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# Ab initio molecular dynamics of H<sub>2</sub> desorption from Si(100)-2 × 1

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### Abstract

We present the first ab initio molecular dynamics (AIMD) trajectories of two competing mechanisms proposed for H<sub>2</sub> desorption from Si(100)-2 × 1. We show that silicon dihydride species are the most likely desorption precursors and that surface corrugation is responsible for focusing desorbing trajectories, based on comparisons with experimental dynamical data. The equal roles played by the transition state (TS) structure and post-detachment dynamics is emphasized. © 1997 Elsevier Science B.V.

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Hydrogen on silicon has been the subject of great attention in the past few years [1-4]. There are many reasons for this interest. From a basic point of view, H<sub>2</sub> on Si(100)-2 × 1 is probably the simplest system to study adsorption/desorption of molecules on semiconductors, and therefore it can be analyzed in great detail both experimentally and theoretically. Moreover, desorption of H<sub>2</sub> from Si is technologically important. The hydrogen atoms passivate the Si surface dangling bonds, and H<sub>2</sub> desorption is thought to be the rate-limiting step in growth of, e.g., silicon by silanes [5]. But probably the factor that has attracted most attention is the intriguing kinetic and dynamic behavior of H<sub>2</sub> adsorption on or desorption from Si surfaces. First, desorption of H<sub>2</sub> from metal surfaces and the Si(111)-7 × 7 surface generally follows second-order kinetics [1], whereas

H<sub>2</sub> desorption from Si(100)-2 × 1 follows first-order kinetics [1,2]. Second, the sticking probability for dissociative adsorption of molecular hydrogen on silicon surfaces is extremely low [3], which suggests a large adsorption barrier. On the other hand, measurements of internal and translational energy distributions [4] suggest that the desorbing H<sub>2</sub> molecules have little excess energy, which implies a small adsorption barrier. The latter two observations imply an apparent violation of microscopic reversibility.

As we can see, a model for the mechanism of H<sub>2</sub> desorption from the Si(100)-2 × 1 surface has to be able to explain not only the unusual kinetic behavior but also the seemingly puzzling dynamic observations. One of the most popular models is the preparing mechanism (PPM) [1,6], where the two desorbing hydrogens are prepared on a silicon dimer before desorption. It has been shown [7] that the preparing of hydrogen atoms on a Si dimer leads to first-order kinetics, and density

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functional theory (DFT) calculations [8,9] obtain activation energies that are in good agreement with experiment. Moreover, it has been suggested [10] that excitation of lattice degrees of freedom upon desorption can explain the apparent violation of microscopic reversibility. However, a recent dynamical calculation [11] for  $D_2$  dissociative chemisorption on and associative desorption from a Si(100) surface, based on a DFT potential energy surface (PES) for the PPM, has shown that this model cannot be reconciled with quantitative aspects of the experimental data. Also, calculations by Nachtigall et al. [12] have cast some doubt on the DFT results. They show that for the elimination of  $H_2$  from silane, where the exact, atomic-level mechanism is well characterized (unlike on the surface), the exchange-correlation functionals used in the surface DFT calculations [8,9] significantly underestimate the barrier for  $H_2$  elimination. In addition, we have performed detailed ab initio [13–15] and kinetic Monte Carlo [16] studies of various mechanisms for  $H_2$  desorption, and concluded that the isolated dihydride mechanism (IDM), by which the two hydrogens are bonded transiently at atomic defect sites, is in much better agreement with experiments than the PPM, for all kinetic parameters. Furthermore, the IDM is able to explain the apparent violation of detailed balance in a very natural and simple way, without the need to invoke large energy transfer to phonons [14,15].

Internal energy distribution measurements [4] have shown that desorbing  $H_2$  is rotationally cold and vibrationally hot when compared to the surface temperature, and angular distribution measurements [17] have shown that desorbing  $D_2$  molecules have a distribution significantly narrower than  $\theta$ . The correct mechanism for  $H_2$  desorption must also be able to explain these dynamical observations. The main objective of the present work is to study the dynamics of  $H_2$  desorption from the Si(100)- $2 \times 1$  surface for the IDM and the PPM, and compare the results with the experimental observations to determine further which mechanism is likely to be operative. We use the method of ab initio Born–Oppenheimer molecular dynamics [18] to generate a number of desorbing trajectories, and the main conclusion of this

analysis is that the IDM is in much better agreement with the experimental measurements.

