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Adsorbate-Level Splitting in Hydrogen Chemisorption

B. Feuerbacher and R. F. Willis

Surface Physics Group, Astronomy Division, European Space Research and Technology Centre, Noordwijk, Holland

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The electronic energy levels of a hydrogen (1×1) monolayer adsorbed on the (100) tungsten single-crystal face have been investigated by angle-resolved photoemission. *Three* bands of adsorbate levels are found that disperse and split with angle, at energies of about 2, 6, and 12 eV below the Fermi level. The results suggest that hydrogen chemisorption takes place by interaction with localized directional surface-group orbitals of the tungsten *d* band.

The adsorption of hydrogen on the (100) surface of tungsten can be regarded as a system that models the bonding of a simple *1s* adsorbate to a tight-binding *d*-band substrate. As such it has received considerable theoretical attention,¹⁻⁷ particularly as regards the extent to which a localized-orbital approach provides a viable model. Distinct practical advantages of the hydrogen-tungsten system have stimulated a large amount of experimental work using surface-sensitive techniques such as thermal desorption,⁸ low-energy electron diffraction (LEED),⁹ electron-stimulated desorption,¹⁰ and field-emission¹¹ or photoemission spectroscopy.¹²⁻¹⁴ This Letter describes results of a complete series of angle-resolved photoemission studies on adsorbate-induced resonance levels of a hydrogen monolayer (full coverage) on a W(100) surface. *Three* bands of adsorbate-resonance features are found at energies around 2, 6, and 12 eV below the Fermi level, which disperse and split with polar angle. The relatively narrow width of the adsorbate-induced photoemission spectral features, and their apparent grouping in the angular distribution, is interpreted as being indicative of chemisorption bonds involving only selective groups of substrate *d* orbitals,^{2,5} leading to localized, directional bonding within a surface molecular complex.¹⁵

The experiments have been performed in an ultrahigh-vacuum system with a base pressure below 1×10^{-10} Torr. The cleaned crystal was placed in the center of a metallic sphere¹⁶ that ensured an electrostatic and magnetically shielded "field-free" region. Light was incident at 45°

to the crystal surface, and a slot along the periphery of the sphere allowed the emitted photoelectrons to enter a 127° electrostatic deflection analyzer with 0.2-eV energy resolution, sampling a $2^\circ \times 2^\circ$ solid angle. Polar scans were possible for all azimuth directions, but the results presented here are restricted to the principal $\langle 10 \rangle$ and $\langle 11 \rangle$ azimuths. Measurements were performed on saturation-coverage (1×1) hydrogen monolayers to avoid complications due to adsorbate-induced surface-umklapp processes that occur at submonolayer coverages.¹⁴ The light source was an open helium resonance lamp, which caused the pressure in the system to rise during operation to 1×10^{-8} Torr due to He gas. The present data were taken after initial saturation coverage had been obtained with a background hydrogen pressure of 1×10^{-7} Torr in the chamber. The results were later cross checked against data obtained in a closed vacuum system of better than 1×10^{-10} Torr at 10.2-eV excitation energy, to ensure that the stream of neutral He atoms from the light source did not cause changes in the observed adsorbate system.

Measurements of photoelectron energy distribution spectra were recorded for clean and hydrogen-covered surfaces consecutively in 5° polar-angle steps along the two principal azimuth directions $\langle 10 \rangle$ and $\langle 11 \rangle$. Typical results are shown in Fig. 1 for normal emission ($\theta = 0^\circ$), 30° , and 60° polar angle along the $\langle 10 \rangle$ azimuth. The spectra for normal emission agree with previously published results.^{12,17} A prominent peak of twice the intensity of the substrate emission is found in the

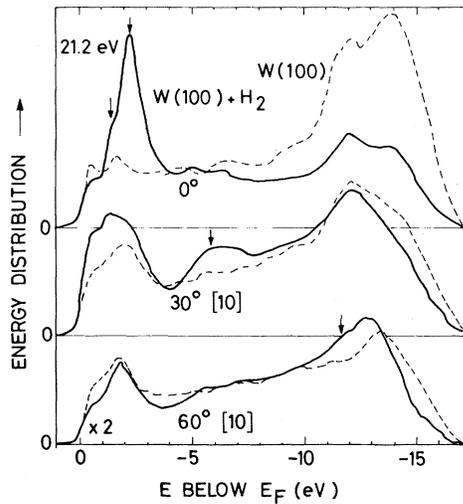


FIG. 1. Angle-resolved photoelectron energy distribution spectra for normal emission and 30° and 60° polar angles along the $\langle 10 \rangle$ azimuth. Spectra are shown for the clean (100) face of tungsten (dashed line) and after saturation hydrogen adsorption.

