Chapter 5

Structural investigation of a chiral adsorbate: α-alanine on Cu(110)

The manner in which biologically active molecules, such as proteins, peptides, etc. bind to surfaces is of relevance due to a number of applications such as the development of biosensors and biocompatible materials. The structure, conformation and local order of these molecules upon adsorption influence their interaction with further incoming species and the process of molecular recognition. Many of these complex molecules are made up mainly of α-amino acids (in which the amino group, NH_2, is bonded to the so called α-carbon; see description in the following section). Therefore the usual surface science approach to understand their essential interaction with inorganic surfaces has been initially to study model systems consisting of these smaller units adsorbed on metal surfaces. However, and in spite of the interest of these biological molecules and the growing importance of the technologies based on them, only a few α-amino acid/metal systems have been investigated so far. Most of these studies have been devoted to the adsorption of glycine (NH_2CH_2COOH) on Cu surfaces. Glycine is not only the simplest of the α-amino acids but also the only one that is non-chiral [1]. Therefore, the natural step forward in this bottom-up approach would be to study the adsorption of the simplest chiral amino acid, alanine (NH_2CHCH_3COOH).

Moreover, the study of the adsorption structure of chiral substances on surfaces is significant for heterogeneous enantioselective catalysis. This kind of catalysis is based on the use of chiral substances as *modifiers* of conventional metallic catalysts to achieve what is called *enantioselectivity*, that is, to attain catalytic production of pure *enantiomeric* forms (or *enantiomers*[2]) of a certain molecule. This is important in particular for the pharmaceutical industry. The reason for this is that most of the pharmaceutical drugs are chiral, and opposite enantiomers of the same substance interact quite differently with

[1] A chiral molecule is a molecule that is distinguishable from its mirror image in the same way that left and right hands are distinguishable

[2] The two forms of a chiral molecule which are mirror image of each other. These two enantiomers are denoted with the prefixes R- and S- according to the CIP rules (see page 80)

living organisms. This has sometimes led in the past to tragic consequences[3] that could be avoided by the production of optically pure chiral molecules.

One example of how heterogeneous enantioselective catalysis works is the asymmetric hydrogenation of methyl-acetoacetate ($CH_3COCH_2COOCH_3$) over modified Ni surfaces. When performing the reaction over the unmodified metal, both types of hydrogen addition can occur, leading to a racemic product mixture, in which both enantiomeric forms of the resulting methyl-3-hydroxybutyrate ($CH_3CH(OH)CH_2COOCH_3$) are present. However, when the Ni surface is modified either by R,R-tartaric acid ($COOH(CHOH)_2COOH$) or by S-alanine, the reaction is "enantiodirected" to give, almost completely, the R-product. That is, adsorption of a chiral substance lends chiral character to the metal surface, leading to different activation energies for the two enantiomers, and therefore, to the preferential formation of only one of them. It is therefore believed that enantioselectivity is due to the manner the modified surface aligns the reactants so that the reaction is effected along one selected direction. Thus, the structure of the active site is intricately involved in the determination of enantioselectivity.

Additionally, it would be very convenient to have available physical methods to distinguish between both enantiomers of the same substance. The accustomed procedures used to determine the configuration of chiral molecules in solution (such as the difference between absorption coefficients for left and right circularly polarised light) tend not to work when diluted species are probed. This is mainly due to the relative weakness of the physical effect on which these methods are based. In the case of randomly orientated chiral molecules in the gas phase, it has recently been proved [150] that differences in core level photoelectron intensities for right and left circularly polarised light can be related to the chiral geometry of the molecule. This effect is opposite for the two enantiomers of the same molecule. However, in the case of a molecule adsorbed on a surface, and therefore fixed in space, there are some other 'sources' of CDAD, as we discuss in section 5.5. Therefore, to use CDAD as a tool to differentiate enantiomers of the same molecule, it would be necessary to be able to discriminate between the CDAD effect due to adsorbate chirality from that due to other effects. This implies that knowledge about how these molecules are oriented on the surface is needed.

The intention of the present work was to gain a deeper understanding on how these organic chiral molecules bind to surfaces. Therefore we have studied the local adsorption structure of the model system formed by the adsorption of α-alanine on a Cu(110) surface by means of the photoelectron diffraction technique. The obtention of this piece of structural information is also relevant to the application of CDAD to characterise opposite enantiomers of chiral molecules adsorbed on surfaces.

[3]At the end of the 50's, a drug called thalidomide was introduced in the market as a non-addictive sedative which was prescribed to pregnant women to combat morning sickness. Three years later it was withdrawn from the market as responsible for an estimated 10,000 to 20,000 babies born with limb malformation and other severe birth defects. One enantiomer of the drug was responsible for producing the birth defects, while the other enantiomer produced the sedative effect.

5.1 α-alanine: A chiral amino acid

Any organic acid which possesses one or more amino (NH_2) substituents may be classified as an amino acid. From this potentially vast array of compounds, only a relatively small group of about 20 α-amino acids are commonly found to form part of proteins (the imino acids proline and hydroxyproline in which the primary amino group is replaced by a secondary imino group (NH) present in a aromatic ring also occur in proteins). All α-amino acids consist of a basic amino group (-NH_2), an acidic carboxyl group (-COOH), and an organic radical group or side chain (R), which is unique to each amino acid. These three groups are attached to the same tetrahedrally-bonded carbon atom, called the α-carbon. The α-carbon is bonded in addition to a H atom (see Fig. 5.1). The properties common to all α-amino acids are due to the relative special arrangements of the carboxyl and amino groups, either or both of which could potentially be involved in the bonding to a surface, while the physical and chemical properties unique to each amino acid are the result of the structure and chemical properties of the side chain.

The general formula of an α-amino acid can be written as $NH_2CHRCOOH$. The simplest of all possible α-amino acids occurs when the side chain, R, consists only of a H atom. In this case, the corresponding molecule, glycine, is non-chiral. Chirality[4] is a geometric property; a chiral object and its mirror image are non-superimposable by any translation or rotation. For this to hold, the chiral object cannot possesses any inversion centres. When R is a more complicated side chain the α-carbon becomes an asymmetric centre (chiral centre) of the molecule allowing the existence of two distinguishable mirror or enantiomeric forms, the so called enantiomers[5] (see Fig. 5.1). Molecular enantiomers have identical chemical properties, except in their chemical reaction with other non symmetric molecules and with polarized light. Indeed, with the exception of glycine, all α-amino acids (in aqueous solution) can rotate the plane of polarised light passing through them. Any material which rotates the plane of the polarised light is termed *optically active*. Opposite enantiomers of the same optically active substance rotate the polarised light in opposite directions by the same amount[6].

Different nomenclatures exist to refer to opposite enantiomers of a molecule, which occasionally cause confusion and can even lead to important misunderstandings. In order to clarify this point, we describe in the next paragraphs the different conventions used in the literature to label distinct enantiomers. In the older literature, the enantiomers of sugars and amino acids were designated with the prefix *d* or *l* in order to show whether the compounds exhibited *dextrorotation* (i.e. they rotate the plane of polarised light clockwise) or *levorotation* (when the rotation is counter-clockwise).

However, these empirical designations were abandoned when it was realised that all α-amino acids (as well as all carbohydrates) have the same geometrical configuration

[4]From the Greek word for hand; term first introduced by Lord Kelvin in 1904

[5]From the Greek word for opposite

[6]In 1848 Pasteur separated the two optically active components of tartaric acid and suggested that they were mirror images of each others

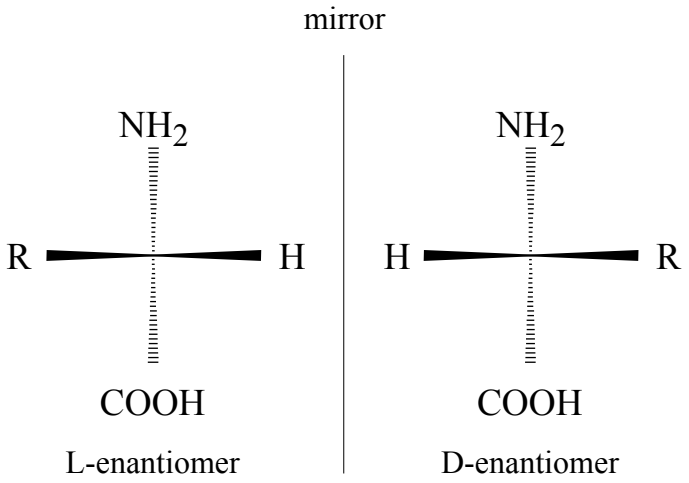

Figure 5.1: The two enantiomers of a general α-amino acid. The four bonds to the tetrahedral α-carbon make a cross at the intersection of the horizontal and vertical lines. The two horizontal bonds are directed towards the viewer, while the two vertical bonds are pointed away from the viewer.

around the asymmetric α-carbon atom. When the central chiral carbon atom is held so that both amino and carboxylic groups are pointing away from the observer and the amino group is in the "12 o-clock position" (as shown in Fig. 5.1), all the α-amino acids involved in the building of proteins have been shown to have the side chain on the left, and are all denoted with the letter L (from the Latin word *laevus* which means left). The corresponding opposite enantiomers have the side chain on the right side, so they are named with the letter D (from the Latin word *dexter* which means right). Nevertheless, this new convention proved to be rather confusing, since the D and L are similar to the *d* and *l* of the previous nomenclature based on the sense the polarisation plane of light is rotated. The confusion arises since some L-amino acids, like L-alanine, L-arginine, L-aspartic acid, L-glutamic acid, L-lysine, L-valine and others, rotate the polarisation plane of the light to the right, while some others, like L-leucine, L-serine, L-tryptophan, etc, are levorotatory or dextrorotatory depending on the pH of the aqueous solution. Furthermore, the L/D system becomes even more ambiguous for more complicated organic molecules which have two or more tetrahedral carbon atoms or *stereogenic*[7] centres.

