densation. If this state can be created, from curve *c* Fig. 2(b) we see that a sharp interface or "surface" in coordinate space should be a characteristic of the condensate at low temperature. At low density the gas behaves classically. The maximum density that can be loaded into a magnetic field for a gas stabilized against recombination is limited by $\exp(B/T)$ and the zero-field density.

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Surface-Reflectance-Spectroscopy Studies of H on W(110): Surface Band Structure and Adsorbate Geometry

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The dielectric function derived from polarized surface-reflectance-spectroscopy studies of the H/W(110) system is compared with that calculated for different hydrogen configurations. The orbital symmetry of the adsorbate states is identified and features of the surface band structure are characterized. It is found that the most likely adatom position is in a bridged site.

The determination of the electronic structure of surfaces has recently received increasing attention in both experimental and theoretical studies. In this Letter we show that surface-reflectance spectroscopy (SRS) may be a powerful tool in elucidating the relationship between the surface band structure and the adatom bonding for chemisorbed systems.

In SRS the change of reflectance caused by chemisorption on an atomically clean single-crystal surface is measured as a function of the energy of incident polarized photons.[1-4] Using this technique, we have studied the optical properties of a monolayer of hydrogen chemisorbed on tungsten(110). The results show a pronounced anisotropy in the reflectivity change which permits an investigation of the orbital character of the wave functions. Anisotropy of this type has been previously reported for O/W(110) and H/W(110) (Ref. 4) and also for Cu/Pt(110).[5]

A partial description of the surface band structure is obtained from the study of the dielectric properties that may be deduced from the reflectance spectrum. The energies of the peaks in the dielectric function[3] correspond to the excitation energies of the optical transitions and their magnitude is proportional to the dipole matrix elements between the initial- and final-state wave functions. By a change in the direction of the electric field, the matrix elements are altered either because new optical transitions are induced or because the strength of the existing ones is modified as a consequence of the directionality of the wave functions.

For each model of the adsorbate geometry there is a corresponding set of valence band orbitals. The transition matrix elements may be calculated for each model and their azimuthal dependence compared with that observed for the adsorbate peaks in the dielectric function. This type of analysis of SRS data for H/W(110) shows that bridge sites are the most probable location of the H atoms.

The experimental procedures used in SRS have been described previously.[2,3] The present study was done on a thin W(110) ribbon under ultrahigh-

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vacuum conditions. Measurements were made of the near-normal–incidence change of reflectance, $(\Delta R/R)(\varphi,\omega)$, for photon energies in the range $0.6\text{ eV} \leq \hbar\omega \leq 6.0\text{ eV}$ and for different azimuthal orientations of the electric field between $\varphi = 0°$ (the $\langle 1\bar{1}0\rangle$ direction) and $\varphi = 90°$ (the $\langle 001\rangle$ direction).

$\Delta R/R$ can be calculated by an extension to the case of an anisotropic surface of the methods described by Feibelman[6] and by Bagchi and Rajagopal.[7] If the symmetry of the clean surface changes upon adsorption, the reflectance change is given by a relation of the form

$$(\Delta R/R)(\varphi,\omega) = A(\omega) + B(\omega)\cos^2(\zeta-\varphi) + C(\omega)\cos^2\varphi. \quad (1)$$

The effect of the symmetry change is to rotate the principal axes of the surface dielectric tensor by an angle ζ relative to that of the clean substrate. $B(\omega)$ and $C(\omega)$ measure the degree of anisotropy for the covered and clean surface, respectively. Equation (1) fits the experimental data[4] when $\varphi = 0°$ and the principal axes are along the $\langle 001\rangle$ and $\langle 1\bar{1}0\rangle$ directions. This shows that the rectangular symmetry of the clean surface is not altered by the adsorbate; as a consequence, any H coordination that would give a different symmetry can be rejected. It also follows that the spectral dependence of $\Delta R/R$ is needed only along the principal directions in order to describe the chemisorption-induced changes of the surface electronic structure. The McIntyre-Aspnes model[8] can then be used to relate the reflectance spectra to the changes in the corresponding component of the complex surface dielectric tensor.

