

## COMMUNICATIONS

## Hydrogen adsorption and desorption on silicon revisited

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Recent molecular beam data on the energy dependence of sticking coefficients for dissociative adsorption of hydrogen molecules on silicon are analyzed in terms of the five dimensional (5D) quantum reaction dynamics used before to describe data on sticking as a function of surface temperature and on state resolved desorption. The sticking coefficient of the 5D model depended strongly on the energy of surface phonons but weakly on the kinetic energy of the incoming H<sub>2</sub> molecules. In a recent molecular beam experiment the latter dependence was measured directly and found to be substantially stronger than concluded from the earlier data. These results have important consequences for the energy and angular distribution of desorbing particles: If the parameters of the 5D model are adjusted so as to describe the new data, it predicts a mean normal kinetic energy of desorbing particles which is now about twice the thermal value. This prediction is rather model independent and can be derived almost directly from the measured data by invoking “detailed balance.” This new increased normal mean energy then is closer to *ab initio* generalized gradient approximation (GGA) slab calculations predicting about three times the thermal value. The increased kinetic energy also leads to a more forward-peaked angular distribution  $\propto (\cos \theta)^{11 \text{ to } 12}$  instead of  $\propto (\cos \theta)^3$  to  $^4$ . © 2000 American Institute of Physics. [S0021-9606(00)70707-0]

The interaction of hydrogen with silicon surfaces has led to extensive experimental<sup>1–10</sup> and theoretical<sup>11–26</sup> efforts, and to a new aspect of surface reactions. So far mainly two energy dissipation mechanisms were considered in an adsorption process: (a) for *nondissociative* processes (atomic and molecular adsorption), energy transfer to the substrate (phonons and/or electrons) is the dominant effect; (b) For *dissociative* adsorption only conversion of center-of-mass energy into internal molecular energy, in particular kinetic energy has been sufficient to explain the data of, for instance, H<sub>2</sub>/Cu and H<sub>2</sub>/Pd. H<sub>2</sub>/Si seems to be the first example where both energy transfer processes have to be taken into account on equal footing.

In the absence of a detailed *ab initio* potential energy surface (PES), a simple two-dimensional model was proposed to study such reactions.<sup>12</sup> It contained, besides the center-of-mass distance of the molecule from the surface, only a single additional coordinate, namely the amplitude of a “representative surface oscillator,” associated with lattice distortions. The consideration of only a single lattice degree of freedom is justified *a posteriori* by classical lattice dynamics for Si(001) taking 32 atoms into account.<sup>25</sup> It turns out that for low temperatures immediately after desorption only one atom of the dimer involved in adsorption/desorption has an appreciable oscillation amplitude.

For higher coverages and nonequilibrium situations other mechanisms such as interdimer transition states may contribute.<sup>8</sup>

The variables in terms of which we describe the PES will be, first of all, the reaction coordinate *s* itself. If molecular vibrations are disregarded it is nothing but the center-of-

mass distance *z* from the surface. The molecular vibrations are described in terms of the H–H distance  $\rho$ . In order to simplify the description of the potential, one transforms the pair of variables (*z*,  $\rho$ ) into a “curved” coordinate system (*s*, *r*).<sup>27,28</sup>

The most important variable besides the reaction coordinate *s* is the displacement *x* of the representative surface oscillator describing the motion of the substrate lattice during the adsorption/desorption process. In order to describe the coupling between *x* and *s* we do not introduce a curvature of the reaction path in these coordinates but rather a “displacement” [called  $\Delta(s)$  below] of the potential minimum along the reaction path. Such a PES allows a strong coupling to the lattice without producing strong translational heating as it would do for the usual curved reaction paths in exothermic processes in accord with Polanyi’s rules.

Finally we take surface corrugation (variation of potential parallel to the surface) into account in terms of the two Cartesian coordinates  $\mathbf{y}=(y_1, y_2)$  of the center-of-mass position parallel to the surface. In total then our model covers five degrees of freedom. Molecular rotations produce qualitatively similar effects as corrugation as can be seen in a 5D calculation neglecting corrugation instead of molecular rotations.<sup>29</sup>

In harmonic approximation our potential then has the structure

$$V(x, \mathbf{y}, r; s) = V_t(s) + V_p(x; s) + V_v(r; s) + V_c(\mathbf{y}; s), \quad (1)$$

where the subscript *t* stands for translation, *p* for substrate (“phonon”), *v* for (molecular) vibrations, and *c* for corrugation. The structure of the right-hand side of Eq. (1) contains

no assumption about the physics of the variables involved and the detailed form of the transition state (asymmetric or symmetric intra- or interdimer transition state). It is solely determined by the mathematics of the harmonic expansion. For the variables  $x$  and  $y$  we take anharmonic effects into account, but keep the structure of Eq. (1).

