Angular Dependence of the Photoelectron Spectra of Hydrogen Adsorbed on W(100)

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The ultraviolet photoelectron spectra of hydrogen adsorbed on W(100) have been studied as a function of the angle of emission. An analysis of this angular dependence at saturation coverage shows some indication of a two-dimensional band structure in the hydrogen-induced energy levels. We discuss the nature of the bands in terms of a molecular-orbital calculation of this adsorbed system.

The recent extension of photoelectron spectroscopy to the study of chemisorption has offered the hope of a wealth of new information about the electronic structure of chemisorbed systems.[1] Recent developments in theories of photoemission[2] and chemisorption[3] permit an analysis of the experimental data that may well lead to a fundamental understanding of chemisorption. In this pursuit, studies of the ultraviolet photoelectron spectra of hydrogen adsorbed on tungsten have recently been carried out.[4,5] However, the angular dependence of these spectra has not been studied previously. It is well known that very valuable information can be obtained from the angular dependence of the photoelectron spectra of solids, and this has been the motivation for the present work.[6,7]

The spectrometer design fixes the angle between the photon beam and the detector at 90° (see inset in Fig. 1). The polar angle, θ, can be varied from 0° to 90° by tilting the crystal, while the azimuthal angle is fixed ($k_{\parallel}$ is in the [11] direction). The detector accepts photoelectrons emitted within a cone of apex angle 4°. The resolution of the 127° analyzer is 0.20 at 15 eV. The experiments were carried out in an ultrahigh vacuum chamber with a base pressure of 2×10^{-10} Torr. A careful estimate of the maximum exposure to background CO during these experiments is 1×10^{13} molecules/cm^2 incident. The saturation coverage of hydrogen has been determined to be $(1.75\pm0.25)\times10^{15}$ atoms/cm^2.[8] The crystal was prepared and cleaned by well-established procedures.[9]

The angular dependence of the spectra has been studied by varying θ from 4° to 77° with $h\nu = 21.2$ eV (He I radiation), and 16.8 eV (Ne I). Some spectra have been taken with $h\nu = 26.9$ eV (Ne II). Figure 1 shows representative samples of these data. The spectra have been presented as the difference between the photoelectron intensity before and after adsorption. In these difference graphs the energy dependence of the transmission of the analyzer has been corrected for so that the peak heights correctly reflect the photoemission intensity. Because the work function changes linearly with coverage, $\Delta\varphi$ has been used as a measure of coverage.[9] Saturation coverage is found to give $\Delta\varphi = 0.85$ eV, in good agreement with previous work.[9] The difference graphs are shown only to − 9 eV because changes in the emission intensity of secondary electrons are the only features observed at lower energies.

In Fig. 1 graphs (a) and (b), taken with $\theta = 14°$ and $h\nu = 21.2$ eV, show two main trends. First, at low coverage ($\Delta\varphi = 0.20$ eV) there are two

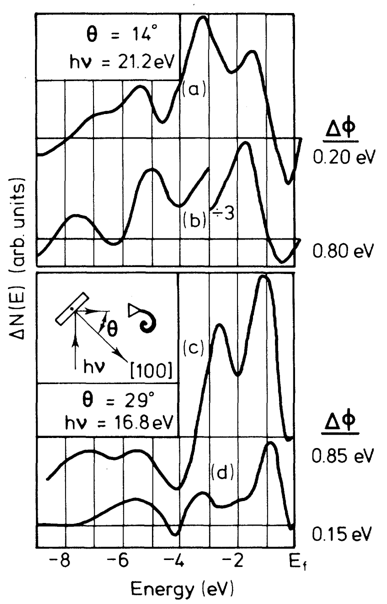

FIG. 1. A graph of the difference in photoelectron intensity between the crystal surface with hydrogen adsorbed and the clean crystal surface for low [graphs (a) and (d)] and saturation [graphs (b) and (c)] coverages. The inset illustrates the experimental geometry. The change in the work function following adsorption is linear in coverage to a value of 0.85 ± 0.05 eV at saturation (Ref. 9).

peaks at -1.4 and -3.2 eV which converge with increasing coverage to a single peak at -1.7 eV at saturation coverage ($\Delta\varphi = 0.80$ eV). Second, the low-coverage structure between -4.5 and -7.5 eV splits up with increasing coverage into two peaks at -5.0 and -7.6 eV at saturation. The first trend has been observed before for this adsorbed system when collecting photoelectrons over the hemisphere around $\theta = 0°$; however, the second trend was not seen.[5] In these two graphs the decrease at -0.5 eV is known to be due to the quenching of the surface state of W(100).[4, 5]

