

## Theoretical study of hydrogen adsorption on Ru(0001): Possible surface and subsurface occupation sites

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We have performed a first-principles calculation of the adsorption of hydrogen on the Ru(0001) surface. The adsorption energies associated with various hydrogen sites above and below the ruthenium surface layer are evaluated using *ab initio* pseudopotentials within the local-density-functional approximation. It is found that the surface threefold hollow site has the lowest energy and is likely to be the adsorption site for one monolayer coverage. The equilibrium position and vibrational frequency are also calculated. On the basis of energy consideration, the subsurface octahedral site is another likely adsorption site, which is separated by an energy barrier from the surface. The occupation of this site may explain the finding of two hydrogen binding states in the measurements of the work-function changes and sticking coefficients. Other electronic properties such as the hydrogen-induced states and work-function changes are also studied and comparisons with experiment are made.

### I. INTRODUCTION

Hydrogen adsorption on transition-metal surfaces has been considered as the prototypical system of surface chemisorption. It is not only the simplest adsorption system of interest, but also an important one related to the catalytic synthesis of hydrocarbons by passing CO<sub>2</sub> and H<sub>2</sub> over certain transition-metal surfaces.<sup>1</sup> Ruthenium is one of the most used catalysts for this process. Therefore hydrogen adsorption on Ru(0001), which is the close-packed surface of this hcp metal, has been the subject of extensive experimental studies. Measurements of temperature-programmed-desorption (TPD) spectra,<sup>2,3</sup> vibrational spectra,<sup>4,5</sup> angle-resolved photoemission,<sup>6</sup> surface diffusion of hydrogen atoms,<sup>7-9</sup> low-energy electron diffraction (LEED),<sup>2,10-13</sup> and work-function changes<sup>2</sup> have been performed for this adsorption system.

One of the most important subjects in the chemisorption study is to determine the atomic arrangement on the surface. It not only provides valuable information for the kinetic process, but it is crucial in explaining and interpreting various experimental data. For H/Ru(0001), possible hydrogen positions include the high-symmetry threefold hollow sites and twofold bridge sites on the surface, and some subsurface sites between the first and second Ru layers. Several experimental studies have either directly or indirectly addressed this question, but some controversies still remain<sup>14,15</sup> and a coherent model consistent with all experimental data has not emerged.

The TPD spectrum for H/Ru(0001) shows one maximum at low coverages.<sup>2,3</sup> As the coverage increases, a second peak at a lower temperature develops and at satu-

ration two broad and overlapped peaks are found in the spectrum.<sup>2,3</sup> This behavior is similar to that of hydrogen on other close-packed surfaces such as Pt(111) (Ref. 16) and Ni(111) (Ref. 17). Correlated with measured work-function changes upon adsorption and desorption, two adsorption states possessing opposite dipole moments and different sticking behavior were proposed.<sup>2</sup> However, the connection with adsorption sites is not fully determined, neither is the surface stoichiometry. In a study of coadsorption of hydrogen and deuterium on Ru(0001), a retardation of the H<sub>2</sub> and HD thermal desorption compared to D<sub>2</sub> was observed at temperatures above 300 K and was attributed to preferential penetration into the subsurface site by adsorbed hydrogen atoms at these temperatures.<sup>3</sup> Annealing a H+D monolayer at above 350 K reduces this isotope effect considerably. This was ascribed to a partial occupation of the subsurface sites by both isotopes,<sup>3</sup> although some questions have been raised for this interpretation.<sup>15</sup> Quantitative determination of the surface and subsurface population was investigated by Cu titration<sup>18</sup> and an approximately equal population was suggested for temperatures above ~320 K.

In the studies of high-resolution electron-energy-loss spectroscopy (HREELS), only two fundamental loss frequencies near 100 and 140 meV, respectively, were found for a saturated hydrogen layer on Ru(0001).<sup>4,5</sup> This result suggests the occupation of threefold hollow sites on the surface from symmetry arguments. The twofold bridge site is excluded since it has three nondegenerate vibrational modes. The finding of two fundamental vibrational frequencies is also common for hydrogen adsorbed on other close-packed transition metal surfaces,

for instance, in H/N(111),<sup>19</sup> H/Rh(111),<sup>20</sup> and H/Pt(111).<sup>21</sup> It has been demonstrated that, contrary to the results of the simple force-constant model, the parallel (asymmetrical) mode is generally softer than the perpendicular (symmetrical) model.<sup>21,22</sup>

Angle-resolved photoemission studies for adsorption below 250 K observed a hydrogen-induced band split-off below the bulk metal bands.<sup>6</sup> This feature disappears when the substrate is raised to room temperature, although about 40% of the saturation coverage is still left on the surface as indicated by the TPD results. Similar behavior was also found in the photoemission studies of H/Pd(111) (Refs. 16, 23, and 24) and H/Ni(111).<sup>16</sup> The position of this split-off band in H/Pd(111) can be obtained from calculations assuming an ordered  $1 \times 1$  hydrogen layer at threefold sites.<sup>24</sup> An overlayer-underlayer transition was first proposed to explain the disappearance of the photoemission spectra in H/Pd(111) at room temperature.<sup>23,24</sup> More data were taken in a recent study for H/Ni(111) and H/Pd(111) and a reinterpretation was given for this effect.<sup>16</sup> It was concluded that the hydrogen split-off band moves upwards continuously toward the bulk bands as the hydrogen concentration decreases until it merges into the metal bands at a certain coverage.<sup>16</sup> However, the question of the existence of subsurface hydrogen is still unresolved.

