Low-Energy K^+-Ion Scattering as a Probe of Adsorbate Ordering

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Overlayers of C, N, and O on Mo(001) have been studied by 500-eV K^+-ion scattering. The energy distributions and their dependence upon incident angle are found to depend strongly upon coverage and annealing temperature. Enhanced specular scattering is extremely sensitive to changes in adsorbate ordering observed by low-energy electron diffraction. The enhancement is explained by a novel scattering mechanism discovered by computer simulation.

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Low-energy ion scattering has been used to determine surface structure and particularly bonding geometry of first-layer adsorbate atoms. Although double or multiple scattering is occasionally seen, low-energy *inert*-gas ion scattering is dominated by single scattering from first-layer atoms. Trajectories with such short-range interaction with the surface give little information about surface ordering as probed by low-energy electron diffraction (LEED). Changes in ion-scattering data have been observed which occur with annealing and correlate with changes in LEED patterns, but they have been explained as a result of different bonding geometries.[1,2] For *alkali*-metal ions, multiple scattering may be very intense and in some cases can be differentiated by energy analysis. More complex trajectories or scattering mechanisms have been identified for these ions.[3-5] These trajectories involve long pathways through the surface region and therefore are sensitive to the crystalline ordering of the first few substrate layers.

We present here, for the first time, evidence that alkali-metal ion scattering is a sensitive probe of adsorbate *ordering*. The evidence is that coverage-dependent or thermally induced changes in adsorbate ordering, as identified by LEED, give rise to large changes in the specular ion-scattering intensity. We use this sensitivity to qualitatively compare the ordering in N, C, and O overlayers on an Mo(001) substrate over a range of about five lattice constants. It is important to probe overlayer ordering in this range to determine the nature of the interatomic forces governing adsorbate-adsorbate interactions. Furthermore, few techniques give quantitative information of ordering on this scale, and it is therefore of interest to explore the capabilities of ion scattering.

Atomic overlayers of N, C, and O on Mo(001), produced by dissociative adsorption of N_2, C_2H_4, and O_2, were examined by alkali-metal ion scattering, LEED, and Auger electron spectroscopy (AES). The experimental equipment used has been described earlier.[6] All O and C coverages were obtained from AES calibrated by CO adsorption.[7] All scattering experiments were conducted with use K^+ ions at an incident energy, E_i, of 500 eV. The glancing angle of incidence, ψ, is measured from the plane of the surface and the laboratory scattering angle, θ, is defined as the angle between the incident ion beam and the detection direction. The scattering plane was along the [100] azimuth ($\phi = [100]$).

Scattered K^+ energy distributions were measured at specular conditions ($\theta = 2\psi = 60°$) for various exposures to C_2H_4 at 550 K. The energy distribution for the clean surface[8] exhibits two maxima at $E/E_i = 0.66$ and 0.75, which can be roughly assigned to focused single and double scattering, respectively ($E/E_i = 0.655$ for a binary collision, $\theta = 60°$). The height of the low-energy peak increases with increasing coverage to a maximum near 0.5 monolayer (ML). The maximum height is about two times larger than that for the clean surface. The peak height then decreases monotonically at higher coverages up to about 0.8 ML of C, the highest coverage obtained. Similarly, the peak position shifts first to lower energies ($E/E_i = 0.63$) and then back to higher energies with increasing carbon coverage. K^+ energy distributions from N_2 adsorption were similar to those for carbon at lower coverages. For a saturated N overlayer, believed to occur at 0.5 ML,[9] the energy distribution was very similar to that for 0.5 ML carbon coverage. However, oxygen adsorption gave quite different results, exhibiting little or no shift in the low-energy peak position and a continuous decrease in peak height with increasing oxygen coverage.[10]

Observation of a shift in peak position and of intensity enhancement near 0.5 ML in the K^+ energy distribution is strong evidence that a new scattering mechanism prevails when either C or N (but not O) adatoms are on the surface. The dependence of the scattering upon both glancing and azimuthal angle of incidence provides further information regarding the enhancement mechanism. The variation of the low-energy peak height with ψ for $\theta = 60°$ is shown in Fig. 1 for the clean surface and two different carbon coverages. The most striking feature is a very intense and narrow peak (full width at half maximum $\approx 3°$) at $\psi = 30°$, which occurs only near a coverage of 0.5 ML. An angular distribution measured for $\theta = 65°$ gave the peak position at $\psi = 32°$ to 33° indicating that this feature is associated with specular scattering rather than a particular crystallographic direction. The intensity also depends strongly upon azimuthal angle, peaking sharply at the [100] azimuth (full width at half maximum $\sim 8°$). The angular distribution obtained for a saturated overylayer of N was nearly identical to that measured for 0.5 ML of C. Exposure to oxygen at 400 K sufficient to yield 0.5 ML of O adatoms gave only a small peak at $\psi = 30°$ ($\theta = 60°$) which disappeared upon annealing with no loss of oxygen.