In Fig. 1 graphs (c) and (d), taken with $\theta = 29°$ and $h\nu = 16.8$ eV, show similar trends. However, this time the two low-coverage peaks at -3.2 and -0.8 eV, graph (d), do not converge completely to a single peak at saturation. This behavior has not been seen previously for hydrogen on W(100), and it indicates the angular dependence of the spectra. Again in graphs (c) and (d) the development of two peaks is seen in the -5 to -8 eV range as coverage increases. In this energy range graph (c) is depressed due to a general lowering of the emission intensity of secondary electrons as the coverage increases.

Since it seems likely that the hydrogen-induced orbitals are localized near the surface, we have considered the possibility that they may have a two-dimensional band structure. If this model is applicable, our data should be amenable to analysis by the method used convincingly by Smith, Traum, and Di Salvo[7] to determine the two-dimensional band structures of the layer compounds $1T$-TaSe$_2$ and $1T$-TaS$_2$.[7] This method assumes that $k_\parallel$ (the component of the wave vector parallel to the surface) is conserved during the photoemission process. The magnitude of $k_\parallel$ is determined from the equation

$$k_\parallel = (E2m/\hbar^2)^{1/2} \sin\theta, \tag{1}$$

where E is the measured photoelectron kinetic energy, and θ is the polar angle. In Fig. 2 the energy of peaks in the difference graphs for the saturated surface at various θ between 4° and 55° have been plotted against $k_\parallel$ for the ΓN or [11] symmetry axis. The solid lines indicate what appear in the difference graphs to be continuous changes in peak position. The shifts in peak energy across the zone appear to indicate two-dimensional band character in the hydrogen-induced levels. The dashed lines in Fig. 2 indicate lines along which Eq. (1) is satisfied for graphs (b) and (c) of Fig. 1.

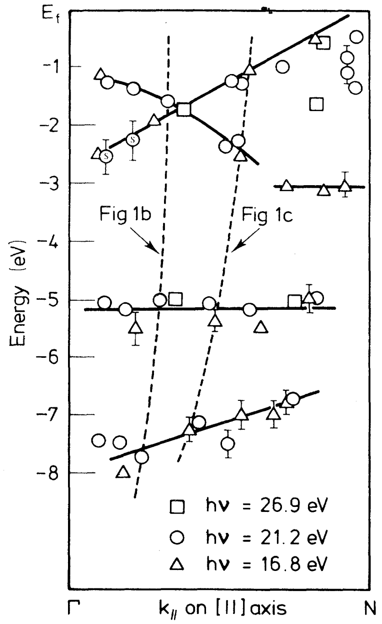

FIG. 2. A plot of the energy of the peak positions in the difference graphs at saturation coverage against the wave vector $k_\parallel$ in the [11] direction of the two-dimensional Brillouin zone at the surface. The dashed lines indicate the allowed values of $k_\parallel$ for the results of Fig. 1. The error bars are used for broad peaks, and the letter "s" indicates a strong shoulder.

In interpreting Fig. 2 it is helpful to consider a relevant molecular-orbital calculation. Anders Hansen, and Bartell[10] have used extended Hückel calculations for a hydrogen atom in the two-coordinate bridge site on a cluster of tungsten atoms to simulate adsorption on W(100).[10] Their lowest energy molecular orbital is formed from the H-1s and W-6s orbitals, and is strongly localized on the hydrogen. If, as expected, orbitals of this type interact at saturation coverage to form a band at the surface with s-like character it would be expected to increase in energy going away from Γ. Just such behavior is seen in the lowest band of Fig. 2 The next to the lowest molecular orbital in the calculations is formed from the H-1s orbital and W-$d_{x^2-y^2}$, d_{yz} hybrids on the two adjacent W atoms. The hybrids point lobes at the hydrogen atom, but point nodes at the hydrogen adsorption sites adjacent in the y direction. When these sites are occupied at saturation coverage,[11] they too would be expected to incorporate such hybrids, and the effect on this orbital of occupying nearest-neighbor sites would be minimal. Evidence for this (as seen in Fig. 1) comes from the observation that there is always a low-coverage peak around -5

or − 5.5 eV which shifts very little as the coverage increases. Furthermore, molecular orbitals of this type would have no two-dimensional band structure, and the absence of shift in energy across the zone, as shown by the − 5.1 eV band in Fig. 2, would be expected.

