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High exposure hydrogen chemisorption on the Si(111)7 × 7 surface: a semiempirical cluster study

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Abstract. The various equilibrium structures of the hydrogen chemisorbed Si(111)7 × 7 surface are investigated using the semiempirical molecular orbital Austin 1 calculational method (AM1). Up to five hydrogen atoms are allowed to adsorb near the corner adatom, centre adatom and restatom adsorption sites of the Si(111)7 × 7 surface. The results obtained from minimizing the energy of the system show very little difference between the chemisorption processes occurring at the two different adatom sites. In both cases, as progressively more hydrogen atoms are chemisorbed, the hydrogen bonded adatom is found to move from its original threefold (T4) site (one hydrogen atom), to an adjacent bridge site (two or three hydrogen atoms) and then on top of a neighbouring first-layer silicon atom (more than three hydrogen atoms). The lowest calculated adatom desorption energies are 1.59 and 1.62 eV, and correspond to the desorption of SiH_3 at a corner adatom and centre adatom site, respectively. In contrast to an adatom, a hydrogen bonded restatom is found to remain close to its original threefold equilibrium position. The smallest desorption energy for this site is 0.75 eV and also corresponds to an SiH_3 surface complex.

1. Introduction

Exposing silicon surfaces to hydrogen is one of the primary methods for controlling such processes as the etching, chemical activation/passivation and structural stabilization of these surfaces. Virtually all hydrogen terminated silicon surfaces are produced by exposure to atomic hydrogen because the reactivity of molecular hydrogen with silicon surfaces is very low [1, 2]. This atomic hydrogen, as suggested in many early studies [2–6], should react with the surface dangling bonds and, via the formation of covalent Si–H bonds, stabilize the surface in the monohydride phase (β_1). Although this picture is now well established for low hydrogen coverage [2, 6], it was also recognized very early on that exposure of the Si(111)7 × 7 surface to atomic hydrogen has the ability to induce major structural changes in this highly complex surface [7–12]. Recently, mainly due to intensive scanning tunnelling microscopy (STM) studies, the structure of hydrogenated silicon surfaces has been shown to be a very complex function of both exposure and adsorption temperature [2, 6]. As a result, the precise nature of the stable hydrogen monolayer phase has become a controversial issue on almost all hydrogenated silicon surfaces [2]. From the chemisorption studies of Cl_2 [13] and NH_3 [14] on the Si(111)7 × 7 surface it is evident that the different dangling bond sites on this surface (restatom, corner adatom and centre adatom) exhibit very different affinities towards the adsorbates. The aim of this paper is to account for the structural changes

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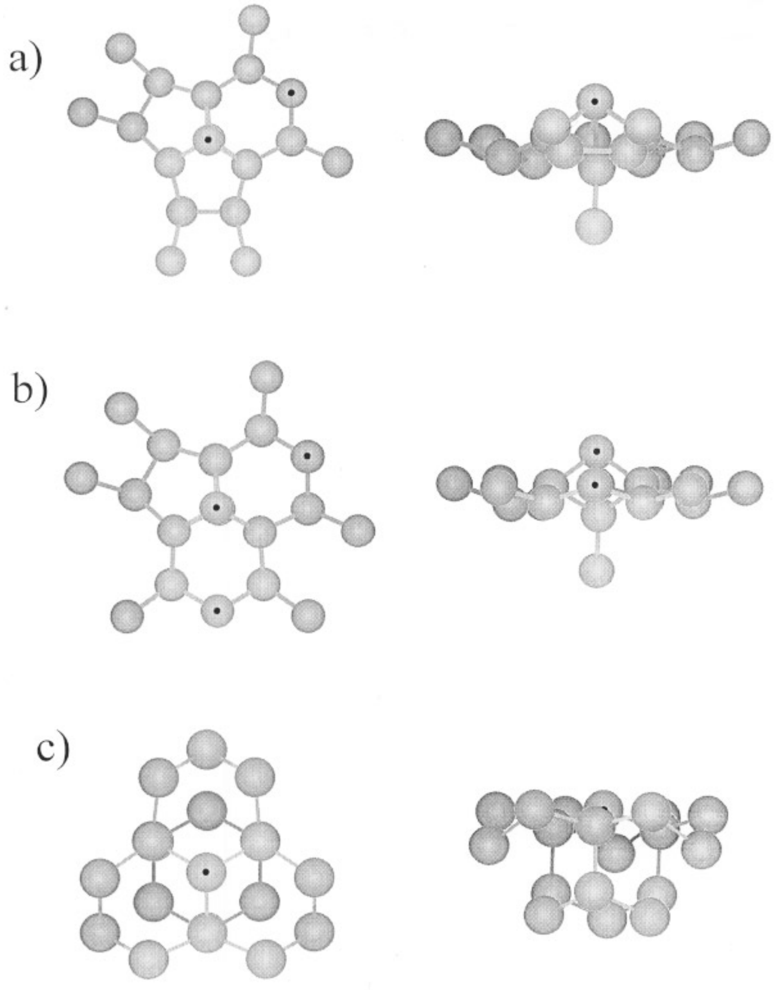

Figure 1. The various clusters employed to model the Si(111)7 × 7 reconstructed surface: (a) top and side views of the $Si_{19}H_{29}$ cluster for an adatom A site; (b) top and side views of the $Si_{20}H_{31}$ cluster for the adatom B site; (c) top and side views of the $Si_{19}H_{27}$ cluster employed to model the restatom C site. The hydrogen atoms which saturate the bulk dangling bonds have been omitted for simplicity. The adatoms and restatoms have been distinguished by a small central black dot.

observed on the hydrogenated Si(111)7 × 7 surface within the context of the local surface affinity of the 7 × 7 reconstructed surface towards hydrogen.

