



# The dynamics of the $\text{H} + \text{D}/\text{Si}(001)$ reaction: a trajectory study based on ab initio potentials

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Received 20 January 1998; in final form 16 March 1998

## Abstract

The adiabatic potential energy surface for the reaction of H atoms with the deuterated Si(001) surface is calculated using a slab geometry and spin-polarized density functional theory with gradient corrections. Its dynamical implications are investigated through classical trajectory simulations. A significant probability for the exothermic production of HD molecules is found. In agreement with recent experiments, the kinetic energy of the HD molecules is the most important channel of energy disposal. For larger energies of incidence of the H atoms, molecular and substrate degrees of freedom take up an increasing amount of energy, leading to a broadening of the HD kinetic energy distributions. © 1998 Elsevier Science B.V. All rights reserved.

## 1. Introduction

In recent years, there has been considerable interest in reactions of hydrogen atoms with adsorbed species on solid surfaces [1–7]. While a better understanding of these reactions is desirable from the point of view of applied science (e.g. for the interaction of a hydrogen-rich plasma with the substrate surface in plasma-enhanced chemical vapour deposition [8]), reactions induced by hydrogen atoms offer also an interesting model system for general studies of gas-surface reaction dynamics proceeding via an Eley–Rideal mechanism. In contrast to the more common class of Langmuir–Hinshelwood reactions, the Eley–Rideal reaction allows the experimenter to vary the energy of the incident atom. Thus the disposal of energy among the different excitation channels of the product molecule can be studied as a function of the incident energy. Recently such stud-

ies have been conducted for the reaction of H atoms with a deuterated Si(001) surface leading to HD formation [4,9–11]. These experiments have revealed that the kinetic energy of the product molecules shows little dependence on the incident energy, suggesting that internal excitations of the molecule or the surface take up sizeable amounts of energy during the reaction.

For an understanding of the details of the energy disposal, an accurate representation of the potential energy surface (PES) of this system is required. While much work has been devoted to the calculation of a PES for Langmuir–Hinshelwood reactions, no reliable PES for an Eley–Rideal reaction is yet available. In this Letter a PES for the reaction  $\text{H} + \text{H}/\text{Si}(001)$  obtained from density functional calculations is presented, and its dynamical consequences by means of Monte Carlo trajectory simulations are studied.

## 2. Total energy calculations

I use the supercell approach to calculate the electronic ground state for various configurations of the reactants, thus obtaining the Born-Oppenheimer energy surface governing the dynamics of the atomic coordinates. The reactive system under study is represented by a slab consisting of 8 layers of silicon atoms, separated by an equal amount of vacuum. On one side of the slab the Si monohydride phase is prepared with the lateral periodicity of a  $2 \times 1$  unit cell, while the opposite side of the slab is passivated by Si dihydride units. For each configuration during the reaction, the electronic ground state energy is obtained by means of total energy calculations using pseudopotentials in connection with a plane wave basis set. The electronic charge density is calculated self-consistently using eight sampling points in the Brillouin zone (two in the irreducible part) and the local spin density approximation (LSDA) [12] for the electronic exchange and correlation effects. The Kohn–Sham equations are solved by alternating conjugate gradient minimizations of the total energy [13] and subspace rotations [14]. The total energy is obtained by applying the spin-polarized version of the gradient corrected functional of Perdew and co-workers (GGA-II) [15] to the electronic density.

A BHS-type pseudopotential is used for Si which is brought to the fully separable Kleinman–Bylander form [16], with the potential in the d-channel treated as the local potential. Hydrogen is described by its full Coulombic potential. All calculations are performed twice using two different basis sets, with plane waves up to a kinetic energy of  $E_c = 10$  and 30 Ry. While relative energies for systems consisting entirely of Si atoms are well converged at 10 Ry, the high quality basis set is required for a correct description of the hydrogen wavefunctions, in particular the Coulomb interaction of the electrons in the H 1s orbitals,  $\psi \sim \exp(-r/a_0)$ . Due to the long range of the Coulomb interaction, even a high quality basis set, including wave vectors up to some cut-off  $G_c = (2mE_c)^{1/2}/\hbar$ , gives rise to an error of the order of