hydrogen-monolayer spectrum at an energy 2.3 eV below the Fermi level, with a width of only 1 eV. A remarkably strong suppression of normally emitted low-energy inelastic electrons is also observed for the hydrogen-covered sample. The measurements at 30° show an adsorbate doublet around -6 eV, while spectra taken at 60° emission angle reveal additional structure around -12.5 eV. The angles of observation for adsorbate-induced peaks depend strongly on the final-state energy of the emitted photoelectron and so on the exciting photon energy. The parameter of interest is therefore not the absolute emission angle, but rather the momentum component parallel to the surface, \vec{k}_{\parallel} , a quantity that is conserved during the electron-emission process. Consequently it is possible to plot the results in the form of a two-dimensional band-structure diagram as demonstrated by Egelhoff and Perry.¹³ Such a diagram of the *energetic position* of the hydrogen-induced features as a function of the parallel k -vector component shows good agreement with previous data obtained over a more limited range,¹³ with the exception of the band near -12 eV, which was not observed before. In addition, the present data allow evaluation in terms of the *intensity* of adsorbate-induced structure, since angular scans are performed at constant and general excitation conditions. This additional information leads to an interpretation different from that of previous data.¹³

The intensity of adsorbate-induced emission

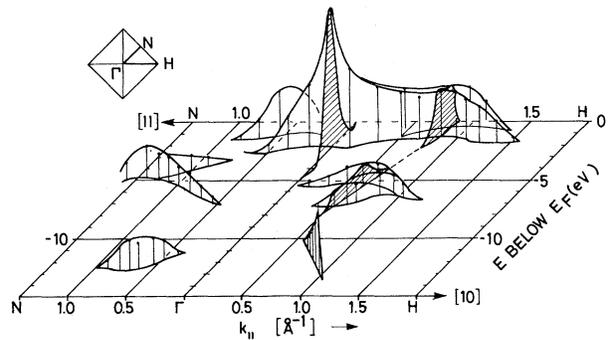


FIG. 2. Three-dimensional plot of hydrogen-adsorbate photoemission features for a (1×1) monolayer on W(100). The plane represents a "band structure" of the energetic position of structure relative to the Fermi level as a function of parallel k vector along two symmetry lines (shown in the inset). The vertical axis gives the intensity of the peaks. Typical widths of the spectral features are indicated for two arbitrary angles $\theta = 0^\circ$ and 25° by the shaded areas.

was determined directly from difference curves, and a background was subtracted only for the case of the low-lying (-12 eV) feature along $\langle 11 \rangle$, since the strong reduction in the broad distribution of low-energy electrons caused this feature to appear in an extended region of negative values in the difference spectra. No correction was made for the $\cos^2\theta$ isotropic emission dependence. The results are presented in the form of a pseudo-three-dimensional plot shown in Fig. 2. Within the horizontal plane the peak energy for the various hydrogen-induced spectral features is plotted as a function of k vector parallel to the ΓN ($\langle 11 \rangle$) and the ΓH ($\langle 10 \rangle$) directions. The E versus \vec{k}_{\parallel} plane is thus a two-dimensional band-structure diagram along the two principal symmetry lines shown in the inset. The peak intensities are plotted on the vertical axis leading to the "ridges." The shaded areas illustrate the "width" of these ridges for two arbitrary angles, 0° and 25° . Figure 2 thus gives a schematic overview of the observed spectral features characterizing hydrogen chemisorption on the (100) face of tungsten. The well-defined peak at the center of the diagram for $\vec{k}_{\parallel} = 0$ represents the strong adsorbate-induced structure apparent at -2.3 eV in Fig. 1 for normal emission. This feature disperses and splits in a complex manner along both principal symmetry directions extending in particular along the $\langle 10 \rangle$ azimuth. The feature around -6 eV has zero intensity at small angles and develops a double-branched structure. The -12 -eV peak also has

zero intensity about $\vec{k}_{\parallel}=0$, and exhibits pronounced dispersion with increasing \vec{k}_{\parallel} . This behavior is distinctly different from the dispersion characteristics of the final-state band gap apparent in the $\theta=0^\circ$ curve of Fig. 1 at -12.5 eV, which indicates that the feature discussed is indeed an adsorbate-induced level and not a final-state or back-scattering effect.¹⁸ However, all of the observed structure disperses with angle in a complex manner such that measurements of the azimuthal-angle behavior of any particular adsorbate-induced resonance are not possible simply by locking onto the appropriate resonance energy and scanning the azimuth angle. Individual energy-distribution spectra have to be scanned for each observation angle in order to relocate the energetic position of the adsorbate levels.

