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Adsorption processes of hydrogen molecules on SiC(001), Si(001) and C(001) surfaces

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Abstract. Adsorption processes of hydrogen molecules on the Si(001)-(2 × 1) and C(001)-(2 × 1) surfaces are discussed in light of our previous studies of H₂ adsorption on the related SiC(001)-c(4 × 2) surface. Very amazingly, there are pathways above the latter on which hydrogen molecules can adsorb dissociatively at room temperature. One of these pathways has not been considered before for adsorption of H₂ on the Si(001)-(2 × 1) or C(001)-(2 × 1) surface. Therefore, we report first-principles investigations of the reaction of molecular hydrogen with the Si(001)-(2 × 1) and C(001)-(2 × 1) surfaces on this new adsorption pathway in addition to those that have been studied before. In spite of a number of similarities, the three surfaces show distinct differences as well, giving rise to spectacularly different reactivities with hydrogen molecules. This is due to the fact that the reaction of H₂ with semiconductor surfaces depends crucially on intricate combined effects of the arrangement of surface dimers, as well as the orientation of their dangling bond orbitals. In addition, the chemical nature of the surface atoms has a pronounced effect on the spatial extent of dangling bond orbitals which influences the adsorption behaviour markedly as well. In agreement with experiments, our results show that Si(001)-(2 × 1) and C(001)-(2 × 1) are inert to H₂ adsorption at room temperature for all investigated pathways which exhibit substantial energy barriers. For the two reaction pathways that have been investigated before, our results are in good accord with those of previous density functional and quantum Monte Carlo (QMC) calculations. As a matter of fact, the new reaction channel studied in

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this work for the first time turns out to have the lowest energy barrier for H\textsubscript{2} adsorption on the diamond surface and should thus be the most important channel for sticking of H\textsubscript{2} on C(001)-(2 × 1).

1. Introduction

The interaction of molecular hydrogen with semiconductor surfaces is of high fundamental interest as well as of technological relevance, e.g. for surface etching and passivation or crystal growth. In theory, it serves as a role model to understand surface reactivity since H\textsubscript{2} is the simplest molecule with a well-known electronic structure. Nevertheless, adsorption and desorption processes of H\textsubscript{2} on group IV semiconductor surfaces are still a matter of vivid experimental and theoretical interest ([1] and references therein). Usually, semiconductor surfaces are considered to be inert to dissociative H\textsubscript{2} adsorption at room temperature because of the large energy needed (about 4.5 eV) to break the molecular H–H bond. For example, the sticking probability of H\textsubscript{2} on an atomically flat Si(001) surface is extremely low at room temperature [2, 3]. Contrary to this general notion, the very amazing observation has been made that hydrogen molecules readily adsorb dissociatively on the group IV compound semiconductor surface SiC(001)-c(4×2) at room temperature [4]. We have been able to clarify this very startling effect by investigating a number of reaction scenarios of H\textsubscript{2} with the SiC(001)-c(4×2) surface [5]. In the course of that work a new reaction pathway that had not been addressed for H\textsubscript{2} adsorption on the Si(001) or C(001) surface before turned out to be of particular interest. It allows for barrierless H\textsubscript{2} adsorption on SiC(001)-c(4×2) explaining the experimental observations [4]. Therefore, it appears expedient to consider this pathway for H\textsubscript{2} adsorption on Si(001) and C(001), as well.

The Si(001)-(2×1), C(001)-(2×1) and SiC(001)-c(4×2) surfaces are all characterized by similar surface dimers which are spatially arranged in closely related patterns. Thus, the structure of the Si(001)-(2×1) surface shows considerable resemblance to that of the SiC(001)-c(4×2) surface. On the basis of our results for H\textsubscript{2} adsorption on the latter [5] one might wonder why H\textsubscript{2} does not adsorb dissociatively on Si(001)-(2×1) at room temperature. This contrast
between the apparent geometrical similarity of both surfaces and their drastically different reactivity with $H_2$ calls for an explanation. Likewise, the structure of the C(001)-(2 $\times$ 1) surface also shows close resemblance to that of SiC(001)-c(4 $\times$ 2). Therefore, it could be expected that $H_2$ should adsorb dissociatively on C(001)-(2 $\times$ 1), as well. But experiment, as far as we know, has never found any evidence for dissociative $H_2$ adsorption on C(001)-(2 $\times$ 1) at room temperature. One might guess that the lack of dissociative adsorption of $H_2$ on Si(001) is simply due to the relatively large lattice constant of Si which is about 25% larger than that of cubic SiC. But if so, that raises the question of why $H_2$ does not adsorb dissociatively on C(001) at room temperature, although the diamond lattice constant is some 18% smaller than that of SiC.

The reaction of $H_2$ with the Si(001) surface has theoretically been studied in detail before [6]–[13]. Its reaction with the C(001)-(2 $\times$ 1) surface, to the best of our knowledge, has been addressed only by Okamoto [12], to date. In all of these studies, only two pathways have been considered. To contribute to a more complete understanding of the spectacularly different reactivities of $H_2$ with the Si(001)-(2 $\times$ 1) and C(001)-(2 $\times$ 1) surfaces, as compared to SiC(001)-c(4 $\times$ 2), we have investigated the three most conceivable reaction pathways of $H_2$ on Si(001)-(2 $\times$ 1) and C(001)-(2 $\times$ 1) by systematic first-principles calculations. Relating our new results to our earlier findings [5] for $H_2$ adsorption on SiC(001)-c(4 $\times$ 2) allows us to gain a better perspective of the peculiar reactivity differences of the three considered surfaces. This appears particularly revealing with Si and C being the constituents of the ionic group IV compound semiconductor SiC. We restrict ourselves to the low-coverage regime of $H_2$.

In section 2, we summarize the calculational procedure. Our results are then presented in section 3. We first briefly address some general aspects of $H_2$ reaction in section 3.1 which apply to all substrate surfaces considered in this work, alike. These general notions are exemplified using our results on the SiC(001)-c(4 $\times$ 2) surface in section 3.2. Then, we address $H_2$ adsorption on Si(001)-(2 $\times$ 1) in section 3.3 and show that the interdimer reaction channel investigated in this work for the first time is energetically less favourable than the optimal adsorption channel identified before. In section 3.4, we investigate adsorption of $H_2$ on the C(001)-(2 $\times$ 1) surface. It turns out that $H_2$ does not adsorb dissociatively on C(001)-(2 $\times$ 1) at room temperature, in spite of the considerably smaller lattice constant of diamond, as compared to SiC. The physical origin of this astonishing behaviour is elucidated. In particular, we find that the new reaction channel is the most favourable for $H_2$ reaction with the C(001)-(2 $\times$ 1) surface. In section 4.1, we compare our results for the different surfaces with one another and with theoretical results from the literature. Finally, in section 4.2, we address adsorption reaction and desorption energies in comparison with experimental data which appear to be available only for $H_2$ on Si(001)-(2 $\times$ 1).