The first term  $V_t(s)$  (the translational potential) then as just described gives the value along the *minimum* of the multidimensional potential with respect to the coordinates orthogonal to  $s$ , i.e., along the line of steepest descent of the PES. We have chosen the parametrization:

$$V_t(s) = (V_d - V_a) \frac{\tanh(\lambda s) - 1}{2} + \frac{1}{4} (V_d + V_a + 2\sqrt{V_d V_a}) \frac{1}{\cosh^2(\lambda s)}, \quad (2)$$

with an adsorption barrier  $V_a$ , a desorption barrier of  $V_d$ , and a potential decay length  $\lambda$ .

The adsorption barrier can be determined so as to yield the observed very low value of the sticking coefficient at room temperature of the order of  $10^{-8}$  leading to  $V_a \approx 0.72$  eV. The desorption barrier  $V_d$  is known from experiment to be  $V_d = 2.3$  to  $2.5$  eV.<sup>30-32</sup>  $\lambda$  has an influence on the translational energy dependence of the sticking coefficient  $s(E)$  and on the translational energy in desorption. In order to represent the recent data<sup>9</sup> on  $s(E)$  we choose a value of  $\lambda = 2.7 \text{ \AA}^{-1}$ .

The additional three terms describe the coupling of center-of-mass motion along the reaction path with lattice vibrations, molecular vibrations, and center-of-mass motion parallel to the surface. To lowest order the potential is quadratic in the variables  $x$ ,  $r$ ,  $y$  as assumed in Eq. (1).

Since the lattice is excited strongly we replace the harmonic potential  $V_p$  by a Morse potential. Also  $V_c$ , which is harmonic near the periodically distributed adsorption sites, will be generalized to a cosine function. Since we omit further anharmonic terms, Eq. (1) describes a *model* and is no longer uniquely determined by mathematics.

We introduce the coupling to the lattice by assuming an  $s$ -dependent shift  $\Delta(s)$  of the potential minimum in the form

$$V_p(x; s) = D(s) \left( 1 - \exp \left( - \frac{\gamma_p(s)}{\sqrt{N_p}} [x + \Delta(s)] \right) \right)^2. \quad (3)$$

The potential depth  $D(s) = N_p \hbar \omega_p(s) / 2$  is given by the frequency  $\hbar \omega_p(s) = E_1(s) - E_0(s)$  defined as the quantum of the first excited state and the number of bound states  $N_p$  which we fix at  $N_p = 39$  independent of  $s$ . The inverse oscillator length is  $\gamma_p(s) = \sqrt{M^* \omega_p(s) / \hbar}$ . We choose the effective phonon mass  $M^*$  to be the mass of one single Si atom and for the asymptotic frequency we use  $\hbar \omega_p(\infty) = 55$  meV. The latter is a mean value of several optical modes.<sup>33</sup> At the barrier we take a frequency smaller than this by 20% and a smooth interpolation on the length scale  $0.5 \text{ \AA}$  between this and the asymptotic value.

For  $\Delta(s)$  we use the parametrization

$$\Delta(s) = \Delta_0 \{ [1 + \tanh(\lambda_d(s - s_0))] / 2 \}^7, \quad (4)$$

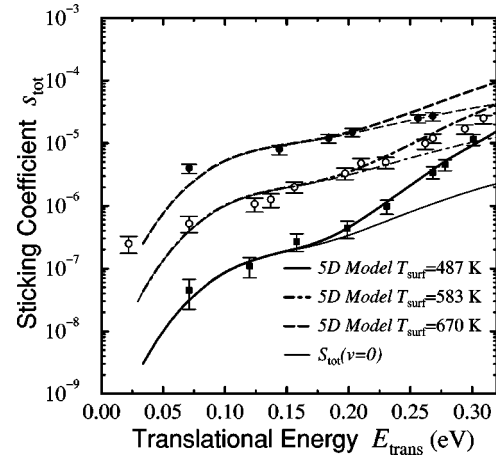


FIG. 1. Sticking coefficient compared to experimental beam data<sup>9</sup> for three different surface temperatures. We include molecular vibrationally assisted sticking for all  $E_{\text{trans}}$  values by taking  $T_{\text{vib}} = T_{\text{Nozzle}}(E_{\text{trans}})$  (thick lines). This is important especially for higher translational energies as can be seen from the sticking coefficient for the vibrational ground state  $\nu=0$  corresponding to  $T_{\text{vib}}=0$  K (thin lines).

