

Orientation Dependence of the Hydrogen Molecule's Interaction with Rh(001)

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First-principles calculational results, that conflict with conventional wisdom, are reported for the orientation dependence of the energy of H_2 , a few bohrs above a Rh(001) surface. In geometric configurations near the saddle point where H-Rh bonds begin to form, the favored molecular axis orientation is along a $\langle 100 \rangle$ direction, corresponding to the attraction of each H atom to a twofold bridge site. This is true even though the final destinations of the H atoms are fourfold hollows, and even though the $\langle 100 \rangle$ orientation corresponds to relatively low symmetry, i.e., C_s rather than C_{2v} .

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Simulation of the trajectory of a molecule impinging on a crystalline surface is only reliable if one starts from an accurate molecule-surface interaction potential [1]. However, such potentials are usually obtained via educated guesswork, or at best, from semiempirical calculations [2-4]. If the past is any guide, one may expect surprises when it becomes possible to calculate the required potentials more realistically [5]. Here I report first-principles local-density-functional (LDF) calculations [6] that provide guidance in the construction of potentials for H_2 impinging on d -band metal surfaces. The results yield a novel picture of H_2 dissociation on a metal, which emphasizes the importance of H-metal-atom coordination, and of the three-dimensional nature of the dissociation trajectory.

Two ideas, called into question here, typically underlie our picture of molecular dissociation on a surface. One is that the favored approach of a molecule is dominated by the *final destinations* of the adsorbed species. This accords with the one-dimensional picture of thermal desorption experiments [7], wherein the heights of the barriers governing desorption-peak temperatures correlate with the strengths of the corresponding adsorption bonds. Dominance of the final adsorption geometry in the case of H_2 dissociation on a fcc (001) surface, where the H-atom adsorption sites are the fourfold hollows, would imply that the H_2 prefers to dissociate with its molecular axis symmetrically oriented, transverse to a bridge. In this "hollow-to-hollow" (henceforth h-to-h) geometry, each H atom is "aimed" at its equilibrium binding site [see Fig. 1(a)].

The h-to-h geometry also accords with the second common idea, namely, that the optimal molecular approach to the surface must involve high symmetry, in this case C_{2v} . This idea, which, however, also allows for the "atop-to-atop" (a-to-a) orientation of Fig. 1(b) [8], is based on the experience that low-lying states are generally symmetric ones. Of course, the *highest*-symmetry approach of H_2 to the fcc (001) surface would be C_{4v} , corresponding to the molecular axis oriented along a surface normal through either a fourfold hollow or an atop site. But this configuration is an unlikely choice for optimal dissociation, because the "upper" H atom is not well situ-

ated for the formation of a bond to the metal. This simple thought provides the starting point for the present study.

In what follows, I present evidence that neither the destinations of the dissociated species nor "high symmetry" should dominate consideration of the optimal H_2 dissociative adsorption trajectory. What *is* important is the difference between the energy gained in forming good H-metal bonds and that which must be expended in stretching the H-H bond. From this perspective, the key consideration is that the gas-phase H-H bond is only 1.40 bohrs long, while fcc Rh nearest-neighbor separation is 5.08 bohrs. This means that the fourfold hollow sites (and similarly the atop sites) on the Rh(001) surface are rather far apart compared to the H-H bond length, and that forming H-metal bonds in fourfold hollows (or in atop sites) requires the expenditure of essentially all the binding energy of the H_2 molecule [9].

Consider, then, an incident H_2 oriented so that the H atoms are aimed at adjacent *bridge* sites [Fig. 1(c)]. There are twice as many bridge sites as fourfold hollows on the fcc (001) surface, and they are therefore only 3.59 bohrs apart on Rh(001), compared to the 5.08 bohrs that separate hollows. Optimal H-atom bonding at a bridge site also occurs considerably higher above a fcc (001) surface than above a hollow, another simple consequence of geometry. The present calculations indicate that optimal bonding at a bridge occurs when a H atom is 2.13 bohrs above the outer Rh layer, while the equilibrium H height in a fourfold hollow is only 1.25 bohrs. Finally, the thermodynamic energy cost of moving a H atom from the equilibrium hollow to the optimal bridge site is rather low, only 0.12 eV [10]. These facts suggest that an incident H_2 can gain almost as much H-metal binding energy in the relatively low-symmetry orientation of Fig. 1(c) as it can in that of Fig. 1(a), while at the same time saving much of the cost of stretching the H-H bond. The premise of what follows is accordingly that the molecular orientation of Fig. 1(c) is optimal for H_2 dissociation on Rh(001), and that the same is true for other fcc metals as well. (This result will be especially important if it extends to the case of the noble metals, for which H_2 dissociation is activated.)

