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LETTER TO THE EDITOR

Dissociative chemisorption of hydrogen molecules on the Si(111) (1×1) surface: first-principles calculations

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Abstract. The dissociative chemisorption for hydrogen molecules on the Si(111) (1×1) surface has been studied using a first-principles method. A direct dissociative chemisorption process was found. The direct dissociation happens at the saddle point of the potential energy surface for hydrogen atoms moving on the Si(111) (1×1) surface. A two-dimensional potential energy surface was presented to show the direct dissociation. Different orientations of H_2 interacting with the surface were also investigated. The calculations showed that H_2 always favours having the molecular axis parallel to the surface.

Being the simplest diatomic molecules, hydrogen molecules interacting with metal surfaces have been studied extensively (Sheng and Zhang 1992, Forni *et al* 1992, White and Bird 1993). However, comparatively fewer studies have been carried out on semiconductor surfaces. Hydrogen atoms being adsorbed on silicon surfaces as a result of exposure to molecular hydrogen had been observed at room temperature (Schulze and Henzler 1983, Wolff *et al* 1989, Ueda *et al* 1991), while no adsorption of molecular hydrogen was found (Schulze and Henzler 1983, Kuramochi *et al* 1994). For the Si(111) surface, the hydrogen-adsorbed surface structure was identified as the (1×1) structure with H atoms bound to the surface silicon atoms (Becker *et al* 1990, Ancilotto and Selloni 1992, Boland 1993). Whether the dissociative chemisorption of H_2 on the Si(111) surface is activated or not is still controversial. That there exist various possible initial surface structures complicates the problem even more. Among these structures, the unreconstructed Si(111) surface is the simplest, and studies of the system will help further investigations on more complex systems.

In this letter we shall present studies of dissociative chemisorption for hydrogen molecules on the Si(111) (1×1) surface using a first-principles method. A *direct dissociated chemisorption process* was found and its corresponding two-dimensional potential energy surface (PES) $V(z, d)$ was evaluated. To locate the most probable chemisorption path, molecular hydrogen approaching the surface from right above the surface to seven different sites in the irreducible zone of the surface was investigated (figure 1). Through each surface-approaching path the molecular axis of H_2 at different orientations was also considered.

The calculations were based on density functional theory (Hohenberg and Kohn 1964) with the local density approximation (Kohn and Sham 1965), and 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).

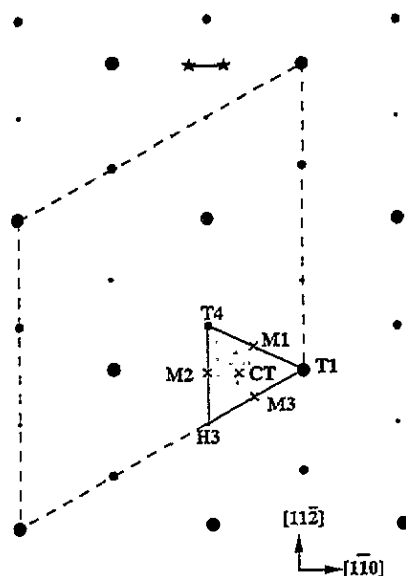


Figure 1. A top view of the Si(111) (1×1) surface. The large, medium and small dots correspond to the silicon atoms on the first, second and the fourth layer of the surface. The T1, T4 and H3 sites correspond to hydrogen atoms on top of the first-, second- and fourth-layer atoms of the surface. The M1, 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 used in the calculations. The two line-connected stars define $\theta = 90^\circ$ and $\varphi = 0^\circ$ for H_2 on the M2 site.

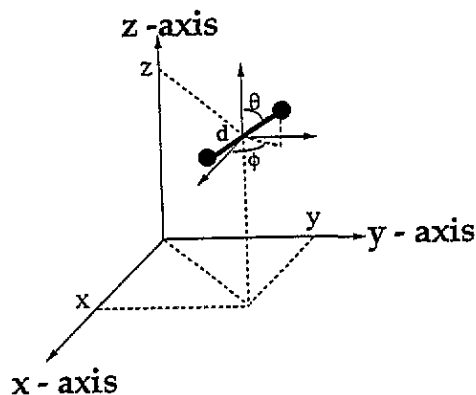


Figure 2. The description of H_2 on the surface. The values of x and y give the position of the centre of mass on the surface; z is the height from the surface; the polar angle θ and azimuthal angle φ are the angular coordinates of the molecule and d is the distance between the two H atoms of H_2 .

