

## Unusual C–O Bond Weakening on a Clean Metal Surface: CO on Cr(110)

Neal D. Shinn and Theodore E. Madey

Surface Science Division, National Bureau of Standards, Gaithersburg, Maryland 20899

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A unique CO chemisorption mode ( $\alpha_1\text{CO}$ ), with the lowest reported CO stretching frequencies ( $1150\text{--}1330\text{ cm}^{-1}$ ) on any clean or promoted metal surface, has been identified on Cr(110) by means of EELS, ESDIAD, LEED, AES, and oxygen coadsorption experiments. A "lying down" binding configuration in twofold-symmetric hollow sites is proposed for  $\alpha_1\text{CO}$  molecules. For  $\theta_{\text{CO}} > 0.25$ , a second mode ( $\alpha_2\text{CO}$ ) bound perpendicular to Cr(110) is populated.

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In this Letter, we present evidence for a previously unreported molecular CO chemisorption mode ( $\alpha_1\text{CO}$ ) on a clean transition-metal surface, Cr(110), at 120 K. This new binding mode consists of molecules adsorbed with the intramolecular axis approximately *parallel* to the chromium surface and is the only CO binding mode at low coverage. In contrast, a second, sequentially populated, CO chemisorption mode ( $\alpha_2\text{CO}$ ) is identified as terminally bonded CO with the intramolecular axis perpendicular to the surface. The observed  $\alpha_2\text{CO}$  stretching frequencies ( $1865\text{--}1975\text{ cm}^{-1}$ ) are within the expected range for chemisorbed CO,<sup>1</sup> but the comparable frequencies for  $\alpha_1\text{CO}$  ( $1150\text{--}1330\text{ cm}^{-1}$ ) are substantially shifted from the gas-phase value ( $2143\text{ cm}^{-1}$ ) and are the lowest reported to date for *any* clean or "promoted" single-crystal metal surface.<sup>2</sup>

High-resolution electron-energy-loss spectroscopy (EELS), electron-stimulated desorption ion angular distributions (ESDIAD), low-energy electron diffraction (LEED), and Auger-electron spectroscopy (AES) experiments were performed in a stainless-steel UHV system with a base pressure of  $4 \times 10^{-11}$  Torr. Gas exposures were made with a microcapillary array doser, which allowed spectroscopic measurements to be made at or below  $7 \times 10^{-11}$  Torr, and thereby minimized contamination problems. The sputtered and annealed Cr(110) surface exhibited a good-quality ( $1 \times 1$ ) LEED pattern against a low-intensity background; faceting or periodic step formation was not observed. The only surface impurity detectable via AES was carbon, which, on the basis of Cr(110)/CO AES studies,<sup>3</sup> was estimated to be less than 5% of a monolayer. Because the Cr *LMM* Auger transitions obscure the oxygen *KLL* lines, EELS was used to estimate the residual oxygen coverage by calibration against Cr(110)/O data.<sup>3</sup> Although a "clean" surface has, typically, 3% of a monolayer of atomic oxygen, coadsorption effects

have been explicitly measured<sup>4</sup> and do not alter the conclusions of this work.

At 120 K, CO adsorbs on Cr(110) with an initial sticking probability of  $\sim 0.9$ , which drops smoothly to  $\sim 0.4$  after a 0.7-L ( $1\text{ L} = 10^{-6}$  Torr sec) CO exposure.<sup>3</sup> A fully developed  $c(4 \times 2)$  LEED pattern is then observed, corresponding to an  $\alpha_1\text{CO}$  coverage of 0.25 monolayer. Corresponding EELS data are shown in Fig. 1. The clean-surface spectrum (Fig. 1, curve *a*) contains one discrete loss at  $595\text{ cm}^{-1}$  due to the residual atomic oxygen.<sup>3</sup> A 0.3-L CO exposure results in three new losses at  $\sim 450$  (weak), 1150, and  $1330\text{ cm}^{-1}$  (Fig. 1, curve *b*), which increase in intensity with CO exposure, and shift to  $\sim 475$ , 1200, and  $1330\text{ cm}^{-1}$  when the  $c(4 \times 2)$   $\alpha_1\text{CO}$  overlayer is complete. Figure 1, curve *c* (0.7-L CO) marks the onset of  $\alpha_2\text{CO}$  by the appearance of a new vibrational triplet at 495, 1865, and  $1975\text{ cm}^{-1}$ ; this indicates that (to within our EELS sensitivity) the  $\alpha_1\text{CO}$  mode is the *only* CO binding mode for  $\theta_{\text{CO}} \leq 0.25$  and that it saturates with the formation of the  $c(4 \times 2)$  overlayer.

