Adsorption of Water on the Si(100) Surface: An Ab Initio and QM/MM Cluster Study†

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Adsorption of Water on the Si(100) Surface: An Ab Initio and QM/MM Cluster Study[†]

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The adsorption of water on the Si(100) surface is investigated using ab initio quantum chemical cluster calculations. A reaction profile is constructed using the multiconfigurational SCF method. The calculations demonstrate that the reactant should be described with a multireference wave function in order to obtain correct energetics, because it contains a bare dimer with significant diradical character. The system becomes almost single-configurational as water approaches the surface and forms a molecularly adsorbed intermediate. Therefore, except for the reactant, a single-configurational wave function seems to be sufficient for a correct description of the reaction. The adsorbed OH group in an *isolated* product can nearly freely rotate between the trans and gauche minima. Interactions between the OH groups and the dangling bonds are small and do not appear to change the OH orientation. However, the interdimer hydrogen bonding is stronger and forces the OH orientation to be perpendicular to the dimer bond. The free rotation of the OH group in an *isolated* dimer model and the hydrogen-bonding picture in an extended cluster model are consistent with the experimental finding for the OH orientation in the product. Si_9H_{12}, $Si_{15}H_{16}$, $Si_{32}H_{28}$, $Si_{48}H_{36}$, and $Si_{64}H_{44}$ cluster models for the Si(100) surface are used, and the SIMOMM (surface integrated molecular orbital molecular mechanics) method is used effectively for these large cluster calculations. The SIMOMM and full quantum results are compared.

Introduction

Adsorption of water on the Si(100)−(2 × 1) surface has been studied extensively[1−5] because of its potential for applications to industry, such as the growth of SiO_2 films by wet oxidation. Even though there has in the past been some controversy[5,6] concerning whether water adsorbs molecularly or dissociatively on the Si(100) surface, dissociative adsorption now seems to be generally accepted as the most likely adsorption mechanism.[3,7,8] A recent theoretical study by Cho et al.,[9] using the generalized gradient approximation (GGA) density functional theory (DFT) method and a slab model, is in agreement with this dissociative adsorption mechanism.

Besides the adsorption mechanism itself, structures of the products and interaction patterns among the products have also been of interest. ESDIAD studies[10,11] and theoretical calculations[8,9] suggest that OH groups are oriented normal to the silicon dimer bond. In their theoretical study, Konecny and Doren[8] used DFT cluster calculations to suggest that either hydrogen bonding between adjacent hydroxyls or dative-bond-type interactions between an oxygen lone pair or hydroxyl hydrogen on one dimer and a dangling bond on an adjacent dimer in the same row is responsible for the orientation of the OH groups. Gurevich et al.[7] investigated these interaction patterns and the structures of the products using broadband infrared spectroscopy in combination with DFT cluster calculations. They concluded that "the water-exposed Si(100)−(2 × 1) surface is comprised of a mixture of single dimers with *isolated* hydroxyl groups and *paired* dimers that are coupled by hydrogen bonding between OH groups on neighboring dimers in the same row of the reconstructed 2 × 1 surface."

However, more recently Cho et al.[9] proposed that, although such hydrogen bonding or dative-bond-type interactions may

have a "profound" effect on the mechanism, the orientation of OH is 'insensitive' to such interactions by showing theoretically that the coverage of the surface with water has only a small effect on the Si−Si−O−H dihedral angle. Thus, there is some disagreement regarding the impact of hydrogen bonding or dative-bond-type interactions on the OH orientation, and it is one of the purposes of this work to investigate and hopefully provide some insight regarding this question.

The uppermost layer of the Si(100) surface is composed of dimers which have significant diradical character.[12−14] This makes the surface very reactive. Redondo and Goddard[15] first demonstrated that a silicon surface with singlet diradical dimers can be correctly described only with a multireference wave function. Many other papers[16−19] agreed with this notion, and more recently, Paulus[20] and Shoemaker et al.[21] confirmed it again. Because the reactants of water/Si(100) also contain the bare surface, a multireference wave function is also required for a correct description of the adsorption reaction. In addition, because the adsorption reaction involves bond dissociation and formation, it is important to determine whether key regions of the potential energy surface are single-configurational or multi-configurational in nature.

