

PHOTOEMISSION STUDY  
OF CO ADSORBED ON K/Cu(110). ANALYSIS  
OF ADSORBATE INDUCED STRUCTURES

P.J. GODOWSKI

W. Trzebiatowski Institute of Low Temperature and Structure Research  
Polish Academy of Sciences  
P.O. Box 937, 50-950 Wrocław, Poland

J. ONSGAARD

Institute of Physics, Odense University  
Campusvej 55, 5230 Odense M, Denmark

S.V. CHRISTENSEN

Institute for Physics and Astronomy, Aarhus University, 8000 Aarhus, Denmark

AND J. NERLOV

Department of Chemistry, University of Copenhagen  
Universitetsparken 5, 2100 Copenhagen, Denmark

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Improved adsorption characteristics of a K predeposited Cu(110) surface with a coverage corresponding to a point before the work function minimum have been confirmed. Analysis of the CO-induced orbitals in the photoelectron spectra of the CO/K/Cu(110) interface for low coverages of carbon monoxide adsorbed at 118 K has been done. Noticeable changes of the parameters of the orbitals with increasing CO coverage have been registered. Elongation of the C-O bond without dissociation of the molecule has been deduced from the energetic separation of 3.4 eV between the  $4\sigma$  and the  $1\pi$  orbital. A weakening of the CO-interface bond with coverage has been found on the base of decreasing  $5\sigma-1\pi$  separation with increasing  $4\sigma/5\sigma$  intensity ratio. Perpendicular orientation of CO molecules to the plane of the substrate surface has been concluded from analysis of the constant initial state spectra of the  $4\sigma$  and  $5\sigma/1\pi$  orbitals.

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## 1. Introduction

Investigations of the interactions of carbon monoxide with the alkali modified metal surfaces are well grounded from both a technological and a scientific point of view [1–3]. Alkali metals play the role of promoters in catalysis, improving some catalytical properties and parameters of catalytic reactions. Frequently promoters are added as a precipitant or in order to poison the support's acidity [4]. The role of alkali promoters can be investigated by comparison of the results based on the clean single crystal surface with those obtained from a surface containing controlled submonolayer quantities of alkali adatoms.

Different surface techniques, such as temperature programmed desorption (TPD), low energy electron diffraction (LEED), photoelectron spectroscopy using X-ray (XPS) or ultraviolet (UPS) excitation, work function changes ( $\Delta\Phi$ ) and high resolution electron energy loss spectroscopy (HREELS) were used to characterize adsorption of CO on different metal surfaces. While LEED, TPD and  $\Delta\Phi$  results describe relatively wide coverage ranges of adsorbed CO, the published photoelectron spectroscopy data for CO on metal or alkali modified metal surfaces concern only the saturation gas coverage [5–11]. Such a case is dictated by relative weak photoemission signal from small quantity of adsorbate. In some cases results of saturated CO layer represent well the whole process, especially for clean metal surfaces with one kind of adsorption site. For coverages near saturation, additional adsorbate–adsorbate interaction may have rather limited influence on the electronic properties of the CO–metal system. However, some metal surfaces with predosed alkali species may change the characteristics of the gas adsorption by modification of the gas–interface interaction.

Carbon monoxide adsorbed on the K/Cu(110) interface at low temperatures gives two basic TPD peaks of 28 a.m.u.: at around 210 K and 650 K [12]. The low temperature feature corresponds to the adsorbed species in the molecular state with a desorption energy around 50 kJ/mol. The second peak is present only on a K-predosed surface and it is due to stronger interaction of the CO molecule with the substrate atoms.

In this paper investigations of the electronic structure of the interface by photoelectron spectroscopy using synchrotron radiation (PSSR) are presented. The present work is a continuation of earlier studies [12] and shows complementary results to the TPD and XPS data because of the technique used. The K/Cu(110) substrate was prepared and characterized using LEED and  $\Delta\Phi$  measurements. The intense photon source from the storage ring improves detection conditions for low coverages of adsorbed CO molecules. Another advantage of PSSR is the possibility of using an incident photon energy corresponding to the maximum photoelectron yield from a given level.