The imperfect alignment of the points on the two lowest bands may well mean that they do not have perfect two-dimensional character. That is, there may be some nonflat band character in the direction perpendicular to the surface. However, the general agreement for three photon energies[12] probably means that such three-dimensional band-structure effects, and also any anisotropic scattering by the substrate lattice,[13] are not of major importance here.

The behavior of the bands nearer E_F is more complicated, and unlike the two lowest bands they do not have a simple interpretation. However, the extended Hückel calculations[10] do not predict simple behavior for the bands in this range.

There is a band around − 1.0 eV at Γ which decreases in energy across the zone. Between the middle of the zone and the zone edge (denoted N) for $h\nu = 21.2$ eV this peak disappears into a shoulder and for $h\nu = 16.8$ eV overlaps with a very intense bulk direct transition.[14] The three triangles at − 3 eV in Fig. 2 may well indicate peaks which arise from enhancement of this bulk emission and may not be connected with the surface band with which they merge between the middle of the zone and the zone edge. There also appears to be a band at − 2.6 eV near Γ which increases across the zone. This band has been observed before by others with $\theta = 0°$ and $h\nu = 10.2$ eV.[4] The Γ point in Fig. 2 corresponds to $\theta = 0°$, and in Ref. 4 a peak was observed at − 2.4 eV which is in close correspondence with the present results. The band at − 1 eV at Γ in Fig. 2 was not seen in Ref. 4 presumably because it was obscured by the decrease of the surface-state peak which, at $h\nu = 10.2$ eV, is larger relative to the emission from the hydrogen-induced bands than at higher photon energies. The two lowest bands of Fig. 2 can not be seen at $h\nu = 10.2$ eV because the photon energy is too low.

Further support for the above interpretation of Fig. 2 comes from our results for θ approaching 90°. At $\theta = 90°$ the photon electric vector is parallel to the crystal surface, and it is known that this does not induce photoemission from delocalized surface bands.[15] This is because the electric vector has no potential gradient to interact with at the surface as it does when it is perpendicular to the surface. In the present studies the intensity of all the peaks due to the adsorption of hydrogen (except the − 5-eV peak) drops to approximately zero as θ approaches 90°.[16] This supports the original assumption that the hydrogen-induced orbitals are delocalized as two-dimensional bands at the surface. It further supports the assignment of the − 5.1-eV peak as being due to orbitals localized around each hydrogen atom. An orbital at the surface that is not delocalized in two dimensions has a potential gradient parallel to the surface with which the electric vector can interact to induce photoemission. It is important here to know that such drops in intensity in the difference graphs near $\theta = 90°$ do not occur for bulk bands (e.g., bulk tungsten oxide relative to clean tungsten) or for localized orbitals [e.g., undissociated methanol on W(100)].[16]

The behavior of the peaks in Fig. 2 near N around − 1 eV is complicated. Changes in θ of only 3° cause marked changes in peak positions. The source of these ambiguities is likely to be three-dimensional band-structure effects in the adsorbate-induced bands. It may be relevant here that in the extended Hückel calculations,[10] half of the orbitals above the lowest two show some density on the hydrogen while having large W-W overlap populations, indicating three-dimensional bands that have been slightly altered at the surface because of adsorption.

In conclusion, we feel that this work indicates that the electronic structure of the W(100) surface saturated with hydrogen can, at least in part, be understood in terms of a two-dimensional band structure. Furthermore, it seems that the information obtained from angular dependence studies on adsorbed layers provides important insight into the electronic structure at the surface. Clearly a more complete theoretical study would be helpful. Our plans are to repeat these experiments with $k_{\parallel}$ in the [10] direction.

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[1] C. R. Brundle, J. Vac. Sci. Technol. 11, 212 (1974).

[2] G. D. Mahan, Phys. Rev. B 2, 4334 (1970); W. L. Schaich and N. W. Ashcroft, Phys. Rev. B 3, 2452 (1971); L. Sutton, Phys. Rev. Lett. 24, 386 (1970).

