

# Poisoning of Hydrogen Dissociation at Pd (100) by Adsorbed Sulfur Studied by *ab initio* Quantum Dynamics and *ab initio* Molecular Dynamics

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We report calculations of the dissociative adsorption of H<sub>2</sub> at Pd (100) covered with 1/4 monolayer of sulfur using quantum dynamics as well as molecular dynamics and taking all six degrees of freedom of the two H atoms fully into account. The *ab initio* potential-energy surface (PES) is found to be very strongly corrugated. In particular we discuss the influence of tunneling, zero-point vibrations, localization of the nuclei's wave function when narrow valleys of the PES are passed, steering of the approaching H<sub>2</sub> molecules towards low energy barrier configurations, and the time scales of the center of mass motion and the other degrees of freedom. Several "established" concepts, which were derived from low-dimensional dynamical studies, are shown to be not valid.

68.35.Ja, 82.20.Kh, 82.65.Pa

The presence of an adsorbate on a surface can profoundly change the surface reactivity. An understanding of the underlying mechanisms is of relevance for, e.g., corrosion, lubrication, and catalysis. Typically the breaking of molecular bonds is the rate-limiting step in a surface chemical reaction, and the model system is the dissociation and adsorption of hydrogen. Whereas on clean Pd (100) the dissociation of H<sub>2</sub> happens very efficiently, it is well known that a small amount of adsorbed sulfur reduces (poisons) the surface reactivity significantly [1,2]. Density functional theory (DFT) calculations have shown that hydrogen dissociation on sulfur-covered Pd(100) is still exothermic, however, the dissociation is hindered by the formation of energy barriers in the entrance channel of the potential-energy surface (PES) [3].

We have recently extended this study and determined the six-dimensional PES of the system H<sub>2</sub>/S(2×2)/Pd(100) in great detail [4] using DFT together with the generalized gradient approximation (GGA) [5]. On an analytical representation of this *ab initio* PES we have now performed six-dimensional quantum and classical dynamics calculations in which all hydrogen degrees of freedom are treated dynamically. The methods are described in detail in Ref. [6]. The study is based essentially on the following approximations: (*i*) Born-Oppenheimer approximation, (*ii*) the substrate is kept rigid (*iii*) the exchange-correlation functional is treated in the GGA, (*iv*) the DFT-GGA calculations are performed in the supercell approach, (*v*) the *ab initio* PES is fitted to an analytical form,

Items *i*) and *ii*) mean that energy dissipation is not

treated *explicitly*. This is appropriate because, while energy dissipation plays a crucial role by taking away the *adsorption* energy, for the *dissociation* of H<sub>2</sub> energy dissipation into substrate or electronic degrees of freedom is not significant. The reason lies in the involved time scales and the mass differences between hydrogen and S and Pd substrate atoms.

The GGA treatment of the exchange-correlation functional [item *iii*)] is the best treatment known to date. It leaves an uncertainty to total-energy differences typically below 0.1 eV (see, e.g., Ref. [7]). The error due to approximation *iv*) was checked to be smaller than 0.1 eV [3,4]. The fit of the PES [item *v*)] by an analytic function has been performed in such a way that the relative error between the fit and the original data,  $|\Delta E|/|E|$ , is smaller than 5 %. For further details of the DFT calculations and the analytical representation of the PES see Ref. [4]. We note that the PES of this system is very corrugated, which represents a significant challenge for a proper treatment of the quantum dynamics. Even earlier empirical studies had not considered such corrugations (energy barriers between 0.09 eV for the optimum pathway and 2.5 eV for an approach over the S adatom [4]). Nevertheless, we ensured that the error due to the finite number of channels considered in the quantum dynamical calculations is below 2 % of the sticking probability.