The centre adatoms have been shown to be the preferred adatom adsorption sites for hydrogen chemisorption onto the Si(111)7 × 7 surface at low exposure and high enough temperature [6]. At room temperature, enhanced reactivity at both the corner and centre adatoms with respect to the restatom sites has been observed [11, 12]. The Si–H bond strength in silane is 38% stronger than the Si–Si bond in silicon bulk [2]. Thus, on a silicon surface, the hydrogen atoms should break the Si–Si backbonds and form more energetically preferred Si–H bonds. Increasing hydrogen exposure at 353 K has been shown to produce both SiH_2 (β_2 phase) and SiH_3 (β_3 phase) on the Si(111)7 × 7 surface, along with a

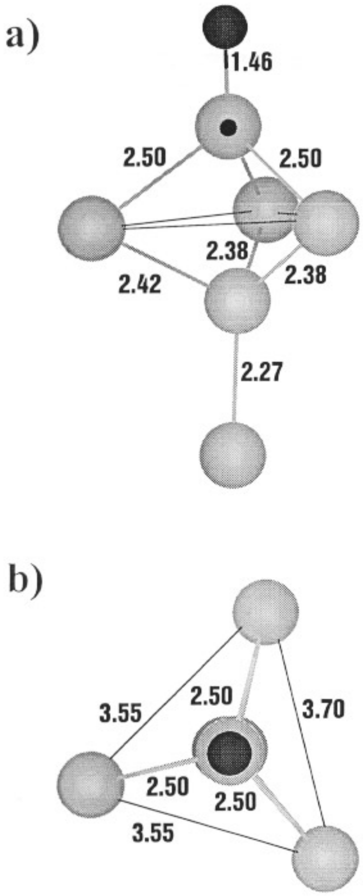

Figure 2. The optimized geometry corresponding to the chemisorption of one hydrogen atom (large black circle) onto an adatom A: (a) side view; (b) top view. All of the bondlengths in this figure, and all subsequent figures, are given in ångströms. Moreover, only the silicon and hydrogen atoms in the centre of each cluster have been drawn for the sake of clarity.

predominantly SiH (β_1 phase) restlayer [9], to give a total saturation coverage of 1.25–1.5 ML [15, 16]. Limited SiH_4 formation has been also observed [7]. In the β_1 phase, both normal and tilted Si–H bonds with respect to the surface normal have been identified [10], with the desorption of the SiH species occurring at 810 K [17, 18]. The origin of the dihydride (β_2) phase is not clear but thermal desorption peaks corresponding to SiH_2 have been observed to occur at 680 K [17, 18]. At this temperature, the SiH_3 radicals from the β_3 phase are also desorbed [17–19]. Strong evidence for the β_3 phase has been provided by ion scattering, ultraviolet photoemission experiments [20] and STM [6, 8]. It is interesting to note that, following the hydrogen adsorption/desorption processes described above, the 7 × 7 superstructure was found to remain intact. This indicates the primary role of the adatom and restatom layers in these processes. Only annealing the saturated surface, or dosing at elevated temperature, produces structural changes in the dimer layer and the observed formation of a 1 × 1 domain [21]. It is believed that this latter process is related to the insertion of isolated adatoms into the restlayer to relax the dimer bonds. This fully

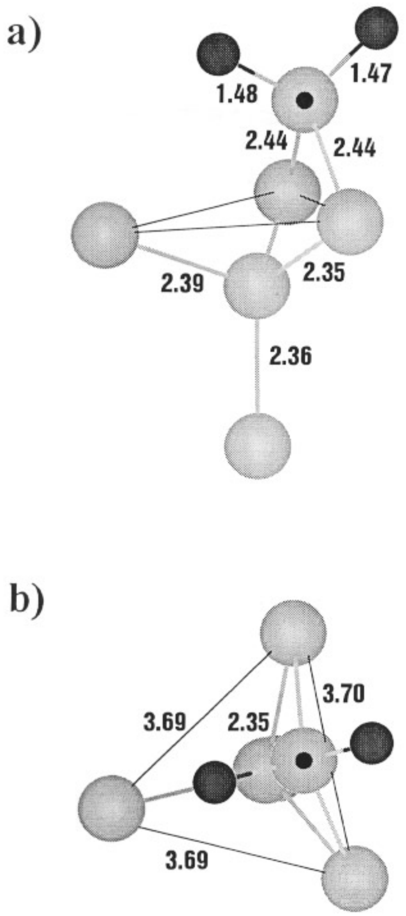

Figure 3. The minimum-energy configuration which results from the chemisorption of two hydrogen atoms near the adatom A: (a) side view; (b) top view.

relaxed surface should thus produce a hydrogen coverage of 1.16 ML [6].

Despite all of this experimental work there has been no theoretical investigation of the high-exposure atomic hydrogen interaction with the Si(111)7 × 7 surface. Most calculations of hydrogen interacting with the (111) surface of silicon have been performed for either a (1 × 1) [3, 22] or (2 × 1) surface periodicity [23–25]. Recent first-principles local density approximation (LDA) cluster calculations of single-hydrogen chemisorption at the centre adatom, corner adatom and restatom sites of the Si(111)7 × 7 surface obtained binding energy values of 3.71, 3.82 and 4.74 eV, respectively [26]. These results indicate that the reactivities of the two adatom sites are very similar. The calculated binding energy for a single hydrogen atom on a restatom site of 4.74 eV is consistent with other LDA calculations performed for hydrogen on the Si(111)1 × 1 surface (4.54 eV [22]), but is very different from the experimental value of 3.6 eV [18, 24]. The initial stages of hydrogenation of the Si(111)7 × 7 surface have also been investigated using a periodic extended Huckel method [27], but again the calculations have been restricted to just a single hydrogen atom chemisorbing at any given site.

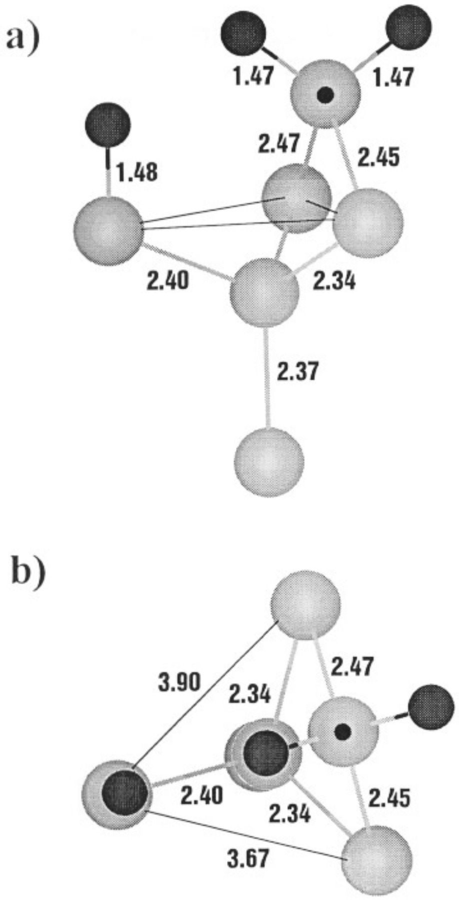

Figure 4. The SiH_2 bridging equilibrium structure which occurs when three hydrogen atoms are chemisorbed in the vicinity of an adatom A: (a) side view; (b) top view.

