Ab Initio Calculation of Coverage-Dependent Adsorption Properties of H on Pd(001)

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The preferential adsorption sites, bond lengths, and vibration frequencies for H on the Pd (001) surface are determined by use of the *ab initio* pseudopotential local-orbital method. From the calculated total energies we derive a coverage-dependent absorption energy in very good agreement with experiment. We establish that at low coverages ($\theta \leq 1$), H occupies fourfold hollow sites. At higher coverages ($1 < \theta \leq 2$), islands of bridge-bonded H (local coverage $\theta = 2$) are predicted to coexist with regions of H in hollow sites.

There is growing interest in the obtaining of microscopic information about adsorption properties of atoms and molecules on transition metals from parameter-free calculations. Only recently, however, have sufficiently powerful methods been introduced[1] which describe adsorbates on extended surfaces with adequate accuracy. We report here the first calculation of coverage-dependent adsorption properties of hydrogen on the Pd (001) surface using the *ab initio* pseudopotential local-orbital method. The hydrogen adsorption properties on this surface have been investigated extensively by a variety of experimental methods such as thermal desorption spectroscopy, work-function measurements, and low-energy electron diffraction (LEED),[2] and further by He scattering[3] and by electron-energy-loss spectroscopy.[4,5] Despite the large amount of experimental information available, the details of the electronic and geometric structure of H on Pd(001) at various coverages remain open subjects. To clarify these points, we calculate the hydrogen binding geometries, adsorption energies, and vibration frequencies for this system from first principles. On the basis of the results of our total energy calculations, we present a model for the surface structure which quantitatively explains the observed[2] coverage dependence of the adsorption energy.

The *ab initio* pseudopotential local-orbital method has been described elsewhere[6] and successfully applied to bulk transition metals and the W (001) surface.[7] The total energy is calculated within the density-functional formalism. Ionic potentials are replaced by norm-conserving ionic pseudopotentials of the Hamann-Schlüter-Chiang type[8] and the basis set consists of Gaussian-type orbitals. We use the Hedin-Lundqvist[9] form of the exchange-correlation potential. The calculations are performed fully self-consistently in a slab geometry.

The adsorption bond energy of hydrogen, E_{ad}, for a given site and height h above the topmost Pd layer, is computed from $E_{ad} = \frac{1}{2}(E_{H/Pd}^{slab} - E_{Pd}^{slab} - 2E_{H}^{atom})$, since hydrogen atoms are assumed to bind to both sides of the slab. Table I summarizes the calculated[10] equilibrium values of E_{ad} for hydrogen in the on-top, bridge, and fourfold hollow adsorption sites on Pd(001). A comparison of these values establishes that at low coverages hydrogen occupies preferentially the hollow sites. This is also supported by the agreement between the calculated and measured adsorption heights[3] and vibration frequencies.[5] In the coverage range $\theta > 1$ new H adsorption sites must be found so that the surface may accommodate more than one H per surface Pd atom. Adsorption configurations involving on-top sites can be ruled out as a result of the very low adsorption-energy value. The simultaneous occupation of neighboring fourfold hollow and bridge sites is unlikely because of the very short dis-

TABLE I. Calculated and observed values of the adsorption bond energy E_{ad}, adsorption height h_0, and vibration frequency ω for H on Pd(001).

Adsorption site	Coverage θ	E_{ad} (eV) Calc.	E_{ad} (eV) Expt.	h_0 (Å) Calc.	h_0 (Å) Expt.	ω (meV) Calc.	ω (meV) Expt.
Hollow	1.0	−2.92	−2.77[a]	0.2	<0.7[b]	77	64[c]
Bridge	2.0	−2.50	· · ·	1.0	· · ·	165	· · ·
On-top	1.0	−1.86	· · ·	1.6	· · ·	217	· · ·

[a]Reference 2.   [c]Reference 5.
[b]Reference 3.

tances between the adatoms.[11,12] We thus conclude that at coverages $\theta > 1$ a monolayer of hydrogen occupying hollow sites is superseded by growing islands of bridge-bonded hydrogen with a local coverage $\theta = 2$ and with a decreased average adsorption energy. By use of the calculated values in Table I, the coverage dependence of E_{ad} can be summarized by

$$E_{ad}(\theta) = \begin{cases} -2.92 \text{ eV if } \theta \le 1 \\ -2.92(2-\theta) - 2.50(\theta - 1) \text{ eV} \\ \quad \text{if } \theta > 1. \end{cases} \quad (1)$$

This behavior, shown in Fig. 1 by the solid line, is in very good agreement with experimental data from Ref. 2. {Note that E_{ad} is related to the measured isosteric heat of adsorption H_{ad}, given in Ref. 2, and the hydrogen dissociation energy $D(H_2)$ by $E_{ad} = -\frac{1}{2}[H_{ad}^{H_2} + D(H_2)]$}. To our knowledge this is the first time that the coverage dependence of the adsorption energy has been obtained from a calculation which uses the atomic numbers as the only input. These results also support the underlying assumption that the highly mobile hydrogen atoms tend to form few large islands with bridge-bonded adsorption sites and reduce the boundary to the hydrogen phase with hollow sites.

