

Structures of Adsorbed CO on Atomically Smooth
and on Stepped Single Crystal Surfaces

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Abstract

The structures of molecular CO adsorbed on atomically smooth surfaces and on surfaces containing monatomic steps have been studied using the electron stimulated desorption ion angular distribution (ESDIAD) Method. For CO adsorbed on the close packed Ru(001) and W(110) surfaces, the dominant bonding mode is via the carbon atom, with the CO molecular axis perpendicular to the plane of the surface. For CO on atomically rough Pd(210), and for CO adsorbed at step sites on 4 different surfaces vicinal to W(110), the axis of the molecule is "tilted" or inclined away from the normal to the surface. The ESDIAD method, in which ion desorption angles are related to surface bond angles, provides a direct determination of the structures of adsorbed molecules and molecular complexes on surfaces.

I. Introduction

A continuing need in studies of atoms and molecules on surfaces concerns the location of surface bonding sites and the geometrical structure of molecules and molecular fragments on surfaces. That is, where are adsorbed species bonded, what are the directions of the bonding orbitals between the atom (molecule) and surface, and what are the bonding directions of ligands in adsorbed molecular complexes? In a continuing series of experiments, (1,2) we have established that the electron stimulated desorption ion angular distribution (ESDIAD) method has clear potential for providing direct information regarding the site location and geometrical structure of molecules adsorbed on surfaces.

In this method, a surface containing adsorbed molecules is bombarded by a focused low energy electron beam. Electronic excitation of the adsorbed species by electron bombardment can result in the desorption of atomic and molecular ions from the surface. The ions desorb in discrete cones of emission in directions determined by the orientation of the surface molecular bonds which are "broken" by the excitation. The resultant ESDIAD patterns provide a visual display of the geometrical structure of surface molecules in the adsorbed layer.

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In the present application, we have observed that when molecular CO is adsorbed on the close packed Ru(001)⁽³⁾ and W(110) surfaces, the dominant mode of bonding is via the carbon atom with the CO molecular axis perpendicular to the plane of the surface. For CO on atomically rough Pd(210)⁽⁴⁾ and for CO adsorbed at step sites on surfaces vicinal to W(110), the axis of the molecule is "tilted" or inclined away from the normal.

In two cases (CO on Ru, Pd), ESDIAD has been used to complement and verify structural information predicted using other methods, such as angular resolved ultraviolet photoemission spectroscopy, low energy electron diffraction, and surface vibrational spectroscopy. For the case of CO on stepped surfaces vicinal to W(110), entirely new insights into CO bonding configurations have been provided by this work.

II. Experimental

The ultrahigh vacuum apparatus used for most of these studies has been described previously⁽¹⁾ and is shown in Figure 1. Briefly, a focused electron beam (50 to 1500 eV) bombards a crystal surface onto which gases have been deposited using a molecular beam doser. The ion beams which desorb from the crystal by electron stimulated desorption (ESD) pass through a hemispherical grid and are accelerated to a micro-channel plate (MCP) assembly. The output signal from the MCP assembly is displayed visually on a fluorescent screen and photographed. By reversing the potential on the input of the MCP assembly, the elastic low energy electron diffraction (LEED) pattern from the sample can also be studied. Mass identification of ESD ions are made using a quadrupole mass spectrometer (QMS). In addition, the QMS may be used as a detector in thermal desorption studies from the adsorbed layers. The cleanliness of the sample crystal is verified using Auger Electron Spectroscopy.

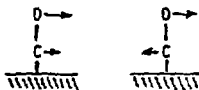
A schematic illustration of the ESDIAD process is shown at the bottom of Figure 1. A focused electron beam (e^-) bombards a single crystal containing a monolayer of adsorbed oxygen. The ESD O^+ ions are liberated in cones of emission, in specific directions related to the bonding geometry. The beams are intercepted by the MCP detector assembly, and displayed visually.

