Molecular beam investigation of hydrogen dissociation on Si(001) and Si(111) surfaces

M. Dürr and U. Höfer

Fachbereich Physik und Zentrum für Materialwissenschaften,
Philipp-Universität Marburg, Renthof 5, D-35032 Marburg, Germany

(Dated: Mar 16, 2004, submission to J. Chem. Phys.)

The influence of molecular vibrations on the reaction dynamics of H$_2$ on Si(001) as well as isotopic effects have been investigated by means of optical second harmonic generation (SHG) and molecular beam techniques. Enhanced dissociation of vibrationally excited H$_2$ on Si(001)2×1 has been found corresponding to a reduction of the mean adsorption barrier to 390 meV and 180 meV for $\nu$ = 1 and $\nu$ = 2, respectively. The adsorption dynamics of the isotopes H$_2$ and D$_2$ show only small differences in the accessible range of beam energies between 50 meV and 350 meV. They are traced back to different degrees of vibrational excitation and do not point to an important influence of quantum tunneling in crossing the adsorption barrier. The sticking probability of H$_2$ on the 7×7-reconstructed Si(111) surface was found to be activated both by H$_2$ kinetic energy and surface temperature in a qualitatively similar fashion as H$_2$/Si(001)2×1. Quantitatively, the overall sticking probabilities of H$_2$ on the Si(111) surface are about one order of magnitude lower than on Si(001), the influence of surface temperature is generally stronger.

I. INTRODUCTION

The interaction of molecular hydrogen with single crystal silicon surfaces is of considerable interest as a model for understanding adsorbate reactions on semiconductor surfaces [1–6]. Dissociative adsorption of H$_2$ on clean Si(001) and Si(111) surfaces is an energetically favourable, but strongly activated reaction (Fig. 1). The chemisorption energy of H$_2$ on Si(001) and Si(111) at low coverages is slightly less than 2.0 eV [7] whereas the activation energy for desorption is around 2.5 eV [8–11]. The difference allows for an adsorption barrier in excess of 0.5 eV, a value that is consistent with the well-established chemisorption energy of H$_2$ on the Si(111) surface was found to be activated both by H$_2$ kinetic energy and surface temperature in a qualitatively similar fashion as H$_2$/Si(001)2×1. Quantitatively, the overall sticking probabilities of H$_2$ on the Si(111) surface are about one order of magnitude lower than on Si(001), the influence of surface temperature is generally stronger.

The interaction of molecular hydrogen with single crystal silicon surfaces is of considerable interest as a model for understanding adsorbate reactions on semiconductor surfaces [1–6]. Dissociative adsorption of H$_2$ on clean Si(001) and Si(111) surfaces is an energetically favourable, but strongly activated reaction (Fig. 1). The chemisorption energy of H$_2$ on Si(001) and Si(111) at low coverages is slightly less than 2.0 eV [7] whereas the activation energy for desorption is around 2.5 eV [8–11]. The difference allows for an adsorption barrier in excess of 0.5 eV, a value that is consistent with the well-established chemisorption energy of H$_2$ on the Si(111) surface was found to be activated both by H$_2$ kinetic energy and surface temperature in a qualitatively similar fashion as H$_2$/Si(001)2×1. Quantitatively, the overall sticking probabilities of H$_2$ on the Si(111) surface are about one order of magnitude lower than on Si(001), the influence of surface temperature is generally stronger.

The first quantitative measurements of the initial sticking coefficients of H$_2$ on well-defined Si(111) and Si(001) surfaces have been conducted by Bratu et al. [14, 15] using SHG as a sensitive monitor for hydrogen chemisorption at the silicon dangling bonds [4]. These authors observed a strong dependence on surface temperature. In the case of Si(111)7×7 the sticking coefficient for the dissociative adsorption of a thermal H$_2$ gas is 2 × 10$^{-9}$ at 580 K. It increases to 5 × 10$^{-6}$ at 1050 K in an Arrhenius-like fashion [14]. The behaviour of H$_2$/Si observed in the SHG-experiments confirms a prediction by Brenig and co-workers [23]. In their
model of “phonon-assisted sticking” thermally activated distortions of the silicon lattice lead to configurations with greatly reduced dissociation barriers for the incident H2-molecules (Fig. 1). The motivation for the introduction of this model was twofold. First of all, due to the covalent nature of the Si–Si and Si–H bonds, lattice relaxation is generally expected to strongly affect reaction barriers. In the case of surface diffusion of hydrogen, e.g., calculated barriers are lowered by as much as 1 eV when the Si atoms are allowed to relax [24–28] and reach good agreement with experimental values [29–32]. Secondly, experiments by Kolasinski and co-workers show that the translational energy of the desorbing H2 molecules is remarkably small [33]. One possibility to reconcile this observation with the small sticking probability is the assumption that most of the excess energy in the transition state is rather released into Si phonons than into the H2 molecule itself. Phonon assisted sticking is then a consequence of detailed balance between recombinative desorption and dissociative adsorption [6, 23].