Regular LEED measurements for H/Ru(0001) observed a  $1 \times 1$  pattern for all coverages at a temperature above 80 K.<sup>2,12</sup> Because of the low scattering power of hydrogen atoms, it is difficult to separate the weak signal induced by hydrogen from that of the  $1 \times 1$  substrate to determine the hydrogen positions. The existence of some other superstructure was suggested<sup>25</sup> below 60 K and at around half of the saturated coverage, but the data have not been fully analyzed yet. Recent studies of very-low-energy electron diffraction (VLEED)<sup>12,13,26</sup> uses electrons of energy less than 40 eV to explore empty bulk and surface states above the vacuum level. The best agreement between the calculated and experimental  $I$ - $V$  curves at saturation is obtained with hydrogen occupying the fcc sites on the surface.<sup>12</sup> In addition, the measured  $I$ - $V$  curve is a function of coverage only and is insensitive to the sample temperature.<sup>11</sup> Thus the results do not support the previously suggested overlayer-underlayer transition model.

With numerous experimental data in the literature, a detailed theoretical study should aid our understanding of this adsorption system. A total-energy calculation for hydrogen occupying the fcc sites as well as the corresponding vibrational properties has been performed recently using the linear augmented-plane-wave (LAPW) method.<sup>22</sup> In this study, we will investigate the possibilities of different adsorption sites. In addition, other physical properties of interest such as the vibrational frequency, work-function change, and surface- and hydrogen-induced electronic states will also be studied. The theoretical methods include the pseudopotential approach<sup>27</sup> to describe the electron-core interaction and the local-density-functional approximation<sup>28</sup> to evaluate the total energy. A Gaussian-orbital basis set is used to represent the one-electron wave functions,<sup>29</sup> and the self-

consistent procedure is carried out in momentum space.<sup>30</sup> This method has been tested in various transition-metal systems including the bulk and surfaces and yields satisfactory results.<sup>30-33</sup> As discussed in the following sections, the surface threefold hollow sites are found to be of the lowest energy for one monolayer of hydrogen. The subsurface octahedral site may also be energetically favorable, but there is a energy barrier to get it occupied. These results will be used to reexamine some experimental data and the connection and implication will be discussed.

## II. CALCULATIONS

Total-energy calculations are performed for this chemisorption system with hydrogen atoms occupying various adsorption sites. The atomic arrangement for the (0001) surface of the hexagonal close-packed (hcp) structure is shown in Fig. 1. There are two kinds of threefold hollow sites in each  $1 \times 1$  unit cell, which differ in the relative position with respect to the second surface layer. They are labelled as fcc and hcp sites in Fig. 1, for these are the positions of the next layer of metal atoms if this is a fcc or hcp crystal. Also shown in Fig. 1 are two subsurface sites considered in our calculation: the tetrahedral and octahedral sites. The experimental lattice constants  $a=2.71$  Å and  $c=4.28$  Å were used. Some preliminary results have been reported previously.<sup>34</sup>

The pseudopotential method<sup>27</sup> is employed together with the local-density-functional approximation (LDA)<sup>28</sup>

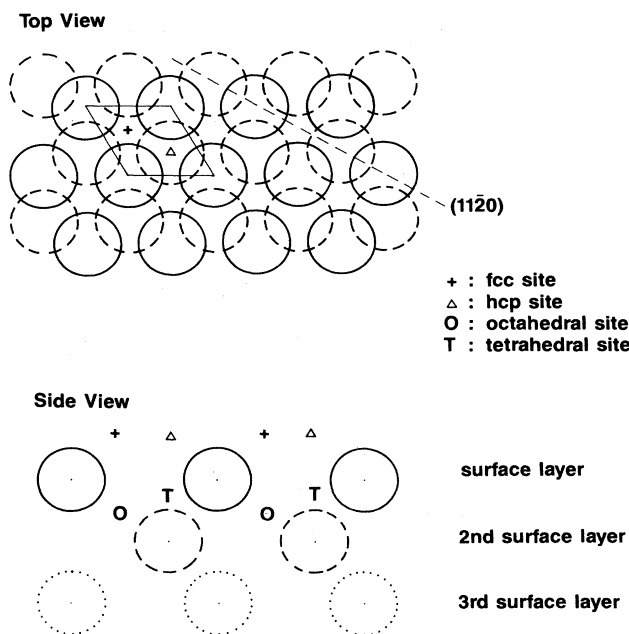


FIG. 1. Atomic arrangement of the Ru(0001) surface. The Ru atoms of first, second, and third surface layers are marked by solid, dashed, and dotted circles, respectively. The surface unit cell is also indicated. Various hydrogen adsorption sites considered in this study are labeled. The side view is shown in the (1120) plane.

in which the many-body interaction is represented by a set of one-electron equations and the exchange-correlation functional form suggested by Hedin and Lunqvist<sup>35</sup> is used. Because of the localized character of the charge density in transition metals, a basis set consisting of Gaussian orbitals is used to expand the wave functions.<sup>29</sup> The optimal decay constants for Ru and H Gaussian orbitals are determined in the calculations for the Ru crystal and for the H<sub>2</sub> molecule. Three decay constants are chosen, respectively, for H and Ru (Refs. 36 and 37) which yield reasonably good lattice constants for the Ru crystal and bond length for H<sub>2</sub>. For each decay constant, basis functions with the angular symmetry of *s*, *p*, and *d* are included for Ru while *s* and *p* functions are incorporated for H.

