NAG3-341

Why CO Bonds Side-on at Low Coverage and Both Side-on and Upright at High Coverage on the Cr(110) Surface

by

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Abstract

An atom superposition and electron delocalization molecular orbital study of CO adsorption on the Cr(110) surface shows a high coordinate lying-down orientation is favored. This is a result of the large number of empty d-band energy levels in chromium, which allows the antibonding counterparts to σ and π donation bonds to the surface to be empty. When lying down, backbonding to CO π^* orbitals is enhanced. Repulsive interactions cause additional CO to stand upright at $>\frac{1}{4}$ monolayer coverage. Our results confirm the recent experimental study of Shinn and Madey.

It has been known for quite some time, both experimentally[1-3] and theoretically,[4,5] that CO adsorbs in an end-on orientation with the carbon-end towards the surface on the metals in the right side of the transition series e.g. Ni, Pt, Pd, and Cu. On a potassium promoted Pt(111) surface CO shifts from the 1-fold to higher coordinate sites.[6,7] On a clean Ru(001) surface, CO adsorbs perpendicular to the surface but on alkali metal promoted ($\theta<0.15$) Ru(001), it lies down.[8] However, when potassium coverage exceeds one-third monolayer CO stands up even on Ru(001).[9] A qualitative molecular orbital explanation for this effect has been provided for the negatively charged Ru(001) surface in terms of d-electron count.[10] On going further left in the transition series one expects, on the basis of theoretical results from Ref. 10, that side-on bonded CO will be more stable than end-on bonded CO even on the unpromoted surface. A very recent high-resolution electron energy loss spectroscopic (HREELS) study of CO adsorbed on a Cr(110) surface has provided confirmation for this.[11,12]

In this paper we have theoretically examined CO adsorption on the Cr(110) surface, both at low and high coverage, using the atom superposition and electron delocalization molecular orbital theory.[13] The usefulness of the method has been amply demonstrated in the previous CO adsorption studies on Pt(111),[4] potassium covered Pt(111)[6], and negatively charged Ru(001)[10] surfaces. C and O atomic parameters used in the present work are the same as used in Ref. 4, and those for Cr are taken from Ref. 14. Cr ionization potentials are increased by 1.5 eV and the exponents are increased by 0.15 a.u. from the literature values to give reasonable charge transfers and bond lengths for diatomic CrO and CrC.

We have employed a two-layer thick cluster consisting of 33 chromium atoms (see Fig. 1) for all our calculations and used the bulk nearest neighbor distance of 2.498 Å. Because of the high degree of electron pairing in bulk Cr, the cluster model is assigned low spin. Six types of binding sites are considered (see Fig. 2). On the three sites marked 1-fold, 2-fold, and 3-fold, CO is adsorbed in the end-on orientation with the carbon-end down; on the other three sites, marked di-σ, 3-fold bridging, and 4-fold, CO is adsorbed in the side-on orientation with the molecular axis parallel to the surface. The CO bond length is optimized to the nearest 0.01 Å, heights above the surface and the lateral displacements of the CO molecule to the nearest 0.05 Å, and the rotation angle for CO on the 3-fold bridging site to the nearest 5 deg.

The calculated results for the adsorbed CO on all the sites are given in Table I. It may be seen that all the lying-down orientations are favored over all the standing-up orientations. The 4-fold site is the most stable binding site. Our results confirm the experimental findings of Shinn and Madey, who have proposed a lying-down binding configuration for less than quarter monolayer CO coverage on the Cr(110) surface.[11,12] These authors chose the two-fold symmetric hollow sites with the CO molecules oriented roughly along the [1$\bar{1}$0] direction. In our notation this is the 4-fold site. This site uniquely allows both C and O to bind to three surface Cr atoms, accounting for its stability. On this site we calculate a bond stretch of 0.16 Å from the gas phase value suggesting considerable weakening of the bond as will be discussed later. The 3-fold site is the most stable binding site for the

