Chemical Shift Photoelectron Diffraction from Molecular Adsorbates

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By using the chemical shift in core-level photoemission from adsorbed species, we apply the technique of energy-scan photoelectron diffraction to molecules containing nonequivalent atoms of the same element. As an example, we demonstrate the complete structural characterization of the surface acetate species on Cu{110} including independent determination of the sites of the two inequivalent carbon atoms.

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Since the majority of molecular adsorption systems form disordered overlayers and are thus not accessible to conventional diffraction techniques, there is considerable interest in surface structural probes which do not require the presence of long-range order [1-3]. In this context, we have shown recently that energy-scan photoelectron diffraction is particularly useful for determining the structural parameters of small, adsorbed molecules containing C, N, and O atoms (e.g., Refs. [4-6]). The intensity of a core-level photoelectron peak, corresponding to an atom of the adsorbate, is measured at a selected emission angle as a function of photon energy and thus of the photoelectron kinetic energy. In the plot of peak intensity versus kinetic energy ("the photoelectron diffraction spectrum") modulations occur as a result of interference between the primary photoelectron wave and the secondary waves elastically scattered at surrounding atoms. These modulations provide information on the scattering path lengths and thus on the local bonding geometry, i.e., on the surface site and the distance to neighboring substrate atoms.

In the case of larger molecules adsorbed on surfaces there are often several atoms of the same element present, as, for example, in hydrocarbons. If these atoms are chemically distinct and have different core-level binding energies in the photoelectron spectrum, then the possibility exists of performing *chemical shift* photoelectron diffraction. The modulations in the corresponding photoelectron diffraction spectrum of each atom will be different, if the surface site and/or the separation from the surface is different. In some cases, atoms which are equivalent in the free molecule will become chemically distinct on the surface due to the bonding geometry, e.g., in adsorbed molecular fragments resulting from heterogeneous reactions. By performing appropriate scattering calculations the photoelectron diffraction spectra can be simulated and the site of each atom determined *separately* relative to the surface.

An example of an adsorbed molecule containing nonequivalent atoms of the same element is the surface acetate species (CH_3COO-) which can be formed on a Cu{110} surface by decomposition of acetic acid. The polarization dependence of the oxygen and carbon *K*-edge absorption spectra [7] shows that the molecular plane is perpendicular to the Cu surface in the ⟨110⟩ azimuth. Further, vibrational spectra of the same species on the Cu{100} surface [8] indicate a symmetric configuration with two equivalent oxygen atoms. A plausible bonding geometry based on that of the corresponding surface formate species [5] on Cu{110} is shown as an inset in Fig. 1. Note that in this proposed structure, which is in fact confirmed by the present study (see below), the so-called aligned bridge site [5] is occupied. From literature data [9] on acetic acid and acetates it is known that the carboxyl carbon atom has a 3.5–4.0-eV higher 1*s* photoelectron binding energy than the methyl carbon atom. Figure 1(a) shows that this is also the case for the surface acetate species on Cu{110}. In the corresponding *trifluoroacetate* species (CF_3COO-) on the same surface the binding energy of the outermost carbon atom increases by ~6 eV (spectrum not shown in Fig. 1) and the peak thus shifts to the low kinetic-energy side of the peak from the carboxyl carbon, again in agreement with literature data [9]. (The surface trifluoroacetate species, in which the H atoms are replaced by F atoms, can be prepared analogously to the acetate species by the decomposition of trifluoroacetic acid.) Thus the surface acetate is ideally suited to demonstrate the potential of chemical shift photoelectron diffraction. At the same time, we obtain valuable structural information on an interesting chemisorption system.