In our calculation, the norm-conserving pseudopotentials<sup>38</sup> as well as the initial guess of Hartree and exchange-correlation potentials are also fitted by Gaussian functions.<sup>29</sup> The self-consistent procedure is carried out in the momentum space.<sup>30</sup> In this approach the final self-consistent potential does not have any special shape constraint. More importantly, the self-consistent potential is independent of the initial fitting of the input screening potential. We included reciprocal-lattice vectors of length up to 6 (a.u.)<sup>-1</sup> in our study.<sup>39</sup>

To restore the periodicity, we used a supercell which consists of a four-layer slab plus an empty region equal to four atomic layers. This set of parameters for Ru has been tested in the calculation of the clean Ru(0001) surface<sup>36</sup> and the calculated surface relaxation and work function are both in excellent agreement with the observed values. Some detailed discussions on the calculational procedure and setup have been presented previously<sup>36</sup> and will not be repeated here. When the origin is chosen at the center of the slab at the bulk octahedral site of the hcp crystal, the corresponding space group  $D_3^3$  with 12 symmetry operations including inversion. Three special *k* points<sup>40</sup> in the two-dimensional irreducible Brillouin zone are used to carry out the summation over *k* space.

### III. ADSORPTION ENERGY

In this study ordered hydrogen layers are placed on both sides of the slab. The adsorption energy is determined by taking the energy difference between the slabs with and without hydrogen adsorbed and comparing it with the energy of isolated hydrogen atoms (13.6 eV/atom). The zero-point energy is not included.

#### A. Monolayer coverage: $\theta=1$

First we consider the configuration with one hydrogen atom per surface unit cell, which gives a ratio between H and Ru atoms of 1:1. The adsorption sites with highest symmetry on the surface are the threefold hollow sites. We place the hydrogen atoms at either of the two different hollow sites (fcc or hcp site, see Fig. 1) and evaluate the total energy as the height varies. The adsorption energy per hydrogen atom at either site is shown

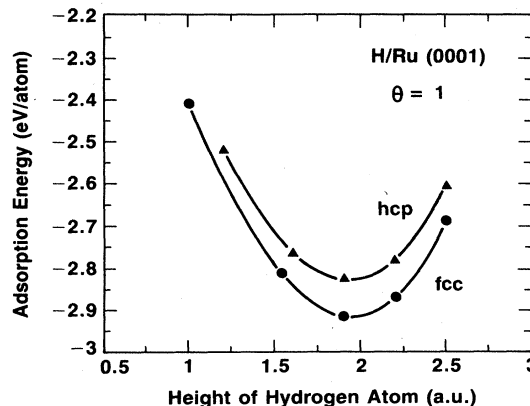


FIG. 2. Adsorption energy of hydrogen at the fcc (circles) and hcp (triangles) threefold hollow sites as a function of height measured from the surface Ru layer for monolayer coverage  $\theta=1$  (H:Ru=1:1). The energy of an isolated hydrogen atom is taken to be zero.

in Fig. 2 as a function of vertical displacement. The equilibrium position is determined by the competition between the exchange-correlation attraction and the kinetic energy repulsion in the interaction of hydrogen electrons with the substrate. In Fig. 2 the two curves have a similar equilibrium height at about 1.9 a.u. ( $\sim 1.0$  Å) measured from the surface Ru layer and an energy difference of 0.1 eV. This energy difference is similar to that found in an embedded cluster model study.<sup>41</sup> Both curves are fitted by a cubic polynomial and the minimum of the curve is determined in the fit. Our calculated adsorption energy in this  $\theta=1$  coverage is 2.9 and 2.8 eV/atom for the fcc and hcp site at a height of 1.03 and 1.02 Å, respectively. Both energies are larger than the calculated dissociation energy of 1.9 eV/atom for H<sub>2</sub> using the same theoretical parameters, indicating a dissociative adsorption. As expected, the difference in the adsorption energy for the two hollow sites is not significant, because metallic screening effectively diminishes the distinction of the two sites which differ only in the relative position with respect to the second surface layer.

We also studied the adsorption energies associated with some subsurface sites for this  $\theta=1$  coverage. The results are summarized in Table I. It is not energetically favorable for hydrogen to be adsorbed at the tetragonal site, since the energy is higher than that in a molecule. On the other hand, with an adsorption energy of 2.2 eV/atom, the subsurface octahedral site is a possible site from the energetics point of view. Yet it is less favorable in energy and more difficult to access than the surface hollow sites. To arrive at the subsurface octahedral site, the hydrogen atom has to pass through the surface fcc site (see Fig. 1). The upper limit of this migration barrier can be estimated in the present calculation by moving one layer of hydrogen atoms into the surface. It is an upper limit because no relaxation of Ru layers is considered and the barrier is therefore overestimated. The energy variation along this path calculated with the layer movement

TABLE I. List of the calculated equilibrium position  $h$ , adsorption energy  $E_{ad}$ , work-function change  $\Delta\phi$ , and the perpendicular (symmetric) vibrational frequency  $\omega_1$  for one hydrogen per surface unit cell ( $\theta=1$ ) on Ru(0001). Comparison is made with other theoretical studies and experiments. The experimental frequency listed is the higher peak in EELS measurements. The calculated  $E_{ad}$  should be compared with the calculated dissociation energy of  $H_2$ , which is 1.9 eV/atom.

	$h$ (Å)	$E_{ad}$ (eV/atom)	$\Delta\phi$ (eV)	$\omega_1$ (meV)
Present study				
fcc	1.03	-2.9	+0.2	140
hcp	1.02	-2.8	+0.2	140
octahedral	-0.88	-2.2	+0.0	100
tetrahedral		-1.7	-0.1	
LAPW (fcc) <sup>a</sup>	1.06	-2.4		140
Experiment	$1.10 \pm 0.06^b$	-2.90 to -2.51 <sup>c</sup>		141 <sup>d</sup> , 138 <sup>e</sup>
		(coverage dependent)		

<sup>a</sup>Reference 22.