Our calculations are based on an embedded cluster model for the Si surface. DFT calculations have shown that embedded clusters and periodic slabs yield similar results, suggesting that cluster truncation is not a problem [9]. For the IDM, the surface is represented by a cluster (Fig. 1) composed of 10 Si atoms, which is terminated with 14 “siligens” ( $\bar{H}$ 's). These are H atoms modified [19,20] in such a way as to minimize spurious charge transfer between the Si atoms and the  $\bar{H}$ 's. The cluster contains three surface atoms (the isolated Si atom defect and a neighboring surface dimer proposed in the IDM [13–16]), four second layer Si atoms, two third layer Si atoms and one fourth layer Si atom, and we denote it by  $Si_{10}\bar{H}_{14}$ . The cluster used to study desorption from the PPM (Fig. 2) is identical to the one used in previous calculations [13–15]. It includes two surface Si atoms (the dimer), four second layer Si atoms, two third layer Si atoms and one fourth layer Si atom, and it is denoted by  $Si_9\bar{H}_{12}$ . In all the simulations, the  $\bar{H}$ 's are kept fixed in bulk-like tetrahedral positions [13,15] whereas all the Si atoms are allowed to move.

We examine here the  $H_2$  desorption dynamics starting from geometries that capture the essential features of the TSs found on ab initio PESs for both mechanisms [14,15]. To start a simulation, we need a set of initial coordinates and velocities for each of the Si and H atoms. For the  $Si_9\bar{H}_{12}$  cluster modelling the PPM TS, the initial coordinates for the Si and H atoms were identical to the geometry found by Radeke and Carter [15] for  $H_2$  desorption from the PPM TS (Fig. 2,  $t=0$ ), since this was the same cluster model used in previous work [14,15]. Since the coordinates for the IDM TS were calculated previously on a different  $Si_{10}\bar{H}_{14}$  cluster model, we had to devise an alternative means for choosing initial coordinates for the model chosen here (which retains more of the surface structure than our previous IDM model) by having both the IDM TS and a dimer on the surface rather than just the IDM TS. Thus, the initial coordinates for the Si atoms in the  $Si_{10}\bar{H}_{14}$  cluster were chosen as follows. The cluster geometry was first fully optimized at the