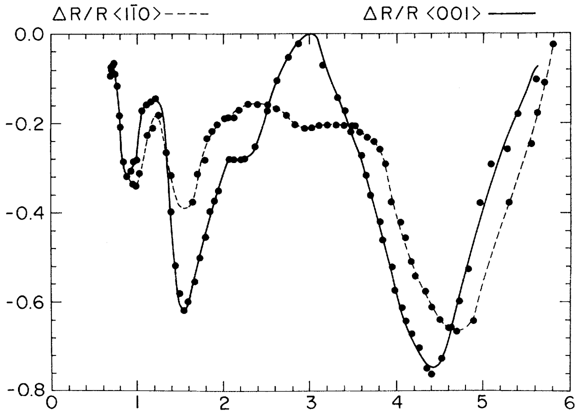

FIG. 1. Dependence of the normalized change of reflectance $\Delta R/R(\omega)$ on photon energy, for a W(110) surface saturated with hydrogen at room temperature. The electric field is along the $\langle 1\bar{1}0\rangle$ and $\langle 001\rangle$ directions.

Two regions may be distinguished in the reflectance spectra (Fig. 1): the near-infrared region ($0.6\text{ eV} \leq \hbar\omega \leq 1.5\text{ eV}$) and the visible–uv region ($1.5\text{ eV} \leq \hbar\omega \leq 6.0\text{ eV}$). In the near-infrared region the peak heights, but not the positions, are seen to vary with the azimuthal orientation of the electric field. In the visible-uv, $\Delta R^{\langle 1\bar{1}0\rangle}/R$ is almost flat up to 3.4 eV, where it decreases to a minimum at 4.8 eV, and $\Delta R^{\langle 001\rangle}/R$ shows a shoulder at 2.1 eV, a maximum at 3.0 eV, and a minimum at 4.4 eV.

Figure 2 shows the frequency dependence of the change in the imaginary part of the dielectric function, $\Delta\epsilon_2$. Depending on the nature of the states involved in the optical transitions, the contribution to $\Delta\epsilon_2$ may be positive or negative. Three types of spectral features can be identified: bulklike peaks (positive contribution), intrinsic surface resonances (negative), and adsorbate-induced features (positive). The bulklike peaks, located at 1.0, 1.8, 3.3, and 5.0 eV, have already been analyzed in detail.[3]

The 1.4-eV dip in $\Delta\epsilon_2$ is associated with the quenching upon chemisorption[9,10] of optical transitions between two surface resonances.[3,11,12,13] The initial state (an occupied resonance level) was studied by Holmes, King, and Inglesfield.[14] It has mainly *yz* *d*-orbital character and exists over most of the surface Brillouin zone (SBZ) (Fig. 3[15]). To determine the orbital character of the final state (an unoccupied resonance level) the azimuthal dependence of the matrix element

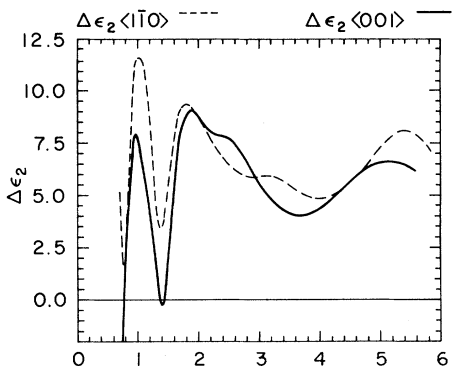

FIG. 2. Frequency dependence of the change in the imaginary part of the dielectric function caused by hydrogen adsorption. The electric field is along the $\langle 1\bar{1}0\rangle$ and $\langle 001\rangle$ directions.

