

## Electronic-structure changes for “ $\pi$ -bonded” CO chemisorbed on Cr(110)

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Synchrotron photoemission measurements of carbon monoxide chemisorbed in lying-down (“ $\pi$ -bonded”) and terminally bonded configurations on Cr(110) have revealed significant binding-geometry-dependent differences in the CO(ads) valence electronic structure, including an anomalous 0.8-eV increase in the CO  $4\sigma$  binding energy for the lying-down molecules relative to that of the terminally bonded CO.

Carbon monoxide is known to bond to transition-metal surfaces via the carbon end in either a terminal or bridged configuration, much like the CO ligand bonds to metal atoms in metal carbonyl complexes.<sup>1</sup> The well-known model of a synergistic combination of CO  $5\sigma \rightarrow$  metal  $d$ -band electron donation and metal  $3d \rightarrow$  CO  $2\pi^*$  back donation<sup>2,3</sup> successfully explains these structures and accounts for observed variations in the chemisorbed CO electronic structure and vibrational frequency. However, a “ $\pi$ -bonded” or “lying-down” adsorption geometry is frequently considered as a plausible molecular precursor (or transient intermediate) to CO dissociation on a metal surface.<sup>4-6</sup> A recent study<sup>7</sup> of CO chemisorption on Cr(110) using vibrational spectroscopy and stimulated desorption found the first evidence for “ $\pi$ -bonded” carbon monoxide on a clean transition-metal surface; the observed  $\sim 800\text{-cm}^{-1}$  reduction in the CO stretching frequency was attributed to enhanced electron back donation into the antibonding CO  $2\pi^*$  orbitals, thereby weakening the intramolecular bond. In this paper, the first comparison of the electronic structure of “ $\pi$ -bonded” and terminally bonded carbon monoxide on a single-crystal surface, Cr(110), is reported. Using synchrotron ultraviolet photoelectron spectroscopy (UPS), unmistakable binding-geometry-dependent effects in the valence electronic structure of “ $\pi$ -bonded” CO are found, including an anomalous binding-energy shift in the nominally nonbonding<sup>8</sup> CO  $4\sigma$  orbital.

Synchrotron photoemission studies were performed on a dedicated surface science beamline at the SURF-II Synchrotron Storage Ring at the National Bureau of Standards. The ultrahigh vacuum chamber (base pressure  $2 \times 10^{-11}$  Torr) is equipped for sample cleaning and cooling to 90 K, Auger electron and photoelectron spectroscopies, low-energy electron diffraction, and both photon- and electron-stimulated ion-desorption measurements.<sup>9</sup> The Cr(110) crystal preparation and cleaning procedure have been described elsewhere.<sup>7</sup> CO was adsorbed by ambient exposures or by using a collimated microcapillary array doser. Valence-band photoemission spectra were obtained over a  $26\text{ eV} < h\nu < 80\text{ eV}$  photon-energy range using a non-angle-apertured double-pass cylindrical mirror analyzer (CMA), fixed at  $90^\circ$  with respect to the incident photon direction. The combined monochromatized photon bandwidth and CMA resolution varied with photon energy between 0.30 and 0.38 eV.

Below  $\sim 150\text{ K}$ , carbon monoxide chemisorbs on Cr(110) in two molecular binding states.<sup>7</sup> Initially, a lying-down state ( $\alpha_1$  CO) is populated up to  $\theta_{\text{CO}} = 0.25$  monolayer, forming an ordered  $c(4 \times 2)$  overlayer. One monolayer corresponds to the surface density of Cr atoms on the ideal

(110) plane,  $1.705 \times 10^{15}\text{ cm}^{-2}$ . Above  $\theta = 0.25$ , CO adsorbs in a terminally bonded state ( $\alpha_2$  CO) at atop and bridge sites until saturation is reached at  $\theta_{\text{CO}} = 0.35$ . This sequential population of two distinct binding states enables a direct comparison of “ $\pi$ -bonded” and terminally bonded CO on the same metal surface.

