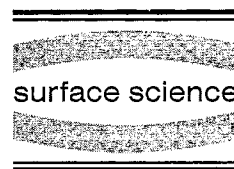




ELSEVIER

Surface Science 363 (1996) 1–10



# Dynamical quantum processes of molecular beams at surfaces: dissociative adsorption of hydrogen on metal surfaces

Axel Gross

*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany*

Received 19 July 1995; accepted for publication 22 September 1995

## Abstract

Due to the improvement of computer power and the development of efficient algorithms it is now possible to combine high-dimensional quantum dynamical calculations of the dissociative adsorption of molecular beams with reliable ab-initio potential energy surfaces (PES). In this brief review two recent examples of such studies of the systems  $\text{H}_2/\text{Cu}(111)$ , where adsorption is hindered by a noticeable energy barrier, and  $\text{H}_2/\text{Pd}(100)$ , where activated as well as non-activated paths to adsorption exist, are presented. The effect of lateral surface corrugation on the sticking probability in the tunneling and the classical regime and the role of additional parallel momentum are discussed in the context of the  $\text{H}_2/\text{Cu}(111)$  results. For the system  $\text{H}_2/\text{Pd}(100)$  it is shown that the initial decrease of the sticking probability with increasing kinetic energy, which is usually attributed to a precursor mechanism, can be explained by dynamical steering. In addition, the influence of rotation on the adsorption and desorption dynamics is examined.

**Keywords:** Atom–solid interactions; scattering, diffraction; Chemisorption; Computer simulations; copper; Density functional calculations; Hydrogen; Low index single crystal surfaces; Metallic surfaces; Models of surface chemical reactions; Molecule–solid reactions; Palladium; Quantum effects; Sticking; Surface chemical reaction; Thermal desorption

## 1. Introduction

In recent years the dynamics of dissociative adsorption and associative desorption of hydrogen has been studied in great detail, experimentally as well as theoretically (see, e.g., Refs. [1,2]). One of the key motivations for these investigations is that by studying this simple surface reaction one hopes to learn about the crucial principles underlying more complex surface reactions which occur, e.g., in heterogeneous catalysis. In the following I will focus on quantum dynamical investigations aimed at the understanding of dissociation. For a much

more detailed discussion see the recent excellent review by Darling and Holloway [3].

Chemical reactions at surfaces represent the interaction of a system with a limited number of degrees of freedom (the molecule) with the half-infinite solid which possesses in principle an infinite number of degrees of freedom. However, for the dissociative adsorption of hydrogen, especially on metal surfaces, there is little energy transfer to the substrate phonons due to the large mass mismatch. The crucial process in the understanding of the dissociation is the conversion of the kinetic and internal energy of the molecule into translational energy of the atoms relative to each other, the subsequent energy dissipation to the solid is not relevant for the dissociation. In addition, electronic

\* Corresponding author. Fax: 49 30 8413 4701;  
e-mail: axel@theo22.rz-berlin.mpg.de.

levels of hydrogen molecules in front of metal surfaces are broadened significantly [4] so that electronic excitations are very effectively quenched.

This situation seems to be different for hydrogen adsorption on semiconductor surfaces, especially in the well studied system  $\text{H}_2/\text{Si}$ . It had been proposed [5] that the experimental puzzle of low sticking coefficient and almost thermal distribution in desorption – the former result indicating a high barrier to adsorption, the latter a low barrier (see Ref. [6] and references therein) – can be reconciled if lattice distortions on adsorption are taken into account. The strong rearrangement of the silicon surface due to hydrogen adsorption has been confirmed in total-energy calculations [7,8], and also the predicted strong surface temperature dependence of the sticking probability of  $\text{H}_2/\text{Si}$  [5] has been found experimentally [6,9].

The dynamics of dissociative adsorption of hydrogen on the more densely packed metal surfaces, however, can be described using low-dimensional potential energy surfaces (PES) because of the large mass mismatch, the smaller space for surface rearrangements, and the quenched electronic excitations [3]. In principle the PES should be six-dimensional describing all the degrees of freedom of the hydrogen molecule. However, up to recently there had been no six-dimensional quantum dynamical investigations of the adsorption and desorption dynamics because the calculations were computationally too demanding. Hence the quantum dynamicists were restricted to low-dimensional model calculations. Since the crucial coordinate for the dissociation process is the intramolecular spacing, a large number of studies were devoted to the dynamics on two-dimensional so-called “elbow” potentials where the  $\text{H}_2$  center of mass distance from the surface and the H–H distance were considered [10–15]. These studies provided us with a qualitative understanding of the topological features that realistic potentials should have in these two coordinates in order to describe surface reactions. Further quantum mechanical model studies coupled the two-dimensional elbow potential to one surface oscillator in order to account for recoil and surface temperature effects [5,16–18]. Just recently there have been a large number of papers dealing with

the effects of rotations on the sticking probability, especially with steric effects and the non-monotonous dependence of the sticking probability on rotational quantum number  $j$  in the system  $\text{H}_2/\text{Cu}(111)$  [19–23].