The aim of this paper is to report theoretical calculations of the various geometries which arise from high-hydrogen-exposure chemisorption on the Si(111)7 × 7 surface. Such calculations are difficult because of the very large 7 × 7 surface unit cell. Fortunately, hydrogen chemisorption on the Si(111)7 × 7 surface is thought to result from short-range interactions, as evidenced by the occurrence of a (7 × 1) LEED pattern [28]. We have therefore chosen to restrict our considerations in this paper to reasonably large atomic clusters which we believe will simulate reliably the various chemisorption sites on the Si(111)7 × 7 surface.

2. Method and procedure

For the Si(111)7 × 7 reconstructed surface we have used the dimer–adatom–stacking fault (DAS) model proposed by Takayanagi *et al* [29], and later confirmed by both STM [6, 30] and low-energy electron diffraction (LEED) studies [31]. According to this model, each surface unit cell is a two-layer reconstruction consisting of a pair of faulted and unfaulted triangular subunits. These subunits are bounded by rows of dimers which intersect,

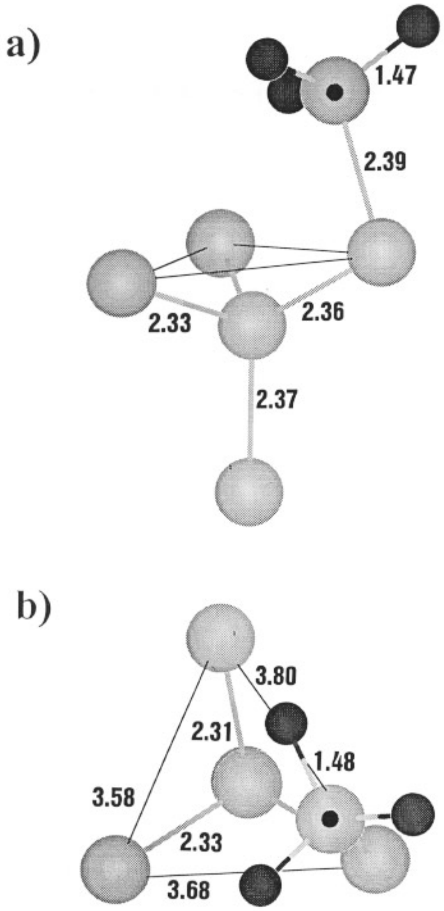

Figure 5. The SiH_3 optimized geometry corresponding to the adsorption of three hydrogen atoms near an adatom A: (a) side view; (b) top view.

producing holes at the corners of each surface unit cell. Each triangular subunit consists of an outer Si adatom layer (six atoms at T_4 positions), bonded to the so-called silicon restlayer. As a result, only three of the 21 restatoms in each triangular subunit are explicitly exposed to the vacuum.

In the DAS model, the total number of dangling bonds per 7×7 reconstructed surface unit cell is 19. This is in comparison with 49 unsaturated bonds per 7×7 unreconstructed surface unit cell for the ideal Si(111)7×7 surface. The dangling bonds of the 7×7 reconstructed surface unit cell are positioned at the 2×6 adatoms and $2 \times 3 + 1$ restatoms (including the restatom located at the bottom of the corner hole). The STM spectra [30] show that the restatom dangling bonds are doubly occupied, while the adatom dangling bonds are half filled so the Si(111)7×7 reconstructed surface is metallic.

In this study only the three most reactive adsorption sites of the Si(111)7×7 surface have been considered. These are the centre adatom, corner adatom and restatom sites. The corner adatom site (adatom A) is represented by the $Si_{19}H_{29}$ cluster shown in figure 1(a). Here the corner adatom is surrounded by one restatom, three nearest neighbours and six other first-layer silicon atoms. Two dimers are formed from the seven second-layer atoms and one of the second-layer atoms bonds to a third-layer atom directly below the adatom. For the centre adatom (hereafter referred to as adatom B), the $Si_{20}H_{31}$ cluster shown in figure 1(b) was used. This cluster contains the centre silicon adatom, its three nearest neighbours, two adjacent restatoms and six other first-layer atoms. Of the seven second-layer atoms, two form a dimer and one bonds to a third-layer atom immediately below the adatom. All of the boundary dangling bonds and restatom dangling bonds are saturated by hydrogens. The $Si_{19}H_{27}$ cluster shown in figure 1(c) was used to simulate the restatom site (restatom C). In this case, the central silicon restatom is surrounded by six other restlayer atoms and six second-layer atoms. The nearest-neighbour second-layer atoms are bonded to six atoms from the third and fourth layers.

All of the atoms in these clusters were located at their experimentally determined LEED positions [31]. The equilibrium configurations were then obtained by minimizing the total energy with respect to all of the coordinates of the chemisorbed hydrogen atoms, the adatom (or restatom) and its three nearest neighbours. For the adatom clusters, the second-layer silicon atom lying directly below the adatom T_4 site was also allowed to vary. This optimization of the geometry was performed using the Berny optimization method [32] contained within the AM1 component of the GAUSSIAN94 code [33]. The AM1 method, which was originally formulated by Dewar *et al* [34], is a fairly sophisticated self-consistent, semiempirical molecular orbital method. In this approximation, the energy of the system is represented as the sum of an electronic contribution due to electron delocalization and the repulsive interatomic interaction. While existing parametrizations of these terms in other semiempirical methods such as MINDO or MNDO reproduce correctly the homoatomic bonds and energies, the modification and reparametrization of the core repulsion function in AM1 improves significantly the description of the bonding and energetics arising from the heteratomic interactions and has been shown to provide a good description of many different systems [35–37].

To ensure that the calculated equilibrium structures were true global minima, rather than local minima, several different starting geometries were employed for each configuration. One of the main advantages in using a semi-empirical method is the ability to perform an adequate search of coordinate space. The actual geometries which are presented in this paper are, unless stated otherwise, the minimum energy structures which have been determined in each case.

In order to calculate the etching energy for a given $Si(A)H_x$ complex, both the energies of the original geometry-optimized chemisorbed system, and that corresponding to the $Si(A)H_x$ complex sufficiently removed from the remaining substrate for their effective interaction to be negligibly small, are calculated. The difference between these two energy values gives the binding energy of the $Si(A)H_x$ complex to the substrate, and hence the net amount of energy required to remove this species from the surface. This binding energy is thus referred to as the etching energy.

