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Precise molecular orientation determination for adsorbates using x-ray photoelectron diffraction: Methoxy (CH_3O) and CO on Cu(110)

K. C. Prince, E. Holub-Krappe, and K. Horn
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-1000 Berlin 33, West Germany

D. P. Woodruff
Physics Department, University of Warwick,
Coventry CV4 7AL, England

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Using photoelectron diffraction from the 1*s* states of carbon and oxygen with x-ray excitation, we show that while CO stands perpendicular to a Cu(110) surface, the catalytic intermediate, methoxy, is tilted. The most probable interpretation of the data involves a mixture of two species, one tilted by 18° ±3° in the $[1\bar{1}0]$ azimuth, and the other tilted by 40° ±5° in the [001] azimuth. The origin of this unusual tilt is discussed.

Determinations of the orientation of molecular species adsorbed on surfaces provide considerable information on the nature of the molecule-surface bond and the likely adsorption site. Selection rules in vibrational spectroscopy allow positive identification of this orientation only in the case of highly symmetric adsorption states,[1] while methods based on the optical matrix elements of photoemission and photoabsorption[2,3] typically depend on the square of the cosine of orientational angles, and so generally have poor precision ($\gtrsim \pm 10°$). Much stronger directional effects are possible in high-kinetic-energy photoelectron diffraction,[4] and here we show that this method can be used to establish the orientation of a catalytic intermediate species methoxy (CH_3O) and of adsorbed CO on Cu(110); the methoxy species is positively identified as tilted on the surface providing a unique case of tilting on a high symmetry surface at low coverage.

The high angular resolution of photoelectron diffraction in a molecular species at high electron energies (~ 1 keV) arises from the fact that at these energies elastic scattering involves small phase shifts and predominantly forward scattering, so that there is always constructive interference along the molecular axis (zero-order diffraction), while a short photoelectron wavelength relative to interatomic distances along the axis ensures that the first diffraction minimum is displaced in angle by only $\sim 10°$.[4,5] Figure 1 shows this schematically. For adsorbed CO species *A* is carbon; for methoxy species *A* is oxygen. Because of the weak scattering of hydrogen atoms, methoxy behaves essentially like inverted CO with a longer bond length for the purposes of the photoelectron diffraction. In addition to the zero-order diffraction, which leads to an emission lobe from one species directed towards the other end of the molecule, weaker higher-order diffraction peaks can occur at higher angles, but have not yet been positively identified.

Initial experiments were conducted with CO adsorbed on Cu(110), as this adsorbate [on Ni(100)] was used successfully in the first such molecular orientational study,[4,5] and so provides a model system for which there is considerable prior information. Figure 2 shows the results of this experiment in the form of the ratio of the C 1*s* and O 1*s* photoemission intensities as a function of polar emission angle (0° being normal emission). The experiments were conducted in a VG Scientific Escalab spectrometer in which the angle between the incident light and electron emission is fixed (at 50°) and the takeoff angle relative to the surface is varied by rotating the sample. Ratioing the two photoemission signals removes most of the instrumental effects involved in this rotation. The incident x rays were from an aluminium target, so the kinetic energies of the two photoemission peaks were about 1200 and 955 eV, respectively. Experiments were performed at saturation coverage (~ 0.6 monolayer[6,7]) of CO at a sample temperature of 80 K. Long-

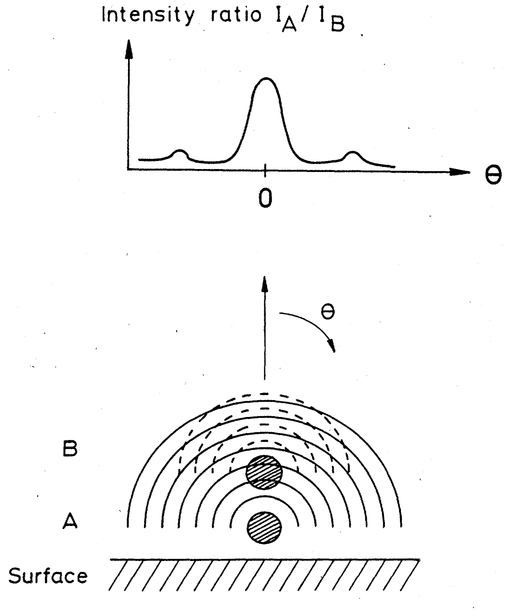

FIG. 1. Schematic diagram of photoelectron diffraction involving interference between the direct emitted waves (solid curves) and scattered waves (dashed curves), for emission from the species *A* nearest the surface. The intensity of emission from species *A* in ratio to that from species *B* shows a zero-order diffraction peak along the interatomic axis.

