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Quantum Steering Effects in the Dissociative Adsorption of H_2 on Rh(100)

A. Eichler, G. Kresse, and J. Hafner
Institut für Theoretische Physik and Center for Computational Materials Science, Technische Universität Wien, Wiedner Hauptstr. 8-10, A-1040 Wien, Austria

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We show on the basis of *ab initio* local-density-functional calculations (with generalized gradient corrections) that the dissociative adsorption of a H_2 molecule on a Rh(100) surface is dominated by quantum-mechanical steering effects arising from the formation and modification of covalent metal-H bonds: As the molecule is lowered towards the surface, bond formation occurs first with the s, p_z, and $d_{3z^2-r^2}$ orbitals extending farthest from the surface. This attracts the molecule to the on-top position. Interaction with the t_{2g} orbitals orients the axis of the molecule towards the bridge sites and drives the dissociation in a bridge-top-bridge configuration. Finally, bonding with the $d_{x^2-y^2}$ orbitals attracts the dissociated atoms to the fourfold hollows. [S0031-9007(96)00483-8]

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The dissociative adsorption of hydrogen molecules on metal surfaces is of great interest as a key intermediate step in many catalytical reactions [1]. Any classical or quantum simulation of the trajectory of a molecule impinging on a surface must be based on a realistic description of the multidimensional potential energy surface (PES) for the molecule on the surface. Attempts have been made to construct the full six-dimensional PES for a diatomic molecule on the basis of low-dimensional cuts calculated from first principles [2–5] and to use it as input for a quantum-mechanical description of dissociative adsorption and associative desorption [6]. The selection of the cuts through the PES is usually made by following two guidelines: (i) The favored adsorption pathway is dominated by the stable adsorption sites, i.e., by the final destination of the adsorbate. (ii) The optimal approach of the molecule to the surface must involve high symmetry. For a hydrogen molecule over an fcc (100) surface where the stable adsorption sites are the fourfold hollows [7–9] the dissociation is expected to occur over the bridge site with the molecular axis perpendicular to the bridge ("h-b-h" geometry).

Recently, this view has been challenged by Feibelman [10]. He emphasized that the key consideration must be that the energy necessary to stretch the molecular H-H bond can be gained only by forming strong metal-H bonds. Now the bond length in the H_2 molecule is only 0.74 Å, while the distance between two adjacent hollows across the bridge is 2.71 Å on a Rh(100) surface. This means that strong metal-H bonds in the hollows can be formed only *after* almost all the energy necessary to break the H-H bond has already been spent. Supported by *ab initio* local-density-functional (LDF) calculations for selected configurations, Feibelman proposed that the strong metal-H bonds are formed first in a bridge-to-bridge (b-b) configuration of the H_2 molecule where adjacent adsorption sites are only 1.90 Å apart. Hence the prediction is that the molecule dissociates in a b-b configuration and that afterwards the isolated H atoms drift into the hollow positions. More recently, similar steering effects induced by molecule-substrate interactions have been discussed by Wilke and Scheffler [11] for the dissociation of H_2 on Pd(100). However, Wilke and Scheffler argue that at larger distances (>1.8 Å above the surface) the on-top position of the H_2 molecule with the axis oriented towards the hollow sites ("h-t-h" configuration) is energetically most favorable and that the optimal reaction pathway involves a gradual shift of the center of mass of the molecule from the top to the hollow position. This is in agreement with the frontier-orbital concept [12] stressing the importance of the covalent bonding to the orbitals with the largest extension from the surface and in contradiction to the Harris-Anderson model [13] based on the minimization of the Pauli repulsion between the adsorbate and the substrate. However, in view of the similarity of the stable adsorption geometries for H on Pd(100) [8] and Rh(100) [7,9], the difference in the proposed reaction pathways is intriguing.

Here we present the results of an extended *ab initio* LDF study of the dissociative adsorption of H_2 on Rh(100). We show that metal-H bonding occurs first on the top site (in agreement with Wilke and Scheffler [11]) through the interaction of the σ MO's (molecular orbitals) of the molecule with the substrate orbitals extending farthest into the vacuum. However, the atoms are oriented towards the bridge sites in a b-t-b configuration, differing from both the h-t-h configuration proposed by Wilke and Scheffler [11] and the b-b configuration proposed by Feibelman [10]. Dissociation occurs in this configuration, and finally the single H atoms drift from the bridges into their stable hollow positions. This pathway may be explained in terms of the formation of covalent Rh-H bonds with different Rh-s, p, d orbitals as the distance of the molecule from the surface decreases.

