Trends in the chemical reactivity of surfaces studied by *ab initio* quantum-dynamics calculations

Andreas Eichler* and Jürgen Hafner*
Institut für Theoretische Physik and Center for Computational Materials Science, Technische Universität Wien, Wiedner Hauptstrasse 8-10, A-1040 Wien, Austria

Axel Groß and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany
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Trends in the chemical reactivity of transition-metal surfaces have been studied at the example of the dissociative adsorption of hydrogen on the (100) surfaces of Rh, Pd, and Ag. Detailed calculations of the six-dimensional potential-energy surfaces have been performed using density-functional theory. The adsorption dynamics has been investigated by solving the time-independent Schrödinger equation via a coupled-channel technique. The results are discussed in the light of current concepts for a reactivity theory.
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A quantitative understanding at a microscopic level of the chemical reactivity of solid surfaces is fundamental to chemisorption, catalysis, and corrosion.[1] Ultimately such an understanding must be based on the knowledge of the potential-energy surface (PES) in the nuclear coordinate space of the reactants and of the features of the PES (presence/absence of barriers in certain reaction channels, angular and translational corrugation, . . .) determining the reaction dynamics. Due to the recent progress in density-functional calculations it is now possible to perform first-principles studies of multidimensional PES.[2–5] In addition, a few quantum dynamic simulations based on the high-dimensional PES have been performed,[6,7] allowing us to establish a comparison with molecular-beam experiments[8] probing the PES over a wide range of energies. If such studies could be performed for a series of metals showing a systematic variation in the band filling and other physical properties, this would provide the most stringent test of current concepts of the chemical reactivity of surfaces.

In essence, such concepts are based on experience with gas-phase chemistry where they are successfully used to predict reactions in terms of the properties of the noninteracting systems. In the earliest attempts correlations of the surface reactivity with the local electronic density of states $N(E_F)$ at the Fermi level[9] or with the number of holes in the *d*-band N_h (Ref. 10) have been proposed. More general measures of the surface reactivity are based on approaches used in the theory of the chemical reactivity of molecules, in particular the concept of frontier orbitals,[11] which has been widely used in the chemistry community for analyzing and understanding bonding at surfaces.[12] This concept has been reexpressed within the exact framework provided by density-functional theory.[13,14] The simple reactivity measures $N(E_F)$ or N_h appear as the limiting cases of a more general dependence of the reactivity on the softness (or local softness) defined as derivatives of the number of electrons (or electron density) with respect to the chemical potential. More recently, it has been pointed out that the key factor determining the reactivity is the formation of new adsorbate-substrate bonds providing the energy for the breaking of the intramolecular bond.[15] Dissociative adsorption is nonactivated, if not only the bonding, but also the antibonding molecular orbitals (MO) hybridize with the metallic *d* band, leading to a partial occupation of the antibonding states and a weakening of the molecular bond. Hammer and Norskov[16] argued that the reactivity depends on the difference in the positions of the *center of gravity* E_d of the *d* band and the bonding and antibonding MO's. Still an analysis of the now available first-principles calculations of the PES does not lead to a definitive assessment of the validity of these rival concepts. The reason is that they may serve to interpret certain features of the calculated PES or of the experimental observations such as the preference for certain adsorption sites,[14] the existence or absence of barriers for certain reaction geometries, or the variation of the barrier height,[16] but that the dissociation probability as a function of the translational energy and the rotational and vibrational states of the impinging molecule depends in a complex way on the form of the PES in a wide region of the configuration space.[6,17] In order to determine the reactivity of a particular system, it is therefore necessary to perform dynamical simulations of the reactants moving on the relevant PES.

In this paper we present the results of detailed quantum dynamic simulations of the dissociative adsorption of hydrogen molecules on the (100) surfaces of rhodium, palladium, and silver with the aim of achieving a microscopic understanding of the trends in the chemical reactivities. Our investigations are based on six-dimensional (6D) PES (corresponding to the six degrees of freedom of the H_2 molecule above the metal surface) constructed by *ab initio* density-functional theory (DFT) calculations and the solution of the time-independent Schrödinger equation for the two H nuclei moving on the 6D PES. Rh, Pd, and Ag have been chosen for our study because the PES calculated for these metals cover the range from nonactivated adsorption along most pathways (Rh) over activated as well as nonactivated paths (Pd) to activated reactions only (Ag). We show that the static information gained from the electronic structure and the form of the PES is not sufficient in order to predict sticking probabilities. Adsorption systems with rather different barrier distributions such as H_2/Rh(100) and H_2/Pd(100) have the same sticking probability at low kinetic energies caused by the complex dynamical behavior on the multidimensional PES.

