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Photoemission and electron-energy-loss spectroscopy investigation of CO+K/Cu(100)

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We have investigated the system CO+K/Cu(100) at a potassium precoverage of $\Theta_K \sim 0.3$ using the techniques of low-energy electron diffraction, angle-resolved ultraviolet photoemission spectroscopy (UPS) with a synchrotron radiation source, angle-integrated UPS and x-ray photoemission spectroscopy, electron-energy-loss spectroscopy (EELS), thermal desorption spectroscopy, and work-function measurements. Our UPS results demonstrate a reduction in symmetry of the CO molecules in the presence of K, a strong splitting and hybridization of the CO 5σ and 1π levels, *lack* of a substantial shift in the position of the σ resonance, a dramatic reduction in the intensity of CO satellite peaks, enhancement at E_F in the promoted system, and significant changes in the K $3p$ core levels at different coverages of K and CO. EELS demonstrates a dramatically weakened C—O bond in the presence of K on Cu(100), with a shift in the C-O stretching frequency from 2070 to 1530 cm^{-1} in the coadsorbed system. The work-function results are similar to changes reported in other coadsorbed systems with high alkali-metal precoverages. Our multiprobe results are best explained by a CO molecule bound to the clean surface primarily through a σ bond. The local presence of a K atom causes the bonding to become predominately π-like, involving both charge transfer into the CO 2π orbital and significant 1π-K direct interaction.

I. INTRODUCTION

In the past few years a number of studies using a variety of surface-sensitive techniques have been made of systems involving the coadsorption of atoms or molecules with alkali-metal atoms on single-crystal metal surfaces.[1-12] The primary focus of these investigations has been to obtain a better understanding of the promoting ability of alkali metals in catalytic reactions. The most thoroughly studied system has been CO coadsorbed with potassium on transition-metal surfaces.[2-12] The promotionlike effects of potassium on CO for these systems is quite general and include the following.

(1) Significant increase in the thermal desorption temperature of CO.

(2) Dramatic lowering of the C-O stretching frequency.

(3) Enhanced dissociation in some cases.

(4) Small shifts in CO core- and valence-level binding energies.

These changes have been explained in general by invoking the Blyholder picture of π back bonding of CO.[13] Specifically, most or all of these effects have been attributed to enhanced donation into the antibonding 2π level of CO with the addition of potassium to the surface. The exact mechanism for this donation is not clear, however. In particular, the nature of the interaction between alkali-metal atoms and the CO molecules has not been ascertained. The predominant interaction may be a short-range, direct interaction between coadsorbates, a long-range indirect interaction mediated by the substrate, or possibly a combination of the two.

In this paper we present a detailed study of the system CO + K/Cu(100) using primarily ultraviolet photoemission spectroscopy (UPS) and electron-energy-loss spectroscopy (EELS). We have chosen this substrate because the bonding of CO to noble metals such as copper is significantly weaker than the bonding to transition metals.[14] The question addressed in this paper is, how universal is the promoting ability of potassium when applied to a different class of substrates?

Since the beginning of this work, several other studies of similar systems have been undertaken. Vibration studies by Wallden[15] of CO + Na/Cu(100) and King and coworkers[16] of CO + Na,K/Cu(100),(110) have revealed large downward shifts in the C-O stretching frequency with the addition of alkali-metal atoms, similar to the shifts reported on promoted transition-metal surfaces. UPS studies have also been performed on the above systems by King and co-workers[16] and Somerton *et al.*[17] The connections of the above experiments to the present study will be discussed later in this paper.

This paper is organized as follows. In Sec. II experimental details are given. In Sec. III our results on the systems CO/Cu(100), K/Cu(100), and CO + K/Cu(100) are presented. Sections IV and V contain discussions and conclusions, respectively.

II. EXPERIMENTAL PROCEDURE

The angle-resolved photoemission measurements presented in this paper were performed at the Synchrotron Radiation Center of the University of Wisconsin. The light from the storage ring was monochromatized by a toroidal grating monochromator described elsewhere.[18] The electrons were analyzed by a hemispherical angle-resolved analyzer[19] with an angular resolution ±2.5°. The overall energy resolution was ~0.4 eV. The Cu(100) crystal was cleaned by sputtering and annealing with the surface cleanliness judged by Auger electron spectroscopy and UPS. The sample could be cooled to ~110 K, at which temperature both CO and potassium were deposited. The K source was a commercial alkali-metal dispenser from SAES-Getters.[20] The potassium was deposited as a thick film (~4 monolayers) on the copper substrate, then annealed to some particular temperature to achieve a desired K coverage. Considerable outgassing and repeated depositions were performed before potassium overlayers could be obtained which were relatively free of contamination, as judged by Auger electron spectroscopy and UPS. During the depositions reported here, the pressure rose no higher than the high 10^{-10}- or low 10^{-9}-Torr range from a base pressure of less than 2×10^{-10} Torr. Contamination or conversion of the surface was a problem as noticeable changes in low-energy electron diffraction (LEED) patterns and UPS spectra were observed within one to two hours. Therefore, most results reported here involved less than two hours of collection time before the sample was recleaned and a fresh surface was prepared. The effects of contamination will be discussed in more detail. All angle-resolved photoemission measurements were made with the A vector parallel to the $\overline{\Gamma}\overline{X}$ direction of the Cu(100) surface (in reciprocal space). Likewise, the collection plane was the one always containing this axis.

A separate study was made on this same system using x-ray photoemission spectroscopy (XPS), work-function, and angle-integrated UPS measurements. The XPS results will be described in more detail in a subsequent publication.[21] The work-function measurements reported in this paper were performed using He I or He II radiation, biasing the Cu crystal, and measuring the cutoff of the secondary electrons with a commercial VG analyzer.

The EELS experiments were performed at Exxon Research and Engineering Company, Annandale, NJ in a three-level stainless-steel ultrahigh-vacuum chamber equipped to perform high-resolution electron-energy-loss-spectroscopy, Auger electron spectroscopy, multiple-mass thermal desorption spectroscopy, and work-function measurements. Experimental details are described elsewhere.[22]

III. RESULTS

A. CO/Cu(100)

1. EELS, LEED, and work-function measurements

A typical EELS spectrum of CO/Cu(100) is shown as A, Fig. 1, which is in good agreement with previous investigations of this system.[23] All spectra were recorded at 100 K with instrumental resolutions ranging from 35 to 80 cm^{-1} (4 to 10 meV) and elastic count rates of $30-60\times10^3$ counts/sec. On the clean Cu(100) surface (spectrum A in Fig. 1), two prominent losses are visible: the C-O stretch at 2070 cm^{-1} (257 meV) and the M-C stretch at 355 cm^{-1} (44 meV). The relatively high C-O stretching frequency and the single low-frequency mode indicate that the CO molecules are terminally bonded and oriented normal to the surface. For comparison, the C-O stretch for gas phase CO is 2144 cm^{-1} (266 meV).

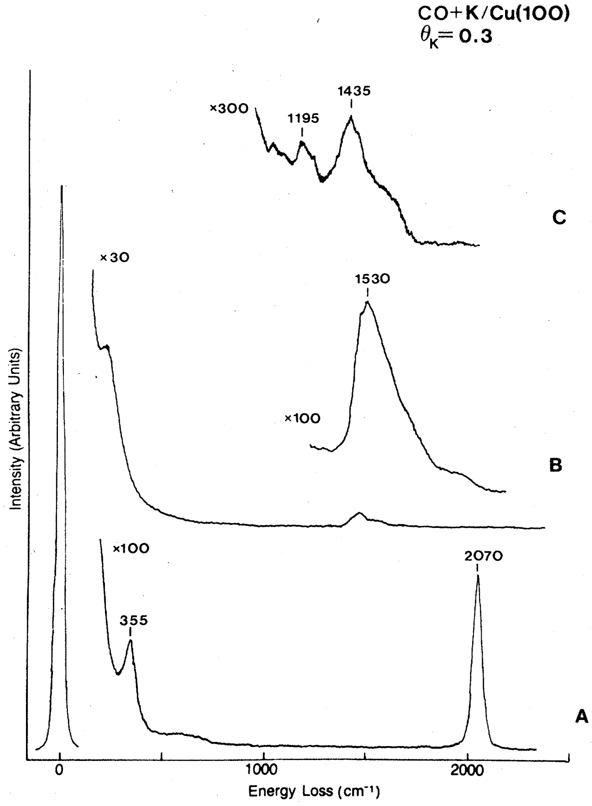

FIG. 1. EELS spectra of, A, CO/Cu(100), $\Theta_{\text{CO}}=0.5$; B, CO + K/Cu(100), $\Theta_K=0.3$, $\Theta_{\text{CO}}\approx0.4$, $T=100$ K; C, CO + K/Cu(100) after annealing the surface depicted in B to room temperature.

The coverage in this case was $\Theta_{\text{CO}}\cong0.5$, corresponding to an exposure of ~2 L CO (1 L = 1 langmuir = 10^{-6} Torr sec) at 100 K. This was determined by the observation of a $c(2\times2)$ LEED pattern, in agreement with a previous study of Andersson.[23] A higher CO exposure (~5 L at 100 K) produced a compressed LEED pattern at $\Theta_{\text{CO}}=0.57$, also in agreement with Andersson.[23]

Figure 2(a) shows the results of our measurements of the changes in the work function, $\Delta\phi$, of Cu(100) upon the adsorption of CO on the clean surface. Specific results are listed in Table I. When CO is added to the clean surface at 100 K, the work function decreases initially to a minimum value of ~ −200 meV at ~0.6 L CO, then increases to saturation at ~ −70 meV after 2–5 L CO are added. These results are in good qualitative agreement with a previous investigation by Pritchard[24] of the CO/Cu(100) system (−230 meV for $\Delta\phi_{\min}$ and −70 meV for $\Delta\phi_{\text{saturation}}$). This work function behavior, an initial decrease and then an increase back towards 0, is typical of

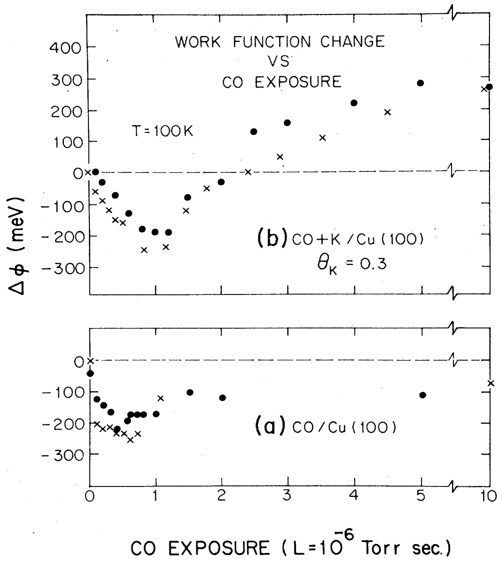

FIG. 2. Change in work function, $\Delta\phi$ (meV), is plotted versus CO exposure. (a) CO/Cu(100) at 100 K; (b) CO + K/Cu(100), $\Theta_K=0.3$, at 100 K. The ×'s and ●'s refer to separate runs using He I and He II radiation, respectively. Note the break in the horizontal axis between 5 and 10 L.