As in all local-density-functional calculations, we find our adsorption system slightly overbound. Previous calculations indicate that this overbinding does not significantly affect energy differences in the solid state and should only result in a rigid shift of adsorption energies for *all* coverages. Indeed, displacing our predicted coverage-dependent $E_{ad}(\theta)$, shown by the solid line in Fig. 1, by a constant amount of 0.155 eV yields a remarkably good representation for the data observed in Ref. 2.

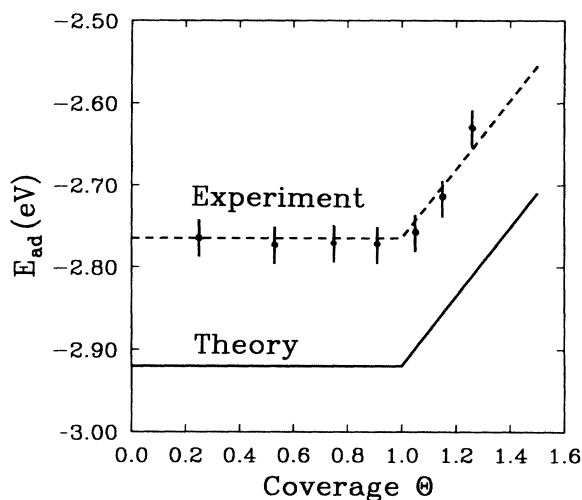The calculated small value of the hydrogen adsorption

height $h_0 = 0.2$ Å given in Table I for the hollow site also agrees with experiment.[3] It is explained by the large distance between the hydrogen and its Pd neighbors which, along the line of the hollow site, is always larger than the sum of their atomic radii. This is also the physical origin of the relatively flat H-Pd interaction potential as a function of h near the equilibrium, as shown in Fig. 2, which causes a very low value of the vibration frequency perpendicular to the surface. The H-Pd interaction potential is very anharmonic and shows a sharp increase for low values of h due to an increased charge-density overlap between the hydrogen and second-layer Pd atoms. Similar results for the hollow-site hydrogen on Pd(001) have previously been obtained from an effective-medium calculation,[12] which characterizes the adsorption system by few parameters.

As seen in Fig. 2, the hydrogen adsorption bond strength decreases in the sequence hollow → bridge → on-top site. For different adsorption sites and bond lengths, the changes in total energy result from a delicate balance of large band-structure, Hartree, and exchange-correlation terms on the one hand, and Ewald energies constituting the adsorbate-substrate ion-ion interaction energy on the other hand. The simple argument that strong adsorption bonds result from large adsorbate-substrate hybridization in highly coordinated sites is supported by comparison of the energy difference $\delta\varepsilon$ between the bottom of the Pd band and the split-off H-Pd bonding band. This quantity reflects the hybridization between the palladium and the hydrogen bands. Inspecting the densities of states, we find no split-off states for the on-top adsorption, $\delta\varepsilon \approx 0.3$ eV for the bridge site, and $\delta\varepsilon \approx 1.1$ eV for the hollow site. Of

FIG. 1. H adsorption bond energy E_{ad} as a function of coverage θ. The solid line is the behavior predicted by Eq. (1); the dashed line is a guide to the eye connecting experimental data points from Ref. 2.
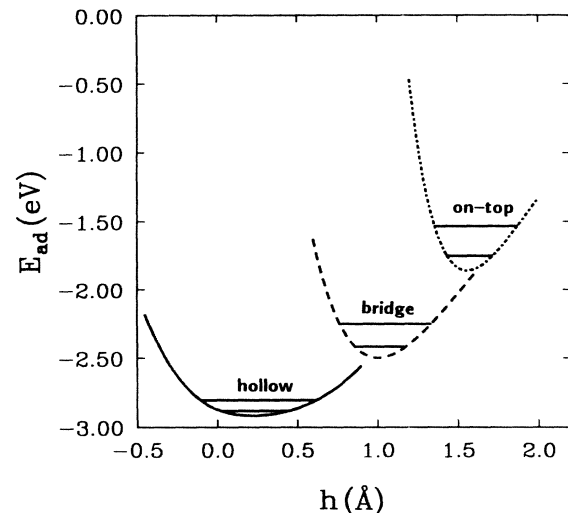

FIG. 2. H adsorption bond energy E_{ad} as a function of the adsorption height h above the Pd (001) surface. The solid, dashed, and dotted lines correspond to the fourfold hollow, the bridge, and the on-top sites, respectively. The lowest two vibrational levels are shown in the potential wells.

course, we observe a decrease of $\delta\varepsilon$ with increasing H-Pd distance. The shallow potential $E_{ad}(h)$ for hydrogen in the hollow site results from a very slow variation in the adsorbate-substrate hybridization for a large range of h, which is reflected in relatively small changes of $\delta\varepsilon$ and of the band-structure energy.

