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Mix of Molecular Adsorption Sites Detected for Disordered CO on Pt(111) by Diffuse Low-Energy Electron Diffraction

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Complete local-bonding geometries in a disordered molecular overlayer have been determined for the first time, together with the relative occupation of different coexisting adsorption sites. Diffuse-LEED intensities were measured with a new, highly sensitive, low-noise, digital-LEED detector, and calculated with an extension of the efficient beam-set-neglect theory. At one-third of a monolayer of carbon monoxide on Pt(111) at 160 K, $(88\pm5)\%$ of the molecules are found to occupy top sites and $(12\pm5)\%$ bridge sites, with bond lengths consistent with earlier results for ordered layers.

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In many cases adsorbates on ordered single-crystal substrates occupy one or more sites with distinct local geometries but without long-range order. Structure determination for these systems is a major challenge to low-energy electron diffraction (LEED). Fine-structure techniques such as surface extended x-ray-absorption fine structure, near-edge x-ray-absorption fine structure, and angle-resolved photoelectron emission fine structure also provide information on disordered adsorbates, but these techniques are limited to adsorbates chemically distinct from the substrate and normally require a synchrotron light source. The "diffuse-LEED" method extends the techniques of LEED structure determination developed for ordered overlayers to all types of "lattice-gas" disorder. No other technique can yield the complete detailed bonding geometry of disordered adsorbates.

Significant theoretical advances are needed to deal with the lack of periodicity, and superior experimental techniques are required to measure the diffuse intensities, which can be 2 or more orders of magnitude smaller than the intensities from the ordered substrate. This paper describes the first application of a low-noise digital-LEED system and an efficient new method for diffuse-LEED calculations to determine bonding geometries in a low-coverage disordered overlayer adsorbed on a single-crystal surface.

The only successful structure determination with diffuse-LEED intensities to date is the study by Heinz, and co-workers of disordered oxygen atoms on the W(100) surface.[1,2] These studies used conventional analog (video) LEED measurements in the experiments[3] and a relatively accurate but calculationally intensive "three-step" theory.[1,4] The three-step theory has also been extended to disordered steps[5] and vacancy defects.[6] We have for the first time applied an extension of the beam-set-neglect theory to a disordered system. This new approach is more efficient than the three-step theory, with a minimal loss of structural accuracy.[7,8] The three-step and beam-set-neglect theories were previously checked against each other.[8]

We chose carbon monoxide adsorbed in a disordered monolayer on the Pt(111) single-crystal surface for our studies. The adsorption behavior of CO on Pt(111) has been studied by both high-resolution electron-energy-loss spectroscopy (HREELS)[9] and infrared reflection-absorption spectroscopy[10] as well as conventional LEED,[11] but there still is no general agreement on the site occupancy with coverage or temperature. At low coverages ($\theta < 0.17$ ML, where 1 monolayer corresponds to 1 CO per Pt surface atom) at a temperature of 92 K, a single C-O vibrational frequency is observed at 2100 cm^{-1} in the HREEL spectra which is attributed to CO adsorption at a onefold-coordinated top site. As the coverage is increased, a new loss peak grows in at ~ 1850 cm^{-1}. This mode is assigned to CO bonded to two metal atoms in a twofold-coordinated bridge site.[9] However, according to the infrared reflection-absorption spectroscopy results of Hayden and Bradshaw,[10] the bridge sites are not occupied until the coverage is greater than 0.33 ML. They also observe an additional lower-frequency mode at ~ 1810 cm^{-1} which is attributed to a threefold hollow site.

In the coverage range $0.35 < \theta < 0.5$ and just below room temperature, CO orders into a $c(4\times2)$ arrangement on the surface. Ogletree, Van Hove, and Somorjai[11] have carried out a LEED structural analysis of this ordered overlayer at 0.5-ML coverage. The LEED structural results confirm the vibrational assignments of the two modes to top and bridge sites. Both CO molecules bond with their molecular axis perpendicular to the surface and the carbon end down with a C—O bond length of 1.15 Å. The Pt—C distances perpendicular to the surface are 1.85 and 1.55 Å for the top and bridge sites, respectively.

We observed no long-range order when the coverage was below 0.35 ML at a temperature of 160 K. Yet there remains weak diffuse scattering from the disordered overlayer and this is the focus of our investigation.

We have recently developed a fast, sensitive "digital" or electron-counting LEED apparatus. It uses hemispherical grids for energy selection, two microchannel plates as the amplification stage, and a wedge-and-strip position-sensitive detector to collect the electrons.[12] The new apparatus allows a reduction in beam current to less than 1 pA. This largely eliminates beam-stimulated desorption or decomposition in the overlayer during the course of the experiment, which is especially important for CO on Pt(111). Digital LEED has no significant background noise and is only limited by statistical noise with a signal-to-noise ratio determined by counting time.

By comparison, conventional LEED uses currents of $\sim 1\ \mu$A, and a fluorescent screen with a video camera for detection.[13] Such currents can cause beam damage to the sensitive CO overlayer on Pt(111).[11] Because of the limited dynamic range, the signal-to-noise ratio is about 80 for a typical video camera. Video detection can therefore only be used when the diffuse intensity is strong.

