UPS studies of virgin CO on W(100)*

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The adsorption of CO on W(100) at 80 K has been studied by photoelectron spectroscopy at $h\nu = 21.22$ eV, and the results have been correlated with previous data for room temperature adsorption. Initial adsorption produces a peak in the emission spectrum at ~ -7.6 eV (relative to the Fermi energy), which is characteristic of the virgin state of adsorbed CO, as well as additional structures which have been previously shown to be characteristic of α- and β-CO. Upon heating the sample to 260 K the -7.6-eV level is depleted and apparent conversion to the β state occurs as indicated by an enhancement of the emission near -5.5 eV. Additional data taken with $h\nu = 16.85$, 26.9, and 40.81 eV are in general agreement with the measurements at 21.22 eV; however, the peak at -7.6 eV for $h\nu = 21.22$ eV is shifted to lower kinetic energies by several tenths of an electron volt at the other photon energies.

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INTRODUCTION

The adsorption of CO on W(100) has been studied by a number of groups using a variety of techniques.[1–9] The bulk of these data are consistent with the model of three distinct binding states of CO on W(100) called α, β, and virgin. β-CO is strongly bound to the substrate. It adsorbs on clean tungsten at temperatures below $\sim$1000 K (Ref. 7) and desorbs in the temperature range between 1000 and 1500 K.[7,8] α-CO is electropositive and is clearly molecular.[2,10] It is adsorbed only after appreciable adsorption of β-CO has taken place,[7] and, upon heating above 300 K, α-CO partially desorbs and partially converts to β-CO.[3,9] Virgin CO is electronegative and is adsorbed only on a clean substrate at low temperatures. Upon heating to 200–400 K this state, like α-CO, partially desorbs and partially converts to β-CO.[3,9]

Although this picture is fairly complete and previous experiments have yielded a good deal of information, a number of questions relating to the nature of adsorbed CO, and of virgin CO in particular, are unresolved. One question is concerned with the distinction between the structure of virgin CO and the other forms. Although virgin CO is electronegative and α-CO is electropositive, only minor differences in the electron stimulated desorption (ESD) and thermal desorption behavior have been found for CO adsorbed at 100 K as compared to CO adsorbed at higher temperatures.[9] Ultraviolet photoemission spectroscopy (UPS) can be used to study the valence electronic energy level structure of the low temperature and higher temperature forms and should be able to shed some light on this question.

Another question is concerned with whether adsorption at $\sim$100 K produces a pure virgin layer or whether significant amounts of β-CO and α-CO are present as well. Gomer[1] has argued from ESD results that the β states are not present in the initial virgin layer and are formed only when this layer is heated to 200–400 K. On the other hand, the ESCA data of Yates *et al.*[3] indicate that, although heating a monolayer of adsorbed CO produces a conversion from virgin to β-CO, significant quantities of both α- and β-CO are present in the layer formed by adsorption at 80 K.

In order to help resolve these questions we have made UPS measurements on the virgin-CO/W(100) surface complex at photon energies of 16.85, 21.22, 26.9, and 40.81 eV. Previous measurements by Baker and Eastman[4] and Plummer *et al.*[7] on CO adsorbed on W(100) at 300 K have demonstrated significant differences between the electronic structure of the β and α states and have indicated that, whereas α-CO is molecular, the most tightly bound state of β-CO on W(100) may be dissociated.[7] The UPS measurements were not extended to low temperatures, however, so that the electronic structure of virgin CO was not studied.

The apparatus used for the present experiment has been described previously.[7] In addition, we have made two modifications. First, a liquid-nitrogen cold stage was added to cool the sample to a temperature of 80 K as measured by a W–3%Re/W–25%Re thermocouple. Second, the microwave-discharge uv source was modified to produce usable fluxes of 26.9 and 40.81 eV photons.[11] Bulk carbon was removed from the sample by a prolonged heating in oxygen.[12] Prior to adsorption the tungsten crystal was flashed to $\sim$2500 K.

SEQUENTIAL ADSORPTION

Figure 1 shows photoemission spectra measured after successive exposures of CO accumulated up to a near

