Theory of Adsorption and Desorption of H_2 Molecules on the Si(111)-(7 × 7) surface

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The physics of adsorption and desorption of H_2 molecules on the Si(111)-(7 × 7) surface is investigated through first-principles density functional theory calculations. The calculated adsorption and desorption energy barriers are 0.8 and 2.4 eV, respectively. The process of adatom *backbond breaking* is identified as the fundamental microscopic mechanism determining the adsorption energy barrier and the kinetic energy of the desorbed H_2 molecule. These results shed light on controversial experimental findings for this classic surface–molecule system. [S0031-9007(97)04863-1]

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The interaction of molecules with solid surfaces is a subject of great practical and theoretical interest. It is the essence of surface catalysis and it represents one of the most challenging problems to theory, because of the complexity of the systems involved and the wide variety of possible outcomes. Typically, such phenomena are studied on metal surfaces which have spatially extended electronic states that can be shared easily with molecular states, thus affecting drastically the structure of the molecule when it is in the vicinity of the surface [1,2]. There exists a different class of systems, namely surfaces of covalent solids, where the surface electronic states tend to be spatially localized and provide a different perspective into the physics of surface–molecule interactions. Experimental studies of such systems have proliferated recently [3–5], while in most cases a detailed understanding of the microscopic phenomena, such as adsorption and desorption mechanisms, is lacking except for some empirical model studies [6]. In this Letter we report a theoretical investigation of a classic covalent surface–molecule interaction, and demonstrate a novel effect, whereby the localized dangling bonds on the semiconductor surface "bend toward" the incoming molecule to facilitate its dissociation.

One of the most interesting equilibrium structural patterns of a covalent solid is the Si(111)-(7 × 7) dimer-adatom-stacking fault (DAS) surface reconstruction [7] (Fig. 1). The complexity of this structure reflects the extensive atomic rearrangement that the system undergoes in order to minimize the number of broken covalent bonds on the surface without introducing excessive strain. Even after this elaborate reconstruction, there remain a number of dangling bonds, of which seven are inequivalent types. The simplest chemical probe of this surface is atomic hydrogen [3,8], and the simplest molecule that reacts in nontrivial ways with this surface is the H_2 molecule. Despite our relatively good understanding of H-H bonding and Si-H bonding, at present there exists no detailed microscopic picture of the adsorption and desorption processes of H_2 on the Si(111)-(7 × 7) surface. In fact, H_2 adsorption and desorption experiments have produced controversial results concerning the adsorption energy barrier. Adsorption experiments at room temperature give a very small H_2 sticking coefficient, indicating the presence of a significant adsorption energy barrier, and the reported activation energy of H_2 adsorption is 0.9 ± 0.1 eV [4]. On the other hand, a low coverage desorption experiment has shown the H_2 desorption energy barrier to be 2.4 ± 0.1 eV [9], while measurements of the kinetic energy indicate that the desorbed H_2 experiences a very small energy barrier of 0.1 ± 0.1 eV [5]. The desorption kinetics has also indicated the presence of two different surface sites from which the two H atoms, forming the H_2 molecule, are dissociated [9].

Here, we report the results of an extensive and accurate theoretical investigation on the dissociative interaction of the H_2 molecule with the Si(111)-(7 × 7) surface. We have identified a fundamental microscopic mechanism associated with the adsorption and desorption processes which resolves the controversy of the adsorption energy barrier.

