Angle-resolved photoemission study of the clean and hydrogen-covered Rh(111) surface

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We have determined the band structure for the surface-localized states on a clean and hydrogen-covered Rh(111) surface using angle-resolved photoemission. Several of our observed bands are strikingly similar to those observed previously on Pt(111) if the Fermi level is shifted appropriately given the fewer valence electrons in rhodium. A deviation from this rigid-band behavior is observed for surface bands in the vicinity of the Fermi level near the $\bar{K}$ point of the surface Brillouin zone. We also compare our results to existing calculations. We find that these generally provide a good match to our results, although more surface bands are observed than calculated.

I. INTRODUCTION

Despite numerous studies of the properties of the Rh(111) surface, to date few have addressed its electronic structure.[1-3] This is surprising since this must play an important role in governing various important processes that occur on this surface. For example, the formation of a carbidic overlayer on this and other transition-metal surfaces is believed to be the rate-limiting factor in the catalytic-methanation reaction.[3-6] Feibelman modeled such an overlayer on Rh(111) and calculated the surface-band dispersion relations for both this system and for clean Rh(111).[3] A simple model was proposed to explain the catalytic activity.

In this paper, we report an accurate study of the surface electronic structure of a clean and hydrogen-covered Rh(111) surface at room temperature using high-resolution angle-resolved photoemission spectroscopy (ARP). Similar to our previous results on Pt(111),[7,8] we observe a rich surface electronic band structure along the symmetry lines of the surface Brillouin zone (SBZ) of the clean Rh(111) surface, while many fewer surface bands are observed on the hydrogen-saturated surface. We report a striking similarity between the electronic structure of these two surfaces if the Fermi level is shifted appropriately to take account of the fewer valence electrons in rhodium. Our current data also provide some experimental verification of Feibelman's calculation of the clean Rh(111) surface.[3] The complete verification of his model must await inclusion of data for the carbidic-overlayer surface preparation. Although successful formation of stable, periodic carbidic-carbon overlayers on low-index metal surfaces has been reported,[9-11] these results remain controversial.[12] To date, we have not been able to produce similar structures on Rh(111).

II. EXPERIMENTAL PROCEDURES

Our ARP system, located at the National Synchrotron Light Source, has been described in detail previously.[13,14] The total instrumental energy and angular resolutions are typically less than 120 meV and 1°, respectively, at full width at half maximum. A 99.999% purity Rh(111) crystal of 1 cm diameter and 0.5 mm thick was oriented to within 0.5° of the (111) bulk-crystalline axis by Laue x-ray back reflection. The surface was cleaned by many cycles combining oxygen treatment (5×10^{-7} Torr O_2 with the sample at 1100 K) and annealing to 1500 K to desorb chemisorbed oxygen, and also of neon ion sputtering (6×10^{-5} Torr Ne with the sample at 1000 K) followed by annealing to 1500 K to remove surface damage. The order and cleanliness of the sample surface was monitored by low-energy electron diffraction (LEED) and Auger electron spectroscopy. Both the clean and hydrogen-covered surfaces exhibited sharp (1×1) LEED patterns. The surface remained clean for typically 30–45 min at an operating pressure of $(0.8-1.2)\times10^{-10}$ Torr, as evidenced by the gradual disappearance of some of the more contaminant-sensitive features in the photoemission spectrum. The residual surface contaminants (CO and H) could easily be thermally desorbed by flashing the crystal to 800 K, a procedure that was done often enough to maintain spectra closely representative of the clean surface. The surface temperature during measurement was <400 K for the first spectrum following the desorption procedure, and approached room temperature after that. Hydrogen was dosed in the form of H_2 5–6 min after a cleaning cycle at which time the crystal was near room temperature. The hydrogen-saturated surface typically was prepared by exposure to H_2 at 1×10^{-8} Torr for 8 min.

