

The Adsorption Structure of Glycine Adsorbed on Cu(110); Comparison with Acetate/Cu(110)

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The molecular orientation of an ordered monolayer of glycine adsorbed on Cu(110) has been studied using XPS, NEXAFS, X-ray Photoelectron Diffraction, LEED and theoretical calculations. In connection, results from the related molecule acetate adsorbed on Cu(110) will be considered.

The measurements were carried out at beamline 8.0 at the Advanced Light Source (ALS), using a modified spherical grating monochromator. The experimental station, consists of two UHV chambers, one for sample preparation and one for analysis. The analysis chamber is comprised of an electron energy analyzer and an X-ray emission spectrometer, both mounted perpendicular to the incoming photon beam. It also houses a partial yield detector for X-ray absorption measurements. For the NEXAFS measurements a retarding voltage of 200 V, 300 V and 400 V was applied for the carbon, nitrogen and oxygen *K*-edges, respectively. Due to the fact that the substrate has two-fold symmetry, two Cu(110) crystals were mounted on a manipulator, rotated 90° with respect to each other. This enabled us to obtain NEXAFS spectra with the **E**-vector along the close-packed copper rows ($[\bar{1}\bar{1}0]$ -direction), perpendicular to these rows ($[001]$ -direction), and with the **E**-vector normal to the surface ($[110]$ -direction). In order to prepare the acetate overlayer, acetic acid was adsorbed at 450 K, after preadsorbing half of a monolayer of oxygen (ordered (2×1) structure) [1]. Glycine was evaporated

from a resistively heated tantalum Knudsen cell. The sample temperature was kept at 400 K during the evaporation. All the measurements were performed at room temperature.

The structure of glycine on Cu(110) was investigated through theoretical calculations at the gradient-corrected DFT level. To determine the structure full geometry optimizations were performed for glycine on a fifteen atom cluster model of the Cu(110) substrate. All degrees of freedom were completely relaxed for the adsorbate, while keeping the internal structure of the cluster model fixed.

LEED for acetic acid adsorbed on a (2×1) oxygen-covered copper surface is known to give a $c(2 \times 2)$ pattern. It is only stable for a few seconds [1]. In contrast, glycine exhibits a sharp (3×2) LEED pattern which is found to be stable for several minute.

Fig. 1 shows the O 1s and C 1s XP spectra obtained for acetate and glycine adsorbed on Cu(110). Only one symmetric O 1s XP line is observed for both adsorbates. This is a consequence of the loss of the acidic hydrogen atom in the adsorption process, which results in two identical C-O bonds. In the carbon region, two peaks are found for both adsorbates. The one at lower binding energy corresponds to the methyl group, whereas the other peak corresponds to the carbon atom of the carboxylic group.

In order to learn about the orientation of the C-C axis in the adsorbates we performed XPD. A photon energy of 1050 eV was used, giving the emitted photoelectrons

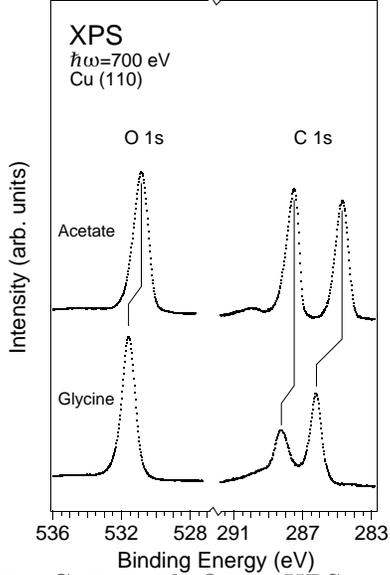


FIG. 1. C 1s and O 1s XPS spectra for glycine (bottom) and acetate (top) adsorbed on Cu(110).

a kinetic energy of around 700 eV. The carboxylic-carbon/methyl-carbon C 1s intensity ratios were measured for different polar angles along the $[1\bar{1}0]$ - and $[001]$ -directions. For acetate, the XPD-polar scan showed a distinct forward-scattering peak at normal emission, indicating a perpendicular geometry of the C-C axis with the carboxylic group closest to the surface. On the other hand, the glycine XPD spectra showed no pronounced features indicating that the molecular C-C axis is highly tilted.

Turning to the NEXAFS data we will start by considering acetate/Cu(110) shown in Fig. 2. The absorption data gives rise to three clearly different spectra indicating that the adsorbate is azimuthally ordered on the surface. In both the C and O spectra the π -resonance is observed with maximum intensity in the $[001]$ -spectrum. This shows that the molecular plane of the carboxylic group is oriented along the $[1\bar{1}0]$ -azimuth.

