Interactions of hydrogen molecules with the Si(111) (1×1) surface: first-principles calculations

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Abstract. The interactions of hydrogen molecules with the Si(111) (1 × 1) surface have been investigated using a first-principles method. We have calculated the energy curves for H_2 approaching seven distinct sites in the irreducible zone of the Si(111) (1 × 1) surface and considered different orientations of H_2 in each path approaching the surface. The most favoured and disfavoured sites for the hydrogen molecule on the Si(111) (1 × 1) surface correspond to the saddle point (M2) and the chemisorbed site (T1) of the potential energy surface for atomic hydrogen moving on the surface. The effect of the orientations of the molecule depends strongly on the position of H_2 on the surface and the distance of H_2 from the surface. Several possible dissociative chemisorption processes for H_2 on the surface were studied and, except for the approach path through the M2 site, all require the overcoming of an energy barrier in the dissociative process. The approach path through the M2 site was found to be a direct dissociative chemisorption path.

1. Introduction

Hydrogen chemisorption on the Si(111) (1 × 1) surface is one of the simplest chemisorption systems which can be studied theoretically in detail to further the understanding of chemisorption processes on semiconductor surfaces. In studying chemisorption processes, the potential energy of the adsorbate on the surface is usually the starting point. With the knowledge of the potential energy, much of the reaction dynamics of the adsorption and desorption processes can be deduced from the appropriate Monte Carlo simulations (see, e.g., Rice *et al* 1987).

In a previous paper (Wu and Cheng 1994a), we presented our studies of the atomic hydrogen interacting with the Si(111) (1 × 1) surface using a first-principles method and some interesting results were found. Except the chemisorbed site (T1, figure 1(a)) for the H atom, two other threefold symmetry sites (T4 and H3, figure 1(a)) of the Si(111) (1 × 1) surface were found to be local maxima on the potential energy surface (PES) for a H atom moving on the surface. These two sites were used to be expected as local minima on the PES owing to their high-symmetry character. We have also found a possible channel for H atoms penetrating into the silicon bulk.

The interaction of molecular hydrogen with the Si(111) (1 × 1) surface is much more complicated than the atomic case and it needs three more coordinates to describe the system. In addition to the position of the hydrogen molecule on the surface, the orientation of the

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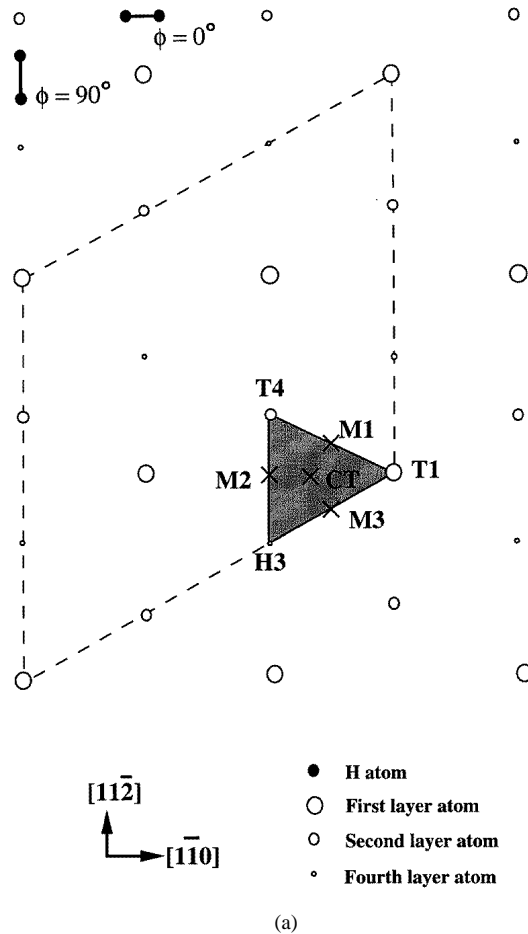
Figure 1. (a) A top view of the Si(111) (1 × 1) surface. The T1, T4 and H3 sites correspond to hydrogen atoms on top of the first-, second- and fourth-layer atoms of the surface. M1, M2 and M3 are the three positions in the middle of the lines connecting T1 and T4, T4 and H3 and H3 and T1 while the CT position is the centre of the irreducible zone (the shaded area) of the surface. The region enclosed by the dashed line is the surface unit cell of (1/3)-monolayer coverage of H_2 which was used in the calculations. (b) The description of H_2 on the surface. x and y indicate the position of the centre of mass of H_2 on the surface; z is the height of H_2 above the surface; the polar angle θ and azimuth angle ϕ describe the orientations of the molecule and d is the interatomic distance of H_2. The x-axis, y-axis and z-axis are along the $[1\bar{1}0]$ direction, the $[11\bar{2}]$ direction and the [111] direction, respectively.

molecule (θ and ϕ in figure 1(b)) and the interatomic distance of the molecule (denoted as d) should also be specified. A concise report of our studies on the system has been published (Wu and Cheng 1994b) and we have shown that there exists a possible direct dissociative chemisorption path for hydrogen molecules dissociating on the Si(111) (1 × 1) surface. In this paper, we will present the detailed results of our studies of hydrogen molecules interacting with the Si(111) (1 × 1) surface.

