

# Six-Dimensional Quantum Dynamics of Adsorption and Desorption of H<sub>2</sub> at Pd(100): Steering and Steric Effects

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We report the first six-dimensional quantum dynamical calculations of dissociative adsorption and associative desorption. Using a potential energy surface obtained by density functional theory calculations, we show that the initial decrease of the sticking probability with increasing kinetic energy in the system H<sub>2</sub>/Pd(100), which is usually attributed to the existence of a molecular adsorption state, is due to dynamical steering. In addition, we examine the influence of rotational motion and orientation of the hydrogen molecule on adsorption and desorption.

The dissociative adsorption and associative desorption of hydrogen on transition metals is of direct technological relevance as well as of general interest for the very fundamental understanding of elemental chemical processes occurring in catalysis and surface chemistry. Molecular beam experiments of the dissociative adsorption of H<sub>2</sub> on various transition metal surfaces like Pd(100) [1], Pd(111) and Pd(110) [2], W(111) [3], W(100) [3,4,5], and Pt(100) [6] revealed that the sticking probability initially decreases with increasing kinetic energy of the beam. Such a behavior is usually explained by a *precursor mechanism* [7]. In this concept the molecules are temporarily trapped in a molecular physisorption state, the so-called *precursor state*, before they dissociatively adsorb. The trapping occurs because the molecules lose energy when impinging on the surface, mainly to the substrate phonons [7]. The energy dependence of the sticking probability is thus related to the trapping probability into the precursor state, and it is this trapping probability which decreases with increasing energy. In all experiments mentioned above the sticking probability rises again at higher energies which is interpreted as such that adsorption via direct activated paths then becomes dominant.

The relevance of the precursor mechanism for the dissociative adsorption has been discussed for a long time, and the discussion remains quite lively [8,9]. One may argue that especially for hydrogen adsorption on metal surfaces the energy transfer to the phonon system should be relatively small due to the large mismatch in the masses of adsorbate and substrate making the precursor mechanism ineffective. Therefore also direct non-activated adsorption together with a dynamical steering effect has been suggested in order to explain the initial decrease of the sticking probability (see, e.g., [5,6]), however, there

had been no theoretical analysis of the importance of this effect. Recent density functional theory calculations [10] of the potential energy surface (PES) of H<sub>2</sub>/Pd(100) show that there exist non-activated as well as activated paths to dissociative adsorption in this system, but they do not yield any *molecular* adsorption well. These results motivated dynamical calculations using a model PES with activated as well as non-activated path to dissociative adsorption [11], in which three degrees of freedom of the hydrogen molecule were taken into account. This investigation suggested that the steering mechanism could be operative in the system H<sub>2</sub>/Pd(100), but the results showed large quantitative discrepancies to the experiment [11].

In order to clarify the nature of the dissociation process, we parametrized the *ab initio* PES of H<sub>2</sub>/Pd(100) thereby obtaining a well-defined function describing the potential energy surface on which the hydrogen molecule moves. This function depends on six coordinates, and together with the kinetic energy operator it defines the Hamiltonian for the nuclear motion. The Hamiltonian is then used for a quantum dynamical study where for the first time *all* six degrees of the hydrogen molecule have been treated fully quantum mechanically in a simulation of dissociative adsorption and associative desorption. The specific coordinates considered in our study are the three coordinates of the center of mass of the molecule  $X$ ,  $Y$ , and  $Z$  ( $Z$  is the distance from the surface), the azimuthal orientation  $\phi$  and the polar orientation  $\theta$ , and the H-H distance  $d$ . The potential in the  $Zd$  plane is described in reaction path coordinates  $s$  along the reaction path and  $r$  perpendicular to it [12]. The potential is then given in the following form

$$V(X, Y, s, r, \theta, \phi) = V^{corr} + V^{rot} + V^{vib} \quad (1)$$

with

$$V^{corr} = \sum_{m,n=0}^2 V_{m,n}^{(1)}(s) \cos mGX \cos nGY, \quad (2)$$

$$V^{rot} = \sum_{m=0}^1 V_m^{(2)}(s) \frac{1}{2} \cos^2 \theta (\cos mGX + \cos mGY) \\ + \sum_{n=1}^2 V_n^{(3)}(s) \frac{1}{2} \sin^2 \theta \cos 2\phi (\cos nGX - \cos nGY) \quad (3)$$

and

$$V^{vib} = \frac{\mu}{2} \omega^2(s) [r - \Delta r(X, Y, s)]^2. \quad (4)$$

$G = 2\pi/a$  is the basis vector of the reciprocal lattice,  $a$  is the lattice constant,  $\mu$  is the reduced mass of the hydrogen molecule, and  $\omega(s)$  is the frequency perpendicular to the reaction path. The functions  $V_{m,n}^{(i)}(s)$ ,  $\omega(s)$ , and  $\Delta r(X, Y, s)$  are determined such that the difference between  $V(X, Y, s, r, \theta, \phi)$  and the *ab initio* total energies, which have been calculated for more than 250 configurations, on the average is smaller than 25 meV.