A final solution to this ambiguity was devised by R.S. Cahn, C.K. Ingold and V. Prelog. The CIP system of nomenclature assigns a prefix (R or S) to each stereogenic centre in a molecule, according to whether its configuration is right- or left-handed. The assignment of these prefixes depends on the application of two simple rules. The *sequence rule* assigns sequence priorities to the four substituents by looking at the atoms attached directly to the stereogenic carbon atom. The higher the atomic number of the immediate substituent

[7]A stereogenic centre is a place within a molecular entity that may present differences in the spatial arrangement of atoms around it without causing any differences in connectivity or bond multiplicity between isomers. Note that a stereogenic centre do not have to be a chiral centre. *Stereomers* not related as mirror images are called *diastereomers*

atom, the higher is its priority. If different isotopes of the same element are connected to the tetrahedral carbon their priorities are assigned according to their atomic mass. When two substituent groups have the same immediate substituent atom, the atoms that are bonded further away from the tetrahedral carbon are evaluated progressively according to their atomic numbers until a difference is found. If double or triple bonded groups are encountered as substituents, they are treated as an equivalent set of single-bonded atoms. Once the relative priorities of the four substituents have been determined, the *viewing rule* states that the tetrahedral carbon must be viewed from the side opposite to the lowest priority group. If a curved arrow drawn from the # 1 position to the # 2 location without crossing the position # 3 (see Fig. 5.2) turns in a clockwise manner, the configuration of the centre is classified as R (from the Latin *rectus* for right-handed). If the turn is counter-clockwise, the configuration is S (from the Latin *sinister* for left-handed).

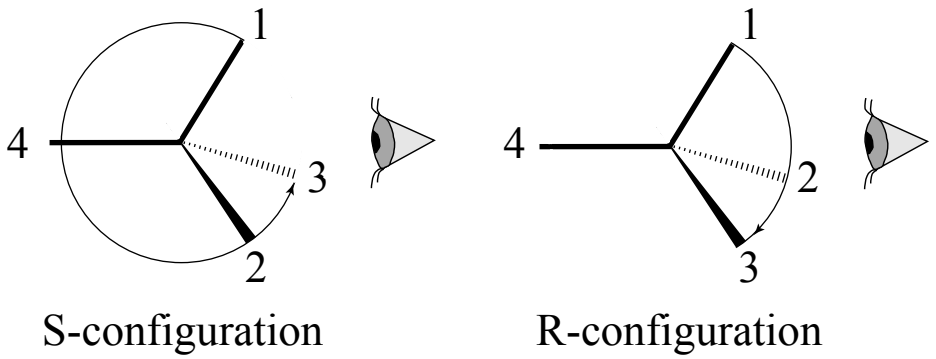

Figure 5.2: Application of the viewing rule to opposite stereogenic centres.

The application of these rules to both enantiomers of α-alanine is shown in Fig. 5.3. According with the sequence rule, the amino group has the highest priority, followed by the carboxylic group, the methyl group, and the H atom, which is the lowest priority substituent. If a viewer is now placed as established by the viewing rule and curved arrows are depicted from the amino group to the carboxylic group and then to the methyl group, the α-carbon for L-alanine has clearly an S configuration, and the corresponding centre for D-alanine presents the opposite R-configuration. As for alanine, most L-enantiomers of α-amino acids have an S-form according to the CIP nomenclature. Only in the case of L-cysteine does the arrangement at the central carbon have an R-form. The side chain of cysteine contains a sulphur atom, which gives it a higher priority than the carboxyl group. Although the consistency of the relative arrangement of substituents provided by the L/D designation has led to the general retention of this nomenclature in the case of α-amino acids (as well as for sugars), in the following we will used the CIP nomenclature to refer to the different alanine enantiomers.

As stated earlier, the simplest chiral amino acid is α-alanine (NH_2CHCH_3COOH), the side group consisting of a methyl group (-CH_3). We have shown above that depending on how the methyl group is arranged with respect to the so called C-C back-bone of the

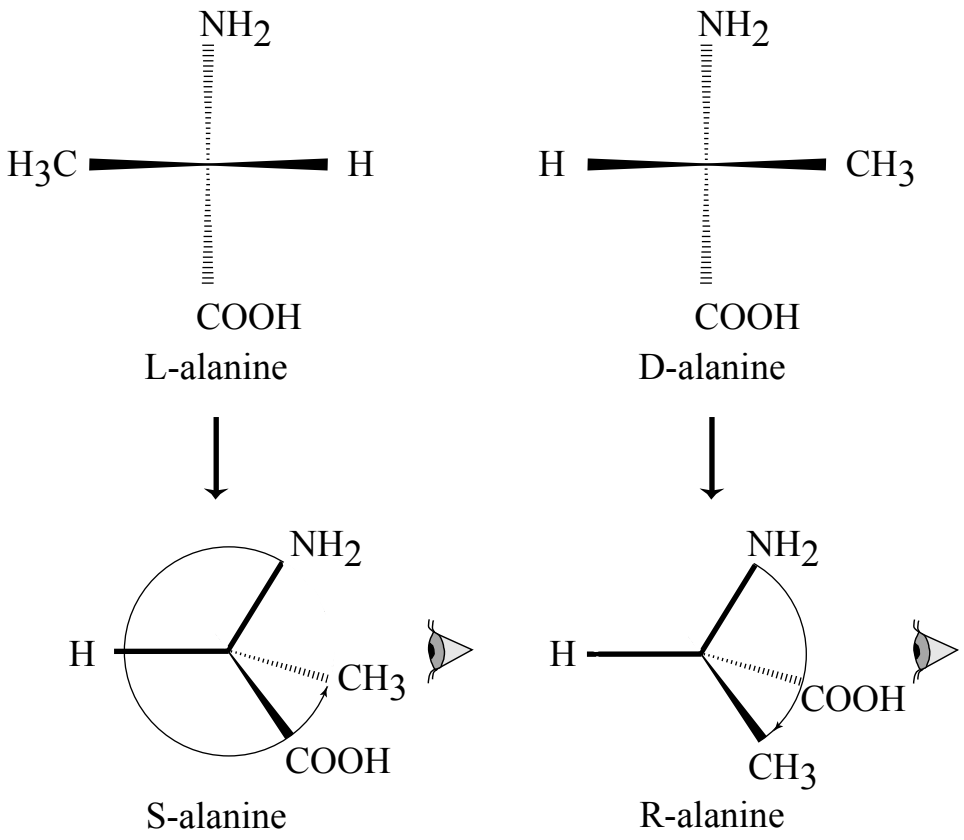

Figure 5.3: Different nomenclatures for both enantiomers of α-alanine.

molecule (the bond between the α-C and the C atom of the carboxylic group), two different enantiomers are possible, S(or L) and R(or D). Both enantiomers of α-alanine occur in nature, although only the S-form has been found to be involved in building proteins. α-alanine is an aliphatic molecule that can have different geometric and electronic structural forms due to the range of inter- and intramolecular interactions that are accessible for it. In the solid phase, the monomer species exists in the so called *zwitterionic* form ($^{+}H_3NCHCH_3COO^{-}$), in which a proton is transferred from the carboxylic acid to the amino group. In solution cationic ($^{+}H_3NCHCH_3COOH$), anionic ($NH_2CHCH_3COO^{-}$) and zwiterionic forms are all found depending on the pH of the surrounding media. In the gas phase, the thermodynamics of gaseous alanine favour the neutral molecular state.

In the following we will refer to the α-alanine molecule simply as alanine, but we should bear in mind that the present work concerns itself with the *alpha* form of the molecule and not with its *beta* counterpart ($NH_2CH_2CH_2COOH$), in which the amino group is no longer bonded to the α-carbon, but to the next C atom in the chain, which is called the β-carbon.

5.2 Adsorption structure

Although the first studies of the adsorption of alanine on metals date back nearly 30 years [151, 152], there have not been many studies since then [153–158]. Most of these studies deal with the adsorption of alanine on Cu substrates [151, 154–158]. On Cu(111), Cu(001) and Cu(110) surfaces alanine has been shown to create ordered overlayers. In all cases studied, the amino and the carboxylic group were found to be involved in the bonding to the metal, with the methyl group pointing away from the metal except in the cases of alanine adsorbed on silver colloid particles [153] and on Cu(001) [156], in which it has been speculated that the methyl group is directed towards the surface.

