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H on Mo(100): Photoemission Result and Its Significance to the Correlation between the Surface Resonances and the Surface Reconstruction

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Photoemission indicates that the surface resonances on Mo(100) are not removed entirely by the adsorption of H₂. It also shows two H-induced states below the bulk *d*-band edge with the binding energies independent of coverage and in good agreement with a calculation. The results indicate that H on Mo(100) is bridge bonded with the local bonding configuration relatively unchanged by reconstruction. A significant correlation between the surface resonances and the surface reconstruction is suggested.

It has long been known that the intrinsic surface resonances on the (100) face of W are extremely sensitive to adsorbed gases.¹⁻³ For instance, the resonances are removed entirely by the adsorption of H₂ at more than 15% of a monolayer (or $\theta \geq 0.15$).³ Recently it has been suggested that if the adsorbates are sufficiently substratelike, such as Hg,⁴ Au,^{5,6} and Cu,⁶ and more importantly, if the overlayer structure is (1×1),^{6,7} the resonances can survive. Furthermore, it has been shown that the adsorption of H on W(100) induces a second-order structural phase transition.⁸⁻¹¹

At low coverages ($\theta < 0.15$), H atoms stabilize the reconstruction characteristic of the clean surface at room temperature and below,¹⁰⁻¹² and produce a full *c*(2×2) low-energy-electron-diffraction (LEED) pattern. With increasing coverage, H atoms induce a second-order phase transition and restore the surface to its unreconstructed (1×1) structure at saturation.⁸⁻¹⁰ At all coverages, H atoms are bridge bonded onto the (100) face of W.^{9,13} However, the binding energies of the H-induced states exhibit a significant dependence on the coverage,¹⁴ suggesting a drastic

change in the local bonding configuration during the phase transition.

Angle-resolved photoemission¹⁵ measurements indicate that the surface resonances on the (100) face of Mo are very similar to those of W. In each case there are three occupied bands of surface resonances with the first and the third being of d_{z^2} character and the second $d_{x^2-y^2}$ and $d_{zx, zy}$. Consequently, one would expect that the adsorption of H_2 and O_2 , which are nonmolybdenumlike and do not form a simple (1×1) overlayer structure at submonolayer coverages,^{16,17} would remove the surface resonances on the (100) face of Mo. Although this is the case¹⁸ for O_2 , we have found that H_2 does not destroy the surface resonances. Furthermore, we have observed two H-induced states below the bulk d -band edge. Their binding energies are independent of coverage and in good agreement with a calculation¹⁹ based on a bridge-bonded model. The results strongly suggest that H on Mo(100) are bridge bonded at all coverages and that the H-induced reconstruction does not differ appreciably from that of the clean surface.¹⁷ The results also suggest that the surface resonances are responsible for the reconstruction characteristic of the clean surface,¹⁷ and vice versa.

The angle-resolved photoemission spectra of clean, O_2 - and H_2 -adsorbed Mo(100) were obtained at the 240-MeV storage ring at the Synchrotron Radiation Center of the Physical Sciences Laboratory of the University of Wisconsin. The experimental system has been described elsewhere.^{15,20} In this study, only normal-emission photoelectron spectra were taken as a func-

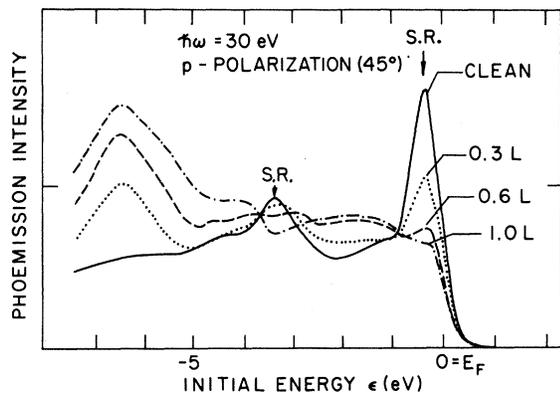


FIG. 1. Angle-resolved photoemission spectra of clean and O_2 -adsorbed Mo(100) at normal exit. The two arrows indicate the energy positions of the two surface resonances which disappear upon adsorption of O_2 .

tion of O_2 and H_2 exposure with the sample at room temperature.

