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Application of molecular symmetry in near-edge x-ray-absorption spectroscopy of adsorbed species

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The importance of symmetry and selection rules in the near-edge x-ray-absorption spectra of adsorbed molecules is discussed. We show how the number of allowed resonances, their degeneracy, and polarization dependence can be predicted by reference to the appropriate molecular orbital scheme. Further, the effects of symmetry lowering, due to the presence of the surface, and of symmetry breaking, due to the creation of the core hole, may need to be considered. Recent data for the formate species adsorbed on a Cu{110} are used to illustrate some of these points.

I. INTRODUCTION

The polarization dependence of the soft x-ray-absorption spectrum (often referred to as NEXAFS, near-edge x-ray-absorption fine structure) of adsorbed molecules has been used extensively in recent years to determine molecular orientation on surfaces.[1-3] In a recent paper[4] we have argued that most NEXAFS studies ignore several important aspects of this problem which can lead to an incorrect interpretation of experimental data. In particular, we maintain that the expected number and symmetry of the resonances in the x-ray-absorption spectrum of a polyatomic molecule or molecular fragment can be obtained by considering the bonding scheme in the molecular orbital (MO) picture and by including the effect of symmetry breaking due to core hole creation. Using the polarization dependence of the resonances the effective point group of the *adsorbed* molecule can then be established, whereby the effects of symmetry lowering due to the interaction with the surface have to be considered. An example showing the validity of this approach is provided by a recent x-ray-absorption study of the surface carbonate species adsorbed on Ag{110}.[5] Using a simple MO model the expected resonances were identified and the corresponding dipole selection rules established. It could then be shown that, at least for the two σ-type resonances, the effective symmetry remains D_{3h} and that only one σ-type resonance is expected at the C K edge in agreement with experiment.

Currently accepted NEXAFS usage,[3] on the other hand, considers a polyatomic molecule to be "assembled" from diatomic and/or ringlike subunits. Associated with each of these moieties are then resonances polarized parallel or perpendicular to the internuclear axis or the ring system. A superposition of these "local" polarization dependences then gives the polarization dependence for the molecule as a whole. Some of the inadequacies of this building-block model have been recognized, for example, in the case of conjugation in aromatic systems, although even here NEXAFS is still apparently able to yield molecular orientation. When delocalization effects lead to nondegenerate orbitals, which in an MO picture do not lie along or perpendicular to the local internuclear axis, NEXAFS resonances are thought to show a polarization dependence characteristic of the spatial orientation of the orbitals. The sum of the corresponding intensities should nevertheless follow the angular dependence characteristic of the internuclear axes.

This somewhat anachronistic picture fails to take account of the effective point group, the symmetry of the (delocalized) molecular orbital and the dipole selection rules governing the transitions between initial and final states. In the present paper we illustrate these points by reference to new x-ray absorption data for the surface formate species adsorbed on Cu{110}. First, however, we briefly discuss symmetry and selection rules in connection with photoabsorption in adsorbed molecules.

If the surface species possesses at least one symmetry element (i.e., belongs to a point group), the transition from a core level into an unoccupied molecular orbital will be polarized and its intensity given by

$$I \propto [\mathbf{E}\langle f|\mathbf{M}_u|i\rangle]^2 , \tag{1}$$

where $\mathbf{E}$ is the electric vector of the incident radiation and $|i\rangle$ and $|f\rangle$ the initial and final states.[6] $\mathbf{M}_u$ is a Cartesian component of the electric dipole associated with the transition. For nonzero intensity the product of the irreducible representation corresponding to $|i\rangle$, $|f\rangle$, and $\mathbf{M}_u$ must belong to, or at least contain, the totally symmetric representation of the point group. The angular dependence of an allowed transition is then given by

$$I \propto [\mathbf{E}\cdot\mathbf{M}_u]^2 = \text{const}\cos^2\theta , \tag{2}$$

where θ is the angle subtended by the $\mathbf{E}$ vector and the relevant Cartesian coordinate u. The application to orientation determination then follows.