III. Results

A. CO on Ru(001)

Data previously reported using UPS (ultraviolet photoemission spectroscopy) and EELS (electron energy loss spectroscopy) have indicated that CO is terminally bonded to the Ru surface through the C atom, with the CO axis perpendicular to the surface. The ESDIAD results for CO confirm this orientation⁽³⁾: for all CO coverages in the temperature range 90 K to >350 K, the angular distributions of O^+ and CO^+ ESD ions are centered about the surface normal. The widths of the ion beams are

temperature dependent; for both O^+ and CO^+ , the corrected half widths at half maximum, α , of the ion cones are $\sim 14.5^\circ$ at 300 K, and $\sim 11^\circ$ at 90 K. This temperature dependence, coupled with a simple model calculation, indicates that the dominant factors contributing to the width of ESD ion beams are initial state effects, i.e., CO surface bending vibrations of the type



Thus, the data suggest that both the directions and widths of ESDIAD beams from adsorbed molecular species are determined largely by the structure and dynamics of the initial adsorbed state.

B. CO on Pd(210)

ESDIAD has been used to verify an unusual bonding configuration for CO on the (210) surface of fcc palladium⁽⁴⁾. In an infrared reflection-adsorption study⁽⁵⁾ of CO on Pd(210) and (100), the measured values of the C-O stretching frequency indicated that at low coverage, the CO was bridge-bonded to two Pd atoms via the C atom. The Pd(210) is a rather open surface, and top layer atoms with the nearest neighbor distance of 2.73 Å do not exist (cf. Fig. 2); the shortest distance between top layer atoms is 3.88 Å in the [001] direction. Bridge-bonding is not known to occur in transition metal carbonyls for metal-metal spacings greater than ~ 2.78 Å. On Pd(210), it therefore appears that bridge-bonding can only occur on sites of the kind which exist between atoms in the first and second atom layers, so that the axes of adsorbed CO molecules are expected to be inclined away from the normal by $\sim 18^\circ$, as shown for the type C site in Figure 2.

The ESDIAD data are consistent with the infrared results, and for CO coverages \leq less than 0.5 monolayers, two-fold symmetric ion desorption patterns dominated by emission in directions away from the normal are observed. In addition, the ESDIAD patterns provide specific information about the desorption sites. CO populates the two equivalent type C sites at $\theta < 0.5$, and type B sites at higher coverages. Furthermore, the ESDIAD results indicate that the surface bending vibrational amplitudes for the bridge-bonded CO are different in orthogonal directions, in agreement with recent calculations. At the saturation CO coverage ($\theta=1$) at 90K, at least a fraction of the adsorbed CO appears to be bonded with the molecular axis normal to the Pd(210) surface.

C. CO on W(110) and stepped surfaces vicinal to W(110).

The above results demonstrate that the ESDIAD method yields CO structures consistent with adsorbed molecular geometries deduced using other techniques. Based on these data, we have examined the role of surface steps in molecular adsorption in an ESDIAD study of CO on a multifaceted tungsten monocrystal. The questions to be answered are: how do the CO adsorption geometries compare on flat surfaces and on stepped surfaces, and are new structures seen on stepped surfaces?

The experiments were performed on a 7mm diam. tungsten crystal cut to expose 5 separate facets. It was used in a previous ESDIAD study of oxygen adsorption (6) and was similar to one used in studies of oxygen adsorption kinetics on stepped W surfaces (7). The central facet was oriented within 0.3° of the (110) plane, and the four surrounding facets were stepped surfaces of different step densities (6° and 10° off the (110) plane), and with step orientations parallel to [100] and [110] directions.