The peak in the ψ dependence is quite sensitive to adsorbate ordering, which may be changed by annealing at different temperatures. The ratio of the intensity at $\psi = 30°$ to that at 24° was used as a relative measure of the intensity of the peak. A ratio was used to reduce errors due to ion-beam current fluctuations which could not be measured accurately during scattering. The value of this ratio after annealing is shown in Fig. 2 for carbon and oxygen overlayers. The adsorptions described were carried out on a clean annealed surface near 375 K followed by 60-s anneals at successively higher temperatures. Following each anneal, the crystal was cooled to below 450 K and the ratio measured. Therefore, variations in the ratio reflect thermally induced irreversible changes. Ethylene adsorption yielded a strong variation in the ratio as a function of temperature. Similar annealing of a 0.5 ML oxygen overlayer displayed only a gradual decrease in this ratio compared to the carbon overlayer.

With use of a similar annealing program, the 0.5 ML carbon surface was monitored by LEED and AES. A direct correlation was observed between the measured ion-scattering intensity ratio and changes in the LEED pattern. Ethylene adsorption at 375 K resulted in a $p(1\times1)$ which was streaked in $(1,\bar{1})$ and $(1,1)$ directions. Hydrogen desorption (as determined with a quadrupole mass filter) and formation of a sharp $c(2\times2)$ LEED pattern resulted from annealing to 550 K. Annealing to 750 K

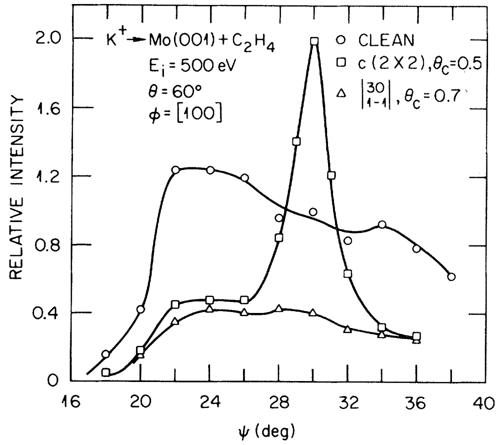

FIG. 1. The dependence of the single-scattering peak height is shown as a function of angle of incidence, ψ, for three different surfaces specified by carbon coverages and observed LEED pattern. The curves for each coverage are scaled relative to each other within an accuracy of $\sim 30\%$.

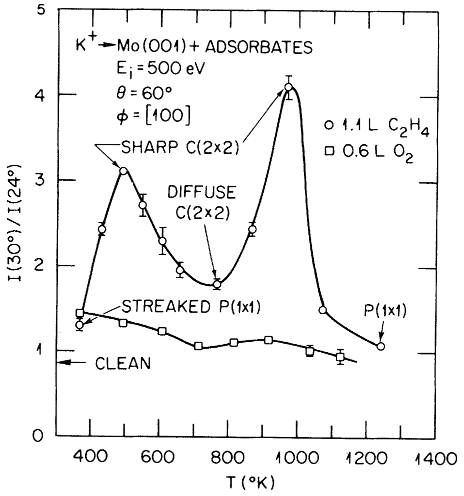

FIG. 2. The ratio of single-scattering peak height at $\psi = 30°$ to that at 24° is given as a function of annealing temperature for near 0.5 ML coverages of O and C. The ratio characteristic of a clean surface is also shown.

resulted in a blurring of half-order spots, but annealing to 970 K produced a sharp $c(2\times2)$ once again. No change in C coverage was detected up to this temperature. Heating to 1250 K resulted in a loss of surface carbon and disappearance of the half-order spots. On this basis, it was concluded that the scattering mechanism responsible for the sharp peaking in the ψ distribution is associated with the occurrence of an intense $c(2\times2)$ LEED pattern. A $c(2\times2)$ LEED pattern also occurs for a saturated N overlayer, but was never seen for the 0.5 ML oxygen overlayer, in agreement with other studies.[11]

Previous analysis of the azimuthal dependence of computed and experimental K^+ energy distributions led to the conclusion that carbon and oxygen adatoms are located on fourfold hollows.[7] Scattering along the [100] azimuth of a clean surface is dominated by an enhancement in intensity due to focused single and double scattering from *second*-layer Mo atoms.[8] The presence of 1.0 ML of adatoms in fourfold sites blocks this focused scattering, leaving only single and double scattering from first-layer [100] chains.[8]