To our knowledge there are only two published studies of the adsorption of alanine on a Cu(110) surface [155, 157] (although there are apparently another two in preparation [159]). The results of these investigations have been reviewed recently in a report on adsorption of complex organic molecules at metal surfaces by Barlow and Raval [159].

Reflection absorption infrared spectroscopy (RAIRS) [155] showed that exposure of S-alanine to the Cu(110) at room temperature led to deprotonation of the carboxylic acid group. This was deduced from the absence in the RAIRS spectra of the ν(C=O) stretching vibration, which would be expected to be intense, and from the appearance of vibrations attributable to the COO^- group. The nature of the group containing the N atom is, however, more difficult to determine on the basis of these RAIRS data since both NH_2 and NH_3 are known to show deformation vibrations which are difficult to distinguish unambiguously. However, Barlow and Raval mentioned that a N 1s binding energy between 399.5 and 399.9 eV has been measured, which is claimed to be consistent with the presence of a NH_2 unit, since the $NH_3{}^+$ group displays a N 1s binding energy which is almost 2 eV higher [160, 161]. This would imply that alanine adsorbs as alaninate ($NH_2CHCH_3COO^-$) on the Cu(110) surface.

In this low coverage phase, only two of the three vibrational modes expected from the COO^- group in the mid-infrared region were observed, the symmetric ν_s(OCO) stretch and the δ_s(OCO) scissoring deformation. Bearing in mind that the local dipole moment of the asymmetric stretching is aligned along the O-O axis, the absence of the ν_{as}(OCO) stretch indicated that both O atoms in the carboxylate group are placed equidistant to the Cu surface. Similarly, it was deduced that the NH_2 plane is almost parallel to the surface and that the CH and CH_3 units are held at an angle away from the surface normal, with the CH and C-CH_3 bonds having large components parallel to the surface. The approximate local adsorption geometry of this low-coverage alaninate species is shown in Fig. 5.4.a.

As the coverage of alanine was increased, new bands in the infrared spectra appeared, while those already existing at low coverage remained the same. This behaviour was explained by the presence of a new alaninate species differently bonded to the surface, which coexisted with the species present in the low-coverage phase. The development of a band ascribed to the asymmetric OCO stretching mode indicated that the new alaninate molecules have their COO^- group with a sideways-tilted orientation. The two O atoms of

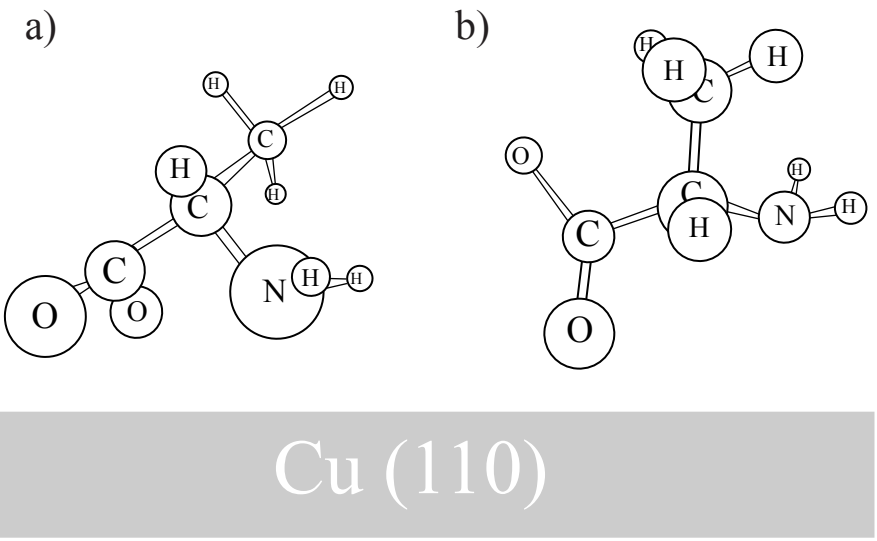

Figure 5.4: a) low-coverage S-alaninate species; high-coverage S-alaninate species (as proposed in reference [155]

the carboxylate are no longer equidistant to the surface and the carboxylate is proposed to be monodentate. The amino group of this new species is largely (but not entirely) held with its plane parallel to the surface. The vibrations associated with the CCN stretches do not increase in intensity after adsorption of the high-coverage alaninate species, which may imply that the C-N bond of this second species is not directed towards the surface. The methyl group is concluded to be reoriented to be more nearly normal to the surface, although it is not aligned completely along the surface normal (see Fig. 5.4.b).

The annealing of this disordered high coverage phase in the temperature range 420-460 K leads to a (2 -2, 5 3) LEED pattern [157], which can be seen in Fig. 5.5. On the basis of RAIRS data (not yet published [159]), the authors suggest that this phase consists of both orientations of alaninate described above. As depicted in Fig. 5.6, the two alaninate species would be arranged in groups of six or eight molecules through a network of H-bondings interactions which occurs at two levels. Between alaninate molecules with the same orientation, the bonding is formed via lateral N-H to O bonds, involving the amino group of one molecule and the carboxylate of the neighbouring molecule. For alaninate molecules differently orientated, transverse C-H to O bonds are formed, which involve the upwards tilted oxygen of the monodentate carboxylate and the CH_3 groups of a molecule in a neighbouring row. The manner in which the alaninate molecules self-organize on the Cu surface generates a unique growth direction that is not coincident with either of the major direction of the Cu(110) surface. This destroys the two mirror planes of the face centered cubic (110) surface, creating a truly extended "handed" surface which cannot be superimposed on its mirror image. Thus, the (2 -2, 5 3) phase is chiral at both local and global levels. STM data [157] show that the 2D order of the S-alaninate on Cu(110) extends over distances larger than 400 Å.

Adsorption of R-alanine in the same conditions is found to switch the global organi-

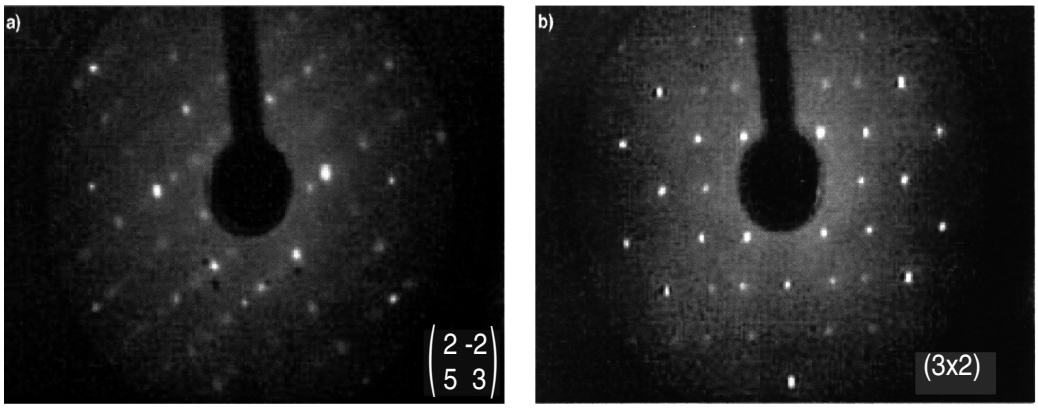

Figure 5.5: LEED patterns corresponding to the two S-alaninate structural phases (data taken from [157])

sational chirality of the modified surface to form the mirror (5 -3, 2 2) structure [157].

Upon heating the (2 -2, 5 3) phase to temperatures above 460 K, the LEED pattern converts into a (3x2) structure with some missing half-order diffracted beams (Fig. 5.5). This absence of half-order spots in the LEED pattern cannot be related to the existence of a true glide plane as has been argued for glycine adsorbed on Cu(110) ([5] and references therein). For a chiral amino acid only homochiral domains are possible, so the presence of mirror-image molecular adsorbates required for a true glide line cannot occur. However, STM images [159] are consistent with there being two alaninate molecules placed within the (3x2) mesh, so that the mirror plane of the substrate must be transformed into a pseudo-glide plane. For this phase, the IR band associated to the asymmetric OCO

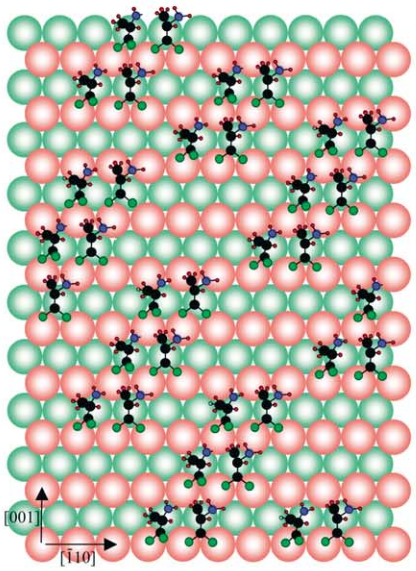

Figure 5.6: Schematic of the (2-2, 5 3) S-alaninate structure as suggested in [159]

stretching mode completely vanishes[8], which suggests that all the alaninate molecules adopt the local structure in which the carboxylate is bidentate.

