

Interaction of H₂ with Si(001)-(2 × 1): Solution of the Barrier Puzzle

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The sticking probability of H₂ on Si(001) is immeasurably small at room temperature, indicating the presence of a large energy barrier to adsorption. Surprisingly, the final state energy distributions of H₂ molecules desorbing from Si(001) show no signs of having traversed such a barrier, in apparent contradiction with microscopic reversibility. Here we report experimental and theoretical evidence resolving this long-standing puzzle. Adsorption and desorption proceeding along two distinct, microscopically reversible pathways can explain all observations.

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The interaction of hydrogen with silicon is of immense technological importance because of hydrogen's crucial role in passivating dangling bonds. Dangling bonds (associated with defects, surfaces, and interfaces) need to be efficiently passivated during electronic device fabrication as they severely degrade device performance. On the other hand, unpassivated dangling bonds at surfaces are essential for deposition, thin-film growth, surface diffusion, oxidation, and etching processes, making H₂ desorption an important and often rate-limiting step in these reactions [1]. Furthermore, the interaction of H₂ with Si(001)-(2 × 1), involving the simplest of all molecules and one of the most thoroughly investigated surfaces, has emerged as an important model system for fundamental studies of dissociative adsorption and associative desorption on covalent surfaces [2]. But despite great experimental and theoretical efforts, the microscopic mechanisms and dynamics of adsorption/desorption have remained elusive and are subject to intense debate. Among the many unusual observations are desorption kinetics closer to first order than second order [3], and the so-called "barrier puzzle" [2,4,5]. The presence of a large energy barrier to adsorption is inferred from the fact that the dissociative sticking probability of H₂ on Si(001) is immeasurably small ($<10^{-10}$) at room temperature. An adsorption barrier is expected to manifest itself in desorption by imparting hyperthermal amounts of kinetic energy to the desorbing molecules, as in the case of H₂ associatively desorbing from Cu(111) [6]. Surprisingly, however, H₂ molecules desorbing from Si(100) monohydride show no signs in their final state distributions of having traversed such a barrier [4,7], in apparent contradiction with microscopic reversibility. This paradoxical situation has puzzled the gas-surface dynamics community for many years (see [2] for a review), and has raised questions about the applicability of the principle of detailed balance [4].

The discussion of this problem has recently focused on a promising proposed mechanism called "phonon-assisted sticking" [5,8–10]. Because the buckling angle of surface Si dimers changes considerably during adsorption/desorption of H₂, it was hypothesized that during desorption the excess potential energy of the adsorption barrier

may be transferred into lattice vibrations rather than the degrees of freedom of the H₂ molecule, explaining relatively cold desorbing molecules [4,7]. *Ab initio* molecular dynamics simulations [5,10] have made it clear, however, that coupling to the buckling coordinate does not correctly account for the observed desorption dynamics. The simulations show that although a fraction (~ 0.1 eV) of the barrier energy can be transferred to the lattice, much more energy (~ 0.55 eV) ends up in the translational energy of the desorbing molecule, contrary to experimental observation [5]. A new possibility was opened when Heinz and co-workers discovered in a scanning tunneling microscopy (STM) study that H₂ can easily adsorb on specific sites of a Si(001) surface preexposed to atomic hydrogen following an interdimer pathway [11]. Adsorption along this pathway was found to occur without a barrier [11–13].

By combining laser-based measurements of the adsorption/desorption kinetics with statistical mechanical modeling and *ab initio* calculations, we arrive at a quantitative, mechanistic description of adsorption and desorption consistent with all observations and providing a natural explanation of the long-standing barrier puzzle. We find that at intermediate and high H coverages, thermal adsorption (i.e., without preexposure to atomic H) and desorption are dominated by this adsorption-barrier-free, autocatalytic pathway [11–13], while a phonon mediated, nonautocatalytic pathway with a ~ 0.7 eV adsorption barrier dominates at very low coverages.

Experiments were performed on an atomically clean, well-ordered Si(001)-(2 × 1) surface [14] using the technique of surface second harmonic generation (SHG). Isothermal adsorption and desorption rates were determined by measuring the hydrogen coverage as a function of time by monitoring the SHG efficiency, and numerically differentiating the resulting coverage vs time curves. Figure 1 shows the measured sticking probability S vs H coverage for different sample temperatures and exposure pressures. It is evident that contrary to Langmuirian site-blocking kinetics, which would predict S to decrease with coverage, the sticking probability actually increases dramatically (up to tenfold) with coverage for most