Although already in the earliest studies on dissociative adsorption [24] the important role of surface corrugation was stressed, except for in the studies of Nørskov and co-workers [25–27] and Holloway and co-workers [28–30], little attention has been paid to the influence of corrugation on the adsorption dynamics. There are two main reasons for this. Firstly a large number of adsorption systems shows the so-called normal-energy scaling [31–33], i.e., the sticking probability is a function of the normal component of the kinetic energy of the impinging molecules alone. This scaling behaviour is usually associated with a flat, structureless surface. And secondly, the magnitude of the corrugation had to be more or less guessed since the mapping out of the whole PES by ab-initio methods was much too time-consuming. Since also the electronic density in front of metal surfaces is rather smeared out [34], the picture of low-corrugated metal surfaces was widely accepted.

Due to the improvement of computer power and the development of efficient algorithms it just recently has become possible to map out the six-dimensional PES of hydrogen dissociation on metal surfaces [4,35–37] by reliable density-functional calculations. It came as a surprise when elaborate studies of the  $\text{H}_2/\text{Cu}$  system [4,35] revealed that the PES is strongly corrugated although this system obeyed normal energy scaling in the beam experiments [32,33]. These theoretical findings renewed the interest in the role of corrugation for the dissociation dynamics [38–40]. In a three-dimensional model study Darling and Holloway [38] showed how the apparent contradiction between normal energy scaling and strongly corrugated PES can be reconciled if the PES exhibits topological features now termed “balanced corrugation” [3].

The availability of high-dimensional potential energy surfaces has brought about new efforts for the improvement of the quantum dynamical algorithms. While up to recently it was believed that the inclusion of all molecular degrees of freedom

in a quantum dynamical calculation is too computationally expensive [22,23], there is now the first six-dimensional quantum study of dissociative adsorption and associative desorption [41]. High-dimensional quantum dynamical studies using ab-initio potentials serve a twofold purpose. Firstly, they can yield a quantitative as well as also a novel qualitative understanding of the dissociation process because all relevant degrees of freedom are included. But secondly, also the reliability of the total-energy calculations can be checked. The results for the  $\text{H}_2/\text{Cu}$  system showed that one has to go beyond the local-density approximation (LDA) in the treatment of exchange-correlation effects in order to obtain realistic barrier heights [4,35]. But still the non-local corrections are approximative and their validity is highly debated, especially in the  $\text{H}_2/\text{Si}(100)$  system [7,8,42]. Since from just looking at a PES one cannot extract whether the PES is accurate, one has to perform dynamical calculations on this PES in order to find out.

In the following I will present two examples of high-dimensional quantum dynamical studies on ab-initio potential energy surfaces. The first example deals with the  $\text{H}_2/\text{Cu}(111)$  system [43] where dissociation is hindered by noticeable barriers. I will focus on the effect of lateral surface corrugation on the sticking probability in the tunneling and the classical regime and on the role of additional parallel momentum. The second example is then devoted to  $\text{H}_2/\text{Pd}(100)$  [41], a system where activated as well as non-activated paths to dissociative adsorption exist. It will be shown that the initial decrease of the sticking probability with kinetic energy found in this system [31] is not due to a precursor mechanism, as was commonly believed, but can be explained by dynamical steering. In addition, rotational effects will be discussed. The paper ends with some concluding remarks.

## 2. $\text{H}_2/\text{Cu}(111)$

$\text{H}_2/\text{Cu}$  has been the benchmark system for the study of dissociative adsorption. An abundance of experimental [33,44–46] and theoretical [12,13,19–23] investigations about this system

exists, just to mention a few. The calculated barrier heights varied substantially over the years (see Ref. [4]) and the discussion still goes on [35,47]. For the  $\text{H}_2/\text{Cu}(111)$  system it was found that the barrier to dissociative adsorption for the molecular axis parallel to the surface varied between 0.73 and 1.43 eV within the surface unit cell for a four-layer substrate in the slab calculations. Convergence tests suggested that the minimum barrier should be lowered to 0.5 eV. A five-dimensional parametrisation of the ab-initio PES has served as an input for a dynamical study of the adsorption and desorption [43], where the consistent four-layer results have been used. Further convergence tests which were finished after the completion of the dynamical calculations showed that the whole barrier region of the PES should be shifted by approximately the same amount as the minimum barrier [48]. In the dynamical study the three center-of-mass coordinates and the interatomic spacing of the  $\text{H}_2$  molecule have been treated quantum mechanically, while the azimuthal orientation of the molecule has been taken into account in a classical sudden approximation which works quite well in the  $\text{H}_2/\text{Cu}$  system [49]. The polar orientation is not varied which means that the molecular axis is kept parallel to the surface. The quantum dynamics were determined in a time-independent coupled-channel scheme using the concept of the *local reflection matrix* [50,51] and the *inverse local transmission matrix* [52]. This very stable method also yields the wave function of the scattering problem [40]. It is closely related to the logarithmic derivative of the solution matrix and thus avoids exponentially increasing evanescent waves which cause numerical instabilities.