CO chemisorption on other copper faces as well.[24,25] This is in sharp contrast to CO adsorbed on transition-metal surfaces.[7,26,27] In these latter cases, the addition of CO results in a steady increase of ϕ to saturation at $\sim+500$ meV.

2. *Angle-resolved UPS measurements*

A typical angle-resolved UPS spectrum of CO/Cu(100) is shown in curves *b* and *c* of Fig. 3 [curve *a* is a UPS spectrum of clean Cu(100) for the same geometry and photon energy]. The coverage in this case is $\Theta_{CO}=0.5$ and the photon energy is 37 eV. The CO significantly attenuates the Cu *d* bands, a general feature of CO chemisorption,[28,29] and gives rise to four new peaks, centered at 8.9, 11.8, 13.5, and 16.4 eV (see Table II). The peaks at 11.8 and 8.9 eV have previously been shown to be due to emission from the 4σ and superimposed 5σ and 1π levels of molecular CO, respectively, with the 5σ level having undergone a shift, due to interaction with the surface, of ~3 eV downward with respect to the other two levels.[28,29] The peak at 13.5 eV has been identified as a shake-up peak or multielectron excitation[30–32] and has been observed on all copper surfaces studied so far.[14] The peak at 16.4 eV is a feature which has not been previously reported but was observed for CO/Cu(111).[33] We identify this peak as a second shake-up peak which may be associated with a 1π-2π excitation coupled to a 4σ hole, analogous to explanations of some core-level shake-up peaks.[21,34]

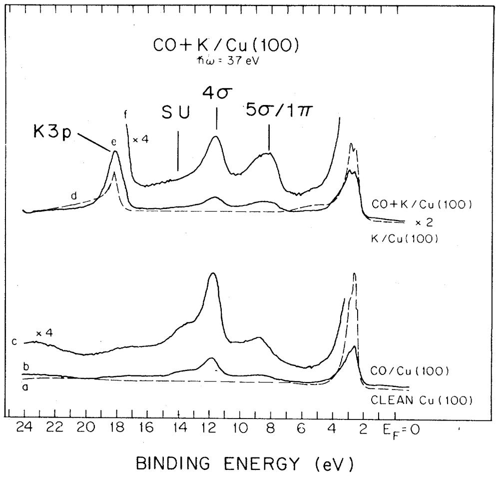

FIG. 3. UPS spectra of CO/Cu(100) and CO + K/Cu(100) at $\hbar\omega=37$ eV, $\Theta_I=45°$, 15° off-normal emission. *a*, Clean Cu(100); *b* and *c*, 2 L CO at 110 K, $\Theta_{CO}=0.5$, $c(2\times2)$ overlayer; *d*, K/Cu(100), $\Theta_K\sim0.3$; *e* and *f*, 2 L CO deposited on surface of *d* at 110 K.

The photon-energy dependences of these CO valence levels are shown in Figs. 4 and 5 for *p*-polarized light and normal emission, and in Fig. 6 for *s*-polarized light and emission 20° off normal in the "allowed geometry." Most of these results agree quite well with a previous study by Allyn *et al.* on this system.[30,35] He found the peak of the 4σ resonance to be at a photon energy of 36 eV, as opposed to 35 eV in this study (see Table III). Also, we observe some peaking in the $5\sigma/1\pi$ resonance at ~32 eV

TABLE I. Work-function changes of Cu(100) and K/Cu(100) upon CO adsorption.

	CO	CO + K $\Theta_K=0.3$
ϕ (eV) at $\Theta_{CO}=0$	4.59[a]	1.9±0.3
$\Delta\phi_{min}$ (meV)	−200±30	−220±30
CO exposure (L) at $\Delta\phi$ minimum	0.6±0.1	1.0±0.1
$\Delta\phi_{sat}$ (meV)	−70±20	+260±20
Saturation CO exposure (L)	2–5	5–10
$\Theta_{CO,saturation}$	0.57	0.4±0.1

[a] Reference 26.

TABLE II. K 3*p* level.

Θ_K	Θ_{CO}	Binding energy (eV)	Width[a] (eV)
3–4 monolayers	0	18.5	≤0.5
0.3	0	18.1	≤0.5
0.3	~0.5	17.9	1.05
0.05	0	18.3	1.1
0.05	~0.1	18.1	1.2

[a] Widths not corrected for instrumental resolution of ~0.3–0.5 eV.

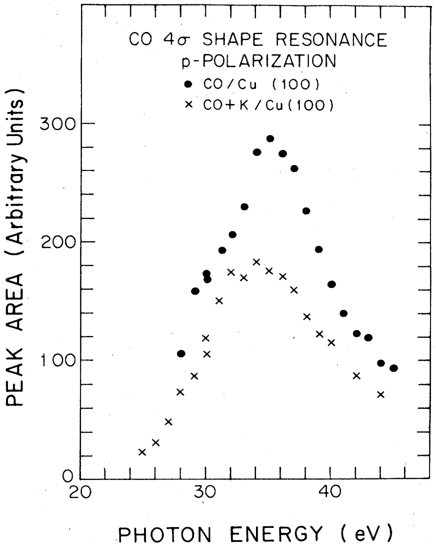

FIG. 4. Normalized photoionization cross sections of 4σ level for CO/Cu(100) and CO + K/Cu(100) with p-polarized light as a function of photon energy. CO/Cu(100): $\Theta_I=45°$, normal emission, $c(2\times2)$ CO overlayer. CO + K/Cu(100): $\Theta_I=50°$, 10° off normal, $\Theta_K\sim0.3$, 2 L CO at 110 K.

(Fig. 5). In Allyn's study there was a more or less continual rise in the peak area at low photon energies. We believe that this 32-eV shoulder is a remnant of the 5σ resonance which is observed at approximately this photon energy for CO adsorbed on Ni(100),[30] Ni(111),[30] and Co(0001).[28] One more apparent difference between these studies is the observation of a resonance in the $5\sigma/1\pi$ level for s-polarized light at 20° off normal, while no resonance was observed at 45° off normal by Allyn *et al.*[30,35]

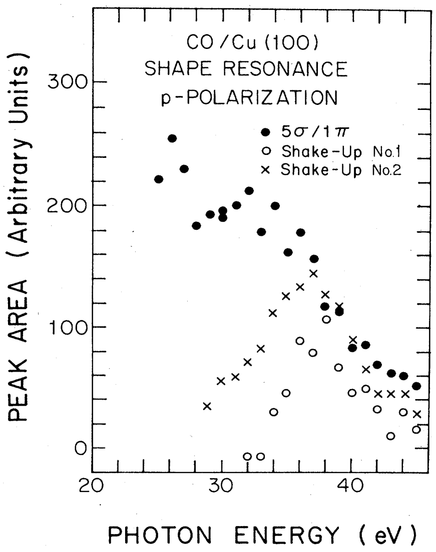

FIG. 5. Normalized photoionization cross sections of $5\sigma/1\pi$, shake-up 1 (at 13.5-eV binding energy), and shake-up 2 (16.4 eV) of CO/Cu(100) are plotted as a function of photon energy. The intensity scale is the same as that in Fig. 4. $\Theta_I=45°$, normal emission, p polarization, 2 L CO at 110 K.

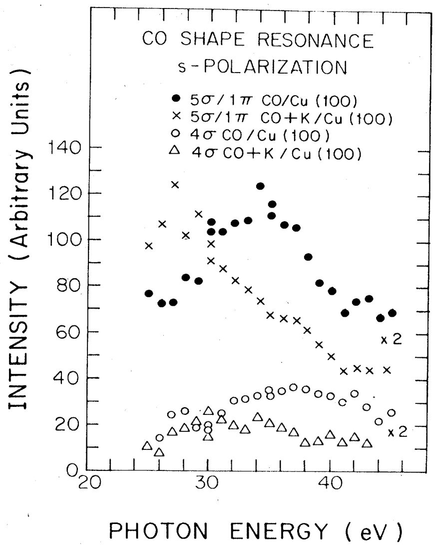

FIG. 6. Normalized areas of 4σ and $5\sigma/1\pi$ levels of CO/Cu(100) and CO + K/Cu(100) for s-polarized light. $\Theta_I=0$, 20° off-normal emission, allowed geometry. 2 L CO at 110 K.

We would not expect the difference of 25° in exit angle to have such a large effect; however, these resonances are not well understood, particularly shape resonances occurring with s-polarized light which should be forbidden by symmetry.[31,36]

The lower-binding-energy satellite peak (13.5 eV) resonates at $\sim$37 eV (Fig. 5), in approximate agreement with Allyn's results.[30,35] The peak at 16.1 eV binding energy, which we are assigning as a second shake-up peak, goes through a resonance at a photon energy of $\sim$38 eV. The similarity in the cross sections of the two satellite peaks and of these peaks and the 4σ level (Fig. 4) supports the assignment of the 16.4-eV peak as a shake-up peak associated with the creation of a 4σ hole.

Angle-resolved photoemission can be used to determine the orientation of simple molecules such as CO on a surface.[28–30] Using simple selection rules, and the polarized nature of synchrotron light, it can be shown[28–30] that for a geometry in which the light is incident normal to the crystal and the detector is in the incident plane (defined by the radiation direction and the direction of the A vector), only emission from even orbitals about this plane is permitted (this is the so-called "allowed" geometry). For

TABLE III. CO valence level binding energies in eV.

CO level	$\Theta_K=0$	$\Theta_K=0.3$
4σ	11.8[a]	11.6[b]
5σ	8.9[c]	9.0[c,d]
1π	8.5[c]	7.9[c,d]
SU 1	13.5[a]	13.1[b]
SU 2	16.4[a]	

[a] Measured at $\bar{\Gamma}$ (normal emission).
[b] Measured at 20° off normal (allowed and forbidden geometry).
[c] Measured 15° off-normal emission.
[d] Tentative assignment (see text).

