

Evidence for a Novel Chemisorption Bond: Formate (HCO₂) on Cu(100)

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(Received 19 November 1984)

Surface extended-x-ray-absorption fine-structure measurements reveal that formate (HCO₂) groups on Cu(100) chemisorb via the two oxygen atoms in adjacent fourfold hollow sites with an average O-Cu nearest-neighbor bond length of 2.38 ± 0.03 Å. This distance is significantly (~ 0.4 Å) longer than typical O-Cu bonds in bulk compounds and all known surface complexes. The unusually large O-Cu distance is attributed to a steric effect involving the C atom in HCO₂ and the nearest-neighbor Cu surface atoms.

PACS numbers: 68.20.+t, 78.70.Dm, 82.65.Jv

The development of various surface structural probes over the last decade has allowed the determination of the precise location of chemisorbed *atoms* on surfaces.¹ Although it is still difficult to predict atomic chemisorption sites *a priori* the chemisorption bond lengths appear to be better understood. As shown by Madhukar² and Mitchell,³ experimentally derived bond lengths for a variety of chemisorbed atoms on metal surfaces can be well accounted for (within 0.1 Å) by Pauling's bonding concepts in molecular complexes and bulk compounds.⁴ In contrast to the case of atomic chemisorption the structural data base for chemisorbed *molecules* is still relatively small as a result of the difficulty of many techniques to deal with such systems. From the available structural data⁵ it appears, however, that the bond lengths between atoms in the molecule and surface substrate atoms are similar to those of the individual atoms in either surface or bulk complexes.

Here we report the first observation that the molecular chemisorption bond can be significantly different from the corresponding bond for an atomic adsorbate or for bulk complexes. Surface extended-x-ray-absorption fine-structure (SEXAFS)⁶ complemented by near-edge x-ray-absorption fine-structure (NEXAFS)⁷ measurements reveal an unusually long O-Cu distance for the formate (HCO₂) species on Cu(100). The derived bond length is larger by about 0.4 Å than the O-Cu nearest neighbor (nn) bond lengths for atomic oxygen and the methoxy (CH₃O) species on the same surface and for various bulk compounds (e.g., oxides and formates). This unusual bonding is attributed to a steric effect involving the C atom in a bridge position between two Cu surface atoms. The nonbonding C-Cu interaction which coun-

teracts the O-Cu bond pushes the molecule away from the surface and leads to the unusually long O-Cu distance.

Experiments were performed on beam line I-1 at the Stanford Synchrotron Radiation Laboratory with use of the grasshopper monochromator (1200 lines/mm holographic grating). SEXAFS and NEXAFS spectra were obtained by partial-electron-yield detection using a retarding voltage of -450 V.⁶ The angle of incidence of the x rays on the sample could be varied from grazing (**E** vector close to surface normal) to normal (**E** in surface plane). The Cu(100) surface was cleaned by Ar⁺ bombardment. Surface cleanliness and order after annealing were checked by Auger spectroscopy and LEED (base pressure 8×10^{-11} Torr). The formate was prepared^{8,9} by predosing the Cu(100) surface with 50 L O₂ [1 L = (langmuir) = 10^{-6} Torr sec] followed by a saturation dose of formic acid at 300 K. This predose maximized the amount of surface formate formed. The SEXAFS and NEXAFS spectra were measured at 300 K. Thermal-desorption studies following these measurements confirmed the integrity of the formate overlayer and Auger spectra after thermal decomposition of the formate showed no excess atomic oxygen.

NEXAFS and SEXAFS spectra above the O *K* edge for HCO₂ on Cu(100) are shown in Fig. 1 for two x-ray incidence angles $\theta = 15^\circ$ and 90° . The NEXAFS spectra in Fig. 1(a) are dominated by two resonances *A* and *B* which are readily assigned to π and σ resonances, respectively.⁷ According to dipole selection rules⁷ the π resonance will be maximized for the **E** parallel to the π orbitals of HCO₂, i.e., **E** perpendicular to the molecular symmetry plane which contains all atoms. Since for $\theta = 90^\circ$ (**E** parallel to surface) peak *A*