For CO exposures beyond  $\sim 0.7\text{ L}$ , the following are observed: (1) The measured CO sticking probability declines to 0.1; (2) the  $\alpha_2\text{CO}$  vibrational intensity increases (Fig. 1, curve *d*) while the 1200- and  $1330\text{-cm}^{-1}$  EELS peaks merge and are slightly attenuated; and (3) the  $c(4 \times 2)$  LEED pattern reverts to a diffuse ( $1 \times 1$ ) pattern with a high-intensity background at  $\theta_{\text{CO}} \approx 0.3$ . After 2–3-L CO exposure ( $\theta_{\text{CO}} \sim 0.35$ ), broad  $\alpha_2\text{CO}$  vibrational losses dominate the EEL spectrum and the ( $1 \times 1$ ) diffraction beams are barely visible above the intense background, which indicates extensive adlayer disorder. Additional experiments at higher CO coverage have shown that some CO dissociation and surface reconstruction can occur even below 300 K.

Coverage-dependent ESDIAD measurements also reflect the sequential population of distinctly different  $\alpha_1\text{CO}$  and  $\alpha_2\text{CO}$  modes. When one starts with the clean surface and continues through an

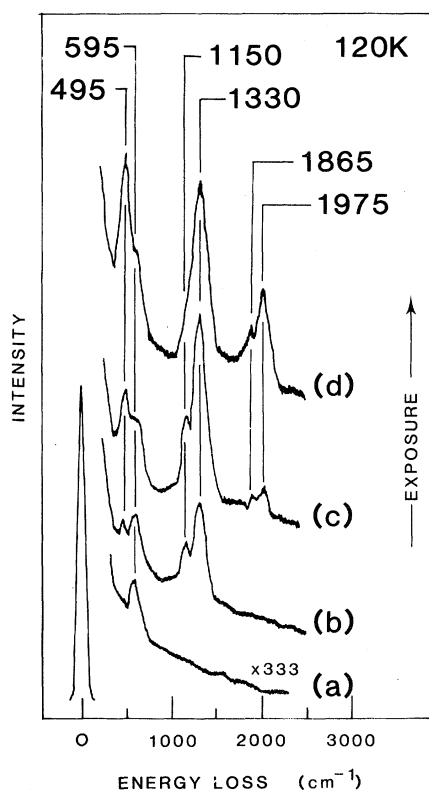


FIG. 1. High-resolution ( $90 \text{ cm}^{-1}$  full width at half maximum) EELS data for CO on Cr(110) at 120 K: Curve *a*, clean; curve *b*, 0.3-L CO; curve *c*, 0.7-L CO; curve *d*, 0.9-L CO. All spectra are normalized to the elastic peak height for the clean surface (shown).

$\sim 0.7$ -L CO exposure, only vanishingly weak  $\text{O}^+$  ion emission normal to the surface is observed. This extremely low signal is consistent with ESD (electron-stimulated desorption) of the residual atomic oxygen but is remarkably weak for  $\sim 0.25$  monolayer of  $\alpha_1\text{CO}$ , if it were bound in a conventional manner.<sup>5</sup> With the onset of the  $\alpha_2\text{CO}$  EELS vibrational features, a single  $\text{O}^+$  beam along the [110] normal ( $\pm 20^\circ$ ) is observed, increasing in intensity along with the normalized EELS  $\alpha_2\text{CO}$  losses. Additional tests for  $\alpha_1\text{CO}$  ESD  $\text{O}^+$  ions with use of incident electron energies up to 1 keV failed to produce detectable ion desorption along any azimuth.

