

Normal Versus Anomalous Formate-Copper Surface Bonding and the Application of X-Ray-Absorption Fine-Structure Studies to Molecular Adsorption

Recent applications^{1,2} of the techniques of near-edge and surface-extended x-ray absorption fine structure (NEXAFS and SEXAFS) to the structure of formate (HCOO) on Cu(100) and Cu(110) have led to remarkably different results. On Cu(110)^{2,3} formate was found atop top-layer Cu atoms with the O atoms in near-bridge sites with a *true* Cu-O nearest-neighbor distance of about 1.90 Å, while on Cu(100),^{1,4} the site was bridging with O atoms in near-fourfold hollows and a *true* Cu-O nearest-neighbor distance of about 2.30 Å. This latter bond length is ~ 0.3 Å longer than other known Cu-O nearest-neighbor bond lengths and has been cited as an example of an anomalous surface bond caused by the special geometry of the chosen adsorption site.^{1,4,5}

The low adsorption-site symmetry of the O atoms in both cases, brought about by the mismatch of the molecular O-O distance and the substrate Cu-Cu distance, means that at least two unresolved Cu-O near-neighbor distances contribute to the "first shell" of the Fourier transform of the SEXAFS so that the true Cu-O nearest-neighbor distance must be deduced from *some average distance* in the usual method of analysis. We have therefore reanalyzed the data from both experiments using a multishell simulation technique, described in detail elsewhere,⁶ which takes proper account of these contributions. The conclusion of this analysis is that while the site proposed for Cu(110) gives the best description of these data within the quoted errors, the site proposed for Cu(100) gives unacceptable results. In particular, the fit to the 15°- (grazing-) incidence data [Fig. 1(a)] is poor although the fit to the 90°- (normal-) incidence data is fair. Both the result of Fig. 1(a) and reanalysis by the Fourier-transform method indicate that the (100) data can only be reconciled with the originally proposed structure by use of an energy zero which differs by some 15 eV for the data collected at the two different incidence angles. This is clearly unphysical. By contrast we find we can fit both experimental spectra using an alternative atop site on Cu(100) with O again in off-fourfold hollow sites but a *true* Cu-O nearest-neighbor distance of 1.99 Å [Fig. 1(b)]. The different polarization direction dependence of the component Cu—O bonds to the near-neighbor peak in the Fourier transform for this structure accounts for the different periodicity of the SEXAFS measured at the two different incidence angles.

We therefore conclude that (a) the adsorption sites

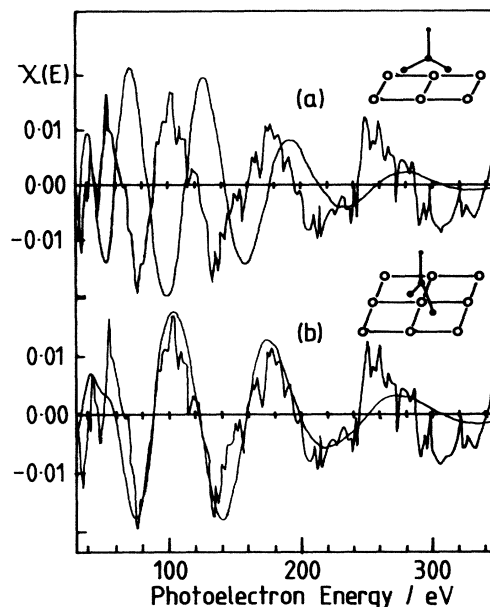


FIG. 1. Comparison of experimental (Refs. 1 and 4) O K-edge SEXAFS collected at 15° grazing incidence for formate on Cu(100) with simulations for (a) the originally proposed structure, and (b) the new structure proposed here.

and true Cu-O nearest-neighbor bond lengths for formate on Cu(100) and Cu(110) are similar, and the Cu(100)-formate bond is not anomalous; (b) multishell simulations have a valuable role in the analysis of SEXAFS data from molecular adsorbates which will commonly have atoms in low-symmetry adsorption sites.

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Received 4 June 1986

PACS numbers: 61.10.Lx, 68.35.Bs, 78.70.Dm

¹J. Stöhr, D. Outka, R. J. Madix, and U. Döbler, Phys. Rev. Lett. **54**, 1256 (1985).

²A. Puschmann, J. Haase, M. D. Crapper, C. E. Riley, and D. P. Woodruff, Phys. Rev. Lett. **54**, 2250 (1985).

³M. D. Crapper, C. E. Riley, D. P. Woodruff, A. Puschmann, and J. Haase, Surf. Sci. **171**, 1 (1986).

⁴D. A. Outka, R. J. Madix, and J. Stöhr, Surf. Sci. **164**, 235 (1985).

⁵T. J. Upton, J. Chem. Phys. **83**, 5084 (1985).

⁶M. D. Crapper, C. E. Riley, and D. P. Woodruff, to be published.