In this work, the potential energy surface is constructed using multireference wave functions to determine whether the system is single-configurational or multiconfigurational, by comparing the results with the results based on a single-configurational wave function in terms of energetics and structural parameters. The structures of the products and the interactions among the products are considered in detail. The OH orientation with respect to the silicon dimer is discussed in relation to the interactions among the products. The results obtained from those calculations are compared with the experimental findings.

Recently, a new embedded cluster model, the surface integrated molecular orbital molecular mechanics (SIMOMM) method, has been developed for the study of surfaces.[22]

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TABLE 1: Relative Energies of the Structures along the Minimum Reaction Path

	reactant	intermediate	TS	product
Full QM (Si$_9$H$_{12}$/H$_2$O)				
RHF/HW(d)	35.5	0	6.9	−63.7
MP2//RHF/HW(d)	33.0	0	2.4	−52.5
GVB-PP(1)/HW(d)	22.1	0	6.2	−65.7
MCQDPT2//TCSCF/HW(d)	27.0	0	3.0	−53.6
RHF/MIXED[a]	14.5	0	13.1	−66.3
MP2//RHF/MIXED[a]	12.7	0	5.6	−54.2
GVB-PP(1)/MIXED[a]	1.3	0	12.3	−68.0
MCQDPT2//TCSCF/MIXED[a]	6.9	0	6.4	−55.0
RHF/DZV(d)	15.2	0	15.9	−60.4
MP2//RHF/DZV(d)	10.2	0	7.4	−49.0
GVB-PP(1)/DZV(d)	2.5	0	14.7	−62.7
MCQDPT2//TCSCF/DZV(d)	5.8	0	8.4	−49.9
RHF/6-31++G(d,p)	13.4	0	15.2	−58.2
MP2//RHF/6-31++G(d,p)	8.2	0	7.2	−46.5
GVB-PP(1)/6-31++G(d,p)	0.9	0	14.0	−60.2
MCQDPT2//TCSCF/6-31++G(d,p)	4.3	0	8.5	−46.8
SIMOMM (Si$_9$H$_{12}$/H$_2$O)				
RHF/HW(d)	32.4	0	7.1	−65.6
MP2//RHF/HW(d)	31.0	0	2.3	−55.6
GVB-PP(1)/HW(d)	17.9	0	6.5	−67.4
MCQDPT2//TCSCF/HW(d)	24.1	0	3.1	−55.9
RHF/MIXED[a]	11.5	0	13.2	−68.5
MP2//RHF/MIXED[a]	10.9	0	5.6	−57.7
GVB-PP(1)/MIXED[a]	1.9	0	12.7	−69.8
MCQDPT2/TCSCF/MIXED[a]	4.2	0	6.6	−57.7
DFT[b]				
B3LYP/6-31++G(d,p)	14.1	0	7.0	−44.4
B3LYP/6-311G(d,p)	12.9	0	1.6	−49.9
B3LYP/6-311++G(2df,2p)	7.2	0	1.1	−51.8

[a] Mixed basis set: HW(d) for Si and 6-31G(d) for H and O.
[b] Previous DFT study by Konecny et al. (ref 8).

SIMOMM can save considerable computational effort by representing many of the atoms with inexpensive MM potentials, while maintaining the quality of results. SIMOMM is also tested in this work for the water/Si(100) system, via a comparison with the full quantum mechanical results.

Computational Details

The GAMESS electronic structure program was used for all calculations reported here. Recently, Shoemaker et al.[21] investigated basis set effects for surface clusters and concluded that the Hay−Wadt effective core potential (ECP) with its associated double-ζ plus polarization valence basis set is a viable method for investigating the properties of large clusters. In this work, the Hay−Wadt ECP plus polarization function basis set was used. This HW(d) basis set consists of double-ζ plus d polarization for the valence electrons and ECPs for the core electrons for Si. The 6-31G(d) basis[23] was employed for O and H. To assess the reliability of this mixed basis set, we also used two different all-electron basis sets, DZV(d), consisting of the Dunning-Hay[24] double-ζ valence basis set plus d polarization functions, and 6-31++G(d,p). Results obtained with the 6-31++G(d,p) basis set are directly compared to those of the previous DFT/B3LYP/6-31++G(d,p) study in Table 1.