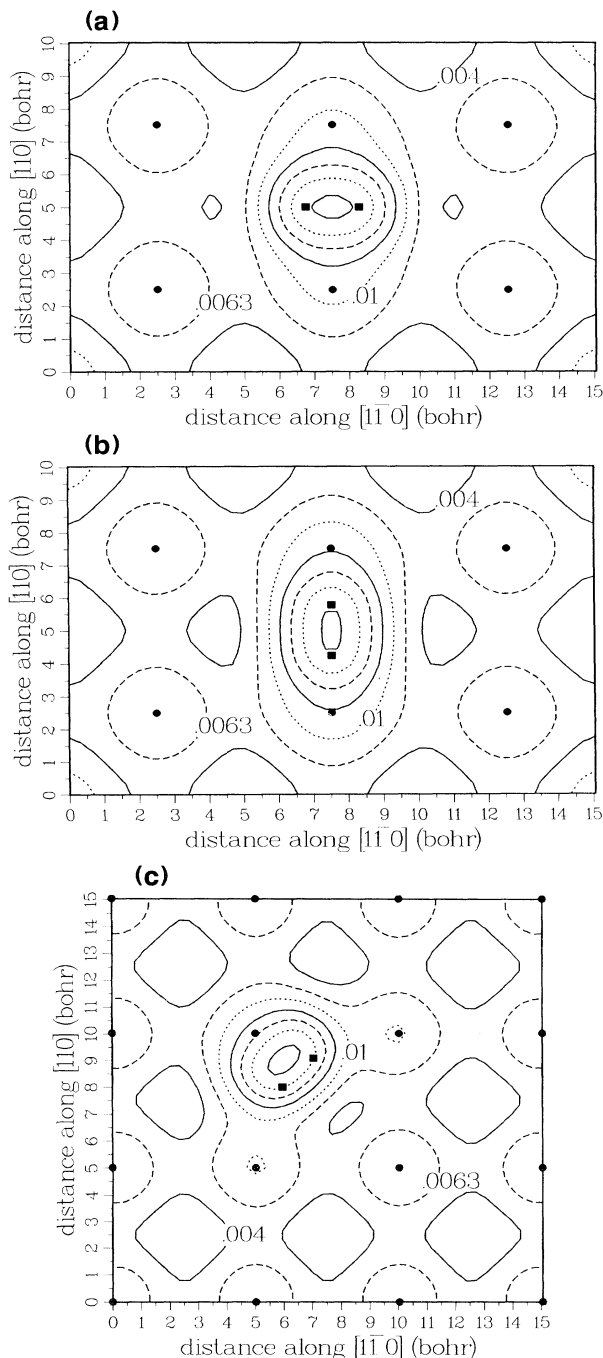


FIG. 1. Charge contour plots in a plane 2.98 bohrs above the outer Rh nuclei, for three different $H_2/Rh(001)$ orientations with the H nuclei residing at a height of 3.98 bohrs. Heavy dots represent the projections along the surface normal of the outer Rh nuclei. Heavy squares represent the projections of the protons. Contours are labeled in e/bohr^3 , and are geometrically spaced. Every fifth contour represents a change in charge density of a factor of 10. (a), (b), and (c) correspond to cases (1), (2), and (3) in Table I. (a) A hollow-to-hollow molecular orientation, (b) atop-to-atop bonding, and (c) a bridge-to-bridge case.