A detailed experimental investigation of the interplay between H2 translational energy and Si(001) lattice excitation in overcoming the adsorption barrier has been carried out by Diirr et al. [34] who combined molecular beam techniques for H2 dosing and SHG for the detection of hydrogen adsorption. The measured initial sticking coefficients $s_0$ as function of kinetic energy $E$ exhibited an s-shaped form, $s_0(E) \propto 1 + \tanh[E - E_0/W(T_s)]$, with a mean barrier height $E_0 \geq 0.6$ eV. Unlike to systems as H2/Cu, which have a comparable barrier [35–38], the temperature-dependent width-parameter $W(T_s)$ is large in the case of H2/Si, e.g. $W(670 \text{K}) = 190$ meV [39]. As expected for a phonon-assisted process, $W$ increases as a function of surface temperature $T_s$. At higher surface temperature, when thermally activated low-barrier pathways become more and more important, the sticking probability depends less on the kinetic energy of the gas molecules corresponding to an increase of $W$ with $T_s$. Conversion of the broad adsorption functions $s_0(E)$ into desorption flux $\Phi(E)$ according to detailed balance gives a maximum of $\Phi(E)$ at 170 meV, i.e. far below the barrier height. This result is in qualitative agreement with the lack of translational heating reported by Kolasinski et al. [33]. Recent desorption experiments by Sagara et al. [40] that have been performed under conditions that are closer to those of Ref. [34], i.e. lower coverage and lower surface temperature, show excellent agreement of $\Phi(E)$ with the inverted adsorption experiments.

Due to this strong influence of the surface degrees of freedom, the theoretical modeling of the reaction dynamics of H2/Si is quite difficult. Brenig and co-workers have constructed a parameterized multi-dimensional potential energy surface that is capable of explaining most of the available experimental data [6, 41, 42]. However, this potential is not unambiguous and more or less independent of the detailed microscopic pathways. Up to now, dynamical calculations based on ab-initio potential energy surfaces have only been conducted for dihydride adsorption [43, 44] and for the intra-dimer mechanism for Si(001) [45–47]. However, the latter pathway, that has been discussed intensively over many years [46–53], as it provides a natural explanation for the desorption kinetics of H2/Si(001), i.e. the so-called “pairing model” [9–11, 54], can be excluded on the basis of recent STM experiments [55, 56]. On Si(001)2 × 1, both the dissociative adsorption and the recombinative adsorption of H2 take place at the dangling bonds of two dimers of the same row (inter-dimer pathway, Fig. 1) [55–57]. The inter-dimer pathway which has been treated only sporadically in earlier theoretical work [50, 58] is indeed energetically favouré over the simpler intra-dimer pathway according to the most recent calculations [59, 60]. On Si(111)7 × 7, H2 is likely to interact with both the rest-atoms and the ad-atoms dangling-bonds [16, 61, 62].

Considerable insight into the nature of lattice distortions in the inter-dimer pathway on Si(001) has been gained by studying adsorption at steps and H-precovered surfaces [17, 57, 59, 63]. It has been shown, both experimentally and theoretically, that the geometric and electronic distortions of the Si surface caused by steps and pre-adsorbed hydrogen can lower the adsorption barrier at the remaining dangling bonds drastically. In case of the so-called H4 adsorption pathway where the two non-reactive dangling bonds of two dimers are saturated with hydrogen, the barrier even vanishes completely [57]. This leads to a coverage dependence of the sticking coefficient that depends on surface temperature and hydrogen flux [19]. In desorption, the H4 pathway dominates at high coverages and models have been proposed that account for the deviation from 2nd order kinetics, characteristic for H2 desorption from Si(001) [19, 64, 65].

Information about the lateral corrugation of the dissociation barrier of H2/Si(001) has recently been obtained by angular dependent measurements of the sticking probability on single-domain surfaces [66]. A strong forward peaking along the direction of the dangling bonds was observed. Comparison with the results of angular distributions found for recombinative desorption from two-domain surfaces shows that adsorption and desorption are closely related by detailed balance [66–68].

In this paper, we present experimental results concerning three further aspects of the dynamics of H2 adsorption on silicon:

1) The dynamics of dissociative adsorption cannot be satisfactorily described without considering molecular vibrations. We apply seeded molecular beam techniques in combination with SHG and measure the energy dependence of the sticking probability on single-domain surfaces [66]. A strong forward peaking along the direction of the dangling bonds was observed. Comparison with the results of angular distributions found for recombinative desorption from two-domain surfaces shows that adsorption and desorption are closely related by detailed balance [66–68].

2) In dissociation reactions involving hydrogen the possibility of tunneling has frequently been discussed in
FIG. 2: Experimental setup for the determination of sticking probabilities by means of supersonic molecular beam and optical second harmonic generation techniques. The hydrogen beam is expanded from the continuous nozzle in chamber 1 (C1) and can be chopped by the chopper (Ch) in chamber 2 (C2) for time-of-flight measurements with the quadrupole mass spectrometer (QMS). The beam enters the main chamber (C4) after passing an additional differential pumping stage (C3). Chamber C5 can be used as a stagnation detector for determination the hydrogen flux in the beam when it is pumped only through its aperture. For optical second harmonic generation, pulsed laser light of the frequency \(\omega\) shines on the sample under 45°. The specularly reflected signal at 2\(\omega\) is detected after separation of the laser fundamental. Additional windows allow for angle dependent measurements of sticking coefficients [66].