3. Results

3.1. Clean Si(111)7 × 7 surface

As a reference point for studying the interaction of hydrogen with the Si(111)7 × 7 surface, we have first calculated the binding energies for an adatom A, adatom B and restatom C on this reconstructed surface using the clusters shown in figure 1. Compared to the results of Tong *et al* [31], an adatom A and adatom B is found to move up by 0.166 Å and 0.232 Å respectively, while a restatom moves up by only 0.001 Å. The corresponding binding energies were determined to be 5.60 eV (adatom A), 5.70 eV (adatom B) and 7.57 eV (restatom C). These results are in reasonably good agreement with the values of 6.34 and 8.46 eV which have been obtained for the adatom and restatom binding energies on the Si(111)7×7 surface from Hartree–Fock cluster calculations using the 6-31G*(3df, 2p) basis set and including correlation effects via the BECKE3LYP option within GAUSSIAN94 [38]. Our AM1 restatom binding energy value of 7.57 eV is also in excellent agreement with the measured value for the binding energy of a silicon atom on the ideal Si(111) surface of 7.80 eV [39].

3.2. One to five hydrogen atoms chemisorbed near an adatom A

3.2.1. Single-hydrogen-atom chemisorption. To obtain the structure appropriate to a single hydrogen atom chemisorbed at an adatom A site, we have minimized the total energy of the $Si_{19}H_{29}H$ cluster with respect to the x, y and z coordinates of the chemisorbed hydrogen, the adatom A, its three nearest-neighbour silicon atoms and the silicon atom lying immediately below the adatom in the second layer. The minimum-energy configuration corresponds to the hydrogen atom sitting almost directly above the threefold adatom site with an Si–H bondlength of 1.46 Å, as shown in figure 2. The adatom has moved downwards by 0.03 Å compared to its clean surface equilibrium position. The H atom has gained 0.03 e from the substrate (as determined by a Mulliken population analysis) and has an adsorption energy of 2.58 eV (see table 1). The calculated Si–H bondlength is in reasonable agreement with the value of 1.50 Å obtained from *ab initio* HF–DFT calculations [40]. The binding energy values for a single hydrogen atom at an adatom A site derived using the LDA [26] and *ab initio* HF–DFT [40] methods are, however, considerably higher at 3.82 and 3.45 eV, respectively. The binding energy of the SiH complex for this adatom A site is determined to be 3.95 eV. The etching energy for a single adatom A on the clean Si(111)7×7 reconstructed surface has been determined to be 5.60 eV, as indicated above. It is thus clear that the chemisorption of a single hydrogen atom greatly reduces the bond strength between an adatom A and its underlying substrate.

3.2.2. Two-hydrogen-atom chemisorption. When a second hydrogen atom is chemisorbed near an adatom A site, the adatom is found to move from its original threefold position to an adjacent bridge site between two of its nearest-neighbour first-layer silicon atoms to form an approximately tetrahedral structure, as shown in figure 3. The Si–H bondlengths are 1.47 Å and 1.48 Å, while the Si(A)–Si backbond lengths are about 4% longer than the bulk nearest-neighbour distance of 2.35 Å. The two hydrogen atoms gain 0.16 e from the nearby silicon atoms. The binding energy of the $Si(A)H_2$ configuration on the substrate is calculated to be 3.22 eV, while the total chemisorption energy for the two hydrogens is 5.13 eV.

3.2.3. Three-hydrogen-atom chemisorption. Chemisorbing a third hydrogen atom near an adatom A site results in the two structures shown in figures 4 and 5. In the former case, the additional hydrogen atom has simply saturated the dangling bond on the unbonded nearest-neighbour silicon atom whilst, in figure 5, one of the Si(A)–Si backbonds has been broken to yield an essentially tetrahedral SiH_3 configuration. Of these two structures, the fully saturated SiH_2–SiH configuration of figure 4 is the more stable by 2.33 eV. The etching energy of the SiH_2 complex for this minimum-energy bridge site structure is 5.18 eV, almost 2.0 eV greater than for the two-hydrogen configuration of figure 3.

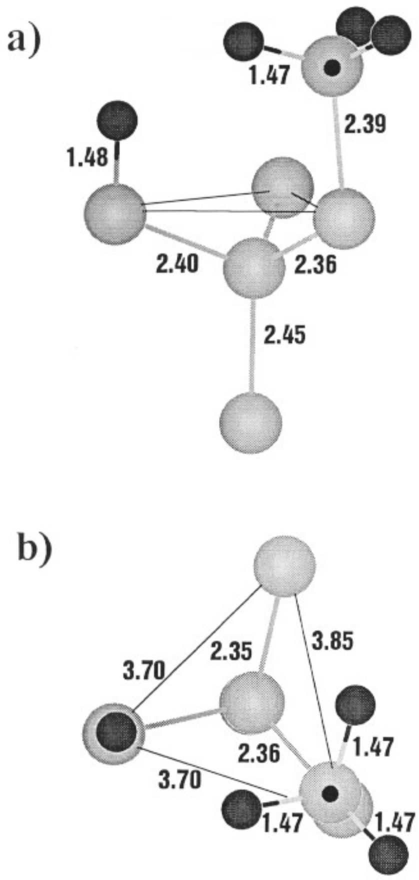

Figure 6. The SiH_3 minimum-energy structure for four hydrogen atoms chemisorbed adjacent to an adatom A: (a) side view; (b) top view.

3.2.4. Four-hydrogen-atom chemisorption. Adsorbing four hydrogen atoms in the vicinity of the adatom site of the $Si_{19}H_{29}$ cluster gave rise to the two structures in figures 6 and 7. Both of these structures have one unsaturated bond. They are thus very similar in energy, with the SiH_3 configuration of figure 6 being more stable by just 0.15 eV. The binding energy of the SiH_3 complex for this preferred structure is 3.77 eV. The Si–H bondlengths are all approximately 1.47 Å and the Si(A)–Si backbond is only 0.04 Å longer than the silicon bulk nearest-neighbour distance of 2.35 Å.