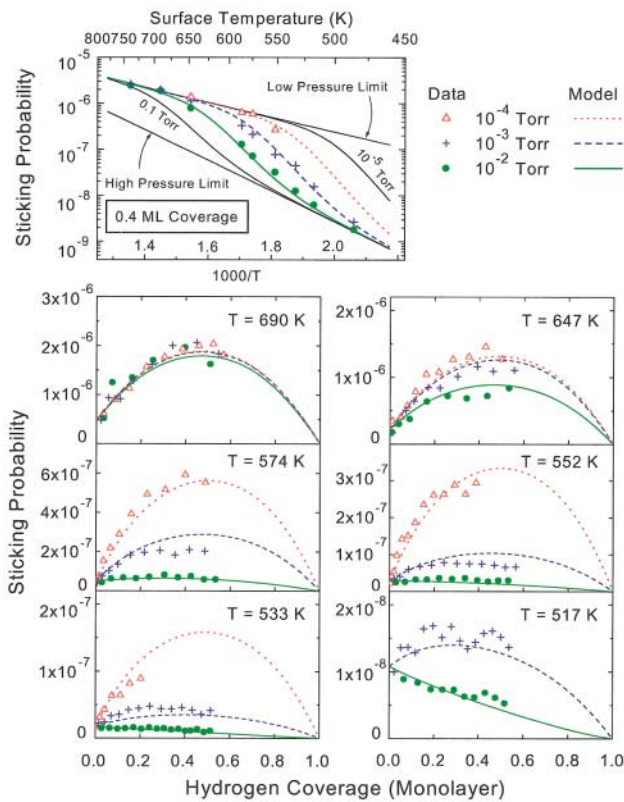


FIG. 1 (color). Sticking probability of H₂ on Si(001) as a function of H coverage, for different exposure pressures and surface temperatures. Also shown is an Arrhenius plot of the sticking probability at a hydrogen coverage of 0.4 monolayer.

temperatures and pressures [15]. In addition, at temperatures below 650 K, there is a strong reduction of *S* with increasing exposure pressure. Such behavior is quite remarkable since in any “simple” adsorption mechanism the probability that an impinging molecule sticks to the surface should not depend on the rate of other molecules impinging elsewhere. This unusual coverage and pressure dependence of *S* places severe constraints on any model of the adsorption process. Figure 2 shows isothermal desorption rates from the monohydride phase vs coverage, at several temperatures.

The large increase in sticking probability with coverage implies that hydrogen atoms adsorbed on the surface facilitate further adsorption, i.e., lower the adsorption barrier. However, this autocatalytic mechanism cannot be the only adsorption pathway, since the sticking probability at zero coverage is greater than zero at all temperatures (Fig. 1). We conclude that a second, nonautocatalytic adsorption mechanism exists. A model based on the two pathways (depicted in Fig. 3) can explain all observations. In the nonautocatalytic mechanism (called “2H” in the following, reflecting the number of participating H atoms) the H₂ molecule dissociates on a clean surface site via an interdimer pathway [16], as observed by Heinz and co-workers with the STM [17]. It is associated with an appreciable adsorption barrier, due to Pauli repulsion between the closed-

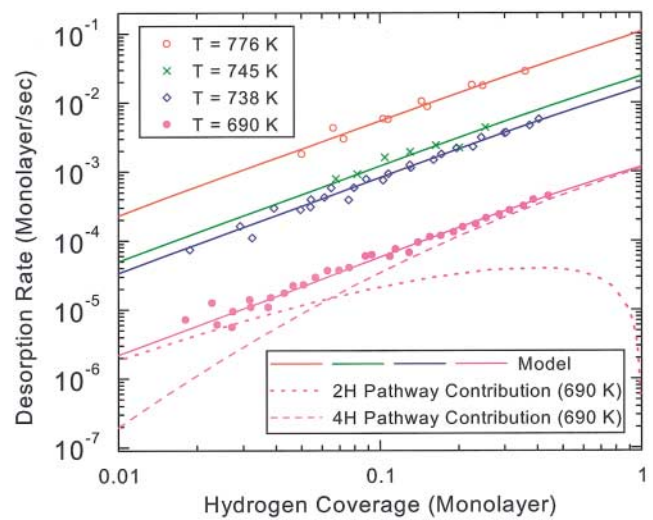


FIG. 2 (color). Isothermal desorption rate of H₂ from Si(001) as a function of H coverage and surface temperature.

shell H₂ molecule and the closed-shell Si dimers. The autocatalytic mechanism (“4H” in the following), on the other hand, appears to correspond to a different interdimer pathway, also discovered with the STM [11]. The STM study suggested, and molecular beam experiments and *ab initio* theory [12,13] confirmed, that adsorption along this pathway occurs without an activation barrier. The 4H pathway is characterized by “active sites” consisting of two adjacent Si dimers, each singly occupied with H atoms in the initial state, as shown in Fig. 3, explaining the autocatalytic nature of this adsorption process. The two preadsorbed H atoms break the π bonds of both dimers, resulting in a pair of reactive radical lobes (dangling bonds occupied with a single electron) which can efficiently