We have studied by means of the photoelectron diffraction technique the local adsorption structure of the (3x2) phase formed by the adsorption of S-alanine on Cu(110). Our intention was to investigate the possible structural differences between this system and the previously studied glycine/Cu(110) [5, 162, 163] system. A potential source of difference is the presence in the alanine molecule of a methyl group as a side chain. This could affect both the local adsorption geometry of the molecule on the Cu substrate and the manner in which the molecules self-arrange on the surface upon adsorption.

5.2.1 Description of the experiment

The Cu(110) crystal was cleaned in situ by several cycles of Ar ion bombardment followed by brief annealing to 800 K. Since the vapor pressures of amino acids are of the order of 10^{-10} Torr at room temperature and become appreciable at temperatures below the decomposition temperature, they can sublime without being decomposed, which make them suitable for vapor deposition. Alanine powder of 99% of purity was obtained from the firm Sigma-Aldrich[9]. S- and R-enantiomers were mounted in two different home-made ovens in which the alanine powder is placed inside a glass cylinder which has one of its ends capped with a tantalum piece to prevent the powder from falling out. A K-thermocouple was attached to this tantalum piece to measure the dosing temperature. The glass tube is contained within a ceramic cylinder heated by passing a current through a copper wire coiled around it. The purpose of this ceramic tube is to make the heating homogeneous. The ovens containing the alanine powder were placed in two differentially pumped six-way crosses separated from the main chamber by gate valves, so both enantiomers of the molecule could be dosed independently. Cu gaskets with a 7 mm diameter hole were placed between the alanine sources and the gate valves, so that the alanine fluxes could be collimated. This limits the pressure rise in the experimental chamber during dosing.

In order to prepare an S-alaninate overlayer, the source was first heated to a temperature around 350 K and the Cu substrate was kept at a temperature within the range of 400 to 430 K. The Cu crystal was placed facing the gate valve to the corresponding doser chamber. When the temperature of the alanine was seen to be stable the gate valve was opened. It was found that to achieve a saturated alaninate overlayer, as judged by monitoring the heights of the O 1s, N 1s and C 1s photoemission peaks, the crystal had to be exposed to the alanine flux for about 30 minutes. After this dosing procedure the surface presented a clear (2 -2, 5 3) LEED pattern. Since the alaninate overlayer was found to be rather sensitive to electron beam induced damage, further adsorbate overlayers were checked by comparing the photoemission peak heights and shapes of the O 1s, C 1s and N 1s core levels with those corresponding to a preparation for which a

[8] Raval, private communication

[9] S-alanine product number: A2,680-2; R-alanine product number: 16,265-5

(2 -2, 5 3) structure was observed. Brief annealing (around 5 min) of this (2 -2, 5 3) overlayer at a temperature of 470 K changed the LEED pattern into an (3x2) phase. This is accompanied by changes in photoemission from the core levels, in particular in the case of C 1s photoemission, as can be seen in Fig. 5.7. At temperatures of 500 K the LEED pattern became a (1x1) corresponding to the Cu(110) clean surface.

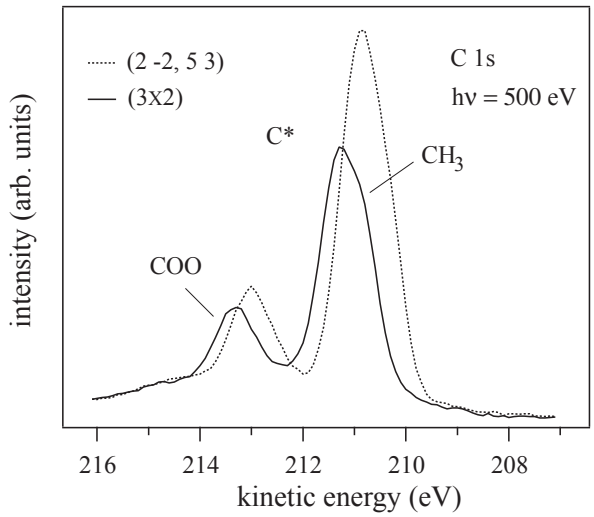

Figure 5.7: C 1s photoemission spectra corresponding to the (2 -2, 5 3) phase (dashed line) and the (3x2) phase (thin line). C* denoted here the α-carbon.

The application to the other alanine enantiomer (R-alanine) of the dosing procedure described above produced the mirror (5 -3, 2 2) LEED pattern. After brief annealing of this surface phase, a (3x2) LEED pattern similar to that obtained for S-alanine under the same conditions was observed.

The PhD spectra were measured at the undulator beamline UE56-2 at the BESSY II synchrotron radiation facility in Berlin, whose undulator gap can be stepped synchronously with the spherical grating monochromator. This allowed the use of the peaks of the first and third harmonic undulator radiation throughout the measurement of the energy-scanned O 1s photoelectron diffraction spectra and of the N1s and C 1s photoelectron diffraction spectra, respectively. The alaninate overlayers were stable over long periods (6 to 8 hours), so that several PhD spectra could be measured for each preparation.

5.2.2 Structure determination

In order to investigate the adsorption structure of S-alaninate on Cu(110), a total of 15 N 1s and O 1s photoelectron diffraction spectra were measured in all four principal azimuths at different polar emission angles. The PhD spectra were integrated and normalised as detailed in chapter 2. The resulting modulation functions are shown in figure 5.8. A striking feature of these data is the large difference in the modulation amplitudes shown by the PhD spectra corresponding to the N 1s and O 1s core levels. While the N 1s

PhD spectra show rather large modulations near normal emission, those spectra corresponding to the O 1s core level have much weaker amplitudes. As has been explained in chapter 2, strong modulations are commonly due to the presence of a scatterer atom right behind the emitter relative to the emission direction. This implies that the N atom most probably occupies a site on top of one of the Cu substrate atoms. Moreover, the weak modulation amplitude shown by the O 1s PhD spectra indicate that the oxygen atoms adsorb in low symmetry sites, and possibly even in two or more inequivalent sites.

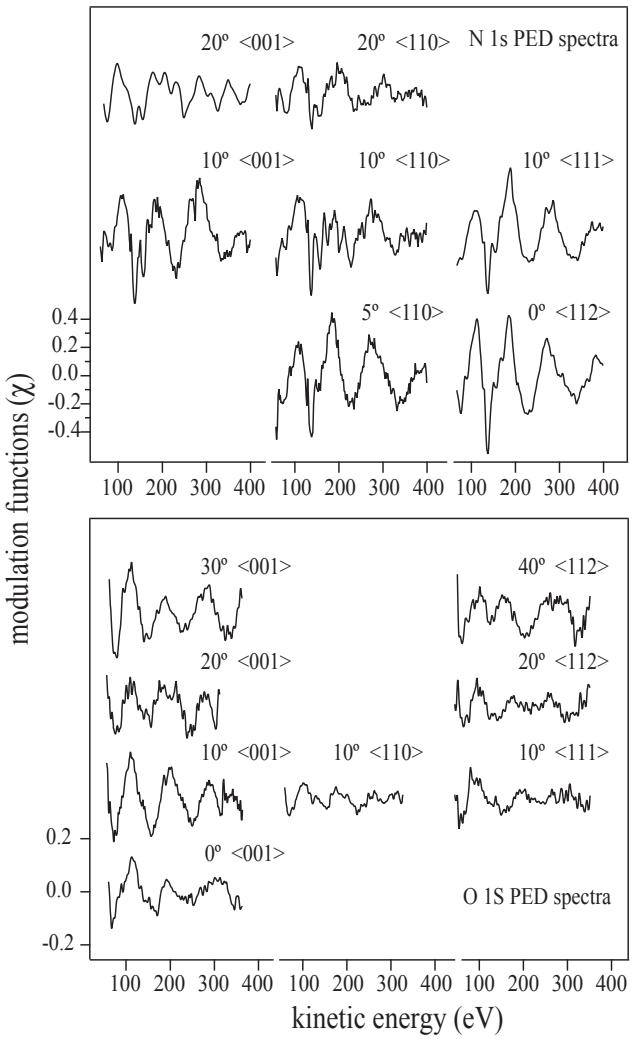

Figure 5.8: N 1s and O1s PhD spectra measured from the (3x2) created by the adsorption of S-alaninate on Cu(110)

PhD measurements were also attempted using the C 1s core level peak. However, while the spectral resolution did allow separation of the carboxylic C, it was not good enough to fully separate the two component peaks corresponding to the α-carbon and the C atom in the methyl group, so reliable curve-fitting for these components could not be achieved through the whole energy range in which the C 1s PED spectra were measured. Fig. 5.9 shows two C 1s PhD spectra corresponding to the carboxylic C measured at

normal and at 40 off-normal emission. As can be clearly seen, the modulations are rather weak. This can be attributed to the fact that the carboxylic carbon may be (at least) more than 4 Å away from the nearest neighbour Cu scatterer. No further analysis of the C 1s PhD spectra was performed.