The changing environment of the hydrogen atoms in the different adsorption sites also modifies the shape of the H-Pd interaction potential, as shown in Fig. 2. With decreasing coordination number, $E_{ad}(h)$ resembles more a pairwise interaction potential which gives rise to an increasing vibration frequency. The increase in the adsorption height h_0 as one goes from the hollow to the bridge and to the on-top site is consistent with a H-Pd bond length of 1.6–1.7 Å in the two latter cases, which is equal to the sum of their atomic radii.

To illustrate the nature of the hydrogen-palladium surface bond, in Fig. 3 we present charge-density contour plots for H in the fourfold hollow site at the equilibrium height h_0. The total charge density, given in Fig. 3(a), shows a very small corrugation in this case, as observed by the He diffraction experiment in Ref. 3. An analysis of the charge-density difference shows a charge transfer
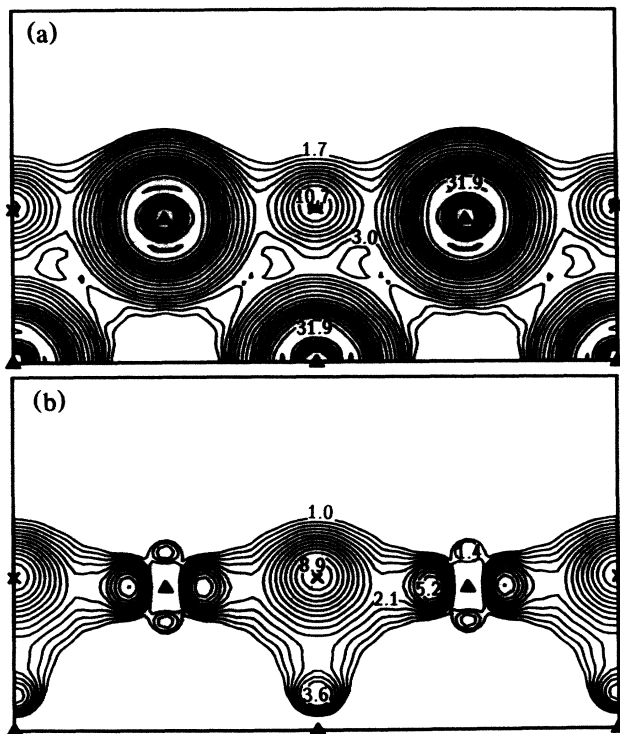

FIG. 3. (a) Calculated total charge density ρ for hydrogen occupying the hollow sites on the Pd (001) surface. The cut is perpendicular to the surface in the (110) plane. The position of Pd atoms is marked by black triangles, that of H atoms by crosses. The charge density is in units of $10^{-1}e/\text{Å}^3$; the ratio of two consecutive contours is $\rho(n+1)/\rho(n)=1.2$. (b) Charge density corresponding to the adsorbate-induced H-Pd bonding band. The plot parameters are same as in (a).

of ≈ 0.2 electron towards hydrogen, stemming mainly from Pd atoms in the topmost layer. The nature of the H-Pd bonding mechanism can be seen from the charge density associated with the H-Pd split-off band, shown in Fig. 3(b). The covalent bonds result mainly from the hybridization of hydrogen wave function with the Pd d states and are mostly localized in the topmost surface layer.

Most of our calculations have been performed on a five-layer slab consisting of three Pd layers covered on both sides with a film of hydrogen. In a three-dimensional periodic arrangement, the slabs were separated by four "layers" of vacuum and charge-density calculations did not show any charge in the vacuum region. A comparison of the adsorption-energy results to a five-Pd-layer calculation showed the deviations to lie within the experimental error indicated in Fig. 1. Similar agreement was obtained for the vibration frequencies. The completeness of our basis set and the k-point sampling of the Brillouin zone have been tested by investigation of the dependence of the total energy on an increase in the basis size and number of k points and also by comparison of calculated properties of molecular H_2 and bulk Pd to experimental values. The criterion for self-consistency requires the change in the total potential $\delta V(\mathbf{G})$ to be smaller than 10^{-4} Ry between two successive iterations for all values of $G \leq 8$ (a.u.)$^{-1}$, which in our case yields total energy differences of the order $< 10^{-4}$ eV. Our calculated work function $\phi = 5.25$ eV is in excellent agreement with available experimental values[13] of $\phi = 5.2$–5.5 eV for polycrystalline films.