III. RESULTS AND DISCUSSION

As described in more detail elsewhere,[7,8,15-18] we identify the surface states or resonances on the clean surface by doing two experimental tests. First, we apply the so-called "crud test." That is, we adsorb a certain adsorbate (H_2, in this case) on the surface to see if it causes any changes in the ARP spectra. Emission originating from surface-localized bands is often particularly sensitive to the modification of that surface, so that either the photoemission feature will be quenched or it will be shifted in binding energy. Some bulk features also exhibit pronounced sensitivity to contamination, and additional information is thus required. The other test is to check the dependence of the binding energy of those features pass-

ing the "crud test" on the momentum normal to the surface, $k_\perp$. We do so by changing the photon energy while keeping the momentum parallel to the surface $k_\parallel$ fixed. This procedure requires simultaneous variation of photoelectron-emission angle and kinetic energy. The latter is controlled by varying the photon energy between 24 and 60 eV in the present experiment. Due to their two-dimensional character, the surface features should have little dispersion with $k_\perp$. Theoretically, no dispersion at all would be observed for a true, intrinsic surface state. Some small dispersion can be expected for a surface resonance, since these may be understood to be hybrids between a true surface state and a bulk state.[19] Such an effect, for example, has been observed for a well-characterized surface resonance on Ta(011).[20] A reasonable working definition of a surface resonance is that its measured bandwidth in a direction normal to the surface is substantially smaller than the width of the bulk band in which it is embedded.[19,20] Once an observed feature is determined to be surface related, we compare it with the bulk band structure projected normal to the surface. In this way, in principle, we can determine whether it is a true surface state if the feature is located in a gap of the projection, or a surface resonance if it falls into the projected continuum having a broader bandwidth. Of course, these assignments are not precise in the absence of a measured bulk continuum. In some systems [e.g., Ta(011) (Ref. 20)] the projected bulk bands are simple enough that they can be determined experimentally and any remaining ambiguity is thereby removed. We have not found this to be possible for Rh(111) due to the complexity of the bulk bands, particularly at points off the bulk symmetry lines. This being the case, we have used calculated bulk bands.[21] This comparison with a calculated projection is not without limitation, since photoemission inherently measures an excited quasiparticle state while the calculated bands do not. Existing measurements of bulk-band dispersions for Rh(111) (Refs. 1 and 2) and the closely related Ru(0001) surface[22,23] are typically predicted by calculations to an accuracy of 0.5 eV, at least for states within a few eV of the Fermi level. We use the projections as useful guides in interpreting our data, and acknowledge some ambiguity in interpreting surface features lying close to the edge of a projected band gap or associated with relatively narrow bulk bands. The same criteria can be applied to distinguish hydrogen-induced states or resonances except that we then search for new features observed upon hydrogen adsorption instead of those modified by it.

Figures 1 and 2 provide two samples of our ARP data. These present spectra collected at $h\nu=42$ eV as a function of emission angle (or, using a simple kinematic relationship, $k_\parallel$) in the $\bar{T}$ and $\bar{\Sigma}$ azimuths of the SBZ, respectively. The spectra of the clean and hydrogen-saturated surfaces are plotted on top of each other to allow direct comparison. The peaks connected by guide lines were determined to be of surface character on the clean surface according to our criteria outlined above. The dispersion relations of these surface features give the surface band structure of clean and hydrogen-covered Rh(111) along the symmetry lines of the SBZ and are summarized in

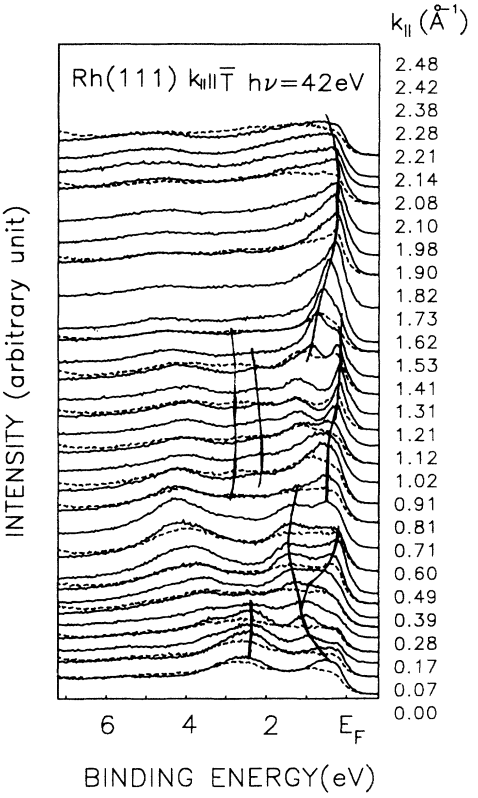

FIG. 1. ARP spectra of the clean (solid curves) and hydrogen-covered (dashed curves) Rh(111) collected along the $\bar{T}$ azimuth at a photon energy of 42 eV. The parallel momenta shown are calculated for electrons emitted from the Fermi level.

