Structure of an Unusual Tilted State of CO on Fe(001) from X-Ray Photoelectron Diffraction

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The highly tilted α_3 state of CO on Fe(001) has been studied using combined polar and azimuthal x-ray photoelectron diffraction. A more accurate structural picture is derived, with the molecule being tilted at an angle of 55° ± 2° with respect to the surface normal along ⟨100⟩ azimuths and probably occupying fourfold hollows. An estimate is also made of the vertical C distance above the Fe surface. The utility of combined θ/ϕ x-ray photoelectron diffraction measurements for such unusual adsorbate structures is demonstrated.

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The existence of an "abnormal" or "unusual" type of surface bonding state of CO that involves a tilted or lying-down geometry and a considerably lowered CO stretch frequency has been discussed recently for several different transition-metal surfaces including Fe(001),[1-3] Cr(110),[4,5] and Mo(001).[6] This state is of considerable interest because it may represent a precursor to dissociation with a weakened CO bond due to additional electronic interactions with the metal substrate.[1] However, little is known about the exact geometric structure of the CO for any of these cases. For the case of α_3 CO on Fe(001) that we will consider here, electron-energy-loss (EELS) measurements show a very low CO stretch frequency of 1210 cm^{-1}.[1] Near-edge x-ray-absorption fine-structure (NEXAFS) measurements on this state have been used to deduce an elongation of the CO bond by 0.07 ± 0.02 Å from a shift in the position of the σ resonance.[3] From the relative lack of a change in the absolute and relative intensities of the π and σ resonances with a change in radiation polarization, an estimated tilt angle with respect to normal of 45° ± 10° has been deduced.[3] However, the precision of this determination is not high, and it also was not possible in this study to specify whether there is any preferred azimuthal orientation of the tilt. Measurements of electron-stimulated-desorption ion angular distributions (ESDIAD) are consistent with such a high tilt in showing a very weak signal for O^+, but no bond angle information could be derived, probably due to the strong image forces which deflect and attenuate the desorbing ions.[2]

We have thus applied x-ray photoelectron diffraction (XPD) for the first time to this intriguing adsorption state in an attempt to better understand its structure, combining both polar and azimuthal scans of core-level intensity in a way that has not been attempted before for such adsorbate structure studies. This method makes use of the dominance of highly-peaked forward scattering in core-level emission at energies of greater than approximately 500 eV.[7-10] As these peaks have typical FWHM values of only about 20°, the precision of bond tilt determinations should be considerably higher than in measurements such as NEXAFS where the dependence on variable polarization goes as a more slowly varying $\cos^2$ function.[3,8,10] Also, a simple single scattering cluster (SSC) model has been shown in prior studies to model very well this kind of intramolecular scattering,[7-10] although useful structural conclusions can often be drawn directly from the position of the through-bond forward scattering without any comparison to theory.[7-10] For the case at hand of a diatomic adsorbate, high kinetic energy, and high takeoff angles relative to the surface, multiple-scattering effects should be completely negligible.

The instrumentation utilized is described in detail elsewhere[10] and consists of an x-ray photoemission spectroscopy (XPS) system equipped with a two-axis specimen manipulator capable of automated scanning of either the polar or azimuthal angles of electron emission with high precision (approximately ±0.2°-0.3°). LEED characterization is also possible. The Fe(001) surface was cleaned and prepared using standard procedures.[11,12] After cleaning, less than 0.1 monolayer (ML) of combined C and O impurity was present on the surface. CO was adsorbed on the clean surface at ambient temperature up to a total exposure of 15 Langmuirs (10^{-7} Torr × 150 sec). Prior work on this system using a combination of XPS, temperature-programmed desorption (TPD), and EELS[1,11,12] indicates that this should lead to a very high fraction of the CO being present in the desired α_3 state. From a comparison of our C 1s and O 1s core spectra with those published previously,[11] we estimate this fraction to be greater than 80%. The C 1s and O 1s intensities yield coverages after adsorption of 0.33 ± 0.05 ML for C and 0.52 ± 0.05 ML for O; the latter number is in excellent agreement with recent work for the O coverage based upon XPS and TPD data[12] and the former suggests the presence of atomic oxygen from CO dissociation that blocks some CO adsorption sites and thus reduces the C coverage. Precise calibration of the polar (θ) and azimuthal (ϕ) scales was made by using strong, narrow XPD peaks in Fe $2p_{3/2}$ emission from the clean surface;[10] the accuracy of this calibration is ±0.5°. Polar scans of both C 1s and O 1s intensities were carried out in two different azimuths above the (001) surface: [100] and [110]; the θ scale is measured with respect to the surface. Polar data will be reported as the normalized ratio $I(\mathrm{C}\ 1s)/I(\mathrm{O}\ 1s)$ in order to approximately divide out the θ-dependent instrument response function;[7,10,13] in any case the $I(\mathrm{O}\ 1s)$ profile was smooth and structureless so that this division does not affect any of our conclusions. Azimuthal C 1s scans were also carried out over a range of 200° for selected polar angles. All data shown represent sums of seven or more separate scans with cleaning and reabsorption in between. All features discussed here were reproducible in all of the individual scans.

