

A NEXAFS study of the orientation of CO on Cu(110)

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 S297

(<http://iopscience.iop.org/0953-8984/3/S/047>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 11:25

Please note that [terms and conditions apply](#).

A NEXAFS study of the orientation of CO on Cu(110)

R Davis†, R Lindsay†, K G Purcell†, G Thornton†, A W Robinson‡,
T P Morrison†, M Bowker§, P D A Pudney§ and M Surman||

† Interdisciplinary Research Centre in Surface Science and Chemistry Department,
Manchester University, Manchester M13 9PL, UK

‡ Interdisciplinary Research Centre in Surface Science, Liverpool University, Liver-
pool L69 3BX, UK

§ Interdisciplinary Research Centre in Surface Science and Leverhulme Centre,
Liverpool University, Liverpool L69 3BX, UK

|| SERC Daresbury Laboratory, Warrington WA4 4AD, UK

Received 25 April 1991

Abstract. We have determined the molecular orientation of CO adsorbed on the Cu(110) surface at 150 K as being within 20° of the surface normal, using x-ray absorption spectroscopy in the near-edge region. Measurements were carried out in the [011] azimuth, using Auger yield detection. We discuss the difficulties of using NEXAFS spectroscopy whilst performing Auger yield measurements with a fixed electron energy analyser.

1. Introduction

Near-edge x-ray absorption spectroscopy (NEXAFS) of adsorbed molecules has been used extensively in recent years to determine molecular orientation on surfaces [1-3]. This is achieved by measuring the polarization dependence of intra-molecular resonances. The resonances arise from excitation of core-level electrons into unfilled molecular orbitals. The CO molecule is particularly suitable for study with NEXAFS as it exhibits two clear resonances, one corresponding to excitation into the unfilled $2\pi^*$ antibonding orbital and the other into a so-called σ^* shape resonance.

Adsorption of CO on the (110) face of FCC metals is particularly interesting, as it is known that CO often forms well-ordered overlayer structures with the CO molecular axis tilted away from the surface normal [4, 5]. This is usually manifested in a 'missing row' low-energy electron diffraction (LEED) pattern, indicative of glide plane symmetry in the adlayer. No such pattern has been reported for CO on Cu(110). In addition, a photoelectron diffraction study [6] has indicated that the C-O axis is oriented to within 10° of the surface normal.

In this article we report a NEXAFS study of the adsorption of CO on Cu(110) at 150 K at the C K-edge. The results confirm the geometry determined by photoelectron diffraction.

2. Experimental details

NEXAFS experiments employed the high-energy spherical grating monochromator ($200 \leq h\nu \leq 1000$ eV) on beam line 1.1 at the SRS, Daresbury Laboratory [7]. The

experimental chamber was equipped with LEED and an HA100 100 mm mean-radius hemispherical analyser with multichannel detection (VSW Scientific Instruments Ltd). The entrance lens of the HA100 electron energy analyser was fixed at 40° to the incoming radiation in the horizontal plane. C K-edge NEXAFS spectra were recorded using Auger detection, monitoring the yield of C KVV electrons at a kinetic energy of 267.5 eV. The analyser resolution was ~ 1 eV full width at half-maximum (FWHM) and the monochromator resolution was ~ 0.28 eV (FWHM) in the photon energy range studied.

The Cu(110) sample was cleaned by cycles of Ar^+ bombardment and annealing to 800 K until a well-ordered (1×1) LEED pattern was observed. Photoemission and C K-edge NEXAFS were used to monitor surface cleanliness. The CO adlayer was formed by exposing the clean sample to 60 L (1 Langmuir = 1.32 mbar s) of CO at 150 K. A series of NEXAFS spectra was recorded over a range of incidence angles (5° – 90°). Here we adopt the NEXAFS convention [1] and define the incidence angle as the angle between the incoming photon beam and the surface plane. The experiment was repeated by first desorbing the adlayer by heating to room temperature and then re-adsorbing CO at 150 K. While at room temperature the C K-edge NEXAFS was checked to ensure the presence of a clean surface.

3. Results and discussion

Normalized C K-edge NEXAFS spectra recorded at the two extreme incidence angles (5° , 90°) in the [011] azimuth are shown in figure 1. As expected, two resonances are observed. A relatively sharp resonance arising from C $1s \rightarrow 2\pi^*$ excitation [1] lies at lower photon energy, having maximum intensity when the x-ray *E*-vector lies parallel to the surface. The second, broad resonance is the σ^* shape resonance [1], which has the opposite polarization dependence.