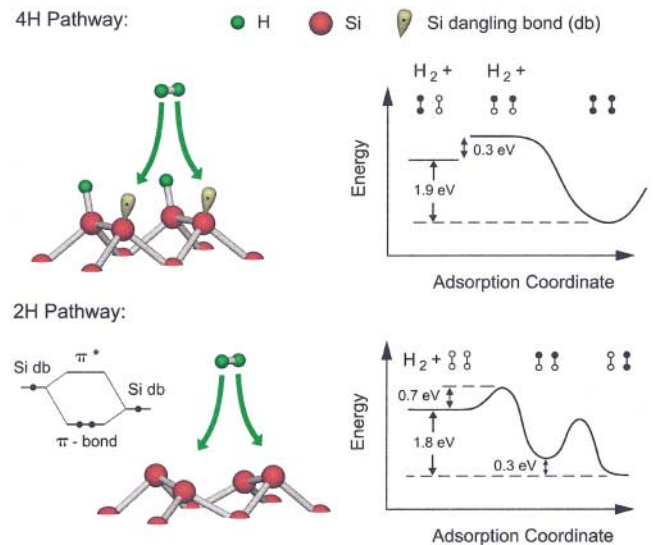


FIG. 3 (color). Schematic of adsorption pathways underlying the theoretical model (see text). In the energy diagrams, \circ denotes Si atoms (in dimers) and \bullet denotes Si-H.

dissociate an impinging H_2 molecule without a barrier. The surface density of these active sites is very low, however, since adsorbed H atoms tend to pair up on the same dimer, which lowers the energy by minimizing the number of broken π bonds [18,19]. Because of the absence of an adsorption barrier, desorption along this pathway is expected to result in nonhyperthermal energy distributions of the desorbed molecules. The unpaired final state of the surface relaxes after the H_2 molecule has left by pairing the remaining two adsorbed H atoms, dissipating the excess energy into the crystal.

To arrive at a prediction for the sticking probability $S = S_{2H} + S_{4H}$, we calculate the thermal equilibrium density of active sites from a lattice gas model of H/Si(001) [19]. In addition to the pairing energy ϵ we also consider the clustering interaction between occupied dimers of the same dimer row, parametrized by the clustering energies ω_{22} , ω_{12} , and ω_{11} , corresponding to interaction between doubly-doubly, singly-doubly, and singly-singly occupied pairs of dimers, respectively. Since this lattice gas model partially maps onto the one-dimensional Ising model, which can be solved analytically, we can add up the partition function Q and determine the relevant equilibrium properties for a given coverage and surface temperature T , such as the surface density of adjacent pairs of unoccupied dimers n_{00} , and the density of active sites for 4H adsorption n_{11}^{cis} (i.e., singly-singly occupied pairs of adjacent dimers in *cis* configuration) [20]. According to Fig. 3, the sticking probability corresponding to the activated 2H process is expected to be proportional to n_{00} ,

$$S_{2H} = \sigma_{2H}^0 n_{00} \exp(-E_{2H}/k_B T), \quad (1)$$

where the prefactor σ_{2H}^0 and the activation energy E_{2H} are adjustable parameters, and k_B is the Boltzmann constant. For the nonactivated 4H process

$$S_{4H} = \sigma_{4H} n_{11}^{cis}, \quad (2)$$

where $\sigma_{4H} = 2.4 \times 10^{-18} \text{ cm}^2$ is the adsorption cross section of 4H sites measured by Biedermann *et al.* [11].

It is evident in Fig. 1 that the pressure dependence approaches zero in the limit of zero coverage, indicating that the dependence of S on pressure is a property of the 4H process only. To understand the effect of exposure pressure on S_{4H} we note that every 4H adsorption event destroys an active site for adsorption, reducing the number of available adsorption sites and therefore S_{4H} . While at low impingement rates the active-site density n_{11}^{cis} is given by the thermal equilibrium value, at high impingement rates the thermal creation rate of active sites cannot keep up with their continuous depletion by adsorption. This leads to a steady-state density lower than the equilibrium value, reached when the active-site depletion rate (by hopping and adsorption) becomes equal to the creation rate (including creation by hopping, r_{hop} , and by desorption through the 4H channel, $r_{d,4H}$). Quantitatively, we obtain

$$S_{4H} = \sigma_{4H} n_{11}^{cis} = S_{4H}^{\text{eq}} \frac{r_{\text{hop}} + r_{d,4H}}{r_{\text{hop}} + r_{\text{imp}} S_{4H}^{\text{eq}}}, \quad (3)$$

where S_{4H}^{eq} is the thermal equilibrium sticking probability, obtained from the equilibrium active-site density, and r_{imp} is the pressure-dependent impingement rate of H_2 molecules. For the rate of active-site creation by hopping we use an Arrhenius expression

$$r_{\text{hop}} = \nu_{\text{hop}} n_{02} \exp(-E_{\text{hop}}/k_B T), \quad (4)$$

with a prefactor of $\nu_{\text{hop}} = 10^{13} \text{ s}^{-1}$ for hydrogen diffusion along Si dimer rows [21]. The creation rate is assumed to be proportional to n_{02} , the density of dimer pairs with one dimer unoccupied and the other doubly occupied.

