Theory of Adsorption and Desorption of H_2/Si(001)

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While the small sticking coefficient for molecular hydrogen on the Si(001) surface apparently requires a large energy barrier of adsorption, no such barrier is observed in desorption experiments. We have calculated the potential-energy surface of an H_2 molecule in front of a Si(001) surface. If we relax the Si substrate, we find an optimum desorption path with a low (≤ 0.3 eV) adsorption energy barrier. While molecules impinging on the surface will mostly be reflected at the larger barrier of some frozen substrate, molecules adsorbed on the surface can desorb along the low-barrier path.

Adsorption and desorption processes represent the initial and final steps of catalytic reactions of gases on solid surfaces, which are of importance both in fundamental research and for technological applications. Typically, the adsorption and desorption dynamics of diatomic molecules are described within a simple conception that the molecule is moving in a fixed, elbow shaped potential $E(Z, d)$, with Z denoting the distance of the molecule from the surface and d being the separation of the atoms forming the molecule [1,2]. Of course this potential may additionally depend on the remaining four molecular coordinates [i.e., the position of the center of mass of the molecule along the surface (X, Y), and the azimuthal and polar orientation of the molecular axis], however, this does not alter the basic assumption behind this potential, namely, that there are *no surface atomic degrees of freedom,* i.e., the surface atomic geometry is frozen. Therefore, the trajectories for adsorption and desorption are connected by time reversal, and, consequently, the height of the adsorption energy barrier measured in either an adsorption or a desorption experiment has to be the same.

However, recent experimental results for H_2/Si(001) have revealed a puzzling apparent contradiction to the principle of microscopic reversibility [3,4]: On the one hand, the small sticking coefficient of molecular hydrogen on Si(001) requires that there is a substantial energy barrier of dissociative adsorption. On the other hand, no such barrier is found in associative desorption experiments: Kolasinski *et al.* [3] measured the distribution of the translational, vibrational, and rotational energies of molecules desorbing from the monohydride surface and found that the hydrogen molecules do not have any significant energy in access of the thermal energy corresponding to the surface temperature. From this they estimated the height of the adsorption energy barrier to be 77 ± 80 meV.

This experimental result severely challenges the widely employed conception of adsorption-desorption dynamics outlined above. If the energy barrier were in fact high, some mechanism must be at work nevertheless allowing the molecules to desorb with a thermal energy distribution.

Extrinsic effects, e.g., the diffusion of hydrogen atoms to special defect sites on the Si(001) surface with a low local energy barrier towards desorption, seem to be at variance with experimental evidence [4]. Furthermore, no anomalous isotope effect was found [5] that would corroborate the model of hydrogen molecules tunneling through the barrier [6]. Recently Brenig *et al.* [7] suggested another mechanism. Their model potential has an order of 1 eV barrier, but additionally it possesses a surface oscillator degree of freedom modeling Si lattice vibrations. After having crossed the barrier, the desorbing molecule gets decoupled from the surface, and the excess energy due to the potential drop behind the barrier cannot be transferred to the molecule, but Si phonons are excited instead. Thus, despite the large barrier, the energy distribution of the desorbing molecules looks approximately thermal.

Other suggested scenarios start from the assumption that there is no, or only a small, adsorption barrier in the adiabatic potential-energy surface, in accordance with the desorption data. Still the sticking coefficient can be small, if the adsorption and desorption processes follow different pathways on the potential-energy hypersurface [3,4].

Kolasinski *et al.* [4] have carried out detailed measurements of the sticking coefficient of D_2 on Si(001) using molecular beam techniques. They found an increase of the sticking probability both with nozzle temperature (i.e., with the energy of the impinging molecules) and with surface temperature. The increased sticking coefficient for fast molecules demonstrates that the dissociative adsorption of hydrogen on Si(001) is activated, and the fit to the experimental data indicates an average barrier height of 1 eV and a large width of the barrier height distribution of 0.6 eV. The fact that sticking is facilitated by surface temperature corroborates the idea that surface atom motion is important [4]: There may be certain surface atom configurations which correspond to low-barrier adsorption pathways; however, heating the surface is necessary to excite surface atom vibrations that dynamically generate these configurations. Cluster calculations have lead to adsorption energy barrier heights larger than 1 eV [8,9], which appear to be at variance with the above explanation.