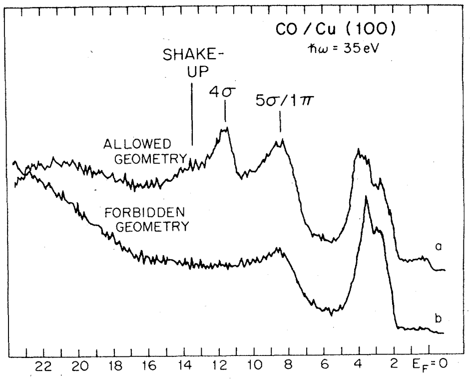

FIG. 7. Allowed- and forbidden-geometry measurements of CO/Cu(100). $\hbar\omega=35$ eV, $\Theta_I=0°$, 65° off-normal emission in both cases.

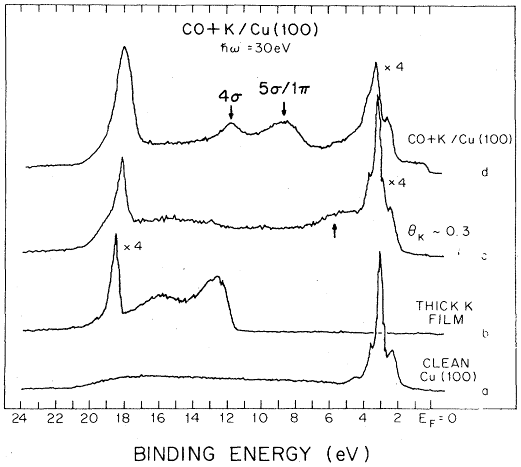

FIG. 8. $\hbar\omega=30$ eV, $\Theta_I=45°$, 15° off-normal emission. *a*, clean Cu(100); *b*, 3—4 monolayers of K; *c*, hexagonal overlayer of K/Cu(100), $\Theta_K \sim 0.3$; *d*, 2 L CO added to surface in *c* at 110 K.

CO molecules with their principal axis perpendicular to a surface, the 4σ, the 5σ, and one component of the 1π level should be detected in such a geometry. When the detector is positioned perpendicular to the incident plane (the "forbidden" geometry), only emission from odd levels (i.e., one component of the 1π in the case of CO) is allowed. Figure 7 illustrates measurements in the allowed and forbidden geometries for CO/Cu(100) at a photon energy of 35 eV. The disappearance of the 4σ level in the forbidden geometry (curve *b*) demonstrates that the CO molecules are perpendicular to the clean Cu(100) surface ($\leq 15°$ tilt), as has been previously shown by Allyn *et al.*,[30,35] and is in agreement with EELS measurements as discussed above.

B. K/Cu(100)

1. LEED, work-function measurements

Deposition of 0.3 monolayers of K on a Cu(100) surface causes a work function decrease of ~2.7 eV, to ~1.9 eV (Table I). This is typical of alkali-metal adsorption on metal surfaces,[7,37,38] with the alkali overlayer in a metalliclike regime at this relatively high coverage.[7,37,38]

At this K coverage, an ordered hexagonal potassium overlayer is formed, as observed by LEED. Similar LEED structures have been reported by Aruga *et al.*[39] for K/Cu(100) and by Andersson and Jostell for K/Ni(100).[40] Annealing to ~220 °C reduces the K coverage further to $\Theta_K=0.25$, and a $p(2\times2)$ overlayer of potassium was observed. Both of these LEED patterns were found to be very sensitive to beam damage and/or contamination as both were obscured within 10—15 min while being exposed intermittently to the LEED beam. No other alkali-induced LEED patterns were observed. For the rest of this paper the relevant potassium overlayer is the hexagonal overlayer at $\Theta_K \sim 0.3$.

2. UPS results

Several of the important photoemission features of potassium adsorbed on Cu(100) are illustrated in Fig. 8. Spectrum *a* in Fig. 8 shows a clean Cu(100) surface at a photon energy of 30 eV. Deposition of a thick film of potassium onto this surface at 110 K produces the characteristic spectrum *b* shown in Fig. 8. Based on Auger peak heights and approximate electron escape depths, it is estimated that ~3—4 monolayers of potassium are deposited on the substrate under normal running conditions. At this coverage the substrate photoemission features are completely suppressed. The photoemission peaks at binding energies of 12.5, 15.8, and 18.5 eV correspond to emission from an $M_{23}VV$ Auger transition,[41] plasmon loss off of the Auger,[41] and potassium $3p$ levels, respectively. The Auger transition is the result of initial ionization of the $3p$ level followed by decay into the $3p$ hole by a valence $4s$ electron accompanied by emission of a second $4s$ electron to conserve energy. On an expanded vertical scale, the potassium $4s$ level can also be observed at E_F.

As the potassium coverage is decreased from a thick film to a third of a monolayer, the $3p$ binding energy shifts from 18.5 to 18.1 eV, as can be seen from spectrum *c* in Fig. 8. A similar shift has also been observed by Eberhardt *et al.* for K adsorbed on Ru(001),[2] for which there is a good correlation with the changes in work function. The dispersion of the $3p$ level was measured to be less than 0.1 eV as a function of $k_{\parallel}$ (by varying the emission angle). The width of the $3p$ level for both the thick film and hexagonal overlayer was less than 0.5 eV, limited by the instrumental resolution (see Table IV). The line shape changes dramatically, however, with a significant asymmetry appearing on the high-binding-energy side for the thin film, as can seen in Figs. 8 and 9.

Comparing spectra *b* and *c* in Fig. 8, several other changes can be seen due to the change in the thickness of the K overlayer. There is a fairly uniform attenuation of Cu *d* bands (note that spectrum *c* is multiplied by a factor of 4 with respect to *a*). This appears to be a general feature of alkali-metal adsorption.[31,32,36] No sign of the $4s$ level of K at E_F can be detected even in an expanded

TABLE IV. Shape resonances of CO + K/Cu(100).

CO level	Polarization	Resonance peaks (eV) $\Theta_K=0$[a]	 $\Theta_K=0.3$[b]
4σ	p	35	34
$5\sigma/1\pi$	p	32[c]	32
SU 1	p	37	35
SU 2	p	38	?
4σ	s	no peak	no peak
$5\sigma/1\pi$	s	28	34

[a] Measured at normal emission for p polarization, 20° off normal for s polarization.

[b] Measured 10° and 15° off normal for p polarization, 20° off normal for s polarization.

[c] Shoulder at 32 eV.

scale at these photon energies. This level should, however, lie at the Fermi level (and not above) since at this coverage the potassium is believed to be in a basically metallic form.[42] The lack of observation of the 4s level at E_F may be due to the low cross section for this excitation at the photon energies used in this experiment (>20 eV). The 5s valence level of Cs has been observed for submonolayer coverages of Cs on Cu(111) but at much lower photon energies (4–6 eV).[37]

A comparison of spectra a and c of just below the copper d bands shows that K adsorption has induced a new, broad feature centered at $\sim$(5–5.5)-eV binding energy.[43] This new peak was observed at several photon energies from 23–27 eV and dispersed toward E_F by less than 0.5 eV as $k_{\|}$ was varied. Similar alkali-metal-induced features have been observed in other systems: K/Fe(110),[32] Na/Ag(110),[44] K/Ni(100),[36] K/Ru(001),[2] and Na/Cu(111).[45] In all cases the induced feature is one to several volts below the d bands of the metal surface. In the case of copper, the peak lies fairly close in binding energy to atomic oxygen.[46] However, we have reproduced this feature in more than a dozen surface preparations. In addition, the peak is almost completely attenuated by adsorption of CO, as will be discussed later. This is inconsistent with it being due to contamination. Another possible explanation is that the new feature is an interfacial plasmon loss off of the Cu d bands. We cannot rule this out absolutely, but feel that its strong intensity relative to the d bands makes this explanation unlikely. In addition, we do not see an equivalent loss off of the K 3p line.

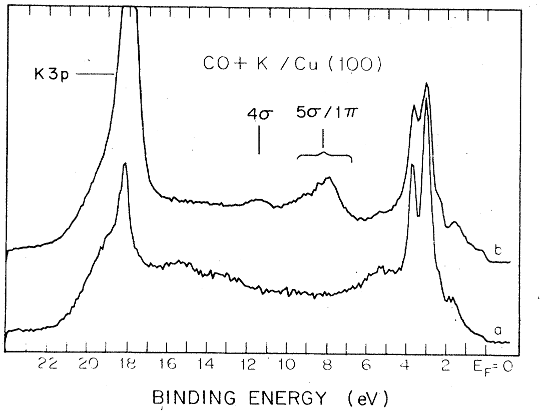

FIG. 9. $\hbar\omega=30$ eV, $\Theta_I=0$, s polarization, 20° off-normal emission in the allowed geometry. a, K/Cu(100), $\Theta_K\sim0.3$; b, CO + K/Cu(100), 2 L CO at 110 K.

When the hexagonal overlayer of potassium is formed, the Auger and plasmon-loss features shown in spectrum b of Fig. 8 for the thick film persist, although at slightly different energies. This is best illustrated in curve a of Fig. 9, in which two peaks are clearly seen at approximately 12.8- and 15.3-eV binding energies. The plasmon-loss energy has decreased from 3.3 eV for bulk potassium to 2.5 eV for the thin film. This latter value is close to the surface-plasmon energy of potassium of 2.4 eV.[41] A similar observation for the Auger peak has also been reported by Broden and Bonzel[32] in their study of K/Fe(110).