To test this idea, I have performed self-consistent local-density-functional total-energy calculations, using the "matrix-Green's-function" method which permits the study of an isolated molecule on an otherwise perfect metal crystal surface [11,12]. For several H_2 orientations with the molecular axis parallel to the Rh(001) surface (cf. Figs. 1), I determine geometric parameters that approximately zero the force parallel to the surface, on each proton. For these geometries, I compare bond lengths and total energies, as well as the forces on the H's along the surface normal. The results unambiguously indicate that in a search for the lowest potential energy, the "bridge-to-bridge" (b-to-b) orientation is preferred to the atop-to-atop configuration, which in turn is better than the hollow-to-hollow state. Thus, what is most important in dissociating the H_2 is to maximize the H atoms' coordination to metal atoms, not to maintain the highest symmetry or to aim the H atoms at their final destinations.

The matrix-Green's-function version of the LDF scattering theory of adsorption energies has previously been described in detail [11]. It relies on two basic approximations, representation of exchange and correlation via a local exchange-correlation energy density, and selection of a set of localized basis orbitals. Here, the Perdew-Zunger parametrization [13] of the Ceperley-Alder (CA) exchange-correlation energy density [14] was used, while electron-nuclear interactions were represented via the norm-conserving pseudopotentials (for Rh) of Bachelet, Hamann, and Schlüter [15] and (for H) of Hamann [16]. The orbital basis of Ref. [17] was used for Rh(001). It has been shown to yield energy levels throughout the surface Brillouin zone that agree to 75 meV with a converged, linearized augmented-plane-wave calculation [18]. The H-centered basis orbitals of Ref. [17] were also employed. Additionally, "floating" s -like Gaussians (with attenuation constants 0.5 and 0.7 bohr^{-2}) were centered at the midpoint of the H-H bond, in each H_2/Rh geometry, to allow for the buildup of H-H bond charge.

With this orbital basis, the minimum in the energy of gas-phase H_2 corresponds to a bond length of 1.45 bohrs, and, referencing to the experimental H-atom energy of 1 Ry, a dissociation energy of 3.50 eV [19]. Within the LDF approximation, using the CA exchange-correlation potential, the optimal Rh-Rh nearest-neighbor distance is 5.015 bohrs [17]. This value was used in the calculations, rather than the experimental 5.083 bohrs. Thus the LDF ratio used, of Rh-Rh to gas-phase H-H separations, is 5% less than in nature, and according to the arguments presented above, the estimate obtained for the favorableness of the b-to-b orientation relative to the h-to-h should therefore be a conservative one. The Rh(001) substrate was modeled as a seven-layer slab, as in Ref. [17], with the outer-layer separation contracted by 3.1% relative to the interior, in accordance with calculated forces. Rh nuclei were fixed at their clean-surface positions, independent of the assumed location of the H's.

TABLE I. $H_2/Rh(001)$ geometric parameters (in bohrs), corresponding forces (in Ry/bohr), and binding energies (BE) (in Ry). Surface-layer Rh nuclei are located at $3.546((n+m), (n-m), 0)$ bohrs. For each geometry, the first line of data refers to one of the H atoms and the second line to the other.

Orientation	x	y	z	F_x	F_y	F_z	BE (2H)
Free	0.7250	0.0000	...	0.000	0.000	0.0000	0.2573
	-0.7250	0.0000	...	0.000	0.000	0.0000	
(1) h-to-h	1.2367	2.3093	3.98	0.000	0.000	-0.0092	0.2809
	2.3093	1.2367	3.98	0.000	0.000	-0.0092	
(2) a-to-a	1.2271	1.2271	3.98	0.001	0.001	-0.0114	0.2830
	2.3189	2.3189	3.98	-0.001	-0.001	-0.0114	
(3) b-to-b	-0.7637	-2.0930	3.98	-0.002	0.007	-0.0141	0.2891
	0.7637	-2.0930	3.98	0.002	0.007	-0.0141	
(4) h-to-h	1.1225	2.4235	2.98	0.022	-0.022	-0.0283	0.3162
	2.4235	1.1225	2.98	-0.022	0.022	-0.0283	
(5) h-to-h	1.1649	2.3811	2.98	0.007	-0.007	-0.0238	0.3185
	2.3811	1.1649	2.98	-0.007	0.007	-0.0238	
(6) a-to-a	1.1366	1.1366	2.98	0.009	0.009	-0.0164	0.3242
	2.4094	2.4094	2.98	-0.009	-0.009	-0.0164	
(7) b-to-b	-0.9192	-2.1920	2.98	0.005	-0.010	-0.0267	0.3374
	0.9192	-2.1920	2.98	-0.005	-0.010	-0.0267	
(8) h-to-h	1.2497	2.2963	4.48	0.003	-0.003	-0.0049	0.2727
	2.2963	1.2497	4.48	-0.003	0.003	-0.0049	