Figure 1 shows CO-coverage-dependent UPS data obtained with the experimental configuration shown in the inset. In these experiments, the [110] surface normal is aligned with the CMA acceptance cone direction. The photon plane of incidence contains the [110] and [100] crystal azimuths and the photon polarization vector,  $A$ . A photon energy of 40 eV was used to avoid interfering Auger and second-order UPS features,<sup>10</sup> enhance the CO  $4\sigma$  cross section by being near resonance,<sup>11,12</sup> and enable comparisons with UPS data for CO chemisorbed on other metal surfaces. This experimental configuration is optimal, within the experimental constraints, for detection of CO  $4\sigma$  photoemission if the molecule is adsorbed in a terminally bonded arrangement and the intramolecular axis is oriented roughly along the [110] direction<sup>13-15</sup>—i.e., the proposed  $\alpha_2$  CO binding geometry.<sup>7</sup> Hence, based upon symmetry arguments alone, the  $\alpha_2$  CO  $4\sigma:(1\pi + 5\sigma)$  intensity ratio should be much greater than unity. On the other hand, a similar analysis for  $\alpha_1$  CO, lying down on the surface, shows that the  $4\sigma$  intensity should be less than that of the combination  $(1\pi + 5\sigma)$  peak, if the symmetry of the  $\alpha_1$  CO  $4\sigma$  orbital is not changed by bonding to the chromium surface. Therefore, CO-coverage-dependent spectra are expected, *a priori*, to show a large increase in the relative  $4\sigma:(1\pi + 5\sigma)$  intensity ratio only after the  $\alpha_1$  CO is saturated and the  $\alpha_2$  CO binding state is sequentially filled. This does not imply different Cr—CO bonding mechanisms for the two binding states but rather follows directly from the previously proposed models for the orientation of the C—O axis; i.e., roughly perpendicular to [110] for  $\alpha_1$  CO and parallel to [110] for  $\alpha_2$  CO.

Figure 1, curve *a* shows the photoemission spectrum for the sputter-annealed Cr(110) surface. The weak peak at  $\sim 6\text{-eV}$  binding energy ( $E_B$ ) relative to the Fermi level ( $E_F$ ) is attributed to trace amounts ( $< 0.03$  monolayer) of surface oxygen, which was also evident in previous vibrational data.<sup>7</sup> A weak peak at  $E_B = 11.6 \pm 0.1\text{ eV}$  and a more intense broadband centered at  $E_B = \sim 7.5\text{ eV}$  both increase in intensity linearly with CO exposure up to 1 L (1 L = 1 Langmuir =  $1 \times 10^{-6}$  Torr) as the  $\alpha_1$  CO binding state is populated [Fig. 1 (curves *b-d*)]. CO exposures above 1 L [Figs. 1 (curves *e-g*)] result in the appearance of a narrower fourth peak at  $E_B = 10.8 \pm 0.1\text{ eV}$  which grows rapidly