The adsorption measurements have been performed by means of a combination of molecular beam techniques and optical second harmonic generation (SHG) introduced earlier [34]. The experimental setup is sketched in Fig. 2. The hydrogen beam is provided by a continuous, heatable supersonic nozzle consisting of a molybdenum tube with a hole of 30 \(\mu\)m diameter [71]. Hydrogen gas with a purity of 99.9999% is passed through a cooled trap in order to freeze out residual H\(_2\)O. With a backing pressure of 11 bar and a nozzle-sample distance of 30 cm the apparatus allows for a pure hydrogen flux on the surface as high as \(\Phi = 2 \times 10^{16}\) molecules per cm\(^2\). The speed ratio \(S\) between the mean velocity and the width of the distribution is \(S = \bar{v}/\Delta v \approx 10\) at room temperature. Before hydrogen exposure, the silicon surfaces have been prepared by resistive heating of the samples up to 1300 K and a subsequent slow cooling down. They showed clear 2\(\times\)1 and 7\(\times\)7 low-energy-electron-diffraction patterns for Si(001) and Si(111), respectively, and no traces of contaminants were detected in the Auger electron spectra.

II. EXPERIMENT

The adsorption measurements have been performed by means of a combination of molecular beam techniques and optical second harmonic generation (SHG) introduced earlier [34]. The experimental setup is sketched in Fig. 2. The hydrogen beam is provided by a continuous, heatable supersonic nozzle consisting of a molybdenum tube with a hole of 30 \(\mu\)m diameter [71]. Hydrogen gas with a purity of 99.9999% is passed through a cooled trap in order to freeze out residual H\(_2\)O. With a backing pressure of 11 bar and a nozzle-sample distance of 30 cm the apparatus allows for a pure hydrogen flux on the surface as high as \(\Phi = 2 \times 10^{16}\) molecules per cm\(^2\). The speed ratio \(S\) between the mean velocity and the width of the distribution is \(S = \bar{v}/\Delta v \approx 10\) at room temperature. Before hydrogen exposure, the silicon surfaces have been prepared by resistive heating of the samples up to 1300 K and a subsequent slow cooling down. They showed clear 2\(\times\)1 and 7\(\times\)7 low-energy-electron-diffraction patterns for Si(001) and Si(111), respectively, and no traces of contaminants were detected in the Auger electron spectra.

Hydrogen uptake on the surface is monitored in real time by optical second-harmonic generation of the fundamental of a Q-switched Nd:YAG laser, as described previously [14, 15]. At the wavelength of 1064 nm the nonlinear response of Si(001)2\(\times\)1 and Si(111)7\(\times\)7 is resonantly enhanced by dangling-bond derived surface states that are quenched upon hydrogen adsorption [4, 72, 73]. For small coverages this leads to a linear decrease of the square root of the SHG signal \(I^2(2\omega) \propto |\alpha s^2(\theta)|\) with hydrogen coverage \(\theta\). The relationship between the nonlinear susceptibility \(\chi^2_s\) and hydrogen coverage \(\theta\) is \(\chi^2_s(\theta) = \chi^2_s(0)(1 - \alpha\theta)\) with the proportionality factors \(\alpha = 3.1\) for Si(001) and \(\alpha = 1.3\) for Si(111) [4]. The high sensitivity of the SHG probe together with the high gas flux makes it possible to measure sticking coefficients as small as \(10^{-8}\) with our setup. In addition, real time monitoring allows for the detection of different reaction channels on
one surface if present, e.g. at steps or sites pre-covered with H atoms [17, 18, 34, 57, 66, 74].

Typical adsorption traces on a flat and clean Si(111)7×7 surface are shown in Fig. 3. The SHG signal is constant as long as the molecular beam is off and decreases continuously with hydrogen uptake after opening the shutter. Initial sticking probabilities are derived from the slope of the curves by

\[ s_0 = \Phi^{-1} \frac{\Delta \theta}{\Delta T} \simeq -\left(\Phi \alpha \chi^{(2)}_s \right)^{-1} \frac{\Delta \chi^{(2)}_s}{\Delta T}. \]  

The kinetic energy of H\(_2\) in the molecular beam is increased by heating the supersonic nozzle. At the same time, this leads to an increased number of vibrationally excited molecules. By admixing heavier rare gases to the hydrogen gas, the correlation between nozzle temperature and kinetic energy of the H\(_2\) molecules can be decoupled [75]. This so-called seeded beam technique allows the measurement of sticking probabilities as a function of kinetic energy for one fixed nozzle temperature and therefore a certain ratio of the vibrationally excited states. The kinetic energy distribution of the molecules has been carefully determined by means of time-of-flight measurements directly before and after every single of these adsorption measurements. The speed ratio \( S \) of hydrogen in the seeded beam is reduced compared to the pure hydrogen beam with a value of \( S \approx 6 \) for the H\(_2\)/Ne-mixture. The hydrogen flux \( \Phi \) in the seeded beam has been determined by measuring the partial pressure in a stagnation detector (C5 in Fig 2) [76, 77].