In Fig. 1(a), we show normalized polar scans of the C 1s intensity along the two types of azimuths studied. The difference between the two curves is striking: There is a clear peak in the curve for the [100] azimuth, centered at $\theta = 35° \pm 2°$ and with a FWHM of 25°, whereas the curve for the [110]-type azimuth is flat and featureless, with only one possible weak peak at $\theta \approx 17°$. These same differences are seen in the raw data for the C 1s intensities before normalization; as noted above, the normalized O 1s curves for the two cases were smooth featureless curves with no indication of forward scattering peaks. These results alone thus immediately suggest that the CO is bound with the C atom down, that the peak at $\theta = 35°$ is due to forward scattering from O, that the molecular tilt is approximately 55° with respect to the surface normal, and that the tilt is preferentially along ⟨100⟩ azimuths. The overall forward scattering effect for the [100] azimuth at 35° as judged by the quantity [I(maximum) minus the average of the minima at the edges of the peak]/I (maximum) is 16% and thus is comparable to that observed for the case of $c(2\times2)$-CO/Ni(001), which exhibits bonding normal to the surface.[7(a),(b)]

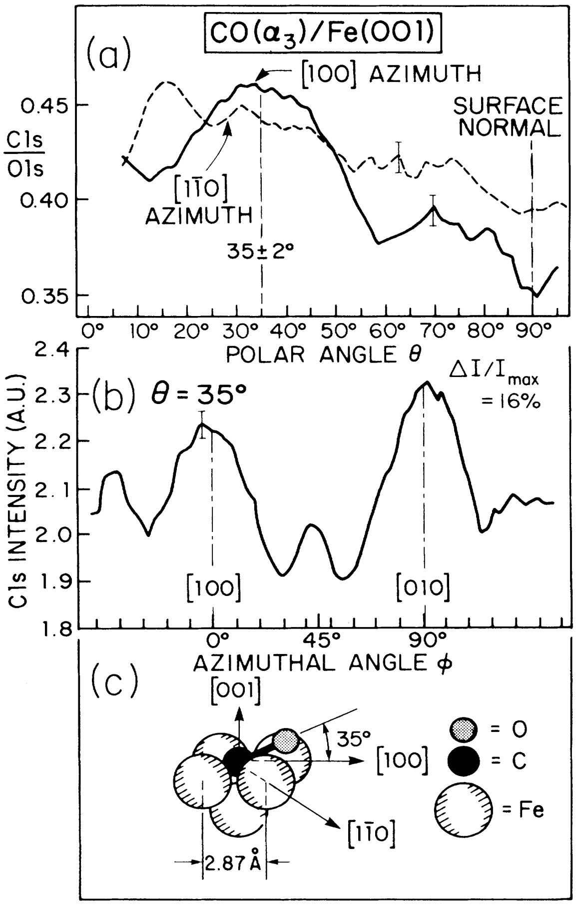

FIG. 1. (a) Experimental polar scans of the C 1s/O 1s intensity ratio for the α_3 state of CO on Fe(001). Curves are shown for two azimuths: [100] (solid curve) and [110] (dashed curve). (b) Experimental azimuthal scan of the C 1s intensity for the α_3 state of CO at a polar angle of 35° with respect to the surface. (c) The bonding geometry deduced from these data.

In order to further quantify these conclusions, we have also performed 200° azimuthal scans of the C 1s intensity at a polar angle of 35° chosen so that the emission directions will pass directly through the strong [100] peak in Fig. 1(a). These results are shown in Fig. 1(b). (Normalization with O 1s is not necessary in this case because θ is constant.) This curve shows its strongest features at precisely those ⟨100⟩ azimuthal positions that are consistent with the peak in Fig. 1(a). These azimuthal results thus lead to the overall conclusion that a high proportion of α_3 CO is tilted in the ⟨100⟩ azimuths, as shown schematically in Fig. 1(c) for the most likely bonding position in a fourfold hollow site.[1-3] Note also the small, but reproducible, peak at $\phi = 45°$ or along ⟨110⟩ azimuths; this we will discuss further below.