The purpose of this Letter is to sort out the correct explanation for the apparent contradiction between the measured adsorption and desorption dynamics. We have carried out *ab initio* total-energy calculations [10] to map the potential-energy hypersurface for a hydrogen molecule in front of a Si(001) surface. To represent the buckled surface (see Fig. 1) we take a (2 × 2) surface unit cell. This is necessary in order to correctly describe the ground state of the Si(001) surface with buckled dimers (Fig. 1). Moreover, we use this unit cell instead of the smaller (1 × 2) cell in order to reduce the interaction between hydrogen molecules in neighboring supercells through electrostatic and electronic H-H coupling and through the mechanical relaxation of the substrate. The Si slab consists of five layers of atoms, the topmost three of them being relaxed, and the atoms in the remaining two layers are fixed at their bulk positions. The dangling bonds on the bottom surface of the slab are saturated with hydrogen atoms. The total energy is computed within density-functional theory together with the local density approximation (LDA) for the exchange-correlation (XC) functional, and it is *a posteriori* corrected for charge inhomogeneity
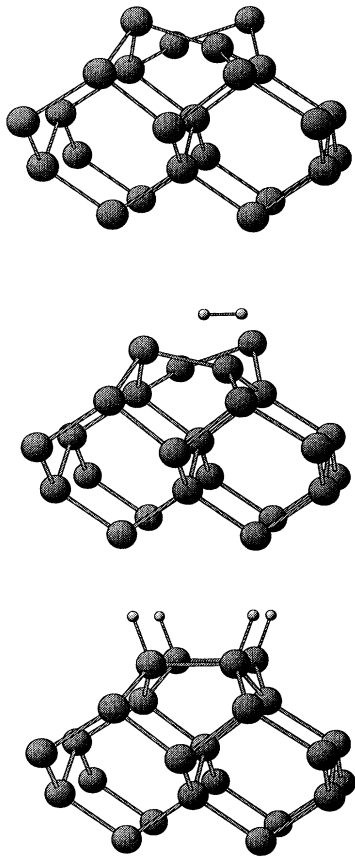

FIG. 1. Atomic structure of, from top to bottom, the clean $p(2 \times 2)$-reconstructed Si(001) surface, the transition state geometry with a hydrogen molecule close to the Si(001) surface, and the monohydride surface.

effects, using the LDA charge density to evaluate the exchange-correlation energy in the generalized gradient approximation (GGA) by Perdew *et al.* [11]. The GGA has proven to be of importance for the calculation of activation energy barriers [12] and barriers of adsorption [13,14]. The dissociation barrier for H_2 on Cu(111), for example, comes out large (order of 0.7 eV) in the GGA calculation, but is almost zero in LDA, and only the GGA result conforms with experiment [14,15]. We have generated the pseudopotential for Si with Hamann's [16] scheme, while we use the full $1/r$ potential for the hydrogen atoms. The main contribution of the GGA correction to the total energy is expected to stem from the hydrogen, thus we do not expect that the usage of an LDA pseudopotential for Si seriously affects our results. Calculating the energy gain due to buckling for the clean Si surface, both the LDA calculation and our *a posteriori* GGA procedure (in combination with the Hamann LDA pseudopotential) yield the same result within some meV, as opposed to GGA corrections of a few hundred meV for, e.g., the height of the energy barrier of dissociative H_2 adsorption. The **k** integration [17] is performed by using one special **k** point for the Brillouin zone of the (2 × 2) cell. This **k**-point restriction induces an error of about 0.1 eV. The cutoff energy defining the plane-wave basis set was chosen to be 30 Ry, leading to an estimated convergence error of about 0.14 eV for the potential-energy surface. To improve the accuracy of the barrier height the energy of the transition state geometry was calculated with 4 **k** points and an energy cutoff of 40 Ry. The calculated endothermicity of H_2 adsorption is 2.1 eV per H_2 molecule [18] (without corrections for zero-point vibrations), somewhat smaller than the values of 2.4 eV [19], 2.9 eV [9], and 2.6 eV [8] from previous cluster calculations. A detailed presentation of the high-dimensional potential-energy surface and convergence tests will be published elsewhere [20].