Because the reactant includes the bare surface with dangling bonds, the generalized valence bond (GVB) or two configuration SCF (TCSCF) method was employed. Because the natural orbital analysis revealed that the occupation number for the virtual orbital in the active space was small ($\leq$0.04) except for the reactant (see below), Hartree−Fock (HF) wave functions were used for the rest of the calculations (except for direct comparisons with reactant), particularly for the study of product structures. However, clusters containing a bare surface were always treated with the GVB wave functions.
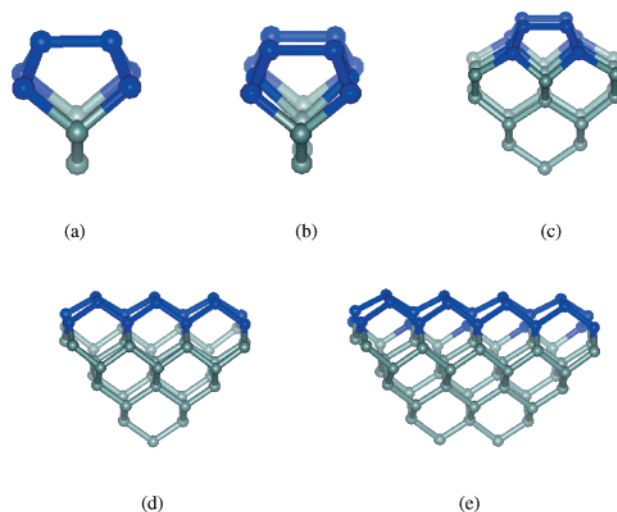

Figure 1. Cluster models used in this study: (a) Si$_9$H$_{12}$, (b) Si$_{15}$H$_{16}$, (c) Si$_{32}$H$_{28}$, (d) Si$_{48}$H$_{36}$, and (e) Si$_{64}$H$_{44}$. The blue atoms are treated quantum mechanically and the light ones molecular mechanically.

For the minimum energy reaction path, all stationary points were identified as minima or transition states by computing and diagonalizing the Hessian matrix. A first-order saddle point (transition state) was characterized by one imaginary frequency from the Hessian diagonalization and a minimum by no imaginary frequency. The intrinsic reaction coordinate (IRC), using the Gonzalez−Schlegel second-order method,[25] was used to connect the minimum energy reaction path with a step size of 0.30 amu$^{1/2}$ bohr. To recover the dynamic electron correlation, the energies at all stationary points at the RHF level of theory were recalculated with the Møller−Plesset second-order perturbation method,[26] denoted MP2//RHF. Similarly, multireference second-order perturbation theory was used to augment the TCSCF multireference wave functions. The MCQDPT2 method (multiconfigurational quasi-degenerate second-order perturbation theory)[27] was used in the present work. The notation MCQDPT2//TCSCF means that a single point energy correction was performed with the MCQDPT2 method at a TCSCF (equivalent to GVB-PP(1)) optimized geometry.

Si$_9$H$_{12}$, Si$_{15}$H$_{16}$, Si$_{32}$H$_{28}$, Si$_{48}$H$_{36}$, and Si$_{64}$H$_{44}$ cluster models (Figure 1) for the Si(100) surface were employed in this work. For the dissociative adsorption mechanism, a Si$_9$H$_{12}$/H$_2$O cluster model was used, and SIMOMM and full quantum results were compared. For the study of the interaction patterns and the structures of the product, Si$_9$H$_{12}$/H$_2$O, Si$_{32}$H$_{28}$/H$_2$O, Si$_{15}$H$_{16}$/2H$_2$O, Si$_{32}$H$_{28}$/2H$_2$O, Si$_{48}$H$_{36}$/3H$_2$O, and Si$_{64}$H$_{44}$/4H$_2$O SIMOMM models were used. The waters are always treated with ab initio wave functions.

Results and Discussion

A. Adsorption Mechanism of H$_2$O within the Single-Dimer Cluster Model. The potential energy surface for the dissociative adsorption of water on the Si(100) surface, on the basis of the Si$_9$H$_{12}$ cluster model, is depicted in Figure 2. Water adsorbs dissociatively on the Si(100) surface with a small *net* reaction barrier. Table 1 summarizes the relative energies along the minimum energy path.