C. CO + K/Cu(100)

1. *LEED and thermal desorption*

An exposure of 2 L of CO on the potassium-precovered surface (which corresponds to $\sim$0.3 monolayer of CO based on XPS measurements described in more detail elsewhere[21]) causes the hexagonal LEED pattern due to the K atoms to disappear, leaving only the substrate 1×1 spots. We believe that this is due to competition between the K atoms and CO molecules, since the potassium forms an incommensurate hexagonal overlayer while the CO forms a square array in a commensurate structure on the clean surface. This should be compared to CO + K/Ru(001), in which both CO and K form hexagonal structures in the coadsorbed system.[7]

In thermal desorption measurements we detected only a very small increase in the desorption temperature of CO from the K-precovered Cu(100) surface (≤10 K) from the clean-surface value of ~180 K. This is in agreement with a similar study of CO + K/Cu(100) by King *et al.*[16] At this temperature, however, CO is only partially desorbed from the promoted surface (all CO desorbs from clean Cu at ~180 K). Upon annealing to room temperature, $\sim$65% of the CO remains on the K/Cu(100) surface in some form, as judged by a reduction in intensity of the O 1s core levels by XPS upon annealing. Lackey *et al.*[47] report that the remainder of the CO desorbs in the range of 400–500 K. This increase in desorption temperature of $\sim$200–300 K is comparable to the increases reported for CO desorption from alkali-metal-promoted transition-metal surfaces.[1–11]

2. *Work-function measurements*

Figure 2(b) illustrates the results of measurements of the change in the work function of the K/Cu(100) surface as a function of CO exposure. The important parameters are listed in Table I. When the K-precovered Cu surface is exposed to CO, the work function initially decreases, reaching a minimum value of ~-220 meV, similar to the behavior when CO is adsorbed on clean Cu (see Fig. 1 and Table I). As more CO is adsorbed, the work function increases back to its initial, zero-coverage value then continues to increase to positive values, saturating at $\sim+260$

meV after an exposure of 5–10 L CO at 100 K. Based on our XPS results,[21] we estimate the saturation coverage of CO to be ~0.4 monolayer on the Cu(100) surface at 100 K with $\Theta_K \sim 0.3$, compared to 0.57 monolayer of CO at saturation on clean Cu(100).

3. *EELS results*

Figure 1 compares EELS spectra of, curve *A*, saturated CO on clean Cu(100) with saturated CO dosed at 100 K on Cu(100), $\Theta_K = 0.3$, curve *B*, annealed to 150 K, and, curve *C*, annealed to 300 K. As in the photoemission investigations, multilayers of potassium were deposited at 100 K and subsequently annealed until hexagonal patterns were obtained (70 °C). The presence of the potassium film dramatically changes the vibrational spectrum of the CO molecule (curve *B*). The C-O vibration has been red shifted by more than 500 cm^{-1} from its frequency on the clean surface and has become broadened to 150 cm^{-1} full width at half maximum (FWHM) (as compared to 45 cm^{-1} on the clean surface). Although the elastic beam has broadened as well (to 80 cm^{-1} FWHM) it can only account for a small increase in the C-O vibrational linewidth. Indeed, the broadening of the elastic beam together with the asymmetry of the C-O stretching vibration (notice the high-energy tail) suggests inhomogeneous broadening, i.e., the presence of several CO environments on the K/Cu(100) surface, which is consistent with the lack of an overlayer LEED pattern for the coadsorbed system. The feature appearing on the shoulder of the elastic beam (~250 cm^{-1}) cannot at present be confidently assigned, although it may be a K-O vibration resulting from dissociated CO. Due to the highly ionic character of the K—O bond, even small amounts present on the surface can be manifested in modes of substantial intensity.

Annealing to 300 K (curve *C*) produces a complex spectrum containing features at 1195 and 1435 cm^{-1} as well as a distinct shoulder at 1500–1600 cm^{-1} which can be assigned with confidence as a CO stretching vibration in comparison to curve *B*. Previous isotopic labeling experiments have established that CO on Ru(001), $\Theta_K = 0.3$, can produce stretching vibrations as low as 1350 cm^{-1}.[48] The lower frequency EELS peaks in curve *C* may also be due to different CO states, but other explanations cannot be ruled out.

4. *UPS measurements*

(a) *K*-induced features. The CO coverage in all CO + K UPS spectra presented here was ~0.3 monolayer, corresponding to 2 L CO at 100 K. No changes in K or CO features were observed when more CO was added to the K-precovered surface, although saturation did not occur until a 5–10-L exposure of CO at $\Theta_{CO} \sim 0.4$, based on XPS intensities.[21] Several significant changes occur in CO/Cu(100) UPS spectra when the CO molecules are coadsorbed with K atoms. Most of these features are illustrated in Figs. 3, 8, and 9. First, consider the effect of CO upon the potassium levels. The 3*p* level shifts from 18.1 to 17.9 eV with the addition of CO (see Table IV). A shift to lower binding energy by a few tenths of an eV has also been seen for the 3*p* level in CO + K/Ru(001),[2] Pt(111),[5] Ni(100),[6] and the 3*p* and $2p_{3/2}$ levels for CO + K/Fe(110).[4] The width of the 3*p* level changes dramatically from less than 0.5 to 1.05 eV (see Table IV), while the asymmetry in the line shape disappears. Simultaneously the peak height increases as shown by spectrum *d* of Figs. 3 and 8. The area of the peak therefore has increased substantially, by a factor of ~2.5. Similar effects have also been noted on CO + K/Fe(110),[4] Ni(100),[6] and Ru(001).[2] In our XPS study of CO + K/Cu(100), as well as in a similar study of CO + K/Fe(110) by Broden *et al.*,[4] no corresponding increase was observed in the K 2*p* intensity. We can rule out diffraction effects since the enhancement persists at a variety of emission angles and photon energies. This 3*p* enhancement may be a result of a stronger coupling of the initial state due to the interaction of the adsorbed K atoms with the CO and leading to a larger 3*p* cross section. Alternatively, the enhancement may be the result of a line-shape change related to the asymmetry of the 3*p* level in the absence of CO. If the presence of CO altered the decay mechanism of the photoinduced 3*p* hole, both the line shape and intensity of the 3*p* level would be expected to change. These points will be discussed further in a later section. It is unlikely that the increased width is a result of inhomogeneous broadening due to the displacement of the K atoms by the CO molecules from their ordered structure (the hexagonal LEED pattern is lost) when CO is adsorbed, since a similar width change is observed for CO + K/Ru(001),[2] in which the K atoms remain in an ordered overlayer upon the addition of CO.

Figure 9 illustrates a second significant change between K/Cu(100) and CO + K/Cu(100); namely the Auger and plasmon-loss peaks at 12.8 and 15.3 eV have disappeared with the addition of CO. This can be explained if the potassium atoms become ionic as CO is adsorbed. If the 4*s* level becomes unoccupied, the Auger decay and accompanying plasmon loss observed for thick and thin K films would no longer be possible. This model of ionicity has also been used to explain the work-function measurement of CO + K/Pt(111).[5] However, if the direct Auger decay process becomes impossible due to the ionicity of the K, then the lifetime of the 3*p* hole should increase substantially, resulting in a narrower linewidth, contrary to observations. In addition, the shift in binding energy of the K 3*p* level is in the wrong direction for increased ionicity of the K in the presence of CO. We will attempt to reconcile these apparent discrepancies later in this paper.

Figures 3, 8, and 9 demonstrate that when CO is adsorbed on the potassium-precovered Cu(100) surface, the K-induced peak at ~5.5-eV binding energy is almost completely attenuated or shifted, although the possibility that it undergoes a shift upward into the *d* bands cannot be ruled out. A similar attenuation of a K-induced feature can also be seen in published spectra of CO + K/Fe(110).[4] This attenuation may imply a significant interaction of the CO molecules with the potassium atoms involving this electronic level, but other explanations are possible.

Figure 3 also illustrates the further attenuation of the Cu *d* bands upon adsorption of CO on the K-precovered surface. The change is similar to that observed for CO adsorbed on the clean surface, although not as substantial even considering the lower CO coverages for

CO + K/Cu(100) versus CO/Cu(100).

One final important effect of the adsorption of CO upon the K/Cu(100) surface is a significant enhancement at the Fermi level, as illustrated by spectrum *b* in Figs. 8 and 9. This enhancement was observed at all angles, polarizations, and photon energies studied, with a larger cross section at lower photon energies, as shown in Fig. 10 and plotted in Fig. 11. A similar enhancement has also been seen in the CO + K/Fe(110) system.[4] No such enhancement at E_F was observed for CO on the clean surface for any angles or photon energies, in disagreement with results on CO/Cu(100) reported by McConville *et al.*,[49] who claimed to see evidence for the CO 2π level below E_F. A recent UPS study of CO/Cu(110) (Ref. 50) also revealed no evidence for the 2π level at or below E_F. The photon-energy dependence of the step at E_F for CO + K/Cu(100) is consistent with that expected from a π-like level, i.e., increasing cross section at lower photon energies. The intensity of this step is comparable in both the allowed and forbidden geometries supporting its assignment as a π-derived level. The enhancement *cannot* be due to emission from the K 4*s* level due to the low cross section of this level as demonstrated by the lack of a peak at E_F for the thick K film in spectrum *b* of Fig. 3.

This enhancement at E_F was confirmed in a separate angle-integrated UPS investigation as illustrated in Fig. 12, using He I radiation at a photon energy of 21.2 eV. The addition of CO to clean Cu(100) results in a *decrease* in intensity at E_F, comparable to the reduction in the *d* bands (spectra *a* and *b* of Fig. 12). On the other hand, when CO is added to the K-precovered surface (spectra *c* and *d* of Fig. 12), a significant *enhancement* at E_F is observed. We attribute this increase to emission from the partially occupied CO 2π level enhanced by the presence of K on the Cu(100) surface, as discussed later.

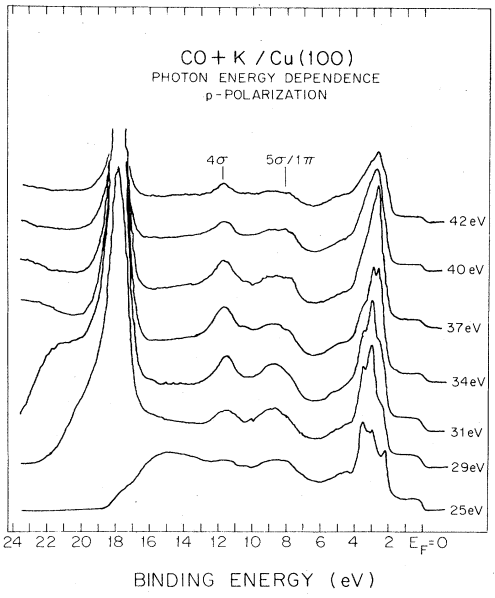

FIG. 10. Photoemission spectra of CO + K/Cu(100) at several photon energies. $\Theta_I = 50°$, 10° off-normal emission.