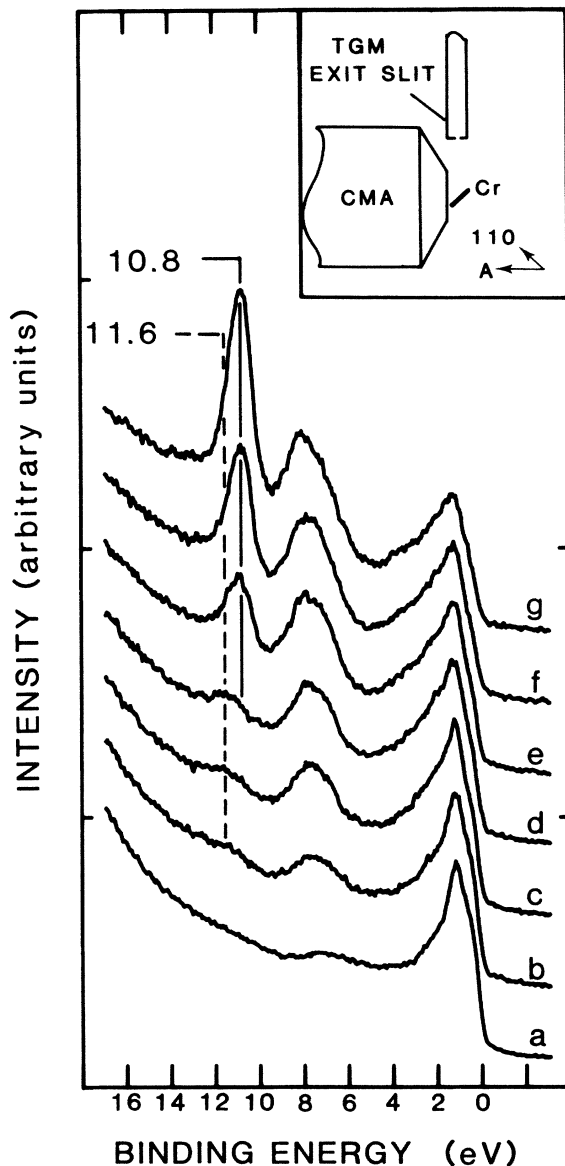


FIG. 1. Representative normal emission UPS data for CO adsorption on Cr(110) at 90 K. Spectra shown are for CO exposures of curves a, 0 L; b, 0.4 L; c, 0.6 L; d, 0.8 L; e, 1.6 L; f, 2.0 L; and g, 3.0 L. Vertical dashed and solid lines indicate the CO  $4\sigma$   $E_B$  for  $\alpha_1$  CO and  $\alpha_2$  CO, respectively. Inset shows the experimental layout, in the plane of incidence, used in this experiment.

to dominate the spectrum until saturation is reached after a total exposure of  $\sim 3.5$  L. Subtle changes in the broad peak centered at  $\sim 7.5$  eV also can be seen.

Based upon the CO-coverage behavior, photon-energy dependence (see below and Ref. 10), and limited measurements<sup>10</sup> of the angular dependence of the 11.6- and 10.8-eV intensities, these peaks have been assigned to the  $4\sigma$  levels of  $\alpha_1$  CO and  $\alpha_2$  CO, respectively, while the broad  $\sim 7.5$ -eV feature is assigned to a combination of  $5\sigma$  and  $1\pi$  emission from both binding states, with the  $\pi$  components being at the lower binding energies. Thus the intensity predictions discussed above are seen experimentally, providing additional support for the lying-down ( $\alpha_1$  CO) and terminally bonded ( $\alpha_2$  CO) models.

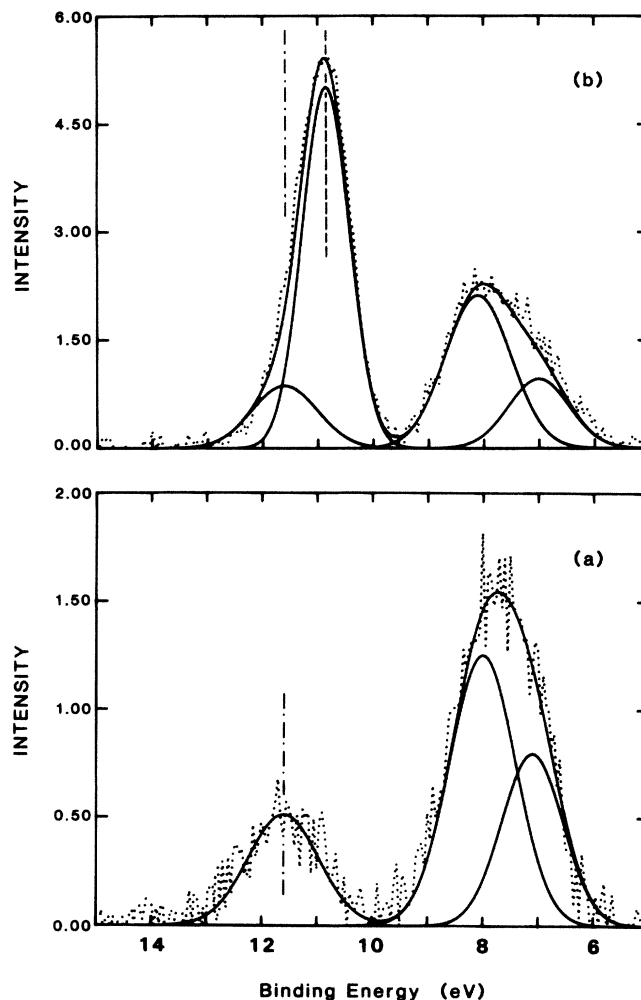


FIG. 2. Sample fitting of the CO-derived UPS peaks after subtracting a spline-function background from the spectra of Fig. 1 (curves d and g). Numerical intensity scales may be compared directly. (a) A three-peak fit for  $\alpha_1$  CO after an 0.8-L CO exposure at 90 K. (b) A four-peak fit for the mixed adlayer of both  $\alpha_1$  CO and  $\alpha_2$  CO after a 3.0-L CO exposure at 90 K. See text for peak assignments and Table I for fitting parameters. Vertical dash-dot and dashed lines indicate binding energies for the  $\alpha_1$  CO and  $\alpha_2$  CO  $4\sigma$  levels, respectively.