## 2. Experimental

The exciting photon beam was achieved from the SX-700 monochromator attached to the storage ring ASTRID in Aarhus, Denmark [13–15]. The pressure of the residual gases in the experimental chamber during measurements did not exceed  $1.33 \times 10^{-8}$  Pa.

The Cu(110) sample was mounted on a heating device connected to a dewar giving the possibility of cooling to 110 K and heating to 1000 K. The cleaning procedure consisted of heating and Ar<sup>+</sup> bombardment until the sample gave a sharp (1 × 1) LEED pattern with low background intensity and free of contamination signals in the PSSR spectrum. During adsorption the sample temperature did not exceed the temperature giving rise to the adsorbate-induced substrate reconstruction, i.e.  $T_{\text{rec}} = 158$  K [16].

Potassium source, bought from the SAES GETTERS company (Milano, Italy), has a form of a metal container which held a mixture of alkali metal chromate (K<sub>2</sub>CrO<sub>4</sub>) with a reducing agent (Zr84%–Al16%). In order to release the alkali metal, the dispenser was heated to a suitable (820–1120 K) temperature under vacuum. Potassium was dosed from a direct heated source positioned approximately 5 cm away from the sample surface. The coverage, expressed relative to the number of copper surface atoms, was determined from the  $\Delta\Phi$  curve, where the work function minimum occurs for a coverage of  $\tau = 0.17$  substrate monolayers (SML). It corresponds to a density of potassium atoms,  $n_K = 1.85 \times 10^{14}$  at./cm<sup>2</sup>, i.e. to the half of the most dense potassium overlayer on Cu(110) [16].

CO was admitted to the whole chamber via a dosing system, typically dose of 1 L corresponded to 100 s of  $1.33 \times 10^{-6}$  Pa. The saturation layer of CO on the clean Cu(110) surface gives rise to the c(5/4 × 2) structure [17] which contains adsorbate molecules of density  $n_{\text{CO}} = 8.68 \times 10^{14}$  molec./cm<sup>2</sup> which corresponds to a coverage of  $\tau_{\text{CO}} = 0.80$  SML. It is assumed that the same molecular density is obtained on the free copper areas as on the K/Cu(110) interface. The saturated layer of CO on the modified surface is obtained after 1 L exposure which coincides with the saturation level of the work function changes. The coverage of CO was determined from the total intensity of the valence band CO-derived peaks, calibrated at the saturation point as corresponding to  $\tau_{\text{CO}} = 0.8(1 - 0.4) = 0.48$  SML, i.e. to a density  $n_{\text{CO}} = 5.23 \times 10^{14}$  molec./cm<sup>2</sup>.

### 3. Results and discussion

Normal emission valence band spectrum of CO adsorbed on a copper surface shows three main features [18]. The one with the highest binding energy (*BE*) of around 13 eV is due to the 4σ satellite, then near 11.5 eV is due to the molecular 4σ, whereas the feature at *BE* of approximately 8 eV is due to the two 5σ and 1π overlapping levels [9, 18]. Careful examination of the 5σ/1π region shows the splitting of the peak into two components, but with an order of *BE* which is reversed relative to the CO gas phase [19, 20]. The overlap and the reverse order are the results of the elongation of the bond distance of adsorbed CO molecule, because it bonds to the substrate mainly through the 5σ level.