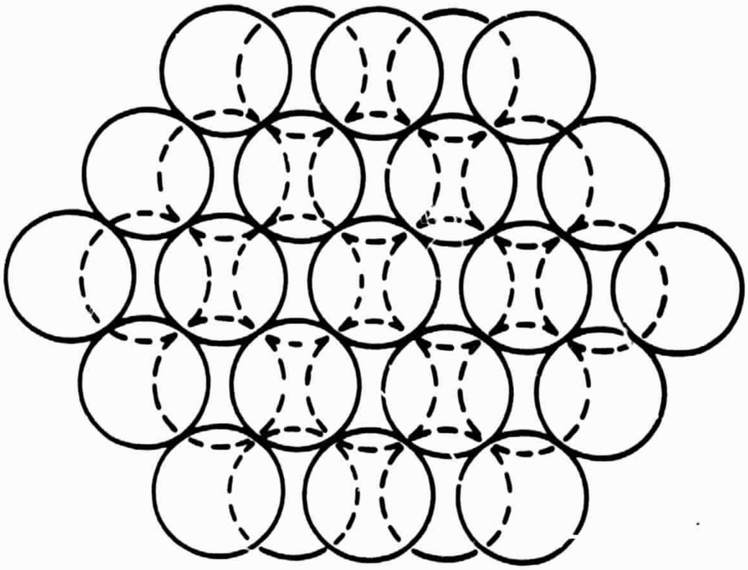

Fig. 1. Cr_{33} cluster model of Cr(110) surface.

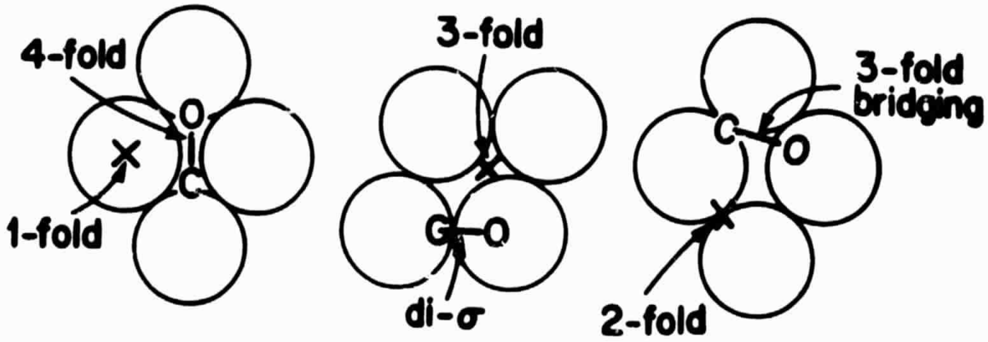

Fig. 2 Adsorption sites studied on the cluster model of Fig. 1.

end-on configuration, with the 2-fold and 1-fold sites close behind for the low coverage model. As will be seen below, binding of CO is stronger at the high coordinate site because of increased π^* participation. Also this order of stability for the upright CO on the 1-fold, 2-fold, and the 3-fold sites will be changed for the high coverage model.

Our calculated CO stretching force constants vary inversely with the binding energies at the various sites, being largest on the 1-fold atop site where the binding energy is minimum, and smallest on the 4-fold site where the binding energy is maximum. Since the force constant of a diatomic molecule is proportional to the frequency squared, a crude comparison is possible with the surface results by omitting CO vibrational coupling to the surface. Our calculated ratio of the square roots of the CO force constants for the 4-fold side-on configuration and the 3-fold end-on configuration is 0.77 as compared to 0.67, calculated from the ratio of the measured frequencies for the two CO binding modes given in reference 20. As will be discussed later for CO coverage more than quarter monolayer, our calculated ratio of the square roots of the CO force constants for the two most favored binding orientations (4-fold and 1-fold) becomes 0.63, which compares more favorably with the observed frequency ratio of adsorbed CO. Our calculations produce a CO dissociation barrier of 0.4 eV when adsorbed on the 4-fold site and when CO bond stretches by 0.55 Å from its equilibrium value. This low barrier is consistent with the observed low temperature (<200 K) dissociation of CO and with the idea that a reclined orientation is a precursor state to CO dissociation.[11,12] Our calculated barrier for CO dissociation is very close to that estimated in Ref. 12 (~40 $kJ.mol^{-1}$).