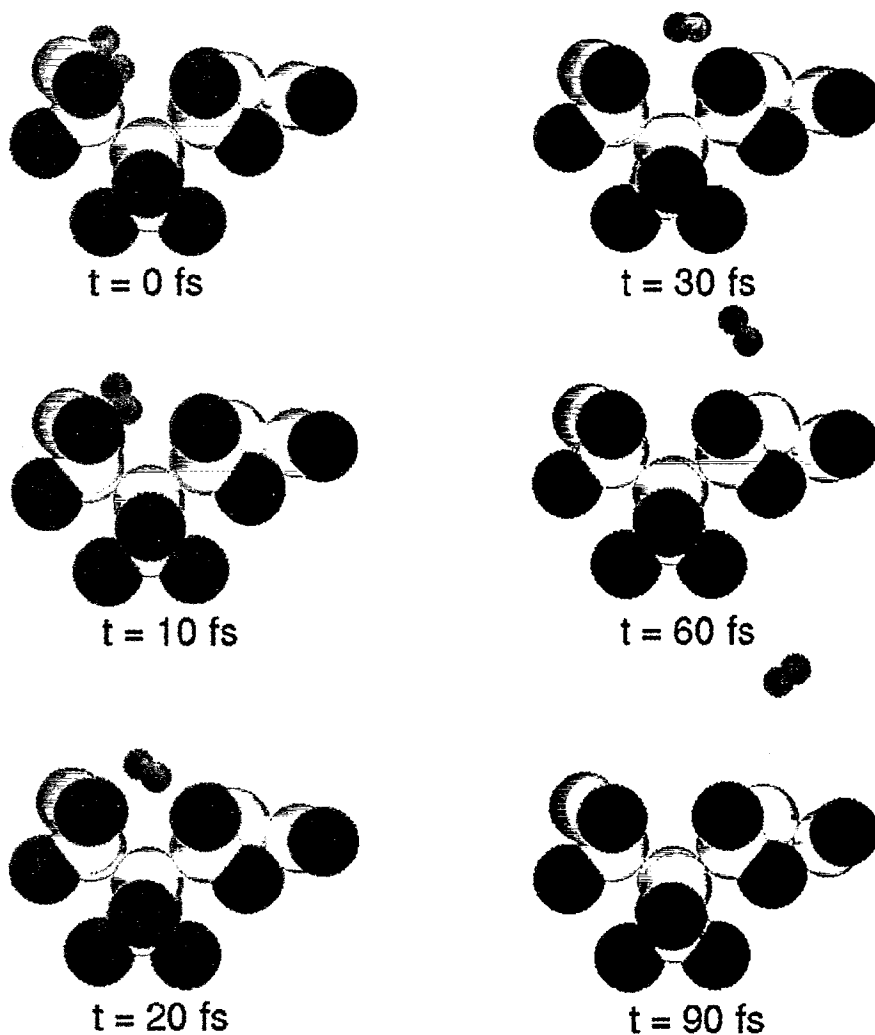


Fig. 1. Snapshots of a typical simulation of the isolated dihydride mechanism (Run 6 from Table 1; Key: Red=H; Light Blue=Si; Dark Blue= $\bar{H}$ ).

Hartree-Fock level, subject to the constrained  $\bar{H}$ 's. We then chose the velocities for each Si atom randomly from a Boltzmann distribution at 780 K, which is the experimentally-observed peak  $H_2$  desorption temperature [2]. The cluster was then propagated for 130 fs and the velocities were rescaled at each time step during this period to ensure that the average temperature of the Si atoms is always within 10 K from the target temperature of 780 K. After this period, the cluster was freely propagated (no velocity scaling) for

$\sim 350$  fs. Time steps along this trajectory were randomly selected and were used as the Si atoms' initial coordinates and initial velocity guesses [21] for the desorption simulations. The two hydrogen atoms were then placed between the isolated Si atom and the Si dimer in such a way that the relative positions of the two H's and the isolated Si atom were the same as those in the complete active space self-consistent field (CASSCF) TS geometry found by Radeke and Carter [15] for the IDM (Fig. 1,  $t=0$ ). The initial velocity guesses