$$\int_{|G| < G_c}^{\infty} dG \frac{|\psi^*(G)\psi(G)|^2}{|G|^2} \sim [G_c(1 + (G_c/2)^2)]^{-1} \sim [\sqrt{E_c}(1 + E_c/4)]^{-1},$$

where  $\psi(G)$  is the Fourier transform of the H 1s Slater orbital,  $G_c$  is given in units of inverse bohr and  $E_c$  in Ry. The error associated with the finite basis set can be estimated by plotting the data as a function of the term in square brackets and corrected by a linear extrapolation to zero. I have checked the validity of the above expression by test calculations at 50 Ry for the binding energy of an H atom at different distances above the surface. A similar scheme was used for the atomization energy of  $H_2$  as a function of the cut-off. The extrapolation gives an atomization energy (without zero-point corrections) of 4.91 eV within LSDA and 4.57 eV within GGA-II. While these results are in excellent agreement with literature values calculated with the help of localized basis sets [15], they once again demonstrate the well-known overbinding of small molecules in LSDA. The GGA result, on the other hand, somewhat underestimates the correct experimental atomization energy of 4.75 eV (again quoted without zero-point corrections). In the following, only numbers obtained with the GGA-II, and corrected for the finite basis set size as described above, are quoted.

In the reaction of H with a hydrogen-passivated Si surface, an Si–H bond is broken while a new H–H bond is being formed. Since the molecular bond is the stronger one, this process is exothermic. The exact amount of energy released depends on the final state of the surface. If we start with a fully covered surface, an isolated dangling bond is formed after the abstraction of one hydrogen, which is occupied by a single electron in a spin-polarized state. For this process I find an exothermicity of 1.17 eV. While the monohydride surface consists of Si dimer units oriented parallel to the surface, the abstraction of one hydrogen leads to a shortening of the Si dimer bond (from 2.43 to 2.37 Å) accompanied by a slight buckling of the Si dimer ( $\sim 2$  degree). The energy associated with this geometrical relaxation (compared to the monohydride surface) is about 60 meV, i.e. it contributes only a small fraction to the energy of reaction. Moreover, electronic relaxation is possible if one or more dangling bonds already exist at one of the Si dimers next to the monohydride. In this case, the newly formed dangling bond will interact with the existing one and form a bonding and anti-bonding linear combination (this applies to the present calculations using the  $(2 \times 1)$  unit cell). Eventu-

ally, for a single reacting monohydride on an otherwise clean surface, the newly formed dangling bond will become part of a surface band state. While an electron in an isolated dangling bond is spin-polarized, the ground state will be non-magnetic for a band of surface states. From the energy difference between the polarized and non-polarized solutions in the  $(2 \times 1)$  unit cell, I estimate that spin relaxation, if advantageous, is associated with an energy gain of 80 meV. For low coverages, Si dimers with only one H atom attached have to be considered as initial states. Abstraction of this H atom is even more exothermic ( $-1.23$  eV) compared to abstraction from H–Si–Si–H, because the final state, the fully buckled Si dimers (buckling angle 16 degree, Si–Si distance 2.29 Å), is stabilized by charge transfer between the two Si dangling bonds. The difference in binding energy for the first and the second H atom in a monohydride group has been noted earlier in connection with the “pairing effect” of hydrogen adatoms on the Si(001) surface [17,18] and was found both in cluster [19,20] and slab calculations [21].

Thus, the exothermicity of hydrogen abstraction lies in the range of 1.2 to 1.3 eV, depending on the local chemical environment. Note that these values are consistent with the results for the H–H bond strength (4.57 eV) given above and the mean Si–H binding energy of 3.45 eV obtained earlier [22]. After the reaction, the energy is disposed among the degrees of freedom of the molecule and the surface. The details of this process are governed by the topology of the potential energy surface (PES).

Since the reaction involves a radical with an open atomic shell, we can follow the highest occupied orbital during the reaction by plotting the spin density for various configurations along the reaction path. Initially the spin density is localized at the incident hydrogen atom, while the hydrogen adsorbate wavefunctions are non-spinpolarized (see Fig. 1a). The reaction involves the transfer of an electron from the H atom into the dangling bond state at one of the surface Si atoms. As long as the nascent  $H_2$  is close enough to the surface, this orbital is hybridized with the anti-bonding  $\Sigma_u^*$  orbital of the molecule, as can be seen from the node in the spin density in Fig.

