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The Bonding of H to Ni, Pd and Pt Surfaces

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Abstract

The bonding of H to the (111) surfaces of Ni, Pd and Pt has been studied using angle resolved photoelectron spectroscopy. H adsorbed onto a cooled substrate produces photoemission spectra characteristic of chemisorption. In this state the H atoms form a diatomic molecule. Heating the chemisorbed layer to 300 K results in an irreversible transition of the H atoms into a subsurface site.
The interaction of a H atom with a transition metal is illustrated by the potential energy diagram shown in Fig. 1a. The surface bond is characterized by the heat of adsorption \( \Delta H_{\text{ads}} \) while the equivalent quantity for the bulk is the heat of solution \( \Delta H_{\text{sol}} \). In general the heat of adsorption is larger than the heat of solution resulting in a higher concentration of hydrogen at the surface than in the bulk. The objective of this study was to investigate the electronic properties, and consequently the nature of the surface bond of adsorbed H on a series of transition metal substrates where the interaction of the H with the bulk metal is quite different. Table 1 lists some of the physical properties of the chosen substrates, Ni, Pd and Pt. The heat of solution for H is positive for Pd, negative for Ni and more negative for Pt, while the heat of adsorption has a different trend (Ni, Pd then Pt).

The chemisorption of H on Ni, Pd and Pt has been studied extensively but the nature of the bond to the surface is still unclear. For example, consider the adsorption of H onto Ni. Angle integrated photoemission spectra of H adsorbed at room temperature on Ni(111) showed a peak in the difference curves 5.8 eV below the Fermi energy, with a 2.5 to 3 eV width. This level was interpreted as the H-Ni bonding level. Its energy position and width were used by Muscat and Newns to show theoretically that the d-bands in Ni play a crucial role in the H bond. Himpsel, Knapp and Eastman demonstrated using angle resolved photoemission that the peak observed 5.8 eV below the Fermi energy was not due to a H-bonding level but to enhancement of the direct transition from the bulk's band of Ni. H adsorption at room temperature quenched a s-p (\( \Lambda_1 \)) surface state on Ni(111) but did not produce a bonding level split-off from the Ni bands. These authors believed that they had observed a "new type of chemisorption bond" on a transition metal, where the bonding was predominantly with the free-electron-like s band.
The reported photoelectron spectra of H adsorbed on Pd and Pt are also inconsistent. Adsorption at 80 K on Pd (Pt) (111) produced a peak in the difference curve at 6.4 eV (7.5 eV) below the Fermi energy for a photon energy of 21 eV, but room temperature adsorption of H on Pd(111) did not produce a bonding state, split-off from the bulk bands. Also, adsorption of H at 200 K onto a stepped Pt(111) surface did not produce a bonding split-off state.

We have investigated in detail the angle and energy dependence of the photoemission spectra obtained from the clean and H exposed (111) face of Ni, Pd and Pt as a function of substrate temperature and H exposure. A quite simple picture emerges for the bonding of H, which is qualitatively the same for the three metals. Adsorption of H onto a clean substrate at low temperature always produces a bonding H level split-off from the d-bands. The presence of this H split-off state is accompanied by a large perturbation of intrinsic d-like surface states. Warming the adsorbed layer to near room temperature causes an irreversible conversion of H into a bonding site where the split-off state is not visible and the d-like intrinsic surface states are unaffected. The qualitative description just given is independent of exposure (coverage). We will show that the nature of the low temperature bonding state can be determined by comparison with theoretical calculations of the H induced surface electronic states, and postulate that the equilibrium site of H, which is achieved by warming the crystal, is in or under the first plane.

Fig. 2 shows a set of characteristic spectra taken at \( \hbar \omega = 40 \text{ eV} \) and normal emission. Each panel contains a spectrum of the clean metal and a spectrum after H exposure.
The spectra on the left are for adsorption of H onto a cooled substrate (T ≈ 100 K). The adsorption of H produces a new energy level (marked by the arrow) split-off from the d-bands and causes dramatic changes in the d-band region of the spectra (especially for Pd and Pt). The $H_L^s$ substrate bonding energy level exhibits considerable dispersion with the parallel component of momentum for the coverages shown in Fig. 2. Fig. 3 shows the measured dispersion of all of the hydrogen induced surface bands in the photoelectron spectra of H on Pd(111), compared to Louie's calculated H induced bands. The split-off state has the periodicity corresponding to a (1x1) overlayer, or islands of (1x1) structure. The energy of the split-off state in normal emission was observed to move towards the Fermi energy (≈ 1 eV for Pd and 1.5 eV for Ni) for low coverages. This is simply a result of the disappearance of dispersion due to increased H-H spacing or more likely to very small island size at low coverage. The split-off state could be observed for exposures as low as $\approx 10^{-7}$ torr·sec, while the effects of the adsorbed H on the d-surface states could be seen at even lower exposures, due to the large cross section. For the (111) Ni surface the s-p ($\Lambda_1$) surface state at the SBZ center (0.25 eV below $E_F$) and d-like surface states at the SBZ edge are quenched or shifted when H is adsorbed onto a low temperature substrate. We have identified six bands of surface states or resonances on clean Pd(111) that are quenched or shifted upon H adsorption at low substrate temperatures (Fig. 3).

For the purposes of this letter it suffices to say that it is possible to understand in microscopic detail the nature of the hydrogen-surface bond in this low temperature state.
scopy (Ni$^6$, Pt$^7$), LEED (Ni$^8$) and theoretical calculations of the photoemission spectra as a function of the binding site (Pd$^9$). The present study determines the electronic states at the surface. The substrate d electrons are undoubtedly involved in the surface bond$^9$.