For the population of excited vibrational states of the hydrogen molecules nozzle temperatures in excess of 1000 K are necessary. Within this temperature range, the equilibrium between atomic and molecular hydrogen in the hot nozzle is shifted towards atomic hydrogen. H-atoms are produced in an amount which can influence the adsorption measurements. In the seeded beam experiments, in particular molecules with low translational energy and therefore reduced sticking probability compete with the highly reactive hydrogen atoms. To test their actual influence, sticking probabilities have been measured as a function of stagnation pressure \( p_0 \) in the nozzle. Results are shown in Fig. 4 for two nozzle temperatures as well as fits to the data following

\[ s_0(T_N, p_0) = s_{0,H_2}(T_N) + \alpha_{\text{diss}}(T_N, p_0)s_{0,H}\]  

\[ \alpha_{\text{diss}}(T_N, p_0) \propto 10^{-11850 K/T_N + 3.18} / \sqrt{p_0} \]  

with sticking probability for atomic hydrogen \( s_{0,H} \). The pressure dependence of the degree of H\(_2\) dissociation \( \alpha_{\text{diss}} \) is derived from simple statistical considerations and the temperature dependence is taken to follow the data in literature [78]. One can clearly observe that at low stagnation pressure and high nozzle temperature, hydrogen uptake is dominated by H-atoms in the beam. However, towards high stagnation pressures the hydrogen molecules dominate the adsorption behaviour in the temperature regime investigated.

III. INFLUENCE OF MOLECULAR VIBRATIONS - SEEDED BEAM EXPERIMENTS FOR H\(_2\)/Si(001)

It is well known from activated adsorption systems on metal surfaces that vibrational excitations can effectively enhance the reactivity of the dissociating molecule [79, 80]. Moreover, for H\(_2\) desorbing from both Si(001) and Si(111), an overpopulation of excited vibrational states has been found [81]. Following detailed balance, an increased reactivity for such excited molecules is expected in the adsorption channel.

Seeding hydrogen in neon results in a lower translational energy of the H\(_2\) molecules as compared to a pure hydrogen beam. If one neglects vibrational cooling during the supersonic expansion, the population of vibrationally excited molecules is given by the nozzle temperature \( T_N \). Sticking coefficients measured at constant nozzle temperature but with varied gas mixture therefore reflect the dependence of sticking probability on kinetic energy for a constant ratio of excited molecules in the beam.

For H\(_2\)/Si(001), such data are shown in Fig. 5 for various nozzle temperatures \( T_N \) and a surface temperature \( T_s = 90 \) K. The low surface temperature minimizes the effect of lattice excitation on the hydrogen dissociation. Therefore, the effect of molecular vibrations on the reaction dynamics is revealed most clearly. At low kinetic energies and high nozzle temperatures, the measured sticking coefficients are much higher than those of the unseeded beam and they show very little energy dependence. According to the the results of the stagnation pressure dependent measurements (Fig. 4), hydrogen uptake in this region is mainly due to the adsorption of atomic hydrogen. Towards higher energies (\( E_{\text{kin}} \geq 150 \text{ meV} \), the sticking probability increases beyond this
FIG. 5: Initial sticking coefficients on Si(001)2×1 at a surface temperature $T_s = 90$ K as a function of kinetic energy for three constant nozzle temperatures, i.e. three different populations of excited vibrational states (filled symbols) and as a function of nozzle temperature converted to $E_{\text{kin}}$ for the pure hydrogen beam (circles). Lines represent fits of the model functions Eq. 4 and Eq. 5 to the data. In the inset, the obtained energy dependence of the sticking coefficient of H$_2$ in the $\nu = 1$ and the $\nu = 2$ state is compared to that of ground-state molecules. The dashed line for $\nu = 0$ indicates a width of the barrier distribution of 190 meV, as measured for a surface temperature of 670 K [34], the solid line corresponds to $W = 80$ meV, the upper limit of $W$ at $T_s = 90$ K.

background. This effect is most pronounced for the lowest nozzle temperature ($T_N = 1268$ K). We attribute it to the sticking of vibrationally excited molecules because the sticking probability of atomic hydrogen is unlikely to depend strongly on kinetic energy and because the amount of hydrogen atoms in the beam is constant. For the unseeded beam, with less excited molecules at the same kinetic energy, we measure considerably smaller absolute sticking probabilities.

In order to quantify the the effect of vibrational excitation we describe the sticking coefficient as function of kinetic energy and nozzle temperature by a model function that properly accounts for the relative population of vibrational excited and dissociated molecules in the beam

$$s_0(E_{\text{kin}}, T_N) = \sum_\nu F_B(\nu, T_N)s_0(\nu, E_{\text{kin}}) + \alpha_{\text{diss}}(T_N, p_0)s_0,_{H}$$

(4)

The contributions $s_0(\nu, E_{\text{kin}})$ of the molecules in the vibrational state $\nu$ are weighted by the Boltzmann factor $F_B(\nu, T_N) = [\exp(E_\nu/kT_N) + 1]^{-1}$ for the state $\nu$ at temperature $T_N$. The state-resolved sticking coefficients $s_0(\nu, E_{\text{kin}})$ are modeled by the s-shaped functions

$$s_0(\nu, E_{\text{kin}}) = \frac{A(\nu)}{2} \left[ 1 + \tanh \frac{E_{\text{kin}} - E_0(\nu)}{W(\nu)} \right].$$

Adsortion of atomic hydrogen is taken into account using a constant sticking coefficient $s_{0, H}$ and the $T_N$-dependent dissociation coefficient $\alpha_{\text{diss}}$.