For the Si(111) (1 × 1) surface structure, the irreducible zone is the equilateral triangle shown as a shaded area in figure 1(a). The Si(111) (1 × 1) surface contains three threefold
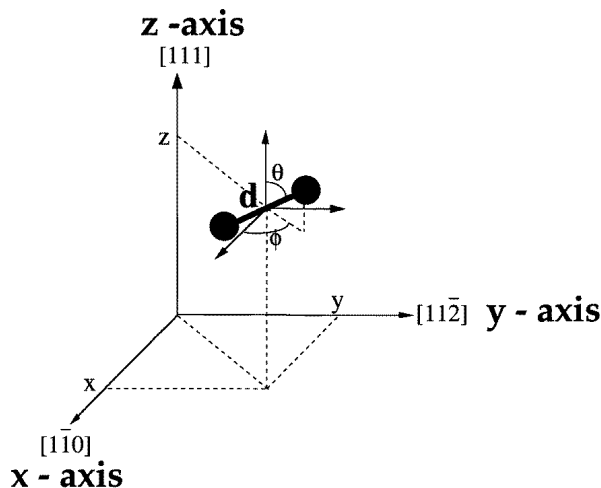
(b)

Figure 1. (Continued)

symmetry sites which correspond to positions immediately above the first (T1), the second (T4) and the fourth (H3) layers of silicon atoms. The dangling bonds of the surface silicon atoms make the T1 site the perfect position for bonding with hydrogen atoms. This is the chemisorbed position for hydrogen atoms on the Si(111) (1 × 1) surface. The T4 and H3 sites correspond to local maxima on the PES as stated above.

Similarly to in the studies of atomic hydrogen on the Si(111) (1 × 1) surface, we can define the formation energy for the adsorbate structure as the potential energy of the adsorbate on the surface. The formation energy (E_{form}) is defined as the energy difference between the energy of the adsorbate structure ($E_{\text{surf}+H_2}$) and the sum of the energies of the unrelaxed Si(111) (1 × 1) surface structure (E_{surf}) and the free hydrogen molecule (E_{H_2}):

$$E_{\text{form}} = E_{\text{surf}+H_2} - (E_{\text{surf}} + E_{H_2}). \tag{1}$$

In order to obtain a thorough picture of the interactions between hydrogen molecules and the Si(111) (1 × 1) surface, the formation energies of hydrogen molecules approaching the surface from immediately above seven distinct sites in the irreducible zone of the surface were evaluated. In additional to the three threefold symmetry sites, the M1, M2 and M3 sites which are the middle points of the lines connecting every pair of the T1, T4 and H3 sites, and the CT site which is at the centre of the equilateral triangle were also selected (figure 1(a)). The different orientations of H_2 along the seven approach paths were investigated and the details are given in section 3.1. Section 3.2 gives the energy curve of H_2 approaching the surface along the seven approach paths with the orientation which is the most favoured on each approach path. The situations which have one H atom of the hydrogen molecule locating immediately above the T1 site were also studied (section 3.3). In these calculations the bond length of H_2 is kept the same as the bond length of the free hydrogen molecule. The bond length of H_2 is then varied to investigate several possible dissociative chemisorptions of H_2 on the Si(111) (1 × 1) surface, i.e., adsorbate structures with various interatomic distances d of the molecule are discussed in section 3.4.

The calculational method is described in the next section.

2. Calculational method

The calculations were based on the density functional theory (Hohenberg and Kohn 1964) with the local density approximation (Kohn and Sham 1965). The Ceperley–Alder form (Ceperley and Alder 1980) was used to calculate the exchange–correlation energy. The norm-conserving pseudopotentials for the silicon and hydrogen ions were taken from Bachelet *et al* (1982). Using the bare Coulomb potential for hydrogen ions gives only a small difference (less than 20 meV/H_2) in the formation energy. This was also confirmed in the paper of Chang and Chadi (1989).

Table 1. Convergence tests of the basis expansion and k-point sampling for hydrogen molecules on the Si(111) (1×1) surface with (1/3)-monolayer coverage of hydrogen molecules. For H_2 at the H3 site, H_2 is at the height of $z = 1.75$ Å above the surface with the molecular axis both parallel and perpendicular to the surface. For H_2 at the M2 site, H_2 is at the height of $z = 1.48$ Å above the surface with the molecular axis parallel to the surface. The formation energy is in units of eV/H_2.

Site	Alignment	z	$E_{cut-offs}$ (Ryd)	Number of k-points		
				1	9	25
H3	Perpendicular	1.75	4	0.017	−0.108	−0.109
			8	−0.278	−0.342	—
			10	−0.254	−0.306	—
H3	Parallel	1.75	4	−0.679	−0.813	−0.804
			8	−0.435	−0.526	—
			10	−0.440	−0.461	—
M2	Parallel	1.48	4	−1.189	−1.217	−1.225
			8	−0.758	−0.716	−0.715
			10	−0.709	−0.596	−0.620
			12	−0.854	−0.556	—

Table 2. Formation energies (in units of eV/H_2) for H_2 on the Si(111) (1×1) surface with coverages (Θ) of 1, 1/3 and 1/4 monolayers of hydrogen molecules. H_2 is at the height of $z = 1.48$ Å above the surface and the molecular axis is along the line connecting the two nearest T1 sites. 4, 8, 10 and 12 Ryd correspond to the tests of the convergence of the basis-set expansion.

Site	$E_{cut-offs}$ (Ryd)	Coverage (Θ)		
		1	1/3	1/4
T1	4	0.751	−0.445	−0.482
	8	1.219	0.211	0.211
M2	4	0.076	−1.217	−1.283
	8	0.257	−0.716	−0.734
	10	0.257	−0.596	−0.622
	12	0.255	−0.556	—

All of the structures in the calculations are periodic systems with slab configurations. The unit cell contains six double layers of silicon along the [111] direction with a period

of nine double layers. The surface area enclosed with dashed lines in figure 1(a) was used as the unit cell which corresponds to (1/3)-monolayer coverage of H_2 on the surface. The theoretical lattice constant of silicon and the equilibrium bond length of hydrogen molecule at energy cut-offs of 4, 8, 10 and 12 Ryd were used for the calculations at corresponding energy cut-offs. The wavefunctions were expanded with plane waves and the calculations were done in the momentum space (Ihm *et al* 1979). The samplings of k-points for integration over the first Brillouin zone were chosen with the scheme of Monkhorst and Pack (1976). The convergence tests in the k-point sampling (using up to 25 points in the first Brillouin zone) and the energy cut-offs (up to 12 Ryd) were carried out for H_2 at different positions on the surface and the error bar is estimated to be less than 0.1 eV/H_2 (table 1). Similar tests were carried out in the calculations of structures with larger (smaller) unit cells, i.e., for the quarter- (one-) monolayer coverages of hydrogen molecules, and the results are listed in table 2. This shows that for *the unit cell that we used the interaction between hydrogen molecules is negligible*. To calculate the energy of the free hydrogen molecule, the corresponding unit cell of the adsorbate structure that consists of one hydrogen molecule is used.