The energy level correlation diagram for CO adsorbed on the 4-fold site in the side-on orientation on the cluster model is shown in Fig. 3. It may be seen that CO binds to the surface by means of 5σ and π donation bonds, the antibonding counterparts of both are high-lying and empty. This is in marked contrast to the CO adsorption bonds on the favored μ/π site of Ru(001) where antibonding counterparts of the π donation orbitals are half-filled,[10] and for the same site on the Pt(111) where they are doubly filled.[4,10] Even if there is a 2.31 spin imbalance, as recently predicted by Victora and Falicov[15] for the (110) surface, our conclusions are unaffected because these orbitals will remain empty. This effect progressively reduces the stability gained due to the donation bonds on going from Cr(110) to Ru(001) to Pt(111) surfaces, to the extent that the lying-down orientation becomes much less favored on the Pt(111) surface compared to the standing-up orientation. These differences are directly attributable to the number of d electrons in the metal valence bands. Furthermore, it has been shown in reference 10 that when more electrons are simply added to the d-band of the Ru (001) cluster model to make it isovalence-electronic with platinum, the 1-fold standing-up orientation becomes favored over the lying-down orientation, as it is for Pt (111).

The backbonding to the CO antibonding π^* orbitals and the loss of σ and π bonding due to donation and electron delocalization to the surface in the 4-fold site both serve to weaken the CO bond. The net effect of these charge transfers is a small positive Mulliken charge on CO.