The mean adsorption barriers $E_0(\nu)$, the widths of the distributions $W(\nu)$, and saturation values $A(\nu)$ were obtained from the best fit of eq. 4 to the full data set of Fig. 5. The resulting parameters are collected in Table I, the solid lines in Fig. 5 indicate the calculated sticking coefficients. Although the number of the data points in Fig. 5 is limited, they impose severe restrictions on the most interesting fit parameters, the barriers $E_0(\nu = 1)$ and $E_0(\nu = 2)$. We estimate an accuracy of 30 meV and 50 meV, respectively. The errors are considerably smaller than that of $E_0(\nu = 0)$ determined earlier from experiments with an unseeded beam at higher surface temperature as these measurements could only probe the energy regime far below the mean barrier of 0.8 eV [34]. Also included in Table I is the parametrization used for the measurements at higher surface temperatures. The contribution of the vibrationally excited H$_2$ and D$_2$ molecules are well described with the same mean adsorption barriers $E_0$ but with a somewhat increased width parameter $W$. It should be noted that the finite width of the energy distribution of the beam appreciably affects values of the width parameters given in Table I only for $W = 40$ meV. The resulting inaccuracy of these width parameters has been calculated to be in the order of ±10 meV.

For the further discussion it is instructive to compare the contributions of molecules in the first and second excited state as well as that of hydrogen atoms to the total sticking of the unseeded beam. Fig. 6 shows that at low nozzle temperature and therefore low kinetic energy, only the molecules in the second excited state may traverse their low adsorption barrier. In the mid-temperature regime, the molecules in the first excited state contribute most to the overall sticking coefficients. This can be explained by the fact that the molecules in the second excited state have already reached the saturation value of

<table>
<thead>
<tr>
<th>$T_s$ (K)</th>
<th>$E_\nu$ (meV)</th>
<th>$E_0$ (meV)</th>
<th>$W$ (meV)</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>$\nu = 0$</td>
<td>–</td>
<td>$\geq 600$</td>
<td>$&lt;80$</td>
</tr>
<tr>
<td>90</td>
<td>$\nu = 1$</td>
<td>520</td>
<td>390 ± 30</td>
<td>40</td>
</tr>
<tr>
<td>90</td>
<td>$\nu = 2$</td>
<td>1020</td>
<td>180 ± 50</td>
<td>40</td>
</tr>
<tr>
<td>487</td>
<td>$\nu = 0$</td>
<td>–</td>
<td>820 ± 200</td>
<td>125</td>
</tr>
<tr>
<td>670</td>
<td>$\nu = 0$</td>
<td>–</td>
<td>820 ± 200</td>
<td>190</td>
</tr>
<tr>
<td>540</td>
<td>$\nu = 1$</td>
<td>520</td>
<td>390 ± 50</td>
<td>70</td>
</tr>
</tbody>
</table>
the applied s-curve. Their contribution follows a softer increase correlated with the number of excited molecules in the beam whereas the molecules in the first excited state reach their adsorption barrier with the consequence of a strongly increasing reactivity. Only for the highest temperatures close to $T_N = 2000$ K, the influence of atomic hydrogen becomes comparable to that of the molecules in the first excited state.

Following the principle of detailed balance, the enhanced reactivity of excited molecules in adsorption can be directly related to the overpopulation (vibrational heating) of the excited state found in desorption measurements. We compare the ratio of molecules found in the $\nu = 1$ state to those found in the $\nu = 0$ state via

$$\frac{P_1}{P_0} = \frac{\int_0^\infty \sqrt{E} e^{-E/kT} e^{-E_{exil}/kT} s(\nu=1,E)dE}{\int_0^\infty \sqrt{E} e^{-E/kT} s(\nu=0,E)dE}$$

(6)

applicable for molecules desorbing perpendicular to the surface [82]. In desorption Shane et al. [81] found $P_1/P_0 = 0.0108 \pm 0.004$ at a surface temperature of $T_s = 780$ K. We obtain the same value for $P_1/P_0$ using width parameters $W(\nu=0) = 200$ meV and $W(\nu = 1) = 80$ meV that are in good agreement with the results obtained at the highest temperature of our experiment, $T_s = 670$ K. Although this suggests that detailed balance is applicable and the microscopic pathways of adsorption and desorption are simply reversed, one should be aware that the desorption measurements of Ref. [81] most likely probed a surface in the mid-coverage regime whereas our adsorption measurements were performed at a coverage below 5%. Indeed it is known that at higher surface coverages, dissociation of hydrogen can proceed via a non-activated reaction path, the so-called H4 mechanism [57, 63]. This reaction pathway accounts for the observed increase of sticking probability with surface coverage [19]. It is operative at saturation coverage [56] and no vibrational heating is expected from such a barrierless pathway. However, one expects a turnover from the barrier-less H4 to the ordinary H2 path at coverages as high as 0.9 ML [64, 65], since this would reconcile the desorption kinetics with earlier findings [10]. Therefore the comparison of vibrational assisted sticking found in the adsorption experiments at low surface coverage with vibrational heating found in desorption experiments at mid and high surface coverage is justified [65].

