

Structure Determination of the Formate Intermediate on Cu(110) by Use of X-Ray-Absorption Fine-Structure Measurements

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A unique assignment of both the orientation and the adsorption site of formate (HCOO) on Cu(110) has been made by analysis of near-edge and extended x-ray-absorption fine structure. The species lies with its molecular plane perpendicular to the surface, aligned along the $[1\bar{1}0]$ directions, and on top of the copper atoms of the outermost layer; the oxygen atoms almost bridge two copper atoms with an average Cu-O bond length of $1.98 \pm 0.07 \text{ \AA}$, essentially identical to that in bulk copper formate.

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While electronic, vibrational, and desorption spectroscopies have identified a number of catalytic intermediate species on well-characterized surfaces,¹ the determination of the local-bonding geometry (the "active site") has so far proved too complex a problem for most structural techniques. Here we show that with use of the combination of analysis of near-edge x-ray-absorption fine structure (NEXAFS)^{2,3} and of surface extended x-ray-absorption fine structure (SEXAFS),⁴ both the local coordination and orientation of one such species, formate (HCOO) on Cu(110), can be determined. The low symmetry of this surface increases the site selectivity and power of the optical selection rules of the techniques to allow an unambiguous structural assignment. An important conclusion of our study is that the Cu-O bond length in this system is essentially identical to that of copper formate in contrast to the conclusions of a recent study of formate adsorbed on the higher-symmetry Cu(100) surface.⁵

The analysis proceeds in two steps. Firstly, the dependence of the NEXAFS intensities on the direction of the polarization vector of the incident radiation is used to determine the orientation of the formate species on the surface. The NEXAFS from the totally symmetric oxygen $1s$ core level is dominated by two absorption peaks,³ one involving transitions to antibonding bound states of the species having π symmetry (antisymmetric relative to the molecular plane) and the second being associated with a multiple-scattering (shape) resonance in the CO band which is usually regarded as totally symmetric (σ symmetry) relative to this CO bond axis. Optical selection rules require that with the polarization vector perpendicular to the molecular plane, the π resonance is strongest, while the σ resonance vanishes; by contrast, if the polarization vector lies parallel to the molecular plane,

the π resonance vanishes. For the twofold symmetric Cu(110) surface these rules allow both the tilt and the azimuthal orientation of the species to be determined. Secondly, the periodicity of the SEXAFS oscillations⁴ is used to determine the nearest-neighbor Cu-O bond length, while the dependence of the SEXAFS amplitude on both polar and azimuthal angles of the polarization vector allows the directions of these neighbors to be determined.

Experiments were conducted by use of normal ultrahigh-vacuum and surface-science methods of sample preparation and characterization and with use of light from the SX 700 plane-grating grazing-incidence monochromator⁶ installed on the BESSY storage ring in West Berlin. Surface EXAFS measurements were made with a partial-yield detector set to exclude electrons having energies less than about 400 eV,⁷ while NEXAFS studies relied on measurements of the oxygen KLL Auger electron emission detected in a cylindrical mirror analyzer. The formate species was formed on the surface by exposing the surface at room temperature to formic acid.^{8,9}

A selection of NEXAFS difference spectra taken with the polarization vector along $[1\bar{1}0]$ and $[001]$ azimuths, and at normal ($\theta = 90^\circ$) and grazing ($\theta = 20^\circ$) incidence are shown in Fig. 1. The strong π resonance seen at normal emission with the polarization vector along $[001]$, and the weak π resonance seen on changing the azimuth by 90° at both incidence angles clearly indicate that the molecular plane lies perpendicular to the surface and lies parallel to $[1\bar{1}0]$. This vertical orientation for the formate has been deduced from vibrational spectroscopy on both Cu(110)⁹ and Cu(100)¹⁰ and from NEXAFS on Cu(100)³; in addition, studies¹¹ on formate on another fcc (110) surface (of Pt) using the angular dependence of electron energy-loss spectroscopy have indicated that the