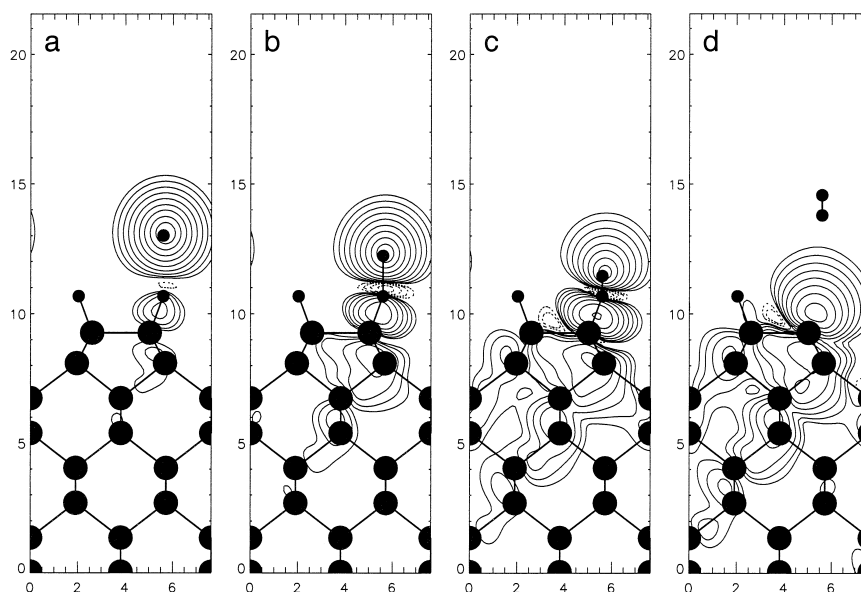


Fig. 1. Spin density for selected configurations during the reaction, shown in the  $[\bar{1}10]$  plane perpendicular to the surface, integrated over the unit cell along the  $[\bar{1}10]$  direction (perpendicular to the plane of view). For clarity contour spacing is logarithmic, with a reduction of a factor of two between subsequent contour lines. Negative values of spin density are marked by dashed contours. Positions of the atoms are superimposed as a ball-and-stick model.

1b and c. Simultaneously the former Si–H bonding orbital evolves into the  $\Sigma_g$  bonding orbital of  $H_2$ . For a single reaction on an otherwise completely hydrogen-passivated surface, the dangling bond state created at the surface is half-filled, i.e. it contains a spin-polarized electron, as shown in Fig. 1d. In the more realistic situation when other empty sites already exist next to the newly created dangling bond, this state will become part of a partially filled, nonpolarized band of surface states. In the later situation, the reaction involves the crossing of two diabatic potential energy surfaces, with spin  $S = 1/2$  and  $S = 0$ , respectively.

I have determined the adiabatic PES for this situation for selected geometries. Fig. 2 shows the PES for a head-on collision of an H atom with an Si monohydride unit. In this geometry the only relevant coordinates are the H–H distance and the distance between the  $H_2$  center-of-mass and the surface. Plot-

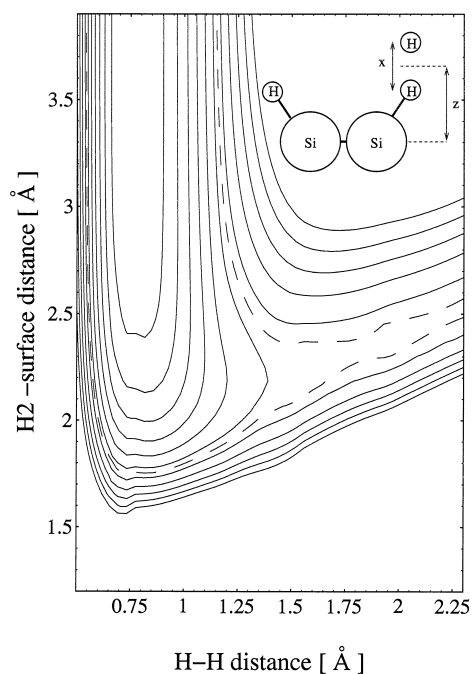


Fig. 2. Potential energy surface for an H atom colliding head-on with an H atom adsorbed on Si(001). Contour lines beginning at  $-1.1$  eV with a  $0.2$  eV spacing and the zero energy contour (dashed) are shown. Energies are for the fixed geometry of the lattice Si atoms in the monohydride phase, corrected for the effect of finite basis set size as explained in the text. Final state effects due to substrate relaxation are smaller than  $60$  meV.