3. Results and discussion

As stated in the first section, six coordinates are needed to specify the position of H_2 on the Si(111) (1×1) surface (figure 1(b)). In our calculations the position of H_2 is represented by the location of the centre of mass of the molecule. x and y specify the position of H_2 on the surface and z is the height of H_2 above the surface. The x-axis and y-axis are defined as along the $[1\bar{1}0]$ and $[11\bar{2}]$ directions of the Si(111) (1×1) surface and the z-axis is along the [111] direction. The orientation of the molecule is described by the polar angle θ and the azimuth angle ϕ. The molecule is perpendicular to the surface at $\theta = 0°$ and parallel to the surface at $\theta = 90°$. The azimuth angle ϕ describes the projection of the molecular axis on the Si(111) (1×1) surface. $\phi = 0°$ and $\phi = 90°$ correspond to the projection of the molecular axis being along the $[1\bar{1}0]$ and the $[11\bar{2}]$ directions, respectively.

3.1. The effect of orientations

For each one of the seven approach paths, at least four heights of H_2 above the surface were studied. At each height of these seven approach paths that we have studied, at least three orientations of H_2 are considered: one perpendicular (i.e., $\theta = 0°$) and two parallel to the surface (i.e., $\theta = 90°$) (figure 1(a)). The molecular axes of the two parallel cases are perpendicular to each other and *one of them is directed to the nearest T1 site*.

3.1.1. The orientation effect of H_2 in the approach process.
Firstly, we investigate the effect caused by the different polar angles in the processes via which H_2 approaches the Si(111) (1×1) surface. This is studied by considering the differences between the formation energies of the structures with the molecular axis perpendicular and parallel to the surface $(\Delta E_\theta = E_{\theta=0°} - E_{\theta=90°})$ while the azimuth angle is fixed at either $\phi = 0°$ or $\phi = 90°$ during the process of H_2 approaching the Si(111) (1×1) surface (figures 2(a) and 2(b)). $E_{\theta=0°}$ ($E_{\phi=0°}$) is defined as the formation energy of the structures with the molecular axis at $\theta = 0°$ ($\phi = 0°$). It was found that the closer H_2 is to the surface, the larger $|\Delta E_\theta|$ is. In both cases, the largest change in energy at various values of θ occurs firstly for the T1 approach path (the solid line with solid circles in figures 2(a) and 2(b)) which is expected as the T1 position is just above the surface-atom layer. $|\Delta E_\theta|$ rises enormously when H_2
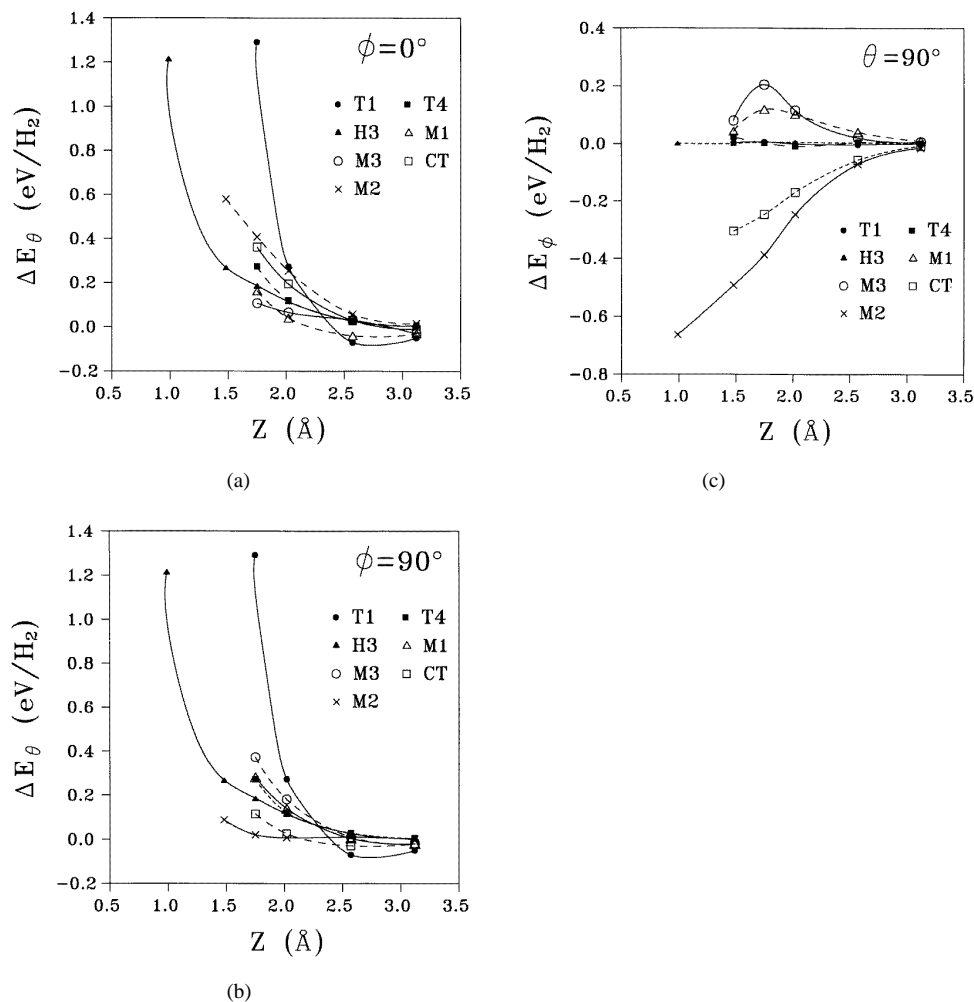
Figure 2. The difference between the formation energies of H_2 for $\theta = 0°$ and $\theta = 90°$ ($\Delta E_\theta = |E_{\theta=0°} - E_{\theta=90°}|$) with the azimuth angle ϕ fixed at (a) $0°$ and (b) $90°$. (c) The difference between the formation energies for H_2 for $\phi = 0°$ and $\phi = 90°$ ($\Delta E_\phi = |E_{\phi=0°} - E_{\phi=90°}|$) with the polar angle θ fixed at $90°$.