Which symmetry elements are expected on surfaces? Only symmetry axes and planes perpendicular to the surface are in fact possible. There can be no reflection in the surface plane and the number of allowed point groups associated with an adsorbed molecule or molecular fragment is thus reduced to ten: C_1, C_2, C_3, C_4, C_6, C_s, C_{2v}, C_{3v}, C_{4v}, and C_{6v}.[7] (C_1 corresponds to the trivial case of there being no symmetry at all.) In NEXAFS this list may only have formal significance: more important is the *effective* symmetry of the molecule for the transition concerned. Thus in the case of the carbonate species cited above the point group remains D_{3h} for the σ-type resonances but is possibly C_{3v} for the π-type resonance. This reflects the extent to which the corresponding bonding orbitals interact with the surface. Similarly, the effective symmetry of the methoxy species on Cu{100} appears to be C_{3v} in NEXAFS although the symmetry implied by the off-bridge bonding site (as determined using photoelectron diffraction) is only C_s.[8] There are other cases, however, where symmetry lowering is strongly apparent. An example is provided by the adsorbed CN moeity,[9,10] where the lying-down configuration (C_s point group) lifts the degeneracy of the unfilled π orbitals.

A useful procedure to determine the number and symmetry of the possible final states is to refer to a molecular orbital scheme for the "free" molecule or fragment. The polarization dependences can then be predicted for successive symmetry lowerings and compared with experiment. Note, however, that the correct assignment of the resonances is still a necessary prerequisite for the orientation determination. There is a similar problem in determining molecular orientation with angle-resolved photoemission. In this technique the symmetry of the initial-state wave functions (corresponding to filled MO's) must be known; the symmetry of the final state is predetermined by placing the electron analyzer in such a position as to detect a continuum wave function of particular symmetry.[11,12]

So far this discussion has implicitly assumed that the photoabsorption process does not break the symmetry, i.e., that the point group in the final state is the same as in the initial state. Symmetry breaking is a consequence of core electron (and thus hole) localization. Thus in the (free) carbonate species the excitation of an O 1*s* electron effectively reduces the symmetry D_{3h} to C_{2v} in the final state. There are several ways of considering this problem, the most simple being to assume the broken symmetry configuration also applies to the initial state. Alternatively, the core levels may be considered as forming delocalized orbitals (which of course in practice they do not) within, in this case, D_{3h} and the selection rules worked out accordingly. Strictly speaking, however, the correct approach is to consider the whole set of broken symmetry configurations and form linear combinations thereof such that the transition can take place within the higher symmetry of the ground state. There are subtle differences in these procedures, but normally they arrive at the same result. We delay further discussion of this problem until the O 1*s* spectrum of the formate species is considered below.

Some other aspects of molecular x-ray absorption are worthy of mention, if only briefly. First, the unoccupied MO's in molecules containing C, N, and O may be regarded as deriving from linear combinations of atomic orbitals in the second principal quantum shell. Higher shells give rise to Rydberg orbitals which form series converging on the ionization threshold. These also belong to the irreducible representations of the molecular point group and may mix with unfilled valence orbitals.[13] It is often assumed that transitions into pure Rydberg states are "quenched" by the surface,[14] which may well be the case, although as yet there is little experimental evidence that this is a general effect. On the contrary, Rydberg features have already been identified in NEXAFS of adsorbed molecules;[15,8] since they belong to irreducible representations they will also show a polarization dependence.[8]

A second point concerns the so-called shape resonances. Although the strong continuum features in the first NEXAFS spectra recorded (e.g., SF_6) were originally assigned to the transitions into unoccupied molecular orbitals,[16] they have also been described in terms of electron scattering,[17] where the photoemitted electron is temporarily trapped in a quasibound state produced by the presence of a centrifugal barrier in the molecular potential. Based on this scattering description a correlation between the energy of such a resonance and interatomic bond length ("bond lengths with a ruler") has been proposed.[18–20] This correlation is quite successful in the case of diatomics and diatomic analogs, but is highly questionable in its application to polyatomic molecules where there are necessarily several σ-type continuum resonances of different symmetry. This is one of the points made by Piancastelli *et al.*[21] in their detailed criticism of the "bond lengths with a ruler" concept.