The corrugation of the PES has several unexpected consequences. For example, it leads to zero-point vibrations (ZPV) in the quantum dynamics which reduce the quantum sticking probabilities compared to the classical results. Since, however, the ZPV energies in the single frustrated modes are rather small, the quantum particles do not realize completely the ZPV in these slow modes. Furthermore we find that steering of molecules to low-barrier configurations is effective at unusually high kinetic energies. And in spite of the fact that the PES exhibits a early minimum barrier for dissociation, initial vibrational excitation of impinging molecules enhances the dissociation probability. These results confirm that results derived from statical analyses of the PES, as e.g. the barrier distribution, are not sufficient to obtain reaction probabilities, but a proper *high-dimensional dynamical* treatment of the dissociation process is essential.

Figure 1 shows two cuts through the six-dimensional PES with the optimum pathway displayed in Fig. 1a. The minimum energy barrier to dissociation ( $E_b = 0.09$  eV) lies at a configuration where the bond-length of the molecule is nearly unchanged compared to the gas

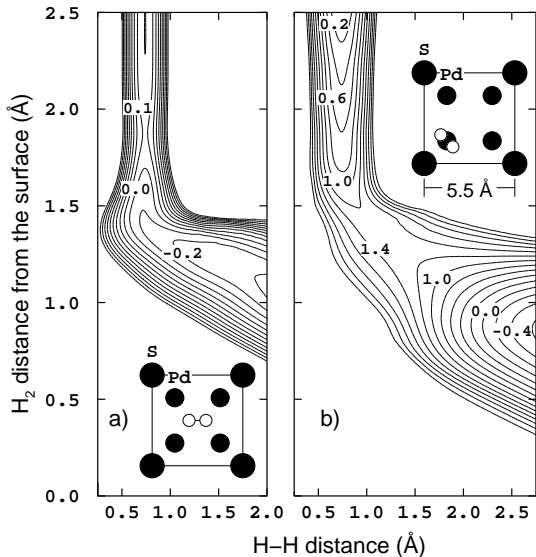


FIG. 1. Lines of constant energy for two cuts through the six-dimensional PES of  $H_2$  at  $S(2\times 2)/Pd(100)$ . The insets show the orientation of the molecular axis and the lateral  $H_2$  center-of-mass coordinates, i.e. the coordinates  $X$ ,  $Y$ ,  $\theta$ , and  $\phi$ . The coordinates in the figure are the  $H_2$  center-of-mass distance from the surface  $Z$  and the H-H interatomic distance  $r$ . Energies are in eV per  $H_2$  molecule. The contour spacing in Fig. 1a is 0.1 eV, while in Fig. 1b it is 0.2 eV. Fig. 1a corresponds to the minimum energy pathway.

phase value [3,4]. In such a situation it is usually anticipated that the vibrational and translational degrees of freedom are almost uncoupled so that vibrational energy of the impinging molecules cannot be used to overcome the barrier (see, e.g., Ref. [8,9]). Consequently, it has been predicted [3] that the sticking probability of  $H_2$  at  $S(2\times 2)/Pd(100)$  should show no strong dependence on the initial vibrational state of the molecule. This prediction corresponds to the so-called Polanyi rules which have been formulated for gas-phase dynamics thirty years ago [10]. We will show that these rules have to be modified for strongly corrugated PESs.

The large repulsion for hydrogen dissociation closer to the sulfur atoms is illustrated in Fig. 1b. While the dissociation path over the on-top position on the clean surface is hindered by a barrier of height 0.15 eV [11], the adsorbed sulfur leads to an increase in this barrier height to 1.3 eV.

Figure 2 compares our results for the sticking probability as a function of the kinetic energy of the incident  $H_2$  beam with the experiment [1]. In addition, also the integrated barrier distribution  $P_b(E)$  is plotted, which is the fraction of the configuration space for which the barrier towards dissociation is less than  $E$  and which is also called the “hole model” [12].