The surface used in this study was prepared by conventional techniques.[7,11] The sample temperature during data collection was $\sim$ 160 K and the CO coverage was maintained at about 0.3 ML. Normal incidence was used. The diffraction pattern within about 50° of the surface normal is projected onto the planar detector and is digitized on a 256×256 pixel grid. Each image contained a total of 10^6 counts and took between 50 and 90 s to collect at count rates well below the saturation level for our detector. Data were collected in energy ranges around 80 and 130 eV. Corresponding diffuse intensities were also measured for the clean surface, for a background subtraction process suggested by Ibach and Lehwald[14] and discussed below.

The experimental data were treated as follows: (1) correction for quantum efficiency of the microchannel plates, which varies with the angle of incidence on the first plate[15]; (2) correction for the radial distortion of the diffraction pattern due to projection onto a planar detector; (3) averaging onto the theoretical pixel grid, which also improves the signal-to-noise ratio; (4) removal of a region around each integral-order spot; (5) optional subtraction of clean-surface intensities; (6) evaluation of the "Y-function," which is essentially the derivative of the diffracted intensity with respect to the energy at constant parallel momentum transfer,[1,4] for comparison to the theory. Figure 1 shows the experimental data at 130 eV after treatment by steps 1 through 4.

A multiple-scattering theory of diffuse LEED should calculate the probability that an electron scatters at least once from a disordered adsorbate. In the three-step theory of Pendry and Saldin,[4] the first step propagates the incident electrons by any path until their first encounter with the adsorbate. The third step propagates the electrons from their last encounter with the adsorbate until the detector. The middle step involves only scattering-path segments that start at the disordered adsorbate and return to it, after scattering from substrate or adsorbate atoms.

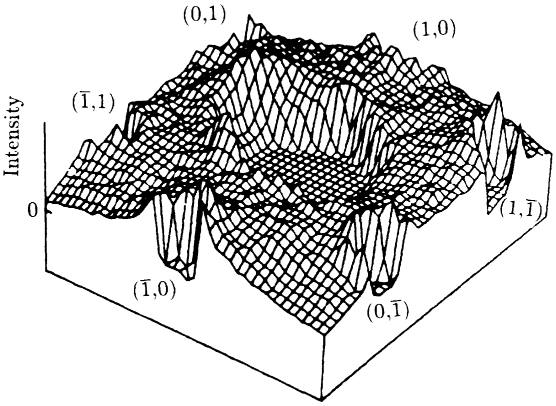

FIG. 1. Experimental intensities after treatment by steps 1 through 4 (see text). The energy is 130 eV and the data set was obtained at normal incidence. A rectangular region in reciprocal space is depicted, where the rectangle edges pass through the centers of substrate-induced spots. The depressions in the pattern are due to the center hole of the detector and a region removed from around each substrate diffraction spot.

The contribution from the middle step is at least of third order in terms of multiple scattering, and is therefore rather weak. At the same time, the computational effort needed to obtain it is relatively large, because it is done in the spherical-wave representation. In the present extension[7,8] of beam set neglect[16] this step is ignored, leaving the first and third steps, which can be efficiently combined and computed in the plane-wave representation. Multiple scattering within the molecule is included exactly.

Diffuse-LEED intensities due to adsorbates at different bonding sites can simply be added incoherently. This is an approximation which becomes exact in the low-coverage limit, but is already very good at the coverages common in adsorbed layers, such as for $\frac{1}{3}$ to $\frac{1}{2}$ monolayers. As a result, it is relatively easy to study simultaneous adsorption at different sites.

We treat the surface as composed of a separate overlayer with one bonding site at a time and individual substrate layers. For each layer, diffraction matrices are obtained as in conventional LEED,[17] but only for two sets of beams: the set of integral-order beams due to of the incident beam and a replica of this set which is shifted in such a way that the detected direction is included. No multiple scattering is allowed between adsorbates because of the low-coverage assumption. But multiple scattering is included within each adsorbate (e.g., within

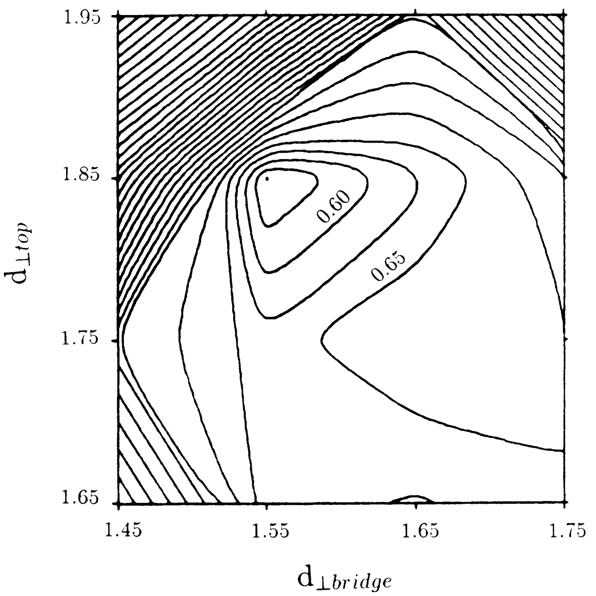

FIG. 2. Pendry R-factor contour plot as a function of the top- and bridge-site perpendicular Pt— C distances for site occupancies of 90% on top and 10% on bridge.