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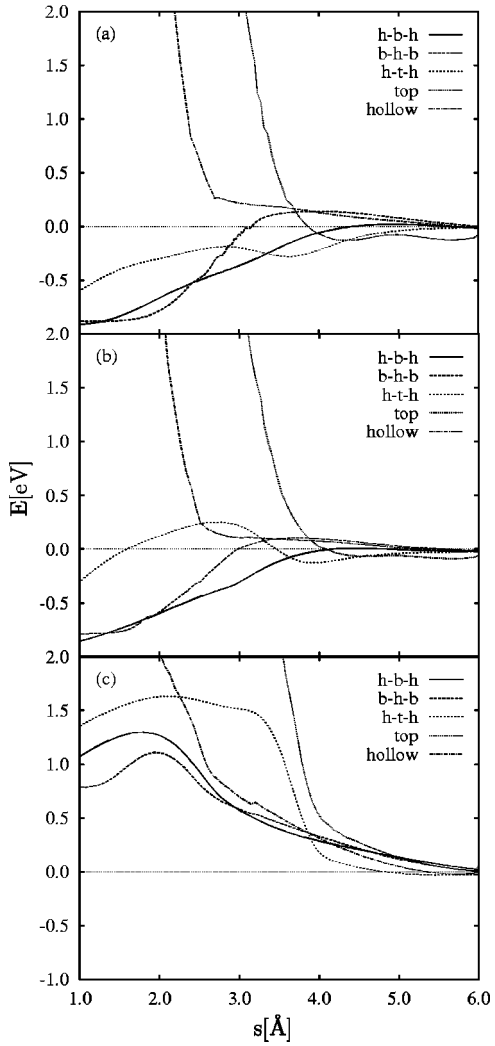

FIG. 1. 2D cuts through the (adiabatic) potential-energy surface for the dissociative adsorption of H_2 on (a) Rh(100) [(b) Pd(100), (c) Ag(100)] surface as a function of the reaction coordinate s along several pathways. For the definition of the reaction coordinate and the nomenclature of the pathways see the text.

The quantum dynamical calculations presented here are based on potential-energy surfaces derived from *ab initio* total-energy calculations[5] within the generalized gradient approximation[20] using the Vienna *ab initio* simulation package VASP.[18]VASP works in a plane-wave basis and uses ultrasoft pseudopotentials[19] to achieve convergence at tolerable cutoff energies.

For each surface, 14 two-dimensional (2D) cuts (consisting of about 200 data points including forces) have been calculated and used as an input for a parametrization similar to that in Ref. 6. The potential is written as the sum of an adiabatic potential V^a, describing the energy of the molecule in its vibrational ground state, and a parabolic vibrational potential V^{v} using a frequency depending on the reaction-path coordinate s.[21] In total we use a set of 15 s-dependent parameters fitted at 200 discrete s values.

Figure 1 shows the adiabatic (parametrized) potential along five representative pathways for the three surfaces. The first three pathways (h-b-h,b-h-b,h-t-h) correspond to molecules oriented parallel to the surface with the center of mass over the high symmetry position equivalent to the letter in the middle (b is bridge, h is hollow, t is on top) and the atoms pointing towards the high-symmetry positions described by the first and third letter. The last two pathways show the energy for molecules impinging in an upright position on the on-top and hollow position, respectively. The first panel in Fig. 1 corresponds to the dissociation over Rh(100). Nearly all pathways for molecules parallel to the surface lead to unactivated dissociation. The lowest-energy reaction path leading to dissociation is over the top site, with the molecule stretching towards the bridge sites. However, as the bridge positions are only saddle points on the PES, the dissociated atoms finally slide into the hollows. Only the pathway over bridge exhibits a barrier of about 130 meV in the entrance channel. There are no barriers in the exit channel. For upright molecules the on-top position is at the beginning attractive, but very soon the molecule is repelled by the substrate. Incidence over hollow allows a closer approach of the molecule with only slightly increasing energy, but finally this particle is also repelled.

