

Unusual State of Adsorbed CO: $\text{CO}(\sqrt{3} \times \sqrt{3})R30^\circ/\text{Cr}_2\text{O}_3(111)$

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A new form of CO is found for adsorption on an oxide surface, where an ordered array of CO is found by angle-resolved photoemission to be bound in a tilted or lying-down mode. This new bonding configuration has very strange features which are discussed, including strange ordering of valence bands and abnormal binding energies. A simple model is presented.

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In the late fifties and sixties surfaces of oxide powders were studied in detail with respect to their chemical reactivity due to the importance of oxides in catalysis. With the advent of surface science and the growing interest in electron spectroscopic techniques the attention shifted towards the study of adsorption and reaction on metal surfaces. During the last decade or so, however, interest has returned to the investigation of oxides with increasing importance attached to clean oxide single-crystal surfaces, but a systematic investigation of molecular adsorbates on well-defined oxide single-crystal surfaces has not been carried out. In particular, studies of ordered structures of molecules on single-crystal oxide surfaces are hardly found [1].

Oxide surfaces are different from metal surfaces in that they are usually insulators or semiconductors. As a consequence, the 2π backbonding contribution to the bonding of CO on an oxide surface is small compared to adsorption on most transition metals. Another point is that oxides are ionic compounds, resulting in strong electric fields at the surface which might shift the adsorbate's electronic states.

In this Letter we report the first detailed study of the electronic and geometric structure of an ordered overlayer of CO adsorbed on an oxide surface, employing electron spectroscopic methods. We have chosen Cr_2O_3 as a substrate for our adsorption studies since the catalytic activity of this oxide for various reactions is rather high [2-4]. It is known that CO adsorbs on Cr_2O_3 powders [5], but a detailed picture of the bonding mechanism does not exist.

The $\text{Cr}_2\text{O}_3(111)$ film was prepared by oxidation of a clean $\text{Cr}(110)$ surface as described elsewhere [6-9]. It is at least 10 Å thick and exhibits chromium- and oxygen-terminated patches on the surface [10,11]. We observe a three-dimensional band structure with pronounced dispersions, which is a good indication that the electronic structure is similar to that of the bulk material [10]. The major advantage, however, over the bulk material is that the system does not charge under photon or electron irradiation even at liquid-nitrogen temperatures.

Upon dosing CO at low temperature (100 K) up to saturation, a clear $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED (low-energy electron diffraction) pattern which is very sensitive to electron or photon irradiation is observed. CO desorbs out of this structure at $T=175$ K with a relatively sharp desorp-

tion signal. With HREELS (high-resolution electron-energy-loss spectroscopy) we observe a C-O stretching frequency of 2167 cm^{-1} . As often found for CO adsorption on oxides [5], this frequency is slightly larger than the gas-phase value (2143 cm^{-1}) [5]. If the clean $\text{Cr}_2\text{O}_3(111)$ surface is exposed to oxygen before CO exposure, CO does not adsorb on the surface. This indicates that the CO molecules adsorb on parts of the surface that expose Cr atoms to the vacuum.

We have employed angle-resolved photoelectron spectroscopy to extract information about the bonding geometry of the CO molecules via the use of symmetry selection rules for the cross sections. Also, we have taken advantage of a well-known intensity resonance of the σ -ion states. This so-called σ shape resonance [12] is observed at a photon energy of about 35 eV if the light is polarized along the molecular axis, which should also be the direction of electron detection.

Figure 1 shows photoelectron spectra of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ CO structure recorded in the so-called forbidden and allowed geometries [13,14] as indicated in the figure, in comparison with a normal emission spectrum of a physisorbed monolayer CO on $\text{Ag}(111)$ [15]. There are two CO-induced features visible in the spectra of the CO adsorbate on $\text{Cr}_2\text{O}_3(111)$: one at 17.5 eV and a slightly asymmetric one at 20.2 eV. As indicated above, the CO σ valence emission should be intense at the photon energy the spectra have been taken with, i.e., 36 eV, whereas the 1π emission should be rather weak. Thus we identify the two CO-induced features as the σ -ion states of molecularly adsorbed CO.

The electronic binding energies of CO on $\text{Cr}_2\text{O}_3(111)$ are larger by several eV compared to those of the CO physisorbate on $\text{Ag}(111)$. This holds also for CO adsorbates on other metals (see, for instance, Refs. [15-18]), indicating that the substrate-CO interaction on $\text{Cr}_2\text{O}_3(111)$ is appreciably different from that on metals.