For our investigation we use the Vienna *ab initio* simulation program VASP [14,15]. VASP performs an iterative solution of the generalized Kohn-Sham equations of LDF

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theory via residual minimization techniques [16]. Exchange and correlation are described within the Ceperley-Alder local-density-functional [17] and the generalized gradient corrections (GGC's) of Perdew *et al.* [18]. The GGC's are applied self-consistently in the construction of the pseudopotentials as well as in the calculation of the Kohn-Sham ground state and of the Hellmann-Feynman forces. VASP has been applied successfully to a wide range of problems, including the adsorption of C on Al(111) surfaces [19], the reconstruction and hydrogen-induced dereconstruction of various diamond surfaces [20], the relaxation of clean Rh surfaces [21], and the adsorption of atomic hydrogen on Rh(100) [9].

Both Rh and H are described by optimized ultrasoft pseudopotentials [22,23]. For the Rh pseudopotentials see Ref. [21]; for H see Ref. [20]. The basis set consists of all plane wave with a kinetic energy up to 200 eV. The calculations of the PES are performed for slabs with 3 and 5 layers of Rh, using $c(2 \times 2)$ and $p(2 \times 2)$ surface cells. We find that the calculated adsorption energies and positions are well converged already for the thinner slabs and vary only little with coverage. Brillouin-zone integrations are performed for a grid of $4 \times 4 \times 1$ special points, using second-order Methfessel-Paxton smearing [24] with a width of $\sigma = 0.2$ eV.

For the calculation of the PES we have relaxed (although not always simultaneously) all six degrees of freedom of the H_2 molecule. The positions of the substrate atoms are fixed in a bulk-terminated geometry. Our work on the adsorption of atomic H on Rh(100) has shown that the adsorption of a monolayer of H reduces the inward relaxation of the top layer from -3.2% for the clean surface to -1.5% for adsorption in the bridge sites and leads to an outward relaxation of 0.5% for adsorption in the stable hollow positions. However, the adsorption energies and positions change by only ± 0.02 eV/atom and ± 0.02 Å relative to the bulk-terminated surface on a complete relaxation of the substrate.

Figure 1 shows the variation of the adsorption energy measured along the bottom of the reaction channel for several straight perpendicular approaches of a molecule positioned parallel to the surface. *h-b-h* means that the center of mass is above the bridge site with the atoms oriented towards the hollow sites; "*b-b*" stands for a position connecting neighboring bridge sites. Table I notes the adsorption barriers (where a barrier exists) and the minimum-energy positions. There are two important conclusions to be drawn from these results: (i) The stable adsorption site is the fourfold hollow, but the bridge sites have only slightly higher energy [25]. (ii) At larger distances from the surface, a straightforward approach to the hollow sites via dissociation over the top or bridge positions (*h-t-h* and *h-b-h* paths) is energetically less favorable than with the atoms oriented towards the bridge sites (*b-b* and *b-t-b* paths). Together these results suggest that the lowest-energy dissociation path is via the top site with the axis of the molecule oriented along the edge of the $c(2 \times 2)$ cell towards the bridge sites and that only in the final stage of the process do the dissociated atoms move towards the hollows (as indicated by the dashed line in Fig. 1).

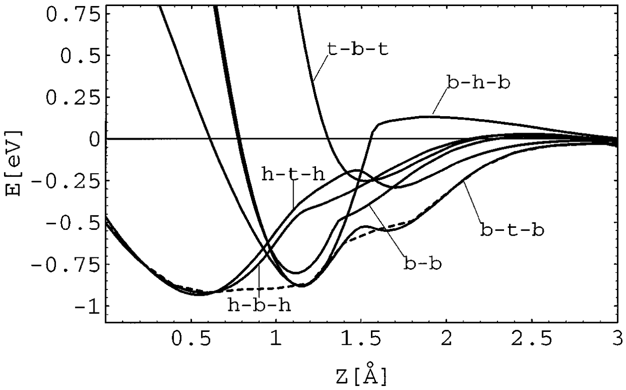

FIG. 1. Variation of the energy of a H_2 molecule above a Rh(100) surface, measured along the bottom of different straight perpendicular reaction channels as a function of the distance z from the surface. h, b, t stand for hollow, bridge, and on-top sites, "*h-b-h*" for a configuration with the center of mass of the molecule over the bridge site and the axis oriented towards the hollow sites. The dashed line marks the energy along the lowest-energy reaction path shown in Fig. 2.

To test this suggestion we performed a simulation with the H_2 molecule initially in an off-symmetry position 4 Å above the surface. The distance from the surface is gradually reduced; at each step the molecule is allowed to relax its length and position, with the only restriction that it remains parallel to the surface. At each step we have monitored the forces that could lead to a canting of the molecule, but we found that these forces are always too small to induce a significant inclination of the molecule relative to a position parallel to the surface. Hence essentially all six degrees of freedom are gradually relaxed. We find that at a distance of ~3.2 Å the

TABLE. I. Minimum energy configurations and dissociation barriers for H_2 on Rh(100), calculated along different reaction paths (E, energy in eV; d, length of H_2 molecule or distance between the dissociated H atoms; z, height of the center of mass of the H_2 molecule above the surface, both in Å).

