

Photoemission and electron-stimulated desorption studies of H on W(110): Single- versus two-binding-site models

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The chemisorption of H on W (110) at room temperature is studied with the use of angle-integrated photoemission and electron-stimulated desorption (ESD). The ESD cross sections of H^+ are found to be so low that no significant H^+ signals with meaningful ion energy distributions are observed. The photoemission results show, however, two types of H adatoms, referred to as β_2 and β_1 states, for this chemisorptive system. Both states are found to appear simultaneously rather than sequentially as suggested by previous studies, and exhibit a simple $1-\Theta$ adsorption kinetics with different initial sticking coefficients. The β_2 state induces two binding energy levels at -2.0 and -6.0 eV, respectively, whereas the β_1 state induces a level at -3.8 eV. The work-function change (with a maximum value of -0.45 eV) is found to follow exactly with the intensity of the β_2 state. These results are found to be compatible with the two-binding-site model, inherently suggested by the reflection high-energy electron-diffraction data. However, the results can also be consistent with a single-binding-site model suggested by a recent angle-resolved photoemission and inelastic electron scattering study. A model based on the present results is proposed and critically compared with previous studies. Unresolved problems associated with both single- and two-binding-site models are also discussed.

I. INTRODUCTION

The chemisorption of H on W(110) has been subject to a variety of experimental studies¹⁻¹⁴ in the past decade, but the models drawn from these studies regarding the binding sites and bonding structure are still controversial. No low-energy electron diffraction (LEED) pattern, other than that of the substrate, has ever been observed for H on W(110) adsorbed at room temperature.¹ However, Matysik,² using reflection high-energy electron diffraction (RHEED), has reported a $p(1 \times 2)$ structure for H on W(110) adsorbed at room temperature. This $p(1 \times 2)$ superstructure appears immediately after H adsorption, and never disappears even for coverages reaching $\Theta=1$. This indicates that there are at least two different binding sites for H adatoms. Thermal desorption spectra^{3,4} show only one peak (referred to as β_2) at $\sim 700^\circ\text{C}$ for coverages below $\Theta=\frac{1}{2}$, but reveal a second peak (referred to as β_1) at $\sim 450^\circ\text{C}$ for coverages larger than $\Theta=\frac{1}{2}$. Both peaks exist at saturation with about equal intensity. Angle-resolved photoemission results of Feuerbacher and Fitton⁶ and Holmes and King,⁷ as well as angle-integrated photoemission results of Plummer *et al.*⁸ show two major states at about -2.2 and -4.0 eV, respec-

tively, for a saturation coverage of H on W(110). Angle-resolved normal photoemission results^{6,7} have shown that the state at -4.0 eV does not appear until the coverage is larger than $\Theta=\frac{1}{2}$, whereas the state at -2.2 eV, after reaching its maximum intensity at $\Theta=\frac{1}{2}$, begins to attenuate for $\Theta>\frac{1}{2}$. Angle-integrated photoemission results have shown, however, that the state at -2.2 eV increases its intensity almost linearly with coverage, and the state at -4.0 eV exists even for coverages below $\Theta=\frac{1}{2}$. Most of the results mentioned above have been interpreted^{6,7} to be indicative of two binding sites for H on W(110). The first state (-2.2 eV) β_2 occupies one site for coverages below $\Theta=\frac{1}{2}$, and the second state (-4.0 eV) β_1 occupies a different site sequentially after the coverage is larger than $\Theta=\frac{1}{2}$. This model has been referred to as a two-binding-site sequential filling model.

In contrast to the model mentioned above, several other studies⁹⁻¹⁴ have favored a single-binding-site model and attributed the thermal desorption multiple peaks and photoemission results to the coverage-dependent lateral interactions of the H adatoms.⁹ The studies favoring this model include field-emission energy distribution measurements of Plummer and Bell,¹⁰ electron-stimulated desorption studies of King and Men-