Obviously, there is no significant difference in the spectra of $\text{CO}/\text{Cr}_2\text{O}_3(111)$ for the two collection geometries in Fig. 1. If the CO molecular axis were oriented perpendicular to the surface, the symmetry selection rules would require the σ -ion states to disappear in the forbidden geometry, and only the ion states of π symmetry should show up. Since both σ -ion states of CO are observed with comparable intensities in both geometries, we conclude that the CO axis is strongly inclined with respect to

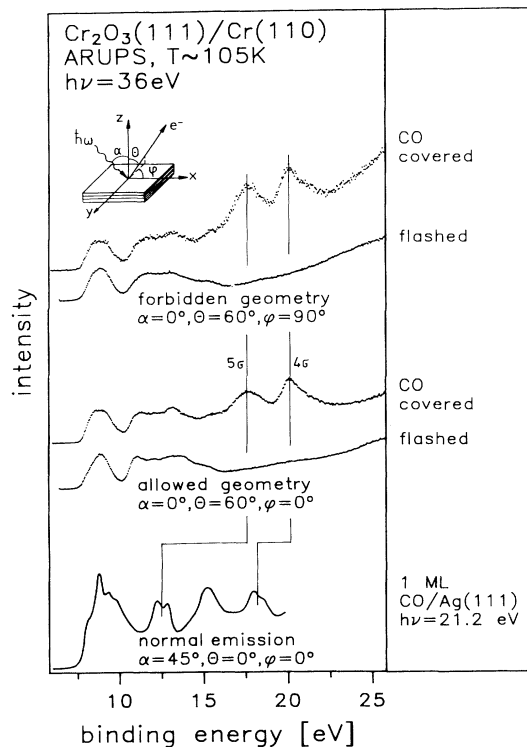


FIG. 1. Photoelectron spectra of clean $\text{Cr}_2\text{O}_3(111)$ and $\text{Cr}_2\text{O}_3(111)$ covered with a saturation coverage of CO. The spectra were recorded in the so-called allowed and forbidden geometries. Binding energy is referenced to the vacuum level. For comparison also a spectrum of a monolayer CO on Ag(111) [15] is shown. The splitting of the σ levels in this spectrum is due to band-structure effects.

the surface normal.

More detailed information on the orientation of the molecular axis can be deduced from Fig. 2, where a set of photoelectron spectra taken with a constant angle, i.e., 90° , between the directions of light incidence and electron detection is shown.

From Fig. 2 it is obvious that the σ -ion states exhibit highest intensities for near-normal light incidence and near-grazing electron emission, whereas at grazing light incidence these features are strongly attenuated, in strong contrast to CO adsorbed standing up on most metal surfaces. Since at a photon energy of 36 eV the σ states emit with highest intensity if the polarization direction and the direction of electron detection both coincide with the CO molecular axis, this behavior is only compatible with an orientation of the molecular axis approximately parallel to the surface.

In the inset of Fig. 2 we compare the emission intensities of the CO σ valence states as a function of photon energy for two different experimental geometries. The data shown in the upper panel were taken at a light incidence angle of 20° with respect to the surface normal, collecting the electrons 70° off normal, whereas the data