gets closer to the surface than the $z = 2$ Å position. At $\phi = 90°$, i.e., where H_2 is parallel to the $(1\bar{1}0)$ plane, $|\Delta E_\theta|$ is tiny for H_2 approaching the surface from immediately above the M2 site (figure 2(b)). This shows that H_2 does not have an obvious preference for the orientation $\theta = 0°$ or $\theta = 90°$ when H_2 is at the M2 position with ϕ fixed at $90°$. It is also demonstrated, in figure 2, that *the θ-dependence in the formation energy can be ignored for H_2 for $z > 2.5$ Å*.

Secondly, we consider the effect of the azimuth angle with the molecule parallel to the surface, i.e., $\theta = 90°$. The difference between the formation energies for the azimuth angles $\phi = 0°$ and $\phi = 90°$ ($\Delta E_\phi = E_{\phi=0°} - E_{\phi=90°}$) (with θ fixed at $90°$) is shown in figure 2(c). The magnitude of $|\Delta E_\phi|$ is less than 0.05 eV/H_2 in the processes by which H_2 approaches the surface from immediately above the T1, T4 and H3 sites. Similar to $|\Delta E_\theta|$ at $\phi = 0°$ and $\phi = 90°$, $|\Delta E_\phi|$ becomes larger as H_2 comes closer the surface for the M2 and CT

approach paths. There are interesting results for the M1 and M3 approach paths. As H_2 comes closer to the surface $|\Delta E_\phi|$ firstly increases and then decreases with the maximum at $z = 1.75$ Å. Similar to the θ-dependence, the ϕ-dependence in the formation energy for H_2 can also be ignored as z is greater than 2.5 Å.
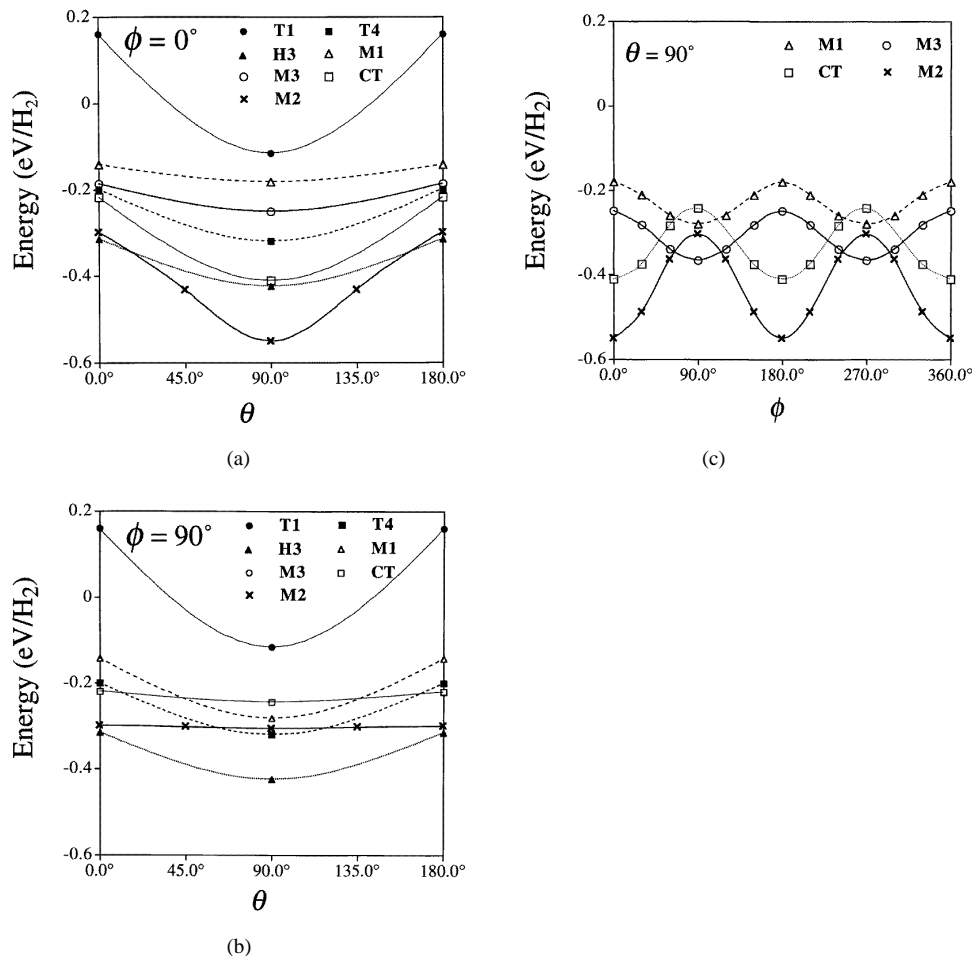

Figure 3. The formation energy of H_2 at $z = 2.02$ Å for various polar angles θ for the azimuth angle ϕ fixed at (a) $0°$ and (b) $90°$. (c) The formation energy for H_2 at $z = 2.02$ Å for various azimuth angles ϕ for the polar angle θ fixed at $90°$.