H_2 adsorption energy.—In Fig. 1 we show a ball-and-stick representation of the (7 × 7) reconstruction, with a side view of a (7 × 7) unit cell. As far as adsorption and desorption of H_2 molecules are concerned, an important consideration is the relative position of pairs of dangling bond sites, to which H atoms can bind upon adsorption of the H_2 molecule or from which H atoms can detach in order to form a desorbing molecule. There are three basic types of dangling bond sites on the surface: the adatom
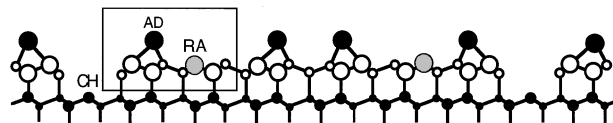

FIG. 1. Ball-and-stick model of the Si(111)-(7 × 7) reconstruction (a side view along the long diagonal of the unit cell). AD, RA, and CH indicate the adatom (large black dots), rest atom (large gray dots), and corner hole sites. The rectangular box indicates the region used to display valence charge densities in Fig. 2.
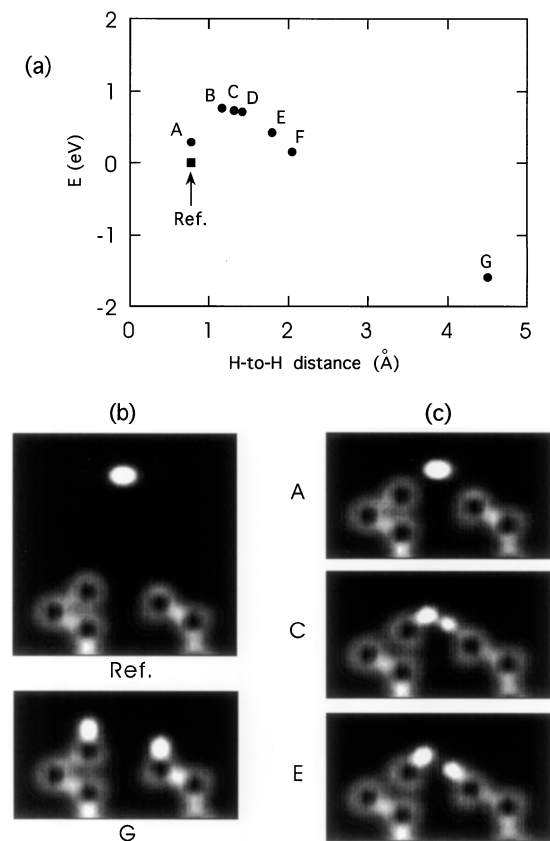

FIG. 2. (a) Total energy relative to the reference state (with the center of the H_2 molecule situated at 7 Å above the surface) along the reaction coordinate of H_2 dissociation (represented by the H-to-H distance). Configurations labeled "Ref." and G correspond to the top (reference) and bottom panels of (b), and A through F correspond to panels of same label in (c). (b) Cross-sectional plots of the total valence charge density in the vertical plane corresponding to the box in Fig. 1. Top panel shows the adatom site on the lower left side and the rest atom site on the lower right side. The H-H covalent bonding charge is shown as a white ellipse in the upper part of the panel. The bottom panel shows two H-Si covalent bonds at the AD and RA sites. (c) Cross-sectional plots of the total valence charge density in the same plane as in (b). Panels A, C, and E correspond to the H_2 breaking states along the reaction coordinate [same labels as in (a)].

(denoted in short by AD), the rest atom (denoted by RA), and the corner-hole atom (denoted by CH). The adsorption energies of a H atom at these sites are calculated to be 2.9 eV at AD, 3.2 eV at RA, and 3.5 eV at CH [8]. Different pairs of dangling bond sites are at various distances, with only the AD-RA pair at a reasonably small distance (4.4 Å) to participate in the adsorption or desorption process (other pairs are at distances larger than 7.6 Å). Considering the equilibrium Si-H and H-H bond lengths (1.54 and 0.76 Å, respectively), under optimal conditions the H-to-H distance in the H_2 molecule would need to increase by only 0.56 Å for the molecule to break and two Si-H bonds to form at the AD-RA pair site. Note that the attachment of the two H atoms at the AD-RA pair

of sites is also consistent with the desorption experiment [9] in which two different surface sites have been invoked to account for the observed desorption kinetics order of 1.5 (i.e., halfway between first and second order kinetics).