2. Calculational method

The calculations are carried out within density functional theory (DFT) using the generalized gradient approximation (GGA). We employ nonlocal, norm-conserving pseudopotentials in separable form, Gaussian orbital basis sets with appropriately determined decay constants, and the exchange–correlation functional of Perdew and Wang [14]. The surface systems are treated within the supercell approach with slabs of six atomic layers per supercell saturated by a hydrogen layer at the bottom. The reaction of $H_2$ with the surfaces is studied at and above the top layer. Neighbouring slabs are separated by a vacuum layer of more than 10 Å thickness.
In the structure optimizations, we fix the two lowest atomic layers and the saturating H bottom layer per slab. The other four substrate layers and the reacting H\textsubscript{2} molecule are allowed to fully relax. To explore reaction pathways, we apply the nudged elastic band (NEB) method [15]. This technique determines a minimum energy path (MEP) by constructing a set of replicas or images of the system between an initial and a final state which correspond to different positions of H\textsubscript{2} along its pathway. We have used eight replicas within the climbing image algorithm [16] where an image is driven to climb up along a path to the saddle point. A MEP is thus a path of minimum local energy that connects the initial and final states in configuration space. More calculational details can be inferred from our previous work on adsorption of molecular [5] and atomic [17] hydrogen at SiC(001) surfaces.

3. H\textsubscript{2} adsorption on group IV semiconductor surfaces

We briefly comment on a few general aspects of H\textsubscript{2} adsorption processes on group IV semiconductor surfaces before we address H\textsubscript{2} adsorption on the SiC(001)-c(4 × 2), Si(001)-(2 × 1) and C(001)-(2 × 1) surfaces, respectively.

3.1. General aspects

All substrate surfaces addressed in this work are characterized by surface dimers which have different distances at the different surfaces and the localization of their dangling bond orbitals is unequally strong. In general, the H\textsubscript{2} adsorption process is accompanied by two counteracting effects. One involves an energy loss which is due to stretching and breaking of the H\textsubscript{2} molecular bond and a displacement of the substrate surface atoms from their equilibrium positions. The other involves an energy gain which results from the interaction of the surface dangling bonds with the antibonding states of the H\textsubscript{2} molecule eventually giving rise to the formation of two new H—Si or H—C bonds, respectively. Of course, the bond energy of two H—Si or H—C bonds is larger than that of one H—H bond. For the adsorption process to actually take place, however, the H atoms in the molecule have to be able to come close enough to the dangling bonds of the surface dimer atoms so that breaking of the H—H molecular bond and formation of two new H—Si or H—C bonds can occur simultaneously. Whether it happens at all depends very much on the arrangement of the surface dimers, as well as on the orientation and spatial extent of their dangling bonds. In general, it is most advantageous for dissociative adsorption of H\textsubscript{2} if the dimer distance is small enough and the dangling bonds of the involved Si or C dimer atoms point towards the H\textsubscript{2} molecule approaching the surface. In addition, the chemical nature of the dimer atoms should be such that the dangling bonds have a sufficiently large spatial extent to allow for an efficient interaction between H\textsubscript{2} and the dangling bonds at the substrate surface. In this latter respect, there is a significant difference between C and Si atoms and their related surface dangling bonds. A carbon atom is much smaller than a Si atom, as evidenced by their covalent radii of 0.77 and 1.17 Å, respectively, and a carbon dangling bond at C(001)-(2 × 1) is much more localized than a Si dangling bond at the Si(001)-(2 × 1) surface [18]. This fact also becomes most evident by the bond lengths of H—C and H—Si bonds which amount to 1.1 and 1.5 Å, respectively. Therefore, a hydrogen molecule has to come much closer to a carbon than to a Si dimer before it can efficiently interact and dissociate.
Figure 1. (a) Top and side views of the AUDD model of SiC(001)-c(4\times2). The unit cell is shown by the dashed diamond. Top layer Si atoms (labelled 1–5) are shown by orange balls. The C atoms in the side view are shown by light green balls. Initial state H\(_2\) positions on the different pathways considered (H atoms denoted by small black balls) are schematically indicated by A–D. Adsorption of one H\(_2\) molecule per 4\times2 surface area corresponds to a H coverage of 0.25 monolayers. (b) Total energy profiles, referred to a free H\(_2\) molecule and the clean reconstructed c(4\times2) AUDD surface, along interdimer pathway A (red triangles) and intradimer pathway B (blue dots). The ‘reaction coordinates’ 0 and 9 refer to the final (two H atoms adsorbed) and initial (H\(_2\) in vacuum) states, respectively. Lines are drawn to guide the eye. The insets (side views) show snapshots of the surface atom configurations at ‘reaction coordinate’ 5 on pathways A and B, respectively.

3.2. SiC(001)-c(4 \times 2) surface

The above general notions are nicely borne out by our results for H\(_2\) adsorption on the SiC(001)-c(4 \times 2) surface [5]. Two structural models are currently considered as the most favourable reconstructions for this surface. One is the alternately up and down dimer (AUDD) model [19] and the other is the missing-row asymmetric dimer (MRAD) model [20]. Here, we concentrate on the AUDD model for simplicity. Top and side views of the model, as resulting from our structure optimization, are shown in figure 1(a). Neighbouring atoms in the surface layer form symmetric Si dimers, half of which are long (2.72 Å) residing slightly above (up-dimers) and half of which are short (2.37 Å) residing slightly below (down-dimers) the ideal surface plane, respectively. Since each long dimer has four short neighbouring dimers and vice versa, the dimer arrangement has c(4 \times 2) symmetry. Yet, it is closely related in effect to a 2 \times 1 surface especially with respect to low-coverage H\(_2\) adsorption.

