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# Ab initio explanation of the apparent violation of detailed balance for $H_2$ adsorption/desorption from Si(100)

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## Abstract

The experimentally observed apparent violation of detailed balance in the adsorption and desorption of  $H_2$  on Si(100)- $2 \times 1$  is explained via a dihydride intermediate that can be accessed via two different transition states, as found by complete active space self-consistent field/multireference single and double excitation configuration interaction (CASSCF/MRSDCI) calculations. Our calculations explain the low sticking probability by predicting an early symmetric transition state to adsorption with a high barrier. We predict that desorption, on the other hand, occurs through an asymmetric transition state and find excellent agreement between our calculated barrier to desorption and experimental values. For the asymmetric transition state we calculate a small barrier to adsorption, however, we suggest that impinging  $H_2$  seldom sees this orientationally constrained late transition state to adsorption, explaining the apparent violation of detailed balance.

**Keywords:** Ab initio quantum mechanical methods and calculations; Adsorption kinetics; Hydrogen; Silicon; Solid–gas interfaces; Thermal desorption

## 1. Introduction

The interaction of  $H_2$  with Si surfaces appears to violate the principle of detailed balance, which assumes that adsorption and desorption occur through the same pathway.  $H_2$  has a tiny sticking coefficient ( $S_0$ ) on bare Si surfaces [1], suggestive of a large adsorption barrier. However, recent experiments [2–4] show that desorbing  $H_2$  molecules do not possess much more energy than the zero point energy (zpe) of  $H_2$  and the bare surface. If  $H_2$  had come down from a large adsorption barrier, then there should have been an excess of energy in the desorbing molecule. Thus, these

experiments suggest that the pathway to  $H_2$  desorption does not include the large adsorption barrier which is required to explain the tiny adsorption probability.

The reaction of  $H_2$  with Si(100)- $2 \times 1$  is also interesting since  $H_2$  desorption follows first-order kinetics [5–8] rather than the second-order kinetics one would expect from a process that presumably involves the random recombination of two atoms. Several proposals attempt to explain the unusual kinetics. The first is the delocalized H mechanism [5], which we previously ruled out since diffusion is predicted to be localized on Si(100)- $2 \times 1$  [9–11]. Other proposals include monohydride–dihydride isomerization preceding desorption [2,12,13]; the “preparing” mechanism

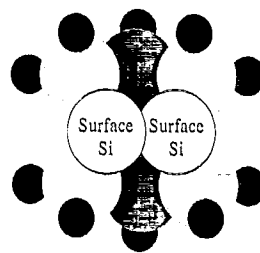
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[6], in which two H atoms are prepared on a Si dimer and desorb in a concentrated fashion; and desorption via isolated dihydrides [14].

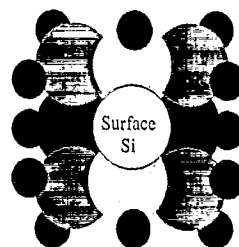
Models invoking orientational constraints [2-4,13], defects [12,14,15], steps [1,16], phonons [1,3,17], and surface dimer buckling [18,19] all strive to explain the apparent violation of detailed balance. However, a mechanism which would meet all of the experimental criteria, i.e., explain the kinetic order of H<sub>2</sub> desorption on the Si(100)-2 × 1 surface, put forth a precursor to desorption which would be common to the mono- and dihydride phases of Si(100) as well as to Si(111)-7 × 7 (as suggested by REMPI measurements which show that H<sub>2</sub> desorbs from all of these surfaces with similar internal state distributions) [2,13], and provide a reason for the negligible S<sub>0</sub> of H<sub>2</sub> on the above three surfaces, has not emerged yet. This report addresses one of the issues that ties these observations together, namely the apparent violation of detailed balance. Our calculations reveal that an orientation effect is in large measure responsible for the violation and that the position of these orientation-dependent barriers explains why the pathways for adsorption and desorption indeed are different.