Although the PES does not have a precursor molecular adsorption state, the results of the six-dimensional quantum dynamical calculations concerning the dependence of the sticking probability on the kinetic energy in the system  $H_2/Pd(100)$  agree very well with the measured results. This will be explained by a purely dynamically steering effect. In addition we will show that rotations in general suppress sticking, but that steric effects, i. e., effects due to the orientation of the molecules, can lead to a strong enhancement of the sticking probability.

The quantum dynamics is determined by solving the time-independent Schrödinger equation for the two hydrogen nuclei moving on the six-dimensional PES. We use the concept of the *local reflection matrix* (LORE) [13] and the *inverse local transmission matrix* (INTRA) [14]. This very stable coupled-channel method has been employed before in a high-dimensional study of the adsorption of  $H_2/Cu(111)$ , where, however, the polar orientation of the molecule has not been varied [15]. In the present calculation up to 21,000 channels per total energy are taken into account; with channels the eigenfunctions of the asymptotic Hamiltonian are meant. The PES is obtained using density functional theory within the generalized gradient approximation (GGA) [16] and the full-potential linear augmented plane wave method (FP-LAPW) (see Ref. [10] and references therein).

Figure 1 presents our results for the sticking probability as a function of the kinetic energy of the incident  $H_2$  beam. The dashed curve corresponds to  $H_2$  molecules initially in the rotational ground state  $j_i = 0$ . This curve exhibits a strong oscillatory structure for low energies in contrast to the experimental results. Such oscillatory structures have already been found in three-dimensional model calculations using potential energy surfaces with activated as well as non-activated paths to adsorption [11,17]. For a PES without a molecular adsorption well the oscillations are related to quantum effects of the hydrogen beam, namely the opening up of new scattering channels for increasing incident energy [11].

In molecular beam experiments the incident molecules are not all in the rotational ground state, the rotational states are occupied according to a Boltzmann distribution with a temperature of 0.8 of the nozzle temperature [1]. In addition, the beam is not strictly monoenergetic, but has a certain energy spread. Both effects, the rotational distribution and the energy spread,

are incorporated in the solid curve where we have assumed a typical energy spread of molecular beams of  $\Delta E/E_i = 2\Delta v/v_i = 0.2$  [1] ( $E_i$  and  $v_i$  are the initial kinetic energy and velocity, respectively). This curve should be compared with the experimental results of Rendulic *et al.* [1]. In view of the fact that *no* parameters are used in our calculations, the agreement between theory and experiment is quite satisfactory. The initial decrease of the sticking probability is well reproduced although no precursor state exists in our PES. Hence a purely dynamical mechanism has to be the origin of this energy dependence.

The mechanism, a dynamical steering effect, is disclosed by the fact that more channels in the dynamical simulation are needed at low energies than at high energies. Usually it is the other way around in coupled-channel calculations since the higher the energy, the more channels become energetically accessible. Thus the calculations reflect that there is a strong rearrangement between the different channels at low energies due to the steering. At high energies the dynamics is closer to the adiabatic limit which means that during the dissociation event there is little redistribution among the channels.

An illustration of the steering effect is given in fig. 2. There a two-dimensional cut through the six-dimensional PES is shown together with two typical trajectories of impinging  $H_2$  molecules. Besides a difference in velocity, both trajectories have equivalent impact parameters. In the case of the left trajectory the incident molecule is so slow that the forces acting on the molecule can steer it towards a configuration where non-activated dissociative adsorption is possible, while in the case of the right trajectory the molecule is too fast for the forces to divert the molecule significantly, it hits the repulsive part of the potential and is reflected back into the gas phase. If the incident energy of the molecule is further increased, from a certain energy on it will have enough energy to directly traverse the barrier. This leads to the increase of the sticking probability at higher energies (see fig. 1).

Of course in a complete description of the adsorption process also energy losses of the impinging molecules to the substrate phonons have to be considered, in spite of the large mass mismatch which makes the energy transfer rather small. Energy losses of the molecules would slow down the molecule and thus make the steering even more effective. Furthermore, the inclusion of the substrate motion would broaden the velocity spread of the incident molecules relative to the substrate atoms [18].