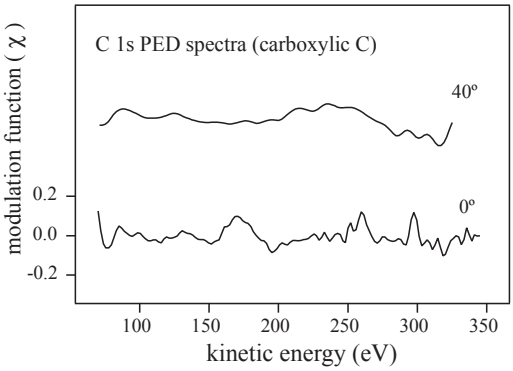

Figure 5.9: C 1s PhD spectra measured from the carboxylic C of the (3x2) S-alaninate phase

Projection method results

To gain a first order indication of the adsorption site of the N and O atoms the projection method described in chapter 2 was used. The result of applying this procedure to the N 1s and O 1s PhD spectra is shown in Fig. 5.10 and Fig. 5.11, respectively. The upper panel of Fig. 5.10 show sections perpendicular to the surface in the [001] and [1$\bar{1}$0] azimuths where the emitter is placed at (0,0,0). The slightly diffuse features that can be seen in both plots suggest the possibility of an atop adsorption site with small offsets in both crystallographical directions. This is corroborated by the slightly broad feature that appears in the section parallel to the surface cut at a 2.08 Å distance below the emitter (lower panel). This finding agrees with our prior suggestion based on the large modulation amplitude shown by the N 1s PhD spectra.

The interpretation in the case of the oxygen atoms is slightly more complex. The cut taken perpendicular to the surface plane in the [001] azimuth (upper right panel Fig. 5.11) implies an atop adsorption configuration but with a large offset along the [001] azimuth. Notice that the appearance of two features can be attributed to the two symmetrically equivalent domains included in the calculation and not to the presence of two equally spaced substrate nearest neighbours. The upper right panel of Fig. 5.11 shows the corresponding perpendicular cut along the [1$\bar{1}$0], which indicates that the O emitter is also slightly offset from the atop position in this direction. The lower panel of Fig. 5.11 shows the section parallel to the surface at a depth below the emitter of 1.68 Å. This indicates the offset of the position of the O emitter along the [001] azimuth to have a value around 1.0 Å. Note again that the two features are due to the two symmetric equivalent domains (in fact, the distance between them is around 2.0 Å , much smaller than the Cu-Cu distance along [001]).

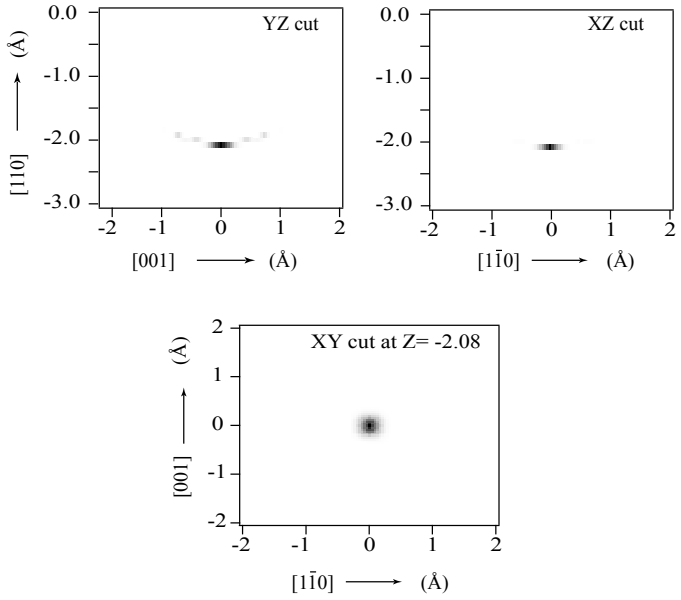

Figure 5.10: Result of the application of the projection method to the N 1s PhD data from the (3x2) S-alaninate adsorbed on Cu(110). The upper panels show sections perpendicular to the surface cut along the [001] and [1$\bar{1}$0] azimuths. The lower panel show a section cut parallel to the surface at a depth below the emitter chosen to cut the main feature seen in the perpendicular sections.

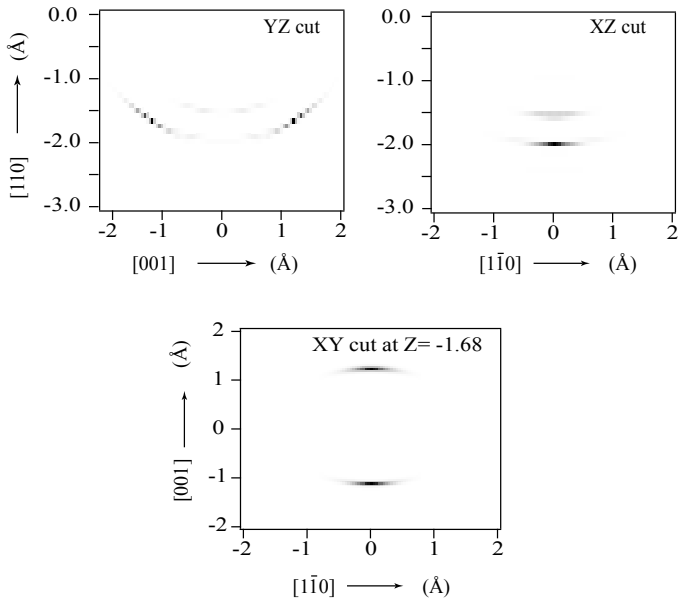

Figure 5.11: Results of the application of the projection method to the O 1s PhD data from the (3x2) S-alaninate adsorbed on Cu(110). The lower panel show a section cut parallel to the surface at a depth below the emitter chosen to cut the main feature seen in the perpendicular sections

Photoelectron diffraction structure determination

The results of the projection method discussed above are quite similar to those of the glycinate molecule adsorbed on the same Cu(110) surface [162]. Therefore, we can use the structural model obtained for the adsorption of glycinate on Cu(110) as a guide for the simulations of the alaninate/Cu(110) structure. The glycinate molecule was found to bond to Cu(110) surface through both of the O atoms of the carboxylate and the N atom of the amino group. The N atom occupied an atop position above the first layer Cu substrate atoms with a slight offset in the $[1\bar{1}0]$ azimuth. In the present work, multiple scattering calculations were run for the N atom on top of a Cu atom of the first layer as well as for a possible atop adsorption on a Cu atom of the second layer. Although both simulations gave relatively good agreement with the experimental N 1s PhD spectra, this agreement was better for the case in which the N atom adsorbs in the first layer. The associated R-factor was smaller than that corresponding to adsorption in the second layer by more than 2 times the estimated variance. Furthermore, as can be seen in Fig. 5.12, adsorption on the first layer reproduced some features of the PhD spectra that adsorption on the second layer does not.

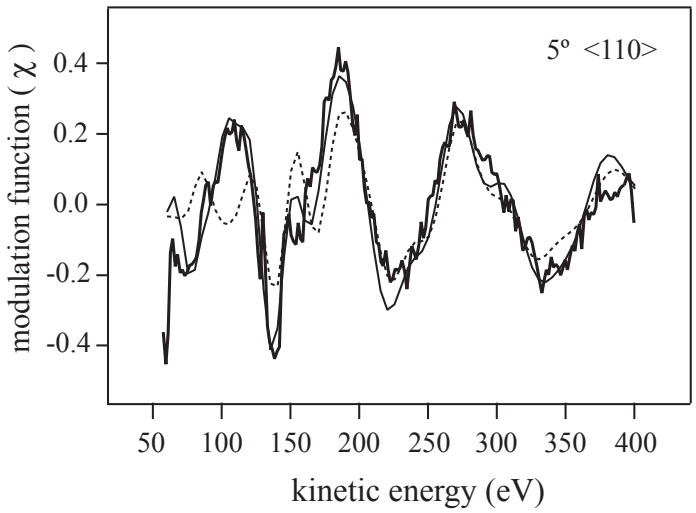

Figure 5.12: Comparison of the experimental N 1s PhD spectrum measured at 5° off normal emission along <001> (bold line), with the results of theoretical simulations for adsorption on top of a Cu atom at different layers: at the first layer (thin line) and at the second layer (dashed line). Notice that in the latter case, the simulation does not reproduce the modulation at 100 eV

Fig. 5.13 shows the comparison of the experimental N 1s PhD spectra with the result of the simulations for the best-fit structure shown schematically in Fig. 5.14. Table 5.1 lists the values of the main structural parameters for this best-fit structure. The agreement is visibly very good, as the value of 0.19 of the R-factor indicates. The N atom is found to be on top of a Cu atom of the first layer at a distance of 2.01 ± 0.02 Å, slightly offset in both [001] and $[1\bar{1}0]$ azimuths by 0.20 ± 0.10 Å and 0.24 ± 0.15 Å respectively. Anisotropic vibrations were found for the N atom with a value of 0.025 Å^2 parallel to the surface, and

a value of an order of magnitude smaller perpendicular to the surface. The best fit value for the mean square vibrational amplitude of the Cu atoms was 0.003 Å^2. The optimal value found for the inner potential was 15 ± 5 eV.