Figures 1a–c show the photoemission spectra of the CO/K/Cu(110) interface for a potassium precoverage of 0.4 of the most dense potassium overlayer ( $\tau_K = 0.14$  SML) taken at 118 K after exposure to 0.1, 0.3 and 0.5 L of CO, respectively. The spectra were recorded at the angle of incidence of the incoming photons equal to 50°, at normal emission and at a photon energy of 40 eV. The peaks in the region of the CO orbitals are synthesized and specified by the use of the ion state labels from the free, gas phase CO molecule (Table). Fitting

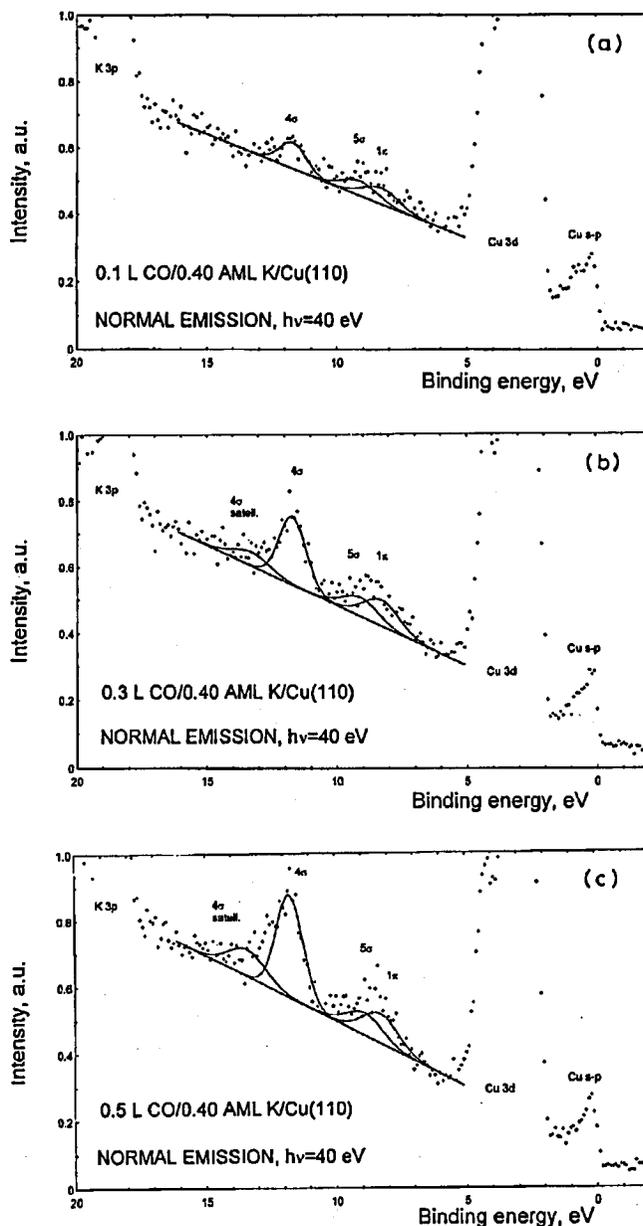


Fig. 1. The valence band spectrum of the CO/K/Cu(110) interface at  $T = 118$  K obtained by an incident photon energy of  $h\nu = 40$  eV (not smoothed data). (a) After a CO exposure of 0.1 L, (b) after a CO exposure of 0.3 L and (c) after a CO exposure of 0.5 L. For clarity, only the individual components and the linear background resulting from the fitting procedure are shown as the solid lines.

TABLE

Results of peaks fitting procedure for the valence band spectra of the CO/K/Cu(110) interface for a potassium precoverage of  $\tau_K = 0.14$  SML and different CO exposures. Peak position, in eV, corresponds to the binding energy,  $BE$ , relative to the Fermi level. The full width at half maximum, FWHM, is given in eV. The orbital intensity,  $I$ , calculated as the area under the peak, is expressed in the same arbitrary units.