The calculated sticking probabilities are significantly larger than the experimental results. The agreement between the adsorption experiment and our calculations is limited to the single aspect that adsorbed sulfur is a strong poison for the  $H_2$  dissociation, and the onset

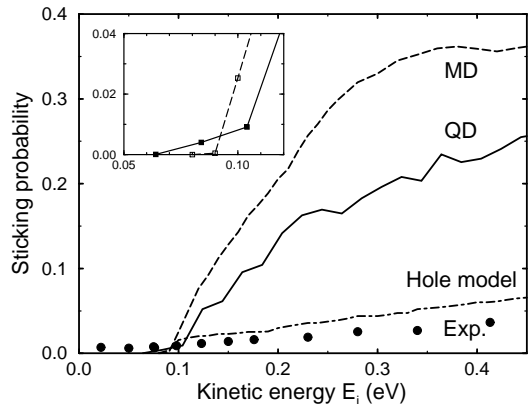


FIG. 2. Sticking probability versus kinetic energy for a  $H_2$  beam under normal incidence on a  $S(2\times 2)/Pd(100)$  surface. Full dots: experiment (from ref. [1]); dashed-dotted line: integrated barrier distribution, which corresponds to the sticking probability in the hole model [12]; solid line: quantum mechanical results for molecules initially in the rotational and vibrational ground-state (QD); dashed line: classical molecular dynamics results for initially non-rotating and non-vibrating molecules (MD). The inset shows the quantum and classical results at low energies.

energy for dissociative adsorption, calculated as  $E_i \approx 0.12$  eV, is in fact in excellent agreement with the experimentally measured mean kinetic energy of hydrogen molecules desorbing from sulfur covered  $Pd(100)$  [13]. Otherwise, in the energy range  $E_i > 0.12$  eV, the calculated sticking probabilities are significantly larger than the experimental results. We consider this a most important result, because progress in science is typically achieved by disagreement between theoretical and experimental results rather than by agreement. What are the likely reasons for the accounted disagreement?

*i)* From the approximations assumed in the calculations (see above) it is mainly the GGA which bears the uncertainty to be good enough for a reliable description of the *topology* of the PES. It should be noted that  $S(E_i)$  probes the details of the energy corrugation of the PES and not just the lowest energy barrier. We note, however, that our results are not very sensitive to an uncertainty of the PES of  $< 0.2$  eV, which we tested by adding some artificial functions to our *ab initio* PES, and that there is no indication in the literature (so far) that the GGA would not be able to deal with such a required, modest accuracy.

*ii)* The other approximations have been carefully tested and we do not believe that they are relevant.

*iii)* Concerning the experimental results we note that the determination of the coverage is not without problems. In fact, it is well possible that the adsorbate coverage in the measurements was higher than reported. The sulfur adlayer was obtained by simply heating the sample which leads to the segregation of bulk sulfur at the surface. The coverage of  $\Theta_S = 0.25$  was then identified

mode	ZPV (eV)
H-H vibration	0.253
polar rotation	0.016
azimuthal rotation	0.013
translation perpendicular to molecular axis	0.027
translation parallel to molecular axis	0.027
sum	0.336

TABLE I. Zero-point vibrations (ZPV) energies of the  $\text{H}_2$  molecule at the minimum barrier position. The  $\text{H}_2$  configuration corresponds to the situation of Fig. 1a. The gas-phase ZPV energy of  $\text{H}_2$  is  $\frac{1}{2}\hbar\omega_{\text{gas}} = 0.258$  eV.

by monitoring the  $\text{S}_{132}$  and  $\text{Pd}_{330}$  Auger signals with respect to those at saturation coverage which is believed to be  $\Theta_{\text{S}} = 0.5$ , and by the presence of a  $(2 \times 2)$  LEED pattern. We speculate that the actual coverage at which the data of Fig. 2 were taken could well have been higher, e.g. due to some significant amount of subsurface sulfur. Subsurface adsorbates can affect the surface reactivity significantly. We hope that more experiments of the type done by Rendulic *et al.* [1] will be performed and that also other techniques for producing the S adlayer will be considered, in order to determine in what form S is actually present at the surface under different experimental conditions.