The equilibrium structure of the clean Si(001) surface [21–23] (see Fig. 1) is characterized by rows of buckled dimers, resulting in a $p(2 \times 2)$ or a $c(4 \times 2)$ surface reconstruction. The buckling is due to the dehybridization of the four sp^3 orbitals into three sp^2 plus one p orbital at the "down" atom (i.e., the Si-dimer atom closer to the bulk), the energetically higher p orbital is unoccupied, and hence the total energy is lower than for symmetric dimers [24]. Furthermore, the down dimer atom tends to push aside its nearest neighbors in the second layer. In the $p(2 \times 2)$ structure the second layer atoms can relax this stress, which is not possible in the smaller (1 × 2) surface unit cell, thus explaining the preference for structures with alternating buckling angle. When the monohydride surface is formed, every dangling bond of the dimerized Si(001) surface is saturated with one H atom. The mechanism leading to buckling does not work any more in this case, hence the dimer bond becomes parallel to the surface. Therefore, comparing the initial and final geometries for a hydrogen molecule dissociatively

adsorbing on a Si(001) surface, it becomes obvious that the adsorption as well as the desorption processes have to be accompanied by rather large movements of the substrate atoms.

The first order desorption kinetics observed in experiment [25] is consistent with a prepairing mechanism of the H atoms on the Si surface dimers, i.e., the H_2 molecule is formed from two H atoms that were bonded to the same Si dimer prior to desorption. Thus we do not have to investigate processes with H atoms coming from different dimers, and we can restrict our geometries to H atoms moving in the plane spanned by the (001) surface normal and the Si-dimer bond. We calculate the potential energy of an H_2 molecule (with the molecular axis kept parallel to the surface) as a function of the hydrogen-atom separation and the hydrogen-surface separation. These cuts through the potential-energy hypersurface are parametrized by the displacement of the center of mass Y of the H_2 molecule along the dimer bond; $(X, Y) = (0, 0)$ refers to the center of the (symmetric) Si surface dimer.

First, we freeze the Si atomic positions to those of the symmetric (1×2) structure. The Si-dimer bond length for the monohydride surface is only by 0.1 Å larger than for the clean symmetric (1×2) surface, and the elastic energy of the clean Si(001) surface corresponding to this expansion amounts to only about 0.1 eV. Freezing the Si coordinates to this geometry corresponds to the physical picture of a "sudden desorption event," i.e., the H_2 molecule is assumed to leave the surface much faster than the Si atoms can relax to the geometry of the clean surface. The calculated potential-energy surface has a large barrier of about 0.7 eV for the symmetric desorption path (i.e., the center of mass of the H_2 molecule is always above the center of the surface dimer, and only moves in the direction perpendicular to the surface) measured with respect to a free H_2 molecule plus a clean symmetric (1×2) surface. Asymmetric pathways lead to even larger barriers. This result is in qualitative agreement with Jing and Whitten's [8] cluster calculations, which yielded a 1.15 eV barrier for a similar geometry.

Next we investigate the adiabatic limit, i.e., all Si atom positions in the topmost three layers are fully relaxed for every fixed position of the two H atoms. The adsorption energy barrier is defined with respect to the total energy of a free hydrogen molecule plus the clean $p(2 \times 2)$ surface. The "adiabatic" adsorption energy barrier determined in this way represents the smallest possible barrier. Paths corresponding to a partial relaxation of the surface will show a larger, or at best equal, barrier.