Path		E (eV)	d (Å)	z (Å)
h-b-h	Barrier	0.02	0.77	2.40
	Minimum	−0.92	2.71	0.55
h-t-h	Local Min.	−0.29	0.87	1.70
	Minimum	−0.93	3.87	0.55
b-h-b	Barrier	0.13	0.77	1.90
	Minimum	−0.88	2.81	1.13
b-t-b	Minimum	−0.88	2.71	1.13
b-b	Barrier	0.01	0.77	2.47
	Minimum	−0.80	1.93	1.10
t-b-t	Barrier	0.03	0.87	2.47
	Minimum	−0.25	1.53	1.03

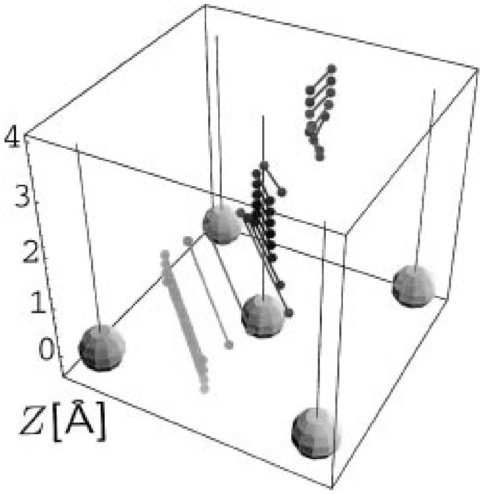

FIG. 2. Lowest-energy reaction path for dissociative adsorption of a H_2 molecule above Rh(100), starting from an arbitrary position 4 Å above the surface and calculated by relaxing the bond length, orientation, and center-of-mass position of the molecule at fixed heights. The dots mark the positions of the H atoms; cf. text.

molecule rotates first such that it is parallel to the *b-t-b* configuration (see Fig. 2). In the next step, at a height of 2.8 to 3.0 Å the molecule is drawn to the on-top site. Even during this critical step, the "canting" forces remain small, hence the restriction to parallel orientation is immaterial to the reaction we want to describe. As the molecule is lowered further, dissociation occurs in the *b-t-b* geometry, at a height of 1.3 to 1.1 Å [note that the height of the equilibrium adsorption site (saddle point) in the bridge is 1.13 Å; cf. Table I]. In the final step, the atoms move further down into the hollows. Note that along this reaction path there is not the smallest barrier for dissociative adsorption, in agreement with the observed high sticking probability for H_2 on Rh(100) [26].

The origin of the "steering" effects directing the molecule along this path is in the interaction with different orbitals of the substrate atoms, depending on the distance from the surface. Interactions between molecule and substrate orbitals set in at a distance of ~3 Å. Initially, the interactions are restricted to the orbitals extending farthest from the surface, i.e., to the s, p_z, and $d_{3z^2-r^2}$ orbitals. The overlap with these orbitals is largest for the on-top position of the molecule. At somewhat smaller distances, there are in addition interactions with the complex of $t_{2g}(d_{xz}, d_{yz}, d_{xy})$ orbitals. This fixes the orientation of the molecule in the *b-t-b* position where the dissociation occurs. At still smaller distances, the overlap is optimized for the $d_{x^2-y^2}$ orbitals and this stabilizes the adsorption in the fourfold hollows. The change of the character of the metal-H bond along the reaction pathway can be monitored by following the change in the densities of states (DOS) projected on the bonding and antibonding four-center orbitals formed by the σ and $\sigma^\star$ molecular orbitals of the H_2 molecule and the orbitals of the two inequivalent Rh atoms in the surface layer. The difference between the DOS's projected on the bonding and antibonding four-center orbitals defines the crystal-orbital overlap population (COOP) function [12,27]. A COOP integrated up to the Fermi energy represents a measure for the strength of the covalent bond [27]. The COOP for the four-center orbitals is defined such that COOP > 0 corresponds to bonding and COOP < 0 to antibonding adsorbate-substrate interactions. Figures 3(a)–3(c) show the differential COOP's at different heights above the surface. Figure 4 shows the variation of the integrated COOP's as a function of the distance of H_2 from the surface. At $z = 1.8$ Å, i.e., just before dissociation sets in, the dominant contribution to the COOP comes from bonding σ-s, σ-p_z, and σ-$d_{3z^2-r^2}$ interactions; their differential COOP is largest at the energy of the bonding H_2-σ