saturation exposure of 2.67×10^{-4} Pa s (2.0 L, where 1 L is equal to 10^{-6} Torr s). Each curve is the difference between the spectra measured immediately before and after a CO exposure and therefore shows the changes in the photoemission spectrum produced by each successive exposure. For an initial exposure of 0.67×10^{-4} Pa s, curve A shows peaks at -1.5, -3.3, -5.5, and -7.6 eV with respect to the Fermi energy. Previous photoemission data[4,7] have shown that the three higher energy peaks are characteristic of β-CO while the ~-8.5-eV peak is characteristic of α-CO. However, the peak (curve A) at -7.6 eV lies about 1 eV higher in energy than the room temperature α peak and is characteristic of virgin CO. The accompanying work-function increase of 0.27 eV is consistent with either β or virgin adsorption. When the previously exposed sample is exposed to an additional 0.67×10^{-4} Pa s (0.5 L), the resulting difference curve (Fig. 1, curve B) reveals only minor changes in the spectrum between -6 eV and the Fermi energy, indicating very little change in the population of the β state. There is, however, a significant increase in the peak at -7.6 eV accompanied by an additional work-function increase of 0.24 V, indicating further adsorption of the virgin state. The assignment of the peak at -7.6 eV to virgin CO is substantiated by the changes shown in curve C for an additional 1.33×10^{-4} Pa s (1 L) exposure. In addition to the continued growth of the main peak, a shoulder grows in at -8.6 eV, the approximate position of the α-CO peak previously observed.[4,7] The work-function change of -0.02 eV is consistent with the interpretation that the effect on the dipole layer of the electronegative virgin state is cancelled by the electropositive α state.[1] Since it has been shown that the α state adsorbs readily on a β layer at temperatures $\lesssim300$ K,[1,7,9] it is likely that α-CO adsorption is taking place on or near those sites of the crystal where β-CO is already adsorbed. Finally, the difference curve relative to the clean surface for the total exposure of 2.67×10^{-4} Pa s (2.0 L) (Fig. 1, curve D) clearly shows the extent of total adsorption into the virgin state as well as the small initial adsorption into the β state.

These data clearly indicate that, in addition to the virgin state, both α and β states are present in the CO layer chemisorbed at 80 K. This observation is consistent with the model that there are two possible channels for CO adsorption on clean W(100)[1]: the virgin state, which seems to be molecular and bonded to the substrate via the carbon atom, and the β state, which probably involves both C–W and O–W bonding. Although the bond energy of the β state to the substrate is larger than that for the virgin state, there is an activation energy associated with the population of β-CO which is consistent with the observations that β-CO forms readily at room temperature[4,7] whereas virgin CO is the principal component at lower temperatures.[1] This model is complicated by the observation that the β state is populated only in the initial stages of adsorption at 80 K (Fig. 1). We can invoke one of two possible

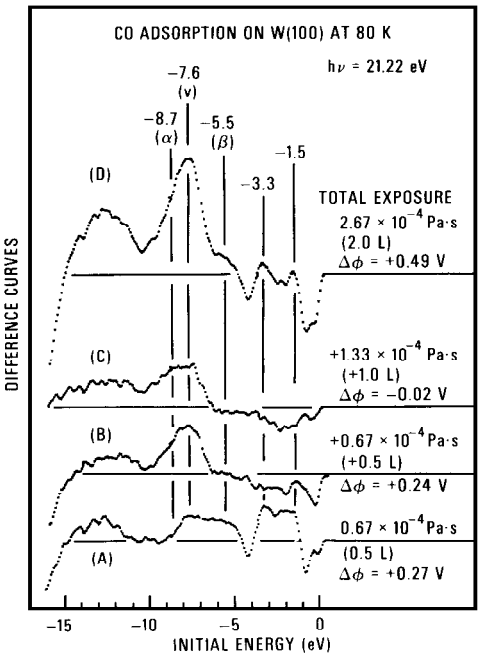

FIG. 1. Photoemission difference curves and work-function changes $\Delta\phi$ measured for W(100) at 80 K after successive doses of CO accumulated up to saturation (the units are arbitrary): A—difference curve and work-function change for an initial dose of 0.67×10^{-4} Pa s (0.5 L); B—the additional changes in the difference curve and the work function due to a second dose of 0.67×10^{-4} Pa s (0.5 L); C—the additional changes due to a third dose of 1.33×10^{-4} Pa s (1.0 L); D—difference curve and work-function change for the total exposure of 2.67×10^{-4} Pa s (2.0 L), equal to the sum of A, B, and C.

mechanisms to account for this point. First, the adsorbed virgin CO may migrate to step and kink sites on the substrate where the activation energy for formation of β-CO is lowered so that it is produced readily. When these sites are filled the adsorption of virgin CO does not lead to further population of the β state at 80 K. Alternatively, there may be a density-dependent activation energy for the formation of β-CO leading to a lower activation energy for its formation on clean W. In either case, continued exposure to gaseous CO results in the adsorption of both the α and virgin states.