Figure 2 illustrates spectroscopic evidence that is suggestive of different Cr:CO bonding mechanisms for terminally bonded and lying-down molecules on Cr(110). The CO-derived UPS features of Fig. 1 (curve d) and (curve g) are compared after subtracting an inelastic electron background approximated by a spline function;<sup>10</sup> Gaussian peak shapes have been numerically fit to the residual features using the following method. For the  $\alpha_1$  CO data, Fig. 2 (curve a), one Gaussian was used to fit the  $4\sigma$  peak at  $E_B = 11.6$  eV and two additional Gaussians of equal full width at half maximum (FWHM) were used for the  $(5\sigma + 1\pi)$  peak at  $\sim 7.5$  eV. Although this conventional notation for CO valence levels is used, it is recognized that these molecular orbitals can be rehybridized and their symmetries altered by bonding to the surface. In addition, the usually degenerate  $1\pi$  orbitals may be energetically split in this binding state, contributing separately to the broad  $(5\sigma + 1\pi)$  peak and

mandating additional Gaussian components. However, the use of more than two components is not necessitated by the present data.

With the addition of the  $\alpha_2$  CO state, Fig. 2 (curve *b*), a fourth Gaussian at 10.8 eV is necessary; additional  $5\sigma$  and  $1\pi$  components are expected also but these spectra cannot be used to extract (reliably) the binding energies of the  $\alpha_2$  CO contributions. This is left to angle-resolved UPS experiments currently in preparation. The fitting parameters are summarized in Table I, which reveals a significant finding of this study: The CO  $4\sigma$  level exhibits *increases* in both its binding energy and the UPS peak FWHM for the lying-down adsorption geometry relative to the terminally bonded geometry.

In the gas phase, the essentially nonbonding CO  $4\sigma$  orbital is well described as an electron lone pair, with the charge density spatially extending away from the oxygen end of the molecule; similarly, the CO  $5\sigma$  orbital spatially extends away from the carbon end.<sup>8</sup> Upon chemisorption in the conventional terminally bonded configuration ( $\alpha_2$  CO), the CO  $5\sigma$  and  $1\pi$  orbitals are rehybridized and energetically stabilized as a result of chemical bonding to the surface and associated relaxation effects. However, the CO  $4\sigma$  orbital is only weakly influenced by chemisorption and its gas-phase symmetry is largely preserved. This is frequently exploited in angular-resolved UPS studies<sup>13-15</sup> to determine the orientation of the adsorbed CO. However, it is clear that in the case of " $\pi$ -bonded"  $\alpha_1$  CO on Cr(110), the  $4\sigma$  orbital is noticeably effected by the proximity of the chromium surface.

The observed  $\alpha_1$  CO  $4\sigma$  binding-energy shift may be due to better screening of the hole as a result of proximity to the metal, an increase in the C—O bond length, or a redistribution of the valence electronic charge among the molecular orbitals and the chromium valence band. The latter reason is equivalent to referring to a "bonding change" in going from a terminally bonded orientation to the " $\pi$ -bonded" configuration. Screening can certainly contribute to the observed  $\Delta E_B$ ; however, a better screened  $\alpha_1$  CO  $4\sigma$  final state is expected to appear at a *lower* apparent binding energy, which is opposite that which is observed experimentally. Although a localized core level can exhibit a binding-energy increase due to final-state effects, this has not been observed previously for a delocalized *valence* level. Increasing the C—O bond length can stabilize the CO  $4\sigma$  level and thereby increase the binding energy. Several calculations illustrating this for gas-phase CO as well as for terminally bonded CO on metal clusters have been published.<sup>16</sup> Recent calculations by Mehandru and Anderson<sup>17</sup> show that increasing the gas-phase C—O bond length by 0.16 Å to lower the stretching frequency to the measured  $\alpha_1$  CO value<sup>7</sup> will increase the  $4\sigma E_B$  approximately 0.3 eV. Although this one calculation may not be conclusive, it suggests that the increased bond length *alone* can account for

less than half of the experimentally measured  $\Delta E_B$  for CO on Cr(110). Their calculations<sup>17</sup> also find a  $4\sigma\Delta E_B$  of  $\sim 1$  eV for terminally bonded and lying-down CO on a Cr<sub>33</sub> cluster, which exceeds the experimental value by  $\sim 0.2$  eV.