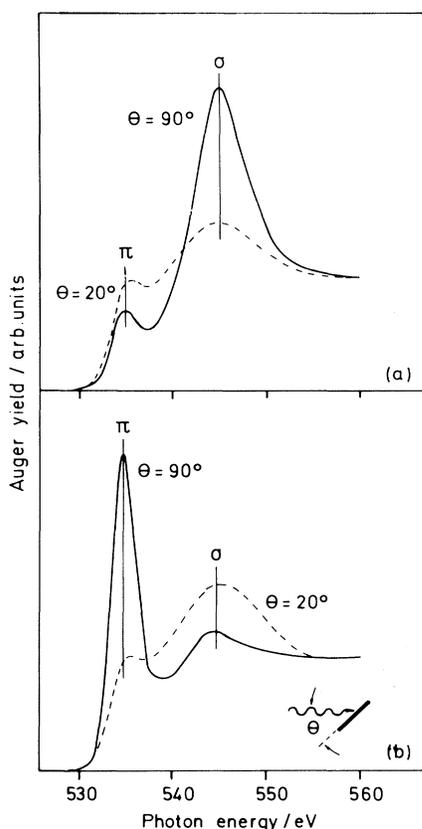


FIG. 1. O K -edge NEXAFS difference spectra for formate on Cu(110) taken with the polarization vector of the x rays along the (a) $[1\bar{1}0]$ and (b) $[001]$ azimuths for grazing ($\theta = 20^\circ$) and normal ($\theta = 90^\circ$) incidence.

species lies parallel to $[1\bar{1}0]$. More quantitative fitting of our data for the angular dependence of both σ and π resonances¹² confirms this assignment and attributes the nonzero amplitude of the π resonance with radiation incident in the $[1\bar{1}0]$ azimuth to imperfect ($\sim 87\%$) source polarization as expected.² If we assume that the σ resonance does behave like that of an isolated CO species, despite the symmetry breaking and scattering of the second oxygen atom, a fit of the dependence of the intensity of this resonance on polar incidence angle (Fig. 1) in the $[1\bar{1}0]$ azimuth yields a O-C-O bond angle of $130^\circ \pm 10^\circ$ consistent with the known bond angle of formate¹³ of 125° . Using the empirical linear relationship of the σ resonance position with bond length found for gas-phase molecules¹⁴ and chemisorbed hydrocarbons,¹⁵ we determine the C-O bond length to be $1.25 \pm 0.05 \text{ \AA}$.¹²

Figure 2 shows a similar set of surface EXAFS spectra. The data are influenced by the intrusion of the C 1s photoemission peak into our partial-yield detector above a photon energy of about 700 eV. The analysis yields a Cu-O bond length of $1.98 \pm 0.07 \text{ \AA}$, in excellent agreement with the value for anhydrous cupric

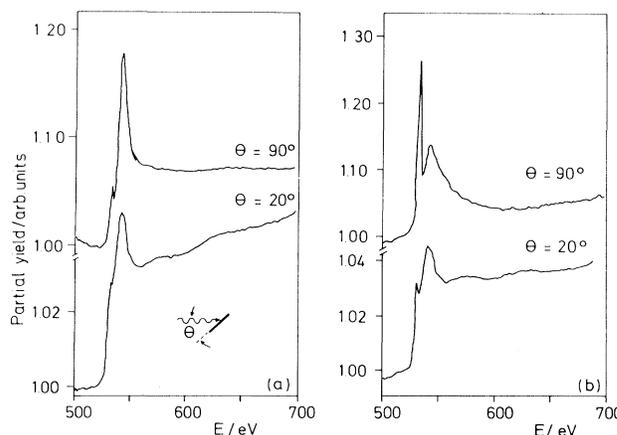


FIG. 2. O K -edge SEXAFS spectra for formate on Cu(110) taken with the polarization vector of the x rays along the (a) $[1\bar{1}0]$ and (b) $[001]$ azimuths for grazing ($\theta = 20^\circ$) and normal ($\theta = 90^\circ$) incidence.

formate¹⁶ (in which four oxygen atoms are spaced at 1.93–1.99 \AA from the central copper atom) and with the Cu-O bond length of 1.98 \AA for a bidentate formate bonded to a binuclear Cu cluster.¹⁷ The Cu-O bond length differs from that for isolated chemisorbed oxygen atoms (1.84 \AA).⁷