The results of the quantum dynamical calculations of the sticking probability of  $\text{H}_2/\text{Cu}(111)$  for molecules initially in the vibrational ground state under normal and non-normal incidence are shown in Fig. 1 versus the normal kinetic energy in a linear and in a logarithmic plot. For comparison also the results of two-dimensional calculations with the minimum barrier are shown. I will first focus on the normal-incidence data in the low-energy regime (Fig. 1b) where sticking is impossible classically. Comparing the 2D and the 5D results shows that the effect of corrugation in the tunneling

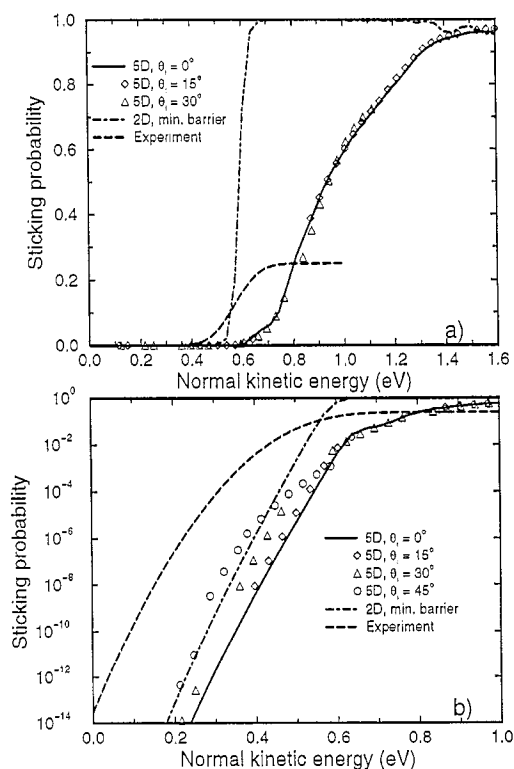


Fig. 1. Sticking probability versus normal kinetic energy for molecules initially in the vibrational ground state. (a) Linear plot, (b) logarithmic plot (note the different energy range). 5D-calculations for different incident angles at the corrugated surface: solid line  $\theta_i = 0^\circ$ ,  $\diamond \theta_i = 15^\circ$ ,  $\triangle \theta_i = 30^\circ$ ,  $\circ \theta_i = 45^\circ$ ; Dash-dotted line: 2D-calculations corresponding to a flat surface with the minimum barrier (from Ref. [43]). Dashed line: Experimental curve (from Ref. [44]).

regime is an almost energy-independent suppression of the sticking probability, in this case by about two orders of magnitude. Since the increase of the sticking probability in 2D calculations is determined by the barrier width [12], this indicates that at energies below the minimum barrier height the adsorption dynamics are governed by the minimum barrier path. This result is also confirmed by wave function plots [39]. It can be simply understood by the fact that the transmission through a barrier in the tunneling regime is exponentially suppressed which on the other hand leads to an exponential preference of the minimum barrier path compared to all other paths.

In the energy regime where sticking classically is possible (which will be referred to as the “classical

regime” in the following) the sticking curves of the 2D and the 5D calculations are no longer parallel (Fig. 1a). Indeed the sticking probability in the 5D calculations starts rising in the linear plot at an energy corresponding to the minimum barrier height and reaches unity at an energy which corresponds to the maximum barrier height (the onset of the sticking in the linear plot occurs already at approximately 0.15 eV below the minimum barrier height due to the softening of the  $H_2$  bond at the surface and the accompanying reduction of the zero-point vibrational energy). Obviously the whole distribution of the barrier heights determines the sticking probability. At these high kinetic energies (larger than 0.6 eV) the dynamics in the classical regime can be described in the sudden limit. A molecule impinging on the surface sticks or not according to whether its energy is larger than the barrier it hits or not, there are little reorientation and steering effects. This means that the sticking in this energy regime can be understood in terms of the available phase space for dissociation which is the basic assumption underlying the so-called hole-model [26].

In the first presentation [43] the theoretical results were compared to data compiled by Michelsen and Auerbach [32]. They fitted existing adsorption data and, via the principle of detailed balance, also desorption data to a functional form of the sticking probability of the form,

$$S_0(E) = \frac{A}{2} \left[ 1 + \tanh \left( \frac{E - E_0}{W} \right) \right]. \quad (1)$$

These experimental data were at variance with the theoretical data of Ref. [43] especially at low and at high energies. In the meantime a new, very detailed experimental study of the adsorption and desorption of  $H_2/Cu(111)$  has been published by Rettner et al. [44]. To describe the sticking function they used,

$$S_0(E) = \frac{A}{2} \left[ 1 + \operatorname{erf} \left( \frac{E - E_0}{W} \right) \right], \quad (2)$$

because this functional form reproduces the adsorption data better at low energies [53]. And indeed, while in the old parametrisation the experimental sticking probability did not drop below

$10^{-4}$  [32], now at low energies in Fig. 1b the experimental and the theoretical curve no longer disagree substantially. The two curves are almost parallel, whereby the shift of approximately 0.25 eV can be related to the minimum barrier height in the calculations which seems to be too high by the same amount [4]. This indicates that, except for the barrier height, the minimum barrier path is properly described by the ab-initio PES. The same shift of 0.25 eV between theory and experiment is also seen at the onset of sticking in the linear plot, Fig. 1a (note the different energy scale in the linear and the logarithmic plot). However, while the experimental curve saturates at a sticking probability of 0.25, the theoretical curve reaches almost one. The issue of the maximum sticking probability for  $\text{H}_2/\text{Cu}(111)$  is still strongly debated. Rettner et al. [44] state that their experimental sticking probabilities fitted equally well with  $A$  values between 0.15 and 0.5 since the measurements do not extend to energies above 0.55 eV. Just one fitting parameter  $W$  for the width of the sticking curve may not be sufficient, since the increase of the sticking probability is determined by two different properties: in the tunneling regime by the barrier width, and in the classical regime by the distribution of the barrier heights. On the other hand the polar rotation of the molecule had not been considered for the theoretical results in Fig. 1. Particles that hit the surface in the upright orientation can not dissociate. So the inclusion of the polar orientation will probably reduce the maximum sticking probability since at high energies molecules will not have enough time to reorientate towards a more favorable configuration towards dissociative adsorption during the scattering process.