All the structures in the calculations are periodic systems with slab configurations. The unit cells contain 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 was used as the unit cell; it corresponds to one third of a monolayer coverage of H_2 on the surface. The wavefunctions were expanded in terms of plane waves and the calculations were done in momentum space (Ihm *et al* 1979). The sampling of k points for integration over the first Brillouin zone was chosen using the scheme of Monkhorst and Pack (1976). The formation energy (E_f) is defined as the energy difference between 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 molecules (E_{H_2}):

$$E_f = E_{\text{surf}+H_2} - (E_{\text{surf}} + E_{H_2}). \quad (1)$$

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 at most 0.1 eV/ H_2 . Similar tests were carried out in the calculations of structures with larger (smaller) unit cells, i.e., the quarter-(one-) monolayer coverages of hydrogen molecules, and they show that, for the unit cell

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. The detailed results of the calculations will be presented elsewhere.

In order to obtain a complete picture of the PES for hydrogen molecules interacting with the Si(111) (1×1) surface, the formation energies of hydrogen molecules approaching the surface from right above seven distinct sites in the irreducible zone of the surface were evaluated (figure 1). In these calculations the bond length of H_2 is kept the same as the bond length of the free hydrogen molecule. Along each path at least three orientations of H_2 are considered: one perpendicular (i.e., $\theta = 0^\circ$) and two parallel to the surface (i.e., $\theta = 90^\circ$) (figure 2). The molecular axes of the two parallel cases are perpendicular to each other and one of them is directed to the nearest T1 site. From our previous studies, the T1 site is the chemisorbed site for H atoms (Wu and Cheng 1994a).

The calculated results show that the hydrogen molecules prefer having the molecular axis parallel to the surface, which is similar to the findings of previous studies of H_2 on a metal surface using a jellium model (Johansson 1981, Nørskov *et al* 1981). For the molecular axis parallel to the surface, the formation energies of H_2 approaching the three high-symmetry sites of T1, T4 and H3 depend little on the orientation. The energy variations due to different orientations are less than 0.01 eV/ H_2 . However, the energy is strongly orientation dependent for H_2 approaching the other four low-symmetry sites. The largest change in formation energy caused by the orientation of hydrogen molecules occurs with H_2 approaching the M2 site of the surface. The formation energies of H_2 on the M2 site (with fixed $z = 1.48 \text{ \AA}$) at different orientations are plotted in figure 3. The H_2 with an orientation of $\theta = 90^\circ$ and $\varphi = 0^\circ$ corresponds to the molecular axis parallel to the surface and along the line connecting the two nearest T1 sites (figure 1). The formation energies of H_2 at various polar angles θ , with the azimuthal angle φ fixed at 0° (solid line with solid circles) and 90° (dashed line with asterisks), are shown in figure 3(a). As θ increases from 0° to 90° the energy is lowered and reaches a minimum at $\theta = 90^\circ$, i.e., H_2 prefers to lie parallel to the surface. Figure 3(b) shows the formation energy of H_2 at various azimuthal angles while the molecular axis is kept parallel to the surface. The orientation of the molecular axis along the line connecting the two nearest T1 sites ($\varphi = 0^\circ$) is found to be to the lowest-energy position for H_2 approaching the M2 site of the Si(111) (1×1) surface. This is also where the formation energy for H_2 approaching the Si(111) (1×1) surface is lowest while the bond length of H_2 is kept the same as that of the free H_2 . As the molecular axis prefers to be parallel to the surface and as the T1 site is the chemisorption position for hydrogen atoms, we shall concentrate on the cases where the molecular axis is parallel to the surface and directed to the nearest T1 site.