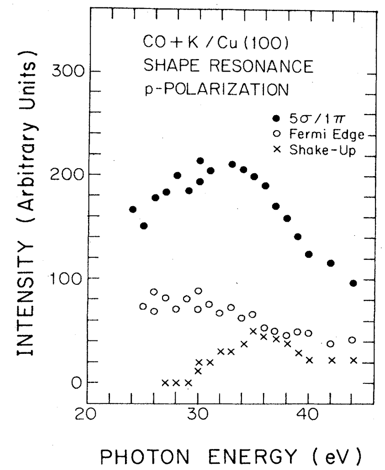

FIG. 11. Normalized intensities of $5\sigma/1\pi$ (peak areas), shake-up (peak areas), and Fermi level (heights at E_F) of CO + K/Cu(100) as a function of photon energy. $\Theta_I = 50°$, 10° off-normal emission, *p*-polarized light, $\Theta_K \sim 0.3$, 2 L CO at 110 K. Intensity scale is the same as that used in Fig. 4 and 5 with the exception of the Fermi-level height which is rescaled.

(b) *CO levels.* Several significant changes occur in the CO valence levels when CO is coadsorbed with potassium. The most dramatic change, as noted by Somerton *et al.*,[17] is the disappearance of the shake-up peak below the 4σ level, at ~ 13.5-eV binding energy. No trace of a peak or shoulder remains, as illustrated by spectrum *f* in Fig. 3, while the 4σ peak width has increased by only 0.1—0.2 eV. We put an upper limit on the shake-up intensity in the following manner.

(1) We subtracted a flat background below the CO valence levels at a number of photon energies. (It is clear that a flat background is justified by spectrum *d* in Fig. 3, which shows the potassium-precovered surface before dosing by CO.)

(2) We fit the 4σ level to a Gaussian, which was in general quite a good fit, and subtracted this peak.

(3) We measured the area of the remainder of the curve,

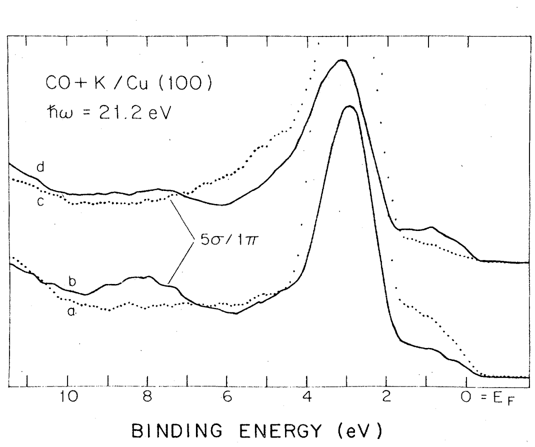

FIG. 12. He I angle-integrated UPS spectra of CO/Cu(100) and CO + K/Cu(100). *a*, Clean Cu(100); *b*, CO/Cu(100), 0.9 L CO at 100 K; *c*, K/Cu(100), $\Theta_K = 0.3$; *d*, CO + K/Cu(100), $\Theta_K = 0.3$, 2.9 L CO at 100 K.

which had a broad, rounded shape centered at 13.6 eV.

(4) We normalized and plotted these areas in Fig. 11. The photon-energy dependence of this "peak" roughly tracks the dependence of the shake-up peak for CO/Cu(100) (see Fig. 5) with approximately the same binding energy (Table II).

Comparing the areas of shake-up I_{SU} to 4σ at the maxima in their respective cross sections yields the following results:

$$(I_{\mathrm{SU}}/4\sigma)_{\mathrm{CO}}=\tfrac{1}{2}\ ,$$

$$(I_{\mathrm{SU}}/4\sigma)_{\mathrm{CO+K}}=\tfrac{1}{3.6}\ .$$

Therefore we can put an upper limit on the intensity of the shake-up peak in CO + K/Cu(100) at approximately $\frac{1}{2}$ the relative intensity of the shake-up peak for CO/Cu(100). Unfortunately, it is not possible to measure changes in the second shake-up peak of CO/Cu(100) at 16.4 eV due to its coincidence in energy with the potassium $3p$ level. A similar UPS study of CO + Na/Cu, for example, would make this determination possible, since the Na $2p$ core level has a binding energy of ~ 30 eV. We have also observed a reduction of 25—50% in the relative intensities of all satellites in the C $1s$ and O $1s$ core regions of CO + K/Cu(100). These XPS measurements and a more detailed discussion of changes in valence satellite peaks in the promoted Cu system will be presented in a subsequent publication.[21]

Comparing spectra c and f in Fig. 3, it can be seen that, while the 4σ level is relatively unperturbed in width or binding energy (see Table II), the $5\sigma/1\pi$ level has changed significantly. The $5\sigma/1\pi$ level in spectrum f of Fig. 3, centered at ~ 8.7-eV binding energy, is clearly broader and more rounded for the CO + K/Cu(100) system than for CO/Cu(100) (spectrum c in Fig. 3). At certain angles and photon energies this broad peak can be resolved into at least two peaks. In Fig. 9 the main peak has a binding energy ~ 7.9 eV with a shoulder at higher binding energy. In a different geometry, this shoulder can be resolved into a separate peak at ~ 9.3-eV binding energy (see Fig. 13 for an example). This indicates a substantial splitting of the 5σ and 1π levels, which are nearly degenerate in energy for CO/Cu(100) (see Table II and Fig. 7). This splitting was also pointed out by Somerton *et al.*[17]

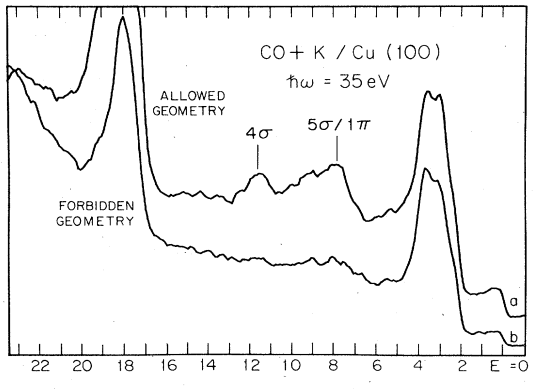

FIG. 13. Allowed- and forbidden-geometry measurements of CO + K/Cu(100). Same geometry and photon energy as in the Fig. 7.

Figure 13 presents symmetry measurements of CO + K/Cu(100) in the so-called allowed and forbidden geometries for the same geometry and photon energy as illustrated in Fig. 7 for CO/Cu(100). In the case of CO/Cu(100), the 4σ level (and associated shake-up peak) completely disappears in the forbidden geometry, curve b. In contrast, a small remnant of this 4σ level, which is more pronounced for some other emission angles, can be seen in the forbidden geometry in curve b in Fig. 13 [the remnant of the 4σ level in the forbidden geometry is $\sim 15\%$ of that in the allowed geometry for CO + K/Cu(100) as compared to less than 5% for CO/Cu(100)]. In addition, substantial intensity in the 5σ-1π region remains for both peaks. These differences between CO/Cu(100) and CO + K/Cu(100), which have also been observed for CO + K/Ru(001),[2] indicate that the symmetry of the CO molecules is reduced on the K-precovered Cu(100) surface compared with that for CO on clean Cu(100).

This reduction in symmetry could be a result of a tilting of the CO molecules in the presence of potassium. Following the analysis of Allyn for CO/Cu and CO/Ni,[30] we find that the remnant of the 4σ level in the forbidden geometry in Fig. 13 and in similar measurements is consistent with a tilt from the surface normal to 20°—40°. Alternatively, this symmetry breaking of the CO could result from strong direct interactions between coadsorbed CO molecules and K atoms without necessarily requiring a tilt of the CO's, as will be discussed later.

Support for a near-normal orientation of CO molecules in CO + K/Cu(100) is found in Fig. 6, which illustrates the photon-energy dependence of the CO levels for s-polarized light. In both cases [CO/Cu(100) and CO + K/Cu(100)] the intensity of the 4σ level is nearly independent of photon energy. In this geometry, for molecules with a perpendicular orientation, σ levels are forbidden by symmetry from coupling to the σ final-state resonance.[29,30] Clearly, the 4σ levels do not couple to this resonance in either case (Fig. 6), implying normal or near-normal orientation of the CO molecules for both surfaces.

The more or less uniform attenuation of both peaks in the 5σ-1π region of CO + K/Cu(100) in the forbidden geometry (curve b of Fig. 13) prevents a definite assignment of these levels based on these symmetry measurements. Measurements in which the angle of incidence of the light was varied in order to change the p component of the A vector are more consistent with an assignment of the low-binding-energy peak to emission from the 5σ level and the high-binding-energy peak to the 1π level. On the other hand, the shape resonance observed for p-polarized light (Fig. 11) at ~ 31 eV for the $5\sigma/1\pi$ levels is due to an increase in intensity on the high-binding-energy side of the peak (see the 29-, 31-, and 34-eV curves of Fig. 10). This result is more consistent with the 5σ level occurring at high binding energy. We believe this apparent confusion results from strong hybridization of the CO 5σ and 1π levels in the presence of K on the Cu surface. The two peaks each possess some σ and π components which are emphasized in different ways depending on the measurement. This hybridization is not unexpected due to the reduction in symmetry implied by the polarization measurements of the 4σ level, and is in agreement with parallel measurements of CO + K/Ru(001).[2,51]

(c) *Photoionization cross sections.* The cross sections of the 4σ and $5\sigma/1\pi$ levels of CO + K/Cu(100) as a function of photon energy for both *s*- and *p*-polarized incident radiation are shown in Figs. 4, 6, and 11. The resonance behavior of the levels for *p*-polarized light is clearly illustrated in Fig. 10. For all of these measurements, spectra such as those shown in Fig. 10 are recorded for photon energies between 24 and 45 eV. A flat background is subtracted below the CO-induced peaks. The areas of the peaks are measured using a data analysis program. These areas are then normalized to the incident photon flux and plotted as shown. The CO + K/Cu(100) measurements were checked several times with consistent results. The results are summarized in Table III. The *p*-polarized measurements for CO + K/Cu(100) were recorded at emission angles slightly off normal (10° and 15°) to improve the signal versus normal emission for CO/Cu(100).

In our measurements the position of the 4σ shape resonance for *p* polarization has shifted by 1 eV to lower photon energy (35 to 34 eV) with the addition of potassium versus CO on the clean Cu(100) surface. This small shift is consistent with similar UPS measurements of CO + K/Ru(001) by Eberhardt *et al.*[2] These results are in apparent disagreement with measurements by Sette *et al.*[52] on CO + Na/Pt(111), who find a shift in the resonance in the promoted system of 4 eV using x-ray radiation and a photoyield-measurement technique. This discrepancy will be discussed further in Sec. IV.