3.2.5. Five-hydrogen-atom chemisorption. Adding a fifth hydrogen atom near the adatom A site results in the saturation of the single dangling bond of the four-hydrogen chemisorbed adatom topologies and produces the equilibrium structure shown in figure 8. This structure is virtually identical to that of figure 6, apart from the additional Si–H bond. Not surprisingly, this fully saturated, and almost completely undistorted, structure showed no inclination to form SiH_4. The energy required to desorb the $Si(A)H_3$ from this structure is only 1.59 eV, 2.18 eV less than the corresponding value for the SiH_3 complex of figure 6. The total charge transferred to the adatom bonded hydrogen atoms from the surrounding

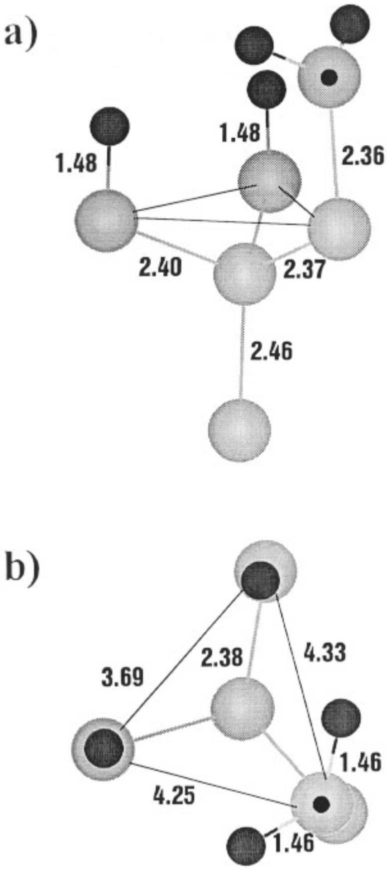

Figure 7. The SiH_2 equilibrium topology for four hydrogen chemisorption near an adatom A site: (a) side view; (b) top view.

silicon atoms is predicted to be 0.44 e.

Permutations of the different complexes, such as having the $Si(A)H_2$ configuration of figure 3 bridging across a five-membered ring rather than a six-membered ring, were also considered. In each case, the energy difference was found to be less than 0.03 eV.

3.3. Chemisorption of one to five hydrogen atoms near an adatom B

The behaviour of an adatom at a B site is very similar to that of an adatom at an A site with respect to hydrogen chemisorption. For both sites, we have found that, as successively more hydrogen is chemisorbed in the vicinity of an adatom, it will move from its original clean surface threefold site (one hydrogen atom), to an adjacent bridge site between two of its first-layer nearest-neighbour silicon atoms (two and three hydrogen atoms) and then to an on-top site above one of these adjacent silicon atoms (more than three hydrogen atoms).

The main results for the chemisorption of one to five hydrogen atoms at both A and B adatom sites are given in table 1. These results include the etching energies for the various SiH_x complexes ($1 \leqslant x \leqslant 3$), E_e, the total chemisorption energies for the adsorption of n hydrogens ($1 \leqslant n \leqslant 5$), E_b, and the net electron transfer to the chemisorbed hydrogen

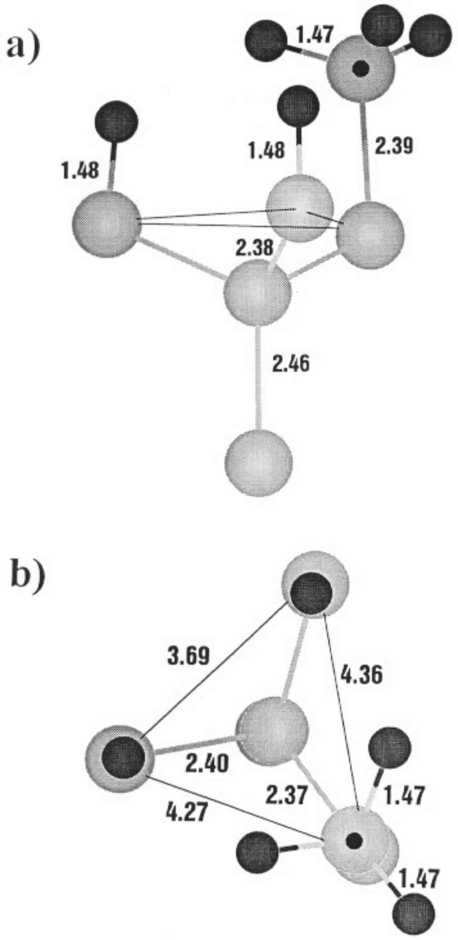

Figure 8. The optimized geometry corresponding to the chemisorption of five hydrogen atoms adjacent to an adatom A site: (a) side view; (b) top view.

atoms, e_t. Not surprisingly, both E_b and e_t increase with increasing n. The minimum binding energies of 1.59 eV and 1.62 eV correspond to the desorption of SiH_3 from the adatom A and adatom B sites, respectively. The most stable complex is SiH_2 for the three-hydrogen bridge site configuration at both adatom sites.

3.4. Chemisorption of one to five hydrogen atoms near a restatom C

3.4.1. Single-hydrogen-atom chemisorption. When a single hydrogen atom is chemisorbed near a restatom C site, and the geometry optimized with respect to the x, y and z coordinates of the hydrogen, the restatom and its three nearest neighbours, the hydrogen is found to sit directly above the restatom at its threefold site, as shown in figure 9. The Si(C)–H distance is 1.48 Å and the restatom lies 0.13 Å above its clean surface equilibrium position. All of the Si(C)–Si backbonds are within 1% of the bulk nearest-neighbour distance of 2.35 Å. The adsorption energy of the hydrogen on the atop site of a restatom C is 2.85 eV and the charge transferred to the hydrogen from the substrate, as determined by Mulliken population

Table 1. The bonding site and etching energy, E_c, for the appropriate SiH_x, the total binding energy, E_b, and the net electronic charge transferred from the substrate, e_t, for n hydrogen atoms ($0 \leqslant n \leqslant 5$) chemisorbed onto the adatom A, adatom B and restatom C sites.