One other notable feature of these data is that the adsorption of molecular CO produces a broad negative region in difference curves B and C between -6 eV and the Fermi energy and a corresponding positive region at energies less than -10 eV: Plummer *et al.*[7] have recently proposed that electrons photoemitted from the substrate may be inelastically scattered by an adsorbate. By using energy-loss data for gas-phase CO,[13,14] they calculated the changes that would occur in the photoemission spectrum due to inelastic scattering when a monolayer of CO molecules are adsorbed on W(100). The results show a 10% depletion in the emission from the substrate between the Fermi energy and -6 eV. Below this energy there is a gradual rise to a region of enhanced emission between -10 eV and the vacuum level. Curves B and C show good qualitative agreement with this model calculation although the use of gas

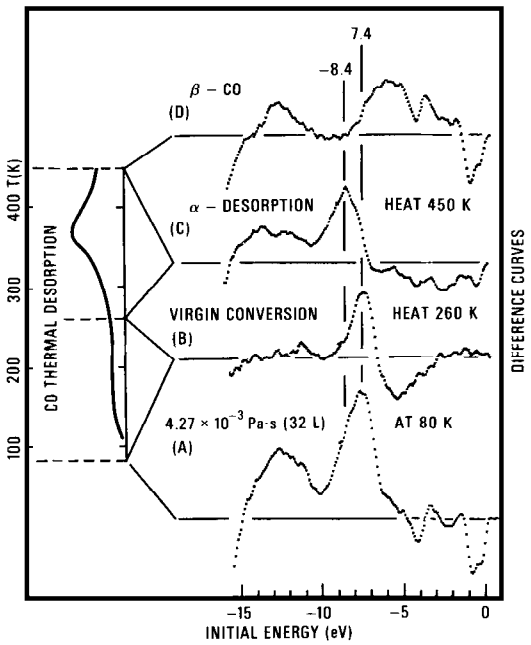

FIG. 2. Photoemission difference curves correlated with CO thermal desorption data (units are arbitrary): A—difference curve for adsorption of 4.27×10^{-3} Pa s (32 L); B—the changes caused by heating to 260 K; C—the additional changes caused by heating to 450 K; D—difference curve for β-CO formed by heating to 450 K.

phase data to calculate electron energy losses for a chemisorbed molecule has not been validated.

CONVERSION AND DESORPTION

In order to characterize more fully the structure and interactions in the chemisorbed layer, we have made a series of UPS measurements during stepwise heating of the sample through a series of temperatures up to 450 K. As shown in Fig. 2, the results may be consolidated into two ranges of temperature and correlated with the thermal desorption data of Yates and King.[9] Curve A in Fig. 2 is similar to curve D in Fig. 1 and simply shows the difference curve measured after a saturation exposure at 80 K. Curve B, however, shows the spectrum measured after adsorption at 80 K minus the spectrum measured after subsequent heating to 260 K. Peaks in this curve (and in curve C as well) indicate where the emission has been reduced by the heat treatment and troughs indicate where the emission has been intensified. The curve shows that upon heating to 260 K the virgin peak at -7.6 eV is depleted substantially and the β peak at -5.5 eV increases. This observation is consistent with the conclusion arrived at by previous workers[1,3,7,15] that virgin CO converts to the β state upon heating to room temperature.

The thermal desorption data[9] reproduced in Fig. 2 show that very little desorption of CO occurs in this temperature range. Absolute coverage data on W(110) by Kohrt and Gomer,[16] however, give a CO/W ratio of 1.1 for a low temperature layer at saturation and 0.5 for the α and β layers. Therefore, if there is very little desorption to produce vacant surface sites for total virgin to β conversion, a form of conversion must be taking place which involves both virgin to β and virgin to α reactions. Because the broad α and virgin peaks are separated by only 1 eV in the photoemission spectra, the large overlap of the peaks does not permit an unambiguous assignment to the latter process.

Heating the sample above room temperature produces a thermal desorption peak at $\sim$370 K from the desorption of α-CO. The corresponding changes in photoemission are indicated by curve C which shows the spectrum measured after heating to 450 K subtracted from the spectrum measured after heating to 260 K. The desorption of α-CO appears as a peak at -8.4 eV, but in contrast to curve B, the absence of a deep minimum between -6 and -4 eV indicates that conversion of the α-CO to β is not competing significantly with the desorption process. The wide trough above -6 eV and the corresponding shoulder at lower energies are more characteristic of the inelastic-scattering spectrum discussed in the previous section. This observation correlates with the thermal desorption data since it suggests that a large fraction of the adsorbed CO molecules producing inelastic scattering of the substrate photoelectrons are desorbed between 260 K and 450 K.

Taken together, the UPS and thermal desorption data clearly indicate that virgin conversion and α desorption take place in different temperature ranges. The former process dominates below 260 K whereas the latter process dominates when the surface is heated from 260 to 450 K.