The $5\sigma/1\pi$ level peaks in intensity at ~32-eV photon energy for *p*-polarized light (Fig. 11). This is close to the peak or shoulder of the $5\sigma/1\pi$ level for CO/Cu(100) (Fig. 5). We feel that this reflects the coupling of the 5σ level to the same final-state resonance as the 4σ in both cases. This resonance behavior is similar to that reported on CO/Ni(100),[29,30] Ni(111),[29,30] and Co(0001).[28]

When the incident light is *s* polarized, the $5\sigma/1\pi$ level for CO + K/Cu(100) behaves quite differently than for CO/Cu(100) (Fig. 6). The $5\sigma/1\pi$ level clearly resonates for CO/Cu(100) at ~34 eV. However, as discussed previously for the 4σ level, the 5σ level should not be able to couple to this resonance in this geometry.[29,30] Similar resonance behavior of the $5\sigma/1\pi$ level has been reported for CO/Ni(100) and Ni(111).[29,30] The $5\sigma/1\pi$ level for CO + K/Cu(100) has a π-like behavior as a function of photon energy for *s*-polarized light (the intensity of the level rises linearly towards lower photon energies). We attribute these differences between CO/Cu(100) and CO + K/Cu(100) to further evidence for hybridization of the CO 5σ and 1π levels in the presence of K.

(d) *CO conversion.* As has been mentioned previously in this paper, data collection times had to be kept relatively short (≤ 1.5 hours, in general) due to the fact that after much longer times spectra were no longer reproducible. This is demonstrated in Fig. 14, in which spectra under identical conditions were recorded after various intervals of time. There are several significant changes with time. A broad peak at ~5-eV binding energy grows in intensity. Simultaneously, the $5\sigma/1\pi$ level broadens and fills in on the high-binding-energy side at ~10.5 eV. It is clear that there is either a buildup of contamination, or that a conversion of the CO is taking place. The conversion possibly involves dissociation of the CO overlayer which can be hastened by annealing the CO + K/Cu surface. Figure 15 shows the results of annealing the sample, after a relatively long time had already elapsed (curve *a*), to room temperature (curve *b*). In this latter case, the peaks at ~5 and 10 eV have grown apparently at the expense of the CO 4σ and $5\sigma/1\pi$ levels. These changes have also been noted by Somerton *et al.*[17] In addition, the step at E_F has decreased in intensity in the annealed spectrum.

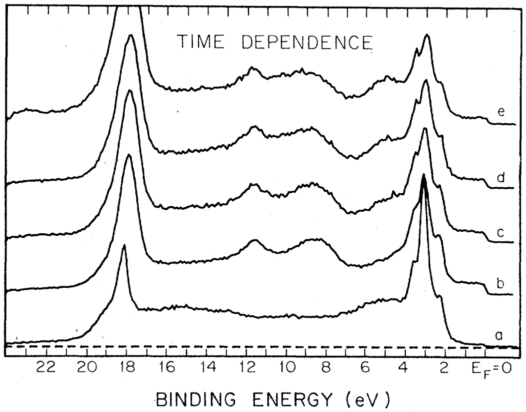

FIG. 14. Time dependence of CO + K/Cu(100) spectra. $\Theta_I = 45°$, 15° off-normal emission. *a*, K/Cu(100), $\Theta_K \sim 0.3$; *b*, 2 L CO added to *a* at 110 K; *c*, ~0.5 hour later; *d*, ~1.5 hours later; *e*, ~2.5 hours later. $\hbar\omega = 30$ eV.

We attribute some of these changes in UPS spectra to a buildup of contamination, probably H_2O, which reacts with the CO + K on the surface upon annealing. Evidence for this is presented in Fig. 16, in which a contam-

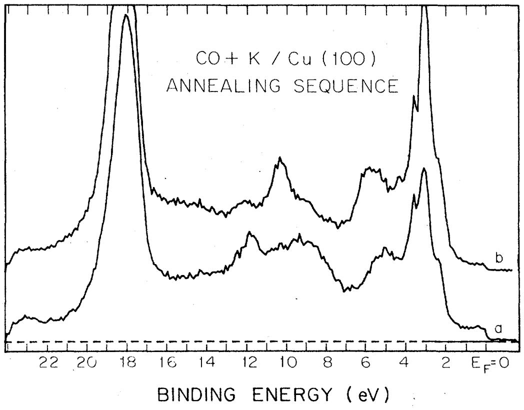

FIG. 15. Annealing sequence of CO + K/Cu(100), $\Theta_I = 45°$, *p* polarization. 15° off-normal emission; $\hbar\omega = 30$ eV. *a*, CO + K/Cu(100) ~2.5 hours after surface preparation; *b*, taken after annealing *a* to 20 °C.

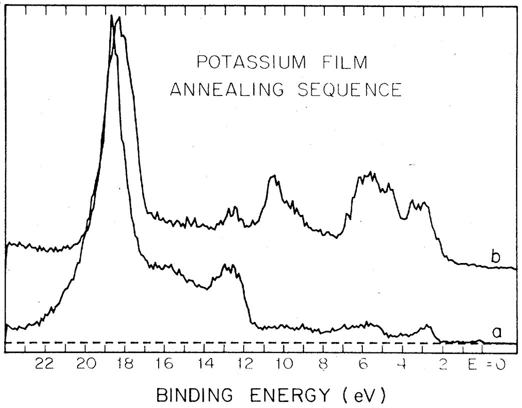

FIG. 16. Annealing sequence of K/Cu(100) at $\Theta_I = 45°$, normal emission, $\hbar\omega = 30$ eV. *a*, Contaminated multilayer of K/Cu(100); *b*, spectrum after annealing *a* to 170°C.

inated multilayer of K (curve *a*), upon which molecular CO does *not* adsorb, is annealed to room temperature (curve *b*). Note the same enhancement of peaks at ~5 and 10 eV as shown by curve *b* of Fig. 15 for the annealed CO + K overlayer. However, the gradual change in UPS spectra with time (Fig. 14), the reduction in intensity at E_F with time and upon annealing, and the significant changes in EELS spectra (Fig. 1) upon annealing as discussed above, also imply that the CO is undergoing a conversion in the presence of K on Cu(100). We cannot determine from our results whether this conversion is related to the contamination of the surface or is intrinsic to the CO + K/Cu system. Lackey *et al.*[47] claim that the coadsorption of CO + K/Cu results in the formation of CO-K salts. We disagree with this assertion and associate the single vibrational mode at 1530 cm^{-1} at low temperatures with UPS spectra taken before too much time has elapsed, and attribute these features to a single species of perturbed molecular CO normal to the surface. Only after annealing the substrate, or possibly after waiting several hours, do we see evidence for conversion or dissociation of the molecular CO.

IV. DISCUSSION

A. Model for alkali-metal promotion

In the investigation reported above, we have observed many significant changes in both CO and K features in the coadsorbed system CO + K/Cu compared with the single-component systems CO/Cu or K/Cu. The most important of these changes are listed below.

(1) The K 3*p* line shape broadens and increases in intensity with the addition of CO.

(2) There is a reduction in shake-up intensities in the core and valence regions of CO + K/Cu(100) versus CO/Cu(100).

(3) A splitting and hybridization of the 5σ and 1π levels occurs in the coadsorbed system.

(4) The 1π shifts to lower binding energy by 0.5—1 eV.

(5) There is little shift in the position of the 4σ shape resonance position.

(6) Substantial changes in the 5σ shape resonance behavior occur.

(7) We observe a reduction in the symmetry of the CO's in the presence of K as evidenced by increased intensity of the 4σ level in the forbidden geometry, and 5σ-1π splitting and hybridization.

(8) There is a substantial enhancement at E_F for CO + K/Cu(100).

(9) A surface resonant state at 5.5 eV is induced by K/Cu(100) and is attenuated by CO.

(10) There is attenuation of Auger and plasmon-loss features associated with the K overlayer by the addition of CO.

(11) The K 3*p* level shifts to lower binding energy by ~0.2 eV upon the addition of CO.

(12) A reduction in the C-O vibrational frequency by ~550 cm^{-1} occurs.

(13) We observe changes in the work-function behavior of CO + K/Cu versus CO/Cu.

(14) Enhanced dissociation of CO is observed in some promoted systems, and is possibly related to the conversion of CO discussed above for CO + K/Cu(100).

(15) There is substantial increase in the bond energy (i.e., in the desorption temperature) when CO is coadsorbed with an alkali metal on a metal substrate. For CO + K/Cu(100), the majority of CO remains on the surface at much higher temperatures than for CO/Cu, although some conversion takes place in the process of annealing the overlayer.

Most of these features and changes have been observed in similar studies of other alkali-metal-promoted systems and appear to be quite universal and any reasonable model of the interactions of CO with an alkali metal on a metal substrate should be able to account for most or all of these observations. We feel that existing models such as those based on a simple Blyholder-type picture of CO bonding are insufficient in explaining the results of this and other studies. We propose here a new model which we feel provides a more complete understanding of measurements of promoted systems. This model, which has also been described elsewhere,[2] was motivated by analogies with other highly perturbed chemisorption systems and with the observation by UPS of a shift of 1—1.5 eV in the binding energy of the CO 1π level for CO + K/Cu(100) and CO + K/Ru(001),[2] compared with CO adsorbed on the clean surfaces. This suggests that the 1π level of CO, which plays little role in the bonding of CO to a surface in simple systems, plays a more important role in the bonding in promoted systems.

In Fig. 17 we schematically illustrate the important steps in our proposed model of the bonding of CO with K on a Cu surface (a similar picture applies to transition-metal surfaces, as well). The main features are described below.