The data were normalized by first dividing by the clean surface spectrum to remove the monochromator structure caused by adsorbed carbon on the optical elements of the beam line. Secondly, the x-ray edge-jump was set to 1 for all spectra to remove contributions caused by changing emission angle, beam decay and effective spot size on the sample. Only the polarization dependence of the π^* resonance was analysed. The π^* intensity was determined from the area above a linear background fitted under the π^* peak. Figure 2 shows how the π^* intensity varies with incidence angle.

The relationship between the NEXAFS π^* intensity of CO, the angle of incidence, degree of polarization and CO tilt angle has been derived by McConville *et al* [8]. We use this relationship to consider a nominal fit to the data which assumes a degree of linear polarization of 80% [9] and a 0° tilt of the CO molecule with respect to the surface normal. Three groups of points deviate from this fit, falling at incidence angles of 70° , 90° and between 40° and 50° . We believe these anomalies arise from the use of a fixed electron energy analyser. We ascribe two groups to the presence of valence band (VB) structure in the NEXAFS close to the π^* resonance, as seen in figure 3. This arises from the VB sweeping through the C KVV Auger energy window just below the C K-edge [8]. In angle-resolved photoemission spectra of Cu(100)/CO the 1π , 5σ and 4σ levels fall ~ 9 and ~ 11 eV below the VB, respectively [10]. These features will appear at higher photon energies than the VB in the NEXAFS spectra and close to the position of the π^* resonance. Two of the groups of anomalous points (labelled a and c in figure 2) occur at special photoemission angles; i.e. at normal incidence (90°) and

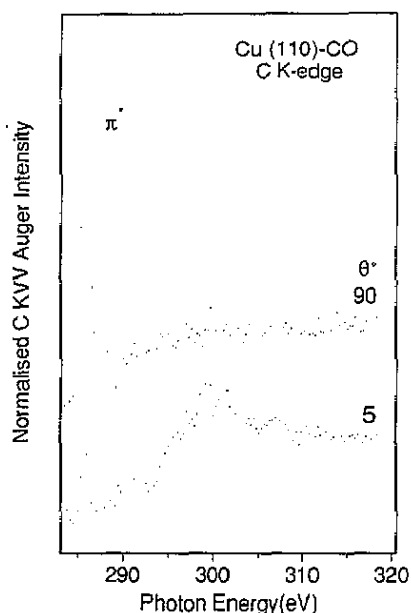


Figure 1. Background subtracted and edge-step-normalized C K-edge NEXAFS spectra of Cu(110)/CO at 150 K at an angle of incidence, θ , of 5° and 90° in the [011] azimuth. Spectra were recorded by monitoring the C KVV Auger yield. The π^* resonance is indicated.

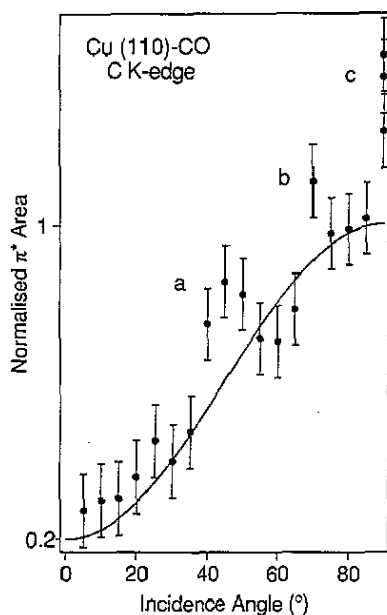


Figure 2. The edge-step-normalized area of the C K-edge π^* resonance from Cu(110)/CO. The full curve is the function $1 - P \cos^2 \theta$, with P , the degree of polarization set to 0.8. This is the variation of intensity expected for CO lying normal to the surface [8]. The points a, b and c are discussed in the text.

around normal emission (40° , 50°). Because of photoemission selection rules which

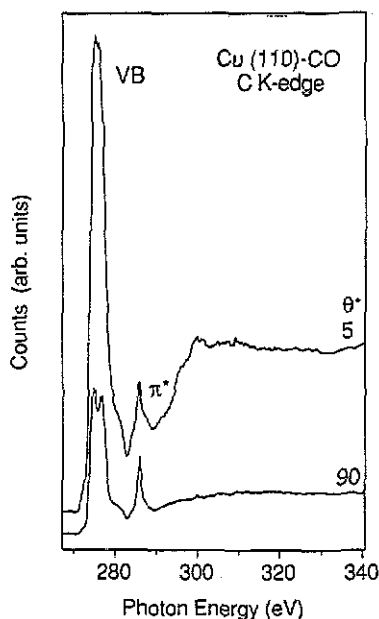


Figure 3. The spectra in figure 1 before background subtraction and normalization. The positions of the valence band photoemission peak and the π^* resonance are indicated.

rely on the polarization and emission angles [11], we expect anomalous behaviour at both of these angles. Since the π^* resonance occurs 9.7 eV above the centre of the VB (figure 3), it straddles the positions of the $1\pi/5\sigma$ and 4σ photoemission features. Anomalous behaviour of these photoemission peaks will affect the derived π^* intensity, entering the data analysis in background-subtraction and edge-step normalization. We therefore feel justified in ignoring data points associated with the anomalous group of points labelled a and c in figure 2. Point b in figure 2 is ignored on different grounds. This point corresponds to an angle of incidence of 70° , which coincides with the angle for specular reflection of the incidence radiation directly into the electron energy analyser.

