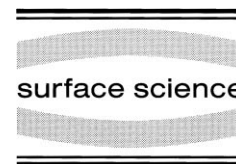




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Surface Science 416 (1998) L1095–L1100



Surface Science Letters

Poisoning of hydrogen dissociation at Pd (100) by adsorbed sulfur studied by ab-initio quantum dynamics and ab-initio molecular dynamics

A. Gross *, C.-M. Wei ¹, M. Scheffler

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

Received 13 May 1998; accepted for publication 3 August 1998

Abstract

We report calculations of the dissociative adsorption of H₂ 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 due to the localization of the wave function of the nuclei when narrow valleys of the PES are passed, steering of the approaching H₂ molecules towards low-energy barrier configurations, and the important role of subsurface adsorbates for the hydrogen dissociation. It is shown that “established” concepts derived from low-dimensional dynamical studies are not necessarily valid in a high-dimensional treatment. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Chemisorption; Density functional calculations; Hydrogen; Models of surface chemical reactions; Molecular dynamics; Molecule–solid reactions; Palladium; Quantum effects; Sulfur

The presence of an adsorbate on a surface can profoundly change the surface reactivity. An understanding of the underlying mechanisms is of relevance, for example, for 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), H₂ dissociates 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 [3], but the dissociation is hindered by the formation of energy barriers in the entrance channel of the potential-energy surface (PES) [4].

We have recently extended this study and determined the six-dimensional PES of the system H₂/S(2 × 2)/Pd(100) in great detail [5] using DFT together with the generalized gradient approximation (GGA) [6]. 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 free-

* Corresponding author. Present address: Physik Department T30, Technical University Munich, D-85747 Garching, Germany. Fax: +49 89 289 14655; e-mail: agross@physik.tu-muenchen.de

¹ Permanent address: Institute of Physics, Academia Sinica, Taipei, Taiwan 11529.

dom are treated dynamically. The methods are described in detail in Ref. [7]. The study is based essentially on the following approximations:

- (1) Born–Oppenheimer approximation,
- (2) the substrate is kept rigid,
- (3) the exchange–correlation functional is treated in the GGA,
- (4) the DFT–GGA calculations are performed in the supercell approach, and
- (5) the ab-initio PES is fitted to an analytical form.

Items 1 and 2 mean that energy dissipation is not treated explicitly. This is appropriate because, whereas energy dissipation plays a crucial role by taking away the adsorption energy, for the dissociation of H_2 , energy dissipation into substrate vibrations or electronic degrees of freedom is not significant. The reason lies in the time scales involved and the mass differences between hydrogen and S and Pd substrate atoms.

The GGA treatment of the exchange–correlation functional is the best treatment known to date. It leaves an uncertainty about total-energy differences typically below 0.1 eV (see, for example, Ref. [8]). The error due to approximation 4 was found to be smaller than 0.1 eV [4,5]. The fit of the PES 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 less than 5%. For further details of the DFT calculations and the analytical representation of the PES, see Ref. [5]. 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 [5]). 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 large corrugation of the PES has several unexpected consequences. For example, it leads to zero-point vibrations (ZPV) in the quantum dynamics that reduce the quantum sticking probabilities compared to the classical results. Furthermore, steering of molecules to low-barrier configurations is extremely effective at unusually

high kinetic energies. Also, in spite of the fact that the PES exhibits an early minimum energy barrier for dissociation, initial vibrational excitation of impinging molecules enhances the dissociation probability. Still large quantitative differences to the experiment remain, which we attribute to the presence of subsurface sulfur in the experimental samples. Our calculations confirm that results derived from a static analysis of the PES, such as the barrier distribution, are not sufficient to obtain reaction probabilities; instead, a proper high-dimensional dynamical treatment of the dissociation process is essential.