In the $[110]$ - and $[1\bar{1}0]$ C K -edge spectra we observe two shape resonances, σ_1 and σ_2 . These resonances are associated to the carboxylic group of the molecule and are also found for formate/Cu(110). At a photon

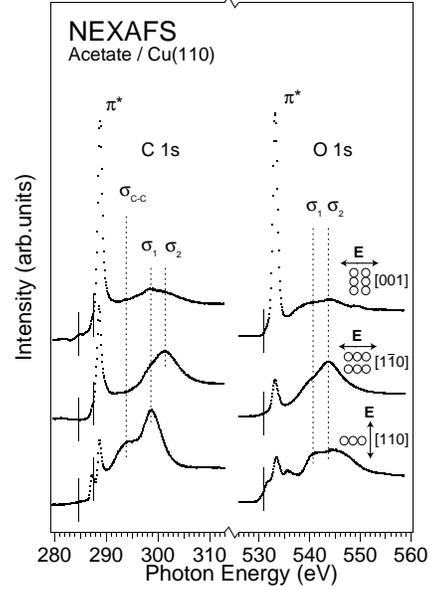


FIG. 2. C 1s and O 1s NEXAFS data obtained for acetate/Cu(110).

energy of 288 eV we observe a sharp state prior to the π -resonance in the carbon $[110]$ -spectrum. This state is associated with the C-H bonds. Finally, the σ -resonance corresponding to the C-C bond is observed in the $[110]$ -spectrum, at 294 eV.

In the oxygen spectra, a relatively sharp σ -resonance is observed at 543 eV in the $[1\bar{1}0]$ -spectrum. In the $[110]$ -spectrum, only a broad distribution of σ states is observed.

Again, this is similar to formate and could thus be assigned to the carboxylic group. In addition, there is a new transition, which we denote σ_1 , at 540 eV. This resonance is found to be most intense in the $[110]$ -spectra and arises from a splitting of the σ -system, caused by the interaction of the adjacent C-C and C-O groups [2]. Hence, the C resonance marked σ_{c-c} in Fig. 2 corresponds to the O resonance marked σ_1 .

From the above considerations, it is clear that acetate adsorbs in a perpendicular geometry, with the molecular plane oriented along the $[1\bar{1}0]$ -azimuth of the substrate, bonding to the surface via the oxygen atoms.

We now turn to the NEXAFS spectra for glycine adsorbed on Cu(110), shown in

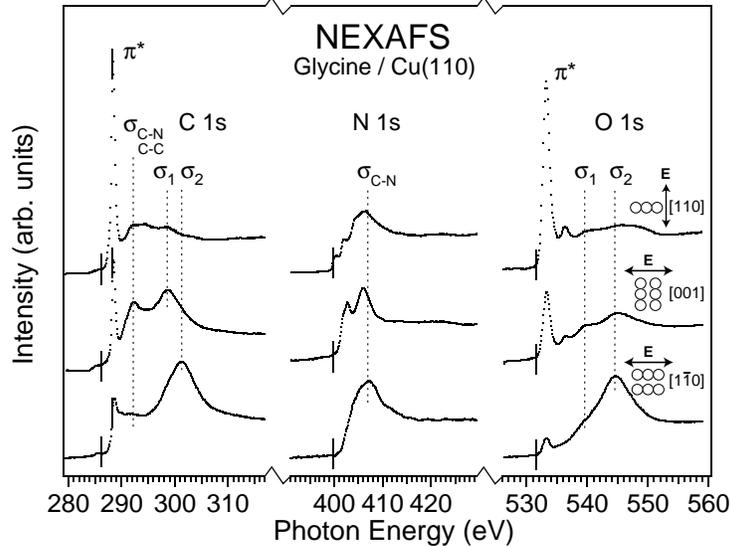


FIG. 3. O 1s, N 1s and C 1s absorption spectra of glycine adsorbed on Cu(110).

Fig. 3. Starting with the oxygen spectra, the π -resonance is observed with maximum intensity in the [110]-spectrum. In accordance with the XPD results, this indicates a highly tilted geometry of the carboxylic group. Shape resonances are found mainly in the $[1\bar{1}0]$ spectrum but also in the [001] spectrum. This is expected for an adsorption geometry where the molecular plane is close to parallel to the surface.

The spectral features can be understood in the same manner as discussed for acetate. Hence, the σ_2 -resonance corresponds to the shape resonances associated with the carboxylic group, whereas the σ_1 -resonance can be viewed as the oxygen contribution to the C-C derived resonance.