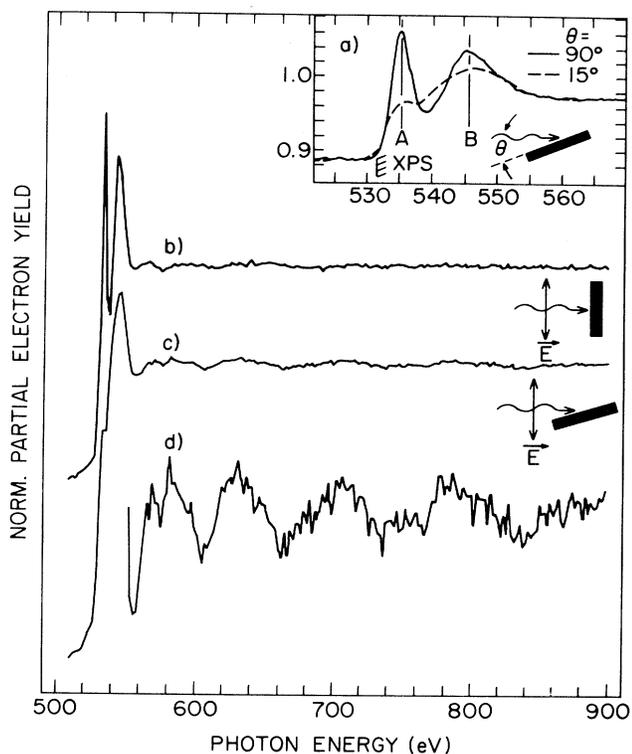


FIG. 1. (a) O K -edge NEXAFS spectrum for formate on Cu(100) at $T=300$ K for grazing ($\theta=15^\circ$) and normal ($\theta=90^\circ$) x-ray incidence on the sample. Peak A arises from a $1s \rightarrow \pi^*$ excitation and peak B is a σ shape resonance. XPS denotes the O $1s$ binding energy relative to the Fermi level measured by photoemission (Ref. 8), which corresponds to the K -shell excitation threshold. Curve b , background-corrected SEXAFS spectrum above the O K edge for the same sample as for curve a at normal x-ray incidence. Curve c , as for curve b for grazing incidence. Curve d , enlarged SEXAFS oscillations of spectrum c .

is large and nearly vanishes for $\theta=15^\circ$, the NEXAFS spectra in Fig. 1(a) show that the molecular symmetry plane is aligned perpendicular to the surface ($\pm 10^\circ$). The molecular symmetry plane is aligned perpendicular to the surface ($\pm 10^\circ$). The σ resonance is strongest for E along the O-C bonds. For HCO_2 the O-C-O bond angle β is expected to be close to 125° as for formic acid ($HCOOH$) and all bulk formates.¹⁰ Therefore the E vector will always have a finite projection onto one of the O-C bonds. This renders the observed angular intensity dependence for the σ resonance more ambiguous with respect to molecular orientation than for the π resonance. The position of the σ resonance relative to the K -edge threshold or $1s$ binding energy [marked XPS in Fig. 1(a)] allows us to determine the C-O bond length to be 1.27 ± 0.04 Å as discussed before.¹¹ Here we have used the empirical linear relationship of the resonance position with bond length found for gas-phase molecules¹² and chem-

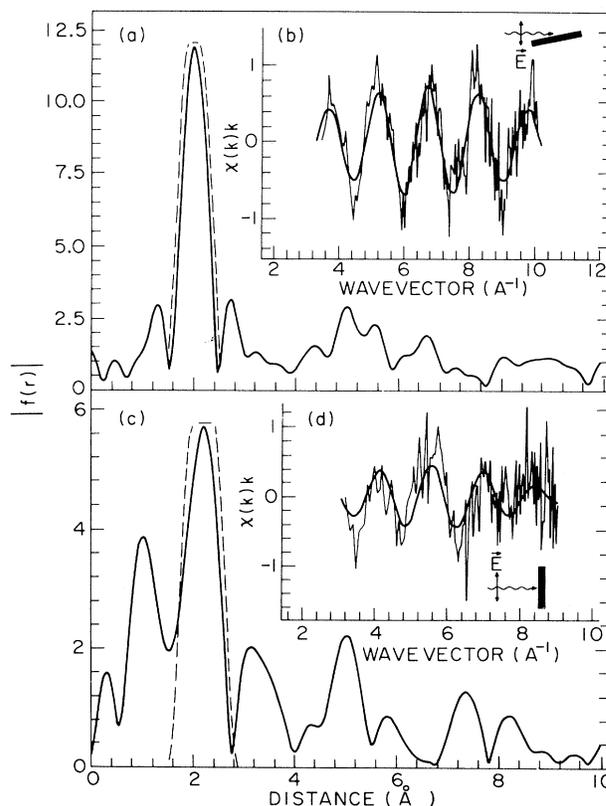


FIG. 2. Absolute Fourier transforms of the SEXAFS signals $\chi(k)k$ obtained at (b) grazing and (d) normal incidence for HCO_2 on Cu(100). The peaks in (a) and (c) around 2.1 Å correspond to the O-Cu distance without phase-shift correction. When isolated by the dashed window functions this peak corresponds to the smooth sinusoidal function superimposed on the data in (b) and (d). The peak around 1 Å in (c) is mostly due to the O-C bond in formate which for normal incidence lies along the E vector.