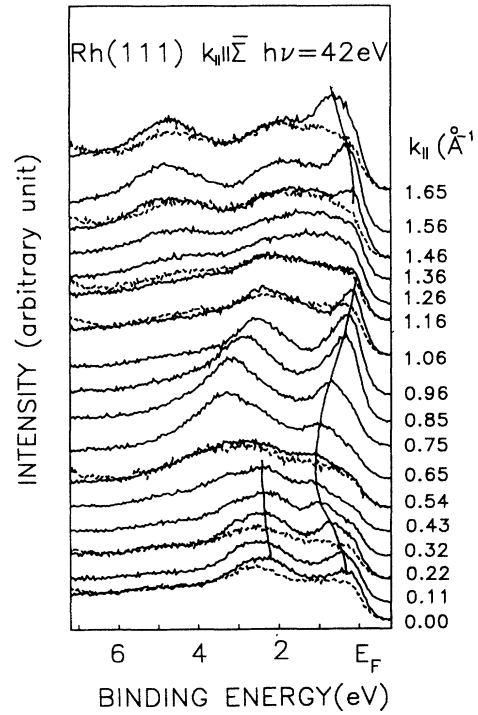

FIG. 2. ARP spectra of the clean (solid curves) and hydrogen-covered (dashed curves) Rh(111) collected along the $\bar{\Sigma}$ azimuth at a photon energy of 42 eV. The parallel momenta shown are calculated for electrons emitted from the Fermi level.

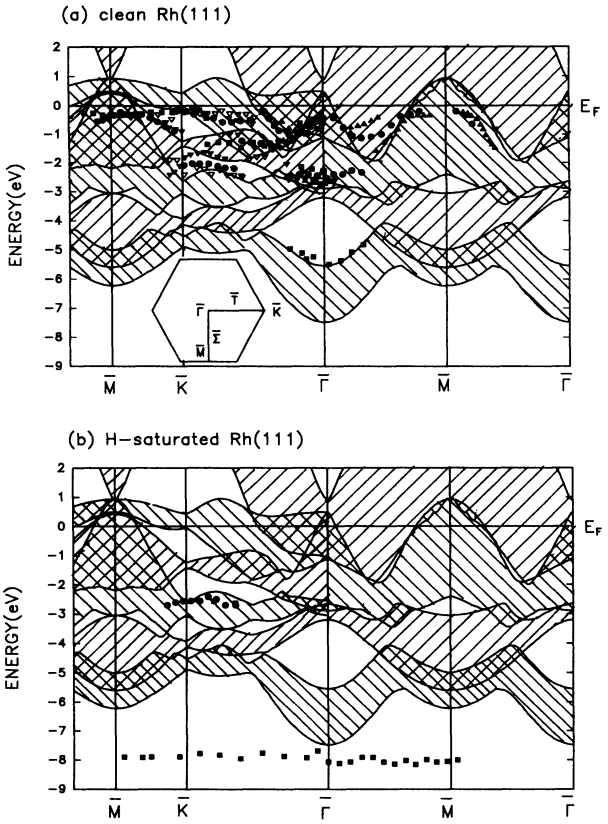

FIG. 3. Experimental surface band dispersion relations for (a) clean and (b) hydrogen-covered Rh(111) in the mirror-symmetry planes of the surface Brillouin zone. Photon energies are as follows: ●, ○: 42 eV; ■,□: 60 eV; ▽,▼: 32 eV; ▲: 24 eV.

Figs. 3(a) and 3(b). The shaded regions are the projection of the bulk-rhodium bulk-band structure calculated using a Slater-Koster three-center nonorthogonal tight-binding interpolation scheme fitted to an augmented plane-wave band structure.[21]

As shown in Fig. 3, there is a rich intrinsic surface band structure on the clean Rh(111) surface, while many fewer states are observed on the hydrogen-covered surface. All the intrinsic surface features are resonances except those inside the gap about 2 eV below the Fermi energy (E_F) around the $\bar{K}$ point. The surface resonance bands along $\bar{\Sigma}$ are of even mirror symmetry with respect to the $\bar{\Sigma}$ line of SBZ. In the following, we give a detailed description of our results by comparing them with the similar results on Pt(111) (Ref. 8) and to Feibelman's theoretical calculation.[3]