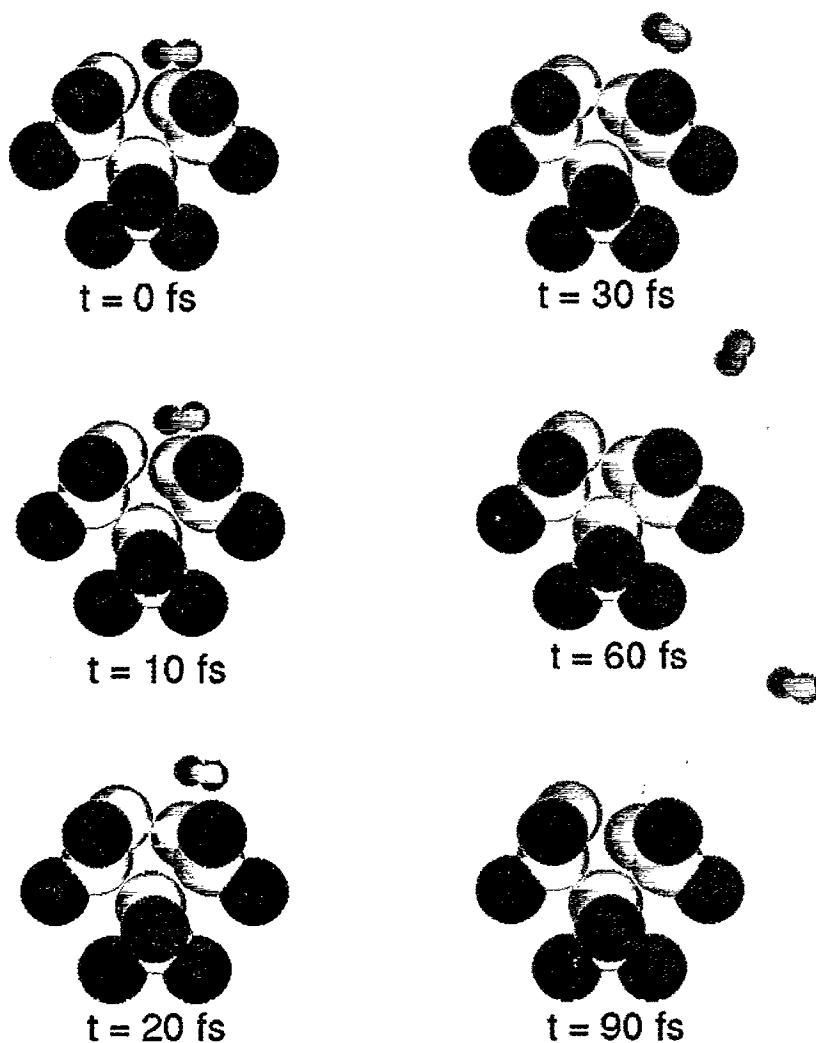


Fig. 2. Snapshots of a typical simulation of the preparing mechanism (Run 6 from Table 1; Key: Red=H; Light Blue=Si; Dark Blue= $\bar{\text{H}}$ ).

[21] for the Si atoms in the  $\text{Si}_9\bar{\text{H}}_{12}$  cluster and for the H atoms in *both* clusters were randomly chosen from a Boltzmann distribution at 780 K. Finally, all the velocities were readjusted to set the total linear and angular momentum of the system to zero and to make the cluster initial temperature 780 K.

Once the initial velocities and coordinates were determined, the nuclei were propagated according to Newton's equations. The equations of motion were integrated using the velocity-Verlet algorithm

[22] with a time step of 0.7 fs. We obtained the forces acting on the atoms by calculating analytically the gradient of the PES with respect to the atomic displacements. All electronic energy and gradient calculations were performed at the CASSCF level using HONDO [23], which is interfaced to our molecular dynamics code. The basis set is exactly the same as used before by Radeke and Carter [14,15]. For the IDM, i.e. for the  $\text{Si}_{10}\bar{\text{H}}_{14}\text{H}_2$  cluster, we used a 4-orbital 4-electron CAS (20 spin eigenfunctions), which corresponds

to the two isolated Si-H bonds and their anti-bonds. For the PPM, i.e. for the  $\text{Si}_9\bar{\text{H}}_{12}\text{H}_2$  cluster, we used a 6-orbital 6-electron CAS (175 spin eigenfunctions). The two extra orbitals correspond to the dimer bond and antibond [14,15].

We initially performed ten desorption trajectories from the TSs for both mechanisms. Snapshots of a typical trajectory for the IDM are shown in Fig. 1. The important features to notice are: (1) it takes  $\sim 10$  fs for the molecule to detach from the isolated dihydride TS; (2) between 10 fs and 25 fs, the  $\text{H}_2$  molecule traverses the surface "pocket" between the isolated Si atom and a neighboring Si dimer. By this time, the  $\text{H}_2$  bond length and vibrational energy are practically at their asymptotic values when the  $\text{H}_2$  is far away from the surface; (3) between 25 fs and 50 fs the  $\text{H}_2$  molecule is scattered by the Si dimer, which more often than not results in a decrease of the component of the  $\text{H}_2$  center-of-mass velocity parallel to the surface and an increase of the component perpendicular to the surface. The overall effect is a focusing of the trajectory towards the surface normal; (4) after 50 fs the  $\text{H}_2$  molecule travels almost in a straight line, which corresponds to the final desorbed trajectory, and by 80 fs the molecule is basically free.

Similar snapshots for a desorption trajectory for the PPM are shown in Fig. 2. An analysis of the data shows that it also takes about 10 fs for the  $\text{H}_2$  molecule to detach from the Si surface atoms, i.e. for the Si-H bonds to break and for the H-H bond to form. However, as opposed to the IDM, the  $\text{H}_2$  molecule immediately starts to fly away from the surface, and after 50 fs it is basically free. Surface corrugation plays no role here because as the hydrogen molecule is ejected its center-of-mass velocity component perpendicular to the surface grows fast enough to prevent further interaction with other Si dimers. However, the component parallel to the surface is significant, which results in an angular distribution that peaks at large angles (Table 1), since there is no focusing effect taking place here. It is therefore hard to reconcile this result for the PPM with the experimental angular distribution [17] and the presence of additional Si dimers in the model would not be expected to change that. The geometry and the forces at