A more quantitative analysis of these results can also be made by using the results of straightforward SSC calculations incorporating spherical-wave scattering.[7,10,14] Such calculations have been carried out for the C 1s intensities so as to model the normalized curve in Fig. 1(a) and the absolute curve in Fig. 1(b); the O 1s intensity is expected and found to have very little modulation due to the absence of any strong forward scatterers between it and the detector. The well-known dominance of forward scattering at the high energy of 1202 eV involved for C 1s also should lead to a very small effective cluster:[7] We have thus used only the tilted CO molecule plus five Fe atoms so as to include the four nearest neighbors and the next-nearest neighbor in an assumed fourfold hollow site, as shown in Fig. 1(c). [The choice of the very open fourfold hollow site is based on its being the most likely site for a highly tilted molecular adsorption, as well as on prior experimental work based upon XPS, LEED, TPD, and ultraviolet photoemission spectroscopy,[1,3,11,12] and prior theoretical calculations for *vertical-standing* CO on Fe(001).[15]] Adding more Fe atoms to this cluster was indeed verified to produce very little change in any of the calculated curves. Reference calculations with *no* Fe atoms have also been carried out to determine precisely what the Fe near neighbors contribute. For simplicity, the C atom is assumed to be centered in the fourfold hollow. The experimental data also suggest that we choose a tilt of 35° with respect to the surface. In some calculations, the vertical position z of the C with respect to the first Fe surface plane has been varied. Four equally probable ⟨100⟩ directions of tilt have been assumed, with intensities from each of these site or domain types being added to yield the final polar or azimuthal curves. The presence of these four site types will reduce the peak-to-background ratios in both polar and azimuthal scans due to the addition of relatively flat backgrounds of intensity from the nonforward scattering sites. Vibrational effects have been included via Debye-Waller factors only, although a more exact treatment including possible wagging or frustrated rotational motion would be expected to additionally broaden features and reduce experimental peak-to-background ratios.[7(b)] Shifting the tilt angle from 35° in the calculations was found to move the peak position in polar scans by exactly the amount of the angle shift; thus we can with certainty use 35° in the remainder of our calculations. Other theoretical results are summarized in Figs. 2 and 3.

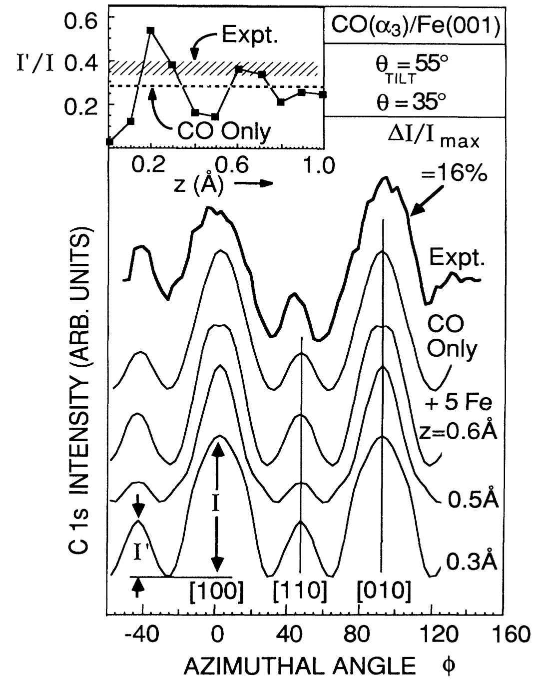

FIG. 2. Comparison of the experimental C 1s azimuthal scan for the α_3 state of CO with theoretical calculations assuming the molecule to be tilted at 35° with respect to the surface along ⟨100⟩ directions and to be in four equally populated site types or domains. In the top curve, no Fe scatterers are included. In the lower curves, five Fe scatterers are added, as shown in Fig. 1(c). The C is taken to be centered in the fourfold hollow, and its vertical distance from the Fe surface plane has been varied from 0.0 to 1.0 Å. Inset: The relative intensity I'/I of the weaker higher-order feature along ⟨100⟩ directions as a function of z.

In Fig. 2, our experimental azimuthal data are compared to calculated curves for an isolated CO molecule (for which z has no meaning) and for a cluster consisting of CO plus five Fe atoms [as shown in Fig. 1(c)]. For the latter, z values of 0.0 (in-plane) to 1.0 Å that span the range of reasonable C-Fe distances in carbonyls[16] have been investigated, although only the curves for 0.3, 0.5, and 0.6 Å are shown. The simple forward scattering peaks along [100] and [010] are well predicted for all of the curves shown, and thus they do not provide any further information concerning vertical position. The weaker peak along [110] by contrast is found to oscillate with z, and its relative intensity I'/I is plotted as a function of z in the inset of the figure. The accuracy of our experimental I'/I values from these first results is only about +0.2, although it could be improved by doing longer full 360° scans and fourfold averaging into one quadrant.[10] Comparing experiment and theory thus suggests two z ranges of about 0.22 ± 0.10 and 0.63 ± 0.10 Å. An analysis of the diffraction calculations shows that the maxima of this weaker peak are the result of successive constructive interferences between a first-order scattering event (that is, with one wavelength difference between direct and scattered waves) from oxygen[7] and second- or third-order event (that is, with two or three wavelengths difference between direct and scattered waves) from the Fe atom in the [110] corner of the hollow. Such simply interpretable features in XPD can thus be directly related to geometry, and this is the first time that they have been used for this. A more accurate analysis of such data should also include the effects of vibration,[7] but these would be expected to more rapidly attenuate the higher-order [110] peak due to the larger scattering angles involved.[10] Thus, our calculated I'/I values should if anything be too low, perhaps favoring the higher values near $z = 0.2$ Å. The z values between 0.2 and 0.6 Å that are suggested by this analysis are also found to yield C-Fe nearest-neighbor distances of 1.64-2.04 Å that are very close to the distances found in CO-Fe complexes.[16]