The absence of  $\text{O}^+$  emission from  $\alpha_1\text{CO}$  could be attributed to a dramatic cross-section difference between  $\alpha_1\text{CO}$  and  $\alpha_2\text{CO}$  for electron-induced dissociation and subsequent ion desorption. However, EELS or LEED measurements following ESDIAD revealed severe electron-beam damage effects for

both  $\alpha_1\text{CO}$  and  $\alpha_2\text{CO}$ . Even low electron-beam doses ( $10^{-8} \text{ C}$ ) caused detuning of the EELS spectrometer (attributed to work-function changes due to CO dissociation) and more diffuse  $\alpha_1\text{CO}$   $c(4 \times 2)$  LEED beams. The significant distinction between the  $\alpha_1$  and  $\alpha_2$  binding modes lies not in their cross sections for electron-stimulated dissociation but rather in their probabilities for  $\text{O}^+$  ion desorption; chemisorption models for  $\alpha_1\text{CO}$  and  $\alpha_2\text{CO}$  must account for this difference.

The  $\alpha_2\text{CO}$  ESDIAD results imply that these CO molecules are oriented nearly perpendicular to the (110) plane, with the carbon end bound to the Cr surface. The simplest interpretation of the two  $\alpha_2\text{CO}$  EELS losses at 1865 and 1975  $\text{cm}^{-1}$  is an assignment to excitations of CO stretching modes for normally bound CO at both bridge-bonded and atop-bonded chromium sites, respectively. The 495- $\text{cm}^{-1}$  vibration is then assigned to the unresolved Cr-CO stretching modes for the two normally bound species. Other possible interpretations are discussed elsewhere.<sup>3</sup>

A suitable  $\alpha_1\text{CO}$  chemisorption model is not immediately obvious. In fact, the intense vibrations at 1150–1330  $\text{cm}^{-1}$  are more suggestive of an adsorbed carbonate, acetate, or formate species<sup>6</sup> (as the product of a surface reaction) than chemisorbed CO. Compelling evidence that these reactions, which require atomic oxygen or some CO dissociation, are *not* occurring is provided by CO/ $\text{O}_2$  titration studies. If the  $\alpha_1\text{CO}$  mode were a reaction product, then deliberate oxygen pre dosing should facilitate product formation. In fact, the *opposite* effect is experimentally observed. Oxygen pre dosing serves to *inhibit*  $\alpha_1\text{CO}$  formation with  $\theta_0 \approx 0.2$  monolayer sufficient to block the  $\alpha_1\text{CO}$  mode completely; only  $\alpha_2\text{CO}$  adsorbs under these conditions.

A more dramatic demonstration that the  $\alpha_1\text{CO}$  mode is indeed chemisorbed CO is its conversion to the  $\alpha_2\text{CO}$  mode, also at 120 K. Figure 2 highlights the results of one such EELS experiment. The clean surface (Fig. 2, curve *a*) is first dosed with CO to form the saturated  $c(4 \times 2)$   $\alpha_1\text{CO}$  layer (Fig. 2, curve *b*), which is then stepwise dosed with oxygen. Two major changes in the vibrational spectrum with oxygen exposure are observed: First, losses appear at 605 and 1030  $\text{cm}^{-1}$  corresponding to adsorbed atomic and molecular oxygen<sup>4</sup>; second, and more importantly, the intensity at  $\sim 1300 \text{ cm}^{-1}$  from  $\alpha_1\text{CO}$  smoothly *decreases* and losses at both 1865 and 1975  $\text{cm}^{-1}$ , due to  $\alpha_2\text{CO}$ , monotonically *increase* in intensity (Fig. 2, curve *c* and inset). AES measurements have demonstrated the conservation of surface carbon, in accord with the rear-