Table 1

Angle (in degrees) between the final center of mass  $\text{H}_2$  velocity vector and the surface normal. See text for definition of cluster labels

| Run                   | Cluster                                       |  |
|-----------------------|---|--|
|                       | $\text{Si}_{10}\bar{\text{H}}_{14}\text{H}_2$ | $\text{Si}_9\bar{\text{H}}_{12}\text{H}_2$ |
| 1                     | 7   | 40   |
| 2                     | 16  | 48   |
| 3                     | 42  | 55   |
| 4                     | 42  | 56   |
| 5                     | 48  | 57   |
| 6                     | 49  | 58   |
| 7                     | 50  | 59   |
| 8                     | 56  | 61   |
| 9                     | 57  | 61   |
| 10                    | 61  | 69   |
| Average               | 43  | 56   |
| Standard deviation    | 17  | 7  |
| $\theta^{\text{TSa}}$ | 71  | 16   |

<sup>a</sup>Angle between the normal and the center of mass vector at the TS ( $t=0$ ).

the TS for the PPM are such that there is no way to reduce the component of the  $\text{H}_2$  center-of-mass velocity parallel to the surface, a necessary requirement to obtain an angular distribution that peaks at a small angle.

The angles  $\theta$  between the asymptotic desorbing trajectories and the surface normal are shown in Table 1. As we do not have enough trajectories to plot an angular distribution function we can only calculate the average value for the angle  $\theta$ . The only experiment that has measured the angular distribution for the desorbing  $\text{H}_2$  molecules was performed by Park et al. [17]. The best fit to their data corresponds to a  $\cos^{5.17}\theta$  angular distribution function for a surface coverage of 0.6 monolayers (ML) and a  $\cos^{3.90}\theta$  angular distribution function for a coverage of 1.0 ML. These functions give an average value for the desorbing angle  $\theta$  of  $\langle\theta\rangle_{\text{exp}}^{0.6} = 28^\circ$  and  $\langle\theta\rangle_{\text{exp}}^1 = 31^\circ$ . Our calculations give  $\langle\theta\rangle_{\text{IDM}} = 43^\circ \pm 17^\circ$  and  $\langle\theta\rangle_{\text{PPM}} = 56^\circ \pm 7^\circ$  (the errors correspond to one standard deviation; see Table 1). Although both results are larger than the experimental values, the IDM result is much smaller. It should be noted that it actually agrees

with the experimental values within one standard deviation, which is a result of the focusing effect described earlier (for the IDM we have calculated nine additional trajectories, which gave a total average of  $\langle\theta\rangle_{\text{IDM}}=41^\circ\pm 16^\circ$ , in very good agreement with the result from ten trajectories). The disagreement with the experimental results is probably related to the fact that in the  $\text{Si}_{10}\bar{\text{H}}_{14}\text{H}_2$  cluster, the absence of other Si dimers besides the cluster Si dimer causes the “pocket” mentioned above to be too relaxed and too open, i.e. the cluster Si dimer and isolated dihydride are too far apart. As a result, the scattering between the desorbing  $\text{H}_2$  molecule and the Si dimer is reduced and the angular distribution is shifted towards larger angles. On the other hand, the fact that the simulations for both mechanisms give somewhat large average desorption angles may indicate that in reality the  $\text{H}_2$  molecules do not desorb with an angular distribution as narrow as measured. As the angular distribution has been measured by only one research group [17], it would be useful to see whether experiments performed in other laboratories will confirm this  $\theta$  dependence. A recent calculation by Bratu et al. [24] reproduces the experimental angular distribution quite well. However, they use a very simple empirical model potential that lacks the microscopic detail of our calculation. Therefore we feel that further research, both experimental and theoretical, is still needed to settle this question.

We should stress that this peaking at smaller angles for the IDM angular distribution is mainly a result of the surface corrugation and not only of the forces acting on the  $\text{H}_2$  molecule during its detachment from the isolated dihydride. Actually, if it were not for the scattering with the Si dimer, the angular distribution would have been much broader, as suggested by the static structures of the IDM and PPM TSs ( $\theta_{\text{IDM}}^{\text{TS}}=71^\circ$  and  $\theta_{\text{PPM}}^{\text{TS}}=16^\circ$ ; see Table 1). This indicates that *knowledge of the TS geometries and the study of the post-detachment dynamics can be equally important in the understanding of surface reactions, at least for surfaces that are highly corrugated.*

Table 2 contains the values of the translational, rotational and vibrational energies for the desorbed  $\text{H}_2$  molecules, averaged over the ten