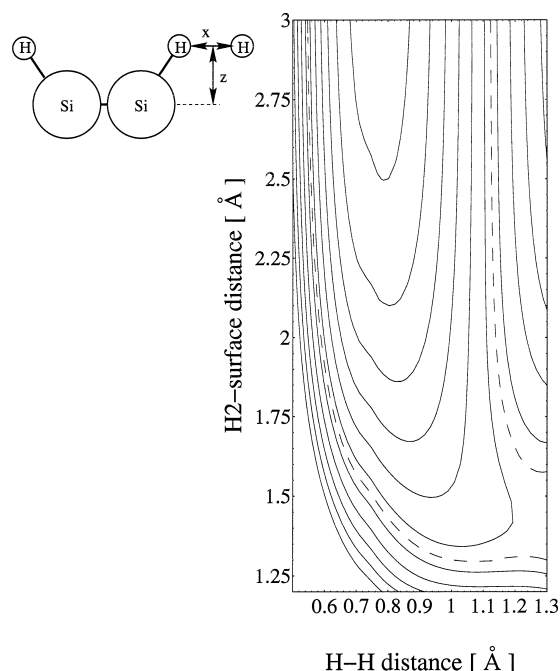


Fig. 3. Potential energy surface for a "broadside" collision between a gas phase H atom and an H atom adsorbed on Si(001). The lateral position of the "target" H atom is held fixed. The molecule is formed with its axis parallel to the surface.

ted against these variables, the PES displays a "valley" structure, the initial and final channel forming a skew angle of  $45^\circ$  typical for an Eley-Rideal reaction of partners with equal mass. Within the calculational accuracy, no activation barrier is found. This is consistent with the low calculated activation energy for H abstraction from disilane [23] and the weak temperature dependence observed for the isotope exchange reaction on the surface [24].

Fig. 3 displays the PES for a geometry where the  $H_2$  molecule is formed with its axis parallel to the surface. Here the lateral coordinates of the target H atom are kept fixed and its reaction partner is incident sideways opposite to the Si surface dimer. This situation may correspond to a direct reaction at a non-vanishing impact parameter, or to a reactive atom that moves laterally on the surface in a trapped state (hot adatom reaction). The PES is again exothermic by  $1.2$  eV.

### 3. Dynamics calculations

In order to investigate the dynamical consequences of the PES and to compare with the experiments, I have performed classical trajectory simulations. The details of such calculations have been described in a previous publication [25]. For an analytical representation of the potential, the total energies, as obtained from the ab initio calculations for 105 different configurations, have been fitted to a modified LEPS potential with adjustable parameters<sup>1</sup>. This representation is flexible enough to fit the data with a mean standard deviation  $< 0.15$  eV per data point. The motion of the incident atom and the adsorbed D atoms is described explicitly, while the surface motion is included by a collective coordinate in the spirit of the ‘soft cube’ model. In this approach energy loss of the incident atom due to inelastic scattering from adsorbate atoms is treated exactly, while the slower and less important energy loss processes to the Si substrate are included approximately. Newton’s equations are solved for H atoms incident under  $45^\circ$  for three different kinetic energies chosen according to the most abundant energies of the photolysis reaction used as the experimental H atom source [10]. The positions and momenta of the adsorbed deuterium atoms are chosen randomly from a thermal ensemble at the surface temperature of 600 K. Test calculations have shown that the results are only weakly dependent on surface temperature. All results have been averaged over various azimuthal angles of incidence and impact sites in the surface unit cell. Typically 80000 trajectories for one incident energy are employed in the averaging procedure. To improve the statistics, the results are reported for product molecules integrated over all final angles. For the lowest energy of incidence, additional runs have been performed where only molecules desorbing in the specular direction are sampled. The final kinetic energy distribution of these molecules is not significantly different from the distribution averaged over all angles, thus justifying the employed averaging procedure.