From the above studies, we conclude that the formation energy differences due to the various orientations are strongly position dependent. That is, they depend strongly on the position of H_2 on the Si(111) (1×1) surface (the x- and y-coordinates) and the distance of H_2 from the surface (the z-coordinate). In most of the cases that we have studied the effect of the orientation becomes stronger as H_2 moves closer to the surface.

3.1.2. The orientation effect of H_2 at fixed height. Following on from the above studies of the formation energy difference at various polar or azimuth angles in the approach process, in the present section we will present the formation energy for H_2 at various polar and azimuth angles θ and ϕ. At least four (and five) heights ($z = 3.12$ Å, 2.57 Å, 2.02 Å,

1.75 Å and 1.48 Å) of H_2 above the Si(111) (1 × 1) surface were chosen for studying the effect of various polar (and azimuth) angles. All of the studies lead to two conclusions, i.e., the H_2 prefers to be parallel to the surface ($\theta = 90°$) and directed to the nearest T1 site. Here we present only the variations of the energy due to different orientations with $z = 2.02$ Å in figure 3. This study not only reveals the preference of the orientation of the hydrogen molecule clearly, but also shows the relative formation energies of H_2 at the seven distinct sites. For various polar angles θ—while the azimuth angle ϕ is fixed either at 0° or at 90°—the formation energies of H_2 are shown in the figures 3(a) and 3(b). In both cases, as θ increases from 0° to 90° the energies are lowered and reach minima at $\theta = 90°$. We conclude that H_2 *prefers to lie parallel to the surface.* The largest change in the formation energy caused by the variations of the polar angle θ occurs as H_2 approaches the T1 site. For ϕ, fixed at 90°, the variations of the formation energy for H_2 approaching the M2 and CT sites are less than 0.01 and 0.03 eV/H_2, respectively. This shows that the formation energies of H_2 approaching the M2 and CT sites depend little on the orientation θ as the molecular axis is parallel to the ($1\bar{1}0$) plane. The result that the hydrogen molecules prefer having the molecular axis parallel to the surface is similar to the conclusion from previous studies of H_2 on metal surfaces using the jellium model (Johansson 1981, Nørskov *et al* 1981).

For various azimuth angles ϕ, while the polar angle θ is fixed at 90°, the formation energies for H_2 at different orientations are plotted in figure 3(c). For the three high-symmetry sites of T1, T4 and H3 the formation energies depend little on the ϕ-orientation, and the energy variations due to different orientations of ϕ are less than 0.03 eV/H_2. However, the energy is more strongly ϕ-dependent for H_2 at the other four low-symmetry sites. As ϕ is increased from 0° to 90°, the energies for H_2 at the M1 and M3 sites are lowered and reach a minimum at $\phi = 90°$, while the energies for H_2 at the M2 and CT sites are raised and reach a maximum at $\phi = 90°$. *The results demonstrate that hydrogen molecules prefer directing to the nearest T1 site.* The largest change in formation energy caused by the ϕ-orientation of the hydrogen molecule occurs as H_2 approaches the M2 site of the surface (the solid line with crosses). H_2 on the M2 site with the orientation $\theta = 90°$ and $\phi = 0°$ corresponds to the molecular axis parallel to the surface and along the line connecting the two nearest T1 sites (figure 1(a)). This orientation is found to be the lowest-energy orientation for H_2 approaching the M2 site of the Si(111) (1 × 1) surface. The most favoured orientation for H_2 approaching the four low-symmetry sites (M1, M2, M3 and CT sites) is that with H_2 parallel to the surface and directed to the nearest T1 site.

As the H_2 prefers having the molecular axis parallel to the surface and the T1 site is the chemisorption position for hydrogen atoms (Wu and Cheng 1994a), we will concentrate next on the cases where the molecular axis is parallel to the surface and directed to the nearest T1 site during the processes of approaching the surface.

3.2. The energy curves for H_2 approaching the Si(111) (1 × 1) surface

The formation energies for H_2 approaching the Si(111) (1 × 1) surface from immediately above the seven distinct sites in the irreducible zone which has been mentioned above were evaluated. The energy curves for H_2 with the most favoured orientation (with the molecule axis parallel to the surface and directed to the nearest T1 site) for the seven approach paths are shown in figure 4. The energy curve for H_2 approaching the T1 site is the highest. This curve tends to be flat before H_2 reaches the height of 1.75 Å above the surface and strong repulsion appears after H_2 passes this point. This shows that there is no obvious attractive force on the T1 approach path for H_2. The energy curves of the other six approach paths
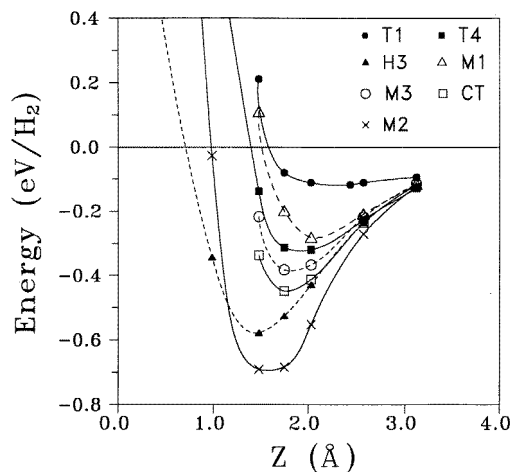
Figure 4. The formation energies for H_2 approaching the T1, T4, H3, M1, M2, M3 and CT sites of the Si(111) (1 × 1) surface while the molecular axis is directed to the nearest T1 sites (see figure 1). The bond length of H_2 is fixed at the bond length of free H_2.