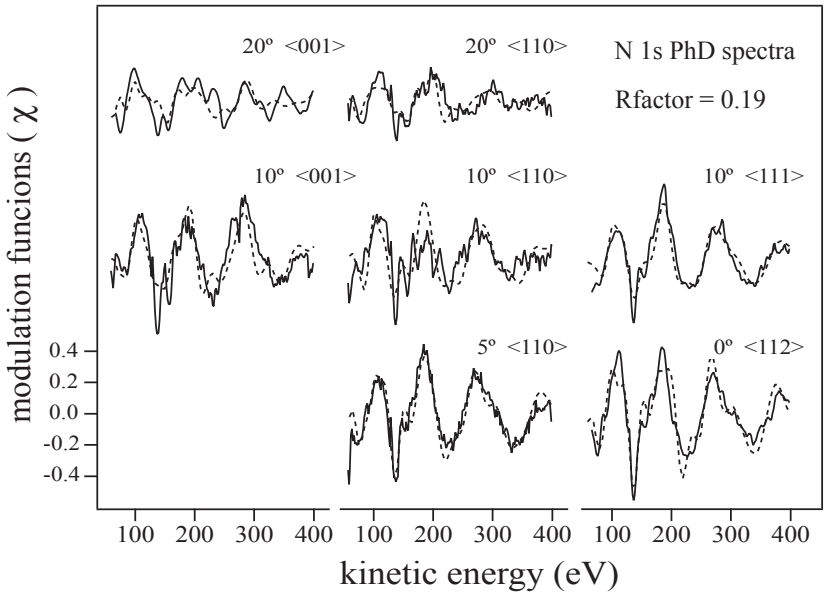

Figure 5.13: Comparison of the experimental N 1s PhD data with the results of the theoretical simulations for the best-fit structure shown in Fig. 5.14 using the values of the structural parameters listed in table 5.1

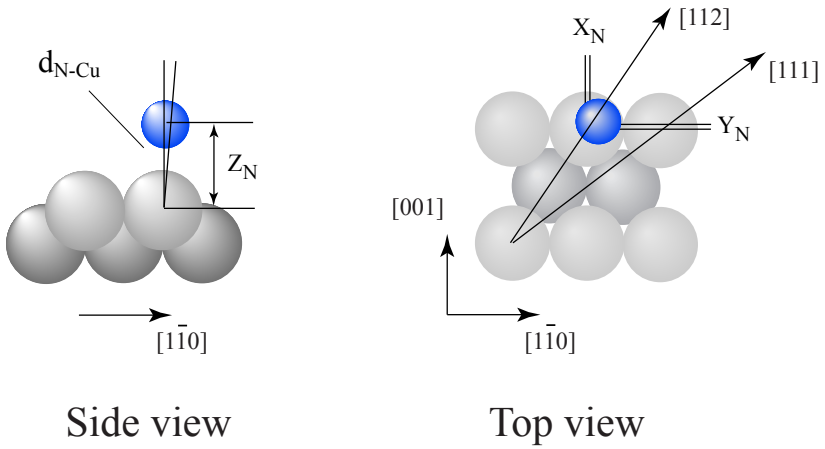

Figure 5.14: Schematic diagram showing the best-fit position of the N atom of the S-alaninate showing the definition of the main structural parameters and the azimuth directions in which the PhD data were collected

Parameters	Best-fit values
X_N(Å)	0.20 ± 0.10
Y_N(Å)	0.24 ± 0.15
Z_N(Å)	2.01 ± 0.03
d_{N-Cu}(Å)	2.03 ± 0.03
Z_{1-2}(Å)	1.32 ± 0.09
Z_{bulk}(Å)	1.28 ± 0.20

Table 5.1: Optimum main parameter values obtained in this study for the N atom position from the (3x2) S-alaninate phase

In the original PhD study of glycinate adsorbed on Cu(110) [162], the two oxygen atoms were assumed to be equivalently bonded to the surface. This adsorption structure implied an unphysically large vibrational amplitude of the O atoms in the [110] azimuth, which was thought to be due to coupling between the vibrational amplitude and a possible static offset in the same direction. However, a recent reanalysis of this work [5], has proved that much better agreement between the experimental and simulated PhD spectra can be achieved by allowing the two oxygen atoms to occupy inequivalent sites, giving an adsorption geometry that coincides more closely with the results of theoretical total energy calculations [164].

Our attempts to reproduce the O 1s PhD modulations based on a model with the two O atoms bonded to the surface in an equivalent manner led to the same results as those of the earlier study of glycinate on Cu(110), that is, unreasonable values for the vibrational amplitudes needed to be used in order to achieve good agreement between the simulations and the experimental PhD curves. Therefore, further efforts were carried out on the basis that the two O atoms of the carboxylate are inequivalently bonded to the Cu substrate. This initially led to an adsorption structure in which the O-O distance had a far too long value of 2.64 Å. Constraining the O-O distance to have reasonable values gave relatively good agreement as shown in Fig. 5.15, although as can be seen from this figure, these simulations failed to reproduce the clear feature that appears at around 100 eV kinetic energy in the modulations observed at normal and at 10° off normal emission along the [001] azimuth.

In view of these unsuccessful endeveours, we decided to explore a model in which half of the alaninate species are adsorbed with the two O atoms almost on top of corresponding Cu atoms, while the other half suffer a smaller azimuthal rotation that causes its two O atoms to occupy inequivalent adsorption positions. This model was proposed as one plausible model for the adsorption of glycinate species on a Cu(110) surface based on total energy calculations [164]. The result of these attempts led, as in the case of the glycinate, to even weaker modulation amplitudes and to some contradictions as to the periodicity of the modulations.

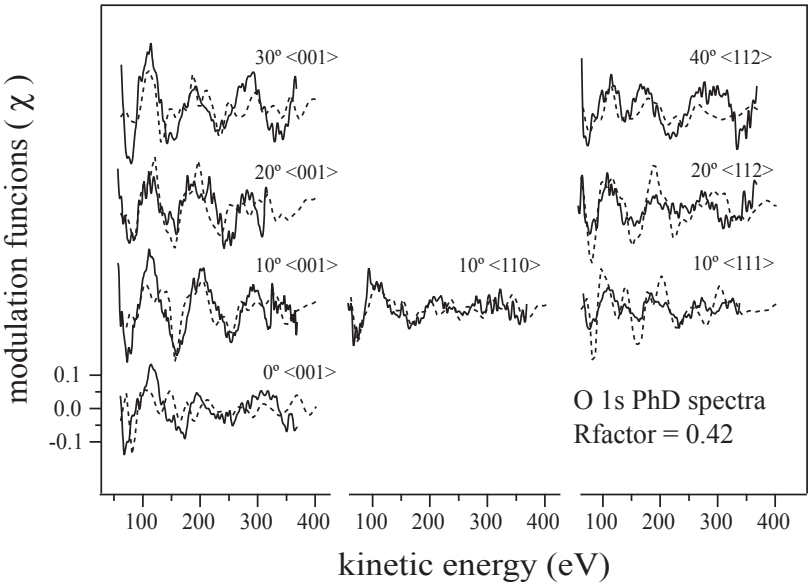

Figure 5.15: Comparison of the experimental O1s PhD modulation spectra (full lines) from the (3x2)-phase formed by adsorption of S-alanine on Cu(110) with the results of theoretical simulations (dashed lines) in which the O atoms are considered to be inequivalently bonded to the surface, and the O-O distance is constrained to have a physically reasonable value

We have already mentioned that STM images favoured the presence of two alaninate species in each (3x2) unit mesh. However, these two alaninate molecules cannot be placed at the surface forming a true centered (3x2) unit mesh, since the center position of a superlattice that is an odd multiple of the substrate periodicity is not in an equivalent position with respect to the substrate. Notice that a shortening of the Cu-Cu distance along the $[1\bar{1}0]$ direction would allow two alaninate molecules to be accommodated in one unit net, which will be no longer a (3x2) mesh, but will have a irrational periodicity along the $[1\bar{1}0]$ direction. This lead us to think that the alaninate adsorption may have caused a reconstruction of the substrate atoms in the vicinity of the O atoms of the carboxylate group. Indeed, if the alaninate molecules are bonded to each other through H atoms as suggested by Raval et al., this bond might be strong enough to cause this reconstruction. Fig. 5.16 shows the result of the simultaneous optimisation of the position of both O atoms and the two Cu substrate atoms to which they may be bonded. Although this calculation included only the first layer of Cu substrate atoms, the agreement with the experimental modulations is surprisingly very good. The simulation showed a clear preference for the two Cu atoms to be closer together in the $[1\bar{1}0]$ direction. The optimal Cu-Cu distance for the Cu atoms involved in the bonding to the O atoms of the alaninate along this particular direction was found to be 11% shorter than that of the unreconstructed Cu(110) surface. Table 5.2 lists the values of the coordinates of the O and Cu atoms involved in the alaninate/Cu(110) bonding relative to the Cu atom positions in the unreconstructed surface. Fig. 5.17 shows the corresponding best-fitting final local structure. The Cu-Cu distance between the two Cu atoms bonded to the O atoms of the alaninate has a value of

2.27 ± 0.05 Å. This allow the O-O distance to have a reasonable value of 2.28 ± 0.06 Å. The Cu-O distances are 2.00 ± 0.06 Å(I) and 1.98 ± 0.06 Å (II). The O emitters were found to have a mean-square vibrational amplitude parallel to the surface of 0.01 Å^2 and perpendicular to the surface of 0.005 Å^2.