First consider basis set effects on the energetics in Table 1. There are large differences between HW(d) and all electron relative energies, whereas the two all-electron basis sets, DZV(d) and 6-31++G(d,p), give very similar results to each other. However, the mixed basis set improves the results significantly, with relative energies that are nearly the same as those obtained

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TABLE 2: Important Structural Parameters along the Minimum Reaction Path

	Si−Si at reactant	Si−O at intermediate	Si−Si−O−H at TS	Si−O at product	Si−Si−O−H at product
			Full QM		
RHF/HW(d)	2.151	1.864	180.0	1.651 (1.651)	179.0 (59.1)
GVB-PP(1)/HW(d)	2.241	1.867	180.0	1.651 (1.651)	179.9 (60.2)
RHF/MIXED[a]	2.151	1.959	126.7	1.652 (1.652)	179.9 (60.5)
GVB-PP(1)/MIXED[a]	2.241	1.972	125.5	1.652 (1.652)	179.0 (60.8)
RHF/DZV(d)	2.185	1.975	137.9	1.659 (1.659)	179.9 (59.8)
GVB-PP(1)/DZV(d)	2.278	1.984	135.0	1.659 (1.659)	179.4 (60.3)
RHF/6-31++G(d,p)	2.189	1.993	135.9	1.670 (1.670)	179.9 (59.9)
GVB-PP(1)/6-31++G(d,p)	2.278	2.003	133.1	1.671 (1.670)	178.2 (61.7)
			SIMOMM		
RHF/HW(d)	2.154	1.863	180.0	1.651 (1.651)	179.7 (57.0)
GVB-PP(1)/HW(d)	2.243	1.869	180.0	1.651 (1.651)	180.0 (57.3)
RHF/MIXED[a]	2.154	1.964	126.0	1.653 (1.653)	179.9 (57.2)
GVB-PP(1)/MIXED[a]	2.243	1.993	124.5	1.653 (1.653)	178.4 (58.5)
			DFT[b]		
BLYP/TZ94P	2.227	2.231	59.0	1.757	62.2

[a] Mixed basis set: HW(d) for Si and 6-31G(d) for H and O. [b] Previous DFT study by Konecny et al. (ref 8).
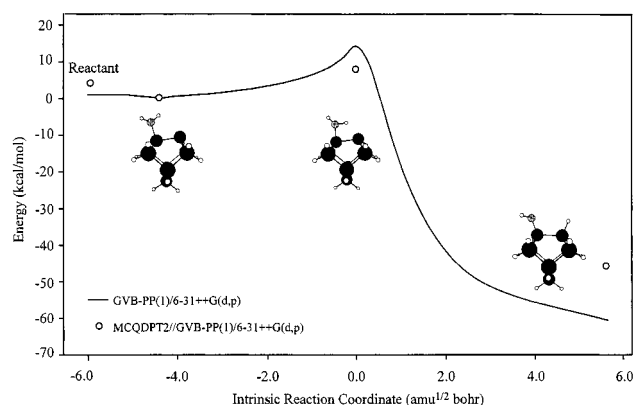

Figure 2. Potential energy surface for the dissociative adsorption of water on the Si(100) surface. IRC calculations connect the intermediate, the transition state, and the product. The data point at the reactant is from geometry optimization.

with the all-electron basis sets. These results suggest that HW-(d) is a reliable and effective basis set for the silicon surface itself, whereas a better basis set is necessary for the lighter elements.

As can be seen in Table 1, except for the reactant, single configuration (i.e., RHF and MP2) energetics are in excellent agreement with the multireference (i.e., GVB and MCQDPT2) results for the same basis sets and analogous levels of theory. RHF structural parameters (Table 2) are also in nearly perfect agreement with the GVB-PP(1) structural parameters except for the reactant. The same calculations were performed with the same cluster model (Si_9H_{12}) using the SIMOMM method in which the water molecule and the first two top surface layers, a dimer layer and the layer directly connected to the dimer layer, were treated quantum mechanically and the rest of the cluster was treated classically. In Figure 1, the blue atoms were treated with quantum mechanics and the light ones with molecular mechanics. The full QM and SIMOMM methods with the Si_9H_{12} cluster model give almost the same results, for the same basis sets, wave functions (RHF or GVB-PP(1)), and levels of theory.