Figure 1 also demonstrates 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. This effect is shown in more detail in fig. 3, which displays the sticking probability versus initial rotational quantum state for a fixed incident kinetic energy of  $E_i = 0.19$  eV. The diamonds correspond to the orien-

tationally averaged sticking probability

$$\bar{S}_{j_i}(E) = \frac{1}{2j_i + 1} \sum_{m_i=-j_i}^{j_i} S_{j_i, m_i}(E), \quad (5)$$

which decreases with increasing  $j_i$ . This means that the faster the molecules are rotating, the more the dissociative adsorption is suppressed, and is caused by *orientational hindering* [19]: molecules with a high angular momentum will rotate out of a favorable orientation towards adsorption during the dissociation event.

From fig. 3 and the principle of microscopic reversibility, 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) [20]. Figure 4 shows a comparison between theory and experiment of the rotational temperatures  $T_{rot}$  of desorbing molecules. These temperatures are determined by fitting the rotational state population in a Boltzmann plot to a straight line. The slope then gives  $(-k_B T_{rot})$ . In order to compare the calculations with the experimental data which were limited to low  $j$  states, for the theoretical analysis only the lowest four rotational states have been considered. There is again a rather good agreement between theory and experiment.

The results of figs. 1 and 4 have been determined by summing over all azimuthal quantum numbers  $m$ . From the PES we know, however, that the most favorable configuration towards dissociative adsorption is met when the molecular axis is parallel to the surface. Rotational eigenstates with azimuthal quantum number  $m = j$  have their rotational axis preferentially perpendicular to the surface, so that the molecular axis is oriented mainly parallel to the surface. Molecules rotating in this so-called helicopter fashion should dissociate more easily than molecules rotating in the cartwheel fashion with the rotational axis preferentially parallel to the surface ( $m = 0$ ) since the latter have a high probability hitting the surface in an upright orientation in which they cannot dissociate. This steric effect has been investigated in a number of model studies for activated adsorption employing three and four-dimensional quantum dynamics [19,21,22,23] or mixed classical-quantum dynamics [24].

In fig. 3 also the sticking probability for initial rotational quantum state for  $m_i = 0$  and  $m_i = j_i$  has been plotted. The results show that the steric effect is operative in systems with activated as well as non-activated paths towards dissociative adsorption. Indeed the difference in the sticking probability between initial  $m_i = 0$  and  $m_i = j_i$  rotations increases with increasing quantum number  $j_i$ . This reflects the fact that the larger the rotational quantum number  $j$  is, the larger is the difference in the orientation between  $m = 0$  and  $m = j$  states. The  $m_i = j_i$  data demonstrate that the steric effect even

over-compensates the suppression of the sticking probability by rotational motion since the  $m_i = j_i$  sticking probability increases with increasing  $j_i$ .

In conclusion, we reported the first six-dimensional quantum dynamical study of dissociative adsorption on and associative desorption from surfaces. We employed a potential energy surface obtained by detailed density functional theory calculations for the system  $H_2/Pd(100)$ . The results show an initial decrease of the sticking probability with increasing energy which, in contrast to common believe, is here not due to a molecular adsorption state, but can be explained by a dynamical steering effect. Rotational motion in general suppresses sticking, however, a strong enhancement in the sticking probability for molecules with their axis parallel to the surface is found. The results clearly demonstrate that a high-dimensional dynamical analysis of the PES is indeed important and provides, due to the microscopic information, *quantitative* as well as new *qualitative* understanding of processes at surfaces.

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FIG. 1. Sticking probability versus kinetic energy for a H<sub>2</sub> beam under normal incidence on a Pd(100) surface. Dashed line: H<sub>2</sub> molecules initially in the rotational ground state; Solid line: H<sub>2</sub> molecules with an initial rotational and energy distribution adequate for molecular beam experiments (see text); circles: experiment (from ref. [1]).

FIG. 2. 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. The molecular axis is 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 H<sub>2</sub> center of mass distance from the surface, for  $s \leq -2.5 \text{ \AA}$  to the distance between two adsorbed H atoms. The left trajectory corresponds to a slow molecule (kinetic energy  $E_{kin} = 0.05 \text{ eV}$ ), the right trajectory to a fast molecule ( $E_{kin} = 0.15 \text{ eV}$ ).

FIG. 3. Sticking probability versus initial rotational quantum state  $j_i$ . Diamonds: orientationally averaged sticking probability (eq. 5), triangles:  $m_i = 0$  (cartwheel rotation), circles:  $m_i = j_i$  (helicopter rotation). The initial kinetic energy is  $E_i = 0.19 \text{ eV}$ .

FIG. 4. Rotational temperatures of desorbing H<sub>2</sub> molecules. Circles: experiment (from ref. [20]), diamonds: theory. The solid line corresponds to molecules in equilibrium with the surface temperature.