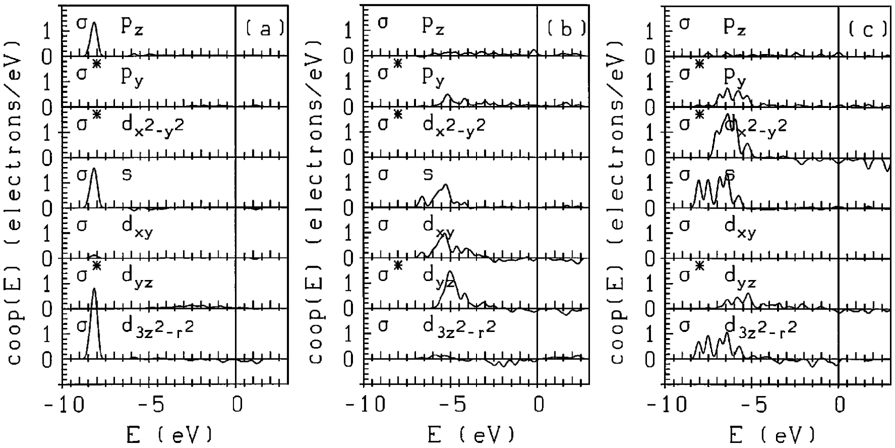

FIG. 3. Differential crystal-orbital overlap population (COOP) functions for four-center orbitals formed by bonding and antibonding H_2 molecular orbitals and local orbitals of the substrate atoms. The calculations refer to the equilibrium configurations at different distances from the surface: (a) $z = 1.8$ Å, (b) $z = 1.2$ Å, (c) $z = 0.6$ Å; cf. text.

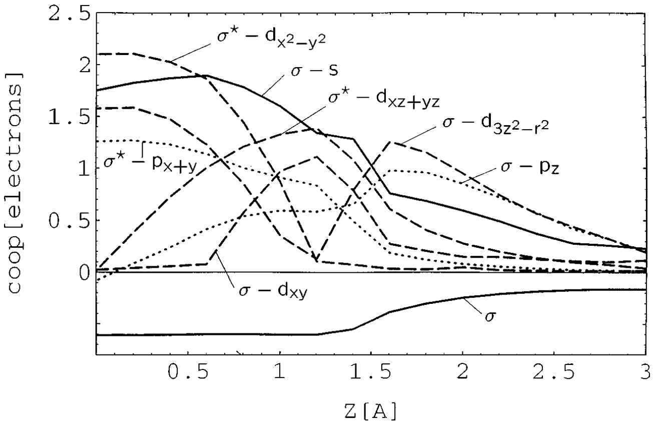

FIG. 4. Variation of the integrated crystal-orbital overlap populations (COOP) for the four-center orbitals of a H_2 molecule on Rh(100) along the lowest-energy reaction path. The lower part of the figure shows the COOP for the σ molecular orbital of the H_2 molecule alone (the scale is reduced and shifted downwards); cf. text.

state. The σ-p_z and σ-$d_{3z^2-r^2}$ interactions attract the molecule towards the top site. As z decreases, the σ peak shifts to smaller binding energies and is broadened through hybridization with the Rh valence band. The COOP's and hence the strength of the bonds increase for $\sigma^\star$-$d_{yz,zx}$, $\sigma^\star$-$p_{x,y}$, and σ-d_{xy} interactions at a distance of $z = 1.2$ Å. These interactions orient the molecule towards the bridge sites; they are also the driving forces for the dissociation. The state of the H_2 molecule is monitored by the COOP for the two-center σ orbital shown at the bottom curve in Fig. 4. The sudden drop near $z \sim 1.5$ Å indicates that dissociation occurs. On the other hand, the σ-$d_{3z^2-r^2}$ COOP decreases. At even smaller distances the interaction with the t_{2g} orbitals decreases at the expense of the interaction with the e_g orbitals ($d_{x^2-y^2}$ and the r^2 part of $d_{3z^2-r^2}$) and these interactions drag the H atoms into the hollows. Hence the energetically most favorable reaction path results from quantum-mechanical steering effects.

In summary, we have shown that a detailed exploration of the reaction path for dissociative adsorption of a diatomic molecule on a fcc surface leads to rather unexpected results. In particular, we find that dissociation and adsorption does not occur in a single step and along a simple straight reaction path. The character of the covalent metal-H bond changes according to the different spatial extension and orientation of the substrate orbitals from the metal surface, and these changing covalent interactions guide the molecule during its approach to the surface. We believe that the "quantum steering" effects discussed here are of quite general importance. At least for transition metals with a nearly completely filled d band we expect that the steering will result in a similar geometry of the reaction path.

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