We have investigated four different reaction pathways A–D with H\(_2\) in respective initial state positions in vacuum above the surface as indicated in figure 1(a). In the calculations, we use 4 \times 2 unit cells to reduce the interaction between neighbouring molecules. In the corresponding
Figure 2. Contours of the total valence charge density on pathway A for H$_2$ adsorption on SiC(001)-c(4 × 2). H, Si and C atoms are shown by black, orange and light green balls, respectively. Figures (a), (b) and (c) show the charge densities for the initial, an intermediate and the final state, respectively.

final states, the H atoms eventually bind to the dangling bonds of the nearest-neighbour Si dimer atoms. On pathways A and C the molecule initially resides in vacuum between two neighbouring Si dimers, whereas on pathways B and D it resides above a single Si dimer. The former are usually referred to as interdimer and the latter as intradimer pathways. We label pathways by the initial state positions of H$_2$ in the following and refer to them as pathways A–D, respectively. Note that pathways A and C are characteristically different, whereas pathways B and D are similar because the long and short Si dimers are not drastically different in length and height. Total energy profiles along minimum energy pathways A and B, as calculated using the NEB method, are shown in figure 1(b). They exhibit distinct differences whose physical origins we address next.

The distance between Si surface atoms 1 and 2 involved in pathway A is 3.83 Å and their dangling bonds on both dimer atoms point towards the approaching H$_2$ molecule. As a result, the total energy decreases monotonically when H$_2$ approaches the surface on pathway A which connects the initial and final states without an energy barrier (see figure 1(b)). The molecule is attracted continually to the surface and its bond is continuously stretched until it finally breaks. At the end of this process, the released H atoms adsorb on the previously unsaturated dangling bonds of Si atoms 1 and 2 forming strong H—Si bonds with a typical bond length of 1.5 Å.

The characteristic properties of this process are also clearly revealed by the evolution of the total valence charge density of the system during the approach of the molecule to the surface, as shown for pathway A in figure 2 for the initial (a), an intermediate (b) and the final (c) state. In the initial state, the two involved Si dimers have different lengths and reside at different heights above the surface and the charge density of the molecule shows only marginal interaction with the nearest-neighbour Si atom in the up-dimer (see figure 2(a)). In the intermediate state
(figure 2(b)), the molecule has been able to come close enough to the surface to strongly increase its interaction with the dangling bonds of the nearest-neighbour Si atoms on the two neighbouring dimers. The dimers start to relax accordingly and the bond length of the molecule has been stretched from its vacuum value of about 0.78 Å resulting within DFT–GGA, to about 1.08 Å. Concomitantly, the H–H molecular bond has become weakened (cf figures 2(a) and (b)). In addition, the molecule has become slightly tilted because the two neighbouring dimers reside initially at slightly different heights. In this intermediate state, the overlap between the charge densities of the molecule and the substrate has become so large that H–H bond breaking and H–Si bond formation can occur simultaneously when the molecule moves further down to the surface. It can do so because the system continuously gains energy on this pathway (see figure 1(b)). Eventually, the molecule dissociates and the two released H atoms form two strong H–Si bonds in the final state as is evident in figure 2(c). Concomitantly, both surface dimers have become oppositely buckled and they attain very similar bond lengths of 2.49 and 2.51 Å, respectively.

It thus turns out that the small lattice constant of SiC giving rise to a relatively small interdimer distance and allowing for a very close approach of the molecule to the surface on a monotonically decreasing MEP during reaction is vital for dissociative adsorption of H₂ to happen. The fact that the dangling bonds of the involved dimer atoms point towards the molecule makes pathway A very favourable for dissociative H₂ adsorption, in addition. The MEP of interdimer pathway C (not shown in figure 1(b)) also turns out to be barrierless, although the involved dimer dangling bonds are orthogonal to the molecular axis so that they do not point initially towards the approaching molecule. Due to the small lattice constant of SiC, however, the distance of the involved Si atoms 3 and 5 is as small as 3.09 Å and the Si dangling bonds are sufficiently extended so that an efficient attractive interaction of the molecule with the surface can take place along the whole pathway C, as well. We note in passing that H₂ can also adsorb dissociatively on a barrierless pathway on the c(4 × 2) MRAD reconstruction of the SiC(001) surface [5]. Thus, our results show that H₂ can reach the SiC(001)-c(4 × 2) surface from vacuum on barrierless minimum energy pathways and adsorb dissociatively by interdimer adsorption explaining why H₂ abundantly adsorbs on SiC(001)-c(4 × 2) at room temperature, as observed in the experiment [4].

Both intradimer pathways B and D, on the contrary, exhibit reaction barriers of 0.37 eV due to the fact that the dangling bonds on the involved Si dimer atoms point away from the approaching molecule (see the inset B₅ in figure 1(b)). As a consequence, large bond-bending forces would have to be exerted on the dangling bonds for adsorption to happen which is very detrimental for an efficient interaction between the molecule and the surface. The minimum energy pathway B in figure 1(b) clearly exhibits the energy barrier related to the transition state which has to be surmounted during adsorption. Most of the thermal H₂ molecules in the Maxwell–Boltzmann distribution at room temperature do not have enough energy to achieve this. As a result, our calculations clearly favour interdimer over intradimer adsorption at room temperature. As noted above, pathways B and D are slightly inequivalent because the down-dimer formed by Si atoms 2 and 3 is short and lies below the ideal surface plane, whereas the up-dimer between Si atoms 4 and 5 is long residing slightly above the surface plane. Nevertheless, the pathways exhibit the same barrier height of 0.37 eV because the dimers adopt the same bond length and height relative to the surface in the respective transition states [5]. Note that the H₂ molecule moves basically straight down to the surface until it dissociates on intradimer pathway B (see inset B₅ in figure 1(b)) because the Si dimers are symmetric in the c(4 × 2) AUDD model.
3.3. Si(001)-(2 × 1) surface

Let us now turn to adsorption of hydrogen molecules on the Si(001)-(2 × 1) surface. Top and side views of the dimer arrangement at the surface are shown in figure 3(a). At the clean surface, the dimers are asymmetric having a dimer bond length of 2.31 Å and a buckling angle of 18.4°. They are all tilted in the same direction, as shown in the side view. Their projections onto the surface plane are shown in the top view. The calculated structure parameters of the Si(001)-(2 × 1) and the related SiC(001)-c(4 × 2) surface are summarized in table 1. The distances $d_\parallel$ and $d_\perp$ in the table are the actual and not the surface-projected atom distances, as indicated in figure 3(a). Note that the dimer distances $d_\parallel = 5.57$ Å and $d_\perp = 3.86$ Å at the Si(001)-(2 × 1) surface are considerably larger (by 1.74 and 0.77 Å, respectively), than the respective dimer distances at the SiC(001)-c(4 × 2) surface.