To obtain the desorption rate as a function of coverage and temperature, we note that the desorption rate into the vacuum is expected to be the same as the desorption rate when the surface (at the same coverage) is in equilibrium with H_2 gas. This rate equals the equilibrium adsorption rate, i.e., the product of the equilibrium impingement rate and sticking probability [from Eqs. (1) and (2)]. To determine the equilibrium impingement rate corresponding to a given coverage and temperature we equate the chemical potentials of the adsorbed phase μ_{ad} and the gas phase μ_{gas} and solve for the pressure. μ_{ad} is determined from the partition function Q of the lattice gas model by

$$\mu_{\text{ad}} = -2k_B T \frac{\partial \ln Q}{\partial N}, \quad (5)$$

where N is the number of adsorbed H atoms. In order for the zero of energy to be the same for both chemical potentials we include the adsorption energy δ in the Hamiltonian of the lattice gas.

The model's predictions for the sticking probability and the desorption rate were simultaneously fit to the data in Figs. 1 and 2, using the pairing, clustering, and adsorption energies, the hopping barrier, and the kinetic parameters of 2H adsorption as adjustable parameters. Good agreement with the measured sticking probability (temperature, coverage, and pressure dependence) and desorption rate (temperature and coverage dependence) is obtained. We find that there is a fairly strong pairing interaction ($\epsilon = 0.31 \text{ eV}$), while clustering is much weaker ($\omega_{22} = 0.06 \text{ eV}$, $\omega_{12} = 0.03 \text{ eV}$, $\omega_{11} = 0.01 \text{ eV}$). This is in agreement with pairing and clustering energies recently determined from STM images by Hu *et al.* [22]. The fit gives a microscopic adsorption energy of $\delta = 1.82 \text{ eV}$, which may be compared with the isosteric heat of adsorption (adsorption enthalpy) of 1.8–2.0 eV measured by Raschke and Höfer [23]. The fitted hopping barrier for active-site creation is $E_{\text{hop}} = 1.73 \text{ eV}$, which is within the range of hopping barriers estimated from STM images (1.68–1.95 eV [21]).

As a further check whether the fitted parameters make sense physically we performed *ab initio* calculations of the various energies with density functional theory in the generalized gradient approximation (GGA), using a five-layer

TABLE I. Comparison of energy parameters obtained by fitting the theoretical model to the data with *ab initio* values and with independently measured values.

Parameter	Model fit (eV)	DFT ^a (eV)	Other expt. (eV)
Pairing energy ϵ	0.31	0.32	~ 0.35 [22]
Clustering energy ω_{22}	0.06	0.06	~ 0.04 [22]
Clustering energy ω_{12}	0.03	0.04	...
Clustering energy ω_{11}	0.01	0.01	...
Adsorption energy δ	1.82	1.88 ^b	1.8–2.0 [23]
Hopping barrier E_{hop}	1.73	1.76	1.68–1.95 [21]
2H adsorption barrier $E_{2\text{H}}$	0.68	...	0.7–0.8 [9]

^aDensity functional theory (GGA), this paper.

^bAfter empirical zero-point correction (2.04 eV uncorrected).

Si slab and ultrasoft pseudopotentials. The results are summarized in Table I. The calculated pairing and clustering energies are all within a few meV of the fitted values, and the calculated adsorption energy (after an empirical zero-point correction) and hopping barrier are within a few percent of the fitted values. Although our model may be simplistic in many respects, the quality of the fit, in conjunction with the good agreement of the fitted parameters with independently determined experimental and theoretical values, is convincing evidence that it captures the basic physics involved.

From Fig. 2 we see that, at coverages exceeding ~ 0.07 monolayer (at 690 K), the desorption rate is dominated by the 4H mechanism, which does not have an adsorption barrier, thus explaining the lack of hyperthermal energy observed in H₂ desorbing from Si(001) at intermediate and high coverages [4,7]. At the same time, despite the absence of a barrier, the corresponding 4H sticking probability is very low because active sites for 4H adsorption are thermal excitations of the surface. The 2H mechanism dominates only at very low coverages, and the likely involvement of substrate vibrations could explain the pronounced activation of the low-coverage sticking probability by the sample temperature [9]. However, the requirement that this phonon-mediated mechanism also give rise to translationally accommodated desorbing molecules (which is in conflict with theoretical results [5,10]) can now be relaxed. Further study is required to determine the detailed dynamics of both pathways, as well as possible contributions of other pathways.

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