zel,¹¹ surface reflectance measurements of Blanchet, Estrup, and Stiles,¹² and inelastic electron scattering (IES) studies of several groups.^{13,14} Surface reflectance measurements have suggested the single binding site to be the long bridge (i.e., along the $\langle 001 \rangle$ direction). The IES data¹³ have been originally interpreted^{7,13,15} in terms of several two-site models (i.e., long bridge and atop,¹³ triangular and short bridge,¹⁵ and long bridge and short bridge⁷), but have recently been reinterpreted¹⁴ in terms of one-site model. Using angle-dependent IES and normal-mode analysis, Blanchet, DiNardo, and Plummer¹⁴ have suggested that the two peaks (96 and 160 meV) in the IES spectra are the symmetric and asymmetric stretching modes of the H adatoms binding to the long or distorted long-bridge site. Although this single-binding-site model is consistent with most of the available experimental data, it does not agree with the RHEED results² that the $p(1 \times 2)$ superstructure remains unchanged even for coverages up to $\Theta = 1$. A single-binding-site model would predict a gradual disappearance of the $p(1 \times 2)$ structure for coverages larger than $\Theta = \frac{1}{2}$, and a $p(1 \times 1)$ structure at $\Theta = 1$. More seriously, however, Blanchet *et al.*¹⁴ have had to assume a $c(2 \times 2)$ structure for coverages below $\Theta = \frac{1}{2}$ in order to explain their angle-resolved photoemission data obtained using synchrotron radiation. This is even in apparent contradiction with the RHEED results.¹⁶

In an attempt to clarify some of the conflicting results mentioned above, in particular the number of binding sites and the coverage dependence of the occupation of these binding sites, we have reinvestigated the adsorption of H on W(110) at room temperature using both angle-integrated photoemission and electron-stimulated desorption (ESD). The ESD results reveal no measurable H^+ intensity with meaningful ion energy distribution curves for H on W(110) at all coverages, but the photoemission results reveal two different types of H adatoms, each inducing different electronic structure and exhibiting simple but different adsorption kinetics. The results seem to favor a two-binding-site model, with both sites being filled simultaneously with different rates, rather than sequentially as suggested previously.³⁻¹⁴

II. EXPERIMENTAL

The experiments were performed at room temperature in an ultrahigh vacuum system containing a double-pass cylindrical mirror analyzer (CMA)

used for measuring the energy distribution curves (EDC's) of photoelectrons and an energy-resolving quadrupole mass spectrometer used for measuring the EDC's of ions in electron-stimulated desorption (ESD). The unpolarized 21.22 eV (He I) of photons were generated from a differentially pumped discharge lamp. The angle of incidence of the light is about 35° . The angle between the axis of the CMA and the normal of the crystal surface is about 42.3° . This geometry results in the measurement of partially angle-integrated photoemission spectra with electron emission angles spanning between $\theta = 0^\circ$ and 85° . The W(110) single crystal had been used extensively in the previous ESD experiments¹⁷ and was cleaned in the present experiments by the routine procedures⁸ (i.e., oxygen treatment and high-temperature flashing). The sample could be rotated in three different directions. During the measurements, the $\langle 011 \rangle$ axis of the (110) face was kept horizontally most of the time. For the ESD experiments, the acceptance angle of the energy-resolving mass spectrometer is about 8° . The photoemission data were collected and processed by a computer-controlled data-acquisition system.

III. RESULTS

The immediate observation from the present ESD studies is that the desorption cross section of H^+ from W(110) is so low (less than 10^{-23} cm²) that no measurable or useful EDC's can be reported for this chemisorptive system. This is in contrast with the case¹⁸ of H on a recrystallized Nb(110), where a sharp H^+ EDC peaked at 2.4 eV in the kinetic energy is observed even though the desorption cross section is also low. We will discuss the implication of this negative result in the next section. For the present we will concentrate on reporting the results obtained from photoemission studies.