We now turn back to the theoretical results. The classical treatment of hydrogen dynamics over-estimate the sticking probability of  $\text{H}_2$  at  $\text{S}(2 \times 2)/\text{Pd}(100)$  compared to the quantum results. For energies smaller than the minimum barrier height  $E_{\text{b}}$  the classical sticking probability is of course zero, whereas the quantum results still show some dissociation due to tunneling, as the inset of Fig. 2 reveals. But for energies larger than  $E_{\text{b}}$  the classical sticking probability rises to values which are almost 50% larger than the quantum sticking probabilities. We have recently shown that ZPV can lead to a suppression of the quantum sticking probability compared to classical results [6,14]. In Tab. I we have therefore collected the ZPV energies of the hydrogen molecule at the minimum barrier position. Since here the hydrogen molecular bond is still almost intact, the zero-point energy in the H-H vibration has only decreased by 5 meV from the gas-phase ZPV energy of  $\text{H}_2$ . However, along the minimum energy path the molecule has to pass through a narrow valley of the PES in the lateral coordinates parallel to the surface due to the strong corrugation of the PES. This causes substantial ZPV energies in the frustrated lateral modes of the molecular center-of-mass of motion already relatively far away from the surface. Note that the ZPV energies in the frustrated rotational modes are fairly small in comparison. This is again due to the fact that the molecular bond is essentially not elongated at the minimum barrier position so that the molecular interaction with the surface is still rather isotropic.

Because the sum of all ZPV energies at the minimum

barrier position is 0.08 eV larger than the gas-phase ZPV energy of hydrogen, the effective minimum barrier height for the quantum particles should be increased by 0.08 eV to  $E_{\text{b}}^{\text{eff}} = 0.17$  eV. And indeed the quantum sticking probabilities are smaller than the classical sticking probabilities for energies larger than the classical minimum barrier height. The absence of ZPV in the classical dynamics leads to the enhanced sticking probability in the classical calculations [14]. However, the quantum sticking probability rises significantly already for energies well below the *effective* barrier height of 0.17 eV. This can be understood by considering the involved time-scales. A vibration with  $\hbar\omega = 50$  meV, e.g., corresponds to a vibrational period of 80 fs. The time it takes for an  $\text{H}_2$  molecule with  $E_{\text{i}} = 0.12$  eV to pass the barrier (width 0.5 Å) is only 25 fs. This means that during the crossing of the minimum barrier region the hydrogen molecule would hardly perform one complete vibration in any of the four frustrated modes given in Tab. I. The concept that in the absence of tunneling a quantum particle needs at least the barrier energy plus the ZPV energies in order to cross a barrier is evidently not applicable for such slow modes. The quantum particles do not completely follow the zero-point motion perpendicular to the reaction path and thus do not additionally need the total ZPV energies in order to cross the barrier.

The question arises why the difference between classical and quantum sticking probabilities even increases with increasing energy although ZPVs should become less important at higher kinetic energies. An analysis of the ZPV shows that the sum of the four ZPV energies of the frustrated lateral and rotational modes actually rises to values of 0.2 eV along the reaction pathways. Although the H-H vibrational energy further decreases, the sum of *all* five ZPV energies becomes even larger than the value of 0.336 eV at the minimum barrier position. This sum plays a crucial role in the quantum dynamics not only at the minimum barrier position, but also later along the dissociation pathways. Since at different kinetic energies different parts of the barrier region with varying ZPV energies are sampled, classical and quantum results are not just shifted by a fixed amount, and the ZPV need to be included in the full dynamical treatment.