## 2. Details of the calculations

We used Si clusters to represent the Si(100)-2 × 1 surface, terminating the clusters with "siligens" ( $\bar{H}$ 's) [20,21] fixed in tetrahedral bulk Si positions during structure optimizations [21]. Details of the atomic basis sets and effective core potentials have been presented previously [14]. To represent the monohydride [H-Si-Si-H<sub>(a)</sub>] and an isolated dihydride [SiH<sub>2(a)</sub>] we used the Si<sub>9</sub> $\bar{H}_{12}$ H<sub>2</sub> and Si<sub>10</sub> $\bar{H}_{14}$ H<sub>2</sub> clusters, respectively (see Fig. 1). The H<sub>2</sub> adsorption/desorption reaction should be primarily influenced by the Si with which it forms the dihydride, since the distance between unpaired Si atoms on the Si(100)-2 × 1 surface is 3.84 Å. Support for the cluster model comes from the comparison of density functional theory (DFT) cluster and periodic slab energy differences that agree to within 4 kcal/mol [18,22]. Moreover, these clusters appear to model adsorbates on the



Top View of Si<sub>9</sub> $\bar{H}_{12}$  Cluster



Top View of Si<sub>10</sub> $\bar{H}_{14}$  Cluster

Fig. 1. The black spheres represent the embedding siligens ( $\bar{H}$ 's). The Si<sub>9</sub> $\bar{H}_{12}$  cluster contains two surface Si atoms (the surface dimer), four second-layer Si atoms, two third-layer Si atoms, and one fourth-layer Si atom. The Si<sub>10</sub> $\bar{H}_{14}$  cluster includes one surface Si atom, two second-layer Si atoms, four third-layer Si atoms, two fourth-layer Si atoms and one fifth-layer Si atom. Adding two adsorbate H's to the Si<sub>9</sub> $\bar{H}_{12}$  and Si<sub>10</sub> $\bar{H}_{14}$  clusters forms the monohydride and isolated dihydride, respectively.

Si surface fairly well, yielding vibrational frequencies in good agreement with experimental values [23].

The initial adsorbed/desorbed minimum energy structures and transition states (TS's) were found using the quasi-Newton [24] and DIIS-Ridge methods [25], respectively. All structure searches were performed at the complete active space self-consistent field (CASSCF) level within C<sub>s</sub> symmetry.

The electronic wavefunction for the isolated dihydride [SiH<sub>2(a)</sub>] was represented with a 4-orbital, 4-electron CAS (20 spin eigenfunctions) with the active orbitals being the Si-H bonds and their corresponding antibonding orbitals. For the monohydride [H-Si-Si-H<sub>(a)</sub>], the Si-Si dimer

bonding and antibonding orbitals were also included, leading to a 6-orbital, 6-electron CAS (175 spin eigenfunctions) [26].

In order to verify that a saddle point obtained is of rank one, we evaluated the numerical Hessian, also at the CASSCF level, using a two-point finite difference method [26]. Additionally, we verified that a given TS connected the appropriate reactant and product by walking down each side of the ridge containing the TS.

Final single point total energies for the reactant, product, and TS were calculated at the multireference single and double configuration interaction (MRSDCI) level using the CAS reference space [27]. Estimates of zpe's were obtained from the vibrational frequencies determined by diagonalizing the CASSCF Hessians. All energies presented below are taken from the MRSDCI calculations corrected by CASSCF zpe's.

### 3. Results and discussion

We find three TS's for the prepairing mechanism: a symmetric TS, an asymmetric TS centered over the Si dimer (asymmetric centered TS), and an asymmetric TS centered over one of the Si dimer atoms (asymmetric TS). These TS's have desorption (adsorption) barriers of 81.8 (14.9), 82.3 (15.4), and 84.9 (18.0) kcal/mol, respectively [23]. The adsorption barriers are in excellent agreement with the experimentally determined activation for adsorption of 16–17 kcal/mol [1]. However, the desorption barriers are much higher than the experimental values [ $45 \pm 2$  to  $66 \pm 4$  kcal/mol] [5–8]. Our calculations agree with those of Jing and Whitten [16] who predicted desorption barriers for the symmetric TS and the asymmetric TS to be 86.3 and 85.0 kcal/mol (with zpe corrections), respectively, using CASSCF level calculations on a  $\text{Si}_{19}\text{H}_{14}$  cluster. On the other hand, several DFT calculations [18,19,22,28,29] find an activation barrier within the experimental values. Recently, however, Nachtigall et al. [30] showed that these DFT predictions utilized functionals that systematically underestimate  $\text{H}_2$  elimination barriers from Si. In fact, using better quality functionals, such as the Becke3LYP functional, Nachtigall et al. [31]

have found the lowest prepairing desorption barrier to be 74 kcal/mol (with zpe corrections). Thus, together with Jing and Whitten [16] and Nachtigall et al. [31] we rule out the prepairing mechanism.

As earlier work [14] and current work [23] have ruled out the isomerization/dihydride desorption pathway, we now consider the only remaining mechanism: desorption via isolated dihydrides. Fig. 2 shows that we find two pathways for desorption via an isolated dihydride, one involving a symmetric TS and the other an asymmetric TS. For the symmetric TS (STS), the barrier to desorption is 101.6 kcal/mol, much higher than the experimentally observed values. This high barrier is expected since symmetry-constrained 4-electron processes such as this are Woodward–Hoffman “forbidden” [32].