The experiments were performed in a purpose-built ultrahigh vacuum spectrometer on the HE-TGM 1 monochromator [10] at the BESSY synchrotron radiation source. The Cu{110} sample was cleaned with the usual methods. The acetate and trifluoroacetate species were prepared in submonolayer concentration by exposing the surface to 1.5×10^{-5} mbars acetic acid at 100 K and subsequently warming to 380 K. A VG Scientific 152-mm mean radius 150° electrostatic deflection analyzer (with

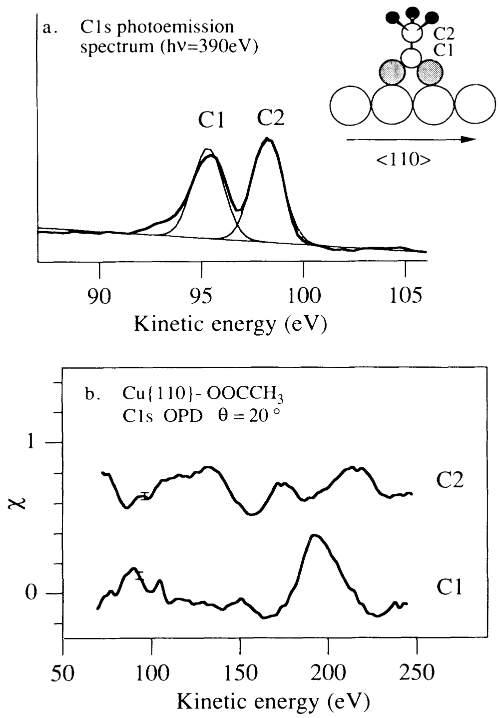

FIG. 1. (a) C 1*s* photoemission spectrum of the surface acetate species at $h\nu=390$ eV. Inset: Structural model assuming adsorption in the aligned bridge site. (b) Energy-scan photoelectron diffraction spectra from the C1 and C2 atoms (carboxyl and methyl carbon, respectively). Polar emission angle $\theta=20°$ in the ⟨110⟩ azimuth. The modulation scale on the ordinate is appropriate to the lower curve, while the upper one is simply offset by a fixed amount. The error bars refer only to statistical (Poisson) noise.

three parallel detectors) was installed at a fixed angle of 60° relative to the photon incidence direction. Photoelectron energy spectra were recorded around the C and O 1*s* photoemission peaks at photon energy intervals of 2 eV in the kinetic-energy range ~70–250 eV at various emission angles in the ⟨110⟩ azimuth. Peak areas after background subtraction were determined at each photon energy to produce the experimental photoelectron diffraction curves shown here; further details of this fitting procedure may be found in Ref. [6].

The 1*s* peaks from the carboxyl carbon (designated C1) and the methyl carbon (designated C2) are, as noted above, easily separable in the photoelectron spectrum [Fig. 1(a)]. Note that the instrumental resolution is ~1.8 eV, but increases to ~2.5 eV at higher photon (and thus kinetic) energy due to the monochromator. Figure 1(b) shows the photoelectron diffraction spectra from the C1 and C2 carbon atoms at a polar emission angle of $\theta=20°$ in the ⟨110⟩ azimuth. The spectra, obtained by summing three separate runs, are plotted in the form of a modulation function $\chi(E_{\rm kin})$ [6]. The error bars correspond to statistical noise in the individual photoelectron spectra; systematic errors associated with the background subtraction procedures are difficult to assess but are certainly no more than a factor of 2 greater than the statistical error. It is immediately obvious that the modulations in the two spectra are completely different, indicating clearly that the two carbon atoms have different coordinates relative to the surface. The same result is obtained at other polar emission angles. The quantitative determination of the sites of the two atoms require, however, theoretical simulations.

Multiple scattering cluster calculations were performed using the approach of Fritzsche [11] based on a magnetic quantum number expansion. An optimized set of basis functions is used in the angular momentum representation, with the result that all sums over magnetic quantum numbers converge rapidly and can be truncated after a few terms without loss of accuracy. Further, by specifically taking into account the finite energy resolution in the photoelectron diffraction experiment, additional damping factors arise in the theoretical expression for the intensity. These systematically suppress the contribution of long scattering pathways [12]. Thus in the present case, third- and higher-order scattering events could largely be neglected due to their longer path lengths. On the basis of the structural model shown as an inset in Fig. 1, C 1*s* and O 1*s* photoelectron diffraction spectra were calculated for both the acetate and trifluoroacetate species at various separations of the atoms from the surface. These calculations were performed for the various polar emission angles used in the experiment both for the structure of Fig. 1 and for a second structural model based on the aligned on-top site [5]. Results obtained for the best fit between theory and experiment at two angles are shown in Fig. 2 for the C atoms ($\theta=20°$) and in Fig. 3 for the O atoms ($\theta=0°$); these two geometries place a nearest-neighbor Cu atom behind the appropriate emitter for the determined adsorption structure (Fig. 1), and this geometry leads to the clearest diffraction effects.