With regard to the effect of additional parallel momentum, Fig. 1a shows that for non-normal incidence the sticking probabilities fall upon the normal incidence sticking curve if they are plotted versus the normal kinetic energy, at least in the classical regime. This normal-energy scaling is surprising considering the strong corrugation of the surface which is shown in Fig. 2. Darling and Holloway [38] have first addressed this issue. They showed that the variation of the barrier height (energetic corrugation) and the variation of the

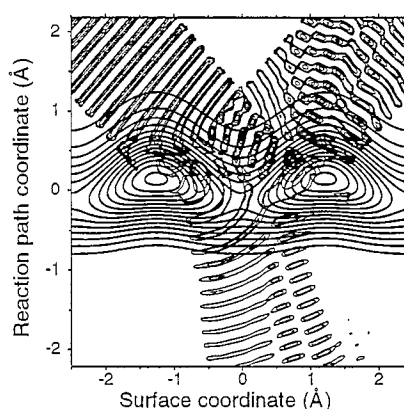


Fig. 2. Positive real part of the wave function of  $\text{H}_2$  scattered at a PES with one-dimensional lateral corrugation simulating  $\text{H}_2/\text{Cu}(111)$ . The incident beam has a kinetic energy of  $E_i = 1.08$  eV, the incident angle is  $\theta_i = 45^\circ$ . The contour spacing for the potential (thick lines) is 0.1 eV. The positions of the Cu atoms are at the potential maxima (from Ref. [43]).

barrier position (geometric corrugation) have opposing effects as far as the role of additional parallel momentum is concerned. The plot of the wave function [40,43] scattered at the corrugated PES in Fig. 2 illustrates these effects. In order to make both the incoming and the reflected part of the beam visible in one single plot, the lateral extension of the beam perpendicular to its propagation direction, which is in principle infinite, is restricted. Thus by following the wave fronts the propagation of the beam and its splitting in a reflected and transmitted part can be followed. Due to the energetic corrugation, molecules with additional parallel momentum will sample a range of energy barriers which leads to an averaging process over the barriers. If their normal kinetic energy is less than the mean barrier height then this averaging process leads to a suppression of the sticking probability [39]. Fig. 2 shows that molecules which encounter the high-barrier sites are scattered back into the gas phase.

On the other hand the area in the surface unit cell where the propagation direction of the incoming beam is aligned to the local gradient of the potential becomes actually larger for additional parallel momentum due to the geometric corrugation. This results in an enhancement of the sticking probability [38,39]. Now if the maximum barriers are at a greater distance from the surface, the

opposing effects of energetic and geometric corrugation can balance [3,38] leading to normal-energy scaling in spite of the strong corrugation.

The question now arises whether this is just a coincidence that nature has hidden the fact of the strongly corrugated surfaces by these peculiar balancing features of the PES. However, total energy calculations show that usually the larger barriers to dissociative adsorption are in front of on-top positions [4,35]. And there the interaction between molecule and surface occurs further away from the surface as compared to, e.g., bridge and hollow sites [35,43] since in front of the atoms the electron density spills further out into the vacuum. So the topological features responsible for the normal-energy scaling do not seem too peculiar regarding the underlying principles of the chemical interaction.

Fig. 1b also reveals that in the tunneling regime additional parallel momentum enhances sticking. This is due to the fact that in the realm of tunneling dynamics parallel momentum is effectively converted into normal momentum for energetic as well as for geometric corrugation [39]. The observation that in beam experiments normal energy scaling is found for all energies in the system  $\text{H}_2/\text{Cu}(111)$  [33,44] can be explained by the fact that a low kinetic energies sticking in the beam experiments is dominated by the vibrationally excited molecules, and for these molecules the range where normal-energy scaling is obeyed is shifted to lower energies [40].

### 3. $\text{H}_2/\text{Pd}(100)$

Molecular beam experiments of the dissociative adsorption of  $\text{H}_2$  on various transition metal surfaces like  $\text{Pd}(100)$  [31],  $\text{Pd}(111)$  and  $\text{Pd}(110)$  [54],  $\text{W}(111)$  [55],  $\text{W}(100)$  [55–57],  $\text{W}(100)\text{--c}(2 \times 2)\text{Cu}$  [58] and  $\text{Pt}(100)$  [59] show that the sticking probability initially decreases with increasing kinetic energy of the beam in these systems. Such a behaviour is usually attributed to a precursor mechanism: before dissociation the molecules are temporarily trapped in a molecular adsorption state, the so-called precursor state, where they accommodate to the surface temperature.

In order to be trapped, the molecules have to lose their initial kinetic energy which is assumed to happen primarily by energy transfer to the substrate phonons [1]. And it is this trapping probability which decreases with increasing energy and thus determines the sticking probability for dissociative adsorption. At higher energies the sticking probability rises again in all systems mentioned above indicating that the adsorption via direct activated paths becomes dominant.