A comparison of the dynamical results with the integrated barrier distribution in Fig. 2 shows that the sticking probabilities are much larger than what one would expect from the hole model [12]. Our analysis of swarms of trajectories with different initial conditions shows that molecules directed towards high barriers are very efficiently steered to configurations and sites with lower barriers [15,16]. Indeed the strongly repulsive potential above the sulfur atoms extends rather far into the gas-phase [4]. Thus the forces re-orienting and re-directing the molecules act on the molecules for a long time; therefore they are so effective up to kinetic energies of more than 0.5 eV. At the clean Pd surface, on the contrary,

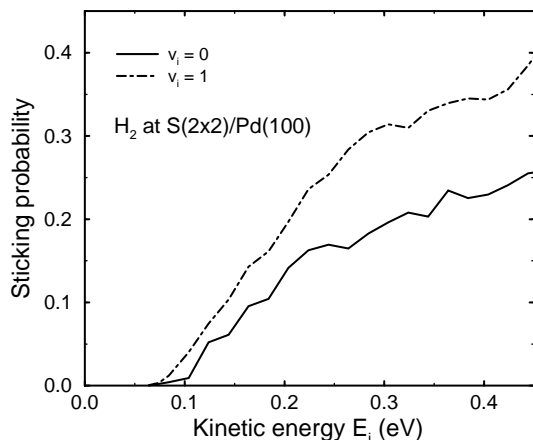


FIG. 3. Dependence of the quantum sticking probability versus kinetic energy for a hydrogen beam under normal incidence at a  $S(2\times 2)/Pd(100)$  surface on the initial vibrational state  $v$ . Solid line:  $v_i = 0$ , dash-dotted line:  $v_i = 1$ . The molecules are initially in the rotational ground state.

at  $E_i \approx 0.2$  eV steering is no longer operative in the dissociation process [15]. This causes the surprising result that at  $E_i = 0.2$  eV the sticking probability at the  $(2\times 2)$  sulfur-covered Pd(100) surface is almost as large as at the clean Pd(100) surface in spite of the fact that at the clean surface the fraction of open dissociation pathways is more than five times larger at this energy [17].

The effect of initial vibrational motion on the dissociation process is illustrated in Fig. 3 where state-specific sticking probabilities as a function of the incident kinetic energy are plotted. As noted above, since the PES has an early minimum barrier for dissociation, no coupling of the initial vibration to the dissociation is expected. However, as Fig. 3 demonstrates, initial vibrational excitation leads to a significant increase in the sticking probability. This shows that the dissociation process cannot be understood by simply analyzing the minimum energy path. As Fig. 1b reveals, there are molecular configurations for which the bond is significantly extended at the barrier position. At higher kinetic energies the adsorbing molecules also probe such pathways along which the vibrational energy can be efficiently used to overcome the dissociation barrier. The unexpected result of the vibrationally enhanced dissociation in spite of an early minimum barrier to dissociation is actually in agreement with the experimentally observed vibrational over-population in thermal hydrogen desorption from sulfur covered Pd(100) [18] invoking the principle of microscopic reversibility. We have also studied the dependence of the sticking probability on the initial rotational quantum number. The rotational effects are similar to the ones found at the clean surface and will be discussed in a forthcoming publication.

In conclusion, we reported a six-dimensional dynamical study of the dissociative adsorption of  $H_2$  at  $S(2\times 2)/Pd(100)$  employing a PES obtained from detailed density functional theory calculations. The dynamical results reproduce the poisoning effect of sulfur adsorption

for hydrogen dissociation on Pd(100), but large quantitative differences to the experiment exist. The huge corrugation and anisotropy of the PES lead to ZPV in the quantum dynamics which reduce the quantum results compared to the classical ones. However, at the minimum barrier the additional ZPV correspond to very slow modes so that the quantum particles do not completely follow these modes. In addition, the huge corrugation and anisotropy cause large steering effects at unusual high kinetic energies. The multi-dimensionality of the PES furthermore leads to an enhancement of the sticking probability for vibrating molecules although the PES exhibits an early barrier for dissociative adsorption.

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