The ESDIAD patterns seen for a monolayer of CO adsorbed on this multifaceted sample at 273K are shown in Figure 3. The electron beam was scanned from facet to facet, and the patterns were photographed from the fluorescent screen. The central W(110) facet yields a single ESDIAD beam which desorbs perpendicular to the surface, giving a single spot in the center of the photograph. Each of the stepped surfaces also yields an ESD ion beam which desorbs perpendicular to the (110) terraces; the images of these normal beams appear in the center of the photos for each of the 4 outer facets in Figure 3. In addition, each stepped facet yields an extra ESD ion beam which desorbs in a down-step direction, along an axis perpendicular to the step edge. All beams consist of both O^+ and CO^+ , in approximately equal intensities. The polar angle between the normal and off-normal beams on the right and left facets is $\sim 40^\circ$.

We interpret these data as follows: At 273K, CO adsorbs in molecular form (the virgin state) along with some dissociated CO (the β states) (8). The ESD signal is due primarily to the molecular CO. Ultraviolet photoemission data demonstrate that the molecular virgin CO is bonded to tungsten through the carbon atom (9). The single normal beam seen in the ESDIAD pattern for CO on W(110) indicates that the molecular CO is bonded perpendicular to the W(110) facet. On each of the stepped surfaces, a fraction of the molecular CO is also bonded with the molecular axis perpendicular to the W(110) terraces. In addition, the observation of the down-step ion beams indicates that the CO molecules are tilted away from the normal to the terraces by $\sim 40^\circ$, and are probably adsorbed directly on the edges of the steps. A detailed account of the temperature dependence of CO bonding configurations on the multifaceted W crystal will be published elsewhere (10).

IV. Conclusions

The ESDIAD data for molecular CO adsorbed on single crystal surfaces of transition metals (Ru, Pd, W) are consistent with simple chemical models in which CO is bonded either perpendicular to the surface, or with the molecular axis inclined away from the normal. In cases where structural information using other techniques is available, the ESDIAD-determined structures provide a direct confirmation. In general, the ESDIAD patterns provide a straightforward visual determination of the molecular bonding geometry.

Finally, we note that the ESDIAD method is also useful for characterizing the structures of maximal valency oxide surfaces, both clean and with adsorbed layers. (11, 12)