Bonding site		$n = 0$	$n = 1$ ($x = 1$)	$n = 2$ ($x = 2$)	$n = 3$ ($x = 3$)	$n = 4$ ($x = 3$)	$n = 5$ ($x = 3$)
E_e (eV)	A	5.60	3.95	3.22	5.18	3.77	1.59
	B	5.70	4.11	3.34	5.30	3.83	1.62
	C	7.57	6.17	4.27	4.78	2.65	0.75
E_b (eV)	A		2.58	5.13	7.78	10.39	13.25
	B		2.64	5.04	7.80	10.39	13.23
	C		2.85	4.13	6.04	7.96	10.36
e_t (e)	A		0.03	0.16	0.22	0.51	0.57
	B		0.03	0.16	0.22	0.50	0.55
	C		0.05	0.10	0.26	0.47	0.52

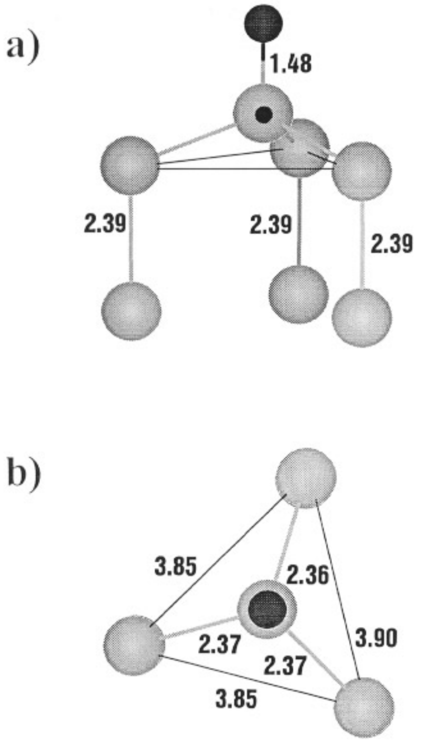

Figure 9. The minimum-energy structure for the adsorption of one hydrogen atom near a restatom C: (a) side view; (b) top view.

analysis, is 0.05 e (see table 1). The etching energy for the SiH is 6.17 eV.

3.4.2. Two-hydrogen-atom chemisorption. Chemisorbing a second hydrogen atom near a restatom C site produces an approximately tetrahedral SiH_2 configuration. In contrast to the adatom results, however, the restatom moves only slightly away its original threefold

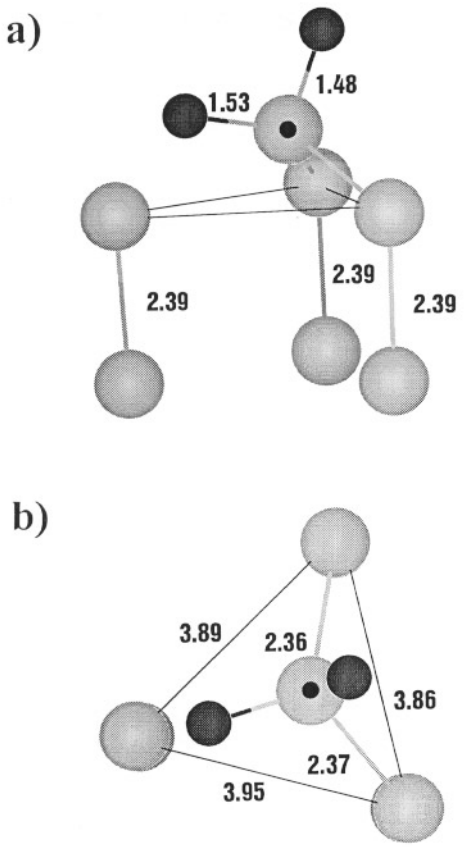

Figure 10. The equilibrium geometry which results from the adsorption of two hydrogen atoms in the vicinity of a restatom C: (a) side view; (b) top view.

site towards an adjacent bridge site, as shown in figure 10. The restatom also moves out of the surface by additional 0.45 Å. The Si(C)–H bonds are 1.53 Å and 1.48 Å, whilst the distances between the restatom C and the two second-layer silicon atoms to which it is bonded are approximately 2.36 Å. The energy required to desorb SiH_2 from this surface is determined to be 4.27 eV, and the total chemisorption energy for the two hydrogens is 4.13 eV.

3.4.3. Three-hydrogen-atom chemisorption. Employing different starting geometries in our geometry optimization procedure for three hydrogen atoms chemisorbed near a restatom site leads to the two structures shown in figures 11 and 12. The SiH_2 bridging configuration of figure 11 is fully saturated, while the SiH_3 topology of figure 12 has two unsaturated dangling bonds, one on each of the two non-bonded nearest-neighbour silicon atoms. The SiH_2 structure is thus more energetically favourable by 0.45 eV. All of the Si(C)–H bondlengths in this structure are 1.47 Å and the Si(C)–Si backbonds are 2.6% longer than the bulk nearest-neighbour distance. The energy required to desorb the SiH_2 is 4.78 eV.

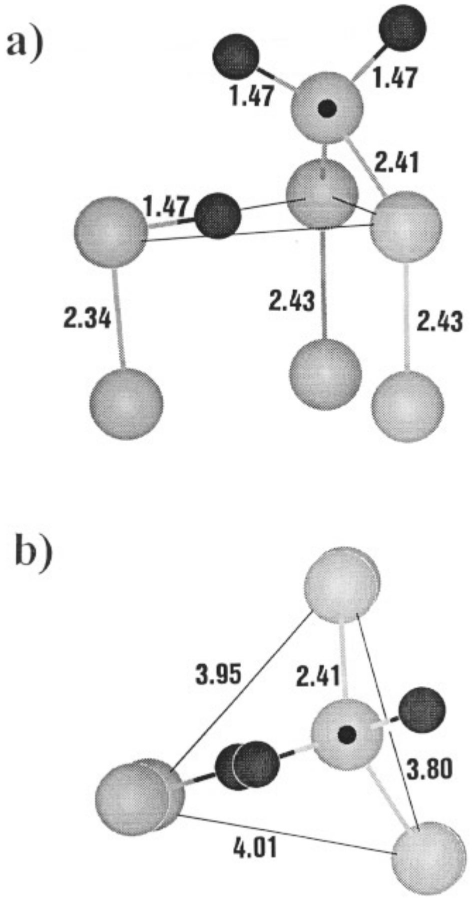

Figure 11. The SiH_2 optimized topology corresponding to the chemisorption of three hydrogen atoms near a restatom C: (a) side view; (b) top view.

3.4.4. Four-hydrogen-atom chemisorption. The chemisorption of a fourth hydrogen atom near the restatom C site is found to produce the minimum-energy structure shown in figure 13. This consists of an essentially tetrahedral Si(C)H_3 configuration bonded to one of the nearest-neighbour second-layer silicon atoms, and a single Si–H bond associated with one of the other neighbouring silicon atoms. There is one unsaturated dangling bond. All of the Si–H bondlengths are approximately 1.47 Å and the Si(C)–Si backbond length is 2.45 Å. The energy required to remove the SiH_3 complex is found to be 2.65 eV.