Before discussing the details of the fit we note that the experimental acetate and trifluoroacetate spectra are very similar for the C1 atom and have a strong resemblance in the case of the C2 atom, although here the modulations are weaker for the fluoroacetate. (The sharp peak at 110 eV is the residual effect after background subtraction of a Cu Auger feature and an excitation of the F 1*s* level with second-order light, so that the detailed structure within a few eV of this feature is not meaningful.) Further, the theory curves for the two species are virtually identical, indicating that the influence of the F atoms on the diffraction spectra is minimal. The same was found to be true for the O 1*s* spectra (Fig. 3). This relative insensitivity of photoelectron diffraction spectra to the presence of other light atoms turns out to be particularly useful in the present situation. The quantitative determination of the position of each atom in the molecule would require in principle a complicated optimization procedure in multiparameter space. To a very good first approximation, however, the simulations can be performed for just the

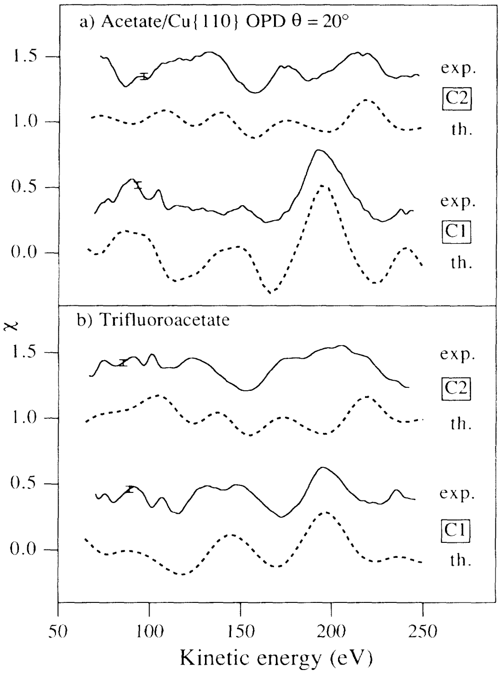

FIG. 2. Comparison of experimental photoelectron diffraction spectra ($\theta = 20°$, ⟨110⟩ azimuth) for the C1 and C2 atoms in the (a) acetate and (b) trifluoroacetate species with the best fit theoretical simulations.

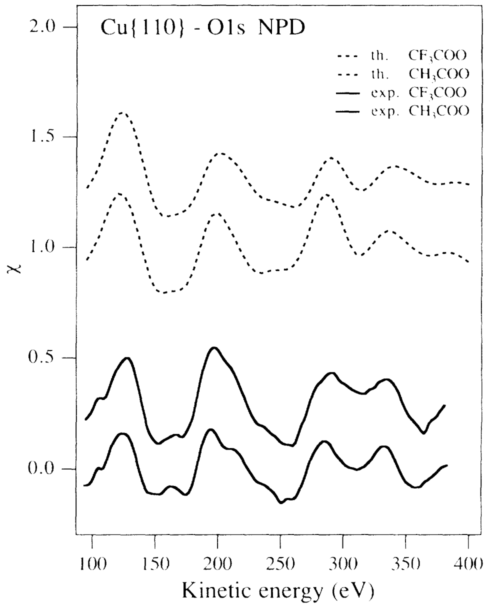

FIG. 3. Comparison of O 1s experimental photoelectron diffraction spectra ($\theta = 0°$) in the acetate and trifluoroacetate species with the best fit theoretical simulations.

emitter atom alone together with the substrate. Inclusion of the other atoms of the molecule at a later stage only shifts the position of the minimum in the reliability factor, or R factor, by ~0.5 Å and marginally improves its value. Two R factors are quoted in this work, R_p and R_m. The former was introduced by Pendry [13] for structural analysis in low-energy electron diffraction (LEED). The latter is based on that used by Shirley and co-workers [14] in their photoelectron diffraction studies, but normalized such that the value of unity corresponds to zero correlation between theory and experiment, as in the case of R_p. Thus $R_m = \sum(\chi_{\text{th}} - \chi_{\text{exp}})^2 / \sum(\chi_{\text{th}}^2 + \chi_{\text{exp}}^2)$.