was calculated and compared with the behavior of the 1.4-eV peak in $\Delta\epsilon_2$. The possible d hybridization of the final-state wave functions was found from group-theoretical arguments and selection rules. In a tight-binding approximation (TBA) the matrix elements are given by

$$M = \langle \psi_i{}^k(\vec{r})|\vec{r}|\psi_f{}^k(\vec{r})\rangle = \sum_{mm'\vec{R}} a_m b_{m'} e^{i\vec{k}\cdot\vec{R}} \langle \varphi_m(\vec{r})|\vec{r}|\varphi_{m'}(\vec{r}-\vec{R})\rangle, \qquad (2)$$

where a_m and $b_{m'}$ are the coefficients in the TB expansion of the initial- and final-state wave functions. M is expressed as a linear combination of matrix elements between pairs of d-like wave functions, one centered at the origin and the other at $\vec{R}$. When the latter is expanded about the origin in terms of d-like and non-d-like components,[16,17] the only nonzero contributions to M are those involving φ_m and the p-like and f-like terms in the expansion of $\varphi_{m'}$. To simplify the calculation, the final state is assumed to be located in the first W layer, and the sum over lattice sites is restricted to the nearest neighbors. For an electric field along the $\langle 001\rangle$ direction, the matrix element $M^{\langle 001\rangle}$ is found to be proportional to the b_{yz} coefficient along ΓH, to b_{yz} and $b_{3z^2-r^2}$ (and/or $b_{x^2-y^2}$) along HP, and to b_{xy} along ΓN. The $M^{\langle 1\bar{1}0\rangle}$ is found to be proportional to $b_{3z^2-r^2}$ (and/or $b_{x^2-y^2}$) along the ΓN, ΓH, and HP directions. We conclude, therefore, that the observed φ dependence of $\Delta\epsilon_2$ can be explained if the character of the unoccupied resonance is mainly yz along ΓH, yz and $3z^2-r^2$ (and/or x^2-y^2) along HP, and xy along the ΓN direction.

The third type of spectral feature, adsorbate-induced changes, includes the peaks at 2.6 eV in $\Delta\epsilon_2{}^{\langle 001\rangle}$ and 5.5 eV in $\Delta\epsilon_2{}^{\langle 1\bar{1}0\rangle}$ (Fig. 2). The initial states of these optical transitions correspond to the low- and high-coverage hydrogen states, respectively, that are observed in both thermal desorption[18] and ultraviolet photoelectron spectroscopy (UPS) studies.[13,19] The final-state energies, E_f, are identified by combining UPS and SRS results. For the 2.6-eV transitions E_f is close to the Fermi level, and for the 5.5-eV transition it is 1.5 eV above the Fermi level. The angular dependence of these peaks in $\Delta\epsilon_2$ reflects the differences between the wave functions associated with each adsorbate level. The position of these adsorbate states in the projected band structure (PBS)[15] follows from UPS studies.[13,19] They are most likely localized in energy gaps only, because their interaction with a wide d band would broaden them over most of the SBZ. It is found that the high-coverage state is located at the edge of the gap around the Γ point and that the low-coverage state is located in the gaps around N and H (Fig. 3).

We have examined two structural models for the saturated surface with the required rectangular symmetry. In one model each H atom is placed on a bridge site (see inset in Fig. 3); in the other, "on-top" sites are used. In each case it is assumed that the strong bond to the surface comes from the interaction of H $1s$ and W $5d$ orbitals,[20] and a group-theoretical argument gives the allowed combination of these orbitals along high-symmetry lines of the SBZ. The matrix elements were calculated within a TBA. In the calculation the initial wave functions are

$$\psi_1{}^k(\vec{r}) = \sum_m a_m \psi_m{}^k(\vec{r}) + c_{1s}\psi_{1s}{}^k(\vec{r}),$$

where

$$\psi_{1s}{}^k(\vec{r}) = \sum_R e^{i\vec{k}\cdot(\vec{R}-\vec{d})}\varphi_{1s}(\vec{r}-(\vec{R}-\vec{d})),$$

$|\vec{d}| = 0$ (on top) or $a/\sqrt{2}$ (bridge sites).