Third, there are problems of assignment and quantitative evaluation of the data. A possible pitfall associated with the assignment of near-edge features is the presence of many-body effects. By this we mean the occurrence of multielectron excitations which can lead to satellites or even, in the case of strong correlation, to a complete disappearance of the single-particle excitation. It has, for example, been recently shown[22] that the $C1s^{-1},b_{2g}{}^{1}$ configuration in benzene is very nearly degenerate with the $C1s^{-1},e_{1g}^{-1},e_{2u}{}^{2}$ configuration and that they mix strongly, leading to two features above and below the ionization threshold. Since the second feature could be accidentally degenerate with other σ-type resonances, problems could arise in the determination of orientation via the polarization dependence. The interpretation of the near-edge spectrum is also made more complicated by the presence of so-called substrate scattering resonances which, in an MO picture, may be considered as antibonding orbitals (or bands) associated with the chemisorption bond. These can lie underneath the molecular-type resonances and lead to incorrect orientation determination as in the case of the methoxy species on Cu{100}.[23,8] Indeed, on an experimental note, there are grave problems in the quantitative application of NEXAFS due to the unknown background under the molecular resonances as well as the difficulties associated with the correct identification of resonances, their line shape, and normalization.

To conclude this section we briefly discuss the surface formate species, which was first identified spectroscopically as a reaction intermediate in the decomposition of formic acid over metal and oxide surfaces.[24] Its presence on Cu{100} and {110} surfaces has been inferred from thermal desorption spectra,[25] and it has been subsequent-

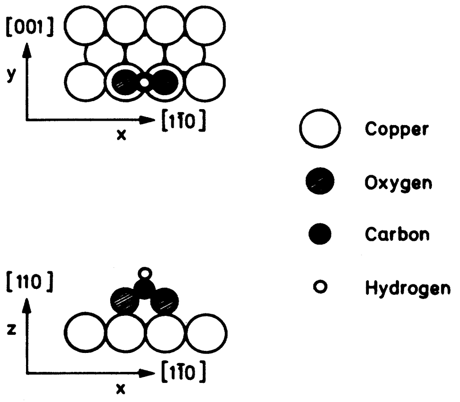

FIG. 1. Chemisorption site for formate on Cu{110}. The coordinate frame is defined such that the x, y, and z directions are parallel to the [1$\bar{1}$0], [001], and [110] crystallographic directions, respectively.

ly investigated with various techniques including infrared spectroscopy,[26] electron-energy-loss spectroscopy,[27] ultraviolet photoelectron spectroscopy,[28–30] x-ray-absorption spectroscopy,[31–35] and photoelectron diffraction.[36] In particular, it is known that the molecular symmetry is C_{2v} and that on the {110} surface the molecular plane is aligned along the ⟨110⟩ azimuth. The exact adsorption site has been the subject of some controversy, but it is now believed that the short bridge site is occupied on both surfaces.[36] This is shown for the Cu{110} surface in Fig. 1.

II. EXPERIMENTAL

The experiments were performed in a VG scientific ADES 400 angle-resolving spectrometer taking light from the BESSY synchrotron radiation source in Berlin. The 1500 lines per mm grating on the high-energy toroidal grating monochromator (HETGM) of the Fritz-Haber-Institut[37] provided light in the 250–600 eV photon energy range. Although the 1100 lines per mm grating yields a substantially higher photon flux below 400 eV, the total absence of carbon absorption structures from the grating with higher ruling density eases the problems associated with photon flux normalization. The Cu{110} crystal was cleaned by the usual combination of argon ion bombardment and annealing cycles until a well-ordered LEED pattern was obtained and XPS and NEXAFS showed no features due to surface contamination. The adsorbed formate species was prepared by exposing the clean surface to formic acid (20 L) at room temperature.

The NEXAFS data were taken at both the carbon and oxygen K edges with the **E** vector in the ⟨110⟩ and ⟨100⟩ azimuths. The Auger yield mode of detection was employed using a ~12-eV-wide kinetic energy window centered at 270 and 510 eV for the carbon and oxygen KVV Auger transitions, respectively. The Auger electron emission was detected at an angle out of the incident plane so as to minimize the intensity of the direct photoemission features.[6] The angle between the electric vector of the light and the surface normal θ_E was varied by rotating the sample relative to the light. The Auger emission angle was kept constant by simultaneously rotating the electron analyzer with the sample. Upon changing the crystal azimuth, however, the Auger detection angle was necessarily rotated 90° azimuthally with respect to the previous position. The clean surface NEXAFS was subtracted from that of the adsorbate-covered surface and the spectra were subsequently normalized to a constant edge-jump height.