Several cuts through the potential-energy surface are shown in Fig. 2. The optimum desorption path is asymmetric, and at the transition geometry (see also Fig. 1) the H_2 molecule is roughly above the Si-dimer atom closer to the bulk. Close to this geometry, the buckling angle of the surface Si dimer below the hydrogen molecule is reduced by about 5° with respect to a value of $\approx 19°$ for the clean $p(2 \times 2)$ reconstructed surface, and the Si-dimer
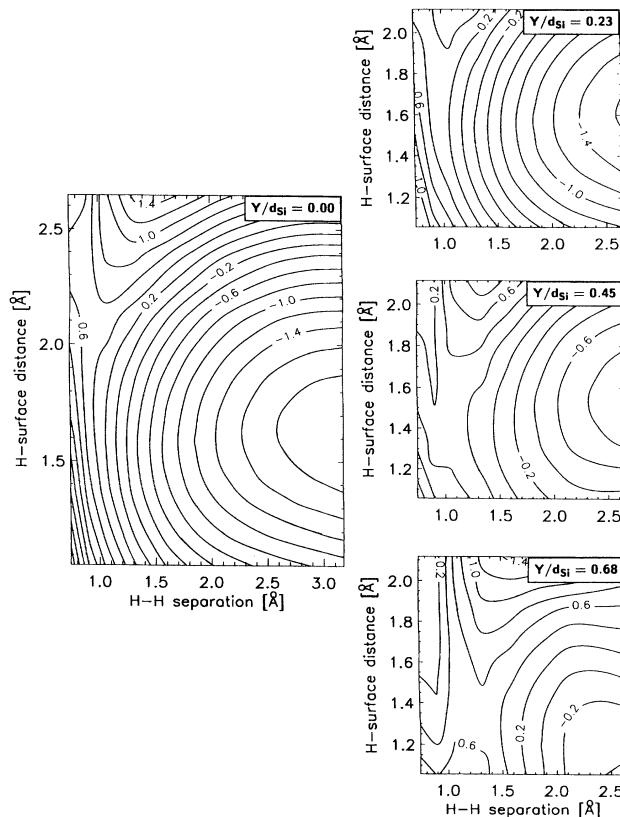
FIG. 2. Potential-energy surface of a hydrogen molecule in front of a Si(001) surface. The contour spacing is 0.2 eV. The Si substrate has been relaxed for each position of the hydrogen atoms. The hydrogen molecule is parallel to the surface and within the plane spanned by the Si surface dimer bond and the surface normal. The cuts plotted here are parametrized by the displacement Y of the center of mass of the molecule along the dimer bond in units of the Si bulk bond length d_{Si}. $Y/d_{Si} = 0.5$ corresponds to a hydrogen molecule coming down onto the surface with the center of mass roughly above the down Si-dimer atom (see middle panel of Fig. 1).

bond length is slightly increased by about 0.1 Å. The adsorption energy barrier height amounts to ≈ 0.3 eV. The energy of zero-point vibration has not been included, however, as bonds are in general softened at the transition geometry, we expect that the energy barrier will even be lowered when vibrational effects are included.

Having found a low adsorption energy barrier path, we tend to exclude those models for the adsorption and desorption dynamics of $H_2/Si(001)$ that depend on a large energy barrier. This does not mean that the corresponding physical mechanisms are absent, but they are not dominant. When the hydrogen molecule desorbs from the surface, some energy will be stored in the Si surface vibrations, but this energy only amounts to < 0.3 eV and not about 1 eV. In fact we calculated that the elastic energy contained in the Si substrate at the transition geometry is only ≈ 0.15 eV. Our results favor the mechanism suggested by Kolasinski *et al.* [3,4] on the basis of their experimen-

tal findings: The sticking coefficient is small because the hydrogen molecules impinging from the gas phase are fast and their momentum transfer to the substrate is ineffective due to the mass mismatch, therefore most of them experience a substantial barrier corresponding to the geometric configuration of the Si-substrate atoms at the moment of the interaction. Though we have not calculated the adsorption energy barriers for such frozen-in configurations we expect them to be large, similar to the barrier we calculated for the frozen symmetric surface. The time scale for scattering of an H_2 molecule can roughly be estimated by the time it takes a hydrogen molecule at 300 K on the average to transverse a length of the order of 2 Å, i.e., ≈ 0.1 ps. The angular oscillation of the Si dimer is expected to be slow ($\lesssim 3$ THz) compared to the optical or acoustical zone-boundary Si bulk phonons, due to the small restoring forces from bond bending at the surface. The time scale on which the dimers flip between their two extremal positions (and thus go through a configuration resembling a symmetric dimer as in the monohydride surface structure) was estimated to be about 10 ps at 300 K [22], which is 2 orders of magnitude larger than the scattering time of the H_2 molecule impinging on the surface. On the other hand, hydrogen atoms adsorbed on the surface stick on the surface until an appropriate fluctuation of the atomic positions of the Si surface atoms allows them to desorb and associate to H_2 following a path close to the optimum one with a small energy barrier. Hence, for the system $H_2/Si(001)$ the adsorption and desorption dynamics crucially depend on surface atom relaxation. Microscopic reversibility is not violated, but time-reversed trajectories are experimentally practically inaccessible as the coordinates of both the molecule and the surface Si atoms have to be considered.

After completion of our work we received a preprint of Kratzer et al. [26]. Their density-functional calculations are very similar to ours and yield a desorption pathway in close agreement to that discussed above. Their calculated energy of the transition geometry is slightly higher (0.5 instead of 0.3 eV), which might be due to their smaller supercell. They assume a (1×2) periodicity of the surface.

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