<sup>b</sup>Reference 12.

<sup>c</sup>Reference 2.

<sup>d</sup>Reference 5.

<sup>e</sup>Reference 4.

is shown in Fig. 3(a). An energy barrier of the order of 1 eV is found in this case.

Among the various sites we have considered for  $\theta=1$ , the fcc hollow site has the lowest energy. The calculated equilibrium position, 1.03 Å from the surface layer, is in excellent agreement with the value of  $1.10 \pm 0.06$  Å ob-

tained from a VLEED study<sup>12</sup> which also suggested a fcc site occupation. Experimental results<sup>2</sup> for the adsorption energy vary from 2.51 eV/atom (saturated coverage) to 2.90 eV/atom (minimal coverage). Without knowing the absolute coverage on the surface in the experiment, a quantitative comparison is not possible. Nevertheless, our calculated adsorption energy for the fcc site occupation, 2.9 eV/atom, falls into the range of measured values. It is 0.5 eV larger than that obtained from a recent linear augmented-plane-wave (LAPW) calculation<sup>22</sup> using a three-layer slab and also the LDA. The origin of this discrepancy is difficult to pinpoint without systematically comparing results for other systems, since both are sophisticated calculations with different approximations involved.

In the above discussion, the relaxation of the surface metal layer is not considered. This effect may be important in certain systems when the subsurface site occupation takes place. For the current hydrogen adsorption system, the relaxation is examined for the  $\theta=1$  case when the subsurface octahedral site is occupied, which is most likely to have the largest effect. Since this Ru(0001) surface has threefold symmetry, no zigzag of surface atoms is allowed if we keep the  $1 \times 1$  symmetry. Therefore we move the whole layer of surface Ru atoms outward while keeping the hydrogen atoms at the center of the first two Ru layers. The change in adsorption energy as a function of surface layer relaxation is shown in Fig. 4. With a maximum energy gain of only 0.06 eV/atom, the effect is not significant for this system. It is therefore concluded that the layer relaxation does not change the above results in an essential manner. However, the horizontal local relaxation of Ru atoms for less than one monolayer coverage of hydrogen may be important, but this is beyond the range of our current study.

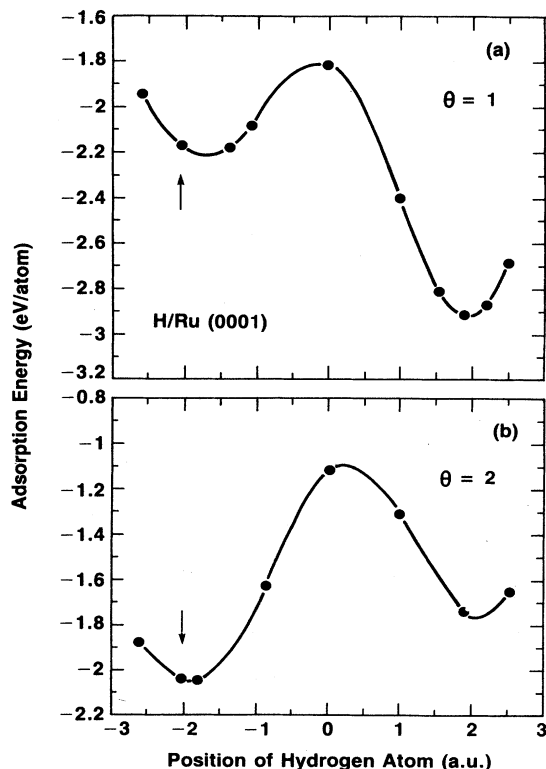


FIG. 3. Adsorption energy of hydrogen on Ru(0001) along the path from the surface fcc hollow site to the subsurface octahedral site (indicated by an arrow) (a) without and (b) with the surface hcp site occupied. The position reference is the surface Ru layer and the energy is relative to that of an isolated hydrogen atom.

#### B. Two monolayer coverage: $\theta=2$

Since the absolute hydrogen coverage could not be accurately determined in the TPD studies, speculations of  $\theta > 1$  were raised to explain some experimental data.<sup>2</sup> In our theoretical study, we can also explore this possibility.

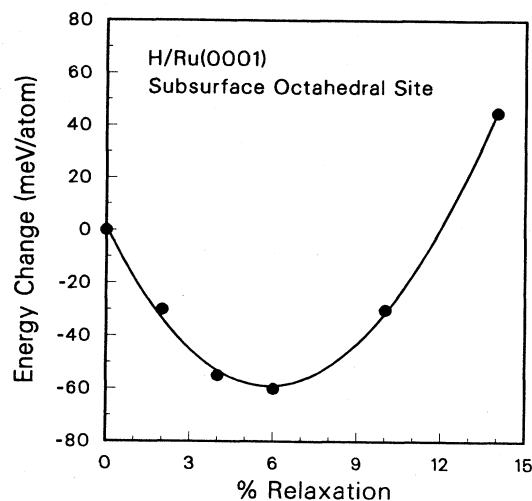


FIG. 4. Adsorption energy change of hydrogen occupying the subsurface octahedral site as a function of the surface Ru layer relaxation. The hydrogen atom is kept at the center of first two Ru layers.