The spectra on the right of Fig. 2 show the consequence of warming an adsorbed layer to near room temperature or exposing at room temperature. The split-off state is not visible and all of the d-like intrinsic surface states are unchanged with respect to the clean spectra. H is invisible, except for quenching the s-p ($A_1$) surface state on Ni(111)$^{13,16}$ and changing the work function. Thermal desorption measurements and comparison of our work function change with previous estimations of the coverage vs. work function indicate that there is $\sim \frac{1}{2}$ of a monolayer of H present in the spectra on the right of Fig. 2$^{17,18,19}$. The conversion which occurs near $\sim 320 \text{ K}$, 270 K and 270 K for Ni, Pd and Pt for 10 sec heating is irreversible for all exposures of H. If the crystal is cooled back down to 100 K the spectra look like the high temperature spectra. Likewise, if H is adsorbed at room temperature and then the crystal is cooled the spectra do not revert back to the low temperature adsorption spectra.

The interpretation of these data is superficially quite easy. H adsorbs on a low temperature substrate as atoms bound in the three fold surface site$^6,7,8,9$. This is not the lowest energy site. Warming the crystal causes a phonon assisted conversion to a lower energy site. Fig. 1b shows a schematic potential energy diagram for the multiple binding states at the surface. This diagram should be viewed with caution, because it is a multiple coordinate plot. For example if the substrate atoms are held in a fixed position the potential well inside the surface may not exist. The substrate atoms move to accommodate the H. The most likely site for the
equilibrium H state is the octahedral site under the surface plane. This is the site which would be occupied in a hydride. The multiple peaks in the thermal desorption spectra \(^{17,18,19}\) result from the competition between conversion and desorption. At low coverage all of the H converts, while at high coverages part of the adsorbed H desorbes. It is possible that the two states coexist at low temperatures.

We postulate the subsurface site for the equilibrium phase because it is consistent with our observation that the d-like intrinsic surface states are unperturbed in this phase\(^20\) and with the fact that inelastic electron scattering has not been able to see H-metal vibrational modes above the transition temperature\(^6,7\). The s-p (\(A_1\)) surface state on Ni(111) is quenched by H under the surface because this type of surface state penetrates deeper into the bulk than the very localized d surface states\(^9,20\).

The only unresolved feature of the spectra for the equilibrium H state is the absence of a H split-off state. Photoemission spectra of Pd hydride show a split-off state 5.4 eV below the Fermi energy\(^21\). Either the photoionization cross-section of the split-off state in our spectra has decreased dramatically compared to the equivalent state for either adsorbed H or Pd hydride, or a split-off state doesn't exist. If it does not exist then the H\(_s\) electron must be mixed in with the substrate s-band. Both explanations require the bonding in the subsurface site to be different than either the hydride bond or the low temperature H bond.

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Figure Captions

1. Schematic potential energy diagram for an atom of H between the gas phase (left) and the bulk of a transition metal (right). (a) Single surface adsorption site; (b) two state diagram proposed for H adsorption.

2. Normal emission photoelectron spectra for H adsorbed on Ni, Pd and Pt.

3. Experimental (points) and theoretical surface bands for (1x1) H on Pd. The shaded region is the projection of the bulk bands onto the SBZ. The theory is for H bound to the surface in a three fold site with a metal-H spacing of 1.7 Å. The open circles are weak peaks observable in a difference spectra.
Table 1: H Interaction Energies

<table>
<thead>
<tr>
<th>Metal</th>
<th>$H^\cdot V$</th>
<th>$E_{\text{H}^\cdot V}$</th>
<th>$E_{\text{H}^\cdot V}$</th>
<th>H-metal bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>eV</td>
<td>eV</td>
<td>eV</td>
<td>H \text{H}^\cdot V</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.10$^2$</td>
<td>0.5$^4$</td>
<td>0.41$^2$</td>
<td>1.84$^2$</td>
</tr>
<tr>
<td>Pd</td>
<td>+0.20$^2$</td>
<td>0.46$^4$</td>
<td>0.23$^2$</td>
<td>2.05$^a$</td>
</tr>
<tr>
<td>Pt</td>
<td>-0.26$^3$</td>
<td>0.23$^4$, 0.37$^5$</td>
<td>0.27$^3$</td>
<td>2.08$^2$</td>
</tr>
</tbody>
</table>

*Surface properties for (111) face.

(a) Pt was estimated using $\Delta V = 2.9$ Å$^3$ for H absorption$^2$.

(b) These bond lengths were determined from the vibrational spectra using a pair-wise interaction model. Ni is Ref. 6 and Pt is Ref. 7.
References

16. The Ni spectrum in Fig. 2 does not show a large reduction near the Fermi energy because the cross-section for the s-p surface state is small at 40 eV. It is seen at lower photon energies.
20. Theoretical calculations show that H and N bound under the first plane of Ti do not destroy d-like surface states.
NORMAL EMISSION, $\hbar\omega = 40$eV

10L AT 150K
$\Delta \phi = 0.15$eV
CLEAN

2L AT 100K
$\Delta \phi = 0.17$eV
CLEAN

10L AT 100K
$\Delta \phi = -0.21$eV
CLEAN

10L AT 100K
CLEAN

5L AT 300K
$\Delta \phi = 0.12$eV
CLEAN

5L AT 300K
$\Delta \phi = 0.14$eV
CLEAN

10L AT 300K
$\Delta \phi = -0.16$eV
CLEAN

INITIAL STATE ENERGY (eV)
H₂ ADSORPTION

E₀
DATE FILMED - 8