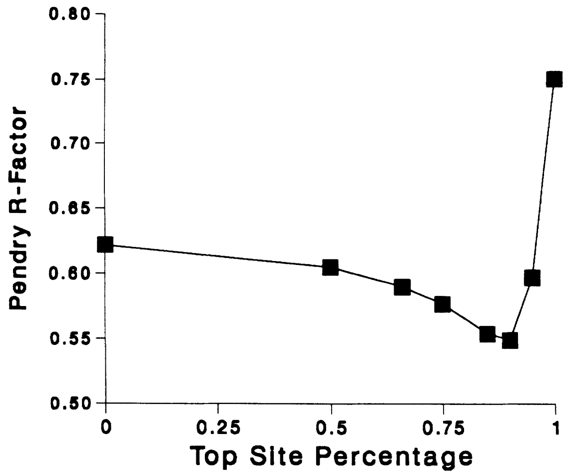

FIG. 3. Pendry R-factor vs top-site percentage occupation for optimum Pt—CO distances.

each CO) through matrix inversion.[17] Renormalized forward scattering is used to stack the layers.[17] The calculation is repeated for each detected direction.

The physical parameters in the calculations are the same as those chosen previously for the ordered system Pt(111)-$c(4\times2)$-2CO.[11] We follow Heinz, Saldin, and Pendry for the comparison between theory and experiment and apply the Pendry R factor to the Y function of the intensity rather than to the intensity itself.[1] This procedure removes long-range pair correlation effects from the data, but not local bonding information.

A number of structural possibilities were tested for our disordered CO layer on Pt(111). We made a few simplifying assumptions based on the solved Pt(111)-$c(4\times2)$-2CO structure.[11] The substrate was kept bulklike, while the CO molecules were taken to be intact and perpendicular to the surface, with a C—O bond length of 1.15 Å. The two metal-carbon interplanar spacings, one for the top site and another for the bridge site, were varied independently. Many mixtures of top- and bridge-site occupations, from 100% on top to 100% on bridge, were also tested.

In Figs. 2 and 3 we show the R factors for representative sets of adsorption structures, using the 130-eV data set. If we choose 90% of top sites and 10% of bridge sites (near the best mix we have found), we can explore the independent variations of the two metal-carbon spacings: This is shown in Fig. 2 with a two-dimensional contour plot. A clear minimum is found near the spacings $d_{\perp\text{top}}=1.85$ Å and $d_{\perp\text{bridge}}=1.55$ Å, the values found earlier in the ordered $c(4\times2)$ structure. The dependence on the site mix is illustrated in Fig. 3, with the assumption of the above interlayer spacings. A surprisingly sharp minimum is visible near 90% top-site and 10% bridge-site occupation. Interpolation yields a minimum at $(88\pm5)\%$ and $(12\pm5)\%$. Subtraction of the clean-surface diffuse intensity has no significant effect on this result.

With the 80-eV data we obtained the same optimal structural parameters. However, the site mix only gave a minimum after the clean-surface background subtraction. The location of this minimum depended on the way in which this background was scaled before subtraction. This effect is probably due to the relatively large clean-surface diffuse intensity at 80 eV.

Ibach and Lehwald have suggested that diffuse-LEED data can contain sizable HREELS contributions,[14] because the measured energy window in LEED (~1 eV in our case) includes quasielastic electrons having undergone phonon losses. They have shown that the HREELS contribution can at some energies and angles be larger than the proper elastic diffuse intensity of interest in diffuse LEED. As a partial remedy, they suggest subtracting the intensities due to the clean surface from those due to the overlayer-covered surface. This approach is supported by theoretical estimates of the phonon contribution to diffuse intensities.[18] Our results, which are the first practical test of this issue, are in agreement with the statements by both groups.[14,18]

The best R-factor value of about 0.55 obtained here is not as good as that found in the O/W(100) structure analysis, 0.13.[3] On the other hand, it is our experience that the R-factor values for ordered molecular adsorbates are rather higher than for ordered atomic adsorbates. The same could be expected in the disordered case.

In conclusion, the two bonding geometries which we obtain for disordered CO on Pt(111) agree to well within our error bars of ±0.1 Å with those obtained earlier for ordered CO on Pt(111). In addition, our 88%-12% mix of top and bridge sites is consistent with and favors the HREELS results[9] rather than the infrared reflection-absorption spectroscopy results,[10] which showed only one adsorption site at $\theta \lesssim 0.33$ ML.

We have shown that our new digital-LEED technique has sufficient sensitivity to easily measure the low intensities from disordered molecular adsorbates on an ordered surface. Conventional techniques would not have worked in this case. Using these diffuse intensities, we were able to obtain the complete local surface structure of a disordered molecular overlayer for the first time. It is not only possible to obtain local molecular bonding geometries, but also to determine the relative occupation of different adsorption sites.

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