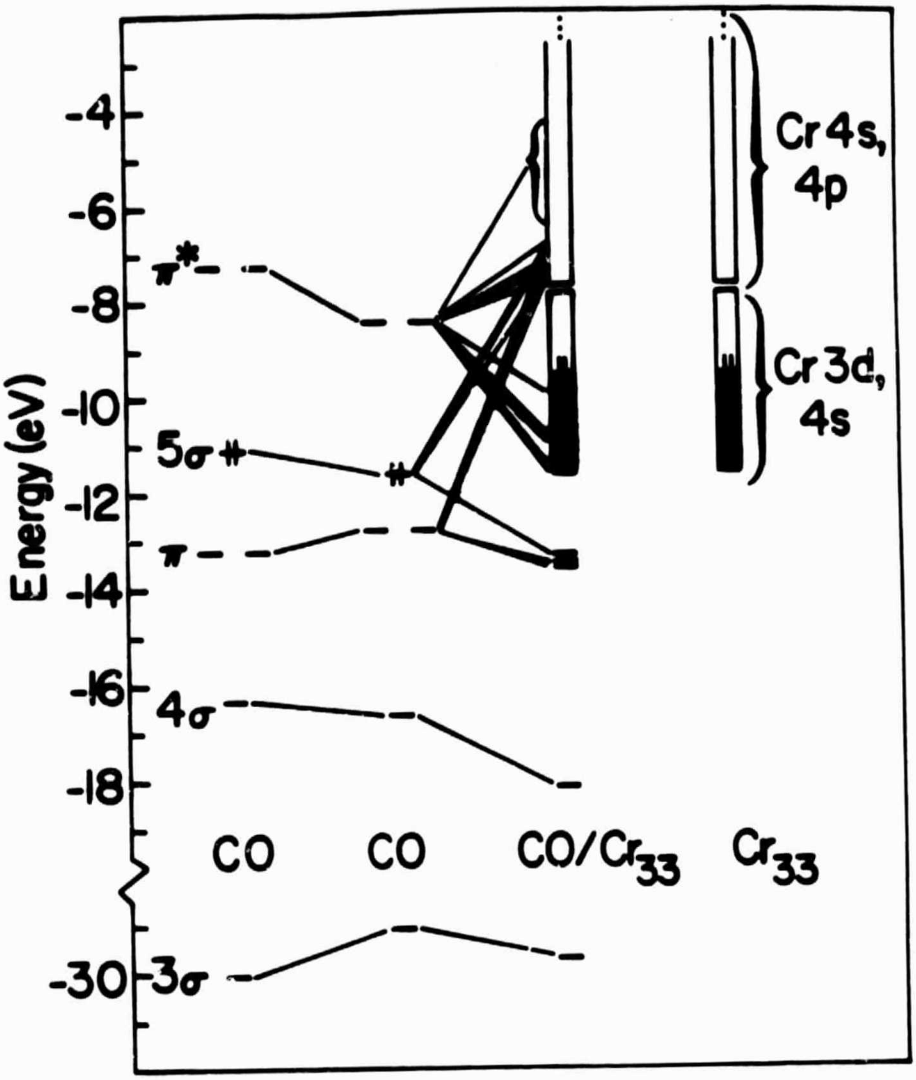

Fig. 3. Energy level correlation diagram for CO adsorbed on the 4-fold site of the cluster model in the side-on orientation. The second column shows the energy levels of CO having the bond length of the adsorbed molecule but with the cluster removed. Correlation lines are drawn for orbitals having 0.05 or more electron on CO.

The 5σ and π donation stabilizations and the π^* back-donation interactions of terminally bonded CO on the 3-fold site are markedly reduced (Fig. 4) compared with the 4-fold lying-down orientation. The backbonding dominates in this orientation since the calculated CO charge is -0.7 electron, which lies predominantly on the oxygen end.

Figure 4 shows the energy levels for all the binding-sites considered in this paper and one can clearly identify the increase in the 5σ and π stabilizations on going from the less stable upright to the more stable reclined orientations. The general stability observed for these orbitals for the reclined orientations is a consequence of having both ends of the CO molecule participating in the bonding. This also enhances the backbonding to the π^* orbitals.

For low CO coverage ($0<\theta<0.25$), CO binds exclusively in the side-on mode as shown by HREELS studies[11,12]. This is understandable considering the large difference (~1.9 eV) in the stability of the most stable lying-down configuration (4-fold) and the most stable terminally bonded configuration (3-fold). However, for CO coverage greater than quarter monolayer a second mode of CO bonded perpendicular to the Cr(110) surface was identified in the HREELS study[11,12]. We have modeled high CO coverage on the Cr(110) surface by employing the cluster model of Fig. 1 with four CO molecules adsorbed in the lying-down orientation in the 4-fold sites according to the observed c(4x2) LEED pattern (see Fig. 5). The structures of these CO molecules are used from the previous calculations involving the adsorption of one CO molecule. The binding orientation and the site for an additional CO molecule was