Despite the fact that the angular emission pattern, Fig. 2, is complex, an attempt is made to interpret the data in terms of the overall features, namely the number of bands and their angular grouping. Experimental evidence to date indicates that hydrogen on W(100) is adsorbed in a single site at full coverage.⁸⁻¹² There is additional evidence^{9,14,19} that this is the bridge site. The present interpretation will therefore be based on identical bonding characteristics for all of the hydrogen atoms on the surface. Figure 2 clearly indicates *three* bands of adsorbate-induced features, of which the energetically lower two are emitted in off-normal directions, while that with the lowest binding energy is peaked strongly about the surface-normal direction. Self-consistent-field molecular-orbital theories of hydrogen chemisorption on *d*-band substrates^{1,2,6} based on the Anderson Hamiltonian^{1,20} predict either one or two peaks only, depending on the magnitude of the adsorbate-substrate hopping interaction relative to the substrate bandwidth. More than two virtual states may be predicted if an unrestricted Hartree-Fock treatment^{4,7} is employed since this takes into account possible intra-adsorbate Coulomb-repulsion effects. Four individual adsorbate peaks may then occur, arising from the the separate hydrogen ionization and affinity levels E_I and E_A that split into bonding and antibonding states by interaction with the substrate orbitals, as indicated schematically in Fig. 3(a). If one of these four levels happens to be situated above the Fermi level [dashed level, Fig. 3(a)], and therefore is not observable in a photoemission experiment, such Coulombic splitting could explain the three distinct adsorbate features observed. On the other hand, since both the ioniza-

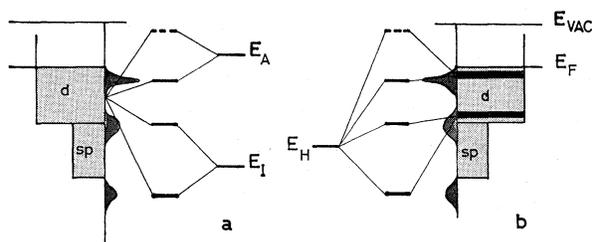


FIG. 3. Schematic illustration of the interpretation of the observed chemisorption features of hydrogen on tungsten. (a) Coulomb interaction gives rise to a splitting into ionization and affinity levels E_I and E_A , which in turn may interact with the *d* band to form bonding-antibonding states. (b) Overlap of a hydrogen level E_H with two surface localized *d* sub-bands leads to four levels of possibly different angular distribution patterns.

tion level and the affinity level of hydrogen have 1s symmetry, hybridization with a band of *d* states would give four peaks having the same overall angular distribution, in contrast to the observed results.

The three individual bands of adsorbate features, Figs. 1 and 2, have fairly narrow widths, varying between 1 and 2 eV. This would indicate that they arise from strong overlap of the hydrogen 1s with specific metal-group *d* orbitals which are strongly localized at the surface, rather than with the *d* band as a whole. Molecular-orbital calculations on such surface-orbital complexes^{2,3,5} are not restricted in the number of adsorbate-induced features they may predict. Extended Hückel calculations of an H atom bonded to a cluster of tungsten atoms³ predict the energetically lowest orbital to arise largely from H1s-W6s hybridization. It has been suggested¹³ that orbitals of this type interact at saturation coverage to form a band of states at the surface with *s*-like character. The present observations do not support this view, since the angular-emission intensity distributions, Fig. 2, for the *two* lowest levels indicates behavior incompatible with *s*-type symmetry.¹⁵ The present interpretation therefore suggests that *s-d* interaction is predominant for all levels observed. The normally emitted narrow peak at -2.3 eV is, in this model, assigned to chemisorption interaction with *d* orbitals that constitute the $\Gamma_{25'}$ level in the tungsten band structure, which is located about 1 eV below the Fermi level.²¹ [It is the *only* *d*-band level along the (100) symmetry line below E_F for $\vec{k}_{\parallel}=0$.] Some support for this view is evidenced by the fact that this level exhibits spin-orbit splitting of about

0.6 eV,²¹ and a similar splitting is observed in the corresponding chemisorption level (see double arrows on -2.3-eV structure in Fig. 1). The two adsorbate bands with higher binding energies in Fig. 2 have zero intensity for normal emission and are assigned to $\vec{k}_{\parallel} \neq 0$ levels as a consequence. The orbital-interaction assignment responsible for these features is not quite so obvious. The bulk energy bands of tungsten, while showing no states just below the Fermi level at the Brillouin-zone boundary, extend from H_{12} along the two symmetry directions observed at energies around -6 eV, with dispersion characteristics compatible with the observations shown in Fig. 2. The suggested bonding scheme is presented in Fig. 3(b), showing schematically the splitting of the hydrogen adsorbate level which arises from interaction with tungsten sub-bands of d symmetry, strongly localized in the surface.

At the present time, these arguments are based on bulk band-structure calculations and must therefore be regarded as tentative. New results now becoming available on calculated densities of states arising from individual surface d orbitals,²² however, do clearly show well-defined peaks localized at the outermost atomic layer. The results of this paper provide strong evidence for hydrogen chemisorption involving overlap with such surface localized and directional d orbitals on tungsten.

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