However, for hydrogen adsorption the large mass mismatch between adsorbate and substrate should make the energy transfer process inefficient. Together with the missing surface temperature dependence this led to a dynamical steering process being proposed in order to explain the initial decrease of the sticking probability [57,59], but there had been no theoretical confirmation whether this mechanism could be effective. Recent density-functional theory calculations show that there exist non-activated as well as activated paths to dissociative adsorption in the system  $\text{H}_2/\text{Pd}(100)$ , but no molecular adsorption well [36]. And three-dimensional quantum dynamical calculations using a model PES with such features suggested that a steering mechanism can indeed be responsible for the initial decrease of the sticking probability [39], but large quantitative discrepancies to the experiment remained.

Using a parametrization of the ab-initio PES of  $\text{H}_2/\text{Pd}(100)$  dynamical calculations of the dissociative adsorption and associative desorption have been performed where for the first time *all* six degrees of freedom of the hydrogen molecule have been treated quantum dynamically [41]. Fig. 3 shows a comparison between experiment [31] and the 6D calculations. The dashed curve which corresponds to molecules initially in the rotational ground state exhibits a strong oscillatory structure which is at variance with the experimental data. Performing three-dimensional model calculations on a PES with similar features as the ab-initio PES of  $\text{H}_2/\text{Pd}(100)$  it has been shown that the quantum nature of the hydrogen beam leads to an oscillatory structure in the sticking probability [39]. Whenever the kinetic energy becomes large enough to open up new scattering channels, the reflection rate has a maximum. Since the reflection

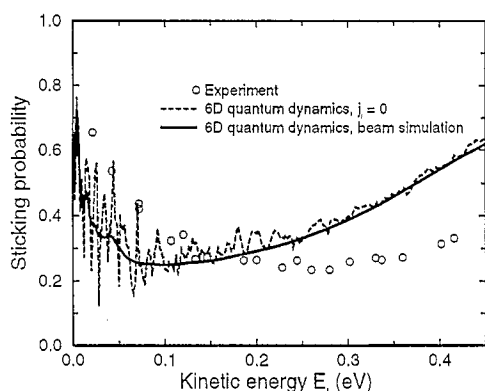


Fig. 3. Sticking probability versus kinetic energy for a  $\text{H}_2$  beam under normal incidence on a Pd(100) surface. Experiment: circles (from Ref. [31]); theory:  $\text{H}_2$  molecules initially in the rotational ground state (dashed line) and with an initial rotational and energy distribution adequate for molecular beam experiments (solid line) (from Ref. [41]).

rate and the sticking probability are related by unitarity, this means that at these energies the sticking probability shows a minimum. Strong oscillations in the sticking probability were also found in three-dimensional wave-packet calculations [29] where the PES included a precursor well. They were attributed to the existence of resonance states in the attractive well which, however, does not exist in the ab-initio potential of  $\text{H}_2/\text{Pd}(100)$  [36,37].

In order to compare the results of the 6D calculations with the beam experiment data one has to take into account that the experimental beam does not correspond to a single quantum state. Firstly, excited rotational states are populated according to a Boltzmann distribution with a temperature of 0.8 of the nozzle temperature in the case of hydrogen beams [31]. And secondly, the beam is not strictly monoenergetic, but has a certain energy spread of typically  $\Delta E/E_i = 2\Delta v/v_i = 0.2$  [31] ( $E_i$  and  $v_i$  are the initial kinetic energy and velocity, respectively). If the theoretical results are averaged over initial states according to the experimental conditions (solid line in Fig. 3), the strong oscillations disappear.

The resulting theoretical curve agrees quite satisfactory with experiment. Although no precursor state exists in the PES and the energy transfer to substrate phonons is not taken into account due

to the fixed substrate atoms, the initial decrease of the sticking probability with increasing kinetic energy is well reproduced. Since the precursor mechanism cannot be responsible, only a dynamical steering effect can cause the initial decrease. This steering effect is confirmed in the coupled-channel calculations by the fact that at low energies more channels are needed in order to get converged results than at high energies. Usually it is the other way around since at higher energies more channels are energetically accessible. This unusual behavior indicates that at low energies there is a strong dynamical redistribution among the different channels while at high energies the dynamics is closer to the adiabatic limit with little transitions between the channels.

The classical analogue to the quantum dynamical description of the steering effect is illustrated in Fig. 4 which shows a two-dimensional cut through the six-dimensional PES together with two typical trajectories of impinging  $\text{H}_2$  molecules. By symmetry, both trajectories have equivalent impact parameters, but while the slower molecule (left trajectory) can be steered towards a non-

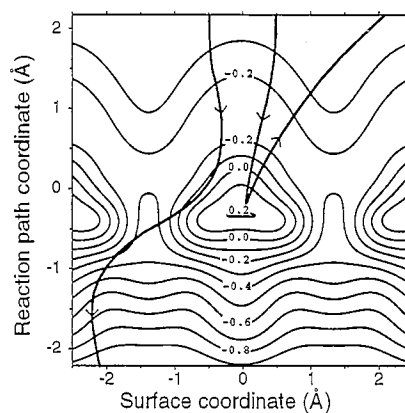


Fig. 4. Classical illustration of the steering effect. The contour lines show the potential energy surface in eV along a two-dimensional cut through the six-dimensional configuration space of a hydrogen molecule with the molecular axis parallel to the surface. The Pd atoms are at the potential maxima. The surface coordinate corresponds to the X-axis, while the reaction path coordinate  $s$  for  $s \rightarrow \infty$  is equivalent to the  $\text{H}_2$  center of mass distance from the surface, for  $s \leq -2.5$  Å to the distance between two adsorbed H atoms. The left trajectory corresponds to a slow molecule (kinetic energy  $E_{\text{kin}} = 0.05$  eV), the right trajectory to a fast molecule ( $E_{\text{kin}} = 0.15$  eV) (from Ref. [41]).

