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# Adsorption structure of glycine on TiO<sub>2</sub>(110): a photoelectron diffraction determination

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## Abstract

High-resolution core-level photoemission and scanned-energy mode photoelectron diffraction (PhD) of the O 1s and N 1s states have been used to investigate the interaction of glycine with the rutile TiO<sub>2</sub>(110) surface. Whilst there is clear evidence for the presence of the zwitterion NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>COO<sup>-</sup> with multilayer deposition, at low coverage only the deprotonated glycinate species, NH<sub>2</sub>CH<sub>2</sub>COO is present. Multiple-scattering simulations of the O 1s PhD data show the glycinate is bonded to the surface through the two carboxylate O atoms which occupy near-atop sites above the five-fold coordinated surface Ti atoms, with a Ti-O bondlength of 2.12±0.06 Å. Atomic hydrogen arising from the deprotonation is coadsorbed to form hydroxyl species at the bridging oxygen sites with an associated Ti-O bondlength of 2.01±0.03 Å. Absence of any significant PhD modulations of the N 1s emission is consistent with the amino N atom not being involved in the surface bonding, unlike the case of glycinate on Cu(110) and Cu(100).

keywords: surface structure; chemisorption; photoelectron diffraction; titanium dioxide; glycine; amino acids

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## 1. Introduction

So far there have been very few structural studies of the adsorption of amino acids at well-characterised surfaces, with the only fully quantitative structure determinations being restricted to those of glycine,  $\text{NH}_2\text{CH}_2\text{COOH}$  on Cu(110) and Cu(100) [1, 2, 3], and of alanine,  $\text{NH}_2\text{CH}_3\text{CHCOOH}$  on Cu(110) [4], achieved by scanned-energy mode photoelectron diffraction [5, 6]. In all three of these cases, the acid is deprotonated by interaction with the Cu surface to form, respectively, glycinate ( $\text{NH}_2\text{CH}_2\text{COO}$ ) and alaninate ( $\text{NH}_2\text{CH}_3\text{CHCOO}$ ) species that bond to the surface through both of the carboxylate O atoms and the amino N atom, all three atoms occupying single-coordinated sites. This bonding configuration is consistent with a number of studies using electronic [7, 8] and vibrational spectroscopy [9, 10, 11], and also scanning tunnelling microscopy [12, 13, 14, 15, 16, 17] and density functional theory (DFT) calculations [18, 19]. Some of these spectroscopic studies, however, do indicate that at different surface coverages, or in less well-ordered overlayers, other chemisorption bonding configurations probably occur involving only one or both of the carboxylate O atoms.

Insofar as one motivating factor for such studies is the issue of biocompatibility in medical implants, studies of  $\text{TiO}_2$  surfaces are potentially more relevant, as many such implants are based on (surface-oxidised) titanium metal or composite ceramics including titania. Much the most studied surface of titania is that of rutile  $\text{TiO}_2(110)$ , and there has been a small number of investigations of amino acids, and particularly glycine, on this surface. Important structural differences between the clean surfaces of Cu(100) and Cu(110) on the one hand, and of  $\text{TiO}_2(110)$  on the other hand, suggest that glycinate, if formed on  $\text{TiO}_2(110)$ , is unlikely to bond in the same ‘lying down’ configuration through both the carboxylate O atoms and the amino N atom. The Cu-Cu nearest-neighbour distance on both Cu surfaces is 2.55 Å, quite similar to the O-O distance in carboxylates of  $\sim 2.27$  Å; the spacing of the undercoordinated (five-fold coordinated) Ti atoms on the  $\text{TiO}_2(110)(1\times 1)$  surface is somewhat larger (2.96 Å), but it is well-established that the simplest carboxylate species, formate ( $\text{HCOO}$ ), does bond to adjacent pairs of these Ti atoms on this surface in a symmetric fashion (Fig. 1) with the O atoms some 0.3 Å off-

atop and the O-O distance equal to  $2.39 \pm 0.08 \text{ \AA}$  [20]. Perpendicular to this carboxylate O-O alignment, however, the metal-metal atomic distances on the three surfaces are very different, namely,  $2.55 \text{ \AA}$  (Cu(100)),  $3.61 \text{ \AA}$  (Cu(110)) and  $6.50 \text{ \AA}$  (TiO<sub>2</sub>(110)). The match of this metal-metal distance to the separation of the amino N atoms from the O-O axis in the glycinate species is closest on the Cu(100) surface, such that all three bonding atoms lie quite close to atop sites [3]. On Cu(110) the larger Cu-Cu spacing leads to the carboxylate O atoms being significantly offset (by  $\sim 0.8\text{-}1.0 \text{ \AA}$ ) from atop, but still in singly-coordinated sites [3]. On TiO<sub>2</sub>(110)(1x1), however, the mismatch is very much larger, and the possibility of N bonding to an adjacent Ti atomic row is further hindered by the intervening row of bridging O atoms that lie higher above the surface (Fig. 1). It seems clear, therefore, on purely geometric grounds, that glycinate cannot bond to TiO<sub>2</sub>(110) through all three molecular sites, and at most two of these sites, either the two carboxylate O atoms or one carboxylate O atom and the amino N atom, can be involved in the surface bonding.