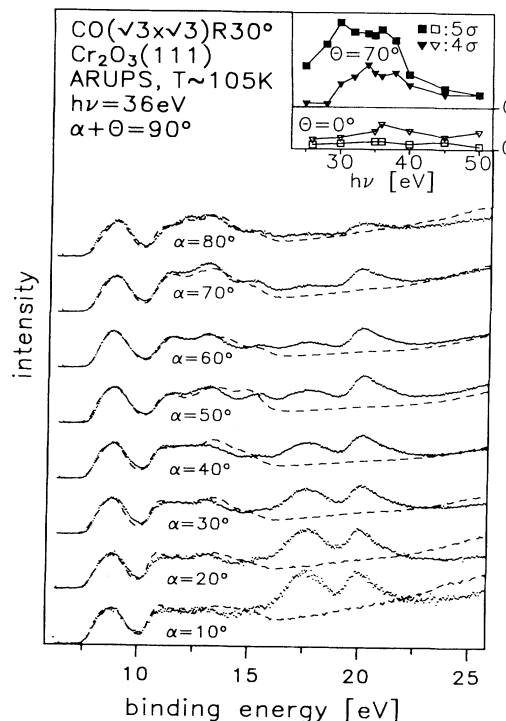


FIG. 2. Series of angle-resolved ultraviolet photoemission spectra for CO adsorbed on $\text{Cr}_2\text{O}_3(111)$. The angle between the incident light and the electron-detection direction has been kept at a fixed value, i.e., 90° (see text). Inset: The emission intensities of the CO valence bands as a function of photon energy for two different experimental geometries (see text). For comparison also spectra for clean $\text{Cr}_2\text{O}_3(111)$ (dashed curve) are shown. Binding energy is given relative to the vacuum level.

in the lower panel were taken at normal electron emission and near-grazing light incidence ($\alpha=80^\circ$). Obviously a strong σ shape resonance is observed only for grazing electron detection, again clearly indicating that the CO molecules must be strongly tilted.

The same conclusion about the molecular geometry must be drawn from the analysis of our NEXAFS (near-edge x-ray-absorption fine-structure) data [11]. These data show that the intensity of the π resonance varies only slightly as a function of the light incidence angle as expected for CO molecules lying flat on the surface, since on 2π component is oriented parallel to the surface, whereas the other one sticks out of the surface. A quantitative estimation of the tilting angle was not possible from our NEXAFS data since the σ resonance was so weak that its intensity only could be evaluated with very large error bars.

From the data discussed so far a quantitative evaluation of the tilting angle was not possible, but, tentatively, we estimate this angle to be larger than about 70° .

An open question is: Where are the 1π orbitals? For flat-lying CO molecules the 1π levels are expected to split into two components, $1\pi_{xy}$ and $1\pi_z$, the first one oriented

parallel to the surface and the other one oriented perpendicular to the surface. Whereas the $1\pi_{xy}$ emission might be hidden below the σ emissions because this level should be intense at grazing emission angles like the σ orbitals, the $1\pi_z$ should be intense at normal emission where the σ emission is weak. As can be seen from Fig. 2, the 5σ emission is nearly totally suppressed at near-normal electron emission so that the $1\pi_z$ level is most likely not situated near the 5σ level as is the case for the 1π levels of CO adsorbed on most metals. One might suppose that the $1\pi_z$ level is located somewhere in the region of the substrate bands, but since the $1\pi_z$ orbital will interact strongly with these bands it will most likely be shifted to higher binding energy, because the substrate levels are energetically located above the 1π levels. Considering this it seems to be rather unlikely that the 1π levels are located somewhere in the region of the oxide emission.

Whereas the 5σ emission is nearly totally suppressed at near-normal emission, a broad feature remains in the region of the 4σ between 19 and 22 eV (Fig. 2). Since the 4σ and 5σ emission intensities should behave similarly, it is tempting to attribute the remaining emission between 19 and 22 eV to the $1\pi_z$ level. Another possible assignment would be that this feature is due to a σ shake-up state. However, we consider this to be unlikely because such shake-up states should be intense at emission angles where the σ main lines are also intense, which is not the case.

Figure 3 compares the binding energies of the present spectra with data reported in the literature [15–20]. All binding energies are larger than the corresponding values known from metal surfaces. They are even larger than the gas-phase values. This holds also for the C $1s$ ioniza-

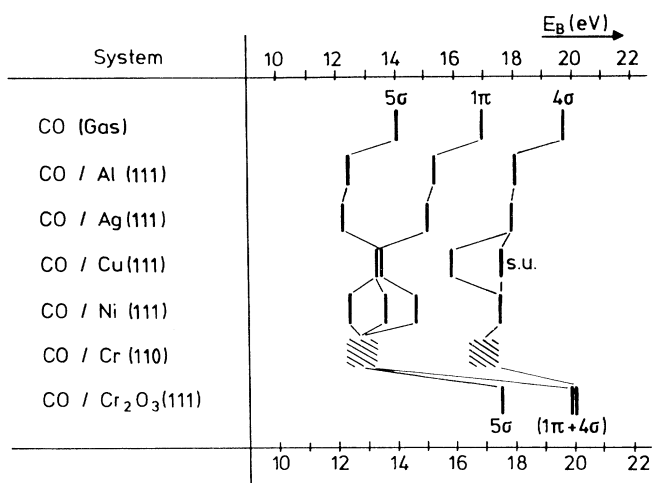


FIG. 3. Binding energies of the valence levels of CO adsorbed on different hexagonal or quasi-hexagonal surfaces with respect to the vacuum level. Since we do not know the work-function change for the adsorption of CO on Cr(110), we have hatched the binding-energy region in which we expect the ionizations to occur. The data have been taken from Refs. [15–20]. S.U. denotes a shake-up state.