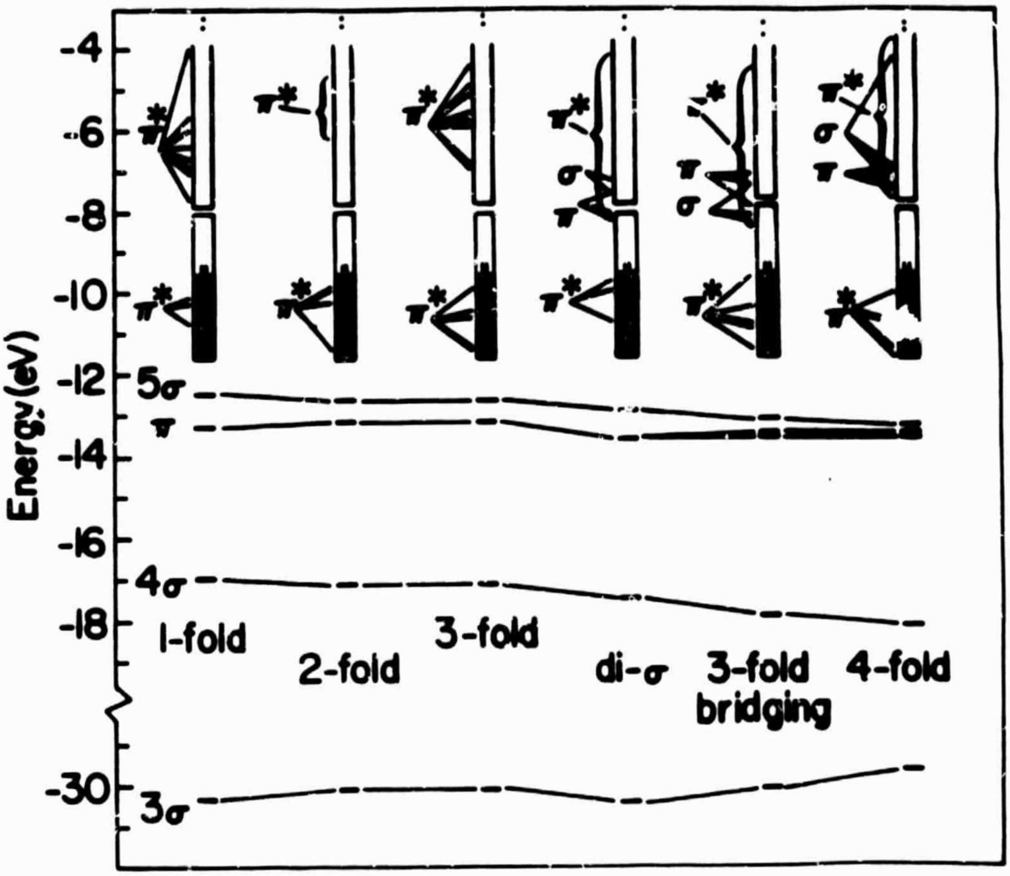

Fig. 4. Energy levels for CO bonded to the six types of sites (shown in Fig. 2) on the 33-atom cluster model. Orbitals with more than 0.05 electron on CO are marked.

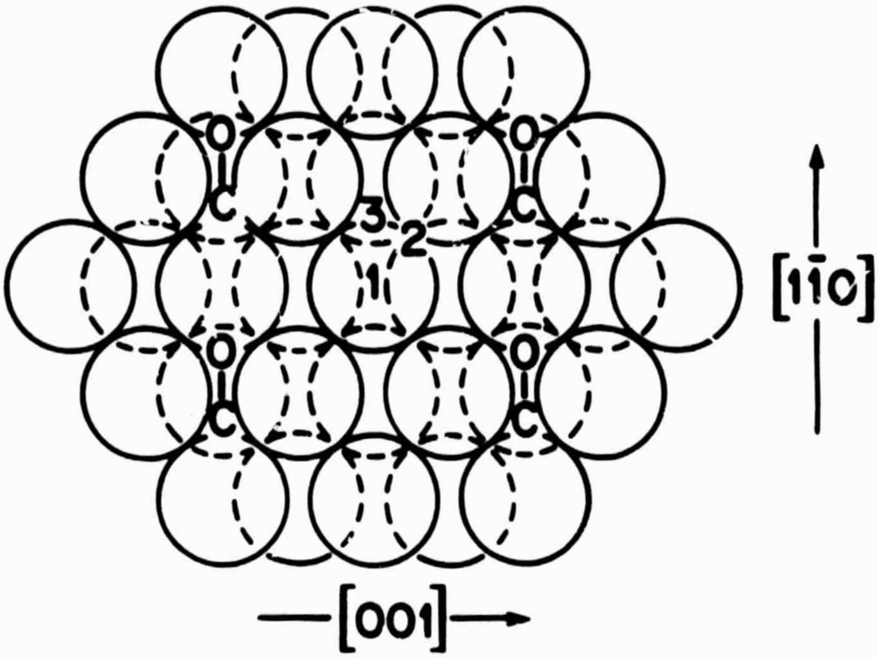

Fig. 5. High coverage model for CO adsorption. 4 CO molecules are adsorbed according to the observed c(4x2) LEED pattern. Another CO molecule is allowed to bind on the sites marked 1, 2, and 3 in the end-on orientation.

then explored in the presence of these four CO molecules. The calculated results are given in parentheses in Table I. Because of the repulsive interactions with the CO molecules already present, this additional CO molecule favors the 1-fold site, shown by the number 1, in the end-on configuration. The 3-fold site (number 3) is the next in terms of stability and the 2-fold site (number 2) is the least stable. The order of stability of the 1-fold, 2-fold, and the 3-fold sites is completely changed compared to the low coverage case for the terminally bonded CO. The presence of a dominant CO frequency at 1975 cm^{-1} and a small peak at 1865 cm^{-1} in the EELS spectrum in Ref. 11 is consistent with the force constants calculated for the 1-fold and the 3-fold sites as given in Table I. Our calculated ratio of the square roots of the force constants on the 3-fold and the 1-fold sites is 0.89 for the high coverage model compared with 0.94 calculated from the observed frequency ratio.