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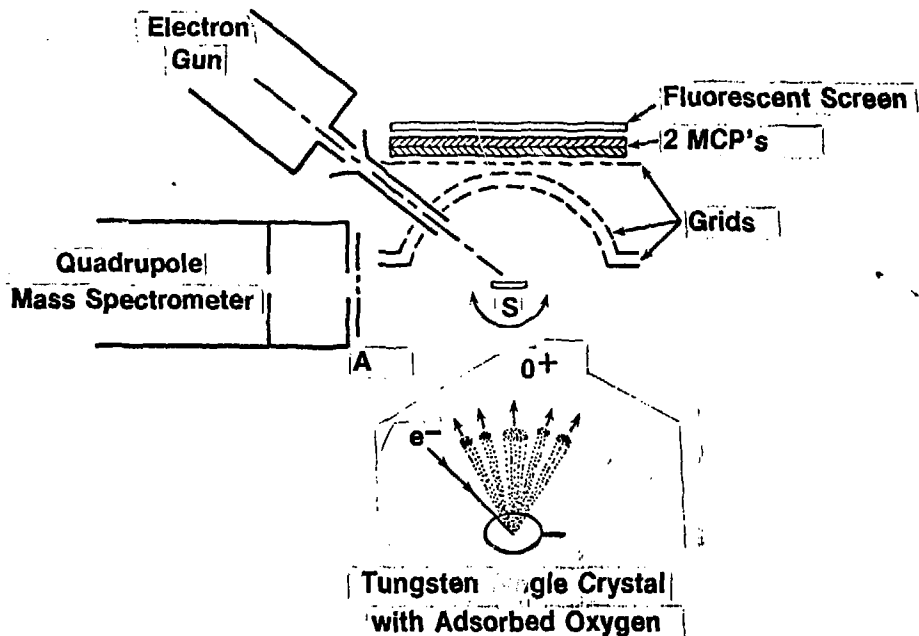
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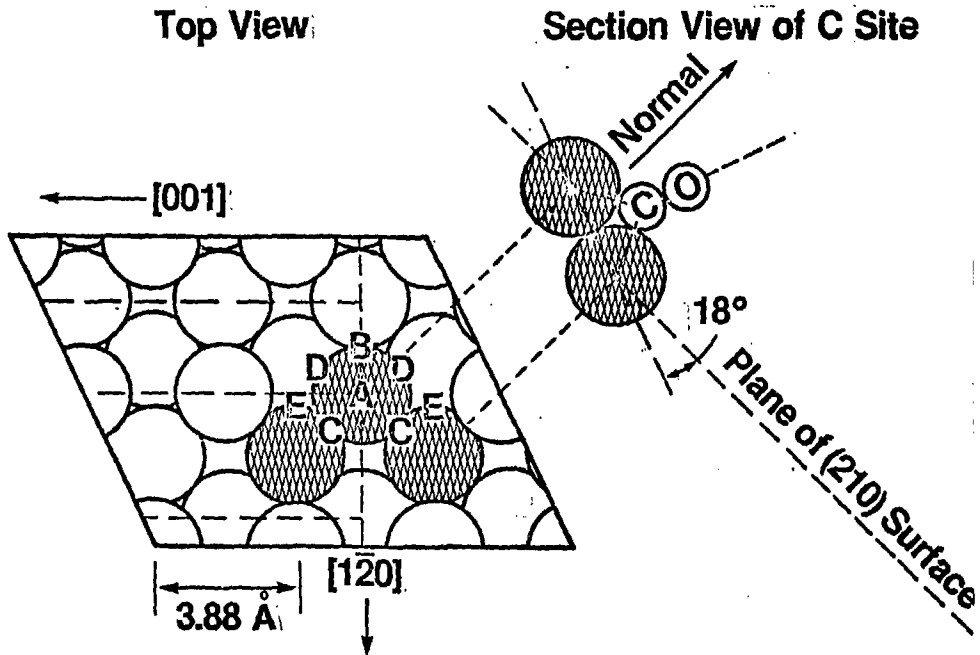
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Figure Captions

- Figure 1.** Schematic of ultrahigh vacuum ESDIAD apparatus. The sample S can be rotated about an axis normal to the plane of the drawing. ESD ions were mass analyzed in the quadrupole mass spectrometer, and ESDIAD patterns were displayed using the grid-microchannel plate (MCP) - fluorescent screen array. The radius of curvature of G_1 is 2.0 cm, and the active area of each MCP has a diameter of 4.0 cm. For most ESDIAD measurements, typical potentials were: $A=G_1 = G_2 = 0$ V, $G_3 = -70$ V, MCP entrance = -700 V, MCP midpoint = 0 V, MCP exit = +700 V, fluorescent screen = +3800 V. The lower drawing is a schematic of the ESDIAD process, in which O^+ ions are liberated in cones of emission during bombardment of the sample by a focused electron beam.
- Figure 2.** Model of Pd(210) surface with possible bonding sites for CO labeled. The section view illustrates how the CO molecule is "inclined" in the C sites (from Ref. 4, with permission).
- Figure 3.** ESDIAD patterns for desorption of O^+ and CO^+ ions from a monolayer of CO adsorbed at 273 K on the multifaceted W crystal described in the text. The central facet is oriented with its surface parallel to the (110) plane; the outer facets are inclined 6° and 10° away from the (110) plane in the directions indicated. The terrace widths on the 6° and 10° stepped surfaces are 13 Å and 22 Å, respectively. In all of the patterns above, the spot in the center of the picture corresponds to a beam of O^+ and CO^+ ions desorbing normal to the surface. The off-normal beams from each of the faceted surfaces provide evidence for "inclined" CO.

ESDIAD Apparatus





**ESDIAD Patterns for
Adsorption of CO on Multifaceted
W(110) Crystal at 273K.**