<sup>1</sup> The best fit was obtained with  $D_{\text{HH}} = 4.62$  eV,  $\rho_0 = 0.74 \text{ \AA}$ ,  $\alpha = 1.383 \text{ \AA}^{-1}$ ,  $\beta = 1.955 \text{ \AA}^{-1}$ ,  $\varepsilon = 0.58$  and  $\eta = 0.83$ , while the other parameters are the same as in Table 1 of [25].

### 4. Results

Reaction probabilities for H atoms hitting a fully D covered surface are shown in Table 1. The most likely reaction is the formation of HD molecules, with a calculated probability of 0.39 at 0.95 eV, decreasing to 0.13 for the highest impact energy. This is in agreement with the measured reaction probability of  $0.3 \pm 0.2$  for all energies used [9]. The rather high reaction probability goes back to the fact that the reaction proceeds by efficient trapping of the incident H atoms as the first step (see discussion below). In the trapping process the projectiles get deflected and loose energy, mostly by scattering from adsorbed D atoms. Note that there is also a probability of a few percent to induce desorption of  $\text{D}_2$  molecules by the impact of H atoms. Induced desorption of deuterium molecules has already been observed in H exposure of a deuterated nickel surface [26], but awaits experimental confirmation for the H + D/Si system.

The energy disposal in the HD reaction channel is analysed in Table 2. About 40% of the energy released in the reaction is converted to kinetic energy of the product molecules. This is due to the fact that the PES shows only weak attraction in the entrance channel, reflecting the low chemical activity of the hydrogen-passivated Si surface. Most of the energy is released after the HD molecular bond has been formed and the molecule experiences the repulsive potential of the surface. As a dynamical consequence, a sizeable fraction of the energy released in the reaction shows up as kinetic energy of the molecules stemming from the acceleration on the repulsive part of the PES. Vibrational and rotational excitation of the molecules are other channels of energy disposal, which become more and more important with increasing incident energy. However, the skew angle for two light particles colliding on a surface built from heavy atoms as the third reaction partner (corresponding to the LLH mass combination in gas phase reactive scattering) limits the energy transfer to molecular vibrations. Eventually, part of the reaction energy remains on the surface as excitation of adsorbate vibrations and surface phonons. The first loss channel is clearly the more important one, because the incident H atom can efficiently loose energy by scattering from an adatom, while

Table 1

Branching ratios for the reaction of H atoms with a fully deuterated Si(001) surface at a kinetic energy of 0.95, 1.9 and 3.25 eV, respectively

$E_{\text{kin}}$ (eV)	0.95	1.90	3.25
backscattering	0.58	0.74	0.85
atomic desorption	0.004	0.003	0.002
HD molecules	0.39	0.23	0.13
D <sub>2</sub> molecules	0.025	0.019	0.01
unclassified	0.004	0.005	0.008

inelastic scattering from a surface atom is inefficient due to the mass mismatch between H and Si. A simple estimate in the Baule limit (collision with a free Si atom) shows that an H atom incident at 3.25 eV may lose at most 13% of its energy by scattering from a Si atom, which is not sufficient to get trapped on the surface.

Fig. 4 displays the kinetic energy distribution of the HD molecules, to be compared with the experimental results reported in Refs. [10,11]. Both in the experiment and in the simulation, the distributions get broader as the incident energy is increased. This can be traced back to the anticorrelation between kinetic and internal energy of the HD molecules: highly vibrationally and/or rotationally excited

Table 2

Distribution of energy among the degrees of freedom before and after the reaction in eV

H on D				
initial	$E_{\text{chem}}$	1.17	1.17	1.17
	$E_{\text{kin}}$	0.95	1.90	3.25
	$E_0$	0.30	0.30	0.30
	$E_{\text{therm}}$	0.25	0.25	0.25
	$\Sigma$	2.67	3.62	4.97
final	$E_{\text{kin}}$	1.17	1.44	1.90
	$E_{\text{vib}}$	0.67	0.86	1.28
	$E_{\text{rot}}$	0.55	0.77	0.93
	$\Sigma$	2.39	3.07	4.11
	$E_{\text{diss}}$	0.28	0.55	0.86

The energy initially available consists of the exothermicity of the reaction, the kinetic energy of the projectile and the zero-point energy contained in the two adsorbate atoms ( $T_s = 600$  K). After the reaction, energy is distributed among the translational, vibrational and rotational degrees of freedom of the molecules. The difference between the total initial and final energy gives the amount of energy dissipated to the substrate, either in the form of adsorbate vibrations or excitation of the surface oscillator.