A. Comparison with Pt(111)

1. Clean surface

Previously we reported an ARP study of the clean and hydrogen-covered Pt(111) surface.[8] The results for the clean Pt(111) surface indicate several striking similarities to the electronic structure of clean Rh(111) which can be explained using rigid-band arguments. Bulk rhodium and platinum both exhibit the fcc crystal structure and have nearly the same valence electronic structure except that the latter has a higher Fermi energy to accommodate one more electron per atom. Several features in the bands shown in Fig. 3(a) closely resemble the corresponding results for Pt(111) if the latter are truncated ~1 eV below the Fermi level. For example, in Fig. 3(a), there are two surface resonance bands located, respectively, at binding energies of 0.6 and 2.5 eV at the zone center ($\bar{\Gamma}$). These have direct counterparts on Pt(111) at energies of 1.5 and 3.2 eV. Our current data indicate strong coupling between the lower of these surface resonance bands and the bulk electronic continuum as evidenced by measurable dispersion with perpendicular momentum. A related resonance has also been observed and predicted on Pd(111).[24,25] A higher energy band at $\bar{\Gamma}$ near E_F reported on Pt(111) is not observed on Rh(111), presumably because it lies above the Fermi level. The more tightly bound surface band near 5.5 eV binding energy on Rh(111) at $\bar{\Gamma}$ was not reported for Pt(111). This feature only appears at photon energies near 55 eV. As observed on the noble-metal (111) surfaces,[26] the final state is strongly coupled to the slowly decaying surface-state wave function at final perpendicular momenta corresponding to the L point of the bulk Brillouin zone which is sampled near this photon energy. On Pt(111), we did not focus on this binding-energy region and collected few spectra in this photon-energy regime. We believe, however, that a similar state exists on Pt(111).

There are also rigid-band relationships between the Fermi contours for the two surfaces. For example, the higher band at $\bar{\Gamma}$ disperses downwards away from the symmetry point in both azimuths before splitting into two bands. The upper of these split bands in both azimuths disperses up in energy, roughly following the edge of the continuum formed by bulk band 6. It eventually crosses the Fermi level at $k_{\parallel}=0.70$ Å along $\bar{T}$ and $k_{\parallel}=0.76$ Å along $\bar{\Sigma}$. We saw exactly the same behavior on clean Pt(111) except for the corresponding crossings which occur at larger values of $k_{\parallel}$ because of the higher Fermi level.[7,8] We traced these crossings throughout the SBZ on Pt(111) and found that they form a hexagonal electron pocket in the two-dimensional (2D) Fermi contours which was nearly degenerate with the edge of the projection of the bulk Fermi surface formed by the sixth bulk band. This pocket would also be observed on Rh(111), except that its size would be smaller due to the reduced number of valence electrons. The heavy nesting of this hexagonal contour might cause the surface-phonon anomalies on Rh(111), as speculated for Pt(111), except that the nesting vector would be somewhat smaller on the former. On Pt(111), we surmised that this feature was associated with the corresponding edge of bulk band 6, and the same is true on Rh(111). To distinguish these bands as "surface resonances" rather than "bulk features which are particularly sensitive to contamination" may appear to be a semantic exercise. However, they are seen with the same 2D dispersion relation at several photon energies implying significant 2D character. Bulk band 6 is highly dispersive, so the features clearly behave more like surface resonances than bulk features.

An additional similarity between Rh(111) and Pt(111) exists for the lower components of the split band along $\bar{\Sigma}$. This disperses briefly downward, and then reverses direction to cross E_F near the $\bar{M}$ point. The band returns below E_F on the other side of the $\bar{M}$ point with the appropriate symmetry to be associated with the SBZ. This result signifies the existence of a hole pocket in the 2D Fermi contours centered at the $\bar{M}$ point. The corresponding band was observed on Pt(111), but in that case the higher Fermi level kept the surface-band extremum below E_F so that no Fermi contour was observed.