The only significant differences between GVB-PP(1) and RHF results occur in the reactant. Because the reactant includes the bare surface with significant diradical character, it is natural that a difference between the single-configurational and multiconfigurational methods exists for this structure. Because RHF gives essentially the same results as GVB-PP(1) along the

TABLE 3: Natural Orbital Occupation Numbers at Critical Points along the Minimum Reaction Path

		reactant	intermed	TS	product
		Full QM			
GVB-PP(1)/HW(d)	bonding	1.63	1.96	1.96	1.98
	antibonding	0.37	0.04	0.04	0.02
GVB-PP(1)/DZV(d)	bonding	1.68	1.96	1.96	1.98
	antibonding	0.32	0.04	0.04	0.02
		SIMOMM			
GVB-PP(1)/HW(d)	bonding	1.68	1.96	1.96	1.98
	antibonding	0.32	0.04	0.04	0.02

reaction path, except for the reactant, in terms of the energetics and the structural parameters, it appears that the whole reaction path except the reactant can be described by single-configurational wave functions. We conclude from these calculations that the bare surface loses its singlet diradical character as water approaches the surface and that the system becomes single-configurational when water undergoes weak molecular adsorption onto the surface.

Natural orbital occupation numbers from the GVB-PP(1) calculation at each critical point are listed in Table 3. Occupation numbers for the antibonding LUMO orbital at all stationary points except the reactant are very small. So the contribution of this virtual orbital is not important at these points. Again, this suggests that the system is single-configurational. It is therefore likely that a GVB-PP(1) wave function is sufficient for the exploration of the entire reaction path and that a RHF-based wave function is sufficient if one is interested only in the intermediate, the transition state, and the product.

The energetics in Table 1 also show that MCQDPT2//GVB-PP(1) results are in reasonably good agreement with those of previous DFT studies[8,9] with the same basis set except for the reactant. The only significant difference is the extent to which the intermediate is stabilized relative to the reactant. The difference is considered to be due to the inadequate treatment of the diradical character in the reactant by the DFT method. This also impacts the predicted sign of the overall reaction barrier. The MCQDTP2//GVB-PP(1) energetics predict a *net* reaction barrier of ∼4 kcal/mol with the 6-31++G(d,p) basis, whereas DFT predicts no *net* reaction barrier. In any event, the small overall reaction barrier implies that water can be adsorbed on the Si(100) surface fairly easily, even with small thermal fluctuations. This is consistent with the experimental observation of the high sticking coefficient for the adsorption reaction.[1]

TABLE 4: Rotational Barrier for the Isomerization and the Buckling Angle in an *Isolated* Product[a]

		E_b (kcal/mol)	ΔE (kcal/mol)	Si−Si−O−H (deg)	buckling angle (deg)
		Single-Dimer Cluster			
Full QM (Si$_9$H$_{12}$/H$_2$O)	MP2//RHF/HW(d)	0.6	−0.3	59.1, 179.0	
	MP2//RHF/DZV(d)	0.5	−0.4	59.8, 179.9	
DFT (Si$_9$H$_{12}$/H$_2$O)[b]	BLYP/TZ94P			62.2	
		Two-Dimer Cluster			
SIMOMM (Si$_{32}$H$_{28}$/H$_2$O)	MCQDPT2//GVB-PP(1)/HW(d)	0.2	−1.6	57.7, 176.7	no buckling, no buckling
		0.4	−1.3	−57.1, −177.0	no buckling, no buckling
	MCQDPT2//GVB-PP(1)/DZV(d)	0.6	−1.0	56.4, 178.0	no buckling, no buckling
		0.8	−0.9	−56.2, −178.0	no buckling, no buckling
DFT (Si$_{15}$H$_{16}$/H$_2$O)[b]	BLYP/TZ94P			84.5	12.7, no buckling
				−81.8	11.4, no buckling

[a] ΔE is the energy difference and E_b is the rotational barrier for the isomerization reaction from the trans to the Gauche form. [b] Previous DFT study by Konecny et al. (ref 8).