For normal emission, only two surface resonances with $d_{3z^2-r^2}$ character are observed due to symmetry selection rules.¹⁵ Both resonances are indicated by the two arrows in Fig. 1 where we have plotted the photoelectron spectra of both clean and O_2 -adsorbed Mo(100) surfaces. Evidently both resonances are removed entirely after 1 Langmuir (1×10^{-6} Torr \cdot sec) of exposure.

By contrast, the surface resonances are not removed entirely by the adsorption of H on Mo(100) even up to the maximum coverage attainable (at room temperature in this study), as clearly seen in Fig. 2 where we have plotted the photoelectron spectra as well as the difference curves with various H_2 exposure. In Fig. 3 we have plotted the photoemission intensities of the intrinsic surface resonances ($\epsilon = -0.3$ and -3.3 eV) and one ($\epsilon = -5.3$ eV) of the H-induced states as function of H_2 exposure. According to previous LEED measurements, the adsorption of H on

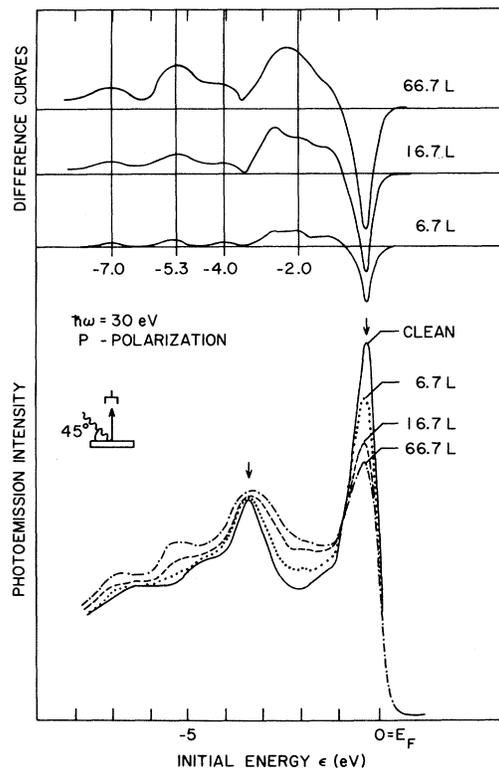


FIG. 2. Angle-resolved photoemission spectra as well as difference curves of clean and H_2 -adsorbed Mo(100) at normal exit. The samples were at room temperature. The two arrows indicate the energy positions of the two surface resonances.

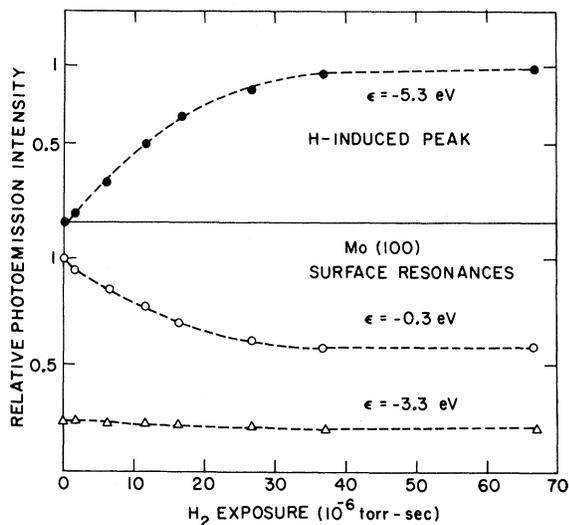


FIG. 3. The relative intensities of the two surface resonances of Mo(100) and one of the H-induced states plotted as function of H_2 exposure.

Mo(100) at room temperature produces LEED patterns corresponding to a $c(4 \times 2)$ unit mesh in one study¹⁶ and a (4×2) reconstruction in the other¹⁷ with exposure less than 1 Langmuir (or $\theta \leq 0.25$). At this coverage ($\theta = 0.25$), the surface resonances on the (100) face of W has already been removed, but those on Mo(100) are hardly affected, as clearly seen in Fig. 3. With increasing exposure, LEED studies^{16,17} of H on Mo(100) are controversial as to whether it is possible to obtain a saturation coverage ($\theta = 1$) at room temperature. For instance, Dooley and Hass¹⁸ obtained a (1×1) LEED pattern, presumably at $\theta = 1$, whereas Estrup¹⁷ suggested that the (1×1) LEED pattern was not obtainable and that the maximum coverage attainable was $0.5 < \theta < 1$. In any case, the results shown in Fig. 3 indicate that the peak intensity of the high-lying resonance ($\epsilon = -0.3$ eV) gradually decreases to half its initial value with exposure, apparently due to increasing coverage, and remains constant at and beyond 40 Langmuirs which may or may not correspond to the saturation coverage²¹ ($\theta = 1$), while the intensity of the low-lying resonance ($\epsilon = -3.3$ eV) is hardly affected. The intensity of the H-induced state gradually increases with coverage and also remains constant at 40 Langmuirs and beyond.