The first surface science study of the TiO<sub>2</sub>(110)/glycine system [21, 22] was concerned mainly with photon-stimulated desorption and dissociation using photons in the energy range from 20-120 eV, but ultra-violet photoemission spectra were interpreted as indicating that in multilayer films the glycine is in the zwitterionic form (NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>COO<sup>-</sup>) that is also found in solid glycine. More recently, a STM investigation of this system [23] identified a local (2x1) ordering of molecular features on the surfaces; this is the same ordering seen for a number of simple carboxylate species including formate. This led the authors to propose that the local bonding configuration is similar to that of formate, with glycinate species bonded symmetrically to an adjacent pair of five-fold coordinated surface Ti atoms through the two carboxylate O atoms with the molecule approximately perpendicular to the surface. This interpretation was reinforced by their observation that the STM images showed no evidence of any asymmetry in the molecular features. An experimental investigation of proline, C<sub>4</sub>NH<sub>8</sub>COOH, on the stoichiometric TiO<sub>2</sub>(110) surface, using core-level photoemission [24, 25], also indicates that both zwitterionic and dissociated (deprotonated) forms are present on the surface, but with the zwitterion desorbing at a lower temperature. Combined with the earlier results on glycine

adsorption, the experiments therefore indicate that the preferred form of these adsorbed amino acids on  $\text{TiO}_2(110)$  is the deprotonated form, with zwitterionic material being present only at higher coverages, particularly in multilayer films. However, this conclusion is in conflict with that of a DFT investigation of the  $\text{TiO}_2(110)$ /glycine system. Specifically, Ojamäe *et al.* [26] identified the lowest energy structure as that of zwitterionic glycine, rather than glycinate (coadsorbed with atomic hydrogen), with the carboxylate O atoms bonded to five-fold coordinated Ti atoms, but with the molecule tilted to form hydrogen bonds between the ammonia H atom(s) and the adjacent row of bridging O atoms. Other recent DFT and molecular dynamics calculations have been of larger amino acids in aqueous solution, thus modifying the relative stability of the zwitterion [27, 28] and rendering the results less relevant to UHV experiments.

Here we show, using a combination of soft X-ray photoelectron spectroscopy (SXPS) and PhD, that at lower coverages (below those of multilayers), glycine reacts with the  $\text{TiO}_2(110)$  surface to form coadsorbed glycinate and atomic hydrogen, the glycinate bonding through the two carboxylate O atoms to a pair of five-fold-coordinated surface Ti atoms, while the atomic H bonds to bridging oxygen atoms to form a local hydroxyl species. Our results confirm the presence of the zwitterionic form of glycine at high (multilayer) coverages, but explicitly exclude the zwitterionic model of Ojamäe *et al.* at low coverage.

## 2. Experimental Details

The experiments were conducted in an ultra-high vacuum surface science end-station equipped with typical facilities for sample cleaning, heating and cooling. This instrument was installed on the UE56/2-PGM-2 beamline of BESSY II which comprises a 56 mm period undulator followed by a plane grating monochromator [29]. Different electron emission directions can be detected by rotating the sample about its surface normal (to change the azimuthal angle) and about a vertical axis (to change the polar angle). Sample characterisation *in situ* was achieved by LEED and by soft-X-ray photoelectron spectroscopy (SXPS) using the incident synchrotron radiation. Both the wide-scan SXPS

spectra for surface characterisation, and the narrow-scan O 1s spectra used in the PhD measurements, were obtained using an Omicron EA-125HR 125 mm mean radius hemispherical electrostatic analyser, equipped with seven-channeltron parallel detection, which was mounted at a fixed angle of 60° to the incident X-radiation in the same horizontal plane as that of the polarisation vector of the radiation.