Without increasing the size of the surface unit cell, we are restricted to the  $\theta=2$  case, i.e., two hydrogen atoms per Ru surface atom. Various combinations were considered in order to extract most information of hydrogen-hydrogen and hydrogen-ruthenium interactions. The results are summarized in Table II.

If all the hydrogen atoms are located on the surface, the most probable configuration is that both the fcc and hcp hollow sites are occupied. It is assumed in our calculation that these two sites have the same height and all the hydrogen atoms are moved together vertically to determine the equilibrium positions and the corresponding energy. Each fcc site is surrounded by three hcp sites and *vice versa*. It is generally recognized that there exists a repulsive interaction between hydrogen atoms occupying nearest-neighbor hollow sites on close-packed [fcc (111) and hcp (0001)] metal surfaces. Indeed it is what we find in the calculation. The average adsorption energy is reduced to 2.3 eV per atom when both fcc and hcp sites are occupied simultaneously. In other words, if the initial system has already had a  $\theta=1$  hydrogen coverage at the fcc site, adding a second hydrogen atom to the remaining hcp site in each unit cell gains only 1.7 eV per atom, which is even smaller than the energy needed to

break a  $H_2$  molecule. If we assume only a simple two-body repulsive potential between nearest-neighbor sites, it can be derived from the individual adsorption energies at the fcc and hcp sites that the effective pair repulsion is about 0.4 eV per pair. This is relatively a moderate repulsion compared with the infinite nearest-neighbor repulsion normally used in the lattice gas model to study order-disorder phase diagrams.<sup>42</sup>

In the above results for the  $\theta=1$  case, the subsurface octahedral site is found to be of interest. Therefore, we also considered the combination with one hydrogen atom on the surface and one occupying the octahedral site. First we calculate the energy change along the path from the fcc site toward the octahedral site, while keeping one separate hydrogen atom at the surface hcp site. The result is shown in Fig. 3(b). Compared with Fig. 3(a), the immediate change one notices is the raising of the energy at the fcc site, which results from the repulsion interaction between hydrogen atoms at nearest-neighbor surface sites. This effectively reduces the barrier of going into the subsurface site, which is more favorable energetically. It is worth mentioning again that the calculated barrier should be considered as an upper limit since it is obtained without including the relaxation of the Ru atoms. In addition, this barrier energy should be coverage dependent. It has been suggested that when one single atom instead of a layer of atoms moves into the surface, the local relaxation of Ru atoms greatly reduces the energy required.<sup>43</sup>

The adsorption energy at the octahedral site is 2.1 eV/atom, which changes only by 0.1 eV compared with the  $\theta=1$  case. This indicates that the interaction between surface and subsurface hydrogen atoms is weak because of the metallic screening in this system. Therefore, it is also expected that moving the surface hydrogen atoms from the hcp sites to the fcc sites with the subsurface octahedral sites occupied should not change the energy considerably. We have calculated the adsorption energy as a function of height for the fcc and hcp sites while keeping the subsurface octahedral site occupied. As shown in Fig. 5, the two curves are close together. The minimum energy positions shift by 0.1–0.2 a.u. away from the surface and the adsorption energy decreases by 0.1–0.2 eV compared with the  $\theta=1$  case, indicating a slightly weaker binding.

#### IV. VIBRATIONAL FREQUENCY

The vertical (symmetric) vibrational frequency at  $\bar{\Gamma}$  of the surface Brillouin zone (which correspond to the

TABLE II. Calculated equilibrium position  $h$ , adsorption energy  $E_{ad}$ , work-function change  $\Delta\phi$ , and the perpendicular (symmetric) vibrational frequency  $\omega_1$  for two hydrogen atom per surface unit cell ( $\theta=2$ ) on Ru(0001) at various combinations of adsorption sites.  $\omega_1$  and  $h$  refer to the surface hydrogen with the subsurface hydrogen atom (if any) fixed.  $E_{ad}$  is the adsorption energy per unit cell (two hydrogen atoms).

	$h$ (Å)	$E_{ad}$ (eV/cell)	$\Delta\phi$ (eV)	$\omega_1$ (meV)
fcc + octahedral	1.02	-4.9	-0.2	120
hcp + octahedral	1.04	-4.9	-0.1	120
fcc + hcp	1.10	-4.6	-1.1	105

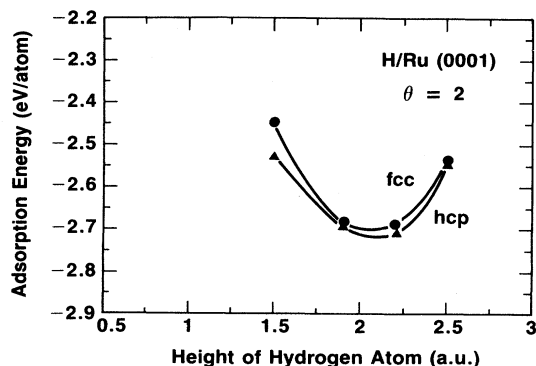


FIG. 5. Adsorption energy of hydrogen at the fcc (circles) and hcp (triangles) threefold hollow sites as a function of height (measured from the surface Ru layer) in the presence of another hydrogen atom occupying the subsurface octahedral site in the same unit cell. The energy is relative to that of an isolated hydrogen atom.

movement of the whole layer) can be obtained from our energy curve within the frozen phonon approximation. Experimentally this is usually measured by the small angle scattering, i.e., low momentum transfer, in the electron-energy-loss spectroscopy (EELS). For the occupation of either fcc or hcp site ( $\theta=1$ ), the data points in Fig. 2 are fitted, respectively, by a cubic polynomial. The vibrational frequency is then calculated from the quadratic term with the cubic term treated as a perturbation and ten lowest levels being averaged. Because of the uncertainty in the fitting, the accuracy of the calculated vibrational frequency is estimated to be 5%.