isorbed hydrocarbons¹³ rather than the more complex correlation predicted by a simplified multiple-scattering theory.¹¹

SEXAFS data for the same two x-ray incidence angles as in Fig. 1(a) are shown by curves b and c in Fig. 1. In order to more clearly show the dominant SEXAFS frequency and the larger amplitude at grazing than normal incidence angle we display the spectra after a smooth background function has been subtracted from the original data. The SEXAFS oscillations for Fig. 1, curve c are shown enlarged in Fig. 1, curve d . Analysis of the SEXAFS signals shown in Figs. 2(b) and 2(d) as a function of wave vector k reveals a dominant frequency which is superimposed on the data as a smooth solid line. This frequency corresponds to a peak at ~ 2.1 Å in the Fourier transform (FT). The k dependence of the SEXAFS amplitude with a maximum around $k \sim 6$ Å⁻¹ reveals that the signal must be due to a Cu neighbor of the central O

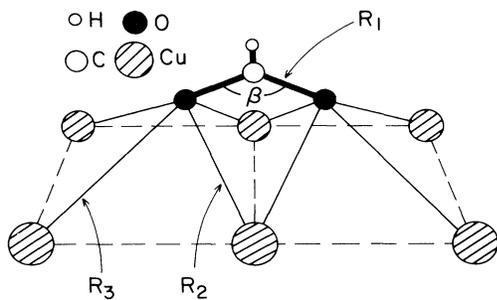


FIG. 3. Proposed structure model for formate on Cu(100) where $R_1 = 1.27 \text{ \AA}$, $2.30 \text{ \AA} \leq R_2 \leq R_3 \leq 2.45 \text{ \AA}$, and $\beta \sim 130^\circ$.

atom.¹⁴ C or O as the other possible neighbor atoms would give a backscattering amplitude which peaks at low k ($< 4 \text{ \AA}^{-1}$) and decreases rapidly at higher k values.¹⁴ By use of an appropriate O-Cu scattering phase shift derived from a Cu_2O single-crystal standard⁶ we obtain a O-Cu nearest-neighbor distance of 2.37 ± 0.02 and $2.40 \pm 0.04 \text{ \AA}$ from the spectra taken at $\theta = 15^\circ$ and 90° , respectively. The experimental amplitude ratio of the two spectra $A(15^\circ)/A(90^\circ) = 1.7 \pm 0.2$ unambiguously establishes that the O atoms occupy (or sit close to) fourfold hollow Cu sites.

Because of the well-defined O-Cu distance revealed by the SEXAFS data, HCO_2 at 300 K is bonded equivalently via its two oxygen atoms to the Cu surface (bidentate configuration). This configuration has been suggested previously by Sexton using electron-energy-loss spectroscopy.⁹ He finds a pure bidentate configuration at 400 K, while at 100 K some of the formate groups have nonequivalent oxygen atoms. Combination of our NEXAFS and SEXAFS results leads to the chemisorption geometry depicted in Fig. 3. The value for $R_1 = 1.27 \pm 0.04 \text{ \AA}$ is most reliably derived from NEXAFS although the O-C distance also appears in the SEXAFS data at normal incidence as revealed by the peak around 1 \AA in the FT [Fig. 2(c)]. Analysis of the SEXAFS data yields $R_1 = 1.30 \pm 0.08 \text{ \AA}$, the accuracy being limited by signal-to-noise considerations. The value derived for R_1 and the nonlinear O-C-O configuration ($\beta < 180^\circ$) in the molecule demand that the O atoms are slightly displaced from the fourfold hollow sites which are separated by 2.56 \AA for an unreconstructed Cu(100) surface. From the Fourier transforms in Fig. 2 we cannot distinguish between the O-Cu distances R_2 and R_3 shown in Fig. 3 but we only obtain a value for $\bar{R} = (R_2 + R_3)/2$. An upper limit for the different $\Delta R = R_3 - R_2$ can, however, be obtained from analysis of the SEXAFS amplitude.¹⁵ Since no amplitude beating is observable over our data range up to 10 \AA^{-1} [Fig. 2(b)] we determine from standard analysis procedures¹⁵ that $\Delta R \leq 0.15 \text{ \AA}$. Therefore R_2 and R_3 have to be within $\pm 0.08 \text{ \AA}$ of the measured average

O-Cu bond length $\bar{R} = 2.38 \pm 0.03 \text{ \AA}$.