activated path to adsorption by the attractive forces, the other molecule (right trajectory) is too fast for the forces to divert it significantly. It hits the repulsive part of the potential and is reflected back into the gas phase. By further increasing the kinetic energy the molecule will eventually have enough energy to directly cross the barrier which leads to the increase of the sticking probability at higher energies (see Fig. 3).

The steering effect should also be observed in desorption properties, e.g., the mean kinetic energy in desorption. In Ref. [39] three-dimensional dynamical calculations on a model potential with non-activated as well as activated paths to dissociative adsorption have been performed where the PES looked quite similar to Fig. 4. In order to desorb the molecules have to have enough kinetic energy normal to the surface to overcome the barrier for desorption. This corresponds to trajectories starting from below in Fig. 4. Now most desorbing molecules propagate along minimum barrier paths [39]. Except for the molecules following the high-symmetry path there are forces acting on the molecules which will divert them from the normal desorption direction. And again, the slower the molecules are, the more they will be diverted. This also means that at high desorption angles primarily low-energy molecules will be found. Indeed the 3D model calculations follow this trend (see Fig. 5) [39]. While for normal desorption the mean kinetic energy is in equilib-

rium with the surface temperature (note that in two-dimensions the flux-corrected mean kinetic energy of a gas in equilibrium is  $3/2 kT$ ), for high desorption angles the mean kinetic energy is strongly lowered. This means that a peaked mean kinetic energy in desorption is not always indicative of non-thermal processes [60]. In addition, it shows that one-dimensional models [61] are not sufficient in order to describe angular distributions in desorption.

A dynamical degree of freedom that has not been considered so far in this brief review is the rotational degree of freedom. As for the influence of additional rotational motion on the sticking probability, there are two different mechanisms operative. Just recently it has been pointed out [20] that, apart from the change in moment of inertia, an isomorphism exists between surface corrugation and a planar rotor which means that there is a close correspondence in the way the lateral surface corrugation and the orientational anisotropy of the molecule-surface potential enter into the dynamics. The barrier to dissociative adsorption strongly depends on the molecular orientation [4,37]. Thus additional rotational motion acts like additional parallel momentum in the case of energetic corrugation. Due to the range of barrier heights which is probed by the rotating molecule the sticking probability is effectively suppressed [20]. However, in the case of the  $H_2/Cu$  system due to the late barrier to adsorption the molecular bond is strongly extended when the barrier region is crossed. The resulting increase in the moment of inertia causes a decrease of the rotational energy. This leads to a lowering of the effective barrier with increasing rotational quantum number  $j$  and to an enhancement in the sticking probability for high  $j$  values [20,21] in agreement with the experiment [53].

Now in the system  $H_2/Pd(100)$  there are non-activated paths to dissociative adsorption so that the concept of early and late barriers is not applicable. Indeed Fig. 3 shows that by taking into account the rotational population of the incoming beam in adsorption, the averaged sticking probability is slightly decreased as compared to molecules in the rotational ground state [41] at all kinetic energies. Especially at low energies

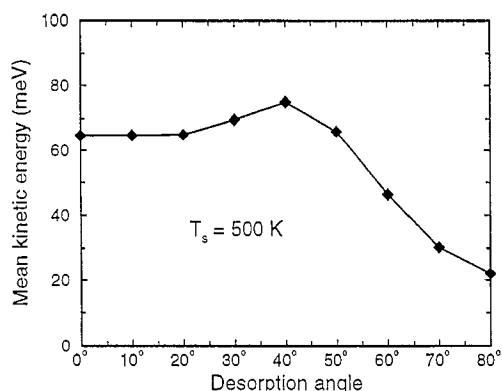


Fig. 5. Angular distribution of the mean kinetic energy of molecules desorbing from a one-dimensional corrugated surface simulating  $H_2/Pd$ . Surface temperature  $T_s = 500$  K (from Ref. [39]).



additional rotational motion strongly reduces the sticking probability. This is shown in Fig. 6 for a initial kinetic energy of  $E_i = 10$  meV. The diamonds correspond to the orientationally averaged sticking probability,

$$S_{j_i}(E) = \frac{1}{2j_i + 1} \sum_{m_i = -j_i}^{j_i} S_{j_i, m_i}(E). \quad (3)$$

The strong decrease is caused by a suppression of the steering effect. The faster a molecule is rotating, the harder the molecular axis can be focused to a favorable orientation towards adsorption, and the more molecules will be reflected at the surface.

In addition, Fig. 6 shows the effect of molecular orientation on the sticking probability. The most favorable orientation to adsorption is with the molecular axis parallel to the surface. Molecules with azimuthal quantum number  $m = j$  have their axis preferentially oriented parallel to the surface. These molecules rotating in the so-called helicopter fashion dissociate more easily than molecules rotating in the cartwheel fashion ( $m = 0$ ) with their rotational axis preferentially parallel to the surface since the latter have a high probability of hitting the surface in an upright orientation in which they cannot dissociate. This steric effect has also been investigated in a number of model studies for purely activated adsorption [19–23].