We have investigated the three highly conceivable but distinctively different reaction pathways $A$, $B$ and $C$, as indicated by the initial state positions of $H_2$ in figure 3(a). They are defined as the pathways $A$–$C$ on the SiC(001)-c(4 × 2) surface discussed in section 3.2. In each case, the molecule is dissociated in the final state and the two released H atoms bind to the respective Si dangling bonds, as shown schematically for pathway $C$ in figure 3(b). However,
Table 1. Calculated bulk and dimer bond lengths ($d_b$, $d_d$) and surface atom distances (in Å), as defined in figure 3. The values quoted for SiC(001) from [5] apply to the c(4 × 2) AUDD model.

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Si(001)-(2 × 1)</th>
<th>SiC(001)-c(4 × 2)</th>
<th>C(001)-(2 × 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_b$</td>
<td>2.36</td>
<td>1.89</td>
<td>1.55</td>
</tr>
<tr>
<td>$d_d$</td>
<td>2.31</td>
<td>2.37/2.72</td>
<td>1.38</td>
</tr>
<tr>
<td>$d_1$</td>
<td>5.57</td>
<td>3.83</td>
<td>3.67</td>
</tr>
<tr>
<td>$d_\perp$</td>
<td>3.86</td>
<td>3.09</td>
<td>2.52</td>
</tr>
</tbody>
</table>

Figure 4. Total energy profiles (in electron volt) along minimum energy pathway $A$ (red triangles in (a)), as well as $B$ and $C$ (blue dots and black squares in (b), respectively) for a hydrogen molecule approaching the Si(001)-(2 × 1) surface from vacuum. For further details, see the caption of figure 1.

the molecule might have to pass through a transition state which is accompanied by an energy barrier before the two H atoms of the molecule can eventually reach their final terminal positions at the surface dangling bonds. Total energy profiles on minimum energy pathways $A$–$C$ are shown in figure 4. The slightly different intradimer pathways $B$ and $D$, discussed in section 3.2 for the SiC(001)-c(4 × 2) surface, are fully equivalent at Si(001)-(2 × 1).

In the actual calculations, we use a 4 × 1 unit cell to investigate pathways $A$ and $B$ and a 2 × 3 unit cell to investigate pathway $C$ to avoid interactions between the H atoms when they are adsorbed in the final state in neighbouring unit cells. These interactions are expected to be small in the low-coverage regime of hydrogen [1]. For the 2 × 3 and 4 × 1 unit cells, we use six and eight $k_\parallel$-points in the sums over the surface Brillouin zone, respectively, which turns out to be sufficient for good convergence. Previous studies of H$_2$ adsorption on the Si(001)-(2 × 1) surface have been restricted to pathways $B$ and $C$ but there appears to be no reason to exclude pathway $A$, as is evident in figure 3(a). Since pathway $A$ has turned out to allow for barrierless dissociative H$_2$ adsorption on the SiC(001)-c(4 × 2) surface, as discussed in section 3.2, we consider it for the Si(001)-(2 × 1) surface, as well.

On interdimer pathway $A$, the dimer bonds point towards the approaching H$_2$ molecule, indeed. The distance $d_\parallel = 5.57$ Å between Si atoms 1 and 2, however, is very large due to the
increase of the Si lattice constant by 25%, as compared to SiC. This situation does not allow for a sufficiently strong interaction of the H2 molecule with the surface dangling bonds to give rise to H—H bond breaking and H—Si bond formation at the same time. As a consequence, the total energy profile of pathway A shows an energy barrier of 0.50 eV. The transition state giving rise to this barrier is shown in the inset of figure 4(a).

Intradimer pathway B exhibits an energy barrier as well, amounting to 0.54 eV. The respective total energy profile along minimum energy pathway B is shown in figure 4(b). Note that the transition state, shown as inset B5 in figure 4(b) is now more intricate than the transition state of pathway B on the SiC(001)-c(4 × 2) surface (cf figure 1(b)). The barrier occurs again because the dangling bonds of the Si dimer atoms 2 and 3 do not point towards the approaching molecule, for one reason. In addition, on Si(001)-(2 × 1) the molecule does not move straight down to the surface because the Si dimers are asymmetric. Instead, it first approaches the electrophilic dimer down-atom 2 whose dangling bond is initially empty. In the transition state (inset B5 in figure 4(b)) both H atoms are relatively far away from the dimer up-atom 3 whose dangling bond is fully occupied. Thus, the molecule has to dissociate close to the dimer dangling bond of Si atom 2 before one of the two released H atoms can bind to Si atom 2, whereas the other has to move over to Si atom 3 to become bound to its dangling bond eventually. This process, which has been alluded to already before [8], is not very efficient energetically. It is accompanied by a significant charge rearrangement in the surface dimer, in addition.

While interdimer pathway C is barrierless on SiC(001)-c(4 × 2), it exhibits a barrier of 0.34 eV on Si(001)-(2 × 1), as is evident in the MEP for pathway C in figure 4(b). This appears to merely originate from the increase in the dimer distance $d_{\perp}$ by 0.77 Å, as compared to pathway C on the SiC(001) surface. The energy barrier of 0.34 eV is the lowest of all barriers on Si(001)-(2 × 1), although the involved dimer-dangling bonds are orthogonal to the molecular axis so that they do not point towards the approaching molecule. The distance between Si atoms 3 and 5 on neighbouring dimers along the [110]-direction, however, is in fact only $d_{\perp} = 3.86 \text{ Å}$ (much smaller than $d_{\parallel} = 5.57 \text{ Å}$ on pathway A) and the Si dangling bonds are fairly extended so that the molecule can apparently interact somewhat more efficiently with the surface on pathway C than on pathway A. As a result, the energy barrier of 0.34 eV on pathway C is lower than the barrier of 0.50 eV on pathway A and the barrier of 0.54 eV on pathway B is the highest. Thus, our results favour interdimer over intradimer H2 adsorption also on Si(001) and they corroborate, in particular, that interdimer pathway C is the most favourable channel for H2 adsorption and sticking at the Si(001)-(2 × 1) surface.