To determine the H_2 adsorption energy on the AD-RA pair of sites, we have performed total energy calculations for two H atoms adsorbed on the AD-RA sites. The computational details are as in previous papers [8,10]. The accuracy of the calculations is 0.1 eV. The calculated H_2 adsorption energy is 1.6 eV, which is equal to the ideal adsorption energy (i.e., the energy obtained from two separate H atom adsorption energies at AD and RA sites: $[2.9 + 3.2 - 4.5]$ eV, where 4.5 eV is the H-H binding energy), indicating that nonlocal interaction between the AD and RA sites is negligible. This is to be contrasted with the AD-CH pair, for which the calculated H_2 adsorption energy is 2.1 eV, corresponding to a nonlocal interaction energy of 0.2 eV (the ideal adsorption energy in this case is $[2.9 + 3.5 - 4.5]$ eV $= 1.9$ eV).

H_2 adsorption energy barrier.—The most important physical quantity for adsorption is the energy barrier involved in the breaking of the H_2 molecule on the surface. To determine the adsorption pathway and the corresponding adsorption energy barrier in going from the initial to the final configurations, which are shown in the cross section in Fig. 2(b), we have performed extensive calculations for various positions of the H atoms in the vicinity of the AD-RA pair of sites. For these calculations, we use a simpler (4×4) surface unit cell which includes four adatom sites and four rest atom sites in the same (2×2) local arrangement as on the (7×7) unit cell. This allows a more extensive exploration of configurational space, which is necessary for accurate determination of the adsorption energy barrier.

We first study the nature of the surface-molecule interaction in which the molecule is moved as a unit and the surface is fully relaxed. As the center of the H_2 molecule is brought toward the surface [above the geometric center of the AD-RA sites, as shown in the top panel of Fig. 2(b)] from a height of 7 Å to a height of 3 Å, the total energy change is negligibly small (less than 0.01 eV), indicating that in this range of distances from the surface the H_2 molecule is very inert, similar to a He atom. As the molecule is brought closer to the surface, a repulsive interaction gradually increases the energy by 0.3 eV at 1.5 Å above the AD-RA geometric center. The energy remains constant as the center of the molecule is further lowered by 1.5 Å down to the geometric center of the AD-RA pair. When the molecule is placed 1.5 Å above the individual AD or RA sites and the system is fully relaxed, the interaction is still repulsive, leading to an increase of the energy by 0.2–0.3 eV, relative to the energy of the molecule in the vacuum. This shows that there is a significant repulsive interaction between a H_2 molecule and the Si(111) surface. Given the inability of the present calculations to capture van der Waals

interactions, we surmise that in the absence of such interactions there would be *no surface physisorbed states* for a H_2 molecule before its dissociation.

We next consider the dissociative adsorption process of a H_2 molecule. A detailed description of the dissociation pathway is given in Fig. 2. Figure 2(a) shows the total energy of the system relative to a reference configuration which corresponds to the H_2 molecule in the vacuum [top panel of Fig. 2(b)]. Initially, the H_2 molecule is placed 0.7 Å above the AD-RA geometric center, and the molecule is constrained to be in a plane perpendicular to the surface, which includes the AD and RA sites, indicated by the box in Fig. 1. The axis of the molecule is parallel to the line connecting the AD and RA sites. The whole system is then fully relaxed under the single constraint that the horizontal component of the center of mass of the H_2 molecule is fixed (the relaxation of this constraint would introduce a small energy change estimated to be smaller than 0.02 eV). The energy of the relaxed configuration corresponds to the point labeled A in Fig. 2(a). The points labeled B-F correspond to a successive increase of the H-to-H horizontal distance, while for each value of this distance the H atoms are relaxed vertically and the surface Si atoms are fully relaxed. The point labeled G corresponds to the final state of adsorption with the two H atoms attached to the AD and RA sites as shown in the bottom panel of Fig. 2(b).