all have clear wells. We remind readers that these formation energies were evaluated with the constraint of the fixed H_2 bond length being the same as the bond length of the free H_2 which has been mentioned before. The well depth of the energy curve for H_2 approaching the M2 site is the deepest, and the position which corresponds to the minimum of the energy curve is at the height of 1.48 Å above the surface. The bottom of this well tends to be flat and it extends over a region from $z = 1.75$ Å to $z = 1.48$ Å. This shows therefore that there are no obvious attractive and repulsive forces between the H_2 and the surface for H_2 in this region. The second deepest well of the energy curves occurs as H_2 approaches the H3 site, and the position corresponding to the minimum of the curve is also at a height of around 1.48 Å above the surface. It was found that as the well depth of the energy curve is deeper, the position of the minimum energy on the curve gets closer to the surface. The most favoured path for H_2 approaching the Si(111) (1 × 1) surface is via the M2 approach path, as the well depth of the energy curve there is the deepest. The second most favoured path for H_2 approaching the surface is via the H3 approach path and the most disfavoured path is via the T1 approach path.

From the above calculations for many different configurations of H_2 on the Si(111) (1 × 1) surface we obtain a fairly complete picture of the interactions of H_2 with the surface. It is found that the T1 site is the most disfavoured site, the M2 site is the most favoured site and the H3 is the second most favoured site for H_2 on the Si(111) (1 × 1) surface. These results are to be compared to those for a H atom on the surface (Wu and Cheng 1994a) where T1 is the global minimum, M2 is the saddle point and H3 is a local maximum on the PES.

3.3. H_2 approaching the Si(111) (1 × 1) surface with one H atom of the molecule fixed exactly above the T1 site

In the previous investigations, the positions of H_2, which are denoted by the centre of mass of H_2, were always located above the seven selected sites. As the T1 site is the chemisorption position of the H atom on the surface, one might suspect that H_2 with one H atom fixed on
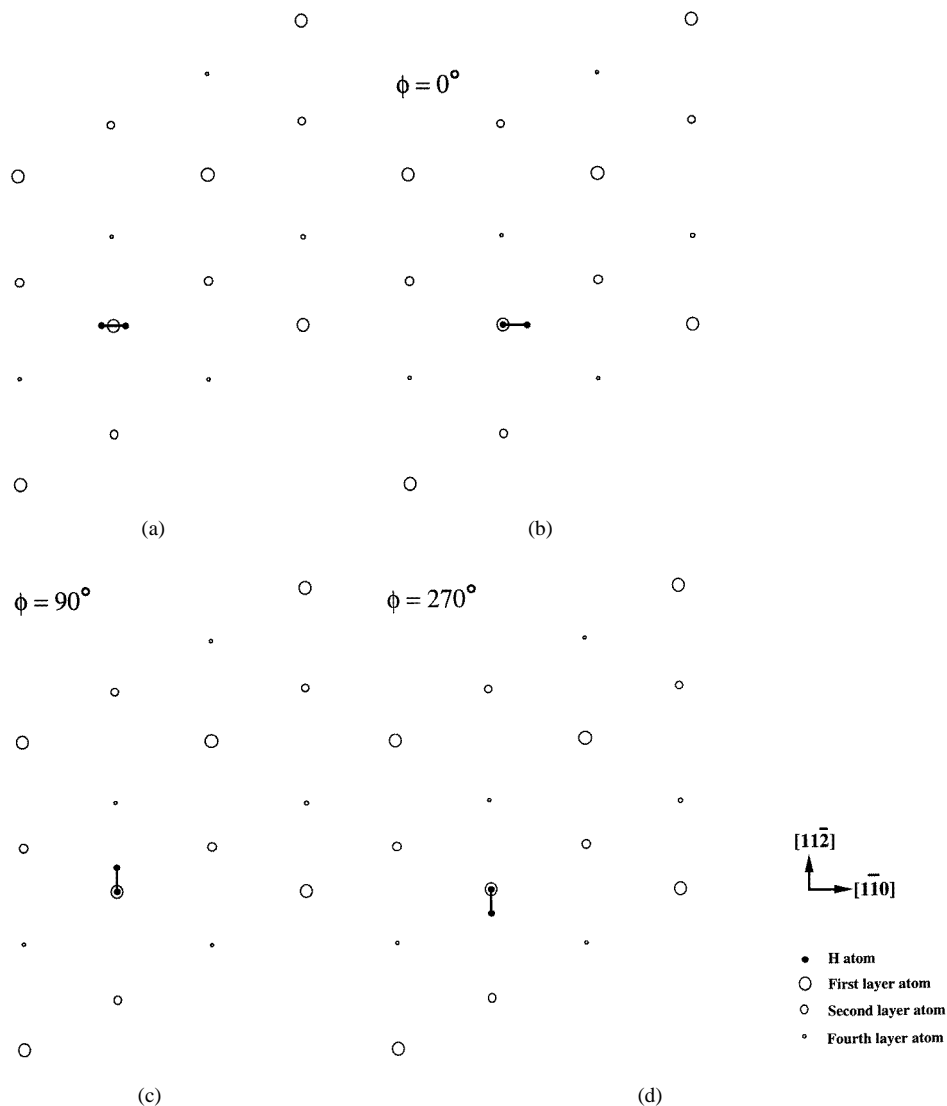
Figure 5. A top view of a hydrogen molecule near the T1 site of the Si(111) (1×1) surface with the molecular axis parallel to the surface. (a) The centre of mass of H_2 is immediately above the T1 site. One H atom of the molecule is immediately above the T1 site with the azimuth angle (b) $\phi = 0°$ (180°), (c) $\phi = 90°$ and (d) $\phi = 270°$.