Results of the calculations are given in Table I, and in the charge-density contour plots of Figs. 1(a)–1(c), which correspond, respectively, to the geometries (1)–(3) of Table I. In these geometries the H_2 molecular axis lies 3.98 bohrs above the surface Rh layer, somewhat below the plane containing the saddle point where the forces on the two protons vanish. The calculated energies, forces, bond lengths, and charge densities for these geometries all tell the same story. For example, in Table I, the x and y forces on the protons are virtually zero, but the downward force in case (2) is larger. This implies that in the a-to-a geometry, the H-metal bonding is stronger than in the h-to-h case. This is consistent with the slightly greater binding energy and longer H-H bond that were also calculated in this case. In Figs. 1(a) and 1(b), one sees that only charge contours near the H_2 , and the Rh bridge over which it is centered, are distorted from their clean-surface shapes. (Notice, e.g., that the nearly circular contours of charge density 0.0063 are unaffected by the orientation of the H_2 molecular axis.) Thus at 3.98 bohrs above the surface, the H_2 only interacts with *two* Rh's, even if, as in Fig. 1(a), the H atoms are aimed at fourfold hollows. This means that the a-to-a orientation should be favored over the h-to-h, because it results in a shorter distance between each H and the nearest Rh, for a given H-H bond length.

Comparing cases (2) and (3) in Table I, one sees that even though the parallel forces on the H's have not quite been relaxed to zero in the b-to-b case, it manifests stronger H-metal forces (F_z 's) and stronger overall bind-

ing than the a-to-a case does. Figure 1(c) shows that in the b-to-b orientation, three surface Rh's participate in the H_2 -metal interaction (note, e.g., that there are small extra charge contours about the Rh's which are second neighbors to the H's), while in the a-to-a case only two Rh's are involved. This is the main message of the present work: The lower-symmetry b-to-b orientation is preferred to the higher-symmetry orientations of Figs. 1(a) and 1(b), because it permits increased H-Rh coordination when the H's are relatively high above the surface. This is true despite the fact that the H atoms in the a-to-a case are about 0.22 bohr closer to their nearest Rh neighbors than they are in the b-to-b orientation and thus occupy sites where the clean-surface charge density is higher than for the b-to-b orientation. This means that preference for the b-to-b orientation is opposite to what an effective-medium picture [2,3] might suggest.

The results for geometries (4)–(7) in Table I show that at a height of 2.98 bohrs above the surface the same preferences remain. The H-metal forces are strongest and the total binding the greatest for the b-to-b orientation of case (7), the next strongest for the a-to-a geometry of (6), and the weakest for the h-to-h case of (5). Comparison of the results for the two h-to-h geometries of (4) and (5) permits an extrapolation to zero parallel forces on the H's. It shows that the changes in energy and F_z that would accompany better optimization of the parallel forces for cases (5)–(7) are small and would not alter the ordering of orientational preferences.

Finally, the results for the h-to-h geometry of case (8)

in the table, corresponding to the H_2 lying 4.48 bohrs above the surface, permit one to extrapolate roughly to a positive binding energy of 0.1–0.2 eV at the saddle point, which lies roughly 5 bohrs above the outer Rh layer. These results are somewhat suspect, because the orbital basis used to describe the Rh(001) surface was not chosen to describe the charge density accurately in the region where it is very small. Nevertheless, the absence of a dissociative adsorption barrier is consistent with the observed high sticking probability for H_2 on Rh(001) [20].

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