For the asymmetric TS (ATS), the barrier to desorption is 57.5 kcal/mol. This activation energy is in excellent agreement with the most reliable experimental values (57–58 kcal/mol) [6–8]. Our calculated barrier is close to the estimate for asymmetric desorption by Wu et al. [14] of 55 kcal/mol and also to barriers of 59.6 kcal/mol and 56.5 kcal/mol (with zpe corrections) obtained by Nachtigall et al. [30,31] at the QCISD(T) level and using DFT with the Becke3LYP functional, respectively, using a similar cluster model. Similarly, Jing and Whitten [33] found a barrier for desorption from a  $\text{SiH}_{2(a)}$  next to another  $\text{SiH}_{2(a)}$  to be 53.1 kcal/mol (with zpe corrections) using a  $\text{Si}_{12}\text{H}_{24}$  cluster at the SCF and limited CI level of theory.

Structural information in Fig. 2 immediately reveals that the ATS can be classified as an “early” desorption TS, while the STS can be classified as a “late” desorption TS. Specifically, the Si–H and H–H bonds in the ATS resemble adsorbed  $\text{SiH}_2$ , while the same bonds in the STS closely resemble the desorbed  $\text{H}_2$  plus bare Si product. The long H–H bond of the ATS is consistent with REMPI measurements [2,13] which show  $\text{H}_2$  desorbing from  $\text{Si}(100)-2 \times 1$  to be vibrationally excited. Although these measurements [2,13] determine that  $\text{H}_2$  desorbs rotationally cold compared to a surface temperature of 800 K, the rotational distributions are characteristic of  $\sim 400$  K, which could

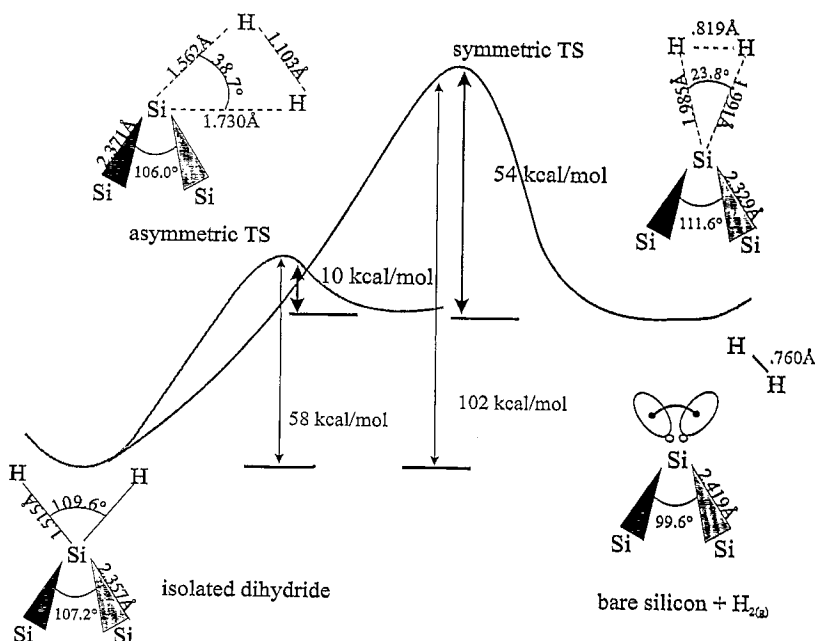


Fig. 2. The energy barriers for desorption from an isolated dihydride via asymmetric and symmetric TS's are illustrated, and the geometries of the product, reactant, and TS's are shown. Only the asymmetric TS has a desorption barrier within the range of experimental values.

still be consistent with an asymmetric TS. Ab initio molecular dynamics (AIMD) simulations [34] provide further support for the ATS and possible rotational (and translational) cooling of  $H_2$ . These AIMD simulations also show, consistently with experimentally observed  $D_2$  angular distributions [35], that  $H_2$  molecules ultimately desorb primarily along the surface normal, due to a surface corrugation effect to be described in detail elsewhere [34]. This occurs despite the fact that the TS itself is asymmetric, which might lead one to expect broad desorption profiles.