The best fits to the experimental data were found for the aligned bridge site, which gives significant minima in both R factors for all emission angles measured. The normal emission acetate data of Fig. 3 give best fit values of $z(\text{O}) = 1.90$ Å, where z is the distance between the adsorbate atom and the outermost Cu layer, $d(\text{O-O}) = 2.25$ Å and a contraction of the outermost Cu-Cu layer spacing relative to the bulk of 0.03 Å ($R_p = 0.19$, $R_m = 0.18$). The corresponding off-normal data give essentially the same values (±0.05 Å) but less satisfactory agreement between theory and experiment (higher R factors). This is not unexpected since the O 1s normal emission spectrum is dominated by the almost 180° backscattering from the single underlying Cu atom; thus the interpretation is particularly clear. From the data of Fig. 2(a), $z(\text{C1}) = 2.44$ Å ($R_p = 0.35$, $R_m = 0.15$) and $z(\text{C2}) = 3.98$ Å ($R_p = 0.36$, $R_m = 0.30$). The normal emission data give identical values with comparable R factors. The data at 27° and 34° give essentially the same values (±0.05 Å) but with R factors that are generally somewhat poorer. Thus for the surface acetate species we conclude that the O-Cu bond length is 1.91 Å, the O-C-O bond angle 129°, the C-O bond length 1.25 Å, and the C-C bond length 1.54 Å. We estimate the precision for these bond length determinations to be ±0.04 Å and for the bond angle ±5°. In inorganic acetate compounds the bond angle and the C-O, C-C bond lengths are typically 119°, 1.26 and 1.50 Å, respectively [15]. From analysis of the trifluoroacetate data $z(\text{O})$ and the $d(\text{O-O})$ appear to remain as in the acetate species; $z(\text{C1})$ and $z(\text{C2})$ shift to 2.47 and 4.02 Å respectively. The r factors are somewhat worse, as might be expected from the poorer agreement seen in Fig. 2(b). Since the measured contraction in the O-C-O bond angle (~3°) is smaller than our estimate of the experimental error, we may conclude that the structural parameters of the surface acetate species do not significantly change on fluorination.

In summary, we have been able to almost completely determine the structure of a relatively large adsorbed molecule, namely, the surface acetate species which is formed as a result of a simple heterogeneous reaction. In particular, using the principle of chemical shift photoelectron diffraction it has been possible to determine *separately* the distances of the two nonequivalent carbon atoms to a copper {110} surface. This technique is likely to have considerable application in the future as attention focuses on the structure and properties of larger molecules at surfaces.

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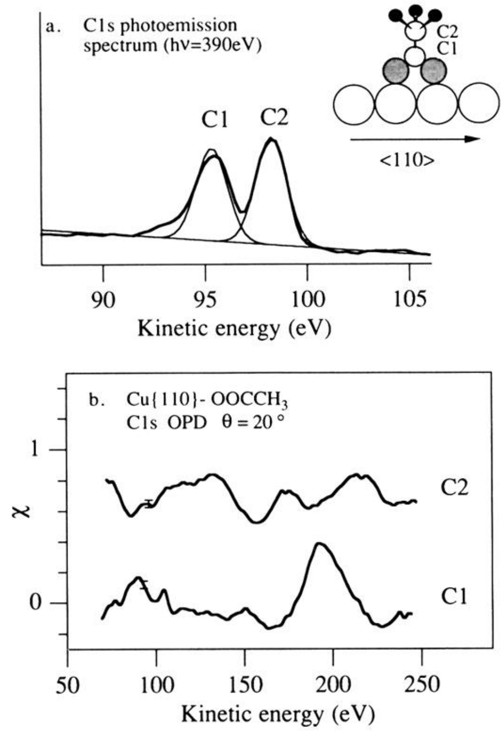

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