All the energy curves of the seven surface-approaching paths exhibit the traditional Lennard-Jones form. The well depths for the paths towards the T1 and T4 sites are shallower, with magnitudes of less than 0.3 eV/ H_2 . The well depth of the path toward the M2 site is 0.6 eV/ H_2 (figure 4)—this is the deepest of the seven energy curves. These energy minima were evaluated with the constraint of a fixed H_2 bond length as stated above. It was found that at these energy-minima positions, the H_2 were subject to elongation forces. With the height from the surface (z) fixed at the minimum-energy positions, the bond lengths of the H_2 were increased to investigate the possible dissociation path. Except for in the case of H_2 on the M2 site, energy barriers had to be overcome in the dissociation process.

From the above discussion, the most probable dissociative path of H_2 on the Si(111) (1×1) surface would be that of the molecule on the M2 site with the molecular axis parallel to the line connecting the two nearest T1 sites. Note that the M2 site is a saddle point of

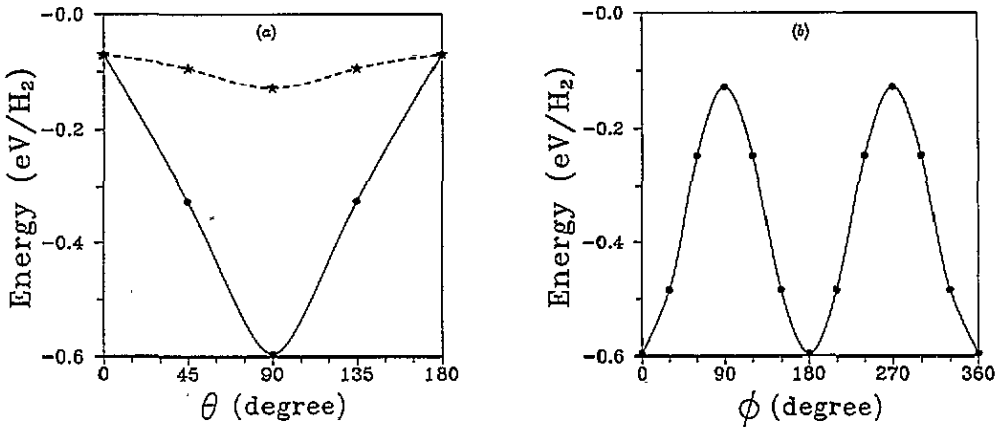


Figure 3. The formation energy of H₂ at different orientations on the M2 site. (a) H₂ at the fixed azimuthal angles $\phi = 0^\circ$ (solid line with solid circles) and 90° (dashed line with asterisks). (b) H₂ at the fixed polar angle $\theta = 90^\circ$.

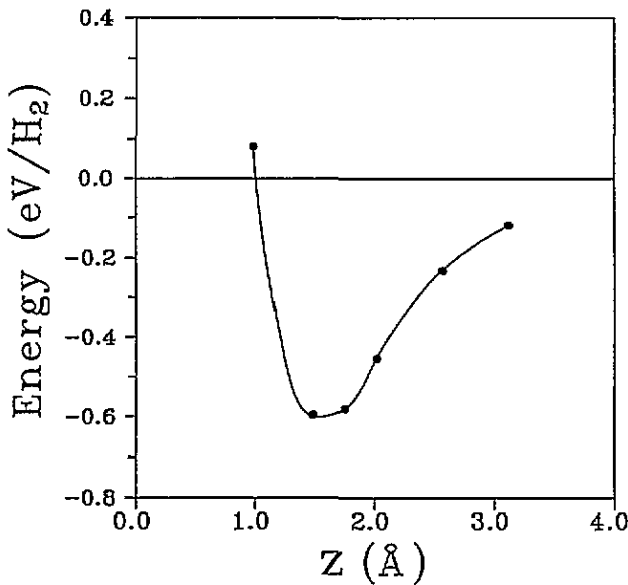


Figure 4. The energy curve of H₂ approaching the M2 site of the Si(111) (1 × 1) surface while the molecular axis is directed to the two nearest T1 sites (see figure 1). The bond length of H₂ is fixed at the bond length of free H₂.