The calculated results for various sites are listed in Tables I and II. For the surface fcc and hcp sites, the vibrational frequencies are the same within the calculational error. Without the occupation of the subsurface octahedral site, the value is 140 meV. This value is in good agreement with the higher frequency peak in the EELS measurements.<sup>4,5</sup> If the octahedral site is also fully occupied and those hydrogen atoms are held fixed, the vibrational frequency for the hydrogen atoms occupying surface hollow sites is reduced to 120 meV. There are certainly coupled oscillations between the surface and subsurface hydrogen atoms which would result in various new modes. However, the current results suggest that the vertical vibrational frequency for the hollow site (140 meV) would decrease slightly if the subsurface octahedral site becomes occupied.

## V. ELECTRONIC PROPERTIES

From the calculated self-consistent charge density, we can examine the nature of binding in this system. Take the surface fcc site as an example. The total charge density in the  $(11\bar{2}0)$  plane is shown in Fig. 6(a), where the position of the hydrogen atom is indicated by a cross. Although some bonding is developed between the hydrogen and the surface Ru atom, there is not significant charge transfer taking place. This feature is manifested in Fig. 6(b), where the difference charge density with

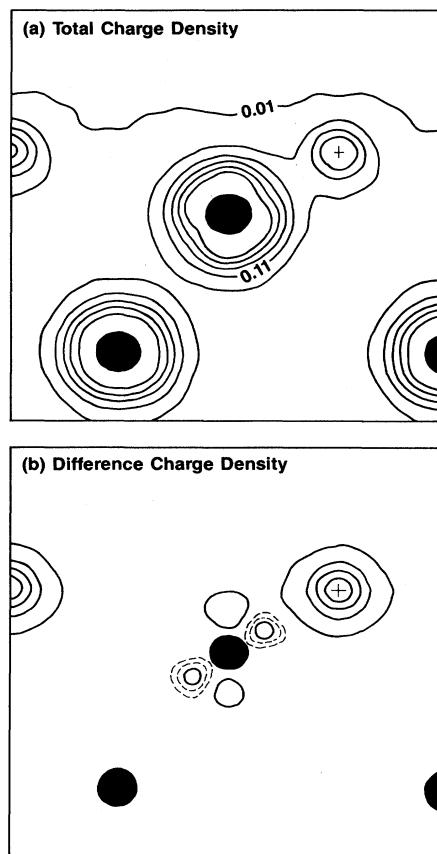


FIG. 6. Charge density [in units of  $e/(\text{a.u.})^3$ ] contour plots of H/Ru(0001) in the  $(11\bar{2}0)$  plane for hydrogen occupying the fcc hollow site (indicated by a cross): (a) total charge density and (b) difference charge density relative to clean Ru(0001). Solid (dashed) lines indicate positive (negative) values with a contour interval of 0.05 (0.01). Positive contours start from 0.01 and 0.02 in (a) and (b), respectively.

respect to the clean surface is plotted. A Mulliken population analysis of the wave function gives 0.95 electrons for the hydrogen with 85%  $s$  character. This is consistent with the fact that hydrogen and Ru have very close values of electronegativity. The interaction between the  $d$  electrons of Ru and the electron of hydrogen can be seen from the charge rearrangement near the surface Ru atom in Fig. 6(b). Similar results are found for hydrogen occupying the hcp site.

We have also studied the projected electronic bands for this surface. In Fig. 7 the electronic states for the clean Ru(0001) surface are shown along several symmetry directions on the two-dimensional surface Brillouin zone. The shaded area is the bulk states of Ru, which are calculated from the perfect crystal and projected along the (0001) direction. A band width of 7.2 eV is found in the calculation, which is in good agreement with the recent experimental value of 7.3 eV.<sup>44</sup> With a slab of four layers, the character of some bulk states, especially those at the bottom of the valence bands, cannot be totally reproduced. Consequently, the lowest eigenvalue at  $\bar{\Gamma}$  is found

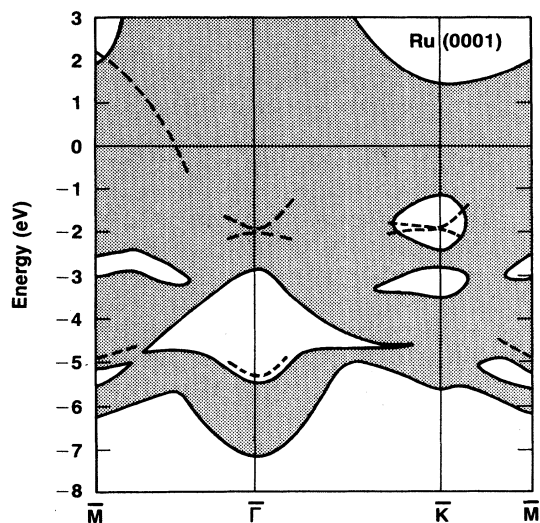


FIG. 7. Calculated energy bands of Ru(0001) along several symmetry directions of the two-dimensional Brillouin zone. Surface states and resonances are indicated by dashed lines. The shaded area is the projected bulk states for the (0001) surface.