The phenomenon that the surface resonances are not removed entirely by the adsorbed atoms has been reported in several studies. A photo-

emission measurement⁴ has shown that the resonance on W(100) was not removed by a saturation coverage of Hg. The resonance also has been shown⁵ to diminish slowly with coverage before vanishing suddenly at just over one monolayer of Au on a W field emitter. A similar field-emission study⁶ has indicated, however, that the resonance exists only at 0, 1, and 2 monolayers of Au and Cu. The survival of the surface resonance has been suggested as being primarily because of the (1×1) structure of the adsorbate overlayer^{6,7} and, secondarily, because of the substratelike potential of the adsorbates.^{5,6} According to this argument, therefore, any non- (1×1) overlayer structure and any nonsubstrate-like adsorbate would remove the surface resonance at submonolayer coverages (or specifically $\theta < 0.5$). Although this argument is consistent with the effect of H on W(100), it clearly conflicts with the present observation that H, which has an entirely different potential from that of Mo, does not remove entirely the surface resonances on the (100) face of Mo. As will be discussed later, we suggest that the survival of the surface resonances depends, at least in the case of H adsorption, essentially on whether the reconstruction characteristic of the clean surface is altered appreciably or not.

In Fig. 2, two H-induced states at $\epsilon = -5.3$ and -7.0 eV are clearly seen in both the photoelectron spectra and the difference curves. (Less obvious are the states around $\epsilon = -2.0$ and -4.0 eV which can only be clearly identified in the difference curves.) The binding energies of these H-induced states are independent of coverage, suggesting that there is only one bonding configuration involved, presumably bridge bonding, at all coverages. This would then be similar to the bonding of H on W(100).^{9,13} The conclusion that H atoms are bridge bonded onto the (100) face of Mo is further supported by a self-consistent pseudopotential calculation.¹⁹ Assuming a bridge-bonded (1×1) saturated overlayer structure and a distance of 0.75 \AA for the H atoms above the substrate Mo(100), the calculation¹⁹ predicts two H-induced states at binding energies of $\epsilon = -5.4$ and -7.1 eV at the $\bar{\Gamma}$ point, in good agreement with the present data. The calculation, however, cannot explain why the two surface resonances are not quenched by the adsorption of H_2 , but it does indicate that the high-lying resonance still exists except that it occurs at lower initial energies.

Although both W(100) and Mo(100) surfaces have

been suggested to exhibit a second-order structural phase transition^{8,11} due to the adsorption of H, which occupies the bridge sites throughout the whole coverage range, there are significant differences between the two systems. First, the reconstruction patterns induced by H adsorption are different between H on Mo(100) and H on W(100), as described previously. Secondly, the binding energies of the H-induced states *shift* with coverage¹⁴ for H on W(100),²² but *do not* for H on Mo(100) as seen in Fig. 2. If the shift in binding energies for H on W(100) is due to dramatic changes in the local bonding configuration because of the phase transition, the above results would suggest that the local bonding configuration of the bridge-bonded H on Mo(100) remains relatively unchanged during the phase transition. In other words, the reconstruction of Mo(100) induced by H-adsorption does not differ appreciably from that of the clean surface, whereas the H-induced reconstruction of W(100) differs markedly from that of clean surface at $\theta \geq 0.15$ where the $c(2 \times 2)$ structure, characteristic of the clean surface, disappears and new structures begin to form.⁸ This phenomenon correlates very well with the behavior of surface resonances as function of coverage, namely, the surface resonances survive when the H-induced surface reconstruction does not differ appreciably from that of clean surfaces, such as H on Mo(100) at all coverages and H on W(100) at $\theta < 0.15$, and disappear when the reconstruction is significantly different from the clean surface structure, such as H on W(100) at $\theta > 0.15$. The significant correlation between the surface resonances and the surface reconstruction suggests strongly that the surface resonances are responsible for the reconstruction characteristic of the clean surface,⁸ and vice versa. This correlation may also be responsible for the results that the adsorption of Hg,⁴ Au,^{5,6} and Cu⁶ on the (100) face of W does not remove the surface resonance under certain circumstances.