For a qualitative discussion of the microscopic origin for the observed enhancement of the sticking probability by molecular vibrations we start with the simplest point of view and compare the relevant bond lengths. In case of the Si(001) inter-dimer pathway the Si–Si–distance of the reacting Si atoms and thus the distance of the dissociated H atoms is 3.8 Å while the bond length of H$_2$ is only 0.9 Å. Clearly, the intra-molecular distance will be an important factor for the dynamics of the dissociation process. Even for the intradimer reaction path with a relevant Si–Si–bond length of only 2.3 Å, ab-initio calculations found a late barrier in adsorption [46], i.e. the molecule first closely approaches the surface and then needs a considerable amount of energy to dissociate within a short variation of distance to the surface. In this case, energy to overcome the barrier can be supplied efficiently by intra-molecular vibrations, provided the incident molecules are oriented parallel to the surface.

Of course, the underlying mechanism for the effective energy transfer from the vibrational to the translational reaction coordinate, and vice versa, may be found not only in purely geometric considerations but also in the electronic structure of the reacting molecule. With greater inter-atomic distance, the splitting of occupied $\sigma$ and unoccupied $\sigma^*$ states of H$_2$ will be reduced. This enables a more effective filling of the antibonding $\sigma^*$ orbitals crucial for dissociation [17, 59]. Comparison of the amount of energy stored in the vibrational excitation with the respective reduction of the mean adsorption barrier, however, shows that vibrational and kinetic energy cannot contribute equally to overcome the reaction barrier. Moreover, the higher excited $\nu = 2$ state is less effective in reducing the adsorption barrier. Very similar behaviour has been found for H$_2$ on Cu(111) [79].

IV. ISOTOPIC EFFECTS - D$_2$/Si(001)

The effect of vibrationally excited molecules is even more pronounced for the sticking probability of deuterium on Si(001). Fig. 7 compares results for unseeded H$_2$ and D$_2$ beams as a function of nozzle temperature at
a surface temperature of 540 K. For low nozzle temperatures the sticking coefficient of D$_2$ is about 50% smaller than that of H$_2$. This result is in agreement with the measurements performed for a thermal gas [15]. However, at $T_N \geq 1000$ K, $s_0(T_N)$ exhibits a stronger increase for D$_2$ and exceeds that of H$_2$ at $T_N \geq 1400$ K.

The increased sticking probability of D$_2$ is mostly a consequence of the lower energy of its first two vibrational states ($E_{\nu=1}$ = 0.36 meV, $E_{\nu=2}$ = 0.70 meV). As a result, the population of vibrationally excited D$_2$ molecules at a given nozzle temperature is higher than in the case of H$_2$. The effect is rather pronounced for the $\nu = 2$ state which can significantly contribute to the sticking of D$_2$ at intermediate nozzle temperatures whereas its effect is negligible in the case of H$_2$ under the same conditions.

If we calculate the sticking probability of D$_2$/Si(001) using the same model functions as for H$_2$/Si(001) we find good agreement using the same barriers. However, we have to reduce either the saturation values or the width parameters as compared to H$_2$. Whereas $W_{H_2}(\nu = 0) = 150$ meV we find $W_{D_2}(\nu = 0) = 140$ meV. For molecules in the first vibrational state, assuming similar saturation values as for H$_2$ and D$_2$ in the vibrational ground state, the width parameter is 70 meV for H$_2$, but only 50 meV for D$_2$.

There are several possibilities how the molecule’s mass may influence the reaction dynamics aside from the different degree of vibrational excitation. First of all, if tunneling through the adsorption barrier would be important one would indeed expect a smaller low-energy sticking probability for D$_2$ than for H$_2$. However, as the mass enters the tunneling rate exponentially, the reduction would be huge if tunneling were decisive. The 50% effect that shows up in Fig. 7, appears to be too small to be associated with tunneling.

Two contrary possibilities remain in the picture of phonon assisted sticking. On the one hand, the reduced ground state energy of the D$_2$ molecule should lead to a higher adsorption barrier (in the order of 0.1 eV), in qualitative agreement with a lower sticking probability. On the other hand, the molecules experience the corrugation as a quantum trough the closer they come to the surface [6]. The resulting zero point energy for the vibration of the center of mass of the molecule in this quantum trough is again higher for the lighter molecule and the difference adds to its adsorption barrier. However, this effect seems to be small. Additionally, a stronger localization of deuterium may influence the effective potential energy surface in such a way that the molecule probes a smaller region of the potential. As a consequence, a smaller distribution of barriers is probed resulting in the smaller width of the adsorption function [83].