These two pathways for H_2 over the Pd(100) surface look very similar. However, due to the higher lattice constant the b-t-b geometry is no longer as favorable in promoting dissociation—at intermediate distances where bond breaking takes place, the most favorable is the one stretching diagonally from bridge to bridge (b-b). Note that both scenarios have also been discussed by Cohen *et al.*[14] from the point of view of the partial density of states (DOS's) at E_F. However, in contrast to the present result, the b-b geometry was predicted for Rh and not for Pd. As a further consequence of the larger lattice spacing, the kink in the hollow curve has moved slightly nearer to the surface. The pathways for the ''flat'' molecules are shifted to higher energy, so that a greater portion of the PES becomes activated, and only a few pathways lead to dissociation without any barriers (h-b-h).

For H_2 over Ag(100), the situation looks different. Now all pathways for ''flat'' molecules have barriers in the exit channel. Along the (h-t-h) pathway that showed already for Rh(100) a tendency for the formation of a barrier in the exit channel, there is now the maximum barrier to dissociation (1.63 eV), whereas the minimum barrier (1.10 eV) is on the b-h-b pathway, which has for Rh(100) and Pd(100) only a low barrier in the entrance channel.

In summary these three surfaces cover the range from a nearly completely unactivated system [Rh(100)] over a surface exhibiting activated as well as unactivated pathways for H_2 dissociation [Pd(100)] to a surface where adsorption is always an endothermic process [Ag(100)]. The Hammer-Norskov concept or the d-hole model predict the global trend rather well but, of course, cannot account for the large local variations in the barrier heights for Pd(100). None of the statical models can explain the high reactivity of Pd for low kinetic energy.

The quantum dynamical calculations have been performed by solving the time-independent Schrödinger equation in the six hydrogen degrees of freedom (6D) in a numerically very stable coupled-channel scheme.[22] The hydrogen vibrations follow the reaction dynamics almost adiabatically,[23] therefore we have analyzed the state-specific sticking probabilities in detail by performing vibrationally

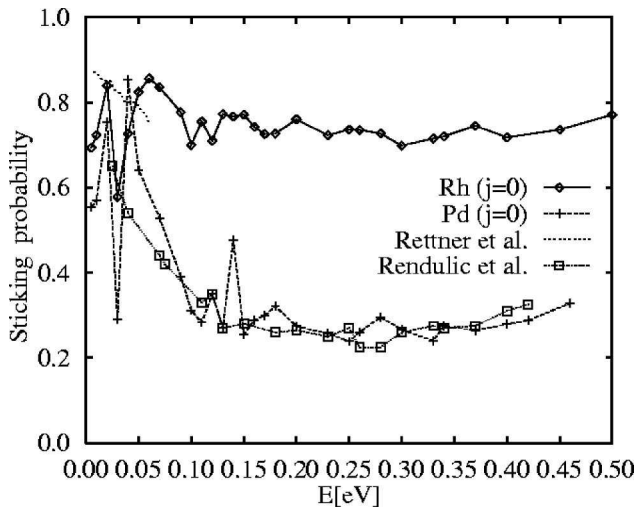

FIG. 2. Sticking probability versus kinetic energy for a H_2 beam under normal incidence on a Rh(100) and a Pd(100) surface. Experimental results for Pd from Refs. 8 and 24.

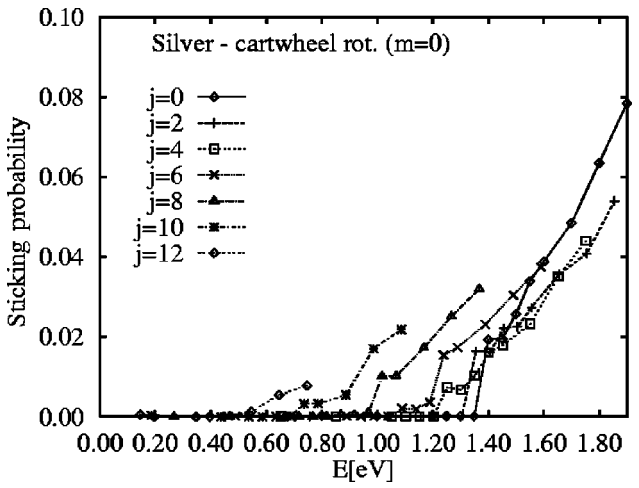

FIG. 3. Calculated sticking probability versus kinetic energy for a H_2 beam under normal incidence on a Ag(100) surface at various j with $m=0$ (cartwheel rotation).

adiabatic 5D calculations (the results of these 5D calculations only differ by less than 5% from the full 6D calculations).