In conclusion, angle-resolved photoemission measurements have indicated that the intrinsic surface resonances on the (100) face of Mo are not removed entirely by the adsorption of H at room temperature and that the binding energies of the H-induced states do not shift with coverage, in contrast to the case of H on W(100). By comparing with the previous results concerning the adsorption of H on W(100)^{3,8-11} and with a theoretical calculation,¹⁹ we suggest that H atoms are bridge bonded onto the (100) face of Mo at

all coverages and that the reconstruction of Mo(100) induced by H adsorption at room temperature does not differ appreciably from that characteristic of the clean surface. The analysis of the results further suggests that the surface resonances on the (100) faces of W and Mo are responsible for the reconstruction characteristic of the clean surfaces, and vice versa.

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²²The binding energies of the H-induced states for H on W(100) are different among the various reports, e.g., W. F. Egelhoff and D. L. Perry [Phys. Rev. Lett. **34**, 93 (1975)] obtained -1.7, -5.0, and -7.6 eV; B. Feuerbacher and R. F. Willis [Phys. Rev. Lett. **36**, 1339 (1976)] obtained -2.0, -6.0, and -12.0 eV; Anderson *et al.* (Ref. 21) obtained -2.0, -4.3, and -6.5 eV; and Plummer *et al.* (Ref. 14) obtained -1.5 and -5.0 eV, respectively. The numbers are approximate values.

Observation of Conduction-Electron Density Oscillations at the Surface of Platinum Particles

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Anomalous large ¹⁹⁵Pt NMR linewidths have been observed in platinum particles with diameters ranging from 33 Å to 200 Å. Spin-echo measurements revealed the presence of nuclear spin-exchange diffusion in large magnetic field gradients attributable to the large indirect exchange interaction in platinum. These data indicate that there are electron spin-density oscillations near the platinum surface consistent with a simple model ascribing free-electron behavior to the *s*-like conduction electrons.

There has been considerable theoretical and experimental interest in the surface electronic properties of the transition metals. In this work we have applied NMR techniques to the study of platinum metal clusters which broach the size regime of interest to heterogeneous catalysis where the fraction of atoms at the surface approaches unity. In such particles the discrete nature of the conduction-electron level spectrum becomes important giving rise to quantum effects¹ that scale inversely with the particle volume. Significantly, in our work, we see no evidence of this phenomenon in particles of diameter as small as 33 Å and at temperatures near 1.7 K. Another important effect is the direct influence of the metal surface on the electron density. We have discovered that ¹⁹⁵Pt NMR is very sensitive to this.

The samples were made from a silica-gel-supported platinum catalyst fabricated by a well-established impregnation technique.² The particles were spheroidal and essentially strain and defect free.³ The silica gel support was removed and 0.3 g of the remaining platinum powder was loaded into a quartz sample chamber and sealed in a helium atmosphere. After NMR experiments were performed the sample was heated *in situ* for five

hours to increase the particle size systematically prior to the next sequence of experiments. For size characterization, electron microscopy, nitrogen adsorption (Brunauer-Emmett-Telks method), and hydrogen chemisorption (titration method)⁴ measurements were performed (Table I).

Pure platinum and its alloys have been investigated extensively⁵ by NMR. Some of the relevant

TABLE I. The characterization of the various samples studied including the heat treatment temperature and particle diameters obtained by electron microscope (EM) studies, and surface areas and diameters obtained by N₂ adsorption [Brunauer-Emmett-Teller (BET)] and by titration of H₂ on the Pt surface (H₂). The surface area measurements of *d* have an estimated accuracy of 10%. The first two samples were not heated. Samples 3, 4, and 5 were obtained by heating sample 2.

No.	<i>T</i> (°C)	EM <i>d</i> (Å)	BET (m ² /g)	<i>d</i> (Å)	H ₂ <i>d</i> (Å)
1		33 ± 11	36
2		50 ± 10	49	57	62
3	450	100 ± 20	20	140	132
4	550	140 ± 20	17	170	160
5	650	200 ± 40	13	218	258