(a) At a coverage of $\Theta_K \cong 0.3$ monolayer, the potassium is in a basically metallic form with the K-atom spacing near that in bulk potassium [~5 Å spacing for K/Cu(100) (Refs. 39 and 40) compared with 4.52 Å for bulk K (Refs. 40 and 53)]. The metallic radius of the K is quite large,[39,40,53] as illustrated in Fig. 17(a), and the pack-

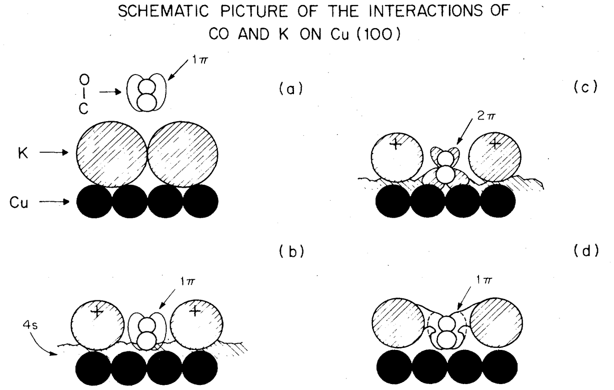

FIG. 17. Schematic representation of a new model for alkali-metal promotion. The CO levels depicted are reproduced from theoretical calculations and are taken from Ref. 29.

ing of the K atoms in a hexagonal overlayer does not allow enough space for the CO molecules to adsorb onto the Cu surface. The 1π orbital of CO is also depicted in this plane.[29]

(b) Since the CO does not adsorb directly onto potassium,[22] the radii of the K atoms must decrease to accommodate the CO molecules on the Cu surface. This will occur if the K atoms become somewhat ionic through interaction with the CO's. (The ionic radius of K^+ is 1.33 Å compared with a metallic radius of 2.26 Å.[53]) The ionicity of K will result from transfer of some or all of the 4*s* valence charge from the atoms to the surface region, as illustrated in Fig. 17(b). This will allow CO to adsorb directly onto the Cu surface, adjacent to several K atoms, as shown. Although the adsorption site or sites of CO in this promoted system are unknown, the CO molecules are directly bonded to K atoms.

(c) Some of the 4*s* charge in the surface region will be back-donated into the CO 2π orbital, which is unoccupied in the gas phase. This is illustrated in Fig. 17(c). We see clear evidence for this 2π enhancement at E_F as discussed above and listed as point (8) in this section. Since the 2π level is antibonding in terms of the C—O bond as shown, partial occupation of the 2π will weaken the interatomic bond while strengthening the CO—substrate bond. To this point, our model resembles the standard Blyholder-type picture of CO bonding applied to promoted systems.

(d) The important new feature of our proposed model is depicted in Fig. 17(d). The 1π orbitals of CO are rather extended spatially and have more weight on the O end of the CO molecule. We suggest that the proximity of K atoms to CO molecules on the Cu surface will lead to a significant interaction between the potassium and the 1π orbitals of CO, as shown. The K is somewhat ionic and will attract 1π charge through Coulomb forces. Charge transfer into the K will occur, somewhat neutralizing the K ions. Due to this charge transfer and the ionicity of the K, the 1π orbitals will become polarized towards the O end of the C-O molecules. The 1π level therefore becomes significantly perturbed from its ground-state configuration; in addition, this polarization of the 1π will tend to weaken the overlap of the 1π orbitals between the C and O ends of the molecule, introducing some antibonding character into the 1π, as shown, thus further weakening the interatomic bond. Finally, this polarization of the 1π away from the surface drives further occupation of the 2π level, allowing an enhancement of the 2π greater than that which would be possible without the perturbation of the 1π [of course, the interactions depicted in Figs. 17(c) and 17(d) are really simultaneous processes]. 5σ donation from the CO to the metal will also occur in a manner similar to that in unperturbed systems and is not illustrated in this figure.

We believe that the model proposed above can more successfully account for experimental observations of promoted systems than any previously suggested model. Consider the 15 key points listed above. Additional 2π occupation compared to CO chemisorbed on the clean surface [Messmer *et al.* in fact suggest that the 2π is completely unoccupied for CO/Cu (Refs. 14 and 54)] is made possible by the polarization of the 1π orbitals away from the surface. This is particularly true since the 1π and 2π orbitals are orthogonal[54] so less 1π weight on the carbon end allows for greater charge transfer from the surface into the 2π. This increased 2π occupation will strengthen the CO-surface bond, which is manifested in all promoted systems by increases of ~200 °C in the desorption temperatures of CO from these surfaces.[1] The 2π occupation will also make possible more efficient screening of core and valence holes, thus reducing the intensity of satellite peaks, as observed in the core and valence regions of CO + K/Cu and the O 1*s* region of CO + K/Ru(001).[51] This will be discussed in more detail in a subsequent publication.[21]

The increased occupation of the 2π *and* the charge transfer and polarization of the 1π levels in the promoted systems both act to decrease the interatomic C—O bond strength. Both of these interactions will result in a weaker bond leading to a decrease in the C-O stretching frequency and enhancing CO dissociation, both of which are observed experimentally. A comparison to electron scattering experiments of CO^- in the gas phase demonstrates that increased occupation of the 2π level in a promoted system is *insufficient* to account for the magnitude of the decreases in C-O frequencies observed. The vibrational frequency of CO^-, which has one electron in the 2π orbital, is reduced by ~ 300 cm^{-1} from that of neutral CO.[55] In contrast, the vibrational frequency of CO coadsorbed with an alkali metal drops by 500—700 cm^{-1} from the unperturbed system [550 cm^{-1} in the case of CO + K/Cu(100)]. In addition, the anharmonicity of CO^- is ~ 40 cm^{-1} (Ref. 55) compared with ~ 70 cm^{-1} for CO + K/Ru(001), according to Hoffmann and co-workers.[56] This clearly shows that 2π occupation is not sufficient to explain the changes observed in promoted systems, and supports our proposal of additional 1π interaction to further weaken the C—O bond.

We attribute the "step" observed at E_F for CO + K/Cu(100) as due to emission from the partially occupied 2π level in the presence of K. Its symmetry and photoionization cross section are both π-like, supporting this model. The fact that we see no indication of this enhancement for CO/Cu(100), but a clear increase in

CO + K/Cu(100) (see Fig. 12) is strong support for the model of Messmer *et al.*,[54] which asserts that the 2π level of CO/Cu is completely unoccupied in the neutral ground state. Our UPS data suggest that the 2π level only becomes occupied in the promoted system, probably to the level of occupation in CO/transition metals, as also discussed elsewhere.[21]

The polarization of the 1π orbital perturbs the 1π charge significantly from the configuration in the neutral molecule. This will weaken the bonding of the 1π to the CO molecule, producing a decrease in the binding energy of the 1π level, as observed [by 0.5—1 eV for CO + K/Cu(100) and 1.5 eV for CO + K/Ru(001) (Ref. 2)].

The direct interaction of the CO molecule through the 1π level lowers the symmetry of the molecule (for example, it is clear from Fig. 17 that the symmetry of the CO molecule is no longer $C_{\infty v}$, as in the gas phase, due to the polarization of the 1π towards the K atoms). This accounts for our observation of an increase in intensity of the 4σ level in the forbidden geometry (Fig. 13) in CO + K/Cu(100) compared with CO/Cu(100), *without* requiring a tilt of the CO molecules. The lack of a tilt is supported by the similarity of the photoionization cross sections of the 4σ levels in the two systems with *s*-polarized light, as described above, as well as by angle-resolved Auger measurements of CO + K/Ru(001) by Weimer *et al.*[51] The lowering of the symmetry of the CO molecule along with the distortion of the 1π level will also allow the 1π orbitals to hybridize with the 5σ, as observed. This hybridization in the promoted system will cause a splitting in energy of the 5σ and 1π levels versus CO/Cu(100) in a simple tight-binding picture, as is observed experimentally.

The K atoms must become somewhat ionic to accommodate the CO molecules on the surface. Subsequent interaction with the 1π levels of CO results in charge transfer and a partial or complete reneutralization of the K ions. This accounts for the lack of a large shift in the binding energies of the K $3p$ or $2p$ (Ref. 21) core levels when CO is added to K/Cu(100). The fact that these levels shift slightly to lower binding energy can be attributed to the change in the work function of the surface upon CO adsorption.[21]

Substantial changes were noted in the line shape of the K $3p$ level (a broadening and intensity increase) and an Auger transition (attenuation) when CO is added to K/Cu(100). The direct interaction between K atoms and CO 1π levels provides a mechanism for understanding these changes. In particular, a new channel has opened up via the 1π for screening and filling a photoinduced hole in the $3p$ level. If interadsorbate charge transfer via the 1π is a more efficient method of filling a $3p$ hole versus decay of a $4s$ electron, then in the CO + K/Cu system the lifetime of a $3p$ hole will decrease, resulting in a broadening of the $3p$ photoemission linewidth, exactly as observed. In addition, if this decay channel is more efficient, it will supercede $4s$ decay into the $3p$ hole, thus inhibiting the associated Auger transition, which is completely suppressed in UPS spectra when CO is added to the surface (Fig. 9). This does not account for the observed intensity increase of the K $3p$ level. One possibility is that much of intensity of the main $3p$ line in K/Cu(100) is transferred into shake-off-type states involving excitations of the $4s$ electrons. The ionicity and subsequent reneutralization of the K atoms by the 1π might suppress these transitions, putting more intensity back into the main line. Further detailed studies of the K $3p$ line shapes (and $2p$ as well), particularly concentrating on changes in the high-binding-energy side, might lead to a better understanding of these features.

Substantial rearrangement of charge occurs in the CO + K/Cu(100) system according to the model proposed above. This could certainly affect the work-function behavior of CO + K/Cu versus CO/Cu. Substantial changes are observed (Fig. 2) and are discussed in more detail in the next section.

We observed very little change in the position or intensity of the 4σ shape resonance in CO + K/Cu versus CO/Cu. (This will be discussed further in a later section.) This would seem to imply that neither the initial 4σ state nor the σ final state are significantly perturbed in the promoted system (in addition, very little change in binding energy, intensity, or width of the 4σ level was observed). On the other hand, substantial changes were observed in the photoionization cross-section behavior of the 5σ level for both *s*- and *p*-polarized light. We attribute these changes to changes in the initial state in the promoted system. In particular, we observed strong hybridization of the 5σ and 1π levels, which will clearly affect the coupling to the σ final resonant state. These shape resonances, particularly for the $5\sigma/1\pi$ levels in chemisorbed systems, are not understood well enough, in general, to allow us to relate the specific changes we observed between CO + K/Cu(100) and CO/Cu(100) to the model of alkali-metal promotion proposed above.

Finally, the addition of K at $\Theta_K = 0.3$ to the Cu(100) surface results in the appearance of a new peak at ~ 5.5 eV, which is almost completely attenuated by CO. This state may be related to the bonding of CO to the promoted surface, although it is unclear how it fits into the model we have proposed. Alternatively, although its origin is still unclear, we prefer to attribute its attenuation by CO to the same changes in screening and core hole filling which produced an attenuation of the K Auger transition with the addition of CO, and which we have related to 1π-K interaction on the promoted surface.