V. INFLUENCE OF RECONSTRUCTION - Si(001)2×1 VS. Si(111)7×7

In order to probe the influence of the reconstruction on the reaction dynamics we measured sticking coefficients for H$_2$ on Si(111)7×7 as function of beam energy and surface temperature. In this section, we compare the results with those obtained earlier for H$_2$/Si(001) [34].

Typical adsorption traces for 4 different beam energies have been shown in Section II, Fig. 3. Each curve is characterized by one single slope, no hints on reaction channels caused by minority species is detectable. The increase of reactivity with coverage, reported earlier for the adsorption of thermal H$_2$ [16], does not play a role for the low coverages of the present investigation, in agreement with the results of Refs. [14] and [16]. The resulting sticking coefficients as a function of nozzle temperature are plotted in Fig. 8b for 4 different surface temperatures. For comparable surface temperatures, they are in general smaller than on Si(001), Fig. 8a, again in agreement with the results reported earlier for thermal gases [15].

For both surfaces, two regimes are clearly distinguishable. At $T_N \geq 1200$ K, the sticking coefficient increases strongly with nozzle temperature due to the onset of vibrational assisted sticking as discussed in Section III. The mean barrier $E_0(\nu = 1)$ and saturation value $A(\nu = 1)$ are found to be similar to those of Si(001) but a smaller width parameter $W(\nu = 1) \approx 40$ meV was obtained. At low nozzle temperatures, the sticking coefficient clearly depends on $T_N$ as well. Since for $T_N < 1000$ K the number of vibrationally excited molecules in the beam is too
small to be responsible for a significant hydrogen uptake (c.f. Fig. 6), this dependence reflects an influence of kinetic energy of the ground state molecules. In this low energy regime, the sticking coefficients of both surfaces show a strong dependence on surface temperature $T_s$. For higher $T_s$, one observes a higher overall sticking probability and in general a lower activation with kinetic energy.

In the case of Si(001), the whole data set is well described by using the model functions (5) with width parameters $W(\nu = 0)$ that monotonously increase as a function of surface temperature [34]. In the case of Si(111), the correlation between the sticking coefficient as a function of kinetic energy and surface temperature is not as clear as in the case of Si(001), e.g., the energy dependence of the data is smaller for $T_s = 600$ K than for $T_s = 666$ K. A description via s-shaped adsorption functions with one common mean adsorption barrier $E_0$ and only the width of the distribution depending on surface temperature matches the data in this region rather poorly (Fig. 8b).

For a better comparison with the results of Si(001), we nonetheless represent the whole set of Si(111) data by fitting s-shaped adsorption functions with $E_0 = 0.8$ eV and a saturation value $A = 10^{-2}$. From this fitting procedure, a linear increase of the width parameter with surface temperature from $W = 120$ meV at $T_s = 535$ K to $W = 230$ meV at $T_s = 727$ K is derived. The comparison with the results of Si(001), see inset of Fig. 8b, shows that the temperature dependence of $W$ is stronger in the case of Si(111).

The differences between the results of Si(001) and Si(111) are further illustrated in (Fig. 9), an Arrhenius plot of the sticking coefficient as function of surface temperature. For Si(001), a continuous decrease of activation with surface temperature is obtained for increasing beam energy. As discussed in Ref. [34], this result is in good agreement with the applied parametrization using a linear dependence of $W$ on $T_s$. Surprisingly, in the case of Si(111), the activation of $s_0$ with surface temperature is lower for $T_N = 297$ K (apparent activation energy $E_A = 0.7$ eV) than for $T_N = 815$ K ($E_A = 0.9$ eV). However, the accessible range of sticking coefficients is rather limited. For $T_N = 297$ K and $T_s = 535$ K the value of $s_0$, e.g., is below $10^{-8}$, the detection limit of our setup. Therefore the data for $T_N = 297$ K clearly cannot follow the Arrhenius law over an extended temperature range. For the adsorption of a thermal gas it was found earlier that the activation with surface temperature is higher in the case of Si(111) than for Si(001) [14, 15]. Comparison of the data for Si(001) in Fig 8a with the data of Si(111) in Fig 8b shows that in a comparable range of sticking probabilities, e.g. between $s_0 = 10^{-7}$ and $s_0 = 10^{-5}$, and beam energies between 70 meV and 250 meV, the data for Si(001) probe a narrower range of surface temperature. Vice versa, the dependence on
surface temperature is stronger when averaged over this region of kinetic energy. As a result, the beam data are indeed consistent with a stronger activation with surface temperature observed for the thermal gas.