In order to obtain accurate values for the heat of adsorption with a localized basis, we extended the basis set by including additional orbitals at sites not occupied by atoms. The basis set for a total-energy calculation of hydrogen in hollow sites also included orbitals at all bridge and on-top sites. The total energy for hydrogen in bridge or on-top sites has been obtained by keeping essentially the same basis and "switching" the hydrogen ionic potential to the respective sites. For the adsorbate-free Pd slab all basis sites at adsorbate positions were kept but carried zero potential. This procedure allows one to treat various geometries on equal footing in the orbital space and to obtain accurate energy differences between the adsorption sites.

The effect of potential anharmonicity on the vibration frequency ω has been considered by expansion of the lowest vibrational eigenstates of a general potential $E_{ad}(h)$ in terms of the eigenstates of a linear harmonic oscillator. Up to nine linear-harmonic-oscillator states have been used in the expansion and ω was determined from the difference of the two lowest vibrational levels. The vibrational levels are shown in Fig. 2 together with $E_{ad}(h)$. In the hollow site, this procedure yielded a vibration frequency which differed by ≈ 8 meV from the harmonic frequency $\omega = 77$ meV. Our calculation of hydrogen vibration frequencies, however, considered only H

displacements perpendicular to the surface at the high-symmetry sites. A coupling to vibration modes parallel to the surface is expected to reduce the lowest vibration frequency and bring it to closer agreement with the observed value.[5]

The adsorption data given in Table I correspond exactly to the coverage θ indicated and can be directly applied to predict average adsorption energies in the range $1 < \theta < 2$. As a result of large average adatom distances for $\theta < 1$ the adsorption energy is not expected to depend strongly on θ. This is a basic assumption for Eq. (1) and is observed in the experiment.[2] We conclude that the adsorption energies for isolated hydrogen atoms in hollow and on-top sites should lie very close to our $\theta = 1$ value. To obtain the correct value of E_{ad} at coverages $\theta > 1$, we considered bridge-site adsorption at a local coverage $\theta = 2$. Because of the small hydrogen-hydrogen distances in this geometry, the effect of interadsorbate interactions on the adsorption energy is expected to be larger. We thus expect the adsorption energy of an *isolated* H atom in a Pd bridge site to be different from our $\theta = 2$ value. The magnitude of the interadsorbate interaction energies is of course important for the determination of the adsorption phase diagrams.[14]

In conclusion, we used the *ab initio* pseudopotential local-orbital method[6] to calculate adsorption energies, bond lengths, and vibration frequencies for hydrogen on the Pd (001) surface as a function of coverage. The very good agreement between the theoretical values of $E_{ad}(\theta)$ and observed adsorption energies supports our model that at low coverages hydrogen occupies fourfold hollow sites. Beyond one monolayer coverage, islands of bridge-bonded hydrogen with a local coverage $\theta = 2$ start to develop, which decreases the average adsorption energy.

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[1]C. Umrigar and J. W. Wilkins, Phys. Rev. Lett. **54**, 1551 (1985); M. Weinert, A. J. Freeman, and S. Onishi, Phys. Rev. Lett. **56**, 2295 (1986); R. Biswas and D. R. Hamann, Phys. Rev. Lett. **56**, 2291 (1986).

[2]R. J. Behm, K. Christmann, and G. Ertl, Surf. Sci. **99**, 320 (1980).

[3]K. H. Rieder and W. Stocker, Surf. Sci. **148**, 139 (1984).

[4]C. Nyberg and C. G. Tengstål, Solid State Commun. **44**, 251 (1982).

[5]C. Nyberg and C. G. Tengstål, Phys. Rev. Lett. **50**, 1680 (1983).

[6]C. T. Chan, D. Vanderbilt, and S. G. Louie, Phys. Rev. B **33**, 2455 (1986); C. T. Chan, D. Vanderbilt, S. G. Louie, and J. R. Chelikowsky, Phys. Rev. B **33**, 7941 (1986).

[7]C. T. Chan and S. G. Louie, Phys. Rev. B **33**, 2861 (1986).

[8]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[9]L. Hedin and B. J. Lundqvist, J. Phys. C **4**, 2064 (1971).

[10]For isolated hydrogen atoms we used the result of a spin-polarized pseudoatom calculation, $E_{tot} = -13.26$ eV.

[11]A. G. Egiluz, D. A. Campbell, A. A. Maradudin, and R. F. Wallis, Phys. Rev. B **30**, 5449 (1984).

[12]P. Nordlander and S. Holmström, Surf. Sci. **159**, 443 (1985).

[13]*Solid State Physics,* edited by J. Hölzl, F. K. Schulte, and H. Wagner, Springer Tracts in Modern Physics Vol. 85 (Springer, Berlin, 1979), p. 92.

[14]K. Binder and D. P. Landau, Surf. Sci. **108**, 503 (1981).