The previous DFT study predicted a transition state with the OH group pointing gauche (~60°) with respect to the silicon dimer. However, in the present calculations, all trial geometries for the gauche (~60°) transition state converged to the gauche′ (~130°) form, even though product structures with the OH oriented gauche (~60°) as well as trans (~180°) with respect to the silicon dimer were found. Therefore, the isomerization reaction between the trans (~180°) and gauche (~60°) product structures was explored. A Si$_9$H$_{12}$ full QM cluster study (Table 4) shows that the thermodynamic stability for the product is nearly independent of the rotation angle and the reaction barrier for the isomerization is very small. This implies free rotation of the OH group on the surface. The experimentally determined orientation of OH is perpendicular to the silicon dimer, neither gauche nor trans. So if the OH group rotates freely, then the experimentally measured value would be the average of the two theoretically possible structures.

It is also possible that the potential energy surface bifurcates at the transition state to produce both trans (~180°) and gauche (~60°) products from one gauche′ (~130°) transition state. If the PES bifurcates, this bifurcation would very likely be coupled to free rotation of the OH group.

A more detailed discussion about the OH orientation and the isomerization of the product is given in the next section.

B. OH Orientation and Interaction Patterns among the Products. Next consider the interaction patterns among the products and the effect of these interactions on the OH orientation using extended cluster models. These discussions are based on SIMOMM RHF calculations because, as discussed in the previous section, SIMOMM is very reliable for this system and the RHF level of theory is also sufficient for a correct description of the product. However the cluster models including the bare surface dimer were treated with the GVB-PP(1) wave function. Second-order perturbation theory single-point energy calculations, MP2//RHF or MCQDPT2//TCSCF, were performed at the RHF or GVB geometries for more accurate energetics.

To investigate the interactions between the hydroxyl hydrogen or oxygen lone pair and silicon dangling bonds, the Si$_{32}$H$_{28}$ two-dimer cluster model ((c) in Figure 1) was employed. One side of the two-dimer model is saturated with OH and H groups, and the other is exposed as a bare surface (dangling bonds). Because of the dangling bonds on the one side, the GVB-PP(1) wave function was used.

In Table 4, we compare the torsion angle of the OH group, the buckling angle, and the rotational barrier between the gauche and trans forms. Increasing the cluster size from the single dimer to the two-dimer cluster model does not have any effect on the

TABLE 5: Selected Geometric Parameters in the Hydrogen-Bonding Picture (Figure 3)[a]

	(H)O···H(O) (Å)	(H)O···H(O) RHF bond order	Si−Si−O−H (deg)
(a) Si$_{15}$H$_{16}$/2H$_2$O	1.90 (2.18)	0.10 (0.06)	83.9 (85.6)
			68.0 (69.0)
(b) Si$_{32}$H$_{28}$/2H$_2$O	1.96 (2.30)	0.09 (0.05)	83.0 (84.8)
			68.8 (70.7)
(c) Si$_{48}$H$_{36}$/3H$_2$O	2.08 (2.48)	0.08 (<0.05)	84.1 (83.7)
	3.04 (3.25)		80.4 (81.8)
			66.8 (67.6)
(d) Si$_{64}$H$_{44}$/4H$_2$O	1.97 (2.34)	0.09 (<0.05)	83.2 (84.8)
	3.93 (3.83)		73.2 (76.7)
	1.99 (2.39)	0.09 (<0.05)	83.9 (86.1)
			68.9 (70.1)
(e) Si$_{32}$H$_{28}$/2H$_2$O[b]	2.32 (2.91)[b]	< 0.05 (<0.05)[b]	82.5 (80.5)[b]
			63.8 (63.6)[b]

[a] Values are from MP2/HW(d) optimized structures, those in parentheses are from RHF/HW(d) geometries. [b] DZV(d) basis set is used.

torsion angle of the OH group with respect to the silicon dimer. The buckling angles for both dimers in the two-dimer model are also still approximately zero, suggesting that the dangling bonds and the OH group do not interact strongly, whereas the previous DFT study[8] predicted more than 10° of buckling for one dimer and zero for the other. In addition, there is no significant change in the rotational barrier from the gauche to the trans form. If there was significant attractive interaction between the OH group and the dangling bonds, one would expect an increase in the potential barrier for the rotation. Therefore, it is concluded that the dangling bonds do not interact with the OH group and do not change the orientation of the OH group. These results are probably due to the long distance between the two dimers in the reconstructed Si(100)−(2 × 1) surface. In contrast, in the previous study,[8] the OH orientation increased from 56° to 84°, apparently as a result of dative-bond-type interactions with the increase of cluster size.