To complete the picture, those parts of the adsorption functions of Fig. 8b which depend only on kinetic energy, i.e., only molecules in the ground state adsorb, are converted to desorption fluxes \( \Phi(E) \) as required by detailed balance \( \Phi(E) \propto E \exp(-E/kT_s)s_0(E) \). Fig. 10 illustrates the result for a surface temperature of \( T_s = 666 \) K. Due to the large width of the adsorption function the maximum of the converted differential desorption flux is shifted to an energy that is considerably lower than the mean barrier height. For \( T_s = 727 \) K, the highest surface temperature in the present adsorption experiments, the fit of a flux-weighted Maxwell distribution \( F_M \propto E \exp(E/kT_M) \) yields a mean energy \( \langle E_{\text{kin}} \rangle = 2kT_M = 400 \) meV. Due to the uncertainty of the shape of the distribution in the high energy tail, this value has to be regarded rather as an upper limit. The converted s-shaped adsorption function, e.g., yields \( \langle E_{\text{kin}}(T_s = 727) \rangle = 345 \) meV. However, the value is clearly higher than the experimental result of \( \langle E_{\text{kin}} \rangle = 225 \pm 70 \) meV obtained at 1520 K desorption temperature [33]. These lower mean energies found in desorption may be explained by taking into account the adsorption measurements of the thermal gas at higher surface coverages [16]. They have shown an increase of the sticking coefficient with increasing surface coverage pointing to a reduced barrier due to next neighbour correlations. It would be interesting to perform time-of-flight measurements for different coverages. Application of detailed balance would predict a reduction of translational heating with coverage as function of hydrogen coverage for both Si(001) and Si(111) surfaces.

To summarize the comparison of the dynamical behaviour of \( H_2 \) dissociating over Si(111) and Si(001): Both surfaces behave rather similar as far as the vibrational excitation of the hydrogen molecules and the activation of sticking probability with surface temperature are concerned. The widths of the adsorption functions \( s_0(E_{\text{kin}}) \) are broad and increase with surface temperature. This can be interpreted as a thermally activated, broad distribution of adsorption barriers on the surface. However, the adsorption functions of Si(111) at constant surface temperatures differ in detail from earlier measurements on Si(001) [34]. Deviations from the trend of lower activation with kinetic energy at higher surface temperature can be observed. At \( T_s = 600 \) K, e.g., the dependence of \( s_0 \) on kinetic energy is very weak for kinetic energies between 50 meV and 250 meV.

In terms of the potential energy surface (PES) describing the reaction dynamics, such a low activation with kinetic energy points towards a low coupling of kinetic energy and lattice displacement. This becomes clearer when studying the reverse process, i.e., recombinative desorption. Fast decoupling between the strong lattice distortion and kinetic energy of the molecule leads to only little excess energy in the translation of the desorbing molecule, exactly as it results from applying detailed balance on adsorption functions with minor dependence on kinetic energy. Earlier suggested PES have been modeled in this way [23]. Dynamical calculations on such PES also suggest that the shape of the single adsorption functions at constant surface temperature depend strongly
on the curvature of the PES and a representation by the commonly applied s-shapes may often be valid only in a smaller parameter space, if at all.

On Si(001), the strong lattice distortion during adsorption is connected with the creation of sites with reactive dangling bonds since the totally filled and unfilled states of the buckled dimer configuration turn out to be highly unreactive [57]. Such reactive sites exist in principle on Si(111) in form of partially filled dangling bonds at the adatoms of the 7×7 reconstruction. However, for an effective reduction of the adsorption barrier, ad- and rest-atom have to get much closer, again resulting in strong lattice distortions. Detailed calculations show that adsorption via a direct reaction pathway almost leads to overcoming of one of the backbonds of the adatoms [62]. Also a reaction path via a dihydride state has been considered [61]. Since both mechanisms may be operative on the surface, a more complex superposition of the potential energy surfaces might be necessary. In both cases, however, the transition states show a high amount of energy stored in the substrate lattice. Therefore lattice distortions can lead to a low adsorption barrier with respect to kinetic energy and a low mean translational energy in desorption.

VI. SUMMARY

In summary, by using seeded molecular beam techniques in combination with optical-second harmonic generation, we found molecular vibrational excitations to enhance the sticking probabilities of H₂ on Si(001) and Si(111) surfaces effectively. A decrease of the mean adsorption barrier with respect to kinetic energy from ∼0.8 eV to 0.39 eV and 0.18 eV has been observed for increasing excitation from the ground state to the first and second excited states. These findings indicate the presence of an early desorption barrier, in agreement with the results of previous state-resolved desorption experiments. For non-excited molecules, we observe only a minor influence of the molecular mass on the sticking probability for kinetic energies between 50 meV and 250 meV. From this, tunneling can be excluded to be a decisive factor in overcoming the adsorption barrier. On the Si(111)/7×7 surface, the adsorption dynamics are found to be qualitatively similar to flat Si(001)/2×1. Dissociative adsorption is activated both by kinetic energy and surface temperature with comparable mean adsorption barriers on both surfaces. The broad adsorption functions are interpreted in terms of a thermally activated distribution of adsorption barriers on the surface caused by Si lattice excitations. Whereas there is a good anti-correlation between the activation by kinetic energy and surface temperature in the case of Si(001), the adsorption functions of Si(111) are more complicated. The effect of surface temperature is generally stronger, at 600 K we find a surprisingly small dependence of the sticking coefficient on kinetic energies below 250 meV.

VII. ACKNOWLEDGEMENT

The authors would like to thank W. Brenig, M. Hilf, K.-L. Kompa, P. Kratzer, E. Pehlke, M. B. Raschke, and J. Wanner for fruitful discussions.