3.4. C(001)-(2 × 1) surface

Let us finally address adsorption of hydrogen molecules on the C(001)-(2 × 1) surface. Top and side views of the dimer arrangement at the surface are shown in figure 5(a). The respective bond lengths are given in table 1, as well. In the case of C(001)-(2 × 1), the dimers are all symmetric and lie in the plotting planes. Their spatial arrangement is the same as in the other cases discussed above (see figures 1(a) and 3(a)). The lattice constant of diamond, however, is about 18% smaller than that of SiC and even about 35% smaller than that of Si. Therefore, one might expect that the interdimer distances $d_{\parallel}$ and $d_{\perp}$ are reduced accordingly and are small enough to allow for an efficient H2 interaction with the C(001)-(2 × 1) surface giving rise to barrierless H2 adsorption. However, the situation is more intricate. For one reason, the carbon
dangling bonds are much more localized than Si dangling bonds, as noted before. In addition, the distance $d_{\parallel}$ between C atoms on neighbouring dimers in the [110]-direction is not reduced by 18% but only by 4%, as compared to $d_{\parallel}$ at the SiC(001)-c(4 × 2) surface (see table 1), because the C≡C surface dimers form strong double bonds with a bond length of 1.38 Å, only. These effects have a crucial influence on H$_2$ adsorption at C(001).

Also for the C(001)-(2 × 1) surface, we have investigated the three different pathways A–C as indicated by the initial states in figure 5(a) and by the schematic final state on pathway A in figure 5(b). The corresponding minimum energy pathways for interdimer pathways A and C strongly resemble those on the Si(001)-(2 × 1) surface, whereas the MEP of pathway B on C(001)-(2 × 1) is qualitatively similar to that on the SiC(001)-c(4 × 2) surface, since the dimers are symmetric on both latter surfaces. We therefore refrain from showing minimum energy pathways on C(001)-(2 × 1) for the sake of brevity.

On interdimer pathway A a substantial barrier of 0.66 eV results, in spite of the fact that the mere geometrical distance $d_{\parallel}$ between the two carbon atoms 1 and 2 is 3.67 Å and the dangling bonds on these dimer atoms point towards the approaching molecule. The dangling bonds are, however, strongly localized and their spatial extent is roughly 0.4 Å smaller than that of Si dangling bonds, as noted in section 3.1. Therefore, it becomes intelligible that the effective dangling bond distance turns out to be too large for a very efficient interaction between the molecule and the surface. As a consequence, the interaction of H$_2$ with the surface is rather inefficient giving rise to the significant energy barrier.
On intradimer pathway \(B\), we find an even larger barrier of 1.05 eV, in spite of the relatively small \(\text{C} \equiv \text{C}\) dimer-bond length and the respectively smaller spatial separation of the carbon atoms 2 and 3 involved in adsorption in this case. The dangling bonds on the carbon dimer atoms, however, point away from the approaching molecule and they are strongly localized. In addition, they are highly directional, as is typical for carbon bonds, and are very resistant to bond bending, therefore.

For pathway \(C\), the distance \(d_\perp = 2.52\, \text{Å}\) between carbon atoms 3 and 5 is significantly smaller than the distance \(d_\parallel\) between carbon atoms 1 and 2 on pathway \(A\), indeed. Nevertheless, a large barrier of 1.08 eV results on pathway \(C\) because the carbon dangling bonds are oriented perpendicular to the axis of the approaching molecule. Since they are strongly localized and highly directional, in this case it also costs a considerable amount of energy to bend them towards the approaching molecule. This fact turns out to be counterproductive for an efficient interaction of \(\text{H}_2\) with the \(\text{C}(001)-(2 \times 1)\) surface on pathway \(C\), as well.

Thus, our results reveal that all the three pathways \(A\)–\(C\) exhibit significant energy barriers on \(\text{C}(001)-(2 \times 1)\) so that dissociative adsorption of \(\text{H}_2\) is very unlikely at room temperature also at this surface. Contrary to the case of \(\text{Si}(001)-(2 \times 1)\), our results show that the new interdimer adsorption channel \(A\) exhibits the lowest energy barrier of all pathways considered for \(\text{H}_2\) adsorption on \(\text{C}(001)-(2 \times 1)\).

4. Discussion

Let us now compare our calculated barriers for \(\text{H}_2\) adsorption on the three surfaces with one another and with related results from the literature before we compare the theoretical results with the available experimental data.

4.1. Comparison of theoretical results

In table 2, our calculated barrier heights \(E_{\text{bar}}\) are compared with theoretical results from the literature. It appears that the differences between the barrier heights for the \(\text{SiC}, \text{Si}\) and diamond \((001)\) surfaces cannot all be interpreted in simple qualitative physical terms because subtle and minute quantitative differences in changes of bonding topology and charge density distributions of the reacting molecule and the substrate surfaces turn out to be of crucial importance. Nevertheless, a few general observations can be made. Firstly, we note that all calculations find intradimer \(\text{H}_2\) adsorption to be less favourable than interdimer adsorption on these surfaces. This appears to be due to the fact that the \(\text{H}_2\) molecule has to break a \(\pi\) bond when it adsorbs on a single surface dimer on intradimer pathway \(B\). The energy cost for doing so is highest for systems containing carbon dimers, in particular for the \(\text{C}(001)\) surface. On interdimer pathways \(A\) and \(C\) only one of the two dangling bonds of neighbouring dimers is an active orbital contributing to the bonding of \(\text{H} - \text{H}\) at the transition state. Therefore, just a weakening of the \(\pi\) bonds of two neighbouring dimers is sufficient at the transition state to bind the activated complex. As a consequence, the energy cost for changing the electronic structure of the surface needed to accommodate the arriving molecule is smaller. Next, we recognize that the barriers on the different pathways are highest for \(\text{C}(001)-(2 \times 1)\). This is due to the fact that the \(\pi\) bonds of a carbon dimer are much stronger than those of a Si dimer and to the higher directionality, as well as the smaller spatial extent of the dangling bond orbitals at the \(\text{C}(001)\) surface, as compared to \(\text{Si}(001)\) or \(\text{SiC}(001)-(4 \times 2)\). The latter peculiarities, characteristic for \(\text{C}(001)\), are
Table 2. Calculated barrier heights $E_{\text{bar}}$ (in electron volt) on interdimer ($A$ and $C$) and intradimer ($B$) pathways for H$_2$ reaction with the different surfaces considered in comparison with theoretical results from the literature. The results for SiC(001) (see section 3.2) apply to the c(4 × 2) AUDD reconstruction.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Pathway</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC(001)-c(4 × 2)</td>
<td>No barrier</td>
<td>0.50</td>
<td>0.54</td>
<td>0.34</td>
</tr>
<tr>
<td>Si(001)-(2 × 1)</td>
<td></td>
<td>0.37</td>
<td>0.20</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40</td>
<td>0.63</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.66</td>
<td>0.70</td>
<td>0.66</td>
</tr>
<tr>
<td>C(001)-(2 × 1)</td>
<td>0.66</td>
<td>1.05</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.14</td>
<td>1.85</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ From [10] Pehlke.