In the above discussion, we have been able to account for most or all significant observations concerning promoted systems. We do not believe that any other model proposed up to this time can explain as comprehensively the experimental results.

B. Work-function changes

As described above, the changes in the work function, ϕ, of a Cu surface upon CO adsorption are substantially Cu different than the changes that occur when CO is adsorbed onto a transition-metal surface. (Similar qualitative differences in work-function behavior are observed for N_2 on transition metals versus CO on transition metals, as well.[57,58]) The increase in work function when CO is adsorbed on a transition-metal surface is generally attributed to the charge which is back donated from the metal into the CO 2π level when the molecules are adsorbed.[26] This results in a net movement of charge away from the metal surface to the CO molecules, thereby causing the work function of the surface to increase.

In contrast, the work function initially decreases when CO is adsorbed on copper, as shown in Fig. 2. This behavior can be rationalized most easily by assuming a substantial decrease in (or complete lack of) charge transfer into the CO 2π level from the metal when the bond is formed, leaving donation from the CO 5σ level to the Cu substrate as the only significant charge transfer. When the coverage of CO/Cu is increased, the work function reaches a minimum and then starts to increase back to a smaller negative value at saturation. Pritchard[24] suggests that this increase is due to a site change of some of the CO molecules at high coverages based on a LEED analysis, but no other measurements tend to support this conclusion.[24] Another possibility is an electrostatic interaction among the dipole moments of the adsorbed CO molecules. Such a "depolarization" has been invoked to account for a minimum in the work function of alkali metals adsorbed on metal surfaces.[37] This latter suggestion cannot be substantiated until quantitative measurements or estimates of such depolarization effects for CO systems are available.

When CO is coadsorbed with a 0.3 monolayer of K on Cu(100), the work function decreases to a minimum, then increases to a positive value of $\sim$260 meV at saturation. As can be seen from Fig. 2, the work-function behavior of CO + K/Cu(100) at low CO exposures is quite similar to the behavior of ϕ for CO/Cu(100). We do not believe these changes are related, however, particularly since Lindgren *et al.*[59] have reported significant initial *increases* in ϕ when CO is adsorbed on top of lower coverages of Na/Cu(111) ($\Theta_{\mathrm{Na}} \leq 0.11$). In addition, work-function measurements of both CO + K/Ru(001) (Refs. 7 and 51) and CO + K/Pt(111) (Ref. 5) yield qualitatively similar results at high-K precoverages to those on Cu presented here: an initial decrease in ϕ as CO is adsorbed, followed by an increase to saturation at positive values of $\Delta\phi$ [the only exception to this behavior reported so far is CO + K/Fe(110),[4] for which the saturation value is -1.1 eV]. We therefore propose that the behavior of ϕ for CO + K/Cu(100) reported here has a common origin with systems such as CO + K/Ru(001) and CO + K/Pt(111).

The explanations offered for the results on Ru(001) (Ref. 51) and Pt(111) (Ref. 5) involve the effects of CO adsorption on the adsorbed K atoms. This is consistent with the model we have proposed above. In particular, if the K atoms become partially ionized when CO molecules are adsorbed in the vicinity, the work function would tend to decrease if such charge transfer (charge from the valence K 4*s* level to the CO surface or neighboring CO molecules) more than compensates initial π back donation from the surface into the CO molecules. As the CO coverage increases, the charge transfer out of the K atoms will eventually saturate; then further back donation would cause the work function to increase, as observed. This model has been proposed to account for the measurements on Ru(001) (Ref. 51) and Pt(111) (Ref. 5), and it is equally applicable to Cu(100). In addition, it may also be important to consider changes in the polarization and charge transfer out of the 1π to the K as proposed above.

Additional support for this model comes from measurements of O_2+Na and Cs/Cu(111) by Lindgren and coworkers.[38] The qualitative behavior of the change in work function when O_2 was coadsorbed onto a Cu(111) surface with a high precoverage of Cs or Na was quite similar to the behavior for CO + K/Ru(001),[7,51] Pt(111),[5] and Cu(100). This similar behavior seems to support a general model, such as the one presented here, which is appropriate for O_2+Cs, Na/Cu(111), as well. The bottom line is that the initial decrease in ϕ when an alkali-precovered surface is exposed to CO is universal and depends upon changes in K. The initial decrease in ϕ for CO/Cu is unique and the similar changes observed in these two systems are *not* related.

C. Shape resonances in promoted systems

Sette *et al.*[52] have recently reported a shift of 4 eV in the position of the σ shape resonance final-state position for CO + Na/Pt(111) versus CO/Pt(111), by measuring the resonance in the C 1*s* and O 1*s* core levels using x-ray radiation and a photoyield technique. They attribute this change to an increase in the bond length of CO in the promoted system according to a recent model proposed by Stohr *et al.*[60] which relates molecular bond lengths to positions in energy of the σ final state. In contrast, we observe a shift of only 1 eV in the position of the σ shape resonance based on our UPS measurements of the photoionization cross section of the 4σ level of CO + K/Cu(100), in agreement with a similar UPS study of CO + K/Ru(001) by Eberhardt *et al.*[61] We believe this represents a real discrepancy and is not simply due to the different systems studied, particularly since the alkali metal and CO coverages were comparable in all cases. This implies one or more of the following: (1) The C—O bond length does not change significantly; (2) the model correlating bond length to resonance position is incorrect; or (3) there is a fundamental difference in the measurement techniques using UPS as in this paper and x-ray photoyield of core levels such as employed by Sette *et al.*[52] We believe that the C—O bond length *does* increase in the presence of an alkali due to the bond weakening induced by 2π enhancement and 1π-K interaction as discussed above. Further study is necessary to determine whether such a bond-length change will produce a measurable shift in the σ resonance position with UPS and/or XPS techniques. The resolution of this question may lead to a better understanding of the photoexcitation process in general. One relevant experiment would be to determine the resonance position with and without an alkali metal by measuring the direct photoemission intensity of the CO core levels as a function of x-ray photon energy in addition to using an x-ray absorption technique such as that of Sette *et al.*,[52] which measures the photoemission cross sections indirectly by detecting subsequent decay products.

D. Analogies with other systems

A number of other chemisorption systems have been studied which we believe provide good analogies to promoted systems and support our model of alkali-metal promotion described above. CO bound at special step sites on the stepped surfaces Pt[6(111)×(111)] (Ref. 62) and Ni[5(111)×(1$\bar{1}$0)] (Ref. 63) and in a deep hollow site on the open Fe(111) surface[64] have exhibited stretching frequencies of 1400, 1520, and 1570 cm^{-1}, respectively. In all cases, CO adsorption sites which are quite different geometrically from those on normal low-index surfaces, are available. Seip *et al.*[64] suggest that the bond weakening associated with all of these systems is a result of interaction between the CO 1π orbitals and the substrate, similar to the model we have proposed for promoted systems. They relate their results to various transition-metal complexes which have highly perturbed CO's.

One example of such a complex is $(\eta^5\text{-}C_2H_5)_3Nb_3(CO)_7$,[65] which exhibits a CO stretching frequency of 1330 cm^{-1}. In this cluster, the C atom of CO is bonded to three Nb atoms, and the axis of the molecule is tilted over such that the O end is coordinated in two of these Nb atoms. This unusual geometry favors interaction of the 1π level with the metal cluster and this has been used to account for the reduced CO vibrational frequency.[65]

These large vibrational frequency shifts described above are comparable to those measured on promoted systems such as CO + K/Cu(100), and suggest that an analogy may be drawn between these different types of systems. In the stepped and open surfaces and metal clusters, the unusual geometry of the substrate makes 1π interaction possible. In our model of alkali-metal promotion, it is the proximity of K ions which facilitates "π bonding." We expect that additional measurements of these stepped and open surfaces, clusters, and other perturbed systems will reveal further similarities with our measurements of CO + K/Cu(100). One particularly significant observation would be of hybridization and splitting of the 5σ and 1π levels by UPS, as we observe in CO + K/Cu(100).

A further analogy exists in N_2/Fe(111), which has been recently studied by EELS and XPS.[66] Not only is there a decrease in the N_2 stretching frequency ($\sim$700 cm^{-1}) comparable to that of CO + K/Cu ($\sim$550 cm^{-1}); in addition, the large satellite peak at $\sim$4 eV below the main N $1s$ line is significantly attenuated[66] compared with N_2 on "normal" surfaces such as N_2/Ru(001), W(110), and Ni(100).[67] These similarities in relation to our model of alkali-metal promotion are discussed in more detail in a subsequent publication.[21]

V. CONCLUSION

We have performed a detailed study of CO + K/Cu(100) ($\Theta_K=0.3$, $\Theta_{CO}=0.3$–0.4) using the techniques of LEED, EELS, UPS, XPS, and work-function measurements. We observe many similarities with other studies of promoted systems and several previously unidentified features as well. Our findings can be summarized in the following picture: CO on Cu(100) is bonded primarily through the 5σ orbital, which is consistent with the bond energy, dipole moment, core-level screening,[21] lack of any sign of the 2π level near E_F, and the measured C-O vibrational frequency. The addition of K to the surface results in a direct K-CO interaction which increases the π bonding both through charge transfer to the CO 2π and direct interaction with the CO 1π. Therefore the π bonding in the promoted system is at least comparable to the typical 2π back bonding found in CO adsorbed on transition metals. Within the context of this model we have been able to account for changes in the line shape of the K $3p$ core level and attenuation of a K-induced Auger transition and surface resonant state by the addition of CO, hybridization and splitting of the CO 5σ and 1π levels, substantial reduction in core and valence CO shake-up intensities, a decrease in the C-O stretching frequency of $\sim$550 cm^{-1}, *lack* of a shift in the σ shape resonance position, and a significant increase in intensity at E_F in CO + K/Cu(100) over that in CO/Cu(100).

This new model must be checked by various theoretical calculations. We would stress that any theory must look at all of the measurable quantities before any conclusion is reached. It is quite clear that our picture of CO on clean Cu is nearly orthogonal to the conclusion reached by Bagus *et al.* in a series of theoretical papers relating the calculated bonding of CO to clusters of Al and Cu atoms to CO on a Cu surface.[68] They state that 2π back bonding is important and that σ bonding is not. However, the theoretical situation is such that at the present time some possibly important physics is left out of calculations in order to make them feasible. With this in mind, it is important that each theoretical calculation presents results for a range of experimental observations in order to make possible an accurate evaluation of various theoretical models and techniques.

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