Very little α-CO remains on the surface after the sample is heated to 450 K.[9] The resulting difference spectrum with respect to clean W (Fig. 2, curve D) is characteristic of β-CO.[4-7] Since the double-peaked

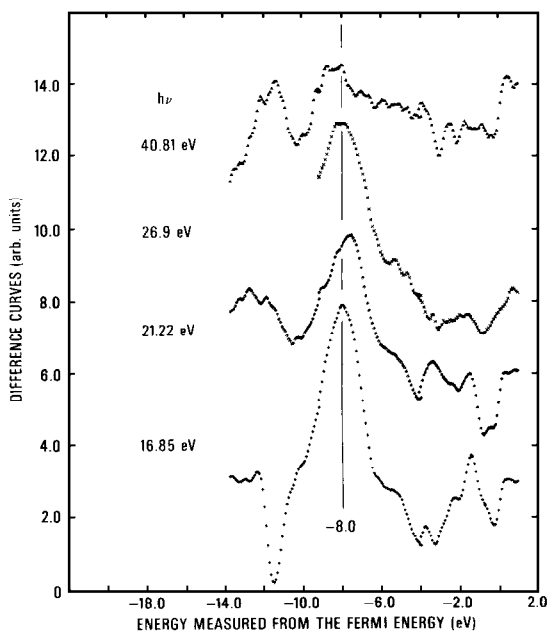

FIG. 3. Difference curves at four photon energies for saturated adsorption of CO on W(100) at 80 K. (For $h\nu=40.81$ eV, adsorption took place over a range of temperature between 145 and 85 K.) Each curve is normalized so that the emission from the d-band peak between 2 and 3 eV below the Fermi level for the clean surface is given a value of 5 (arbitrary units).

structure in the region of W d-band emission between -3 and -1 eV also appears in curve A but not in curve B, it is apparent that this structure is not sensitive to the changes in the bonding character of CO which take place when the sample is heated from 80 K to 260 K. This suggests that the double peak primarily reflects changes in the electronic structure of the substrate due to interaction with the adsorbate.[7]

DATA FOR SEVERAL PHOTON ENERGIES

Figure 3 shows difference curves for photon energies of 16.85, 21.22, 26.9, and 40.81 eV after saturated adsorption at 80 K. For $h\nu = 40.81$ eV, the data were averaged from several runs measured after adsorption at temperatures between 145 and 85 K. In addition to the main peak at -7.6 eV, the 21.22-eV data show a small peak at -11.4 eV superimposed on a feature at -12.5 eV which is due to the disappearance of a dip in the clean W(100) spectrum upon adsorption.[4,5,7] The peak at -11.4 eV becomes much more intense for $h\nu = 40.81$ eV. Furthermore, additional data do not reveal any other levels down to ~ 17 eV below the Fermi energy. This two-level structure and the $h\nu$-dependence of the lower-lying level[17–19] are consistent with the interpretation that the -11.4-eV level of virgin CO is derived from the 4σ level of gaseous CO, whereas the -7.7-eV peak contains two unresolved levels derived from the 5σ and 1π levels of gaseous CO.

Another striking feature of these data is the shift in the position of the main peak for different photon energies. For $h\nu = 16.85$, 26.9, and 40.81 eV, a peak occurs at -8.0 eV. However, for $h\nu = 21.22$ eV, the peak appears at -7.6 eV. (The additional peak at -8.6 eV for $h\nu = 40.81$ eV is thought to be due to adsorption of a larger amount of α-CO owing to the higher adsorption temperature.) It is possible to explain the apparent shift by hypothesizing large changes in the photoionization cross section near threshold for either the 5σ- or 1π-derived levels of adsorbed CO. Plummer *et al.*[20] have observed a peak in the photoionization cross section of the 5σ level of gas-phase CO due to the excitation of an autoionizing level just above threshold. On the other hand, the existence of Cooper minima in photoionization cross sections is well known.[21] The observed shift in the peak would be produced if the energies of the 1π and 5σ levels were at approximately -8.1 and -7.5 eV, respectively, and if there were either a maximum in the 5σ photoionization cross section or a minimum in the 1π photoionization cross section when $h\nu \approx 21.2$ eV. Neither effect has been observed for gas-phase CO near 21 eV,[20] although the adsorbed CO molecule may be perturbed in such a way as to produce one of these effects. Since the 1π photoionization cross section increases relative to the 5σ cross section at higher photon energies,[17] the above hypothesis is consistent with the observation that the peak shifts downward in energy for $h\nu = 26.9$ and 40.81 eV.

SUMMARY

In conclusion, the UPS results indicate the presence of all three binding states of CO adsorbed at 80 K and distinguish between desorption and conversion processes upon heating. Finally, peak shifts of the order of several tenths of an electron volt suggest large variations near threshold in one or more of the partial photoionization cross sections for adsorbed CO.

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