3.4.5. Five-hydrogen-atom chemisorption. The minimum-energy configuration when five hydrogen atoms are chemisorbed near a restatom C site is shown in figure 14. As expected, this structure is fully saturated with an SiH_3 configuration on one of the neighbouring second-layer silicon atoms, and Si–H bonds on the other two. This structure is similar to that of figure 13, apart from the additional Si–H bond, although there has been substantial rotation of the SiH_3 complex about the Si(C)–Si backbond. The etching energy for the SiH_3 complex is now only 0.75 eV, 1.90 eV less than for the four-hydrogen SiH_3 topology of figure 13.

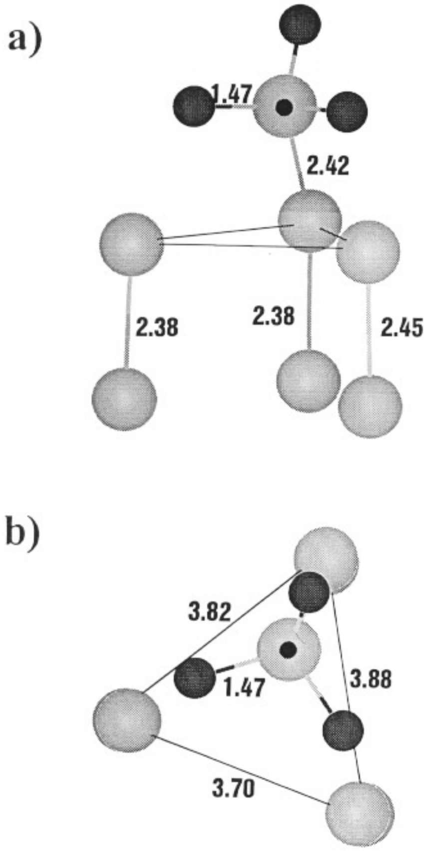

Figure 12. The SiH_3 geometry which is obtained for three-hydrogen chemisorption near a restatom C: (a) side view; (b) top view.

4. Discussion and conclusions

In this paper we have investigated the chemisorption of atomic hydrogen onto the adatom and restatom sites of the Si(111)7 × 7 reconstructed surface. Several important conclusions can be drawn from these theoretical calculations. Firstly, we have found that hydrogen chemisorption behaviour at the adatom A and adatom B sites is very similar. When either adatom is bonded with successively more hydrogen atoms, it moves from its original threefold site (one hydrogen atom), to an adjacent bridge site between its neighbouring first-layer silicon atoms (two and three hydrogen atoms), and then to a position essentially on top of one of these neighbours (more than three hydrogen atoms). The smallest adatom etching energies correspond to the desorption of SiH_3 and are 1.59 eV for the adatom A sites, and 1.62 eV for the adatom B sites. The most stable SiH_x adatom complex is SiH_2 for the three-hydrogen bridge site configuration.

Secondly, we have found markedly different chemisorption behaviour between the restatom and adatom sites. In contrast to an adatom, a restatom interacting with up to five hydrogen atoms remains relatively close to its original threefold site. We believe that these variations are due to the different orientations of the dangling bonds which would

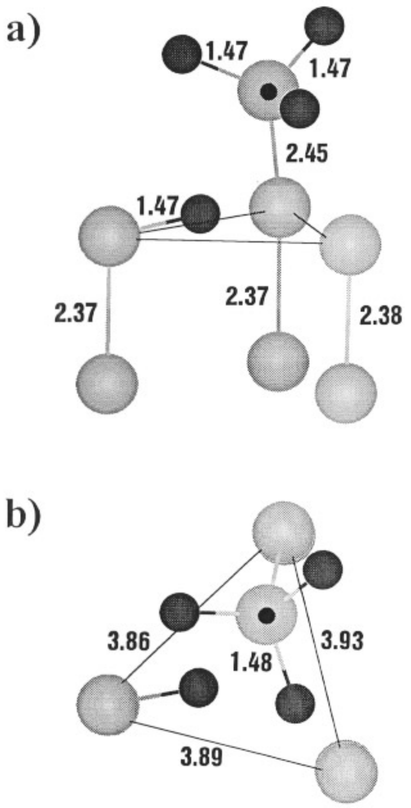

Figure 13. The minimum-energy structure resulting from the adsorption of four hydrogen atoms in the vicinity of a restatom C: (a) side view; (b) top view.

characterize the first- and second-layer silicon atoms of the Si(111)7 × 7 reconstructed surface. For a first-layer silicon atom, the dangling bond is directed upwards, essentially perpendicular to the surface. As a result, a monohydride structure on a threefold site, a dihydride configuration on a bridge site and a trihydride topology on an atop site, correspond to very stable tetrahedral structures for such first-layer silicon atoms, with little deformation of their associated dangling bonds. The dangling bonds which would result from a second-layer silicon atom, on the other hand, are oriented at a relatively small angle to the surface, towards the restatom sites. This prevents the restatom from forming stable tetrahedral structures at its adjacent bridge and on-top sites, and constrains it to remain near its original threefold site. The smallest restatom desorption energy is 0.75 eV for SiH_3, whilst the most stable restatom complex is SiH, corresponding to the chemisorption of a single hydrogen atom onto the restatom site.

Thirdly, it has been shown that when this surface is exposed to atomic hydrogen it modifies its structure to yield stable SiH, SiH_2 and SiH_3 topologies, while still retaining its basic 7 × 7 surface reconstruction. This is in agreement with experiment. No evidence is found, however, for the formation of SiH_4 complexes on this surface, which suggests that the small amount of SiH_4 which has been experimentally observed [7] most likely arises from recombination above the surface. The etching energies in table 1 suggest that, with increasing temperature, some SiH_3 would first be desorbed from a hydrogen covered

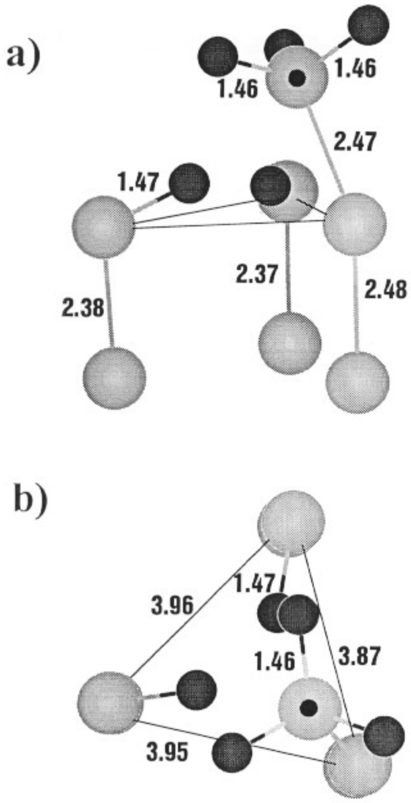

Figure 14. The fully saturated SiH_3 configuration produced by the chemisorption of five hydrogen atoms close to a restatom C: (a) side view; (b) top view.