A final similarity between the two surfaces is observed for the bands which exist inside the gap about 2 eV below E_F near $\bar{K}$. Careful inspection of our spectra collected at the $\bar{K}$ point as a function of photon energy provides a rough estimate of the positions of the upper and lower edges of this gap. These bands lie inside the gap and are thus true surface states. On Pt(111), we were not able to prove whether one or two states exist inside the corresponding gap. On Rh(111), two bands are distinctly observable which appear to become degenerate at $\bar{K}$. Hydrogen adsorption quenches one of these bands and, as shown in Figs. 1 and 3(b), shifts the other band down in energy such that it is located outside the gap upon saturation. Similar behavior is observed on Pd(111).[24,25]

It may be surprising that these two surfaces exhibit such similarity. Platinum is a 5*d* metal and the spin-orbit interaction and other relativistic effects might be expected to have a more pronounced impact upon surface electronic structures. However, most of the surface features we report are associated with band gaps and/or band edges produced upon projection of the bulk bands onto the SBZ. Many of the gaps are produced by symmetry effects so that, aside from energetic shifts of a few tenths of an eV, one should not really expect these relativistic effects to induce a major perturbation.[15]

A significant deviation from rigid-band behavior is observed along $\bar{\Gamma}$ near the Fermi level between $\bar{M}$ and $\bar{K}$. There is a flat band on Pt(111) located just below the Fermi level in the middle of the bulk continuum between the top two gaps around the $\bar{K}$ point. This band, however, is not cut off by the lowered Fermi level on Rh(111) as expected. Instead, it moves down and is shifted closer to the zone center as if squeezed against the gap below it by the Fermi level. Our data do not show clear evidence of this band crossing E_F towards the zone center, as was observed on Pt(111).[8] The spectra are complicated and there is no really well-defined crossing further out in the zone either. On Pt(111), the corresponding band forms a small triangular electron pocket on the 2D Fermi contours, although resonance with the bulk bands implies that the edges of the pocket are not very distinct. There are necessarily significant changes in this part of the Fermi contours on Rh(111).

Perhaps the most surprising facet of our results is for the surface resonance just below E_F near the $\bar{M}$ point of the second Brillouin zone along $\bar{\Gamma}$ (see spectra in Fig. 1). One would expect the same resonance to appear near the equivalent $\bar{M}$ point along $\bar{\Sigma}$. Our data clearly show only the aforementioned surface resonance near $\bar{M}$ along $\bar{\Sigma}$ which moves above the Fermi level (see Fig. 2). The measured dispersion along $\bar{\Sigma}$ is reasonable in light of rigid-band arguments, but the full situation must be more complex.

An interesting perspective of these Fermi contour results near $\bar{K}$ is offered by evaluating the filling of the various surface bands. In bulk platinum, for example, the Fermi surface consists of an electron pocket formed by band 6 and a complex hole structure formed by band 5. Since there is an even number of valence electrons, these must have the same volume to ensure charge neutrality. Qualitatively similar considerations should be operative in the surface orbits. The criterion of overall charge neutrality is more subtle since the surface bands are not entirely localized to the outermost surface layer and surface resonances or the tails of the bulk wave functions contribute to achieving overall neutrality of the surface region. Nonetheless, it is useful to consider charge-neutrality arguments in applying the rigid-band arguments to surface systems. By integrating Fermi contours, we find that the hexagonal electron orbits on Pt(111) and Rh(111) hold ~ 0.9 and ~ 0.5 electrons/atom, respectively. The hole pocket near $\bar{M}$ on Rh(111) holds ~ 0.1 holes/atom. The net increase in electrons from rhodium to platinum in these "rigid-band-like" orbits is thus ~ 0.5 electrons. Since this is less than 1, the change in the number of valence electrons suggests that some other degree of freedom is required to maintain neutrality. We suggest that the diffuse resonances which bracket $\bar{K}$ on both surfaces exist primarily to allow the surface to become approximately neutral. The resonances shift up or down as required to achieve this condition.

2. *Hydrogen-covered surface*

The hydrogen-covered Rh(111) surface resembles hydrogen-covered Pt(111) in its scarcity of the intrinsic surface states and resonances. Our data only show two such states on Rh(111) [see Fig. 3(b)] compared virtually to none on Pt(111). One of the bands in Fig. 3(b) is derived from a clean surface state which is shifted down upon hydrogen adsorption as mentioned above. The other band lies below the bulk projection (8 eV below E_F) and attributed to the H(1*s*) split-off state which is commonly observed on other (111) surfaces of transition metals.[27] It presumably also exists on Pt(111), although we did not seriously search for it.