Table 2

Final energies (eV) averaged over ten trajectories for each cluster. Errors in the calculated numbers represent one standard deviation. See text for definition of cluster labels

|  | Translational    | Rotational         | Vibrational        |
|--|------------------|--------------------|--------------------|
| $\text{Si}_{10}\bar{\text{H}}_{14}\text{H}_2$<br>(IDM) | $0.7\pm 0.1$     | $0.04\pm 0.03$     | $0.2\pm 0.1$       |
| $\text{Si}_9\bar{\text{H}}_{12}\text{H}_2$<br>(PPM)    | $0.6\pm 0.1$     | $0.03\pm 0.02$     | $0.09\pm 0.08$     |
| Experiment <sup>a</sup>                                | $0.34\pm 0.06^b$ | $0.030\pm 0.007^c$ | $0.264\pm 0.002^c$ |

<sup>a</sup>Data from Ref. [4].

<sup>b</sup>Scaled for  $\text{H}_2$ ;  $\text{D}_2$  desorption at 900 K yields  $0.17\pm 0.03$  eV.

<sup>c</sup> $\text{H}_2$  desorption at surface temperature of 780 K.

trajectories for each mechanism. The experimental values [4] are also included for comparison. As can be seen from Table 2, the calculated average translational energy for both mechanisms is significantly larger than experiment. This is a consequence of the overestimation of the adsorption energy barrier at the CASSCF level [15]. The calculated average rotational energies for both mechanisms are in good agreement with experiment, indicating that the  $\text{H}_2$  molecules desorb rotationally cold both in the PPM and IDM. However, the calculated average vibrational energy for the IDM is in much better agreement with experiment. As can be seen from Table 2 our calculated vibrational energy for the IDM agrees well with experiment when the error bars are considered, whereas for the PPM the calculated value is smaller than the experimental value by  $\sim 40\%$  even when the error bars are considered. Most likely this is a result of the longer  $\text{H}_2$  bond in the IDM TS. One should note that the way we chose the initial coordinates for the simulations preserves the longer  $\text{H}_2$  bond distance for the IDM TS when compared to the PPM TS, and therefore we expect that the better agreement with experiment for the IDM is not an artifact of our procedure or of the small sampling of trajectories, but a true feature of the TS geometries. Moreover, because the  $\text{H}_2$  bond distance is a very local feature, the results also should be insensitive to the size of the cluster used, and again the better agreement between the IDM and experiments is not a small size effect.

It is important to stress the fact that the study presented here is only a first step in the process of understanding the dynamics of surface chemical reactions in semiconductors. There are obvious limitations in the cluster approximation employed in our work, for example, the size of the cluster and the fixed boundaries. These approximations limit surface relaxation and energy transfer. Secondly, the expense of AIMD limits the number of trajectories that may be followed and thus prohibits gathering good statistics as of now. Therefore we emphasize only the qualitative features of our study. However, they clearly illustrate the importance of the surface corrugation in the desorption process through the focusing of the H<sub>2</sub> trajectories. Moreover, the analysis of the H<sub>2</sub> internal energies show that SiH<sub>2</sub> species are most likely the precursors to desorption.

In summary, we presented ab initio molecular dynamics of H<sub>2</sub> desorption from the Si(100)-2 × 1 surface. We studied the two most popular, competing desorption mechanisms, the preparing mechanism and the isolated dihydride mechanism. We showed that to understand the desorption dynamics it is important not only to look at the transition state geometries and energies (statics) but also to look at how the desorbing molecules are scattered by the surface after the bonds with the surface have been broken (dynamics). This is especially true for corrugated surfaces, which are common in semiconductors. We have shown that these dynamical effects are crucial in understanding the angular distributions. According to our results the IDM has a smaller value for  $\langle\theta\rangle$  than the PPM angular distribution, in closer agreement with experiment. This is mainly a dynamical effect, caused by the scattering of the nascent desorbing H<sub>2</sub> molecules off the surface Si dimers. We also showed that both mechanisms yield (correctly) rotationally cold desorbed H<sub>2</sub> molecules, whereas the H<sub>2</sub> vibrational energy for the IDM is in much better agreement with experiment than for the PPM. In conclusion, the present analysis suggests, in agreement with our previous calculations of energy barriers, rate constants and kinetic orders [14-16], that the isolated dihydride mechanism for H<sub>2</sub> desorption from Si(100)-2 × 1 is the only

mechanism able to explain all dynamic and kinetic observations.

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