The first dynamical results we are discussing correspond to $H_2/Pd(100)$. This is a very well-studied system, both experimentally[8,24–26] as well as theoretically.[4–6,17,26] In Fig. 2 we compare the calculated sticking probability S_0 with the results of molecular-beam experiments by Rendulic *et al.*[8] and Rettner and Auerbach.[24] It is obvious that the experimental results do not fully agree quantitatively, demonstrating that the determination of sticking probabilities is a challenging task. Still the agreement of our calculated results with the experiments is striking. The most important qualitative feature is that the initial decrease of the sticking probability is well produced. The reason for this decrease is now well understood:[6] The PES of $H_2/Pd(100)$ has some nonactivated paths towards dissociative adsorption but barriers in most reaction channels. At low kinetic energies, molecules impinging in an unfavorable configuration are redirected and reoriented by the corrugation and anisotropy of the PES to nonactivated pathways leading to the high sticking probability. At higher kinetic energies this *steering effect* becomes less effective causing the decrease of the sticking probability.

In the first six-dimensional *ab initio* quantum study of the dissociation dynamics of $H_2/Pd(100)$ there were larger quantitative differences to the experiment.[6] The improved quantitative agreement in our present study is due to the fact that we used more *ab initio* points for the parametrization of the PES, in particular for higher energy paths, which allowed a more detailed representation of the *ab initio* PES. Our results for $H_2/Pd(100)$ show that the *ab initio* quantum dynamics calculations are indeed capable of reproducing sticking probabilities within a high degree of accuracy. This makes us confident that it is meaningful to present in the following calculated sticking probabilities for two systems, namely $H_2/Rh(100)$ and $H_2/Ag(100)$, for which almost no experimental data is available.

According to the barrier distribution (see Fig. 1) Rh(100) is even more reactive than Pd(100). This high reactivity is reflected by the higher dissociation probabilities plotted in Fig. 2, which is consistent with the experimental observation of a high S_0 (''near unity''[27]). However, at low kinetic energies, $H_2/Pd(100)$ and $H_2/Rh(100)$ have the same high sticking probability *in spite of their different barrier distributions*. For the dissociative adsorption of thermal hydrogen gas at room temperature (which has a mean kinetic energy of 0.05 eV), the reactivity of both systems is the same. The steering effect leads to a much higher reactivity of $H_2/Pd(100)$ than would be expected from the barrier distribution. A detailed dynamical analysis of the sticking[28] reveals that steering is also operative in the system $H_2/Rh(100)$, but is much less effective than on the Pd surface. Only at higher kinetic energies, where the steering becomes less effective, the sticking probabilities reflect the differences expected from the different barrier distributions.

On noble metals hydrogen dissociation is hindered by a substantial barrier. For $H_2/Ag(100)$ we have found a minimum barrier of 1.1 eV (without zero-point corrections). To our knowledge, there are no experiments for the hydrogen dissociation on Ag(100). However, the similarity of the PES with that for the extensively studied system H_2/Cu (Refs. 2 and 3) allows us to compare our results qualitatively to the wealth of available data for H_2/Cu.

In Fig. 3 we have plotted the sticking probability for $H_2/Ag(100)$ at various j with $m=0$ (cartwheel rotation). Due to the large minimum barrier for dissociation the sticking probability shows the typical activated behavior. For initially nonrotating molecules the kinetic energy has to be larger than the minimum barrier height in order to rise significantly. In contrast to the reactive systems $H_2/Pd(100)$ and $H_2/Rh(100)$ rotational excitation enhances the sticking probabilities even for cartwheeling molecules, however, in a nonmonotonous way. This behavior is in qualitative agreement with the results found experimentally on the similar system $H_2/Cu(111)$.[29]

Our work shows that it is now possible to start entirely from first principles and to make reliable predictions on the PES and on the adsorption/desorption dynamics. The case of H_2 on Pd(100) demonstrates that these predictions are quantitatively accurate within the experimental error. We present

detailed results on the sticking probabilities of H_2 on the (100) surfaces of Rh and Ag that, together with the results for Pd, illustrate the trends in the chemical reactivities. The similar sticking coefficient at thermal energies we have obtained for Rh(100) and Pd(100) are certainly very surprising—not only from the point of view of the simple reactivity concepts, but also in view of the differences in the calculated PES. This demonstrates that for a quantitative prediction of the reactivity the exploration of the PES by static calculations is not sufficient, but that a quantum dynamic simulation of the adsorption/desorption process is required. We also hope that these results will stimulate new experiments, in particular for the Rh and Ag surfaces.

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*Present address: Institute für Materialphysik, Universität Wien, A-1090 Wien, Austria.

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