Figure 1 shows the photoemission EDC's of both the clean and the H-saturated W(110) surfaces. The geometry of the CMA with respect to the sample and the incident light is illustrated in the lower left side of Fig. 1. The work functions of both the clean and the H-saturated surfaces are found to be 5.25 and 4.80 eV, respectively. This is in good agreement with several previous studies.^{5,7,8,10} The EDC of the H-saturated W(110) surface shows three major H-induced states at -2.0 , -3.8 , and -6.0 eV, respectively. This result is also basically in agreement with the angle-

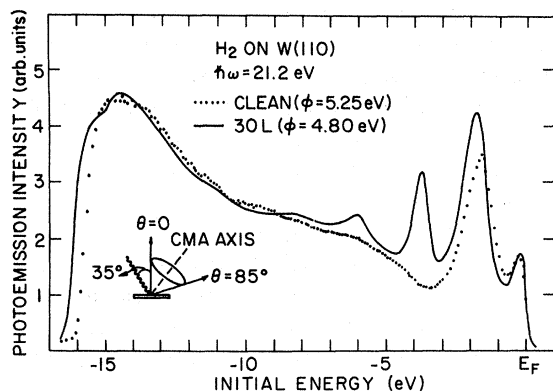


FIG. 1. Photoemission energy distributions at $\hbar\omega = 21.22$ eV for clean W(110) and a saturated exposure of H_2 at 300 K.

integrated photoemission results of Plummer *et al.*⁸

Figure 2 shows the difference curves, obtained by subtracting the clean spectrum from the H_2 -exposed surface spectra, for a variety of H_2 exposure ranging from a few tenths of 1 langmuir ($1 L = 1 \times 10^{-6}$ Torr sec) to 30 L (the pressure reading is not corrected by the gauge factor which is supposed to be 2.2). The corresponding work-function change of each exposure is indicated in the left-hand side of each curve.

The main features revealed from Fig. 2 are the following: (a) The three states at -2.0 , -3.8 , -6.0 eV, respectively, appear *simultaneously* at all

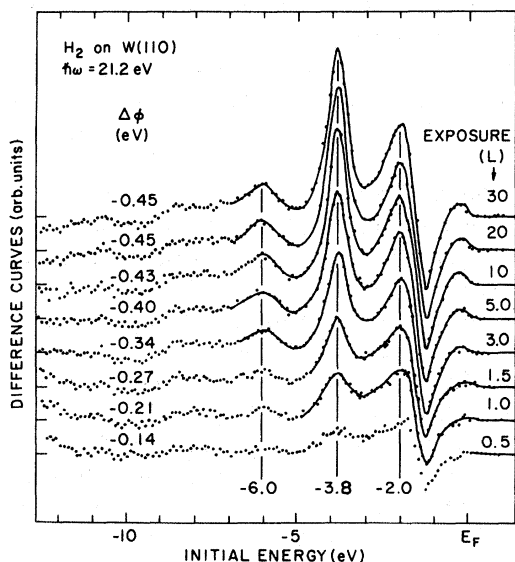


FIG. 2. Difference curves relative to clean W(110), for 300-K adsorption of H_2 on W(110). The photon energy and work-function changes are shown on the left. The H_2 exposures are shown on the right.

coverages, (b) the energy positions of these three states are *independent* of coverage (or exposure), and (c) the variation of the -2.2 - and -6.0 -eV peak heights with exposure is *different* from that of the -3.8 -eV peak height. The third feature can be more clearly seen in Fig. 3, where we have plotted the photoemission peak heights of the two most pronounced states at -2.0 and -3.8 eV, respectively, as a function of hydrogen exposure. Both curves shown in Fig. 3 are obtained by continuously monitoring the photoemission peak heights of both states as a function of time at a fixed pressure (without gauge-factor correction). The result thus obtained is the same as that of measuring the peak heights from all the difference curves.

We find that both curves satisfy a simple equation of adsorption kinetics,¹⁹ namely

$$\frac{d\Theta}{dt} = \frac{2\Gamma S_0}{N_s} f(\Theta), \quad (1)$$

with

$$f(\Theta) = 1 - \Theta, \quad (2)$$

where Γ is the rate of arrival of molecules at the surface, S_0 is the initial sticking coefficient, N_s is the maximum amount adsorbed, and $f(\Theta)$ gives the general coverage dependence.