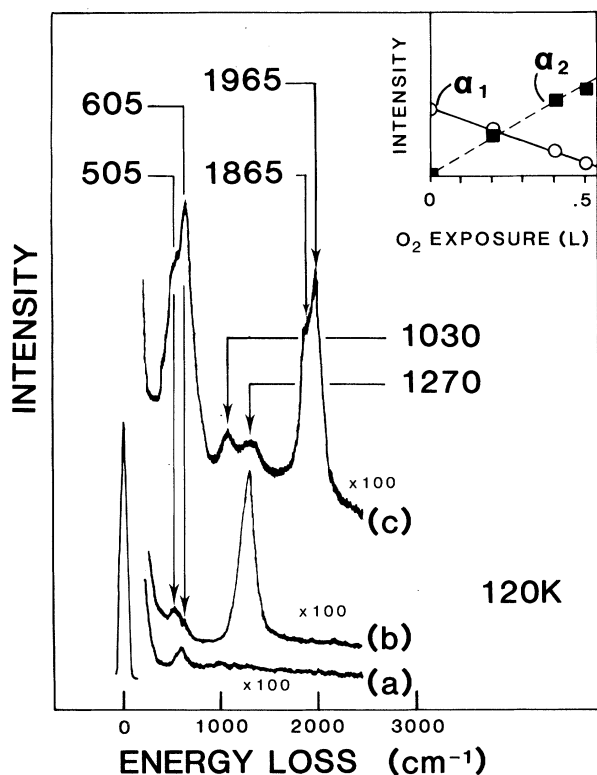


FIG. 2. Sample EELS data for (curve *a*) clean Cr(110); (curve *b*), 0.6-L CO; and (curve *c*), after an additional 0.4-L oxygen exposure. Inset shows normalized peak areas for the  $\alpha_1$  (1150–1330  $\text{cm}^{-1}$ ) and  $\alpha_2$  (1865–1975  $\text{cm}^{-1}$ ) CO vibrational bands.

rearrangement of adsorbed CO. These experiments confirm that the  $\alpha_1$ CO mode is indeed a molecularly adsorbed CO binding state. Additional experiments demonstrate that the  $\alpha_1$ CO mode undergoes dissociation upon heating to  $T \geq 200$  K, indicating that the  $\alpha_1$ CO mode serves as a precursor state to CO dissociation.<sup>3</sup>

A model for the  $\alpha_1$ CO adsorption mode must account for the anomalously low vibrational bands at 1150–1330  $\text{cm}^{-1}$ . Simplistic normal-mode analyses of  $\text{Cr}_n\text{CO}$  clusters, configured to simulate CO adsorbed on Cr(110), have been used to investigate the frequency dependence of the highest-frequency normal mode ( $\nu^*$ ) as a function of CO bond strength and CO binding configuration. The expected finding was that, given reasonable choices for the intracenter force constants and atomic distances, the force constant chosen for the C–O bond largely determines  $\nu^*$ . Hence, the observed 1150–1330- $\text{cm}^{-1}$  vibrations imply substantial CO bond weakening, which within a molecular-orbital description requires electron donation into the anti-

bonding CO  $2\pi^*$  orbital. An alternate explanation is that the CO-chromium bonding, in the  $\alpha_1$ CO mode only, involves molecular-orbital rehybridization. Either of these possibilities is difficult to rationalize if the CO is constrained to be perpendicular to the Cr(110) surface. Greater overlap of the CO  $2\pi^*$  orbitals and the chromium valence electron density could be achieved if the molecular axis were nearly parallel to the surface, thus facilitating CO bond weakening. Such a binding configuration has already been postulated for a transition state during CO dissociation on transition metals<sup>7</sup> and a side-on bonded carbonyl group ( $\nu_{\text{CO}} = 1330 \text{ cm}^{-1}$ ) has been reported in the  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Nb}_3(\text{CO})_7$  cluster.<sup>8</sup>