The actual adsorption site can now be established by comparison of the amplitudes of the SEXAFS for different polarization directions with those predicted for different possible geometries, noting that the amplitude associated with each interatomic vector varies as the square of the cosine of the angle between this vector and the polarization vector. Thus, possible sites considered involving the formate sitting on the "ridge" atoms of the Cu(110) surface are depicted in Fig. 3, while Table I shows the relative amplitudes predicted and measured. The fact that for normal incidence in the $[1\bar{1}0]$ azimuth SEXAFS is observed with a relative intensity of 0.6 ± 0.2 compared with theoretical values of 0 and 0.7 for models A and B, respectively, clearly identifies the correct site as atop with the oxygen atoms almost bridging a pair of top-layer ("ridge") copper atoms (site B), and excludes the bridging configuration (site A). Atop and bridging configurations relative to the second-layer atoms can be excluded as these sites would lead to a strong SEXAFS signal for normal incidence in the $[001]$ azimuth, which is not observed. According to the measured C-O bond length of 1.25 \AA and the O-C-O bond angle of 130° , the oxygen atoms are not exactly bridging two neighboring Cu atoms in the $[1\bar{1}0]$ direction which are separated by 2.56 \AA for an unreconstructed surface. The Cu-O bond lengths of 1.98 \AA , therefore, must be an average value of two bond lengths R_1 and R_2 (cf. Fig. 3), which are within $\pm 0.10 \text{ \AA}$ of the measured average Cu-O bond length. We should note that these

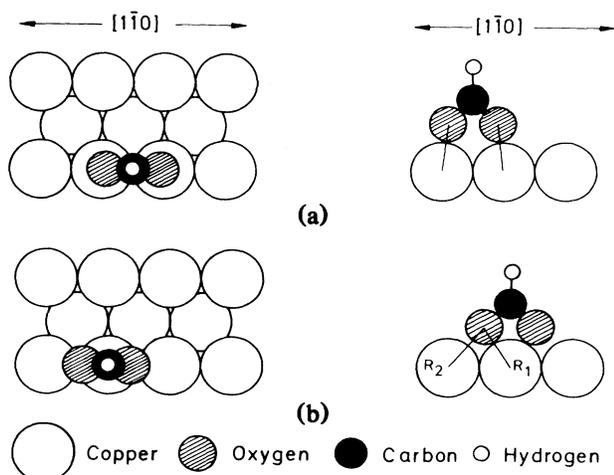


FIG. 3. The considered chemisorption sites for formate on Cu(110). The structural model B is appropriate where $1.88 \text{ \AA} < R_1 < R_2 < 2.08 \text{ \AA}$ and where the C-O bond length and the O-C-O bond angle measure 1.25 \AA , and 130° , respectively.

conclusions contrast strongly with the result⁵ of a similar study of formate on the higher-symmetry (100) surface. Because of this higher symmetry, the molecular azimuthal orientation cannot be obtained from the NEXAFS. Instead, it is established by comparison of SEXAFS amplitudes only. In this study a Cu-O bond length of 2.38 \AA is found, well outside the range of acceptable values for our data and $\sim 0.4 \text{ \AA}$ longer than in any other known Cu-O nearest-neighbor bond length. As the adsorption site found for the (110) surface is also available on the (100) surface, it is far from clear why a different, and chemically surprising, site is adopted on Cu(100). We note, of course, that the adsorption sites for atomic oxygen on Cu(100) and on Cu(110) do differ. In the latter case the bridge site is adopted,⁷ while in the former case there is evidence for both hollow and bridge sites.^{18,19} Nevertheless, no large variations in Cu-O bond lengths are seen, and while Ref. 5 offers an explanation for the long bond length in the Cu(100) formate system in terms of the special site, one might have expected this to be energetically unfavorable relative to the short-bond-length (100)-surface type of site.

In summary, our results provide a clear structural assignment for the formate species on a well-characterized copper surface. The Cu-O bond length differs from that for isolated chemisorbed oxygen atoms, but agrees well with the value for cupric formate.

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TABLE I. Theoretical and experimental SEXAFS amplitude ratios for different incidence directions. The theoretical amplitudes were calculated assuming atop (model A) and bridge sites (model B) for the oxygen atoms (cf. Fig. 3). Values are normalized to unity for $\theta = 20^\circ$, $[1\bar{1}0]$ azimuth.

Azimuth	θ	Theory		Experiment
		Model A	Model B	
$[1\bar{1}0]$	20°	1.0	1.0	1.0
$[1\bar{1}0]$	90°	0	0.7	0.6 ± 0.2
$[001]$	20°	1.0	1.0	1.0 ± 0.2
$[001]$	90°	0	0	0

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