which is now smoother at the barrier compared to our earlier parametrization<sup>12</sup> and has some flexibility by the choice of  $\lambda_d$  and  $s_0$ . Figure 1 shows that we obtain good agreement of our 5D sticking coefficient with the recent experimental beam data,<sup>9</sup> if we use  $\Delta_0 = 0.7 \text{ \AA}$ ,  $\lambda_d = 2.7 \text{ \AA}^{-1}$ , and  $s_0 = -0.15 \text{ \AA}$ . Only at very low translational energies our 5D sticking coefficient decrease more rapidly (see first data point of  $T_{\text{surf}} = 583$  K in Fig. 1). This discrepancy is reduced as recent calculations show if one takes molecular rotations into account.<sup>29</sup>

Our potential leads to a strong lattice excitation in desorption. Application of time reversal to such a desorption process then leads to a large sticking coefficient for an *excited lattice*. Hence, our model predicts strong phonon-assisted sticking with an Arrhenius energy  $E_A = 0.64$  eV for the surface temperature dependence of the sticking coefficient of a thermal gas at  $T_{\text{gas}} = 300$  K. Experimentally, such a strong enhancement of the sticking probability was indeed observed first for  $\text{H}_2$  adsorption on  $\text{Si}(111)7 \times 7$  and then also for  $\text{Si}(001)2 \times 1$ .<sup>4,5</sup>

The molecular vibration dynamics leaves the adsorption/desorption dynamics of the model calculations presented above at low energies essentially unchanged (apart from zero point energy contributions to the PES). The coupling of the molecular vibrations is produced by an  $s$ -dependent stretching of the intramolecular bond length leading to an elbow-like curved reaction path.

Because of the low molecular vibrational energy produced in the reaction it is sufficient to use a harmonic potential  $V_v$  in Eq. (1):

$$V_v(r; s) = \frac{\hbar \omega_v(s)}{2} (\gamma_v(s) r)^2. \quad (5)$$

The inverse oscillator length is  $\gamma_v(s) = \sqrt{\mu \omega_v(s) / \hbar}$  with  $\mu$  the reduced mass of the hydrogen molecule and  $\hbar \omega_v(s)$  the frequency of the molecular vibration.

The value of the curvature as well as a reduction of the vibrational frequency to about 50% at the transition state are

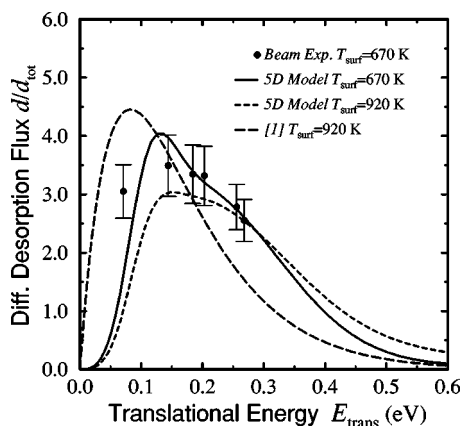


FIG. 2. Differential flux for normal desorption  $d(E_{\text{trans}}, \vartheta=0^\circ, T_{\text{surf}})$  of H<sub>2</sub> calculated directly from the experimental sticking coefficient<sup>9</sup> and with our 5D model. For  $T_{\text{surf}}=920$  K our 5D result and a Maxwell-Boltzmann distribution with  $T_{\text{des}}=960$  K fitted to the desorption experiments of Ref. 1 are also shown, indicating that our model predicts more translational heating in desorption.

taken from *ab initio* calculations,<sup>14</sup> yielding in a 5D treatment in desorption the experimentally observed vibrational heating with its isotopes effects,<sup>2</sup> and in adsorption vibrationally assisted sticking at higher nozzle temperatures.<sup>9</sup> The difference between the sticking coefficient with and without vibrationally assisted sticking is shown in Fig. 1.