Consider first the bridge-site model. The high-coverage state must have mainly $1s$, x^2-y^2 and/or $3z^2-r^2$ character. Calculations showed that to reproduce the φ dependence of $\Delta\epsilon_2$ the final state must have a negligible xy component along ΓN. This orbital character shows that the unoccupied resonance state cannot extend toward Γ

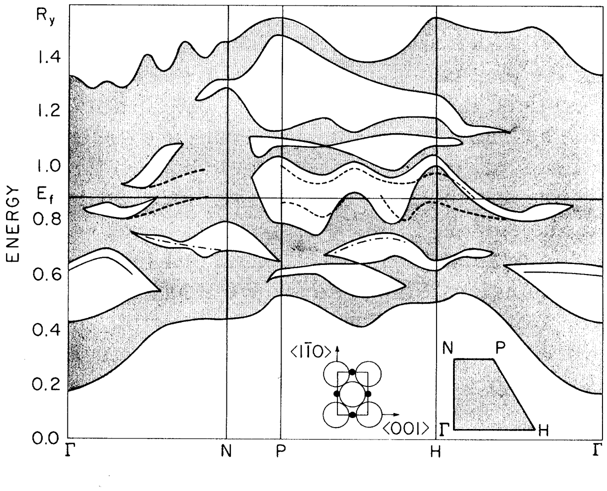

FIG. 3. Projected band structure for the W(110) surface. Dashed lines refer to the surface resonances, full lines to the high-coverage hydrogen state, and dash-dotted lines to the low-coverage hydrogen state. Insets show the corresponding SBZ and the bridge-site position of the atoms (filled circles) on the W direct lattice (empty circles).

further than the occupied one. If it did, it would be a suitable final state, a large xy component would exist along ΓN, and the opposite φ dependence would then have been found in $\Delta\epsilon_2$.

Turning to the low-coverage state, it is seen that its main character must be $1s$, yz. Calculations indicate that the final state (close to E_F), must have the same character as the unoccupied resonance state to reproduce the φ dependence in $\Delta\epsilon_2$. This behavior indicates that hydrogen chemisorption lowers the resonance energy by about 1 eV without major change in the orbital character, in a manner similar to that found by self-consistent calculations for H/Pd(111) (Ref. 20) and H/Mo(100).[21]

Next, consider the model with "on-top" sites. The H($1s$) orbital will hybridize mainly with x^2-y^2, $3z^2-r^2$ orbitals over the whole SBZ. Such mixing for the part of the low-coverage state that is centered at G (mid-point of PH) would imply a mainly yz final state. The lowered unoccupied resonance is an improbable final state because the necessary change in character is forbidden at G for symmetry reasons. Therefore, to explain the φ dependence in $\Delta\epsilon_2$, a new final state would have to exist at E_F with the same orbital character as the occupied resonance level. Since no such state was observed experimentally for the clean surface, we conclude that, of the two models considered, only the bridge site is acceptable.[22]

In conclusion, we have shown that from an analysis of SRS data it may be possible to obtain detailed information about a chemisorbed system. In the particular case of H/W(110), we have determined the most probable H configuration and the hybridization of the adsorbate and resonance wave functions. We also have identified these states and the corresponding optical transitions in the surface band structure.

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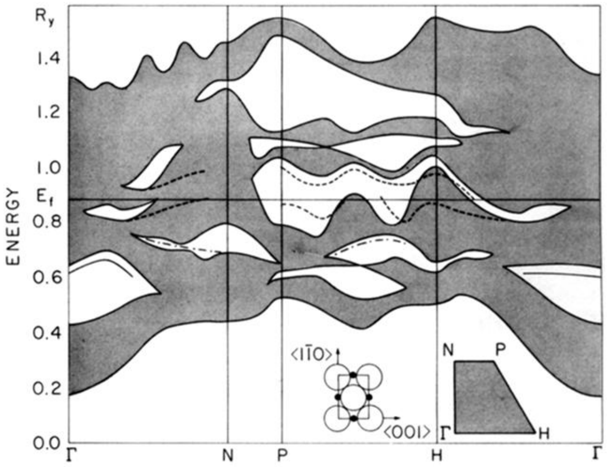

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