In figure 4 we show three fits to the remaining data points. The full curve shows the best fit, which corresponds to a polarization of 80% and the CO molecular axis parallel to the surface normal, i.e. zero tilt angle. This agrees well with the predicted degree of linear polarization of the x-ray beam at the C K-edge [9] and the CO orientation determined by photoelectron diffraction [6]. The other two fits to the data in figure 4 suggest that the polarization cannot be worse than 70% and that CO cannot be tilted by more than 20° if the polarization is 80%.

4. Summary

The C K-edge NEXAFS study of the π^* resonance has shown that CO stands upright on the Cu(110) surface to within 20° . The degree of linear polarization of x-rays from the monochromator employed has yet to be determined accurately, giving rise to large uncertainty in the derived tilt angle. This uncertainty will be reduced when the appropriate measurements have been made. In addition, we have observed anomalous

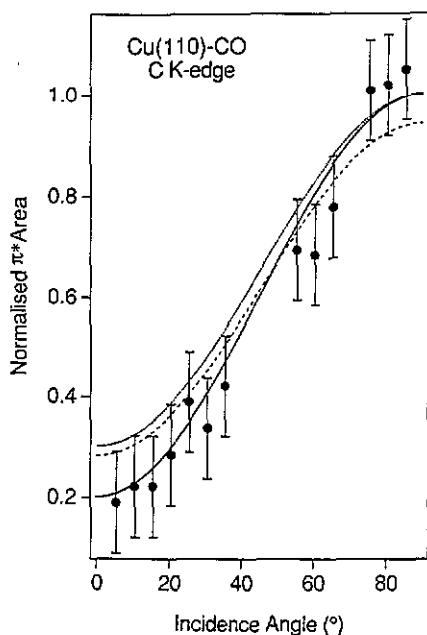


Figure 4. The edge-step-normalized area of the C K-edge π^* resonance from Cu(110)/CO. The full curve corresponds to the polarization dependence expected for 80% polarization of the x-ray beam and the CO axis parallel to [110]. The dotted curve corresponds to the polarization dependence expected for this molecular orientation with 70% polarization of the x-ray beam. The broken curve is for 80% polarization and a CO tilt angle of 20° towards [011].

effects in the NEXAFS which we ascribe to the use of a fixed electron energy analyser in Auger yield measurements. These are associated with the polarization dependence of CO-derived valence band photoemission features.

Acknowledgments

We are grateful to Nick Palmer of VSW for his technical assistance. This work was funded by the Science and Engineering Research Council, including the award of studentships to RD and RL. Additional support was provided by VSW Scientific Instruments Ltd and Harwell Laboratory.

References

- [1] Stöhr J and Jaeger R 1982 *Phys. Rev. B* **26** 4111
- [2] Stöhr J and Outka D A 1987 *J. Vac. Sci. Technol. A* **5** 919
- [3] Stöhr J and Outka D A 1987 *Phys. Rev. B* **36** 7891
- [4] Behm R J, Ertl G and Penka V 1985 *Surf. Sci.* **160** 387
- [5] Comrie C M and Lambert R M 1976 *J. Chem. Soc. Faraday Trans. I* **72** 1659
- [6] Holub-Krappe E, Prince K C, Horn K and Woodruff D P 1986 *Surf. Sci.* **173** 176
- [7] Surman M, Cragg-Hine I, Singh J, Bowler B, Padmore H A, Norman D, Davis R, Purcell K G, Thornton G, Johnson A L, Atrei A, Walter W K and King D A 1991 *Rev. Sci. Instrum.* submitted

- [8] McConville C F, Woodruff D P, Prince K C, Paolucci G, Chab V, Surman M and Bradshaw A M 1986 *Surf. Sci.* **166** 221
- [9] Padmore H A private communication
- [10] Allyn C L, Gustafsson T and Plummer E W 1977 *Solid State Commun.* **24** 531
- [11] Plummer E W and Eberhardt W 1982 *Advances in Chemical Physics XLIX* (New York: Wiley) p 533