–8), 209. Howe, R. T. *Journal Vac. Sci. Technol. B* **1988**, *6* (6), 1809.
- (2) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N. *Acc. Chem. Res.* **2000**, *33* (9), 617. Bent, S. F. *J. Phys. Chem. B* **2002**, *106* (11), 2830.
- (3) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.
- (4) Hamers, R. J.; Wang, Y. J. *Chem. Rev.* **1996**, *96* (4), 1261.
- (5) Gordon, M. S.; Shoemaker, J. R.; Burggraf, L. W. *J. Chem. Phys.* **2000**, *113* (20), 9355. Redondo, A.; Goddard, W. A. *J. Vac. Sci. Technol.* **1982**, *21* (2), 344.
- (6) Shoemaker, J.; Burggraf, L. W.; Gordon, M. S. *J. Chem. Phys.* **2000**, *112* (6), 2994.
- (7) Jung, Y.; Akinaga, Y.; Jordan, K. D.; Gordon, M. S. *Theoret. Chem. Acc.* **2003**, *109* (5), 268.
- (8) Huang, C.; Widdra, W.; Wang, X. S.; Weinberg, W. H. *J. Vac. Sci. Technol. A* **1993**, *11* (4), 2250. Taylor, P. A.; Wallace, R. M.; Cheng,

- C. C.; Weinberg, W. H.; Dresser, M. J.; Choyke, W. J.; Yates, J. T. *J. Am. Chem. Soc.* **1992**, *114* (17), 6754.
- (9) Nishijima, M.; Yoshinobu, J.; Tsuda, H.; Onchi, M. *Surf. Sci.* **1987**, *192* (2–3), 383.
- (10) Sorescu, D. C.; Jordan, K. D. *J. Phys. Chem. B* **2000**, *104*(34), 8259.
- (11) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, *117*(14), 4082.
- (12) Imamura, Y.; Morikawa, Y.; Yamasaki, T.; Nakatsuji, H. *Surf. Sci.* **1995**, *341* (3), L1091.
- (13) Xu, S. H.; Keeffe, M.; Yang, Y.; Chen, C.; Yu, M.; Lapeyre, G. J.; Rotenberg, E.; Denlinger, J.; Yates, J. T. *Phys. Rev. Lett.* **2000**, *84* (5), 939. Mezheny, S.; Lyubnitsky, I.; Choyke, W. J.; Wolkow, R. A.; Yates, J. T. *Chem. Phys. Lett.* **2001**, *344* (1–2), 7. Li, L.; Tindall, C.; Takaoka, O.; Hasegawa, Y.; Sakurai, T. *Phys. Rev. B* **1997**, *56* (8), 4648.
- (14) Wang, F.; Sorescu, D. C.; Jordan, K. D. *J. Phys. Chem. B* **2002**, *106* (6), 1316.
- (15) Shoemaker, J. R.; Burggraf, L. W.; Gordon, M. S. *J. Phys. Chem. A* **1999**, *103* (17), 3245.
- (16) Fletcher, G. D.; Schmidt, M. W.; Bode, B. M.; Gordon, M. S. *Comput. Phys. Commun.* **2000**, *128* (1–2), 190. Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S. *Adv. Chem. Phys.* **1999**, *110*, 267. Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14* (11), 1347.
- (17) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111* (23), 8566. Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111* (23), 8576. Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Am. Chem. Soc.* **1989**, *111* (23), 8551.
- (18) Kundrot, C. E.; Ponder, J. W.; Richards, F. M. *J. Comput. Chem.* **1991**, *12*, 402. Ponder, J. W.; Richards, F. M. *J. Comput. Chem.* **1987**, *8*, 1016.
- (19) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82* (1), 284.
- (20) Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213.
- (21) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- (22) Jung, Y. S.; Choi, C. H.; Gordon, M. S. *J. Phys. Chem. B* **2001**, *105* (18), 4039.
- (23) Ruedenberg, K.; Schmidt, M. W.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71* (1), 41. Ruedenberg, K.; Sundberg, K. R. In *Quantum Science*; Calais, J.-L., Goscinski, O., Linderberg, J., Eds.; Plenum: New York, 1976; pp 505. Cheung, L. M.; Sundberg, K. R.; Ruedenberg, K. *Int. J. Quantum Chem.* **1979**, *16* (5), 1103.
- (24) Truhlar, D. G.; Gordon, M. S. *Science* **1990**, *249* (4968), 491.
- (25) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90* (4), 2154.
- (26) Nakano, H. *J. Chem. Phys.* **1993**, *99* (10), 7983.
- (27) Calculations were one to probe the deviation of MRMP2 from size consistency for this system. The following size consistency errors were determined. $E(\text{surface}) + E(\text{acetylene}) - E(\text{surface+acetylene}) = 21.9 \text{ kcal mol}^{-1}$; $E(\text{surface}) + 2E(\text{acetylene}) - E(\text{surface+2acetylene}) = 49.1 \text{ kcal mol}^{-1}$; $2E(\text{acetylene}) - E(2\text{acetylene}) = 2.2 \text{ kcal mol}^{-1}$. This issue will be addressed more fully by examining a representative set of molecules in a later paper.