The initial sticking coefficients S_0 are determined (after the pressure reading is corrected) to be $S_0 = 0.022$ and $S_0 = 0.055$ for the β_1 (-3.8 eV) and β_2 (-2.0 eV) states, respectively. The expo-

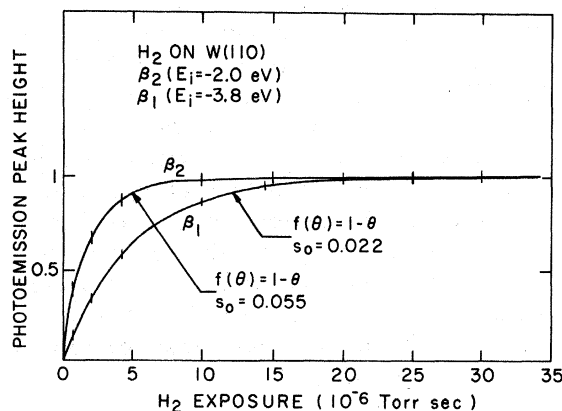


FIG. 3. Photoemission peak heights of both states at -2.0 and -3.8 eV, respectively, shown as a function of H_2 exposure. Both curves are found to exhibit $f(\Theta) = 1 - \Theta$ adsorption kinetics. The initial sticking coefficients (S_0) of both states are found to be 0.022 and 0.055, respectively. $\hbar\omega = 21.22$ eV.

sure dependence of the -6.0 -eV peak height is found to be similar to that of the -2.0 -eV peak height, although its exact behavior is difficult to judge because of poor signal-to-noise ratio.

One remarkable feature also revealed from Fig. 2 is that the exposure dependence of the work-function change is exactly the same as that of the -2.0 -eV peak height. They obey the same adsorption kinetics as illustrated by Eqs. (1) and (2). This interesting feature is shown in Fig. 4(a), where we have plotted the work function, determined from the EDC's, as a function of H_2 exposure. The data points follow a curve exactly identical with that of the -2.0 -eV peak height shown in Fig. 3 if one normalizes both curves at saturation. If one plots the peak height of the -2.0 -eV state as a function of work-function change, one obtains a straight line as shown in Fig. 4(b), where the work-function dependence of the -3.8 -eV peak height is also shown.

IV. DISCUSSION

A. Electron-stimulated desorption

The fact that very few H^+ signals with meaningful ion EDC's are observed for all coverages in

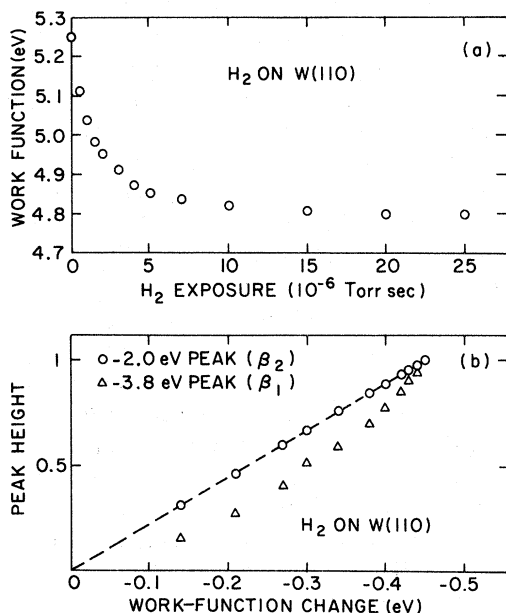


FIG. 4. (a) Work function of H on W(110) plotted as a function of H_2 exposure. (b) Photoemission peak heights of the -2.0 - and -3.8 -eV peaks in the difference curves for 300-K adsorption of H_2 on W(110), plotted as a function of work-function change. $\phi_0 = 21.22$ eV.