less pronounced for Si(001). As a consequence, at the Si(001) surface the dimer distance exerts the dominant effect on H$_2$ reaction behaviour. Since the dimer distance on pathway $C$ is much smaller than on pathway $A$ (see table 1), the barrier on pathway $C$ is the lowest at the Si(001)-(2 × 1) surface. On the contrary, the peculiarities of the stronger bonds of the carbon dimers and of the dangling bond orbitals at C(001)-(2 × 1) give rise to the fact that pathway $A$ has the lowest barrier in this case. Finally, at the SiC(001)-c(4 × 2) surface both interdimer bond lengths $d_\parallel$ and $d_\perp$ are small enough and the Si dangling bond orbitals are sufficiently extended to allow for a very efficient interaction of the molecule with the surface. As a result, both pathways $A$ and $C$ have no energy barrier.

Pathways $B$ and $C$ on Si(001)-(2 × 1) have more recently been studied by DFT–GGA slab [10, 11], DFT hybrid functional cluster [12] and quantum Monte Carlo (QMC) cluster calculations [13]. Our results for these two pathways are in satisfying agreement with the previous results (see table 2). Their difference of 0.17 and 0.14 eV for pathways $B$ and $C$, respectively, from the results of Pehlke’s related DFT–GGA calculations [10], as well as of 0.14 and 0.10 eV from the DFT–GGA results of Kanai et al [11] appear to be due to technical differences in the calculations. In particular, the differences between our calculated barrier heights on intradimer pathway $B$ and interdimer pathway $C$ of 0.20 eV compares favourably with the corresponding values of 0.17 and 0.16 eV from the previous DFT [10, 11] calculations and is in reasonable accord with the value of 0.12 eV resulting from the QMC calculations [13]. The absolute values of the barrier heights show somewhat larger scatter, however. As to the C(001)-(2 × 1) surface, pathways $B$ and $C$ have been studied before by DFT hybrid functional calculations employing a 2 × 2 cluster configuration [12]. The respective energy barriers are about a factor of 2 larger than our results (see table 2).
Table 3. Binding energies $E_b$ (in electron volt) for H$_2$ adsorption on the Si(001)-(2 × 1) and the C(001)-(2 × 1) surfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(001)-(2 × 1)</td>
<td>1.89</td>
<td>2.04</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>1.95$^a$</td>
<td>1.64$^a$</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>1.94$^b$</td>
<td>1.67$^b$</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>2.30$^c$</td>
<td>1.72$^c$</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>2.40$^d$</td>
<td></td>
</tr>
<tr>
<td>C(001)-(2 × 1)</td>
<td>2.65</td>
<td>3.81</td>
<td>2.63</td>
</tr>
<tr>
<td></td>
<td>–</td>
<td>3.70$^c$</td>
<td>1.91$^c$</td>
</tr>
</tbody>
</table>

$^a$ From [10] Pehlke.

Our calculated binding energies $E_b$ for the Si(001)-(2 × 1) and C(001)-(2 × 1) surfaces are compared with theoretical results from the literature in table 3. They are defined as the difference between the initial and final state energies of a particular reaction pathway. Firstly, we note that the binding energies of intradimer pathway $B$ are largest and they are roughly a factor of two larger for C(001) than for Si(001). This fact seems to have a very simple reason. The two released H atoms eventually bind to a single dimer on this pathway forming a Si or C monohydride dimer, respectively. Since the bond energy of two H–C bonds is considerably larger than that of two H–Si bonds (by about 1.5 eV) the binding energy increases accordingly. In particular, the binding energies resulting for Si(001) from all calculations for pathways $B$ and $C$, respectively, are pleasingly close to one another. The same applies for the binding energies of pathway $B$ on C(001).

For both surfaces, the binding energies on interdimer pathways $A$ and $C$ are smaller than those on intradimer pathway $B$. This appears to be due to a salient difference in substrate surface relaxation when the two H atoms bind to a single dimer in the final state of an intradimer pathway, as opposed to two neighbouring dimers on an interdimer pathway. When one or two H atoms adsorb on a dimer (singly versus doubly occupied dimers), respectively, the $\pi$-bond between the dimer-dangling bonds becomes disrupted and the dimer-bond length increases. On intradimer pathway $B$ one dimer per adsorbed H$_2$ molecule becomes doubly occupied by two H atoms, whereas on interdimer pathways $A$ and $C$ two neighbouring dimers become singly occupied by H. Thus, on intradimer pathway $B$ only one $\pi$-bond becomes broken, whereas on interdimer pathways $A$ and $C$ two $\pi$-bonds become broken. As a consequence, the binding

$^3$ At the Si(001)-(2 × 1) surface, the initial states of C-type reaction pathways with H$_2$ approaching dimer atoms 3 and 5 versus 2 and 4 are slightly different because of the buckling of the dimers. The H atoms eventually bind to former dimer down- or dimer up-atoms, respectively. As a consequence, our calculations yield slightly different barriers of 0.35 and 0.33 eV for the two cases, respectively. In table 2, we have listed their mean value for simplicity. As for the interdimer barrier heights of type $C$, it also makes a difference for the binding energies on Si(001)-(2 × 1) whether the H$_2$ molecule approaches up- or down-atoms of two neighbouring dimers, respectively. The binding energy turns out to be slightly larger when the two H atoms eventually bind to dimer up-atoms ($E_b = 1.83$ eV) rather than to dimer down-atoms ($E_b = 1.72$ eV). In table 3, we have listed the average of these two values for simplicity. For C(001)-(2 × 1) this point is of no concern since the dimers are symmetric at the clean surface.
energy is smaller for interdimer pathways A and C than for intradimer pathway B. This general notion is in agreement with all theoretical results in table 3. At Si(001)-(2 × 1), the surface dimers have only a weak π-bond in addition to a σ-bond. The dimer-bond length of 2.31 Å at the clean surface increases to 2.41 Å for the singly or doubly occupied dimers corresponding to an increase by about 4%, when H adsorbs. The respective binding-energy differences between case B versus A and C are fairly small. For pathways B and C, e.g. the difference amounts to 0.27 eV, only. It basically corresponds to the π-bond energy of a Si dimer. At C(001)-(2 × 1), on the contrary, the surface dimers are almost double-bonded at the clean surface with a bond length of 1.38 Å, only, whereas the bond length is 1.62 Å for the doubly occupied dimer in case B and 1.59 Å for the singly occupied dimers in cases A and C corresponding to an increase of the dimer-bond length by about 16%, when H adsorbs. Thus, the binding-energy difference between cases B and C, corresponding to the π-bond energy of a carbon dimer in this case, amounts to about 1.2 eV in our results. This is consistent with the general notion that the π-bond energy of a carbon dimer is much larger than that of a Si dimer and it emphasizes the importance of the chemical nature of surface dimers in H₂ adsorption.