Orbital	0.1 L CO			0.3 L CO			0.5 L CO		
	$BE$	FWHM	$I$	$BE$	FWHM	$I$	$BE$	FWHM	$I$
$1\pi$	8.3	1.60	0.084	8.3	1.60	0.132	8.4	1.60	0.148
$5\sigma$	9.1	1.60	0.075	9.1	1.60	0.096	8.9	1.60	0.112
$4\sigma$	11.7	1.20	0.101	11.7	1.20	0.263	11.8	1.20	0.395
$4\sigma$ satell.	—	—	—	13.3	1.68	0.074	13.4	1.68	0.144

was performed in two steps. First stage, referring to distinct features, comprises a three Gaussian peak synthesis (two in the case of 0.1 L) of the structures lying on linear backgrounds, i.e. the  $4\sigma$  satellite, the  $4\sigma$  and the mixed  $5\sigma/1\pi$ . Second step, i.e. assignment of the  $5\sigma$  and the  $1\pi$  contributions to the structure, was made on the base of angle resolved photoelectron spectra (not shown here). Under some experimental conditions, particularly for small angles of incidence (e.g.  $20^\circ$ ), symmetry arguments require that the  $\sigma$  states are suppressed relative to the  $\pi$  states. Although the energy separation between the  $5\sigma$  and the  $1\pi$  is very small (near the resolution limit), peak positions could be determined by the use of the smoothed spectra. The full width at half maximum (FWHM) of the components is in the range of 1.2–1.68 eV.

After an exposure to 0.1 L, three peaks corresponding to the  $4\sigma$ ,  $5\sigma$  and  $1\pi$  levels could be identified, although the signal-to-noise ratio is small in this case. The  $4\sigma$  satellite lies in the noise level. From the position of the  $5\sigma$  orbital relative to the others, the interaction with the substrate can be probed. The greater  $BE$ , the greater substrate interaction. The determined value of the  $5\sigma$  peak is close to the one corresponding to the CO–Cu interaction [18] which is indicative of CO adsorption on K-free substrate areas. The  $5\sigma$ – $1\pi$  separation of 0.8 eV is greater than one published for the CO/Cu(100) case [19].

The  $4\sigma$  satellite peak appears with an intensity almost 30% of the  $4\sigma$  level for the 0.3 L exposure. The  $5\sigma$ – $1\pi$  separation remains 0.8 eV, but the  $4\sigma/5\sigma$  intensity ratio increases from 1.4 to 2.8. A small value of the ratio is typical of the strong bound form of CO due to a decreased population in the  $5\sigma$ -derived orbital.

For an exposure of 0.5 L the spectrum resembles the one for the saturation case. The  $5\sigma$ – $1\pi$  separation is lowered to 0.6 eV and the increased  $4\sigma/5\sigma$  intensity ratio indicates a weakening of the CO–substrate interaction.

For the purpose of discussion, published data for CO overlayers on different substrates and the present results are collected in Fig. 2. Due to K modification of the copper surface the  $5\sigma$  level is pulled down (from 0.2 to 0.6–0.8 eV) to a deeper  $BE$  than the  $1\pi$  state. This is a probe of the CO–interface interaction

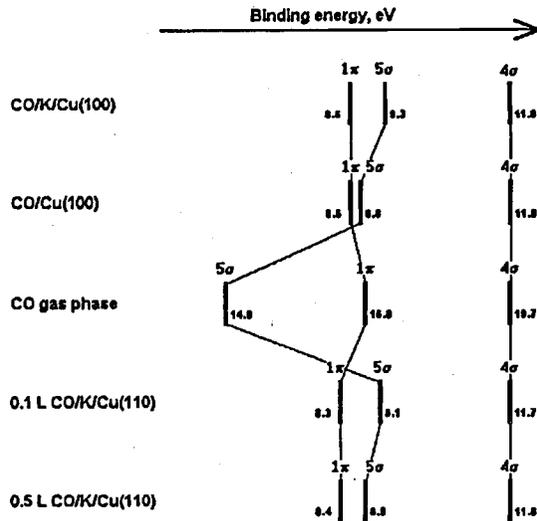


Fig. 2. Peak positions of the CO valence levels for the gas adsorbed and coadsorbed state on copper with respect to the  $4\sigma$  orbital as the reference level. The data for the CO/Cu(100) and the CO/K/Cu(100) interfaces are from Ref. [19], the CO gas data are from Ref. [9] and the data for the CO/K/Cu(110) — this paper.

which indicates a stronger bond for K-modified surfaces. During adsorption of CO on the K/Cu(110) interface, the  $5\sigma-1\pi$  separation slightly decreases which implies a weakening of the CO bond with increasing coverage.