These considerations suggest that initial-state electronic differences are the dominant contribution to the large  $4\sigma$  binding-energy increase associated with the lying-down CO binding state. The increased UPS  $4\sigma$  peak FWHM cannot be attributed to adlayer inhomogeneity since the  $\alpha_1$  CO state forms an ordered  $c(4\times 2)$  overlayer at saturation. Instead, a direct interaction of the  $4\sigma$  orbital with the metal—analogueous to that for the  $1\pi$  and  $5\sigma$  levels of both CO binding states—can lead to more rapid relaxation of the final state (hole) and increased UPS peak width.

Data at other photon energies were obtained to investigate the CO  $4\sigma$  shape resonance<sup>11,12</sup> for CO on Cr(110). Both binding modes exhibit a  $4\sigma$  resonance near 36 eV; however, interference effects<sup>10</sup> from overlapping Auger and second-order UPS peaks in this photon-energy range unfortunately prevent a definitive identification of shape resonance differences. The interference problem is exacerbated by the low  $\alpha_1$  CO  $4\sigma$  intensities measured at all of the limited number of experimentally accessible combinations of photon incidence angle and photoelectron detection angle. A complete report of these measurements is in preparation.<sup>10</sup>

Brucker and Rhodin<sup>18</sup> have argued that the CO  $4\sigma-1\pi$  separation is indicative of the C—O bond weakening upon chemisorption. The present UPS data and previous EELS results<sup>7</sup> showing the  $\alpha_1$  CO binding mode to be a precursor to dissociation on Cr(110) are consistent with this empirical correlation. If the  $1\pi$  levels are assumed to be nearly degenerate (since the present experiment could not clearly resolve a separate  $1\pi$  component for the terminally bonded  $\alpha_2$  CO mode), the  $4\sigma-1\pi$  separation is  $\sim 4.5$  eV for  $\alpha_1$  CO and  $\sim 3.7$  eV for  $\alpha_2$  CO. These values can be compared to values of 3.0 eV for Cu(100),<sup>19</sup> 3.1 eV for Ni(100)<sup>20</sup> and Ir(111),<sup>21</sup> 3.5 eV for Pt(111),<sup>22</sup> 3.7 eV for Pd(111),<sup>23</sup> and 4.0 for Fe(110).<sup>24</sup> The Cr(110) data also are consistent with the correlation of enhanced CO dissociation probability with the proximity of the metal  $3d$  bands to the Fermi level.<sup>25</sup>

In conclusion, these experimental observations indicate that lying-down CO is clearly distinguished from terminally bonded CO in UPS experiments not only by the relative UPS peak intensities but also by  $4\sigma$  binding energy and FWHM increases. We note that the designation as " $\pi$ -bonded" may be misleading in that it implies that the Cr—CO bonding is largely via the  $\pi$  orbitals, rather than a synergistic combination involving charge distribution among the  $2\pi^*$ ,  $1\pi$ ,  $5\sigma$ , and  $4\sigma$  orbitals. The present results show that the most noticeable change in the CO electronic structure is not in the  $\pi$  system but rather in the binding energy of the  $4\sigma$  orbital. Certainly detailed theoretical calculations coupled with the forthcoming angle-resolved UPS data for

TABLE I. Cr(110)/CO UPS peak parameters (in eV).  $\Delta E_B = \pm 0.1$  eV.

Mode	$E_B$	FWHM	$E_B$	FWHM	$E_B$	FWHM	$E_B$	FWHM
$\alpha_1$			11.6	1.5	8.0	1.3	7.1	1.3
$\alpha_1 + \alpha_2$	10.8	1.0	11.6	1.5	8.0	1.3	7.1	1.3

the ordered  $c(4 \times 2)$   $\alpha_1$  CO overlayer will provide further insights into the details of this unusual bonding mechanism.

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