Si(111)7 × 7 surface, followed by SiH_2 and SiH. Moreover, some SiH_2 should persist to relatively high temperatures. These conclusions are broadly consistent with the available experimental data.

Finally, we believe that the observed hydrogen saturation coverage of 1.25–1.50 ML [15, 16] on the Si(111)7 × 7 surface most probably corresponds to the five-hydrogen SiH_3 configuration of figure 8 on the adatom sites, and the single-hydrogen topology of figure 9 on the restatom sites. Both of these configurations are fully saturated and essentially undistorted. Such a hydrogen chemisorbed surface would yield a coverage of $[12\times3+(6+24)\times1]/49$, or 1.35 ML, in excellent agreement with the measured experimental values.

References

[1] Becker G E and Gobeli G W 1963 *J. Chem. Phys.* **38** 2942
[2] Waltenburg H N and Yates Jr J T 1995 *Chem. Rev.* **95** 1589
[3] Appelbaum J A and Hamann D R 1975 *Phys. Rev. Lett.* **34** 806
[4] Sakurai T and Hagstrum H D 1975 *Phys. Rev.* B **12** 5349
[5] Chabal Y J and Raqhavachavi K 1984 *Phys. Rev. Lett.* **53** 282
[6] Boland J J 1993 *Adv. Phys.* **42** 129
[7] Chen D M, Bedrossian R J, Golovchenko J B and Besenbacher F 1991 *Phys. Rev.* B **43** 1816

[8] Boland J J 1991 *Surf. Sci.* **244** 1

[9] Greenliet C M, Gates M and Holbert P A 1989 *J. Vac. Sci. Technol.* A **7** 1845

[10] Kobayashi H, Edamoto K, Ouchi M and Nishijima N 1983 *J. Chem. Phys.* **78** 7429

[11] Boland J J 1991 *J. Chem. Phys.* **95** 1521

[12] Boland J J 1991 *J. Vac. Sci. Technol.* B **9** 764

[13] Yan Chun, Jensen J A and Kummel A C 1995 *J. Chem. Phys.* **102** 3381
Karlsonn C J, Landemark E, Johnsson L S, Karlsson U O and Uhrberg R I 1990 *Phys. Rev.* B **39** 1521

[14] Avouris Ph, In-Wan Lyo, Bozso F and Kaxiras E 1990 *J. Vac. Sci. Technol.* A **8** 3405

[15] Culbertson R J, Feldman L S and Silverman P J 1982 *J. Vac. Sci. Technol.* **20** 868

[16] Oura K, Naitoh M, Shoji F, Yamaure Y, Umezawo K and Hanawa T 1990 *Nucl. Instrum. Methods* A **8** 255

[17] Shultz G and Henzler M 1983 *Surf. Sci.* **124** 336

[18] Koehler B G, Mak C H, Arthur D A, Coon P A and George S M 1988 *J. Chem. Phys.* **89** 1709

[19] Frotzheim H, Kohler U and Lammering H 1985 *Surf. Sci.* **149** 537

[20] Pandey K C, Sakurai T and Hagstrum H D 1975 *Phys. Rev. Lett.* **35** 1728

[21] Memmert U and Behm R J 1991 (Festkorperproblem) *Adv. Solid State Phys.* **31** 189

[22] Wu B R and Cheng C 1994 *J. Phys.: Condens. Matter* **6** 1113

[23] Zheng X M and Smith P V 1993 *Surf. Sci.* **282** 173

[24] Gupta P, Colvin V L and Gregor S M 1988 *Phys. Rev.* B **37** 8234

[25] Ancilotto F and Selloni A 1992 *Phys. Rev. Lett.* **68** 2640

[26] Ye L, Freeman A J and Delly B 1993 *Phys. Rev.* B **48** 11 107

[27] Stauffer L and Minot C 1994 *Catal. Lett.* **23** 1

[28] Uhrberg R I G and Hansson G V 1991 *CRC Crit. Rev. Solid Mater. Sci.* **17** 133

[29] Takayanagi K, Tanishiro Y, Takahashi M and Takahashi S 1985 *J. Vac. Sci. Technol.* A **3** 1502

[30] Hamers R J, Tromp R M and Demuth J E 1972 *Phys. Rev. Lett.* **56** 1972

[31] Tong S Y, Huang H and Wei C M 1988 *J. Vac. Sci. Technol.* A **6** 615

[32] Schegel H B 1982 *J. Comput. Chem.* **3** 214

[33] Frisch M J, Trucks G W, Schlegel H B, Gill P M W, Johnson B G, Robb M A, Cheeseman J R, Keith T A, Petersson G A, Montgomery J A, Raghavachari K, Al-Laham M A, Zakrzewski V G, Ortiz J V, Foresman J B, Cioslowski J, Stefanov B B, Nanayakkara A, Challacombe M, Peng C Y, Ayala P Y, Chen W, Wong M W, Andres J L, Replogle E S, Gomperts R, Martin R L, Fox D J, Binkley J S, Defrees D J, Baker J, Stewart J P, Head-Gordon M, Gonzalez C and Pople J A 1995 *GAUSSIAN94* Revision B.1 (Pittsburgh, PA: Gaussian Inc.)

[34] Dewar M J S, Zoebisch E G, Healy E F and Stewart J J P 1985 *J. Am. Chem. Soc.* **107** 3902

[35] Dewar M J S and Jie C X 1989 *Organometallics* **8** 1544

[36] Jalaliheravi M, McManus S P, Zutaut S E and McDonald J K 1991 *Chem. Mater.* **3** 102

[37] Brewster M E, Huang M J, Kaminski J J, Pop J J and Bodor N 1991 *J. Comput. Chem.* **12** 1278

[38] Wang S, Radny M W and Smith P V to be published

[39] Van den Hoek P J, Ravenek W and Baerends E J 1988 *Phys. Rev.* B **38** 12 508

[40] Que J-Z, Radny M W and Smith P V to be published