tion which is found 0.7 eV below its gas-phase value [11]. The most interesting finding, however, is the energetic position of the $1\pi_z$ level, which is in the present case most likely situated near the 4σ level, indicating a fundamentally different interaction of the molecule with the surface as compared with all cases observed so far: The CO lone pairs (4σ and 5σ) we propose to be bound towards two different Cr ions in the sense of two σ -donor bonds which shift the σ binding energies to higher values. If this is true then it is very reasonable to assume that the 1π levels interact with both the Cr ions but in addition, and more importantly, with the oxygen layer underneath the terminating Cr layer. This latter interaction between the closed-shell O^{2-} ions and CO must be basically repulsive. Since the oxygen levels are situated at lower binding energies than the CO 1π levels, the $1\pi_z$, which is the one that strongly interacts with the O^{2-} ions, is shifted towards higher binding energy and the interacting O^{2-} levels are rearranged as well. The shift of the $1\pi_z$ level is recognized in the data, while it is more difficult to identify the effect on the oxygen levels. If we judge the observed shifts of CO on $Cr_2O_3(111)$ with respect to gaseous CO, we find a shift of all CO levels to higher binding energies. The shift of the 5σ level is larger than that of the 4σ level. This is very reasonable because it follows the individual polarizabilities of the levels involved. The interaction may be separated into the two bonding Cr-CO(5σ) and Cr-OC(4σ) interactions, and into a repulsive O^{2-} -CO(1π) interaction, leading to a weakly chem-

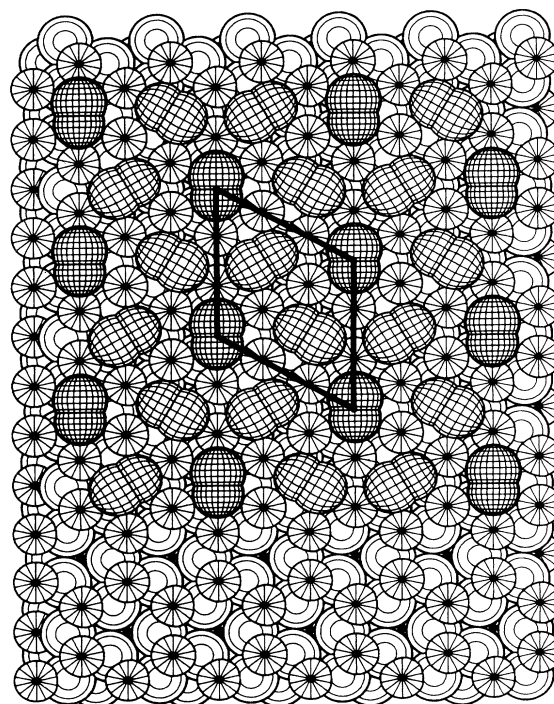


FIG. 4. Structure model for $CO(\sqrt{3}\times\sqrt{3})R30^\circ/Cr_2O_3(111)$. The unit cell of the overlayer is indicated.

isorptive CO-Cr₂O₃ bond. The bonding of CO towards Cr₂O₃(111) is completely different from the bonding of CO to a metallic Cr surface. It is a pure accident that CO binds to metallic Cr in a flat bonding geometry as well. The ion-state binding energies as well as their sequence are clearly different from the situation on Cr₂O₃(111) as may be seen from the data collected in Fig. 3.

A structure model of CO on the Cr-terminated patches of Cr₂O₃(111) is presented in Fig. 4 where we show a schematic representation of the CO-covered surface. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit mesh is indicated. As suggested by the intensity of the CO valence-band emission the surface is most likely rather densely covered with CO molecules, as is, for instance, the case for CO on Ag(111) or N₂ on graphite [16], where the molecules are also lying flat on the surface. A structure with one molecule per unit cell would contain only the molecules on the corners of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ unit mesh. In case the unit cell contains more than one molecule the other molecules have to be added.

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