the present study strongly suggests that the H adatoms bind to high-coordination sites,^{17,18} such as the trigonal (distorted long bridge) or the long-bridge sites, so that the desorption cross section becomes very low for these H adatoms. Our results are different from those of King and Menzel.¹¹ King and Menzel¹¹ have reported the observation of H^+ currents from H on W(110) with significantly higher desorption cross sections (the upper limit has been determined¹¹ to be 1.4×10^{-18} cm²) than our estimation (lower than 10^{-23} cm²). We do not know the exact reason for this difference but we wish to comment on the results reported by King and Menzel.¹¹ The initial sticking coefficient of the β_2 state is estimated to be 0.055 in the present study, in good agreement with the value of 0.06 reported by Tamm and Schmidt.³ The value of 0.025 reported by King and Menzel,¹¹ however, is much lower than the value of 0.06 obtained by us and Tamm and Schmidt.³ Moreover, the exposure dependence of the H^+ -ion current reported by King and Menzel¹¹ does not agree with the exposure dependence of the photoemission peak heights of both the β_2 and β_1 states shown in Fig. 3 or with that of the $p(1 \times 2)$ RHEED intensity.² Specifically, the saturation exposure (about 100 L) reported by King and Menzel¹¹ is much larger than the value (30 L) obtained in the present study or previous studies.^{2,5} The exposure where the β_1 state starts to build up is about 15 L according to King and Menzel,¹¹ which is also much larger than our photoemission observation (0 L) or the results (~ 5 L) of Feuerbacher and Fitton.⁶ In short, the ESD results of King and Menzel¹¹ do not seem to agree with any of the available data except the argument concerning the existence of two states, which is in line with the majority opinion that there may be two states, i.e., β_1 and β_2 , for H on W(110). We are not sure of the exact reason for this discrepancy but we wish to point out a report by Bauer and Poppa²⁰ concerning the effect of impurity on the ESD of H^+ from metal surfaces. Bauer and Poppa²⁰ have found that the existence of impurity such as O on the metal surface or H_2O in the H_2 gas can dramatically enhance the desorption cross section of H^+ from the metal surface. In other words, the H^+ signals observed in ESD could be the result of impurities such as O and H_2O , and not necessarily be due to pure H layers on the clean metal surface. In fact, we have observed significant H^+ signals with well-defined ion EDC's when the surface is contaminated by impurities such as H_2O , CO, or O. But when the W(110)

is judged to be clean from both Auger and photoemission standpoints, very few H^+ signals with recognizable ion EDC's can be observed (the very small amount of H^+ signals could be due to background noises).

B. Photoemission

The interpretation of the -2.0 - and the -3.8 -eV peaks is not entirely clear. It has been suggested⁶⁻⁸ that both peaks are H-induced states and are associated with the occupation of the β_2 and β_1 states, respectively. However, recent angle-resolved photoemission studies by Blanchet *et al.*¹⁴ using synchrotron radiation have suggested that both peaks originate from the bulk bands of the W substrate. The intensities of both peaks vary depending on the symmetry of the surface atomic structure, the photon polarization vector, the photoelectron emission angle, and the H coverage. Blanchet *et al.*¹⁴ have also suggested that the true H-induced states are those at and below -6 eV. Whatever the interpretation it may be appropriate to assume that the intensity of the -6.0 -eV peak observed in the present photoemission study is directly proportional to the coverage of H adatoms. Moreover, since both the -2.0 - and -3.8 -eV peaks appear as a result of H adsorption, and since the intensities of both peaks increase with H exposure, and the exposure dependence of both peak heights can be described by a simple adsorption kinetics which agrees at least for β_2 with the results of Tamm and Schmidt,³ it may not be inappropriate to assume that the peak heights of both the -2.0 - and -3.8 -eV states are also proportional to the coverage of H adatoms. This is substantiated by the fact that the exposure dependence of the -6.0 -eV peak height is the same, within the errors produced by the poor signal-to-noise ratio of this peak, as that of the -2.0 -eV peak height. Based on this assumption we shall discuss the implication of the photoemission data shown in Figs. 3 and 4 regarding the binding states of H on W(110).

The fact that the two "H-induced" states, traditionally referred to as the β_2 (-2.2 eV) and β_1 (-3.8 eV) states, exhibit different adsorption kinetics (see Fig. 3) strongly suggests that both states are induced by two different types of H adatoms. This result seems to substantiate the two-binding-site model. However, in view of the fact that the -2.2 -eV state has the same adsorption kinetics as the -6.0 -eV state (the truly H-induced state) and