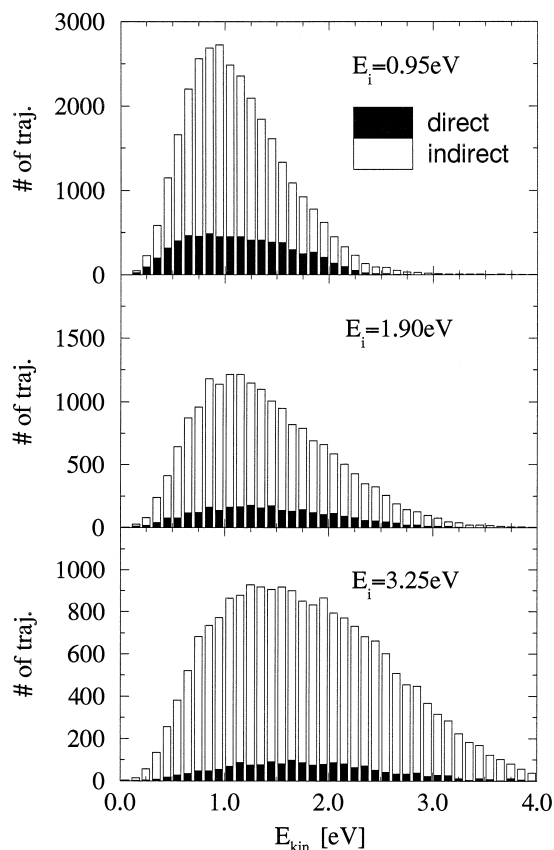


Fig. 4. Kinetic energy distribution of the produced HD molecules for H atoms incident at 0.95, 1.9 and 3.25 eV (top to bottom). Contributions from the direct reaction (filled bar) and indirect reactions (white bars) have been added.

molecules leave the surface with less kinetic energy and thus contribute to the broadening of the distributions. It can also be seen from Fig. 4 that most of the reactions are indirect, with the H atom visiting more than one surface unit cell before forming a molecule (empty part of the bars in Fig. 4), while only a small fraction reacts directly in the unit cell of impact (filled part of the bars). The mean final kinetic energy for H atoms incident at 0.95 eV is 1.17 eV. This is in good agreement with the experimental value of 1.2 eV. For larger energies of incidence, the HD kinetic energy increases, reaching 1.9 eV for the  $E_i = 3.25$  eV. However, the kinetic energy of the HD molecules does not reflect the full rise in the initial energy of the projectiles. Instead, excitations of the substrate, as well as internal excitations of the

molecules, take up a large fraction of the extra available energy. Simultaneously, the fraction of indirect reactive events, i.e. reactions caused by trapped adatoms wandering around on the surface, increases at large incident energies.

In the experiment [10], the maximum of the kinetic energy distribution was found to be nearly independent of the incident energy. In the simulations, the maximum of the distributions is slightly shifted to higher energies on going from top to bottom in Fig. 4. The lower kinetic energy observed experimentally, together with the less pronounced drop of the measured reaction probability at large incidence energy seems to suggest that some mechanism of energy loss other than mechanical coupling to the surface motion comes into play, which leads to efficient trapping of the incident atoms even at these energies. A possible candidate could be electronic excitations in the substrate induced by the reaction.

In conclusion, the potential energy surface of the reaction  $\text{H} + \text{D}/\text{Si}(001)$  has been determined using density functional calculations. The reaction is found to be non-activated and highly exothermic. As a consequence of the topology of the PES, the kinetic energy of the hydrogen molecules is the most important channel of energy disposal. For increased initial energies of the H atoms, the participation of molecular and substrate excitations shows up as an increased width in the kinetic energy distributions of the HD molecules.

### Acknowledgements

I would like to thank W. Brenig and E. Pehlke at TU München for helpful discussions and S. Buntin for communicating his results prior to publication.

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