To examine hydrogen-bonding patterns for the hydrolyzed Si(100) surface, SIMOMM calculations were performed with two-, three-, and four-dimer cluster models (c−e in Figure 1), with all the dangling bonds saturated with OH and H. Table 5 summarizes hydrogen-bond distances and Si−Si−O−H torsion angles. The electron correlated method, MP2/HW(d), produces shorter hydrogen-bond distances between (O)H and O(H) than the HF method. Consequently, the O··H bond orders at the MP2 geometries are larger. This suggests that electron correlation effects play an important role in hydrogen-bond formation. To examine the basis set effect on the hydrogen-bonding patterns, the DZV(d) basis set was employed for the Si$_{32}$H$_{28}$/2H$_2$O cluster model. This better basis set produces a somewhat weaker

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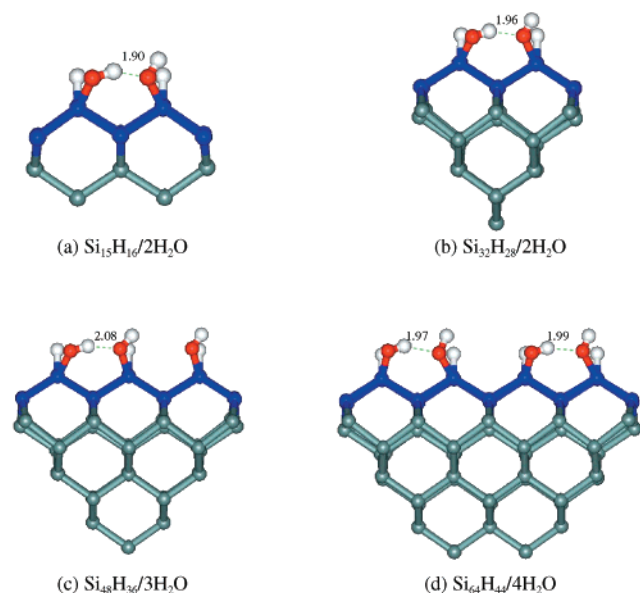*J. Phys. Chem. B, Vol. 105, No. 18, 2001* **4043**

Figure 3. Hydrogen-bonding patterns among the adsorption products. The silicon atoms, in blue, and the OH and H fragments from the water molecule are treated with quantum mechanics and the others with molecular mechanics.

hydrogen bond (2.32 Å O··H) than that of the HW(d) basis (1.96 Å O··H). It is likely the larger basis set will also result in slightly weaker hydrogen bonds in the three- and four-dimer cluster models. The comparison of MP2/DZV(d) and RHF/DZV(d) optimized hydrogen-bond distances also indicates that the MP2 method predicts stronger hydrogen bonds.

MP2/HW(d) optimized structures showing hydrogen-bonding patterns are depicted in Figure 3. As noted earlier, in an *isolated* dimer product (single dimer model), the free rotation between gauche (60°) and trans (180°) forms of the product or the bifurcation of the potential energy surface would lead to a rotation angle similar to that of the experimentally determined OH orientation with respect to the silicon dimer (∼90°). However, if the dimer adjacent to this *isolated* product is also saturated with OH and H, then free rotation is no longer possible, and the trans form is no longer a local minimum. Now, the minimum energy structure is the one in which two adjacent hydroxyls form a hydrogen bond (Figure 3). Because of the formation of hydrogen bonds, the OH orientation with respect to the Si dimer converges to about 85°, not the gauche (60°) or trans (180°) angles found in *isolated* products. Thus, when OH and H saturate the surface there is apparently only one structure, in which OH is oriented normal to the silicon dimer bond because of hydrogen-bond formation. Still, in this hydrogen-bonding picture, dimer buckling is not observed. This agrees with the previous DFT study.[8]