that the work-function changes follow exactly with the appearance of the -2.2 -eV (or the -6.0 -eV) state, the -3.8 -eV state (i.e., the β_1 state) may be the result of lateral interaction. Whatever the case the present study indicates that both states are filled simultaneously, with one state (the β_2 state) being filled about 2.5 times faster initially than the other state (β_1), rather than sequentially as suggested by previous studies.³⁻⁷ This discrepancy may be explained as follows. In thermal desorption, if an equilibrium exists between two distinguishable states there can only be one peak in the thermal desorption spectra²¹ below $\Theta = \frac{1}{2}$. In photoemission the angular distribution of both peak intensities may be coverage dependent, as evidenced by some of angle-resolved photoemission data¹⁴ obtained using synchrotron radiation, so that the absence of the state of -3.8 eV in normal photoemission for coverages below $\Theta = \frac{1}{2}$ does not mean that there are no such states at off-normal angles. This is clearly shown in the angle-integrated photoemission data of Plummer *et al.*⁸ and in the present study. By the same token, the attenuation of the -2.2 -eV peak height for $\Theta > \frac{1}{2}$ reported in the angle-resolved photoemission studies of Feuerbacher and Fitton⁶ and Holmes and King⁷ is also due to the same effect as described above. In other words it may not be appropriate to use the angle-resolved photoemission intensity as a gauge to determine the coverage of the adsorbate.

The adsorption of both types of H on W(110) obeys $1 - \Theta$ kinetics. Kinetics of this form normally are interpreted as requiring adjacent empty sites for adsorption.¹⁹ A random, dissociative chemisorption of H_2 molecules on the surface should have a $(1 - \Theta)^2$ dependence. It is quite possible, therefore, that when H_2 molecules reach the (110) face of W, they somehow dissociate and diffuse to form patches of ordered superstructure on this surface.²² The growth of the ordered superstructure associated with the β_2 state is faster than that of the β_1 state. To be consistent with the RHEED data, the binding sites of both states should be different from each other, and each type of H adatom forms a $p(1 \times 2)$ superstructure, so that even if the coverage reaches $\Theta = 1$, the $p(1 \times 2)$ superstructure still exists. However, in view of the fact that a single-binding-site model seems to be more consistent with the IES data,¹⁴ we propose that the binding site of the β_1 state may not be noticeably different from that of the β_2 state. Specifically, we suggest that the β_2 -H occupies the *distorted* long-bridge site and the β_1 -H oc-

cupies the long-bridge site (or vice versa). The local electronic structure induced by both types of H-W complex can be dramatically different from each other, e.g., the β_2 -H produces and/or enhances two states at -2.0 and -6.0 eV, respectively, and the β_1 -H produces and/or enhances a state at -3.8 eV, but the electron energy losses of both states may not be distinguishable,²³ a "very unfortunate quirk of nature" as described by Blanchet *et al.*¹⁴

If we forget about the $p(1 \times 2)$ superstructure reported by Matysik² and instead, adopt the $c(2 \times 2)$ argument of Blanchet *et al.*,¹⁴ we still cannot fully reconcile with these authors' proposed model. For one thing the model proposed by Blanchet *et al.*¹⁴ still favors a sequential filling process in which the β_2 state, which occupies the (distorted) long-bridge site and forms a $c(2 \times 2)$ superstructure, builds up first until the coverage reaches $\Theta = \frac{1}{2}$. It is only after the coverage is larger than $\Theta = \frac{1}{2}$ that the second state β_1 , which also occupies the same site as β_2 , appears and causes an order-partial-disorder conversion.¹⁴ According to the present studies, both states should appear simultaneously and the order-partial-disorder conversion should appear at low coverages (i.e., $\Theta < \frac{1}{2}$). A more careful calibration of the coverage needs, therefore, to be conducted on this system in order to resolve this discrepancy. Assuming this discrepancy is resolved and indeed, the order-partial-disorder conversion appears at low coverages, our model will then be consistent with a single-binding-site model such as the one proposed by Blanchet *et al.*¹⁴ Basically, the $1 - \Theta$ adsorption kinetics indicates that the incoming H_2 molecules dissociate and form patches (or islands) on the W(110) surface. The β_2 state, which produces two binding-energy levels at -2.0 and -6.0 eV, respectively, is a truly local H-site-induced state, corresponding to the adsorption of a H adatom on the (distorted) long-bridge site. The β_1 state, which induces an energy level at -3.8 eV, is not a local H-site-induced state, but one which measures the H-H lateral interaction and the long-range symmetry (or ordering) of the H overlayer. In light of the observation of Blanchet *et al.*¹⁴ the appearance of the -3.8 -eV peak, which is actually a bulk state of the W substrate, is a result of surface symmetry breaking due to β_1 state of the H overlayers. The total coverage of H adatoms should therefore be measured by the angle-integrated photoemission intensity of the β_2 state. If the total work-function change is linearly proportional to the total cover-