B. Comparison with theoretical calculation

The electronic structure of a clean Rh(111) surface has been calculated by Feibelman using self-consistent linear combination of atomic orbitals.[3] We reproduced the experimental results in Fig. 3(a) in Fig. 4, along with Feibelman's calculated surface bands. Nearly all the surface-localized states predicted by his calculation are confirmed by our results. In the calculation, there are two surface resonances around the center of the SBZ which are bound by 2.5 and 5.4 eV at the $\bar{\Gamma}$ point, respectively. The two more tightly bound bands at $\bar{\Gamma}$ reported here agree with these two calculated resonances very well. They lie 2.5 and 5.5 eV below E_F at zone center, respectively. The lower of these disperses parallel to the

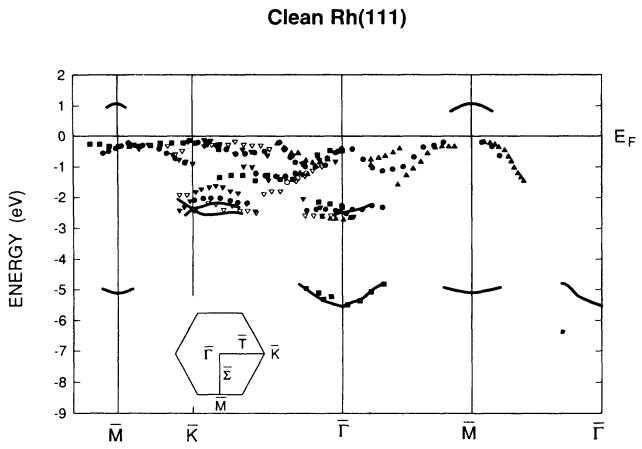

FIG. 4. Experimental surface band dispersion relations for Rh(111) (points) compared to the calculated dispersions (solid curves) from Ref. 3. The data are identical to those in Fig. 3(a). The projected continuum has been removed for clarity.

edge of the lowest bulk-band projection just like the calculated one. The match between the calculated and measured dispersion relations for this state is perhaps better than one might hope, given the limitations of calculations based upon the local-density approximation in treating experimental quasiparticle dispersion relations. On Ru(0001), a similar state is confirmed by both theory and experiment.[3,22] The upper calculated band near $\bar{\Gamma}$ does not extend quite as far as we measured, particularly in the $\bar{T}$ azimuth, but this might reflect simply a different experimental vs computational threshold for distinguishing surface bands. The calculation also shows two surface bands inside the bulk projected gap about 2 eV below E_F near the $\bar{K}$ point. Like the experimental bands, the calculated bands span most of the gap and cross each other at the $\bar{K}$ point. While the shapes of these two bands are well reproduced, the calculated bands are shifted down relative to the experiment by ~ 0.5 eV.

Around the $\bar{M}$ point, Feibelman also predicted a surface state ~ 1 eV above E_F and a surface resonance ~ 5 eV below E_F which apparently have no counterparts in our experimental results. We cannot measure the former using photoemission. However, it is possible that one of the bands which we observe to cross E_F along $\bar{\Sigma}$ is an extrapolation of this band, and that the calculation did not distinguish it due the experimental vs computational threshold problem mentioned above. An alternative origin for the resonances observed but not calculated along $\bar{\Sigma}$ is offered by comparison to noble-metal surfaces.[26,28] These surfaces exhibit related states just above the d bands, but also have shown states at slightly higher binding energy that are related to projected gaps opened by the spin-orbit interaction.[29] If similar states exist on Rh(111), they would very likely connect to the observed band that forms the hole pocket near $\bar{M}$. Concerning the more tightly bound feature near $\bar{M}$ in the calculation, we observed some features in our spectra at high binding energy near $\bar{M}$ which exhibited some surface character. However, the data we have did not enable us to assign them as surface resonances.

Apart from the above similarities, all the other experimental features in Fig. 4 apparently do not have theoretical counterparts. We did not see any substantial difference between these surface features and the ones predicted by the calculation in terms of the 2D surface characteristics. However, all these bands are resonances and thus are often not easily predicted by calculations of slabs having a finite number of layers. The distinction of a surface feature in a slab calculation is arbitrarily determined by a threshold for the amplitude of a particular wave function of the surface layer. It is interesting to note that Louie's electronic structure calculation of the Pd(111) surface[24,25] gives some states that qualitatively resemble some of the surface features in Fig. 3(a) which could not find their counterparts in Feibelman's calculation. It is likely that if a lower threshold to distinguish surface features had been used in Feibelman's calculation, more of our observed bands would be predicted.

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