Computer simulations with the code MARLOWE[12] have been performed for 0.5 ML of oxygen or carbon adatoms located in fourfold sites in a $c(2\times2)$ arrangement on an unreconstructed surface. In contrast to a blocking of all focused second-layer scattering, the scattering (for either adsorbate) is dominated by the mechanism illustrated in Fig. 3. "Single" scattering occurs from the second-layer Mo atoms, which lie directly under an adatom, but the trajectory is strongly modified by additional scattering from the overlying adatom and from the neighboring adatoms located $\pm 2a_0$ away along the [100] direction (a_0 is the Mo lattice constant). Small-angle deflections by the adatoms and also by first-layer Mo atoms lead to focusing (in two perpendicular directions) and therefore to high intensity. The focusing is blocked if either of the nearest-neighbor sites at $\pm 1a_0$ are occupied. The second-layer scattering intensity is therefore affected by the occupancy of five adjacent adsorbate sites (at $\pm 2a_0$, $\pm 1a_0$, and overlying) along the [100] direction. The maximum intensity occurs if the overlying site and the sites at $\pm 2a_0$ are occupied and nearest-neighbor sites at $\pm 1a_0$ are vacant.

Although quantitative agreement between simulated and experimental energy distributions has not yet been obtained, scattering via this mechanism provides a qualitative explanation of the trends observed for N_2 and C_2H_4 adsorption. The simulations explain the intensity enhancement in single scattering observed near 0.5 ML for C and N overlayers and the coverage dependence of the intensity. They also explain (but overestimate) the coverage-dependent shift in energy of the single-scattering peak and the strong specular peaking in the angular dependence (Fig. 1).

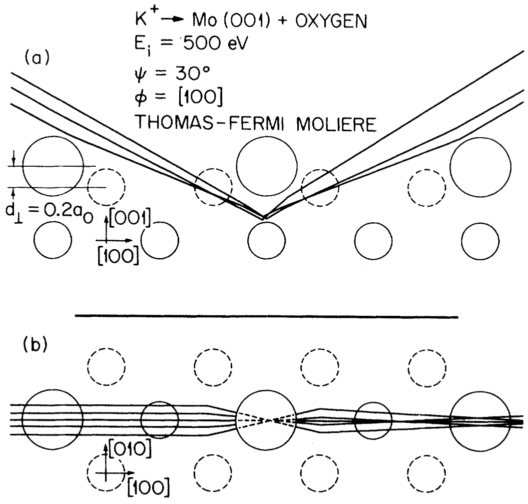

FIG. 3. The focusing effect of adatoms (large circles) and of first-layer Mo atoms (dashed circles) on the approximately single scattering from second-layer Mo atoms (small circles) is shown. In (a) the scattering is viewed along the [010] direction, while in (b) the view is down the surface normal, i.e., in the [00$\bar{1}$] direction. The calculated trajectories in (a) differ from those in (b) in that the trajectories in (a) all lie in the [010] plane containing the adatoms. All trajectories result in a total scattering angle of 60 ± 5°. Mo and O atoms are shown with radii equal to the impact parameters for a laboratory scattering angle of 60° and 10°, respectively.

The sensitivity of scattering by this mechanism to the configuration of adatoms and vacancies over five successive fourfold adsorption sites implies that it is sensitive to overlayer ordering over this range. A relationship can be derived between the measured single-scattering intensity and the frequency of occurrence of various configurations of adatoms distributed in ensembles of five lattice sites.[13] The experimetal results for specular scattering (Fig. 1) show that a perfect $c(2\times2)$ (every second site occupied) yields the highest intensity, a nearly full monolayer (at least four of five successive sites occupied) gives the lowest, while a clean surface (all five sites vacant) is intermediate. Computer simulation allows interpolation of the intensity for other possible combinations of vacancies and adatoms on the five sites. It is then possible to predict the intensity for various coverages and adlayer structures [e.g., $p(2\times1)$ or $p(1\times2)$, island formation, random adsorption, or an imperfectly ordered $c(2\times2)$ characterized by an ordering parameter] by summing up contributions for the various configurations present. The predicted coverage-dependent intensity can then be compared with experiment.[13]

The difference between O and C (or N) can thus be explained. The growth in specular intensity with increasing coverage for C or N corresponds to an increase in the coverage of islands of $c(2\times2)$ configuration. Above 0.5 ML the coverage of $c(2\times2)$ islands decreases along with ion scattering intensity. The perfection or extent of $c(2\times2)$ islands is also affected by different annealing conditions as monitored by ion scattering (Fig. 2). Oxygen does not tend to form the configuration in which every other site is occupied, but instead (depending upon adsorption or annealing temperature) either clusters into islands or randomly fills adsorption sites.

In summary, for the first time it has been shown that alkali-metal ion scattering is sensitive to adsorbate ordering for C, N, and O overlayers on Mo(001). We believe that this result is general, and the extension to other systems is a subject for future experimental and computer simulation studies.

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