In their IR study, Gurevich et al.[7] proposed that hydroxyl-mediated interdimer coupling does not extend to the second adjacent dimer (no consecutive hydrogen bonds in the same row) on the basis of the fact that there was no further shift of the OH stretch frequency as the coverage was increased. As can be seen in Figure 3, our calculations also show that hydrogen bonding occurs only within the adjacent hydroxyls and does not propagate further. This appears to be due to the long distance between two adjacent dimers in the same row. Because of the long distance, in order to form a hydrogen bond, one OH group is tilted forward and the other OH is tilted backward, and this pattern makes the extension of hydrogen bonding difficult.

Conclusions

Adsorption of water on the Si(100) surface was studied by fully quantum mechanical calculations and the hybrid QM/MM SIMOMM method. A comparison of full QM calculations and SIMOMM calculations shows that the computationally efficient SIMOMM method gives reasonable results. It is shown that an all-electron basis set is required for the water molecule, whereas an ECP basis augmented with polarization functions is sufficient and effective for the surface itself. Therefore, it is proposed that the mixed basis set, consisting of an all-electron basis for the target molecule and ECP plus polarization function basis for the silicon surface itself, can be used effectively for the study of various chemical reactions on the Si(100) surface.[28]

The potential energy surface for the adsorption of water on Si(100), modeled with the Si_9H_{12} cluster, was constructed. Because the reactant has significant singlet diradical character, multireference wave functions were used for the correct description of the entire potential energy surface. Calculations with GVB-PP(1)/6-31++G(d,p) followed by MCQDPT2//TCSCF/6-31++G(d,p) energy correction reveal that there is a *net* reaction barrier of ∼4 kcal/mol. This small reaction barrier is consistent with the experimentally determined high sticking coefficient. A natural orbital occupation number analysis and comparison of GVB-PP(1) results with those of RHF illustrate that the entire reaction path, except for the diradicaloid reactant, is actually single-configurational, even though the reaction involves bond dissociation and formation processes.

Two possible structures for an *isolated* product were found, having gauche or trans orientation of the OH group with respect to the silicon dimer. Both the rotational barrier and the energy difference between these two forms were calculated to be small in a single-dimer cluster model. This suggests that the experimentally determined OH orientation in an *isolated* product, normal to the dimer bond, is actually an averaged orientation of the gauche (60°) and trans (180°) forms.

Extended cluster model calculations were performed to identify the interaction patterns responsible for the OH orientation of the product with respect to the dimer bond. Calculations with *isolated* two-dimer cluster models indicate that the dangling bonds next to the dimer in the same row saturated with OH and H do not have any effect on the free rotation of the OH group and do not change the OH orientation. However, when two consecutive dimers are saturated simultaneously with OH and H, a hydrogen bond between these two OH groups is formed. Because of this hydrogen bonding, the trans minimum vanishes and the Si−Si−O−H torsion angle changes to around 85°, close to the experimental observation (∼90°). Therefore, we conclude that there is no interaction between hydroxyl groups (oxygen lone pair or the hydroxyl hydrogen) and the dangling bonds, probably because of the long distance between the two neighboring dimers and that there is a hydrogen-bonding interaction between two adjacent hydroxyl groups in the same row. The latter interaction changes the OH orientation to be nearly perpendicular to the dimer bond. This resolves the question regarding the relative importance of hydrogen bonding vs dative-bond-type interactions on the product configuration (the OH orientation with respect to the dimer bond).

The computations presented here with three- and four-dimer cluster models demonstrate that the interdimer hydrogen bonding occurs only between two adjacent dimers, as originally proposed by Gurevich et al.[7] on the basis of their experimental observation, rather than extended to the hydrogen-bonding network. Electron correlation appears to be very important for an accurate description of the hydrogen bond.

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(28) This mixed basis set, consisting of HW(d) for the surface and 6-31G(d) for cyclopentadiene, worked very well in the study of a cycloaddition reaction of cyclopentadiene on the Si(100) surface recently performed in our group. The results with the mixed basis set were in good agreement with the DZV(d) all-electron basis results.