in this slab calculation to be  $-6.7$  eV,  $0.5$  eV higher than the bulk results. The difference at the bottom of  $\bar{K}$  and  $\bar{M}$  is  $0.4$  and  $0.1$  eV, respectively. In Figs. 7 and 8, the projected bulk results (with a band width of  $7.2$  eV) is used to determine the shaded areas. Some surface states or resonances are indicated in Fig. 7 by dashed lines. The calculated surface states of  $-5.3$  eV at  $\bar{\Gamma}$  and  $-2.0$  eV, at  $\bar{K}$  are consistent with previous theoretical studies<sup>45,46</sup> and also in good agreement with the experimental values of  $-5.6$  and  $-2.0$  eV, respectively.<sup>44</sup>

By comparison, the band structure of the surface with the hydrogen atoms occupying the fcc sites is shown in Fig. 8. Besides shifting down slightly the Ru surface states or resonances, that adsorption of hydrogen induces an extra hydrogen band (shown as a dot-dashed line) below the Ru metal bands. From a Mulliken population analysis, this hydrogen-induced band corresponds to a combination of the hydrogen  $s$  orbital and the surface Ru  $d$  orbitals. The bottom of this calculated energy band is located at  $\bar{\Gamma}$  with an energy of  $-7.5$  eV and the total width is  $1.9$  eV. As mentioned above, the states at the bottom of energy bands obtained in a slab calculation are usually not deep enough. Therefore the actual position of the split-off hydrogen band is expected to be lower than that in Fig. 8 and to have a larger separation from the Ru bulk bands. If we compare the results of the slab calculation for the lowest-energy state at  $\bar{\Gamma}$  for both surfaces with ( $-7.5$  eV) and without hydrogen adsorbed ( $-6.7$  eV) the separation increases to  $0.8$  eV, instead of  $0.3$  eV seen in Fig. 8.

A very similar band structure is found for hydrogen occupying the hcp sites. This is because the fcc and hcp sites are equivalent with respect to the surface Ru layer if the second surface layer locations are not taken into account. For other adsorption sites with  $\theta=1$ , a split-off

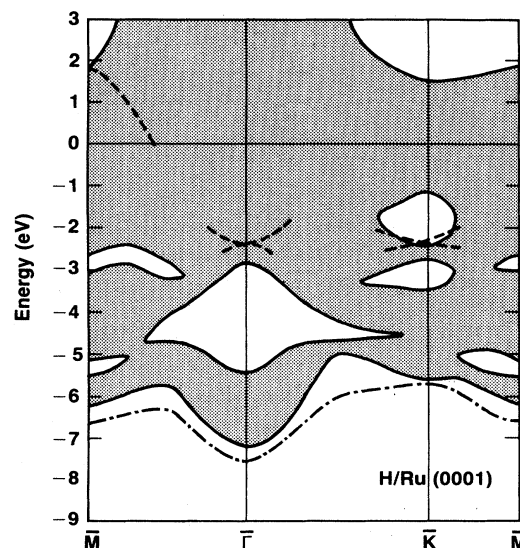


FIG. 8. Calculated energy bands of H/Ru(0001) along several symmetry directions of the two-dimensional Brillouin zone. The shaded area is the projected bulk states for the (0001) surface obtained from Ru bulk calculations. Surface states and resonances are indicated by dashed lines and the hydrogen-induced band is shown by a dot-dashed line. Both are obtained from slab calculations (see text).

hydrogen band is always found. This energy band is deeper in the case of subsurface site occupation compared with the surface site occupation. The calculated energy at  $\bar{\Gamma}$  for the octahedral site is  $-9.7$  eV, about  $2$  eV lower than that of the fcc surface site. For the cases of  $\theta=2$ , two split-off bands are usually found, each associated with one adsorption site.

The data from an angle-resolved photoemission study<sup>6</sup> of this adsorption system at an almost saturated coverage gives a hydrogen band at  $-8.1$  eV at  $\bar{\Gamma}$  with a  $1 \times 1$  dispersion of  $2.2$  eV. The experimental value for the separation at  $\bar{\Gamma}$  between the hydrogen split-off band and the bulk bands is therefore  $0.8$  eV.<sup>6,44</sup> Comparing with results of our calculation, it seems most likely that the sample has  $1 \times 1$  hydrogen atoms occupying the surface hollow sites.

The work functions of these systems can be estimated by taking the difference between the calculated Fermi energy and the average potential at the center the vacuum region between two slabs. A correction is added which sets the exchange-correlation potential to be zero at the center of the vacuum region because a vanishing charge density is expected there. The calculated work-function changes for different combinations of adsorption sites are listed in Tables I and II. A positive change (an increase) is found for hydrogen occupying surface hollow sites in the  $\theta=1$  case, while a negative change (a decrease) for  $\theta=2$ . The accuracy of the calculated values is estimated to be  $0.1$  eV. In contrast, the experimental work function changes are in the range of  $\pm 30$  meV.<sup>2</sup> Hence a direct quantitative comparison may not be possible except comparing the sign and the order of magnitude.



## VI. DISCUSSION

In the effective medium theory of surface chemisorption,<sup>47</sup> an adatom is expected to choose an adsorption site where the average clean substrate electron density has a preferred value [about  $0.01 e/(\text{a.u.})^3$  for hydrogen]. This was obtained by considering the energy gain in placing the adatom in an infinite jellium of a density equal to the average electron density of the substrate at a certain adsorption site. This approximation is expected to work best for hydrogen, since it is the smallest atom available. Our calculated valence charge density of Ru(0001) at the optimal fcc and hcp sites is 0.0142 and 0.0147  $e/(\text{a.u.})^3$ , respectively, which is of the same order as estimated by the effective medium theory and in agreement with the value of 0.0156  $e/(\text{a.u.})^3$  obtained in the LAPW calculation.<sup>22</sup> For the subsurface octahedral and tetrahedral site, the charge density is 0.0175 and 0.0392  $e/(\text{a.u.})^3$ , respectively. The former is still close to that of the fcc or hcp site, but the latter is considerably larger than the preferred value. Thus it is not surprising that the subsurface tetrahedral site is not favorable when the total energy is actually evaluated.