A clean well-characterised rutile TiO<sub>2</sub>(110) surface was prepared which gave a sharp (1x1) LEED pattern and a Ti 2p photoemission spectrum showing no significant high kinetic energy shoulder. The main Ti 2p peaks are generally assigned to Ti in the 4+ charge state expected for a fully ionic stoichiometric bulk site and in the autocompensated surface (e.g. [30]), while any high energy shoulder is assigned to Ti in a 3+ state, most commonly attributed to the presence of surface oxygen vacancies. To achieve this surface, the crystal was bombarded briefly with Ar<sup>+</sup> ions at an energy of 500 eV, followed by annealing in UHV at approximately 830 K.

The glycine powder was contained in a glass tube which could be heated via a surrounding copper coil and its temperature was measured by a thermocouple attached to a wire mesh within the tube. The doser was held within a small, separately pumped side-arm separated from the upper chamber by a gate valve, and was outgassed for prolonged periods (including between dosing) at ~370 K; line-of-sight dosing of the sample was conducted using a slightly higher doser temperature of 410 K for typically 60 seconds with the sample held at 200 K. The sample was then heated to room temperature and held at this temperature during all measurements.

### **3. Results**

#### **3.1 XPS Characterisation**

Fig. 2 shows the photoemission spectra in the energy range of the N 1s and O 1s peaks recorded at photon energies of 500 eV and 630 eV, respectively, following deposition at a sample temperature of ~215 K, and after annealing at ~325 K. A striking feature of the N 1s spectra from the as-deposited film is the appearance of two components, with a

binding energy difference of approximately 2.3 eV, while after annealing to the higher temperature the peak at the lower kinetic energy (higher binding energy) is lost. We attribute the main (high kinetic energy) peak to the  $\text{NH}_2$  amino group and the lower kinetic energy peaks to the  $\text{NH}_3^+$  of the zwitterionic form of glycine. This is consistent with the known behaviour of glycine to take the zwitterionic form in the bulk and in multilayer films, and the implication that the higher surface temperature leads to desorption of the multilayer, leaving only the more strongly-bound first chemisorbed layer. The implication is that the glycine in this first layer is *not* zwitterionic; as we will show below, this is consistent with the PhD data that clearly indicate that this layer is deprotonated glycinate, with the acid hydrogen that has been removed from bonding to surface O atoms to form hydroxyl species.

The O 1s spectrum is dominated by the emission from the oxide substrate, but even after desorption of the multilayer there is a clear chemically-shifted component with a binding energy  $\sim 1.6$  eV larger, associated with the adsorbate(s). This chemical shift is essentially the same as that seen for formate on  $\text{TiO}_2(110)$ , but also for hydroxyl species on this surface [20].

### **3. 2 Photoelectron diffraction**

The PhD technique [5, 6] exploits the coherent interference of the directly-emitted component of the outgoing photoelectron wavefield, from a core level of an adsorbate atom, with components of the same wavefield that are elastically backscattered by the nearby substrate atoms. By measuring the photoemission intensity in specific directions as a function of photon energy, the resulting changes in photoelectron energy, and thus photoelectron wavelength, cause specific scattering paths to switch in and out of phase with the directly-emitted component. This leads to modulations in the intensity which depend on the relative emitter-scatterer location. Simulations of these PhD modulation spectra allow one to determine the local adsorption geometry by adjusting the model structure to optimise the theory-experiment agreement. One special virtue of the method is that it is not only element-specific, in that the binding energies of the core electrons are

characteristic of the atomic identity of the emitter, but it is also chemical-state-specific through the so-called chemical shifts of these photoelectron binding energies. Thus, emission from atoms of the same element in different local environments can be distinguished by these shifts, and the associated PhD spectra can be analysed independently. This chemical-state specificity is exploited here to distinguish the O 1s photoemission from oxygen atoms within the adsorbed glycinate (and hydroxyl) species from emission from O atoms in the underlying TiO<sub>2</sub>.

The PhD modulation spectra were obtained by recording a sequence of photoelectron energy distribution curves (EDCs) around the O 1s and N 1s peaks at 4 eV steps in photon energy in the photoelectron kinetic energy range of approximately 60-300 eV for each of a number of different emission directions in the polar emission angle range from 0° (normal emission) to 60° in the two principal azimuthal planes. Specifically, O 1s PhD spectra were obtained at polar angles of 0°, 10°, 20° and 60° in  $[\bar{1}10]$ , and of 30°, 40° and 60° in  $[001]$ , while a much smaller set of N 1s data (at polar angles of 0°, 40° and 60° in  $[001]$ ) were taken. These data were processed following our general PhD methodology (e.g. [5, 6]) in which the individual EDCs are fitted by the sum of Gaussian peaks (two peaks for O 1s, one for N 1s), a step and a template background. The resulting plots of the integrated intensity of the individual component peaks as a function of photoelectron energy  $I(E)$  are then fitted by a stiff spline,  $I_0(E)$ , in order to obtain the PhD modulation function,  $\chi(E)$ , given by