The photon energy was calibrated by measuring the photoelectron spectrum of the copper $3p$ level in first- and second-order light at a photon energy just below that of the sharp π resonance of the formate species. The error in this calibration procedure is expected to be less than ± 0.5 eV.

III. RESULTS AND DISCUSSION

NEXAFS data taken at the oxygen K edge for the two extreme values of θ_E are shown in Fig. 2. As in the previous investigation by Puschmann *et al.*,[33,34] two features are observed at 532.7 and 542.0 eV which can be assigned to π- and σ-type resonances, respectively. There are, however, some small differences between the data presented here and those previously published. In particular, the π intensity at $\theta_E = 90°$ in the ⟨110⟩ azimuth relative to the corresponding spectrum in the ⟨100⟩ azimuth is larger than would be expected if the molecular plane were perfectly aligned in the ⟨110⟩ azimuth. This follows from the polarization dependence given by Eq. (2) as well as from the assumption that the π orbital (it is actually $2b_2$—see below) has a node in the molecular plane and that the molecular planes themselves are indeed aligned along the ⟨110⟩ azimuth. As the data in the ⟨110⟩ azimuth presented here have been reproduced using the original crystal of Puschmann *et al.*, it is unlikely that there was a higher concentration of molecules on other sites (with another orientation). In later measurements on the monochromator it became clear that the degree of polarization of the incident light had decreased to ~70% compared to the original measured value of ~85%–90% at this energy. This was due to a different position of the electron beam in the storage ring, causing some of the light to be reflected from an ion pump element protruding into the beam line. The problem has since been rectified.

The corresponding data at the C K edge are shown in Fig. 3. It is immediately apparent that there are at least four resonances at 287.9, 290.4, ~297.6, and ~300.4 eV. The sharp feature of lowest energy could be assigned by analogy to the $\pi(2b_2)$ resonance. The weak feature at 290.4 eV—not discernible, or perhaps not resolvable at the oxygen edge—is only observed in the $\theta_E = 20°$ spectra. Compared to the O edge data the "σ" resonance now appears to consist of two features separated by at least 3 eV. This is seen most dramatically when the **E** vector is in the ⟨110⟩ azimuth: For $\theta_E = 20°$ the peak is at 297.6 eV and for $\theta_E = 90°$ it is at 300.4 eV.