age of H adatoms, it should then be proportional to the intensity of the β_2 state. This is indeed the case as shown in Fig. 4. With this interpretation the initial sticking coefficient of the adsorption of H_2 on W(110) becomes 0.11 if we assume that the saturation coverage for the β_2 state is $\Theta = 1$. It remains to be explained, however, why the intensity of the β_1 state, which only measures the lateral interaction and the long-range symmetry of the H overlayer, also obeys $1 - \Theta$ adsorption kinetics.

V. CONCLUSION

We have proposed a model concerning the chemisorption of H on W(110) at room temperature which is consistent with our present photoemission and ESD results. In this model, there are two types of H adatoms which are found to appear simultaneously rather than sequentially as believed previously. Both types of H adatoms induce different binding-energy levels in the photoemission energy distribution curves, but exhibit a simple $1 - \Theta$ adsorption kinetics, with each type having a different initial sticking coefficient. The model is consistent with the RHEED results² if we assume that both types of H adatoms occupy slightly different sites (e.g., the long-bridge and distorted long-bridge sites) and form patches of ordered $p(1 \times 2)$ superstructures, respectively. In order for this model to be also consistent with the IES data,¹⁴ we have to assume that the current IES technique cannot distinguish one site (e.g. the long bridge) from the other (e.g. the distorted long bridge). This remains to be clarified. On the other hand, however, if the superstructure is $c(2 \times 2)$ as suggested by Blanchet *et al.*¹⁴ our model will be basically consistent with the one proposed by Blanchet *et al.*¹⁴ In this model, both types of H adatoms occupy the same binding site (e.g. the distorted long-bridge site). The so-called β_2 state is a truly local H-site-induced state, which measures the total coverage of the H adatoms as well as the total work-function changes. The so-called β_1 state is not a H-induced state and, therefore, does not produce any new energy levels in the photoemission energy distribution curves. The appearance of the -3.8 -eV energy level associated with the existence of the β_1 state is simply a result of the emergence of the W bulk states because of symmetry breaking imposed by the H overlayer. The strength of the β_1 state, as measured in either the thermal desorption or the photoemission study, is therefore a reflection of the strength of the H-H

lateral interaction and the long-range symmetry of the H overlayer. It remains to be explained, however, why this "strength" also obeys a simple $1-\Theta$ adsorption kinetics. Moreover, several discrepancies or problems have to be resolved before this model can be well accepted. First, the order-partial-disorder conversion¹⁴ should occur at coverages much less than $\Theta = \frac{1}{2}$ according to our photoemission data, rather than at and larger than $\Theta = \frac{1}{2}$ as suggested by Blanchet *et al.*¹⁴ Second, the H adatoms form patches of ordered $c(2 \times 2)$ superstructure at room temperature according to this model, but several studies²² indicate that this may not be the case. Third, thermal desorption

data seem to support the two-binding-site model according to the analysis described in Ref. 23. Fourth, and the most important one, the controversy of $p(1 \times 2)$ vs $c(2 \times 2)$ superstructures has to be resolved in a more careful structural study.

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²³In this two-binding-site model, the saturated surface intensity for each (β_1 or β_2) state is 7×10^{14} at./cm² according to previous studies (Refs. 3–5). The total surface density is therefore 1.4×10^{15} at./cm², corresponding roughly to one H adatom per W substrate atom. If we assume that the total integrated intensity of a thermal-desorption spectrum is proportional to the H coverage, we find that this two-binding-site model is consistent with the thermal desorption data. Namely, if we add the intensities of both β_1 and β_2 curves (cf. Fig. 3) together as a function of exposure, the resultant curve roughly follows with the thermal-desorption data points obtained by Barford and Rye (see Fig. 7 in Ref. 5).