We also tried the binding of this additional CO in the side-on orientation on the available 4-fold sites for the high coverage model, and found that its binding energy was only 2.8 eV, showing high repulsive interactions with the four CO molecules already present. These results, therefore explain why CO stands up at coverages greater than quarter monolayer.

In summary, we have made a theoretical study of CO adsorption on the Cr(110) surface both at low and high coverage. We have confirmed the recent HREELS observation that CO bonds side-on on the clean Cr(110) surface at less than quarter monolayer coverage. Our calculated barrier for CO dissociation in the most favored binding configuration is 0.4 eV and is consistent with the experimental estimate of ~40 kJ.mol^{-1}. The stability of the lying-down orientation is a result of relatively few d valence electrons in chromium so that the antibonding counterparts of 5σ and π donation bonds are empty. This orientation also allows increased back-donation from the surface to the CO π^* orbitals. This is in contrast with the CO/Ru(001) system where CO lies down only when the surface is promoted by potassium, which favors strong π^* mixing, and the CO/Pt(111) system where CO adsorbs perpendicularly. This is because on going right in the transition series, as more and more electrons are added to the d-band, the antibonding counterparts of 5σ and π donation orbitals are progressively occupied. This reduces the stability of CO in the lying-down orientation, and makes the standing-up orientation the favored one on the right side of the transition series. For CO coverage greater than quarter monolayer on Cr(110), some CO molecules are adsorbed in the perpendicular orientation because of less repulsive interaction with the lying-down CO molecules.

Acknowledgment: This study was supported by NASA Grant NAG-3-341 from the Lewis Research Center. We are grateful to N. D. Shinn and T. E. Madey for making Ref. 12 and to L. M. Falicov for making Ref. 15 available to us prior to publication.

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Table I. Calculated results for the binding energy (BE), change in CO bond length on adsorption (ΔCO), heights, force constants (k), displacements of C (ΔX and ΔY), CO rotation from the horizontal, and the charges on C and O for CO adsorbed on the 33-atom cluster model.[a]

	Upright orientation			Lying-down orientation		
	1-fold	2-fold	3-fold	di-σ	3-fold bridging	4-fold
BE (eV)	3.56 (3.62)	3.71 (2.91)	3.92 (3.44)	4.46	5.19	5.79
ΔCO (Å)	0.01 (0.01)	0.06 (0.03)	0.06 (0.06)	0.05	0.10	0.16
height C (Å)	1.75 (1.75)	1.40 (1.45)	1.25 (1.25)	1.50	1.30	1.00
height O (Å)	2.95 (2.95)	2.65 (2.67)	2.50 (2.50)	1.50	1.30	1.00
k_{CO}(mdyn/Å)	11.53 (11.92)	8.13 (8.96)	7.78 (9.44)	6.94	5.67	4.59
k_{CrC}(mdyn/Å)	5.53 (5.44)	4.00 (3.21)	4.18 (2.92)	6.47[b]	7.74[b]	4.86[b]
ΔX C (Å)	–	–	–	0.30	0.20	–
ΔY C (Å)	–	–	0.40 (0.45)	0.00	0.70	-0.50
Rotation (deg)	–	–	–	–	15	–
Charge C	0.30 (0.29)	0.14 (0.30)	0.15 (0.15)	0.16	-0.08	-0.10
Charge O	-0.52 (-0.52)	-0.82 (-0.70)	-0.84 (-0.85)	0.04	0.15	0.23

[a] Numbers in parentheses are for the high coverage ($>\frac{1}{4}$ monolayer) of CO as shown in Fig. 5.

[b] For vertical CO displacements; therefore includes a k_{CrO} componenet.

Figure Captions

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