Before attempting to interpret the data, particularly

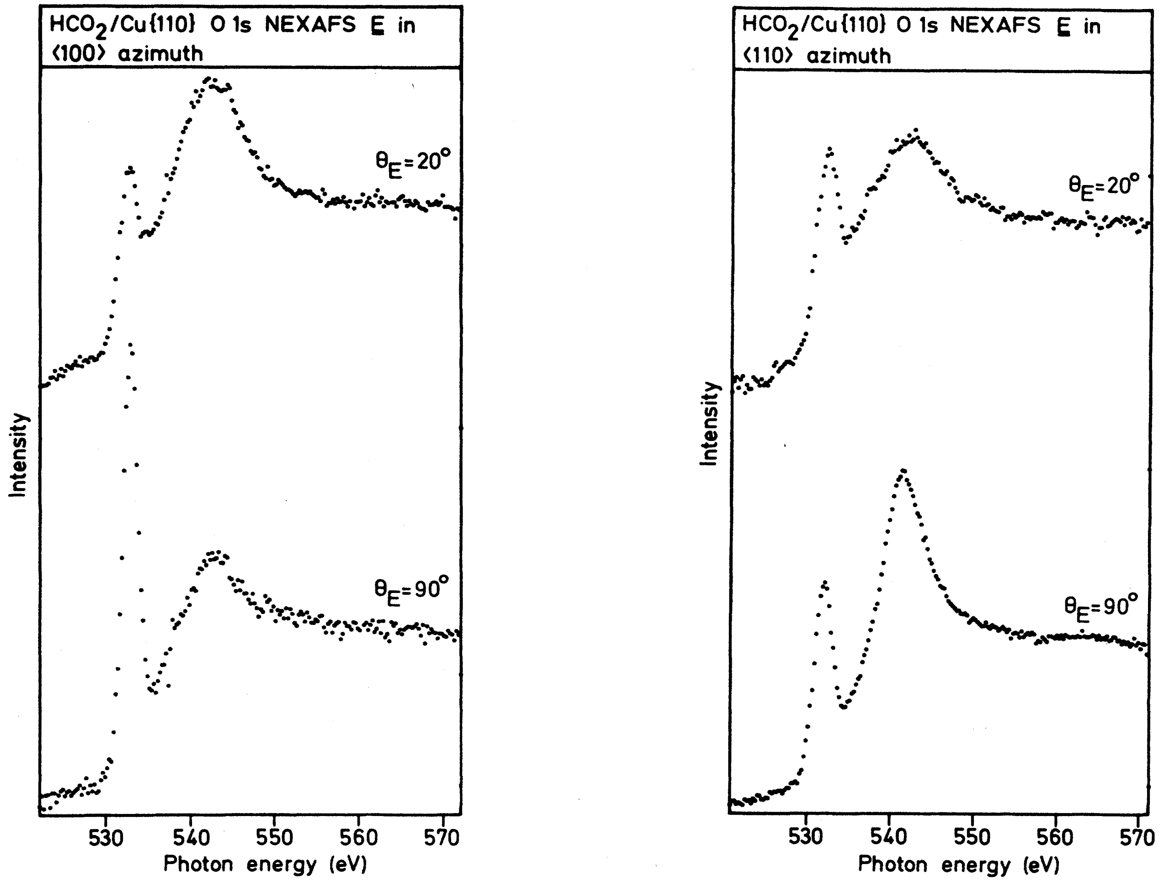

FIG. 2. O K-edge NEXAFS for formate on Cu{110} with the electric vector of the x rays along the ⟨110⟩ (right panel) and ⟨100⟩ (left panel) azimuths. Spectra with the electric vector of the light in the surface plane ($\theta_E = 90°$) and close to the surface normal ($\theta_E = 20°$) in each azimuth are shown.

for the carbon edge, it is first necessary to consider the molecular orbital energy diagram. If the adsorbed formate molecule is assumed to be an anionic species, then we would expect 12 occupied molecular orbitals. Calculation[39–40] and experiment[29,30] indicate that the three highest occupied molecular orbitals are $1a_2$, $4b_1$, and $6a_1$ and that they are of similar energy. A simple analysis shows that there are then four unoccupied molecular orbitals: $2b_2$, $7a_1$, $8a_1$, and $5b_1$. Of these, the $2b_2$ is an unoccupied π^* orbital; the remainder are σ^* orbitals and thus symmetric with respect to reflection in the molecular plane. Such an analysis, however, yields no information on the relative energies of these unoccupied orbitals, nor indeed on the relative energies of the corresponding resonances in the x-ray absorption spectrum. The calculation of Bullett and Dawson,[40] specifically for formate on Cu{110}, puts the $2b_2$ orbital lowest in energy as does the SCF study of the free formate ion by Peyerimhoff.[38] In the latter work the $7a_1$ and $5b_1$ are identified at higher energies. Previous NEXAFS work has correctly assumed the symmetry of the lowest energy resonance in the oxygen spectrum and, as we have seen above, used its polarization dependence to determine the molecular orientation. We first consider the spectra at the C edge and return to the oxygen data later.