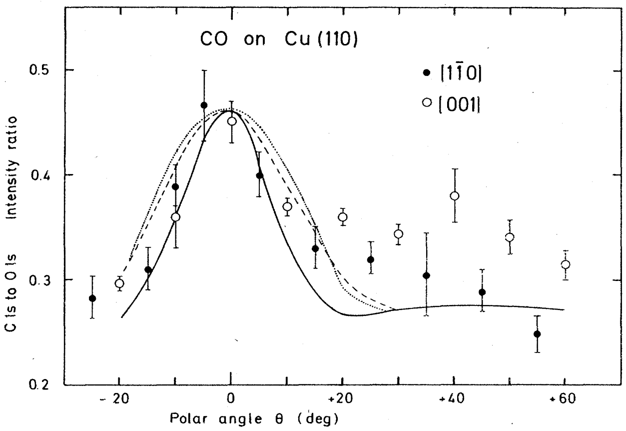

FIG. 2. Experimental photoemitted intensity ratio in the two principal azimuths for CO adsorption on Cu(110), compared with theoretical curves for CO perpendicular to the surface with no vibrations (solid curve), CO perpendicular with a vibrational amplitude of 10° (dashed curve), and CO tilted by 10° but not vibrating (dotted curve). The anisotropies have been reduced by factors of 3.0, 2.0, and 2.1, respectively.

range order is poor at this coverage.[6,7] Further experimental (and computational) details will be given elsewhere.[8] The carbon-to-oxygen photoemission ratio shows a clear peak along the surface normal, consistent with a CO species perpendicular to the surface (with the carbon end bonded to the metal). At these energies a single scattering plane-wave calculation has proved adequate to model all aspects of the experiment except the degree of anisotropy (i.e., the degree of intensity modulation), which is consistently overestimated,[4] and the results of such a calculation in which the anisotropy has been supressed to optimize the match are shown in Fig. 2. Also included are the results of similar calculations showing the effects of frustrated rotational vibrations of the adsorbed molecule and azimuthally averaged tilt. The sharpness of the zero-order diffraction peak in the experiments seems to exclude tilts greater than 10° or average vibrational amplitudes more than ~ 10°. These tight limits stem from a narrower peak [full-width at half maximum (FWHM) is 18°] than that of earlier data on the Ni(100)-CO system; this may be related to the low temperature of our experiment which may more than compensate for the weaker bonding of CO to copper relative to nickel. Although an average orientation normal to the surface is widely established for chemisorbed CO, tilting (by 25°) is seen in the highest coverage ordered structure on Pt(110) (Ref. 9) and is inferred for other fcc (110) surfaces on which the same *plgl* space-group symmetry structure is seen.[10] Clearly, our results show that CO on Cu(110), which does not show the long-range ordered structure, does not display the same molecular tilt. Thus, tilting of CO on Pt(110) probably arises from mutual repulsion at the high associated coverage (one monolayer).

The second system we have studied is the catalytic intermediate methoxy, CH_3O, which is formed by the reaction of methanol with preadsorbed oxygen. Methanol was adsorbed on the oxygen-dosed surface at 80 K and then heated to room temperature to remove excess methanol and the other reaction product, water $(2CH_3OH + O_a \rightarrow 2CH_3O_a + H_2O)$.[11] Photoemission measurements were then conducted at 80 K. Considerable care was taken not to use excessive predoses of oxygen which leads to an adlayer comprising CH_3O and chemisorbed oxygen, thus disturbing the C/O stoichiometry and influencing the angular dependences of the photoemission from the oxygen. Saturation of stable stoichiometric layers occured at 0.25 monolayer of CH_3O as determined by photoemission yields, consistent with two molecular species per unit mesh associated with the streaked (4×2) diffraction pattern seen at this coverage.

As the methoxy is known to bond to the surface through the oxygen atom (e.g., Ref. 12), the photoelectron diffraction data of Fig. 3 for both [1$\bar{1}$0] and [001] collection azimuths are shown as the ratio of oxygen-to-carbon 1*s* photoemission signals. This ratio shows a *minimum* along the surface normal in both azimuths, clearly indicating a tilted species. Moreover, the significant difference between the data taken in the two azimuths shows that this tilt is not azimuthally isotropic.