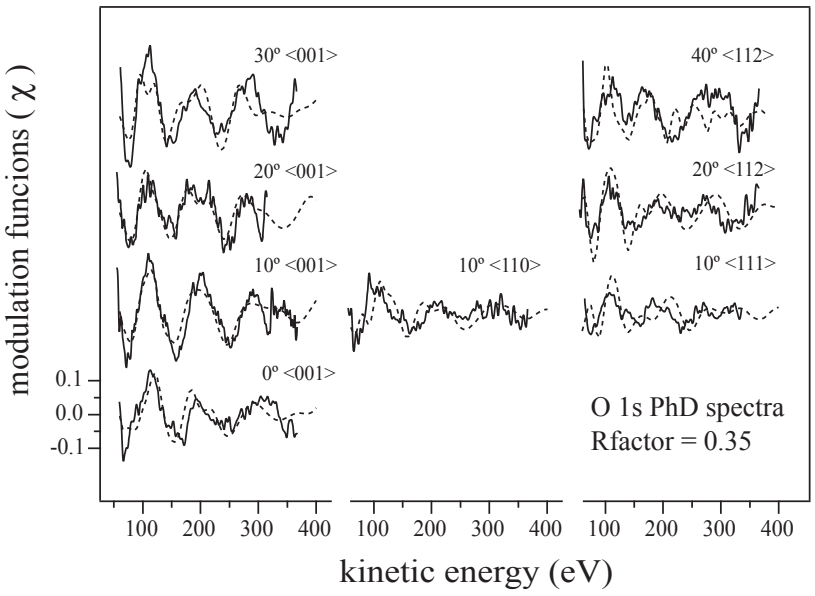

Figure 5.16: Comparison of the experimental O1s PhD modulation spectra (full lines) from the (3x2)-phase formed by adsorption of S-alanine on Cu(110) with the results of theoretical simulations (dashed lines) in which the O atoms are considered to be inequivalently bonded to the surface, and the substrate atoms in their vicinity reconstruct along the [1$\bar{1}$0] azimuth

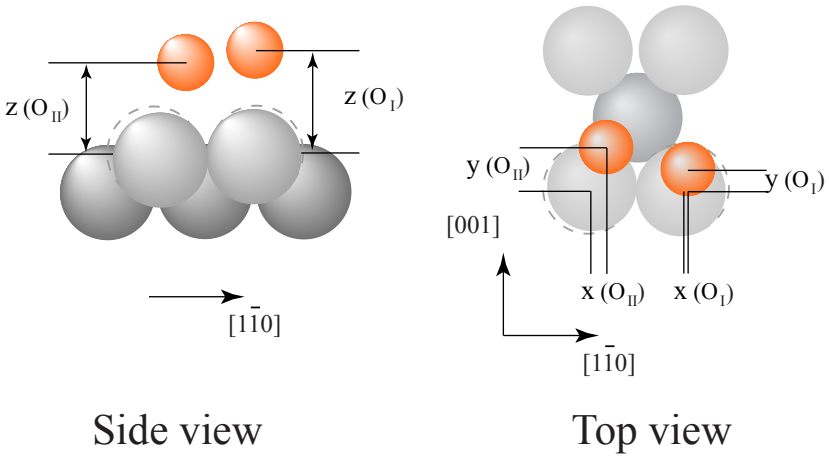

Figure 5.17: Schematic diagram showing the best-fit position of the O atom of the S-alaninate and of the Cu atom involved in the O-Cu bonding. The gray dashed lines indicated the positions of the Cu atoms in the unreconstructed surface

This will render the overlayer incommensurate with respect to the underlying Cu(110) net along the [1$\bar{1}$0] direction, which may explain why the fit shown in Fig. 5.16 is good despite the fact that only the first layer of Cu atoms were taken into consideration in this calculation. Indeed, further inclusion of second and third Cu layers, showed to enpoverish the agreement. This result might cause us to question the nature of the (3x2)LEED pattern.

Coordinates	Oxygen (I)	Oxygen (II)	Cu (I)	Cu (II)
x (Å)	0.12 ± 0.10	0.50 ± 0.12	-0.02 ± 0.20	0.27 ± 0.20
y (Å)	0.46 ± 0.10	1.06 ± 0.09	-0.06 ± 0.09	0.01 ± 0.10
z (Å)	1.90 ± 0.04	1.63 ± 0.04	-0.02 ± 0.04	-0.04 ± 0.03

Table 5.2: Comparison between the optimum main parameter values obtained in this study and those found in the earlier work by Moler et al.

Notice that in the simulations of the N 1s and O 1s PhD data we have so far not taken into account full intermolecular and intramolecular scattering between the oxygen and nitrogen atoms. The inclusion of this possibility did not have any relevant influence in the value of the N and O structural parameters, as might be expected due to the weak nature of N and O as scatterers. The intramolecular N-O separation have a value of 2.84 ± 0.06 Å, for the N to O(I) distance, and of 2.99 ± 0.06 Å, for the distance between N and O(II). Fig. 5.18 shows a plan view of the final structural configuration of S-alaninate on Cu(110), where the C atoms were placed in guessed positions according to the molecular structure.

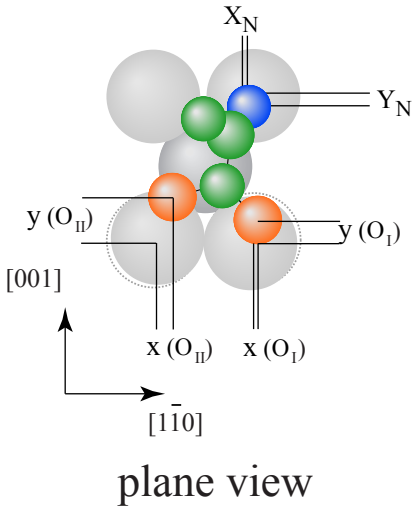

Figure 5.18: Schematic plan view of the final local structure of S-alaninate on Cu(110). The values for the N and O structural parameters are given in tables 5.1 and 5.2. The C atom are placed in guessed positions according to the molecular structure

5.3 Future perspectives: circular dichroism and chiral molecules

The main goal of the present study was to determine the local adsorption structure of S-alaninate on Cu(110) by means of photoelectron diffraction. However, since the beam line UE56/2 (where this experiment was performed) allows measurements with circular polarised light of opposite signs, we have also conducted some preliminary measurements in order to gain some insight into the possibility of using the circular dichroism that we observed appears in the photoelectron angular distribution of core level emission from the alaninate, to distinguish between adsorbed enantiomers of the same molecule. At the time this thesis was being written, this analysis was in a preliminary stage, so no definitive conclusions could be drawn from them. However, since we consider that this measurements are closely related with the general interest of this system (i.e. direct determination of the chirality of adsorbates by means of photoemission) and they are the actual link between the structural study reported in this chapter and our work on this system in the near future, we would like to include here some comments on this respect.

The phenomenon of circular dichroism associated with core level photoemission, that is to say, differences in photoemisison intensity induced by the use of circular polarised light of opposite handedness, was theoretically predicted for the angular distribution of photoelectrons from core levels of chiral molecules by Ritchie [165] and Cherepkov [166]. The magnitude of this effect was later investigated theoretically by I. Powis [167], but it has not been until very recently that this effect has been corroborated experimentally. Hergenhahn et al. [150] has measured circular dichroism in the angle resolved emission from the carbonyl C 1s core level of camphor gas-phase molecules. The effect observed was of opposite sign for the two mirror enantiomers of the molecule, therefore allowing the authors to distinguish between enantiomers by means of photoemission spectroscopy.