In the carbon spectra, two shape resonances associated to the C-C and C-N bonds are in principle expected to appear in the spectra. The interaction between the corresponding σ -orbitals will however result in new hybrid orbitals. Since they are both single bonds, the energies of the bond-prepared “localized” components are expected to be nearly degenerate. The relative weight on the respective hybrid orbitals will be almost equal, making it difficult to distinguish the two resonances from each other.

The contribution from the C-C bond to the σ -resonance arising from interaction between the two adjacent single bonds is expected to appear mainly in the C K [001] absorption spectrum. Inspection of this spectrum reveals that this indeed is the case. As discussed above, it will also contain a strong C-N σ -resonance contribution. We note that there is no enhanced intensity due to this resonance in the $[1\bar{1}0]$ spectrum. This indicates that also the C-N axis predominantly is oriented along the [001]-direction.

In order to identify the σ -resonance arising from the C-N bond in the N spectra it is useful to first consider the N-H resonances in more detail. In free ammonia the $2e$ derived transition is known to consist of two degenerated orbitals, e.g., the N $2p_x$ and N $2p_y$ derived orbitals. When going to methylamine the degeneracy will be lifted and one of the orbitals will constitute the antibonding σ -resonance arising due to the formation of the C-N bond. The other orbital will consequently preserve its pure N-H character. For an oriented adsorbate we would expect very little intensity corresponding to the N-H resonance in a geometry where the \mathbf{E} -vector is close to parallel to the intramolecular axis. Inspection of the N K data re-

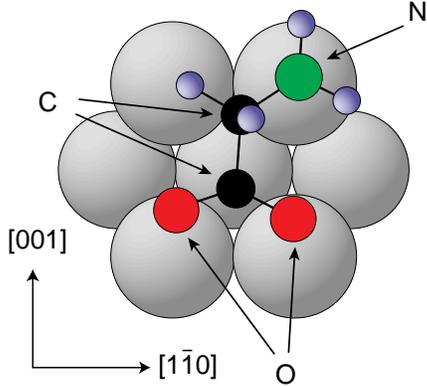


FIG. 4. The optimized adsorption geometry of glycine/Cu(110).

veals that very little intensity corresponding to the N-H resonances in the $[1\bar{1}0]$ -spectrum is present. In the other spectra clear evidence of N-H resonances are observed. Based on these considerations we find it plausible that the broad feature at around 406 eV in the $[1\bar{1}0]$ -spectrum corresponds to the σ -resonance arising from the C-N single bond. We note that in contradiction to the results derived from the C K spectra, where a linear C-C-N configuration was predicted, the N K results indicate that the C-N bond is likely oriented near parallel to the close packed copper rows, i.e., the $[1\bar{1}0]$ -direction.

The starting guess for the geometry optimization was based on qualitative considerations resulting from the experimental data. Thus, the molecule was assumed to span two $[1\bar{1}0]$ rows with the oxygens in equivalent near-on-top positions and the amino group binding to the next row; the C-C-N angle was assumed to correspond to sp^3 hybridization with the $-\text{CH}_2-$ group over the trough between the rows. A model of the optimized structure is given in Fig. 4.

As discussed above, two different adsorption structures can be deduced from NEXAFS: the carbon spectrum could be interpreted as favoring a linear C-C-N structure, while the N absorption spectra seems to indicate a bent C-C-N configuration, much like the optimized structure shown in Fig. 4. In

order to resolve the question of which of the two structures will be favored on the surface we have optimized the structure also starting from the alternative structure that seems to be indicated by the C K data. The result of the optimization is a slow return of the molecule to the bent structure that was the result of the original optimization. No barrier was observed as the oxygens moved from the bridge positions to the favored positions closer to on-top. The energy difference (0.4 eV) between the two proposed structures is not large, but, particularly in combination with the fact that the structure indicated by the carbon absorption data turned out not to be a minimum structure, this is sufficient to allow the conclusion to be drawn that the structure of Fig. 4 should be preferred.

To summarize, it seems that from NEXAFS alone both structures could be supported. Since the structure suggested by the interpretation of the C-C and C-N resonance structures in the C spectra is shown, through the theoretical simulations of the adsorbate structure, not to correspond to a minimum on the energy surface we must exclude this structure. Instead the proposed structure is that of Fig. 4 which was originally obtained through a combination of qualitative results from the experimental data and the theoretical calculations of the adsorbate structure

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 - [2] J. Stöhr, *NEXAFS Spectroscopy* (Springer-Verlag, Heidelberg, 1992).