The ESDIAD results further support a “lying down”  $\alpha_1$ CO binding configuration. The absence of measurable  $\text{O}^+$  ion emission implies that  $\text{O}^+$  ions ejected along the C–O bond axis are recaptured by the attractive image field outside the metal surface. A classical-trajectory approach<sup>9</sup> predicts that  $\text{O}^+$  will be recaptured if CO is tilted at least  $60^\circ$  away from the surface normal; however, the Cr–CO libration should then be visible *via* EELS. But an  $\alpha_1$ CO molecule “lying flat,” with direct Cr–O interaction, would be consistent with both a higher ESD  $\text{O}^+$  ion neutralization probability for  $\alpha_1$ CO and no observable CO libration.

We propose that both the electronic structure and morphology of the Cr(110) surface are significant factors in determining the bonding characteristics of  $\alpha_1$ CO. In particular, unlike the low-index fcc surfaces, Cr(110) exhibits twofold-symmetric hollow sites of appropriate geometry to align the majority of the  $\alpha_1$ CO molecules roughly along the  $[\bar{1}10]$  direction ( $\nu_{\text{CO}} = 1330 \text{ cm}^{-1}$ ). Prior to full  $c(4 \times 2)$   $\alpha_1$ CO overlayer development, other CO molecules adsorbed at defects, near residual surface oxygen atoms, or in small islands could lead to the minority  $\nu_{\text{CO}}$  band which shifts with  $\theta_{\text{CO}}$  (1150  $\rightarrow$  1200  $\text{cm}^{-1}$ ). The weak 450–475- $\text{cm}^{-1}$  loss may be associated with  $\alpha_1$ CO molecules or due to a very low coverage of normally bound CO, since the EELS metal–CO stretch is frequently more intense than  $\nu_{\text{CO}}$  at very low  $\theta_{\text{CO}}$ .<sup>1</sup>

Similar “low CO stretching frequencies” have previously been reported for CO adsorbed on potassium-promoted Ru(001).<sup>2</sup> In this case, it has been argued that the CO molecule is “side-on bonded” with the C–O axis nearly parallel to the surface. However, because of the complicated  $\theta_K$ -dependent behavior and direct interactions between coadsorbates, the local CO adsorption geometry corresponding to the anomalously low  $\nu_{\text{CO}}$  is uncertain. Very recent ESDIAD studies of CO/K/

Ru(001) in our laboratory<sup>10</sup> support the model of CO molecules parallel to the surface; the possible correlation between the electronic structures of CO/K/Ru(001) and the  $\alpha_1$ CO mode is particularly enticing.

In summary, the sequential population of two, generically different CO binding modes on Cr(110) at 120 K has been demonstrated. The low-coverage ( $\theta_{\text{CO}} \leq 0.25$ )  $\alpha_1$ CO mode is without analog on any other *clean* metal surface and may be comparable to certain CO binding states on K-promoted Ru(001). EELS/ESDIAD  $\alpha_1$ CO results are modeled by molecules having weakened C–O bonds oriented parallel to the Cr(110) surface in an ordered  $c(4 \times 2)$  overlayer at saturation. Twofold-symmetric hollow Cr sites are suggested as local adsorption sites for the new  $\alpha_1$ CO mode. The second,  $\alpha_2$ CO mode is modeled as a disordered combination of both bridge- and atop-bonded, terminally bound CO, consistent with the conventional picture of carbon monoxide chemisorption on single-crystal metal surfaces. Finally, CO/O coadsorption results have demonstrated the blocking of  $\alpha_1$ CO by adsorbed atomic oxygen and the low-temperature conversion of  $\alpha_1$ CO to  $\alpha_2$ CO.

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