Fig. 5.19 shows the C 1s photoemission spectra from the (3x2) structure phase of alaninate on a Cu(110) measured with circular polarised light of opposite signs at normal emission, along an azimuth forming 60° with [001] and at a photon energy of 310 eV. As can be seen, unlike the case of camphor gas molecules, differences in intensity are present here not only in the α-carbon signal. This makes us to question which are the differences between our experiment and that performed with gaseous chiral molecules. In the experiment of Hergenhahn et al., the chiral camphor molecules were randomly oriented in space, while in our experiment the alaninate molecule has a fixed spatial orientation. This fixed orientation of the molecule causes a CDAD effect which does not appear in the gas phase due to directional averaging over different random orientation of the molecule. In other words, fixing the orientation of the molecule in space renders all the atom to be in a local chiral environment.

Indeed, the mere fact of being spatially fixed has been proved (both theoretically and experimentally) to be sufficient to induce a CDAD effect in the case of linear (and

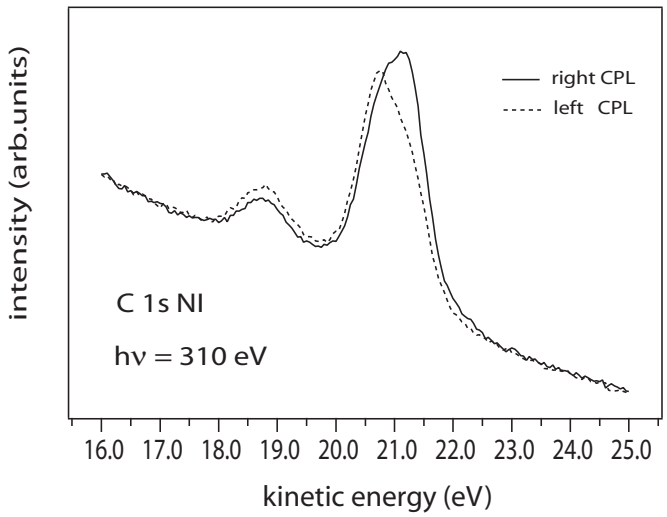

Figure 5.19: C 1s photoemission spectra measured right and left circular polarised ligh(CPL) from the (3x2) S-alaninate on Cu(110), collected at NI and at an azimuth at 40^{circ} from the [001] direction

therefore non-chiral) molecules (see for example [168–170]). However, in the case of linear molecules, the experimental frame defined by the direction of propagation of the photons (**q**), the direction of the ejection of the photoelectrons (**k**) and the molecular axis (**n**) must present a "handedness" or "chirality" (i.e. these three direction must be non-coplanar) in order to observe this CDAD. On the contrary, if two of these vectors are coplanar, the system lacks a handedness and CDAD does not occur. Notice that in the case of non-linear molecules (as it is the case here) the latter does not hold, and in general there are no restrictions on the experimental arrangement for the CDAD due to a fixed orientation of a chiral molecule to be observed [169, 171].

Furthermore, we have hitherto not taken into consideration the fact that the way we have the alaninate molecules oriented in space is by having them adsorbed on a surface. It has been proved that the CDAD from a core level is influenced by the scattering of photoelectrons in the vicinity of the emitter [172–174]. This causes the CDAD effect to have a strong energy dependence at the photon energies used in these experiments. Of course, if **q**, **k** are contained within a mirror plane of the surface, the circular dichroism due to scattering will be zero. That is, there is a way to 'kill' the CDAD effect due to scattering effects from a surface. Notice, however, that even if we measured in such a geometry (in which no contribution from scattering is to be expected in the CDAD), the fact that the molecule has a fixed orientation in space will *a priori* cause a CDAD effect.

The discussion above might cause us to think that CDAD cannot be used to distinguished between enantiomers of chiral substances adsorbed on a surface, at least not in the direct way it can be used in the gas-phase case. However, as can be seen in Fig.5.20, where the azimuthal CDAD patterns corresponding to the two enantiomers of alaninate

(S- and R-) adsorbed on the Cu(110) surface measured at 30° off normal emission are shown, the CDAD is not identical for both enantiomers. Although the number of data may be argued to be not representative, the difference between the CDAD patterns shown by distinct enantiomers might allow to distinguish between them. The dichroic anisotropy χ is measured as the difference in intensity of the C 1s photoemission spectra measured with circular polarised light with different handedness and normalised to the sum of them.

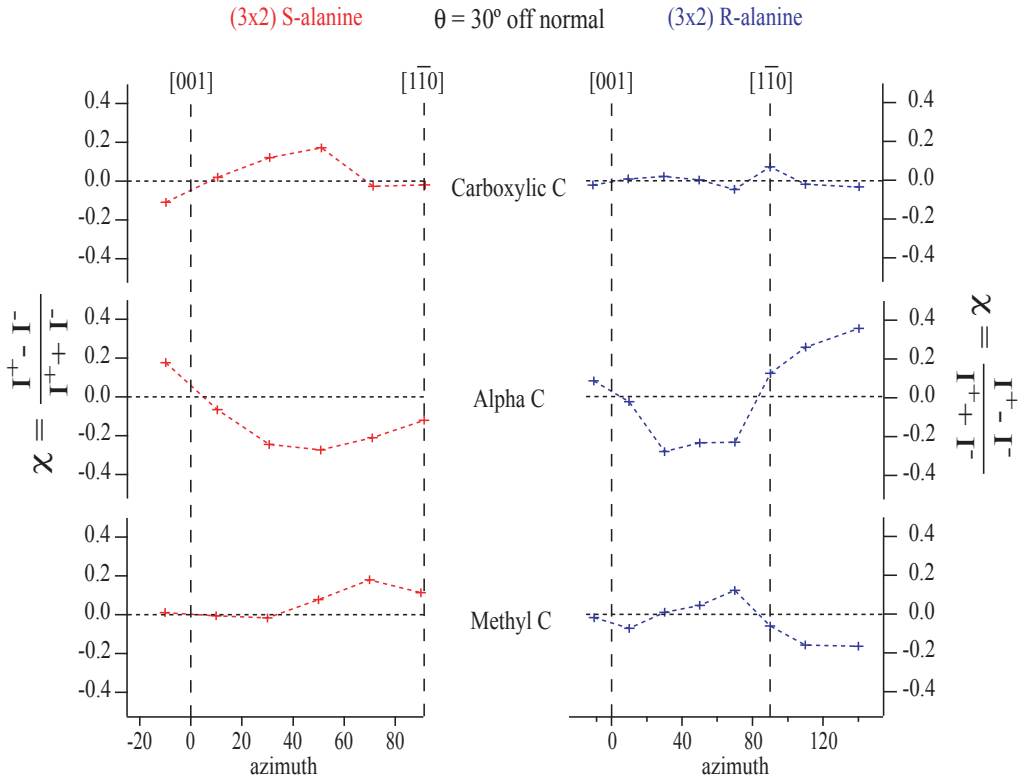

Figure 5.20: CDAD azimuthal patterns of the different C atoms measured from the (3x2) structural phase of both enantiomers alaninate on Cu(110)

We have measured azimuthal as well as polar CDAD patterns for the C 1s, N 1s and O 1s core level spectra for both S- and R-alaninate adsorbed on the Cu(110) surface, and recently even for the glycinate (non-chiral) adsorbed on the same surface. Dr. Martin Polcik has modified Fritzche's code to include the possibility of having emission caused by circular polarised light of opposite signs and he is currently performing some simulations in order to reproduce theoretically these experimental CDAD patterns. Since the CDAD patterns show a strong geometrical dependence, these simulations may allow us to gain also some further information on the positions of the C atoms.

5.4 Conclusions

The detailed bonding geometry of the S-enantiomer of α-alaninate on a Cu(110) surface has been determined by means of photoelectron diffraction. The alaninate molecule is

found to adsorb in a tridentate fashion through the N atom of the amino group and the two O atoms of the carboxylate. The N atom is found to occupy a position on top of a Cu substrate atom in the first layer, with a bonding distance of 2.03 ± 0.03 Å. The two O atoms showed inequivalent adsorption geometries, with one of them having a considerable offset along [001]. These results are similar to those obtained with the PhD technique for glycinate adsorbed on the same Cu(110) surface. The only difference arises from the local reconstruction of the Cu surface observed in the present work. The Cu atoms involved in the bonding to the O atoms have a shorter Cu-Cu distance along the $[1\bar{1}0]$ direction (2.27 Å compared to the 2.56 Å in the unreconstructed Cu(110) surface). The presence of the methyl group in the case of alaninate may allow the formation of H bonding with the neighbouring species. The strength of these intramolecular bonding may originate the modification of the Cu(110) surface.

We have also discussed the possibility of distinguish between the S- and R-enantiomers of alaninate adsorbed on Cu(110) by using circular polarised light. We have argued on the basis of previous theoretical and experimental work that in the case of a chiral molecule fixed in space, the CDAD effect cannot be attributed to the intrinsic chirality of the molecule. However, differences in the CDAD patterns obtained for the two enantiomers of alaninate lead us to believe that distinction between enantiomers may be possible, although not in a straight forward way, as we initially expected.

Moreover, we have shown that PhD is a suitable technique for the structural study of adsorbed organic molecules, which usually have a high fragmentation cross-section for low-energy electron bombardment, hence disabling the use of the most common technique for quantitative surface structure determination (LEED)