Actually, the difference between the binding energy of a doubly occupied (case B) and two singly occupied (case C) Si dimers at the Si(001)-(2 × 1) surface is referred to as the effective pairing energy of two H atoms on a single dimer [21, 22]. Höfer et al [21] have determined a value of 0.25 ± 0.05 eV for the pairing energy, whereas Hu et al [22] have derived a value of 0.31 ± 0.04 eV from their scanning tunnelling microscopy (STM) data. Our respective binding-energy difference of 0.27 eV is consistent with these data.

4.2. Comparison with experiment

In table 4, we finally compare our results for H₂ reaction with the Si(001)-(2 × 1) surface with experimental data for the so-called adsorption [23], reaction [24] and desorption [21] energies available in the literature. We include in this comparison the QMC data [13] as well, since they result from the most advanced calculations on the system, to date. The latter have been extrapolated from QMC cluster calculations to the infinite-system limit (for details see [13]). For a meaningful comparison, we first have to establish the correspondence between our calculated barrier heights, binding energies and desorption energies, defined as \( E_{\text{bar}} + E_b \), and the literature data [13, 21, 23, 24]. The latter refer to the reaction mechanisms labelled H2* and H2 which are defined, e.g. in figure 1 of [13]. For both mechanisms, our calculated barrier heights \( E_{\text{bar}} \) correspond to the adsorption energies defined in [13, 23]. Our binding energy for pathway B, which we label \( E_b^B \) in the following for clarity sake, corresponds to the reaction energy of the intradimer reaction mechanism H2*, as defined in [13, 23], since the latter is identical to our intradimer reaction process B. Correspondingly, our respective desorption energy \( E_{\text{bar}} + E_b^B \) corresponds to the desorption energy of the H₂ molecule for the H2* mechanism. For the interdimer reaction mechanism H2, it is assumed [13, 24] that the molecule first binds to the surface in interdimer state C, acting as an intermediate state in adsorption, and then switches over to intradimer final state B, because the two H atoms have the largest binding energy in the latter. So the reaction energy for the H2 mechanism, as defined in [13, 24], is the energy difference between the initial state with H₂ in vacuum above the surface and the final state with the two H atoms adsorbed in final state B, as well, i.e. it is also given by our binding energy \( E_b^B \) on pathway B. The same argument applies to the related process when H₂ eventually adsorbs in final state B passing through intermediate state A, however. To differentiate between the two
Table 4. Adsorption, reaction and desorption energies (in electron volt), as defined in [13, 21, 23, 24], for H$_2$ adsorption on the Si(001) surface (see text). The first two lines in each section give our results without (first line) and with (second line) vibrational zero-point energy corrections. Experimental data from [21, 23, 24] and results from QMC calculations [13] are given for comparison. Note that the reaction energies in the middle part of the table are the same for all three different pathways (see text) because the adsorption configuration is expected to eventually convert in each case to the final state of pathway B which has the largest binding energy ($E_b^B = 2.04$ eV).

<table>
<thead>
<tr>
<th></th>
<th>H2A</th>
<th>H2(\ast)</th>
<th>H2C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption energy (\hat{\varepsilon} = \varepsilon_{\text{bar}})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work without ZPE</td>
<td>0.50</td>
<td>0.54</td>
<td>0.34</td>
</tr>
<tr>
<td>This work with ZPE</td>
<td>0.59</td>
<td>0.63</td>
<td>0.43</td>
</tr>
<tr>
<td>Experiment (^a)</td>
<td>&gt; 0.6(^a)</td>
<td>&gt; 0.6(^a)</td>
<td>&gt; 0.6(^a)</td>
</tr>
<tr>
<td>QMC with ZPE</td>
<td>–</td>
<td>0.75(^b)</td>
<td>0.63(^b)</td>
</tr>
<tr>
<td>Reaction energy (\hat{\varepsilon} = E_b^B)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work without ZPE</td>
<td>2.04</td>
<td>2.04</td>
<td>2.04</td>
</tr>
<tr>
<td>This work with ZPE</td>
<td>1.84</td>
<td>1.84</td>
<td>1.84</td>
</tr>
<tr>
<td>Experiment (^c)</td>
<td>1.9 ± 0.3(^c)</td>
<td>1.9 ± 0.3(^c)</td>
<td>1.9 ± 0.3(^c)</td>
</tr>
<tr>
<td>QMC with ZPE</td>
<td>–</td>
<td>2.20(^b)</td>
<td>2.28(^b)</td>
</tr>
<tr>
<td>Desorption energy (\hat{\varepsilon} = \varepsilon_{\text{bar}} + E_b^B)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work without ZPE</td>
<td>2.54</td>
<td>2.58</td>
<td>2.38</td>
</tr>
<tr>
<td>This work with ZPE</td>
<td>2.43</td>
<td>2.47</td>
<td>2.27</td>
</tr>
<tr>
<td>Experiment (^d)</td>
<td>2.48 ± 0.1(^d)</td>
<td>2.48 ± 0.1(^d)</td>
<td>2.48 ± 0.1(^d)</td>
</tr>
<tr>
<td>QMC with ZPE</td>
<td>–</td>
<td>2.96(^b)</td>
<td>2.91(^b)</td>
</tr>
</tbody>
</table>

\(^a\) From [23] Dürr et al.
\(^b\) From [13] Filippi et al.
\(^c\) From [24] Raschke and Höfer.
\(^d\) From [21] Höfer et al.

different reaction mechanisms involving intermediate states A or C we label them H2A and H2C in table 4, respectively.