It is tempting to assign the observed four resonances in Fig. 3 to the expected transitions into the four unoccupied orbitals. Using the coordinate frame shown in Fig. 1 and simple group theory, the polarization dependences of these transitions can be predicted in a straightforward way. The $2b_2$ transition can be excited only with the E_y component of the electric vector, $5b_1$ with only the E_x component, and $7a_1$ and $8a_1$ with only the E_z component. This analysis is particularly simple because the excitation of a C 1s electron does not break the C_{2v} symmetry of the adsorbate complex. The spectra in Fig. 3 indicate, as expected, that the lowest energy feature corresponds to the $2b_2$ transition. (The unexpectedly high intensity in the ⟨110⟩ azimuth is due to the relatively low degree of polarization of the incident radiation). Further, the features at 290.4 and at ~297 eV are preferentially excited by the E_z component and are thus of a_1 symmetry. The feature at ~300 eV is preferentially excited by the E_x component, indicating that it corresponds to the transition into the $5b_1$ level. (Again, the small feature observed at this energy in the ⟨100⟩ data is a conse-

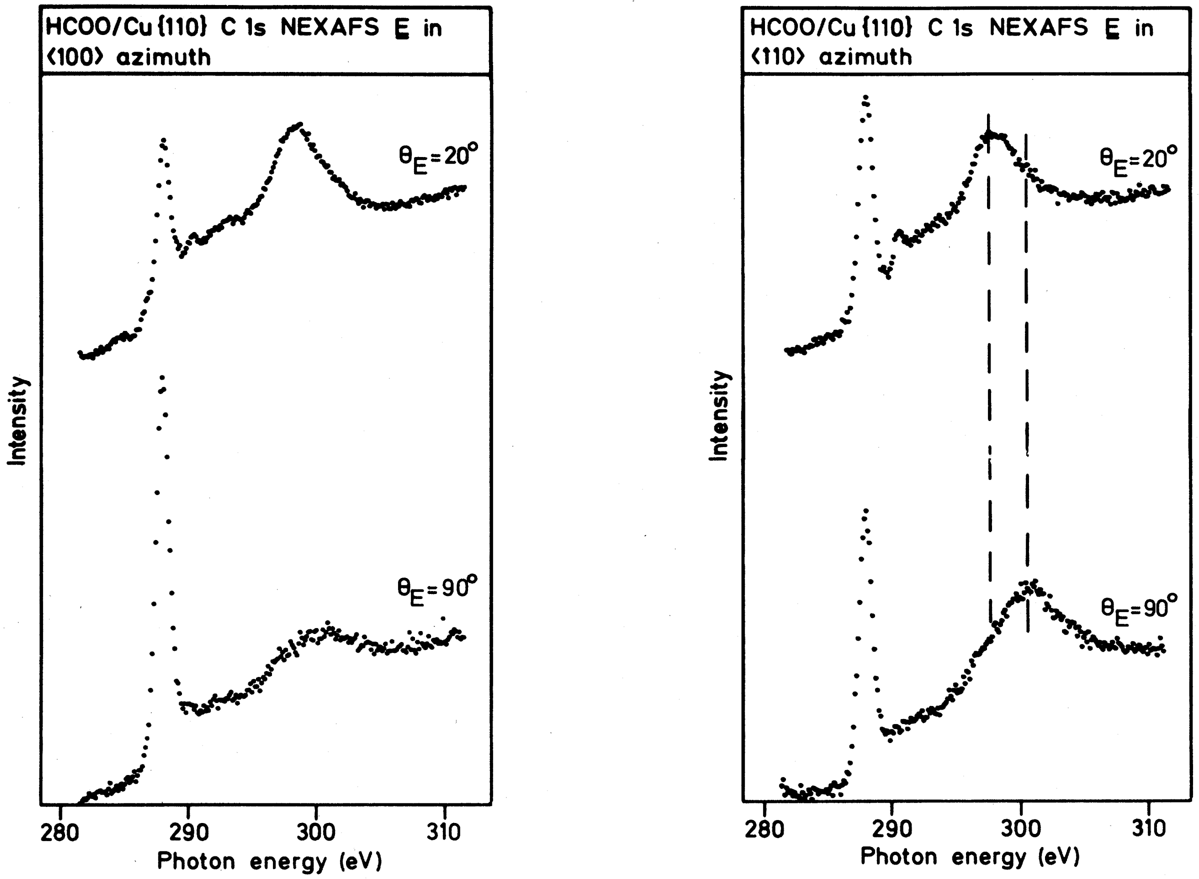

FIG. 3. C *K*-edge NEXAFS for formate on Cu{110} with the polarization vector of the x rays along the ⟨110⟩ (right panel) and ⟨100⟩ (left panel) azimuths. Spectra with the electric vector of the light in the surface plane ($\theta_E = 90°$) and close to the surface normal ($\theta_E = 20°$) are shown for each azimuth.