The derived formate geometry on Cu(100) shown in Fig. 3 is in good accord with the bidentate bonding geometry typically encountered in anhydrous¹⁶ and hydrous¹⁷ formate-copper complexes. For example, for a well-characterized bidentate formate bonded to a binuclear Cu cluster, the values $R_1 = 1.244 \text{ \AA}$, $\beta = 128.4^\circ$, and $R_2 = R_3 = 1.983 \text{ \AA}$ have been reported.¹⁸ The surprising result of our structure determination is the unusually long O-Cu bond length \bar{R} which is considerably longer than the nn O-Cu bond lengths in various Cu formates ($1.93\text{--}2.02 \text{ \AA}$)¹⁶⁻¹⁹ and other bulk compounds,¹⁹ i.e., Cu_2O (1.85 \AA), CuO (1.96 \AA), $\text{Cu}(\text{OH})_2$ (1.94 \AA), $\alpha\text{-Cu}(\text{NO}_3)_2$ (1.98 \AA). Also, it is much longer than the values for $c(2 \times 2)$ atomic oxygen and for methoxy (CH_3O) on the same Cu(100) surface which are $1.94 \pm 0.03 \text{ \AA}$ ²⁰ and $1.97 \pm 0.04 \text{ \AA}$,²¹ respectively, as determined by SEXAFS. In all cases, the chemisorption bond involves an O atom with a preference for binding in the fourfold hollow site.

We attribute the large chemisorption bond length for formate on Cu(100) to steric constraints imposed by the rigid geometry of the nn copper surface atoms. As shown in Fig. 3 the C atom of the formate is located in the saddle point between two Cu atoms. Because it has a saturated valence the C atom does not bond to the surface and hence the C-Cu distance has to be nonbonding. If we assume a "normal" O-Cu distance of 1.97 \AA , which is the average nn bond length in bulk Cu formates,¹⁶⁻¹⁹ the chemisorption geometry in Fig. 3 would predict a C-Cu distance of 1.87 \AA which is strongly bonding.¹⁹ Thus the steric repulsion between the C atom and the two adjacent Cu atoms pushes the molecule away from the surface. We note that a model where the Cu atoms involved in the chemisorption bond are slightly displaced ($\sim 0.05 \text{ \AA}$) from their bulk positions to accommodate the attractive O-Cu and repulsive C-Cu forces, i.e., equalize R_2 and R_3 , is compatible with our bond-length analysis.

There is precedence for longer than normal O-Cu distances in bulk compounds in which a closer approach is prevented by other interactions.¹⁹ For example, in bulk Cu formates there are non-nearest-neighbor O-Cu distances between 2.3 and 2.7 \AA .¹⁶⁻¹⁹ In these complexes the coordination of oxygens about the copper atom (Cu II) are Jahn-Teller distorted from regular octahedral or tetrahedral geometries. The shortest O-Cu distances are all "normal" ($1.93\text{--}2.02 \text{ \AA}$) while other oxygens at larger distances are electrostatically attached to the Cu^{2+} (electronic configuration d^9) ions but are prevented from closer approach by the Jahn-Teller effect. The Jahn-Teller effect is inapplicable on the surface because metallic copper has no unpaired electrons. Here it is a steric rather than an electronic factor which prevents a closer approach of the formate group to the surface. It is hoped that future

calculations will reveal the detailed nature of the unusual chemisorption bond implied by the large O-Cu bond length. We believe that the present results are only a first example of a more general phenomenon and that steric effects may be important in the chemisorptive bonding of other polyfunctional molecules which afford more than one point of attachment to the surface.

We would like to thank A. L. Johnson for help with the experiments. We have greatly benefitted from discussions with T. H. Upton. The work reported here was done at the Stanford Synchrotron Radiation Laboratory which is supported by the Office of Basic Energy Sciences of the U. S. Department of Energy and the Division of Materials Research of the National Science Foundation. This work was supported in part by the National Science Foundation (CPE8320072) and by the Bundesministerium für Forschung und Technologie under Grant No. 05 233 BB.

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