$$\chi(E) = \frac{I(E) - I_0(E)}{I_0(E)}$$

These PhD modulation spectra form the basis of our structure determination and are compared with the results of multiple scattering simulations for trial model structures, the structures being modified until good agreement is achieved. These calculations were performed with computer codes produced by Fritzsche [31, 32, 33] that are based on an expansion of the final state wave-function into a sum over all scattering pathways which the electron can take from the emitter atom to the detector outside the sample. These calculations include double and higher order scattering events as well as the effects due to finite energy resolution and angular acceptance of the electron energy analyser.



Anisotropic vibrations of the emitter atom and isotropic vibrations of the scattering atoms are also taken into account. The quality of agreement between the theoretical and experimental modulation amplitudes is quantified by the use of an objective reliability factor (*R*-factor) [5, 6] defined such that a value of 0 corresponds to perfect agreement and a value of 1 to uncorrelated data.

One immediate finding arising from this data reduction was that the modulation amplitudes of the N 1s PhD spectra are extremely weak ( $\leq \pm 10\%$ ); this is consistent with our expectation that the N atom is not bonded directly to the TiO<sub>2</sub> surface, so there are no strongly-backscattering near-neighbour substrate atoms. In particular, if the N atom was bonded atop a surface five-fold-coordinated Ti atom one would expect reasonably strong modulations with a long period at normal emission; this is clearly not the case. By contrast, if the molecule is 'standing up', we would expect weak PhD modulations due to a combination of intramolecular scattering and scattering from the more distant Ti substrate atoms; the scattering cross-sections of C and O atoms are small, while the scattering contribution from more distant Ti atoms is small, due to the attenuation of the photoelectron wavefield with increasing distance. These weak scattering events will lead to meaningful PhD modulations (even if the upper part of the molecule is freely rotating), but measuring and calculating these weak effects reliably is very difficult. Because of this, we believe that detailed modelling of these N 1s PhD spectra is unlikely to yield any quantitative structural information on the N atom site. However, the fact that the measured N 1s PhD modulations are consistently weak does lead to the clear qualitative conclusion that the N atom is not involved in bonding to the surface.

By contrast, the O 1s PhD spectra show modulations of significant amplitude ( $\sim \pm 20\%$ ) in some directions, suggesting that at least one of the oxygen atoms is bound directly to the substrate. In order to determine the location of these oxygen atoms multiple scattering calculations were performed on a series of structural models for a subset of three of the complete set of seven experimental O 1s PhD spectra. These were those recorded at 40° polar emission angle in the [001] azimuth, and at 10° and 0° in the [ $\bar{1}\bar{1}0$ ] azimuth. The first two of these were chosen as showing the strongest modulations, the third spectrum

was included because it is the highest-symmetry direction. Our general strategy in surface structure determination by PhD is to focus on spectra with the largest modulations. These are the experimental spectra that are most reliable, and are also the spectra that can be modelled most reliably theoretically. Reducing the number of spectra has the added benefit of significantly lowering the computational time required for the analysis, making the whole process more manageable. This general strategy is particularly important in systems, such as the present one, in which even the spectra showing the strongest modulations are only ~20%. Experimental spectra showing only modulations of ~10%, such as those found in many directions in the present study, are commonly found to show inconsistencies in repeated measurements or in different methods of data reduction, and as such cannot be regarded as a sound basis for structural analysis.

In view of the known adsorption geometry of the simplest carboxylate species, formate, on  $\text{TiO}_2(110)$ , our calculations focussed on similar structures, namely bonding of a deprotonated glycinate species through the two carboxylate O atoms that lie close to atop sites above two adjacent five-fold-coordinated surface Ti atoms. An important implication of assuming deprotonation to the glycinate species, of course, is that we need to consider the fate of the H atoms that are removed. In the case of formic acid reaction with  $\text{TiO}_2(110)$ , there is clear evidence from the associated O 1s PhD structural study that the H atoms are adsorbed on the surface on the bridging oxygen atoms to produce local hydroxyl species [20]. Because the O 1s chemical shifts of the adsorbed carboxylate and the hydroxyl species, relative to the emission from the underlying oxide, are essentially identical, this means that the O 1s shoulder in the photoemission spectra contains contributions from both of these coadsorbed species. As a result, the photoelectron diffraction measured from this emission component is expected to comprise an incoherent sum of the diffraction from the three distinct emission sites, the hydroxyl oxygen atom and the two (symmetrically-equivalent) carboxylate oxygen atoms.