quence of the poor degree of linear polarization of the light.) The exact assignment of the two a_1 features is difficult because there is the distinct possibility that the relatively sharp lower energy one is a Rydberg transition (probably $3s$ or $3p_z$). Alternatively, it is possible that the $7a_1$ resonance also occurs in the energy range (below the ionization limit) and mixes with Rydberg states of the same symmetry.[13] We think this is unlikely, however: The two resonances at ~297 and ~300 eV are expected to be largely σ^*(C-O) in origin because of their separation. On the basis of the ordering of the filled levels one might expect the second unfilled a_1 level of σ(C-O) and σ(C-H) character to occur at still higher energy. In which case, it might be so smeared out in the spectrum that it cannot be observed. Without explicitly calculating the transition energies, it will not be possible to clear up this point. Calculations for the related formaldehyde molecule[41] show strong Rydberg features which apparently contain no C-H character. We note there is also some structure in the spectrum between 291 and 295 eV, which of course could also correspond to an a_1 resonance. Our assignment of the carbon near-edge spectrum is summarized in Table I.

Current usage would predict at the most only three features in the near-edge x-ray absorption spectrum of the formate species; the π^*, a single σ^*(C-O), and possibly a σ^*(C-H) resonance. By determining the polarization dependence of the C-O resonance from the two C—O bonds, the transitions for which are apparently polarized along each internuclear axis, it would then be possible to determine the O-C-O angle. This is incorrect as the observation of two σ^*(C-O) resonances with a_1 and b_1 symmetry at the C edge indicates. Puschmann *et al.*[33,34] used this procedure to determine the O-C-O angle using the polarization dependence of the σ^* feature

TABLE I. Polarization dependence of the resonances observed in the C *K*-edge NEXAFS of formate on Cu{110}.

Energy (eV)	Final-state symmetry	Polarization
287.9	B_2	y
290.4	A_1	z
297.6	A_1	z
300.4	B_1	x

at the oxygen edge. As we shall see below, the oxygen case is somewhat more complicated, but the localized resonance picture remains incorrect: There are also two resonances to be considered. A similar situation arises in the determination of the orientation of the hydrocarbon chains in Langmuir-Blodgett films. Outka *et al.*[42] claim that the polarization dependence of the observed σ^*(C-C) resonance results from the superimposed polarization dependences of the individual resonances associated with each C-C moiety. As can be simply shown by consideration of the space group of these quasi-one-dimensional systems,[43] all the resonances are in fact polarized perpendicular and/or parallel to the chain direction.

The x-ray absorption spectra at the oxygen edge are complicated by the fact that in the ground state the formate species possesses two equivalent oxygen atoms. From the localized oxygen 1*s* core levels a linear combination can be formed such that the orbitals transform in C_{2v} symmetry. Hence, within the C_{2v} point group they become the $1a_1$ and $1b_1$ molecular orbitals. Upon creation of a core hole, however, the molecular symmetry is broken due to the localization of the core hole on one of the oxygen atoms. This is a familiar problem in core-level spectroscopy and manifests itself, for example, in the satellite structure on the C 1*s* line in the photoelectron spectrum of benzene.[44] Similarly, the effect has also been included in the calculation of the O 1*s* ionization potential of molecular oxygen.[45] In the case of the formate species, core excitation will reduce the symmetry to C_s in the excited state. The $1a_1$ and $1b_1$ molecular orbitals will then transform as $1a'$ and $2a'$ in the lower symmetry point group, while the unoccupied levels ($2b_2$, $7a_1$, $8a_1$, and $5b_1$) transform as $3a''$, $11a'$, $12a'$, and $13a'$, respectively. The effect of equivalent core holes in the excitation spectra of systems with equivalent atoms has recently been discussed by Schwarz *et al.*[22] By means of a linear combination of all possible localized broken symmetry configurations, the symmetry of the final states can be determined within the higher symmetry point group of the initial state. For the excitation spectra of the formate species, the linear combination for each excited state configuration is given by $\Phi = \Phi_R \pm \Phi_L$, where Φ_R and Φ_L are the molecular wave functions for the core hole localized on the right and left oxygen atoms, respectively.