Comparisons of our calculated results and the measurements of the vibrational spectra,<sup>4,5</sup> photoemission spectra,<sup>6</sup> and low-energy electron reflectivity<sup>12</sup> suggest that at saturation there exist hydrogen atoms occupying hollow sites on the surface with a  $1 \times 1$  symmetry. Although energetically allowed, an additional complete layer at the subsurface octahedral sites seems unlikely, since no extra hydrogen band is observed in the photoemission spectra and this case would be inconsistent with the VLEED data. Nevertheless, partial occupation of the subsurface octahedral sites can not be totally excluded from the existing data. In this situation, the vertical vibrational frequency would shift only slightly toward the lower frequency as mentioned above; new features may not readily appear in the photoemission and VLEED spectra if the occupation fraction is not high enough.

On the other hand, the existence of subsurface hydrogen may be used to explain some puzzling experimental data. In the study of the work-function changes and sticking coefficients during adsorption,<sup>2</sup> some interesting and unusual behavior was found. The nonmonotonic change of the work function as the coverage increases suggests that there exist two different binding states with opposite dipole moments. These two states have totally different sticking properties and are well correlated with the two desorption peaks in the TPD spectra. The first state corresponds to a direct-sticking adsorption and is responsible for the initial increase of the work function. The second one has a much smaller and almost constant sticking coefficient and causes the work function to decrease. The original assignment for these two binding states is to associate them with the surface fcc and hcp sites.<sup>2</sup> This explanation was later-dropped based upon the VLEED data.<sup>12</sup> In addition, this is also an unlikely configuration from the results of the present calculation. The current explanation in the literature is to attribute the appearance of these two binding states to the lateral interactions between hydrogen atoms at the surface fcc

sites.<sup>11,12</sup> However, a recent study on the diffusion of hydrogen atoms on Ru(0001) found that the surface diffusion coefficient to be constant as a function of coverage<sup>9</sup> and no anomaly in the lateral hydrogen interactions was observed.

An alternative interpretation of the experimental data is to assign the two binding states to two sites with the second site being the subsurface octahedral site.<sup>34</sup> The surface hollow sites will be occupied first when adsorption begins since they have the lowest energy. With the energy released from adsorption, the hydrogen atoms could be very mobile on the surface, finding suitable sites to occupy. At this stage, the work function increases accompanied by direct sticking kinetics. When, in a certain region, most of the fcc (or hcp) sites are occupied, the subsurface octahedral site is an alternative to accommodate more hydrogen atoms. The repulsive interaction on the surface could induce the penetration through the energy barrier to a more stable subsurface site [see Fig. 3(b)]. As a result, a precursor adsorption process is observed while the work function starts to decrease. In the thermal desorption, although the surface hydrogen will come out first, the vacancy left behind will be filled by subsurface hydrogen because the energy relation is now better described by Fig. 3(a). Therefore effectively the subsurface hydrogen (the second binding state) gets evacuated first upon desorption even if it gets occupied later upon adsorption. These sequences are consistent with observations.

The occupation of subsurface sites on open surfaces such as Pd(110) (Ref. 48) and Cu(110) (Ref. 49) has been well established and is usually connected to surface reconstruction. For close-packed surfaces, it is still an open question. The above adsorption model is certainly a suggestion based on the present total-energy calculation. It may also be possible that the separation between the surface hydrogen atom and the Ru layer is coverage dependent and thus gives rise to nonmonotonic work-function changes, yet the unusual sticking behavior is difficult to reconcile. Without a detailed kinetic calculation, we can only address here the possibility of the subsurface occupation. Further theoretical and experimental studies are certainly needed to test this suggestion.

In a recent isotope TPD study, the difference in the high-temperature tail of the desorption spectra for  $\text{H}_2$ , HD, and  $\text{D}_2$  was attributed to the preferential penetration into the subsurface site.<sup>3</sup> This difference can be removed by annealing, which presumably establishes thermal equilibrium on the surface. It was, therefore, also suspected that this isotope effect could result from the concentration anisotropy upon adsorption, which could be removed by annealing.<sup>15</sup> However, Cu deposition onto the annealed hydrogen layer produced a new desorption peak near 400 K compared with unannealed samples.<sup>18</sup> The explanation given in Ref. 18 is the occupation of subsurface sites after annealing. It was also suggested that the binding energies of the surface and subsurface sites are similar at this low coverage.<sup>18</sup> However, our calculated results give a noticeable difference of 0.7–0.8 eV/atom between the energies of the surface hollow site and the subsurface octahedral site for a  $\theta = 1$  cov-



erage.

In summary, we have performed a first-principles calculation of hydrogen adsorption on Ru(0001) using the pseudopotential method and local-density-functional approximation. The adsorption energies of various hydrogen sites above and below the surface Ru layer are evaluated. It is found that the surface fcc site has the lowest energy for one monolayer coverage. The calculated equilibrium position, vibrational frequency, and hydrogen induced electronic states are in good agreement with existing experimental data. Possibility of additional occupation of the subsurface octahedral site is also discussed and

may be used to explain the finding of two hydrogen binding states in the measurements of the work-function changes and sticking coefficients.

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