By analogy with the CO results, the most obvious interpretation of the data of Fig. 3 is that the peaks in the O/C photoemission intensities at around 17° in the [1$\bar{1}$0] azimuth and around 40° in the [001] azimuth correspond to the O-C molecular axis direction in these directions. The results of calculations based on two different tilted species, tilted by 18° and 40° on the [1$\bar{1}$0] and [001] azimuths, respectively, are shown as solid curves in Fig. 2. These calculations are based on vibrational (frustrated rotation) amplitudes of 5°, and have been suppressed in polar anisotropy by a factor of 3.0, but the relative average intensities of the two azimuths are as calculated. Note that because of the narrow width of the zero-order lobes in this technique, the data *cannot* be interpreted in terms of a single tilt in an intermediate azimuth which subtends the angles of about 18° and 40° in the two principal azimuths; such a tilted species would not lead to substantial zero-order peaks in either azimuth. What we cannot exclude on this basis, however, is the possibility that there are tilted species in *all* azimuths, but those in intermediate azimuths have intermediate tilts.

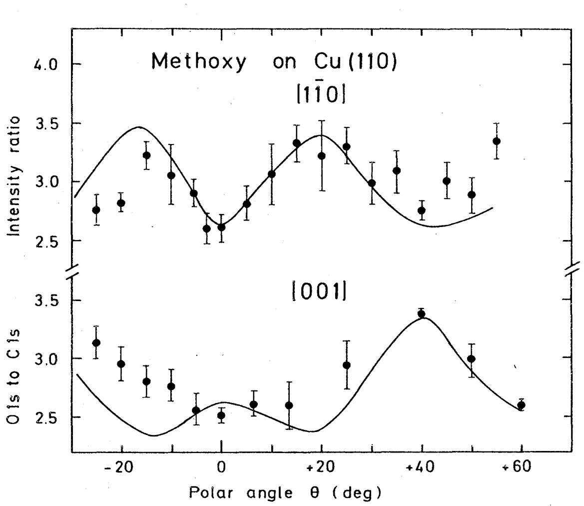

FIG. 3. Experimental photoemitted intensity ratio in the two principal azimuths for methoxy adsorbed on Cu(110). The full curves correspond to the model described in the text, interpreting two tilted species with tilts of 18° in the [1$\bar{1}$0] azimuth and 40° in the [001] azimuth.

Results of calculations on such a model show qualitative features very similar to the full lines of Fig. 3. The main quantitative difference for the results of calculations for this model is that the anisotropies are somewhat weaker, due to the inclusion of the extra azimuthal orientations. This does mean that significantly lower polar anisotropy suppression factors compared to those used for CO must be used, providing a weak counter to this model.

One rather different possibility which we considered is that the methoxy species are tilted *only* in the $[1\bar{1}0]$ azimuths, and that while the peaks in the $[1\bar{1}0]$ azimuths do correspond to the main zero-order diffraction lobes along the molecular axis, the peaks in the [001] azimuth are first-order diffraction peaks from these tilted species. Although this model allows qualitative fitting of the data, the quantitative fits are poor; particularly, the anisotropy introduced by the first-order features in [001] is much weaker than those of the zero-order features in $[1\bar{1}0]$.

The balance of evidence therefore favors a model with two different methoxy species tilted by different angles in the two principal azimuths. Tilting in both azimuths is supported by very recent near-edge x-ray-absorption fine structure measurements,[13] although the data from this technique have been interpreted as consistent with a tilt of 35°, but with random azimuthal orientation.

In summary, therefore, we find the photoelectron diffraction data are compatible with two methoxy species tilted by 18 ± 3° in the $[1\bar{1}0]$ azimuth and by 40 ± 5° in the [001] azimuth. The quoted errors are rather generous as at both 15° and 21° tilts; theoretical calculations are much less like the experiment; these conservative estimates attempt to take some account of the possible defects introduced by our use of a plane-wave approximation.

The origin of the tilting in the methoxy species is unclear. Previous examples of tilted linear molecular species have generally been associated with adsorption at step sites[14] or pseudostep sites on a relatively low symmetry surface,[15] or, in the case of the *plgl* CO structures on some fcc (110) surfaces,[9,10] appear to be associated with steric effects at high packing density. In the present case the packing density is not high (0.25 monolayers), although the presence of a long-range ordered structure does suggest short-range adsorbate-adsorbate repulsion. Of course, in the bonding of methoxy to hydrogen (i.e., in methanol) there is a large "tilt" angle, but our small tilt angles of 18° and 40° cannot easily be reconciled with this feature of the molecular hybridization. The most reasonable suggestion would therefore seem to be adsorption at some relatively low symmetry sites, possibly just off the long bridge site occupied by chemisorbed oxygen on this surface.[16] We note that there are two types of threefold coordinated sites available on the (110) surface, which would give rise to tilts in the [001] and $[1\bar{1}0]$ azimuths. A determination of the local registry site would help to clarify the possibly origins of these unusual tilted species.

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