Fig. 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 almost unchanged compared to the gas-phase value [4,5]. In such a situation, it is usually anticipated that the vibrational and translational degrees of free-

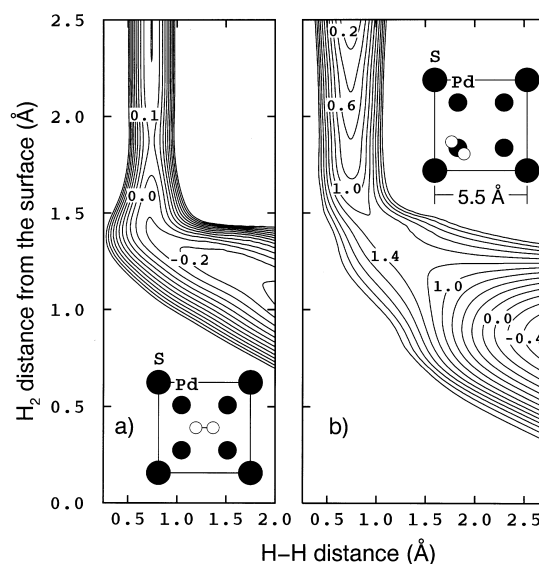


Fig. 1. Lines of constant energy for two cuts through the six-dimensional PES of H_2 at $S(2 \times 2)/Pd(100)$. The insets show the orientation of the molecular axis and the lateral H_2 center-of-mass coordinates, i.e. the coordinates X , Y , θ , and ϕ . The coordinates in the figure are the H_2 center-of-mass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

dom are almost uncoupled so that vibrational energy of the impinging molecules cannot be used to overcome the barrier (see, for example, Refs. [9,10]). Consequently, it has been predicted [4] 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 that have been formulated for gas-phase dynamics 30 years ago [11]. 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. Whereas the dissociation path over the on-top position on the clean surface is hindered by a barrier of height 0.15 eV [12], the adsorbed sulfur leads to an increase in this barrier height to 1.3 eV. Burke and Madix have measured the hydrogen saturation coverage as a function of sulfur coverage [2]. They found that at a sulfur coverage of $\theta_s = 0.28$, i.e. close to the sulfur coverage of 0.25 used in our study, no hydrogen should adsorb dissociatively on the Pd surface. This infers total site-blocking. In contrast, as shown in Fig. 1, the DFT-GGA calculations reveal that hydrogen dissociation is still exothermic, i.e. there is no site-blocking, and dissociation is just hindered by barriers. A possible reason for this apparent contradiction will be given below.

Fig. 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, 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” [13].

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 H_2 dissociation, and the onset 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) [14].

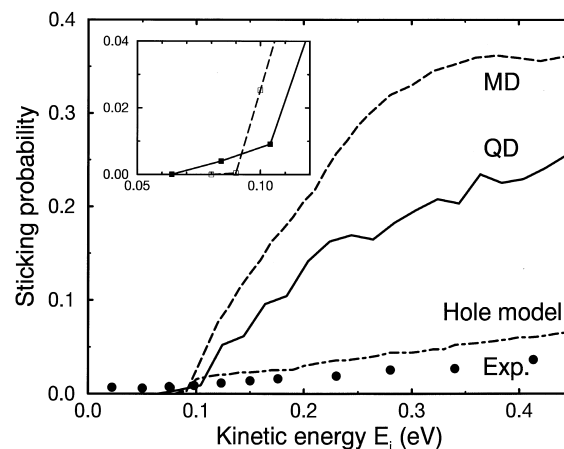


Fig. 2. Sticking probability versus kinetic energy for a H_2 beam under normal incidence on a $S(2 \times 2)/Pd(100)$ surface. Full dots: experiment (from Ref. [1]); dashed-dotted line: integrated barrier distribution, which corresponds to the sticking probability in the hole model [13]; solid line: 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.

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?

- (1) From the approximations assumed in the calculations, it is mainly the GGA that yields sufficient uncertainty 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.
- (2) The other approximations have been carefully

tested, and we do not believe that they are relevant.