the T1 site would be one of the more favoured configurations. That is, it may have lower energy than either the H_2 with the centre of mass fixed on the T1 site (figure 5(a)) or the lowest-energy configuration of H_2 on the surface, i.e., at the M2 site. Furthermore, it might provide a more possible dissociation path. To check this, H_2 approaching the surface with one H atom of the molecule fixed immediately above the T1 site and the molecular axis parallel to the surface (denoted as the n-T1 approach path) was studied. The molecular axes with different ϕ-orientations were also considered: the azimuth angles $\phi = 0°$ (180°), 90° and 270° (figures 5(b), 5(c) and 5(d)). The results are shown in figure 6(a). Because of the
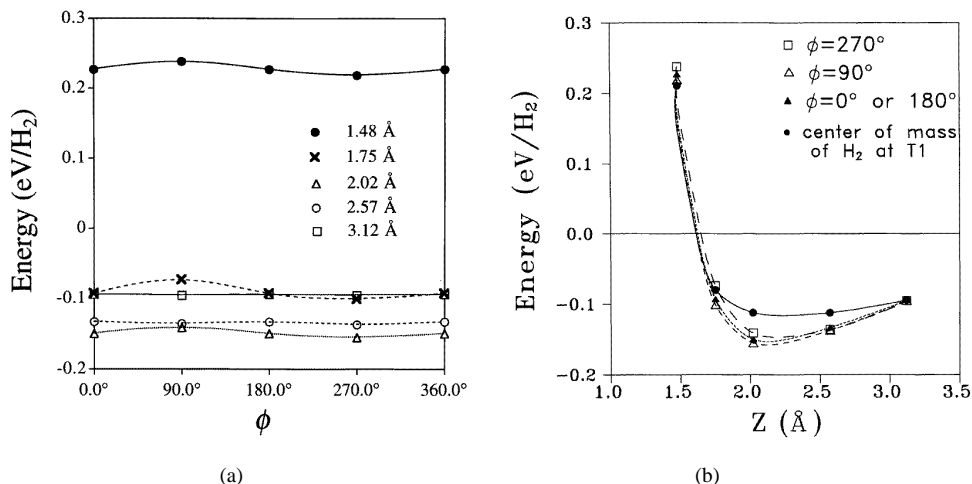
Figure 6. The formation energy for H_2 approaching the Si(111) (1×1) surface with the molecular axis parallel to the surface and one H atom of the molecule fixed immediately above the T1 site. (a) H_2 is at the heights of $z = 1.48$, 1.75, 2.02, 2.57 and 3.02 Å for various azimuth angles ϕ. (b) The molecule axis with the azimuth angle $\phi = 0°$ (180°), 90° and 270° (figure 5) is compared to the centre of mass of H_2 fixed immediately above T1 site at various heights from the surface. The bond length of H_2 is fixed at the bond length of free H_2.
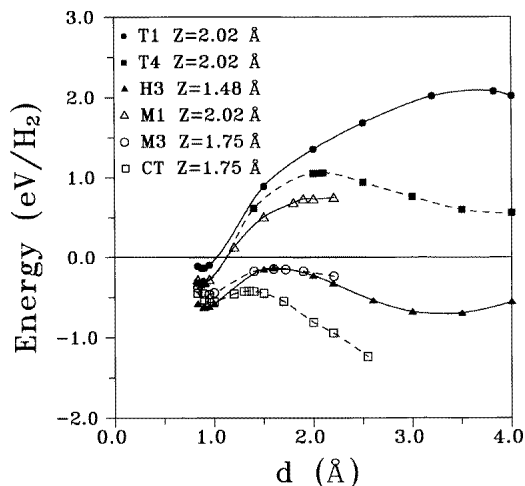

Figure 7. The formation energy of the dissociative process for H_2 at various sites of the surface. H_2 dissociates with the molecular axis parallel to the Si(111) (1×1) surface and directed to the nearest T1 site. The heights of the H_2 are fixed at the minimum-energy positions of the corresponding surface-approach energy curves (figure 4). For example, for the H3 surface-approach energy curves, z is fixed at 1.48 Å.

reflection symmetry of the $(11\bar{2})$ plane, the configuration $\phi = 180°$ is equivalent to $\phi = 0°$. Similarly to the case of H_2 approaching the T1 site, the formation energies also depend little on the orientations, and the energy variations due to different orientations of ϕ are less than 0.02 eV/H_2. The differences between the formation energies for H_2 approaching the

surface along the T1 approach path and along the n-T1 approach path are less than 0.05 eV/H_2 (figure 6(b)). Considering the global picture of the surface-approach energy curves (figure 4), this small difference has little effect on the dynamics of H_2 approaching the surface. Although the T1 site is the chemisorption site of the H atom on the Si(111) (1×1) surface, the formation energies change little for the T1 and n-T1 approach paths. This is due to the effect of the Si(111) (1×1) surface on the interatomic interaction of H dimers (Wu *et al* 1996). This effect is strongly position dependent and it makes the interatomic interaction of H dimers become repulsive when the H dimer is immediately above the T1 site. That is, it is unfavourable for a H dimer to stay above the T1 site of the surface. The formation energies only change little for H_2 approaching the nearby position of the T1 site on the surface (i.e., following the n-T1 approach path) and these approach paths were all disfavoured for H_2 approaching the surface, as the T1 site is the most disfavoured site for H_2 on the Si(111) (1×1) surface.