This calculation gives an adsorption energy barrier of 0.8 eV. As the H-to-H distance increases by 0.4 Å (from configuration A to configuration B), the H-H bond starts to break, and this process increases the total energy by 0.8 eV. From B to D, the two H atoms are in the process of forming Si-H bonds while the H-H bond is being broken. The energy curve is very flat in going from configuration B to configuration D (corresponding to a 0.25 Å increase of the horizontal H-to-H distance). Apparently, the two processes compensate each other over the range of a 0.25 Å change in the H-to-H distance, leading to the flat energy curve. The cross-sectional plots of the total valence charge density in Fig. 2(c) clearly indicate the simultaneous breaking of the H-H bond and formation of the two Si-H bonds. The total energy in going from configuration D to configuration G in Fig. 2(a) is monotonically decreasing. For this part of the process, the H-H bond is already broken [see panel E in Fig. 2(c)], and the total energy decreases as the Si-H bonds are being formed.

The charge density plots in Fig. 2(c) also provide an important clue for understanding the detailed behavior of surface atoms and surface dangling bonds during the adsorption process. Panels C and E suggest that the adatom backbonds are significantly weakened, and the adatom is moved toward the dissociating H_2 molecule. Note that once one of the adatom backbonds is broken, the adatom is free to pivot at the remaining two backbonds, as schematically shown in Fig. 3. This backbond breaking is also involved in the adatom surface diffusion process, and the corresponding energy barrier is 0.8 eV. The following picture of the microscopic mechanism of the adsorption process emerges: As thermal fluctuations provide enough kinetic energy to the adatom to overcome the 0.8 eV activation energy of breaking the backbond, the adatom can move closer to the RA site so that the incoming H_2 molecule can begin to form two Si-H bonds without significantly increasing the H-to-H distance. At this configuration the Si(AD)-H, H-H, and Si(RA)-H bonds are all reasonably close to their equilibrium bond lengths, and the H_2 molecule dissociation is induced without a very high energy cost. After the adsorption process is completed, the adatom backbonds are restored to their original state, as shown in the bottom panel of Fig. 2(b).

H_2 desorption.—The desorption process of H_2 on the Si(111) surface is not necessarily the reverse of the adsorption process since the initial state of the desorption depends on the surface conditions. It is possible that the
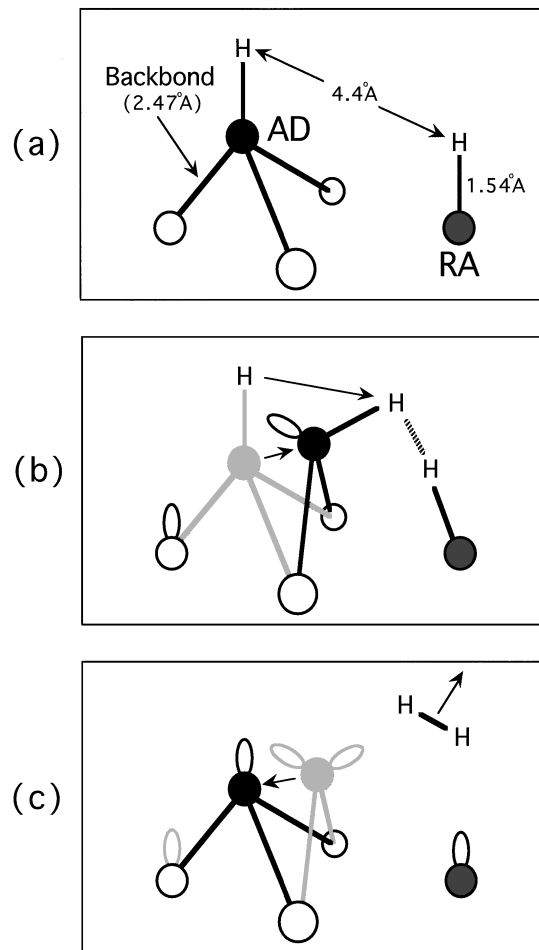

FIG. 3. Schematic illustration of the H_2 desorption process: (a) The adatom backbond length, Si-H bond length, and H-to-H distance. (b) The breaking of one adatom backbond and the motion of the adatom which brings two H atoms close to the H-H bonding distance. (c) The desorption of the H_2 molecule and the subsequent reformation of the broken adatom backbond.