We first consider the transitions from the oxygen 1*s* level into the $2b_2(\pi)$ molecular orbital. In the broken symmetry case, the final state corresponds to a $1a'^{-1},3a''^{1}$ configuration within the C_s point group. Application of a linear combination of the two broken symmetry configurations yields, within the C_{2v} point group, two final states of A_2 and B_2 symmetry for this transition. (Note that the capital letters for the irreducible representation refer to molecular wave functions.) Therefore, excitation from the O 1*s* level into the $2b_2$ orbital corresponds to a transition from the A_1 ground state to A_2 and B_2 excited states. The former is dipole forbidden, the latter is polarized in the *y* direction, enabling the orientation of the molecule to be determined in the same way as at the carbon edge. This was the basis of the orientation determination made by Puschmann *et al.*[33,34] for data taken at the oxygen edge.

Transitions from the O 1*s* level into the $7a_1$, $8a_1$, and $5b_1$ molecular orbitals yield broken symmetry configurations within the C_s point group, given by $1a'^{-1},na'^{1}$ ($n = 11,12,13$). Forming a linear combination from each pair of broken symmetry configurations in the C_s point group result in two final states of A_1 and B_1 symmetry in the C_{2v} point group. Thus for the three transitions into the $7a_1$, $8a_1$, and $5b_1$ molecular orbitals, there is a total of six final states. It should be noted, however, that the energy separation between the A_1 and B_1 states associated with each transition will be extremely small and not resolvable. Therefore a maximum of three σ-type features in the experimental data is expected but each observable transition will be polarized in *both* the *z* (A_1 component) and *x* (B_1 component) directions. It could also be said that these features are polarized in the *xz plane*. This means that their intensity is zero when the **E** vector points in the *y* direction, but nonzero when it lies in the *xz* plane. The dependence of the intensity of a particular feature on the angle of the **E** vector in the plane cannot, however, be predicted and would require calculation.

In the spectra of Fig. 2 and in those in Refs. 33 and 34 only one feature is observed in this region of the spectrum. The polarization dependence of the intensity of this peak in the ⟨110⟩ azimuth indicates that it is indeed excited by *x* and *z* components of the light. Moreover, the overall shape of the peak appears to be polarization dependent, which would suggest that at least two energetically well separated but not resolvable (as is the case at the C *K* edge) transition are present, each of which is comprised of A_1 and B_1 components, i.e., polarized in the *z* and *x* directions.

For the formate species it transpires that this formally more correct way of taking linear combinations of the pair of broken-symmetry configurations gives the same result as treating the core hole as delocalized over both oxygen atoms in C_{2v} symmetry. (For all transitions into the unoccupied molecular orbitals, the hole would be delocalized in either the $1a_1$ or $1b_1$ molecular orbitals; this gives rise to a pair of final states for each transition.) If the excitation occurs into a degenerate unoccupied molecular orbital, only the approach based on linear combinations of broken symmetry configurations can allow for the lifting of the degeneracy of the unoccupied molecular orbital. According to Schwarz *et al.*[22] this effect could induce a splitting of 0.5 eV in the e_{2u}-derived final states of the free benzene molecule.

IV. CONCLUSIONS

The polarization dependence of the two σ-type resonances observed in the carbon *K*-edge excitation spectra of the formate species on Cu{110} have been interpreted using dipole selection rules within a framework based on the number and symmetry of the unoccupied molecular orbitals. The presence of these two resonances prevents the determination of the O-C-O bond angle, and also raises doubts concerning the determination of bond lengths from their energy. The data presented here, and that already published for the carbonate species adsorbed on Ag{110}[5], suggest that current practice of NEXAFS is often oversimplified. We believe that the near-edge structure can only be characterized correctly by reference to the molecular orbital scheme, the application of dipole selection rules within the appropriate point group, and by consideration of symmetry breaking.

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