When comparing the adsorption, reaction and desorption energies defined above with experiment one should take vibrational zero-point energy corrections into account. They have been evaluated for the system at hand by Steckel et al [25] and are already included in the QMC results [13]. We have listed the experimental data for the adsorption, reaction and desorption energies in each column of table 4 since experiment does not reveal a priori which particular type of adsorption mechanism is effectively in action. However, experimental evidence has converged in recent years to the H2 mechanism [1] on Si(001) corresponding to case H2C in our nomenclature. Favouring the H2C mechanism is obviously in agreement with all theoretical results since among all reaction pathways considered on Si(001)-(2 \times 1), interdimer pathway C has the lowest barrier (see table 2). As a matter of fact, mechanism H2C appears to be the most important channel for H$_2$ sticking at this surface, in agreement with the experiment [1].

By and large, our results in table 4 are in very good agreement with the experiment. This also applies for the experimentally favoured mechanism H2C. In particular, the STM data clearly reveal [26] that the H atoms released after dissociation of the H$_2$ molecule bind to the
nearest-neighbour Si atoms on neighbouring dimers in one dimer row, as is the case for pathway C on the Si(001)-(2 × 1) surface (see figure 3(b)). Comparing the two sets of theoretical values in table 4, we see that our results for the experimentally favoured H2C mechanism are also in reasonable accord with the QMC results. While the latter overestimate the measured reaction and desorption energies to some extent our results slightly underestimate the experimental data.

For SiC(001)-c(4 × 2), there are no explicit values for the adsorption, reaction and desorption energies published in the literature. Only the amazing observation that H2 readily adsorbs dissociatively on the surface has been reported [4]. The physical origin of this astonishing effect has been clarified by our calculations.

We are not aware of any H2 adsorption data for C(001)-(2 × 1) in the literature. Thus, our results can only be considered as theoretical predictions, so far. It would be nice if they could be validated by measurements. In particular, the discerning feature of H2 adsorption on the Si(001) versus C(001) surface is the different optimal reaction pathways C versus A, respectively. As opposed to Si(001)-(2 × 1), in the case of the C(001)-(2 × 1) surface the two H atoms released from the molecule after dissociation should bind to carbon atoms on two dimers of neighbouring dimer rows, as shown in figure 5(b), since the A channel and with it the H2A mechanism is the most favourable for H2 adsorption in this case. Thus, we expect that an STM experiment tracing H2 adsorption on C(001)-(2 × 1) could clearly resolve the issue.

5. Summary and conclusions

In summary, we have discussed most conceivable reaction pathways for dissociative H2 adsorption on SiC(001)-c(4 × 2), Si(001)-(2 × 1) and C(001)-(2 × 1) surfaces. In agreement with experiments, we find barrierless reaction pathways only on SiC(001)-c(4 × 2), whereas all pathways investigated on Si(001)-(2 × 1) and C(001)-(2 × 1) exhibit considerable energy barriers which are too high to be surmounted by most of the Maxwell–Boltzmann distributed H2 molecules in the gas phase at room temperature. Intradimer H2 adsorption on the SiC(001) and Si(001) surfaces is accompanied by the highest energy barriers since the dimer-dangling bonds point away from the H2 molecule approaching the surface. This situation does not allow for an efficient attractive interaction between the molecule and the substrate surfaces. This applies for the C(001) surface as well, where the barrier on intradimer pathway B is also very high. Interdimer adsorption crucially depends on the spatial separation and arrangement of the surface dimers, as well as on the direction of their dangling bonds relative to the axis of the reacting H2 molecule and their spatial extent, i.e. the H2 adsorption process depends sensitively on minute structural details of the different surfaces, their lattice constants and the chemical properties of their surface dimer atoms. Both Si(001)-(2 × 1) and the AUDD model of SiC(001)-c(4 × 2) have Si dimers with basically the same dangling bonds which are arranged in a similar pattern. The small lattice constant of SiC, as compared to Si, brings neighbouring Si dimers close enough to one another to significantly increase their interaction with H2 eliminating the adsorption barriers on interdimer pathways typical for the Si(001)-(2 × 1) surface. The interdimer adsorption channel A, investigated on Si(001)-(2 × 1) for the first time in this work, has a barrier which is higher than that on interdimer pathway C. Therefore, the conclusions of more recent work concerning H2 adsorption on Si(001)-(2 × 1) in the literature which are based on mechanism H2C remain unaffected by our complementary results since adsorption channel C remains the most favourable. C(001)-(2 × 1) geometrically resembles SiC(001)-c(4 × 2), as well, but the chemical properties of the carbon dimers differ substantially from those of Si.
dimers. As a result, interdimer pathways $A$ and $C$ show larger energy barriers at C(001)-(2 $\times$ 1), as compared to the respective pathways on Si(001)-(2 $\times$ 1), although the interdimer distance is much smaller than on Si(001)-(2 $\times$ 1). The strong localization of the carbon dangling bonds renders their interaction with H$_2$ very short-ranged so that no efficient interaction of the molecule with the surface occurs and the interdimer pathways exhibit relatively high energy barriers. Actually, reaction channel $A$, which appears to be less important for Si(001)-(2 $\times$ 1) due to its relatively high energy barrier, ends up as the most important channel for H$_2$ adsorption on the C(001)-(2 $\times$ 1) surface. Therefore, we conclude that pathway $A$ should turn out to be the most relevant channel for H$_2$ sticking at C(001)-(2 $\times$ 1). To the best of our knowledge, there are no experimental data available, as yet, to validate this prediction.

In general, we observe that it is not only the distance between dimers at a substrate surface governing the reaction with H$_2$, but also more intricate effects of the dimer arrangement, the topology of their dangling bonds and their spatial extent have a decisive influence on the reaction process. The binding energies of the two H atoms released from the molecule after dissociation at the different surfaces are much larger than the respective barrier heights. For intradimer pathway $B$, in particular, the binding energies can be easily interpreted on the basis of bond strengths and bond lengths of the involved surface dimers and the newly formed H–Si versus H–C bonds at the surface. As a result, the binding energy of two H atoms is roughly twice as large on C(001)-(2 $\times$ 1) as on Si(001)-(2 $\times$ 1).

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References