H atom surface coverage and surface diffusion kinetics do not allow two H atoms to reach a configuration equivalent to the final state of the adsorption process. At low H coverage (Θ) of the Si(111)-(7 × 7) surface, the adsorbed H atoms will first occupy CH sites until they are saturated at 0.02 monolayer (ML) coverage (1 ML is defined to be one H atom per (1 × 1) surface unit area). For the coverage range $0.02 < \Theta < 0.14$ ML, the H atoms will gradually saturate the RA sites, and for $0.14 < \Theta < 0.39$ ML the AD sites will be saturated. For $\Theta = 0.39$ ML, all the dangling bonds on the (7 × 7) surface are saturated so, for $\Theta > 0.39$ ML, the H atoms will begin to destroy the (7 × 7) reconstruction and thereby create additional sites for saturation.

It is evident that the initial state for H_2 desorption depends on the H atom surface coverage. For the range $0.14 < \Theta < 0.39$ ML, the desorption process will be the reverse of the adsorption process since two H atoms can always be found at neighboring AD and RA sites. For the range $0.02 < \Theta < 0.14$ ML, the H atoms on the RA sites need to diffuse close to an AD site before the desorption can follow the reverse path of the adsorption process. The H atom diffusion barrier on the Si(111) surface is experimentally measured to be 1.5 eV [11]; a recent total energy calculation using a (4 × 2) surface unit cell has shown that the energy barrier for H atom diffusion from a RA site to an AD site is about 1.3 eV [12]. Since this diffusion barrier is much smaller than the experimental desorption energy barrier of 2.4 eV, H atom diffusion to AD sites will occur readily before desorption, so that the desorption process will be again the reverse process of the adsorption process. Finally, for $\Theta < 0.02$ ML, H atoms need to diffuse out of the corner hole sites before two H atoms can meet for desorption. This diffusion process is likely to have an energy barrier larger than 2.4 eV since it involves the breaking of Si-H bonds at CH sites, which have a binding energy of 3.5 eV. In this case the diffusion of H atoms from the CH sites would be the rate limiting process.

Thus, for H coverage in the range $0.02 < \Theta < 0.39$ ML, the H_2 desorption process will follow the reverse path of the H_2 adsorption process, as illustrated schematically in Fig. 3. From (a) to (b), the adatom backbond, indicated by an arrow in Fig. 3(a), is broken, which requires an activation energy of 0.8 eV. In (b), two H atoms are close to the equilibrium H-H bond distance so that only 1.6 eV extra energy is required to break two Si-H bonds and to form the H-H bond. The desorption energy barrier is then simply the sum of the adsorption energy and the adsorption energy barrier, i.e. $[1.6 + 0.8 = 2.4]$ eV. This value is in good agreement with the experimental measurement of desorption for low H coverage (2.4 eV at $\Theta = 0.15$ and 0.08 ML [9]). After desorption, the surface adatom is left in a high energy state with a broken backbond, and the H_2 molecule leaves the surface without much kinetic energy as shown in Fig. 3(c). This process explains both the small kinetic energy of the desorbed H_2 molecule and the mechanism of the surface dynamics leading to a 0.9 eV activation energy for the adsorption, and therefore resolves the controversy on the adsorption energy barrier.

Note added.—After submitting this paper, we have found that a similar H_2 adsorption mechanism was proposed by Bratu *et al.* [13] based on a heurstic argument.

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