For the corrugation we take an “energetic corrugation” of the potential into account where only the height but not the position of the barrier is varied along the surface. In this case the overall effect of corrugation is an approximately temperature independent decrease of the sticking coefficient. The corresponding term in Eq. (1) is:

$$V_c(\mathbf{y};s) = \frac{1}{4 \cosh^2(\lambda_c s)} \left\{ V_1 \left[ 1 - \cos\left(\frac{2\pi}{a_1} y_1\right) \right] + V_2 \left[ 1 - \cos\left(\frac{2\pi}{a_2} y_2\right) \right] \right\}. \quad (6)$$

Here  $\mathbf{y}$  means the center-of-mass coordinate parallel to the surface with a periodicity length of  $a_1=3.68$  Å perpendicular, and  $a_2=7.36$  Å parallel to the dimer taken from the Si(001) dimer positions. The range of the corrugation was taken to be  $\lambda_c=2$  Å<sup>-1</sup>. The heights  $V_{1,2}=m(\omega_{1,2}a_{1,2}/\pi)^2$  are determined so as to produce the appropriate keyhole effects for the sticking coefficient. This leads to frequencies  $\hbar\omega_{1,2}$  at the transition state of 8 meV parallel and 5 meV perpendicular to the dimer, 50% smaller than *ab initio* results for an intradimer symmetric transition state.<sup>14</sup>

The quantum dynamics of the 5D model is treated by expanding the wave function in terms of 24 Morse oscillator eigenstates for the lattice and 2–3 harmonic oscillator states for the molecular vibrations. For the two lateral coordinates we expand into 25 to 49 plane wave states. The Schrödinger function then becomes a vector with about 2000 components (“channels”). We compute reflection and transmission coefficients using numerically stable time independent coupled channel methods.<sup>28,34</sup>

Whereas most of the parameters of our 5D PES are determined by the cited *ab initio* and experimental values or

are fixed at *reasonable* values, only  $V_a$ ,  $\lambda$ ,  $\Delta_0$ ,  $\lambda_d$ ,  $s_0$ ,  $\omega_{1,2}$  had to be readjusted to fit the observed sticking curves<sup>9</sup>  $s(E, T_{\text{surf}})$ .

With this 5D potential we find an increased normal mean translational energy in desorption of  $T_{\text{des}} \approx 2T_{\text{surf}}$  (Fig. 2) with for example  $\langle E_{\text{trans}}(\vartheta=0) \rangle = 235$  meV for H<sub>2</sub> at  $T_{\text{surf}}=670$  K, and 300 meV at  $T_{\text{surf}}=920$  K. We can now compare the results of our 5D model for  $T_{\text{surf}}=920$  K directly with earlier laser induced desorption measurements at this surface temperature,<sup>1</sup> showing almost no translational heating with  $\langle E_{\text{trans}}(\vartheta=0) \rangle \approx 170$  meV. Thus, our 5D model based on the beam data of Ref. 9 predicts an increased translational energy in desorption with slightly less than twice the value of Ref. 1. In judging this difference one has to keep in mind: (a) the experimental error of the desorption experiment of about  $\pm 35$  meV (Ref. 1); (b) that both translational energies in desorption are still small compared to the high adsorption barrier.

Our new prediction for the normal mean translational energy in desorption is now closer to results derived from *ab initio* GGA calculations<sup>18</sup> (three times the thermal value).

Note that the energy distribution in desorption is closely related via detailed balance to the translational energy dependence of the sticking coefficient  $s(E)$ .

Due to the increased translational energy the angular dependence of the sticking coefficient is now strongly forward peaked with  $s(E, \theta) \propto (\cos \theta)^{11 \text{ to } 12}$  for  $T_{\text{Nozzle}}=1100$  K and  $T_{\text{surf}}=500$  K, depending very little on corrugation. Such a behavior of sticking has indeed been observed experimentally on a single-domain Si(001) surface.<sup>10</sup>

*Ab initio* calculations for the asymmetric intradimer transition state predict a large anisotropy (40 to 60 degrees, depending on the details of the calculations).<sup>18,25</sup> For our strongly peaked angular distributions, averaging over two opposite dimer orientations would lead to two separate peaks parallel to the dimer. For a smaller anisotropy (e.g.,  $\pm 15$  degrees), however, averaging leads to a broadened single peak. This would be in agreement with the multidomain angular distribution in desorption of Ref. 3 corresponding to an angular dependence of sticking  $\propto (\cos \theta)^3$  to  $^4$ .

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