Now we are able to explain the apparent violation of detailed balance. We predict that the adsorbed Hs will see the early desorption TS and desorb asymmetrically, while impinging  $H_2$  molecules are most likely to first see the symmetric TS, since this is the early TS from the perspective of  $H_2$  adsorption. We find that the adsorption barrier is 9.7 kcal/mol for the ATS compared to an adsorption barrier of 53.7 kcal/mol for the STS. Thus we suggest that the extremely low  $S_0$  of  $H_2$  on Si(100)- $2 \times 1$  is due to most  $H_2$  molecules reflecting off the very high barrier for the STS, in addition,

of course, to scattering off of the high barriers for adsorption directly onto Si dimers. If instead  $H_2$  were to adsorb through the same pathway by which it desorbs, namely the asymmetric pathway, then one would expect a higher  $S_0$ , since the barrier to adsorption would be only  $\sim 10$  kcal/mol. However, looking at the geometry of the ATS, we see that it involves a bend of the surface  $SiH_2$  sideways so that one of the Hs comes to the level of the Si surface. While this type of sideways bend may be possible for the adsorbate Hs, it would be unlikely for an incoming  $H_2$  molecule to approach at this angle to the surface. Note that the existence of two pathways to adsorption/desorption does not violate the second law of thermodynamics, since the laws of thermodynamics only apply at equilibrium and the adsorption/desorption experiments are not done under equilibrium conditions. We have found the available kinetic pathways in this system, corresponding to the non-equilibrium conditions of the experiment.

The barrier we obtain for desorption from an isolated dihydride agrees well with experimental values, suggesting that there could be one or several

fast step(s) with small endothermicities involved in forming the  $\text{SiH}_{2(a)}$  species. In this case, the reaction would appear as first order, dependent only on the rate-limiting step of desorption from the  $\text{SiH}_{2(a)}$ . Nachtigall et al. [31] have suggested that one fast step for creating  $\text{SiH}_{2(a)}$  may occur via a monohydride reacting with a single bare Si (i.e., a single atom defect).

The isolated dihydride mechanism has the advantage of being the only mechanism that explains the REMPI measurements [2,13], which imply a common precursor to desorption from mono- and dihydride Si(100) and from Si(111)- $7 \times 7$ . In particular, Si(111)- $7 \times 7$  has been shown to have a low barrier for H diffusion ( $\sim 35$  kcal/mol) [36] and thus random, fast H diffusion on Si(111)- $7 \times 7$  to form the dihydride precursor is most likely responsible for the observed second-order desorption kinetics (analogous to recombinative desorption of  $\text{H}_2$  from metal surfaces). The measured activation energy for desorption from Si(111)- $7 \times 7$  is  $55 \pm 2$  to  $62 \pm 4$  kcal/mol [6,37–39], which corresponds well to our calculated value for desorption via an isolated dihydride.

We also believe that the isolated dihydride mechanism is compatible with recent experiments, which reveal that  $\text{H}_2$  adsorption on Si(100)- $2 \times 1$  and Si(111)- $7 \times 7$  is enhanced by increasing the surface temperature [1,3,4,40]. Higher surface temperatures could potentially increase the available adsorption sites through both Si adatom diffusion [41,42] and the creation of isolated Si sites through activated processes, enlarging the preexponential factor in the Arrhenius equation for  $\text{H}_2$  adsorption via the ATS, which is otherwise tiny because of orientational restrictions.

#### 4. Conclusions

Our calculations support a mechanism involving a Si dihydride intermediate and also explain the apparent violation of detailed balance in adsorption/desorption of  $\text{H}_2$  on Si(100). In particular, the low  $\text{H}_2$  sticking probability may be due to the presence of an early symmetric TS for adsorption with a very high barrier, such that incoming  $\text{H}_2$  molecules see this barrier or the high barrier for

adsorbing onto a Si dimer and scatter unreactively. In contrast, desorption can occur through the asymmetric TS, a late TS for adsorption, but an early TS for desorption. This asymmetric TS is located with one Si–H bond nearly parallel to the surface, an awkward orientation for impinging  $\text{H}_2$  to assume, but one potentially available to adsorbate Hs which have an essentially infinite amount of time to assume this configuration. The isolated dihydride mechanism can potentially be applied to the Si(111)- $7 \times 7$  surface as well as to the mono- and dihydride Si(100) surfaces, unlike previously proposed mechanisms, and hence can explain the structure insensitivity of the dynamics of  $\text{H}_2$  desorption. Finally, we suggest that this mechanism can be tested by carrying out grazing angle adsorption experiments to see if the adsorption probability increases compared to normal incident adsorption. Furthermore, since the ATS has an H–H distance 45% larger than the equilibrium bond distance for free  $\text{H}_2$ , vibrational excitation of the impinging  $\text{H}_2$  molecule may also be important in enhancing adsorption.

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