the PES for H atoms moving on the surface. The molecule will dissociate into two hydrogen atoms and to be chemisorbed to the two nearest T1 sites on the surface. This PES, $V(z, d)$, of the dissociative chemisorption of hydrogen molecules on the M2 site was evaluated and is presented in figure 5. The formation energies of H₂ at 58 different (z, d) were calculated for this plot. Because of the limitation of the CPU time, these calculations were done at energy cut-offs of 8 Ryd, and nine k points in the first Brillouin zone were included. To check the accuracy of the PES, calculations of energy cut-offs up to 12 Ryd were made for

some selected configurations. The energies are all raised and the raised energy varies from 0.1 eV/H₂ for $d = 0.83$ Å to 0.2 eV/H₂ for $d = 3.82$ Å. As the well of the PES is around 2.3 eV, increasing the energy cut-offs from 8 Ryd to 12 Ryd therefore only made the well of the PES shallower by 4%. The main characteristics of the PES were retained for calculations with higher energy cut-offs.

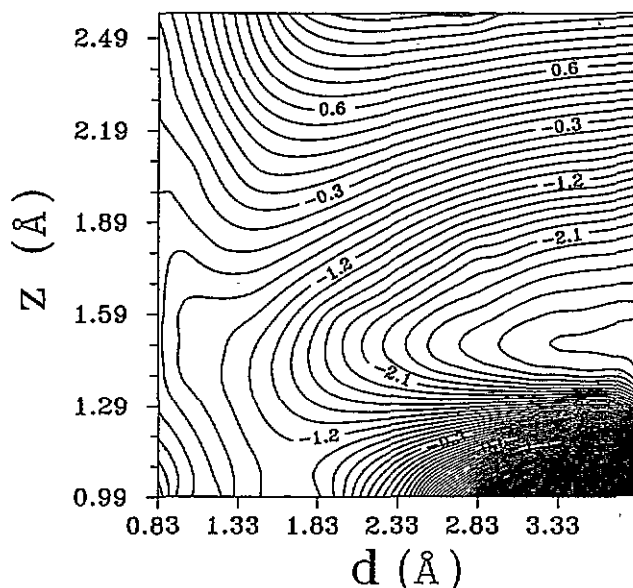


Figure 5. The contour plot of the two-dimensional PES $V(z, d)$ for H₂ approaching the M2 site of the Si(111) (1 × 1) surface. The molecular axis is directed to the two nearest T1 sites.

In the whole process of H₂ approaching the surface with the fixed bond length of free H₂, the H₂ were subject to elongation forces. As the H₂ comes closer to the surface, the forces become stronger. If the molecular bond length is forced to increase when the H₂ is at a fixed height from the surface, the H₂ will finally be dissociated into two hydrogen atoms. In this process, the atomic forces (the components along the direction of the molecular axis) on H reach zero twice before dissociation, once corresponding to the minimum in formation energy (and at which the equilibrium bond length of H₂ at the fixed height from the surface is defined) and once corresponding to the top of the energy barrier. As the height of H₂ is lowered, the equilibrium bond length of H₂ is increased and the barrier lowered. When H₂ reaches the minimum of the formation energy curve (figure 4) of the surface-approaching path, the barrier disappears and the H₂ is dissociated directly to the T1 sites. Investigations show that the interatomic bond strength of H₂ is weakened by the interaction of H₂ and the surface, which leads to a larger bond length when H₂ is closer to the surface and finally to direct dissociation (Wu and Cheng 1994b). In Monte Carlo simulations of dissociative chemisorption (Rice *et al* 1987), it was reported that there was an activation energy of about 0.18 eV in the chemisorption process of H₂ on the unreconstructed Si(111) surface. However, the results of the simulation depend on the interacting potential energy surface of the molecule and surface, which were not constructed *ab initio*.

In conclusion, we have carried out first-principles calculations to investigate the interaction of hydrogen molecules with the Si(111) (1 × 1) surface. Firstly, we found that

H₂ favours having the molecular axis parallel to the surface. Secondly, the orientation of the molecule has little effect on the formation energy of H₂ approaching the high-symmetry sites of the surface. Most importantly, a direct dissociative chemisorption process was found for H₂ on the Si(111) (1 × 1) surface.

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