[3] T. E. Einstein and J. R. Schrieffer, Phys. Rev. B 7,

3629 (1973); T. B. Grimley, Proc. Phys. Soc. (London) 92, 776 (1967); D. M. Newns, Phys. Rev. 178, 1123 (1969); J. W. Gadzuk, in *Surface Physics of Crystalline Materials,* edited by J. M. Blakely (Academic, New York, 1974).

[4] B. Feuerbacher and B. Fitton, Phys. Rev. B 8, 4890 (1973).

[5] E. W. Plummer, to be published.

[6] T. Gustafsson, P. O. Nilsson, and L. Wallden, Phys. Lett. 37A, 121 (1971); N. V. Smith and M. M. Traum, Phys. Rev. Lett. 31, 1247 (1973); M. M. Traum, N. V. Smith, and F. J. Di Salvo, Phys. Rev. Lett. 32, 1241 (1974).

[7] N. V. Smith, M. M. Traum, and F. J. Di Salvo, Solid State Commun. 15, 211 (1974).

[8] T. E. Madey, private communication.

[9] For a detailed discussion of hydrogen on W(100) see T. E. Madey, Surface Sci. 36, 281 (1973).

[10] L. W. Anders, R. S. Hansen, and L. S. Bartell, J. Chem. Phys. 59, 5277 (1973).

[11] P. J. Estrup and J. Anderson, J. Chem. Phys. 45, 2254 (1966).

[12] No peaks are plotted in Fig. 2 below -7 eV for $h\nu$ $=26.9$ eV due to interference of the 19.8-eV spectral line of neon.

[13] A. Liebsch, Phys. Rev. Lett. 32, 1203 (1974).

[14] E. W. Plummer, private communication.

[15] J. G. Endriz, Phys. Rev. B 8, 3464 (1973); B. Feuerbacher and B. Fitton, Solid State Commun. 15, 295 (1974).

[16] W. F. Egelhoff, J. W. Linnett, and D. L. Perry, unpublished results.

One- and Multi-Step Processes in the Reaction ^{144}Nd(^{12}C, ^{14}C)†

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Two very different types of angular distributions, one having a normal bell shape and the other being much more constant with angle were observed in the reaction ^{144}Nd(^{12}C, ^{14}C) for two well-known 2^+ states of ^{142}Nd. The fits to these angular distributions using the distorted-wave Born approximation and/or coupled-channel Born approximation confirms the conclusion that the data give definite evidence for the importance of multistep processes. A comparison with the reaction ^{144}Nd(p, t) is also discussed.

In previous work[1,2] on the reaction ^{144}Nd(p, t)^{142}Nd, the excitation of the ground (0_g^+) state, the first excited (2_1^+) state, the 2.98 MeV (0_2^+) state, and the 3.49 MeV (2_2^+) state in ^{142}Nd ($N=82$) was investigated. The purpose of the present work is to study these and additional states via the reaction ^{144}Nd(^{12}C, ^{14}C)^{142}Nd. Our interests are to learn to what extent the light-ion– and heavy-ion–induced, two-neutron pickup reactions are similar and to determine the effects of multi-step processes in heavy-ion transfer reactions.

The most remarkable feature found in the previous (p, t) work[1,2] was that the transitions to the 0_g^+, 0_2^+, and 2_2^+ final states were strong and were of a one-step nature, while the transition to the 2_1^+ state was much weaker and also had an anomalous angular distribution markedly different from what was expected for a one-step $L=2$ transition. The difference in the behavior of the 2_1^+ and 2_2^+ transitions was attributed to the following distinct properties of those states.[2] The 2_2^+ state is a collective state of two-particle, two-hole nature in the $N=82$ closed shell, i.e., a superposition of monopole and quadrupole pairing vibrations.[3] Therefore, it can be excited strongly by a direct-($L=2$)-type two-neutron pickup reaction. On the other hand, the 2_1^+ state consists dominantly of a proton particle-hole quadrupole vibrational configuration; thus a direct two-neutron transfer process is substantially inhibited and higher-order processes may contribute significantly. Indeed, the anomalous behavior of the 2_1^+ cross section, which defied explanation in terms of distorted-wave-Born-approximation (DWBA) calculations, was well accounted for by coupled-channel-Born-approximation (CCBA) calculations, which took into account the effect of inelastic scattering.[2]

The ^{144}Nd(^{12}C, ^{14}C) experiment was performed