The experimental anisotropy $\Delta I/I_{\max}$ is about 16%-18%, as indicated in Fig. 2. The corresponding values for the theoretical curves of Fig. 2 are about a factor of 2 larger. However, such discrepancies have been noted previously,[7] and could be due to vibrational effects and/or C atoms present in other than the tilted α_3 state.

In Fig. 3, we compare experimental and theoretical curves for the polar variation of C 1s intensity, using for the solid curves a tilt angle of 35° and the two best-fit vertical heights of 0.3 and 0.6 Å. There is excellent agreement here as well, even as to the existence of the weaker feature due to first-order scattering from O that occurs rather near the normal at $\theta \approx 70°$. Adding in the five Fe atoms for the two lower curves is found to change only the fine structure of the principle peak; vibrational

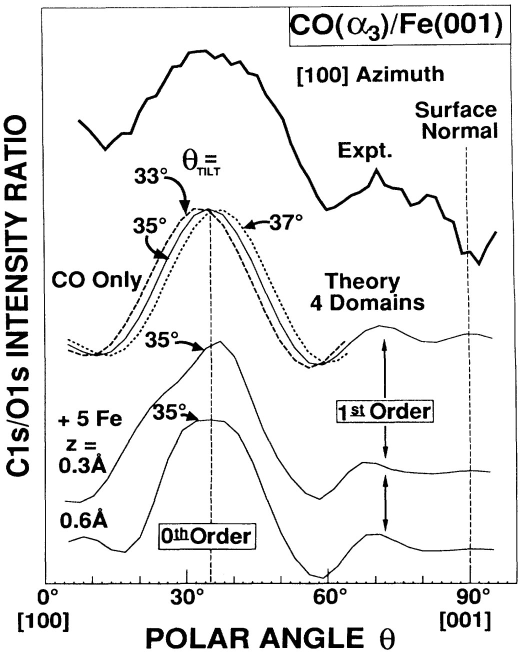

FIG. 3. The experimental polar scan of the C 1s/O 1s ratio in a [110]-type azimuth is compared to theoretical calculations (solid curves) using the same assumptions as in Fig. 2. Such curves (with $\theta_{\text{tilt}}=35°$) are shown for no Fe scatterers and for five Fe scatterers with vertical distances of 0.3 and 0.6 Å as indicated from a comparison of Fig. 2 to experiment. Also shown are the predicted forward scattering peaks for tilt angles of 33° (long-dashed curve) and 37° (short-dashed curve).

effects would be expected to smear out these small changes and to cause all three solid curves to be in equal agreement with experiment.[7(b)] To illustrate the known sensitivity of the main peak to the tilt angle,[7,10] we also show curves for $\theta_{\text{tilt}}=33°$ (long-dashed curve) and $\theta_{\text{tilt}}=37°$ (short-dashed curve); it is clear that the peak position directly follows the tilt angle.

Thus, a fully self-consistent picture of the structure of this unusual bonding state of CO emerges from this study of the system by XPD: CO is tilted at 55° ± 2° with respect to the normal with a preferred orientation in ⟨100⟩ azimuths. This structure information further supports the idea of a fourfold hollow bonding site[1,3,11,12] and for this site, our data suggest that the C-Fe vertical distance is in one of the two ranges of 0.2 ± 0.1 and 0.6 ± 0.1 Å. This tilt angle is thus fully consistent with the less-precise NEXAFS determination of 45° ± 10° by Moon *et al.*,[3] and, as they have conjectured from the insensitivity of the normalized π resonance intensity to changes in polarization direction, it is also extremely close to the magic angle of 54.7°. Although we do not determine here the precise position of the C atom relative to the fourfold hollow including possible offsets from center, such a determination should be possible from similar analyses of additional polar and azimuthal scans of C 1s and O 1s,[17] particularly if the azimuthal scans are made over a full 360°. Overall, the application of such combined polar and azimuthal XPD measurements to highly tilted bonding geometries such as CO on other transition metal surfaces[4-6] is highly promising.

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