3.4. Dissociative chemisorption of H_2 on the Si(111) (1×1) surface

It was found that the hydrogen molecules were subjected to tensile forces in all of the various processes by which H_2 approached the Si(111) (1×1) surface, and the forces were increased as the H_2 came closer to the surface. This is caused by the effect of the Si(111) (1×1) surface on the interatomic interaction of H_2 and the details will be published elsewhere (Wu *et al* 1996). Due to the effect of the surface on the interatomic interaction of H_2, dissociative chemisorption of H_2 is possible. The energy curves for H_2 approaching the surface have a minimum in each energy curve (figure 4) and at the positions of these energy minima the H_2 was also subject to tensile forces. These minimum-energy positions are at the heights of 1.48, 1.75 and 2.02 Å above the surface for H_2 approaching the H3 (and M2), M3 (and CT) and T1 (and T4, M1) sites, respectively. To investigate the possible dissociation paths, the bond length of H_2 was increased until one H atom of the molecule reached the nearest T1 site and the heights of H_2 were fixed at the minimum-energy positions. Except for the case of H_2 on the M2 site, the remaining six dissociation paths all require the overcoming of energy barriers in the dissociation process, and the results are shown in the figure 7. As the dissociation path for H_2 on the M2 site at $z = 1.48$ Å is the only dissociation process which does not need to overcome an energy barrier in the dissociation process and the M2 approach path is the most favoured one for H_2 approaching the Si(111) (1×1) surface, it is expected that the most probable dissociation path for H_2 on the Si(111) (1×1) surface would be the path with the molecule approaching the M2 site and the molecular axis parallel to the line connecting the two nearest T1 sites. Note that the M2 site is a saddle point of the PES for the H atom moving on the surface. The molecule will dissociate into two hydrogen atoms and be chemisorbed on the two nearest T1 sites. Via this path, a direct dissociative chemisorption process of H_2 on the Si(111) (1×1) surface was found (Wu and Cheng 1994b).

If H_2 dissociates via the other six dissociation paths (i.e., H_2 'sitting' on the T1, T4, M1, M3 and CT sites and the bond length of H_2 forced to increase until one H atom of the molecule reaches the nearest T1 site), there exist energy barriers in the dissociative process (figure 7). Three of the six dissociation paths, i.e., for H_2 sitting on the T1, T4 and M1 sites, need additional energy to overcome the energy barriers in the dissociative process. That is, the maxima of the energy curves are positive and the dissociative processes are activated. The additional energies are about 2, 1 and 0.7 eV/H_2 for the dissociation path of H_2 sitting on the T1, T4 and M1 sites. The remaining three dissociation paths which correspond to H_2 sitting on H3, M3 and CT sites do not need additional energy to climb over the energy

barriers. Among these six dissociation paths, the energy barrier for H_2 sitting on the T1 site is the largest (around 2.1 eV/H_2) and the energy barrier for H_2 sitting on the CT site is the smallest (only 0.14 eV/H_2). The dissociation path for H_2 sitting on the CT site is expected to be the second most probable path for the dissociative chemisorption of H_2 on the Si(111) (1 × 1) surface.

Another more probable dissociation path that one may expect is the one with one H atom of H_2 fixed on the T1 site and the other H atom forced to move away from the T1 site. If this dissociation path is probable, the force exerted on the H atom above the T1 site should be tiny and the force on the other H atom of the hydrogen molecule should be strong. However, there exist almost equally tensile forces exerted on the two atoms of H_2 when it approaches the surface via the n-T1 approach path. The T1 site is the most disfavoured site for H_2 on the Si(111) (1 × 1) surface, as has been mentioned above, so the probability is small for the dissociation of H_2 via this path. If the H_2 is to dissociate at the n-T1 site, due to the PES of H atoms on the Si(111) (1 × 1) surface, one of the H atoms needs to climb over a high energy barrier of about 2 eV to reach the nearest chemisorbed site (Wu and Cheng 1994a). Therefore it is not probable that H_2 will dissociate into two H atoms around the T1 site. From the above discussion, the most probable dissociation path for H_2 on the Si(111) (1 × 1) surface would be that in which the molecule approaches the M2 site with the molecular axis parallel to the line connecting the two nearest T1 sites.

4. Conclusions

On the basis of first-principles calculations, the interactions of hydrogen molecules with the Si(111) (1 × 1) surface were investigated. We found that H_2 favours having the molecular axis parallel to the surface. The effects caused by orientations are strongly position dependent. When the molecular axis for H_2 is parallel to the surface, the ϕ-orientations of H_2 have little effect on the formation energy for H_2 approaching the three high-symmetry sites (T1, T4 and H3) of the surface. The path for H_2 approaching the Si(111) (1 × 1) surface from immediately above the T1 site is the most disfavoured one and the approach paths from immediately above the M2 and H3 sites are the most favoured and the second most favoured paths, respectively. For H_2 interacting with the Si(111) (1 × 1) surface, the M2 site is the most favoured site and the T1 site is the most disfavoured site. A direct dissociative chemisorption process was found for H_2 on the Si(111) (1 × 1) surface and it was the most probable dissociative path for H_2 on the Si(111) (1 × 1) surface corresponding to H_2 approaching the M2 site with the molecular axis parallel to the line connecting the two nearest T1 sites.

Acknowledgments

References

Bachelet G B, Hamann D R and Schlüter M 1982 *Phys. Rev.* B **26** 4199
Ceperley D M and Alder B J 1980 *Phys. Rev. Lett.* **45** 566
Chang K J and Chadi D J 1989 *Phys. Rev.* B **40** 11 644
Hohenberg P and Kohn W 1964 *Phys. Rev.* B **136** 864

Ihm J, Zunger A and Cohen M L 1979 *J. Phys. C: Solid State Phys.* **12** 4409
Johansson P K 1981 *Surf. Sci.* **104** 510
Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133
Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
Nørskov J K, Houmøller A, Johansson P K and Lundqvist B I 1981 *Phys. Rev. Lett.* **46** 257
Rice B M, NoorBatcha I, Thompson D L and Raff L M 1987 *J. Chem. Phys.* **86** 1608
Wu B R and Cheng C 1994a *J. Phys.: Condens. Matter* **6** 1113
——1994b *J. Phys.: Condens. Matter* **6** L687
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