The  $4\sigma-1\pi$  separation is determined as 3.4 eV and it is independent of the coverage of CO. Consequently, the CO molecule is stable and although elongation of C-O distance takes place, no dissociation is observed.

Changes of photoelectron excitation from two initial states, namely at  $BE = 11.8$  eV and 8.6 eV, corresponding to the  $4\sigma$  and the  $5\sigma/1\pi$ , respectively, with different final states are shown in Fig. 3. The constant initial state (CIS) spectra were normalized to the background level at a  $BE = 7.5$  eV. Excitation from the  $4\sigma$  CO orbital, shown as the upper graph in Fig. 3, exhibits two maxima for the incident photon energy equal to 21.4 and 34.9 eV. No distinct resonances are found in the broad CIS spectrum from the  $5\sigma/1\pi$  orbitals from the adsorbed CO.

Resonant behavior, characteristic of a given orbital, is observed easily in the CIS spectra when the analyzed emission angle agrees with the maximum value of the angular dependence of the photoelectron cross-section of the orbital [18, 21]. Due to small contributions to the signal, the resonances are usually imperceptible for analyzer orientation far from maxima. Theoretical analysis of cross-sections from an oriented CO molecule shows maximal intensity of the  $4\sigma$  orbital in the direction of the molecular axis, of the  $1\pi$  level in the direction perpendicular to the C-O axis and of the  $5\sigma$  level in a direction between 0 and 90 degree [22]. From Fig. 3 it is seen that the CIS spectra of the  $5\sigma/1\pi$  doublet is without structure which is indicative of registration away from the maxima of the photoemission

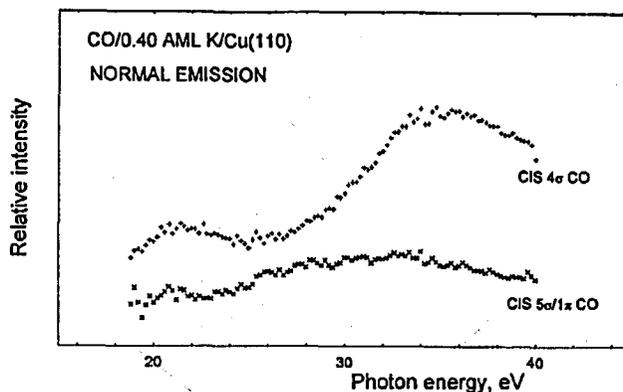


Fig. 3. Normalized photoionization cross-section of the  $4\sigma$  (upper curve) and the  $5\sigma/1\pi$  (bottom curve) CO orbitals for the 1 L CO/0.4 ML K/Cu(110) interface as a function of photon energy. The incident angle and the emission angle with respect to the surface normal were  $50^\circ$  and  $0^\circ$ , respectively.

cross-section of these orbitals. The maxima in the photoelectron emission from the  $4\sigma$  orbital in the CO molecule indicate that the angle of the CO molecule orientation is not far from the normal to the plane of the Cu(110) surface. An orientation of the C-O axis along the normal to the surface is observed on many low-index planes of metal surfaces.

#### 4. Conclusions

1. Adsorbed CO molecules on the K/Cu(110) interface exhibit valence orbitals with an order which is reverse of that occurring in the gas phase.
2. Interaction of CO molecules with the K/Cu(110) interface leads to elongation of the C-O distance; the value of the  $4\sigma-1\pi$  energy separation indicates that the CO molecule is not dissociated.
3. A decreased population in the  $5\sigma$ -derived orbital for weakly bound CO is characteristic of higher CO coverages, resulting in a large value of the  $4\sigma/5\sigma$  intensity ratio.
4. The CIS spectra of the  $4\sigma$  and the  $5\sigma/1\pi$  orbitals suggest an upright orientation of the CO molecules.

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