Invoking the principle of detailed balance, from the suppression of the sticking probability by rota-

tion it follows that the population of rotational states in desorption should be lower than expected for molecules in thermal equilibrium with the surface temperature. This so-called rotational cooling has indeed been found for  $H_2$  molecules desorbing from Pd(100) [62] and is also well reproduced by the six-dimensional quantum dynamical calculations [41].

## 4. Conclusions

In this brief review two recent examples of high-dimensional quantum dynamical studies using ab-initio potential energy surfaces have been presented. For the interaction of light diatomic molecules interacting with metal surfaces the continuous excitation spectrum of the solid can be often neglected. For these systems now an almost complete understanding of the dissociation process can be gained since translational, vibrational, rotational and lateral effects no longer have to be treated separately. Our current understanding of simple surface reactions is mostly based on low-dimensional dynamical studies on model potentials. These studies provided us with a great deal of insight into the crucial principles underlying these simple surface reactions. However, high-dimensional studies do not only enhance the quantitative agreement with experiment. Due to the microscopic information also a new qualitative understanding of dissociation and scattering at surfaces can be obtained. Since this development has just started, many interesting results should be anticipated in the near future.

## Acknowledgements

It is a pleasure to acknowledge the many stimulating discussions and fruitful collaboration with Thomas Brunner, Bjørk Hammer, Peter Kratzer, Eckhard Pehlke, Ralf Russ, Steffen Wilke, and other colleagues at the Technical University Munich and the Fritz-Haber-Institute, Berlin. Special thanks go to Wilhelm Brenig and Matthias Scheffler for guiding and supporting the development of my work. I also want to thank George

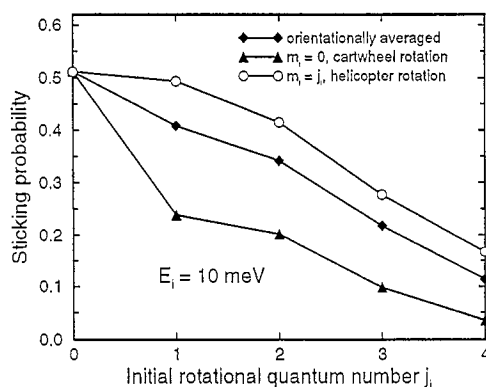


Fig. 6. Sticking probability versus initial rotational quantum state  $j_i$  for the system  $H_2/Pd(100)$ . Diamonds: orientationally averaged sticking probability (Eq. (3)); triangles:  $m_i = 0$  (cartwheel rotation); circles:  $m_i = j_i$  (helicopter rotation). The initial kinetic energy is  $E_i = 10$  meV.

Darling and Stephen Holloway for many discussions concerning dynamical matters and for organizing the Dynamics Workshop in Chester, UK, which offered a great opportunity for exchanging ideas on high-dimensional quantum dynamics.