- (3) Concerning the experimental results, we note that the determination of the sulfur coverage at and below the surface is not without problems. 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 by monitoring the S_{132} and Pd_{330} Auger signals with respect to those at saturation coverage which is believed to be $\Theta_S=0.5$, and by the presence of a (2×2) LEED pattern. Both the experiment [1,2] and the DFT-GGA calculations [3] show that the hydrogen dissociation on the sulfur-covered Pd(100) surface depends sensitively on the actual sulfur coverage. Our calculations are made for a sulfur adlayer on a clean Pd(100) substrate. It might well be that subsurface sulfur and maybe other subsurface species are present in the experimental samples. This will have a decisive influence on the surface reactivity because subsurface species will bind to the Pd atoms and hence make the binding of the hydrogen atoms to the surface Pd atoms more difficult. Thus, the discrepancies between theory and experiment would be reconciled, also with respect to the observed site-blocking [2]. We hope, therefore, 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 the form in which S is actually present at the surface under different experimental conditions.

We now return to the theoretical results. The classical treatment of hydrogen dynamics overestimates the sticking probability of H_2 at $S(2 \times 2)/Pd(100)$ compared to the quantum results. For energies smaller than the minimum barrier height, E_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. However, for energies larger than E_b , the classical sticking probability rises to values that are almost 50% larger than the quantum sticking probabilities. We have recently

shown that ZPV can lead to a strong suppression of the quantum sticking probability compared to classical results [7,15]. In Table 1, 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 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, and so 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 $E_b^{\text{eff}}=0.17$ eV. 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 [15]. However, the quantum sticking probability rises significantly

Table 1
Zero-point vibrations (ZPV) energies of the H_2 molecule at the minimum barrier position

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

The H_2 configuration corresponds to the situation of Fig. 1a. The gas-phase ZPV energy of H_2 is $1/2\hbar\omega_{\text{gas}}=0.258$ eV.

already for energies well below the effective barrier height of 0.17 eV. We have carefully analysed the role of quantum effects for energies close to the minimum barrier height by low-dimensional studies. These studies reveal that the combined promoting effect of tunneling and steering and the hindering effect of the zero-point vibrations almost cancel for energies slightly above the minimum barrier height so that classical and quantum results are rather close.

The question arises as to 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 expected from the hole model [13]. 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 [16,17]. Indeed, the strongly repulsive potential above the sulfur atoms extends rather far into the gas-phase [5]. Thus, the forces re-orienting and re-directing the molecules act on the molecules for a long time; therefore, they are effective up to kinetic energies of more than 0.5 eV. At the clean Pd surface, on the contrary, at $E_i \approx 0.2$ eV, steering is no longer operative in the dissociation process [16]. This causes the surprising result that at $E_i = 0.2$ eV, the sticking probability at the (2×2) sulfur-covered

Pd(100) surface is almost as large as that 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 [18].

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 overpopulation in thermal hydrogen desorption from

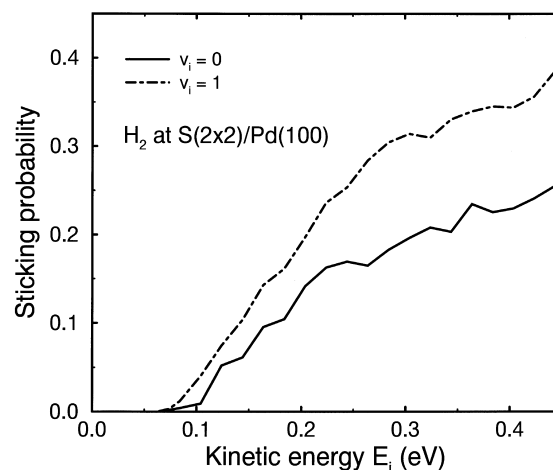


Fig. 3. Dependence of the quantum sticking probability versus kinetic energy for a hydrogen beam under normal incidence at a $S(2 \times 2)/Pd(100)$ surface on the initial vibrational state v . Solid line: $v_i = 0$; dashed-dotted line: $v_i = 1$. The molecules are initially in the rotational ground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

sulfur-covered Pd(100) (H. Zacharias, pers. commun.; [19]) 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 those found at the clean surface and will be discussed in a forthcoming publication.

In conclusion, we have reported a six-dimensional dynamical study of the dissociative adsorption of H₂ at S(2×2)/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. These discrepancies might be caused by the presence of subsurface sulfur in the experimental samples. The huge corrugation and anisotropy of the PES lead to ZPV in the quantum dynamics, which reduces the quantum results compared to the classical ones. 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 minimum barrier for dissociative adsorption.

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