## References

- [1] K.D. Rendulic and A. Winkler, *Surf. Sci.* 299/300 (1994) 261.
- [2] S. Holloway, *Surf. Sci.* 299/300 (1994) 656.
- [3] G.R. Darling and S. Holloway, *Rep. Prog. Phys.* 58 (1995) 1595.
- [4] B. Hammer, M. Scheffler, K.W. Jacobsen and J.K. Nørskov, *Phys. Rev. Lett.* 73 (1994) 1400.
- [5] W. Brenig, A. Gross and R. Russ, *Z. Phys. B* 96 (1994) 231.
- [6] K.W. Kolasinski, W. Nessler, K.-H. Bornscheuer and E. Hasselbrink, *J. Chem. Phys.* 101 (1994) 7082.
- [7] P. Kratzer, B. Hammer and J.K. Nørskov, *Chem. Phys. Lett.* 229 (1994) 645.
- [8] E. Pehlke and M. Scheffler, *Phys. Rev. Lett.* 74 (1995) 952.
- [9] P. Bratu and U. Höfer, *Phys. Rev. Lett.* 74 (1995) 1625.
- [10] B. Jackson and H. Metiu, *J. Chem. Phys.* 86 (1987) 1026.
- [11] D. Halstead and S. Holloway, *J. Chem. Phys.* 93 (1990) 2859.
- [12] G.R. Darling and S. Holloway, *J. Chem. Phys.* 97 (1992) 734.
- [13] S. Küchenhoff, W. Brenig and Y. Chiba, *Surf. Sci.* 245 (1991) 389.
- [14] L. Schröter, S. Küchenhoff, R. David, W. Brenig and H. Zacharias, *Surf. Sci.* 261 (1992) 243.
- [15] G.R. Darling and S. Holloway, *Surf. Sci.* 268 (1992) L305.
- [16] M. Hand and J. Harris, *J. Chem. Phys.* 92 (1990) 7610.
- [17] A. Gross, *Surf. Sci.* 320 (1994) L68.
- [18] G.R. Darling and S. Holloway, *Surf. Sci.* 321 (1994) L189.
- [19] R.C. Mowrey, *J. Chem. Phys.* 99 (1993) 7049.
- [20] G.R. Darling and S. Holloway, *J. Chem. Phys.* 101 (1994) 3268.
- [21] T. Brunner and W. Brenig, *Surf. Sci.* 317 (1994) 303.
- [22] S. Kumar and B. Jackson, *J. Chem. Phys.* 100 (1994) 5956.
- [23] J. Dai and J.Z.H. Zhang, *J. Chem. Phys.* 102 (1995) 6280.
- [24] J.E. Lennard-Jones, *Trans. Faraday Soc.* 28 (1932) 333.
- [25] J.K. Nørskov, A. Houmøller, P.K. Johansson and B.I. Lundquist, *Phys. Rev. Lett.* 46 (1981) 257.
- [26] M. Karikorpi, S. Holloway, N. Henriksen and J.K. Nørskov, *Surf. Sci.* 179 (1987) L41.
- [27] C. Engdahl, B.I. Lundqvist, U. Nielsen and J.K. Nørskov, *Phys. Rev. B* 45 (1992) 11362.
- [28] D. Halstead and S. Holloway, *J. Chem. Phys.* 88 (1988) 7197.
- [29] G.R. Darling and S. Holloway, *J. Chem. Phys.* 93 (1990) 9145.
- [30] G.R. Darling and S. Holloway, *J. Chem. Phys.* 97 (1992) 5182.
- [31] K.D. Rendulic, G. Anger and A. Winkler, *Surf. Sci.* 208 (1989) 404.
- [32] H.A. Michelsen and D.J. Auerbach, *J. Chem. Phys.* 94 (1991) 7502.
- [33] C.T. Rettner, D.J. Auerbach and H.A. Michelsen, *Phys. Rev. Lett.* 68 (1992) 1164.
- [34] J.R. Chelikowsky, M. Schlüter, S.G. Louie and M.L. Cohen, *Solid State Commun.* 17 (1975) 1103.
- [35] J.A. White, D.M. Bird, M.C. Payne and I. Stich, *Phys. Rev. Lett.* 73 (1994) 1404.
- [36] S. Wilke and M. Scheffler, *Surf. Sci.* 329 (1995) L605.
- [37] S. Wilke and M. Scheffler, *Phys. Rev. B* 53 (1996) 4926.
- [38] G.R. Darling and S. Holloway, *Surf. Sci.* 304 (1994) L461.
- [39] A. Gross, *J. Chem. Phys.* 102 (1995) 5045.
- [40] W. Brenig, A. Gross and R. Russ, *Z. Phys. B* 97 (1995) 311.
- [41] A. Gross, S. Wilke and M. Scheffler, *Phys. Rev. Lett.* 75 (1995) 2718.
- [42] P. Nachtigall and K.D. Jordan, *J. Chem. Phys.* 102 (1995) 8249.
- [43] A. Gross, B. Hammer, M. Scheffler and W. Brenig, *Phys. Rev. Lett.* 73 (1994) 3121.
- [44] C.T. Rettner, H.A. Michelsen and D.J. Auerbach, *J. Chem. Phys.* 102 (1995) 4625.
- [45] B.E. Hayden and C.L.A. Lamont, *Phys. Rev. Lett.* 63 (1989) 1823.
- [46] G. Anger, A. Winkler and K.D. Rendulic, *Surf. Sci.* 220 (1989) 1.
- [47] G. Wiesenekker, G.J. Kroes, E.J. Baerends and R.C. Mowrey, *J. Chem. Phys.* 102 (1995) 3873.
- [48] B. Hammer, private communication.
- [49] A. Grüneich, A.J. Cruz and B. Jackson, *J. Chem. Phys.* 98 (1993) 5800.
- [50] W. Brenig, T. Brunner, A. Gross and R. Russ, *Z. Phys. B* 93 (1993) 91.
- [51] Y. Chiba and W. Brenig, *Surf. Sci.* 306 (1994) 406.
- [52] W. Brenig and R. Russ, *Surf. Sci.* 315 (1994) 195.
- [53] H.A. Michelsen, C.T. Rettner, D.J. Auerbach and R.N. Zare, *J. Chem. Phys.* 98 (1993) 8294.
- [54] Ch. Resch, H.F. Berger, K.D. Rendulic and E. Bertel, *Surf. Sci.* 316 (1994) L1105.
- [55] H.F. Berger, Ch. Resch, E. Grösslinger, G. Eilmsteiner, A. Winkler and K.D. Rendulic, *Surf. Sci.* 275 (1992) L627.
- [56] D.A. Butler, B.E. Hayden and J.D. Jones, *Chem. Phys. Lett.* 217 (1994) 423.
- [57] P. Alnot, A. Cassuto and D.A. King, *Surf. Sci.* 215 (1989) 29.
- [58] D.A. Butler and B.E. Hayden, *Chem. Phys. Lett.* 232 (1995) 542.
- [59] St.J. Dixon-Warren, A.T. Pasteur and D.A. King, *Surf. Rev. and Lett.* 1 (1994) 593.
- [60] T. Hertel, M. Wolf and G. Ertl, *J. Chem. Phys.* 102 (1995) 3414.
- [61] W. van Willigen, *Phys. Letters* 28a (1968) 80.
- [62] L. Schröter, R. David and H. Zacharias, *Surf. Sci.* 258 (1991) 259; *J. Vac. Sci. Technol. A* 9 (1991) 1712.