Calculations for the carboxylate O emitter atoms in this symmetric bridging structure were performed for a range of heights of the O atoms above the surface Ti atoms and for different lateral offsets in the [001] azimuth. Different possible relaxations of these

nearest-neighbour surface Ti atoms perpendicular to the surface were also explored. The glycinate species was represented only by the carboxylate O and C atoms, and the influence of the remaining C and N atoms, and the H atoms, was ignored. These are all weakly-scattering atoms, and forward scattering has very little influence on PhD modulations because the scattering path-length differences relative to the directly-emitted path are small. We also note that these neglected intramolecular scattering events are from atoms that, in a standing-up glycinate species, will occupy low symmetry sites, and are also likely to have quite large vibrational amplitudes associated with a soft wagging mode of the whole molecule in the  $[\bar{1}\bar{1}0]$  azimuth. Both factors will further reduce their influence on the measured PhD spectra. On the other hand, the carboxylate C atom was included as a scatterer; this atom occupies a high-symmetry site, the location of which can be estimated with reasonable precision from estimates of the C-O bondlength. Its influence on the calculated PhD spectra is nevertheless weak. Similarly, emission from the hydroxylated bridging oxygen atom did not include scattering from the H atoms, but the location of this O emitter perpendicular to the surface, and the relaxation in this same direction of the two Ti atoms to which it is bonded, were both explored in the calculations.

Fig. 3 shows a comparison of the selected set of experimental O 1s PhD spectra with the results of the multiple-scattering simulations for the fully-optimised versions of two distinct structural models, namely adsorbed glycinate alone, and coadsorbed glycinate and hydroxyl species. In both cases the glycinate is assumed to adopt the symmetric bridging adsorption geometry described above, and the optimised geometries of this species in the two models are essentially identical. For the glycinate species alone, the agreement between experiment and theory for the data collected at normal and  $10^\circ$  emission are reasonable – the main features are reproduced, though there are significant detailed discrepancies. However, for the  $40^\circ$  polar emission angle the agreement is very poor. By contrast, for the model including the coadsorbed hydroxyl species the theory/experiment agreement for this off-normal emission geometry is excellent, while the agreement for the other two geometries is also improved. The overall *R*-factor value for this model is 0.21, a value consistent with generally good agreement, and certainly in

the range (typically below  $\sim 0.30$ ) to be expected for an acceptable solution. The reason for the marked difference in the predictions of the two models can be readily understood. In backscattering photoelectron diffraction, a particularly favourable geometry is one in which a strongly-scattering atom lies directly behind the emitter relative to the collection direction. Under these conditions one commonly observes the strongest PhD modulations with a clear dominant single long-range periodicity in electron wavenumber, attributable primarily to scattering from this single atom. The periodicity, in this case, reflects the pathlength difference for this scattering event which is simply twice the emitter-backscatterer bondlength. At  $40^\circ$  emission in the  $[001]$  azimuth, the bridging O atoms have essentially this favoured geometry relative to one of the two six-fold-coordinated Ti atoms to which they are bound, and it is emission from these hydroxylated bridging atoms that dominates the observed PhD modulations in this direction. By contrast, at normal emission an emitter that is atop a surface Ti atom may be expected to show this behaviour. In the present system the carboxylate O atoms are actually somewhat displaced (by  $0.34 \text{ \AA}$ ) laterally from the atop sites, significantly attenuating the amplitude of the associated PhD modulations. Moreover, the fact that normal emission corresponds to a symmetry direction for the bridging O atoms (with the scattering pathlengths from the two Ti neighbours equivalent) means that significant modulations also arise in the PhD from this site alone. It seems to be for this reason that the  $10^\circ$  emission spectrum, rather than the normal emission spectrum, is more obviously dominated by the PhD contribution from the (two) carboxylate O atoms.

The structural parameter values associated with this best-fit glycinate-plus-hydroxyl structure are summarised in Table 1. Figure 4 shows a diagram of this optimised structure based on the determined positions of the carboxylate O atoms and the implication from our results that the molecule is 'standing up'; the exact positions of the C, N and H atoms are, however, not determined in our study and thus are only schematic in the figure.

#### **4. General Discussion and Conclusions**

In addressing the structure formed by glycine interaction with  $\text{TiO}_2(110)$  there are a

number of key questions, namely:

1. is the molecule deprotonated to a glycinate species or is it intact, and if intact does it have the zwitterionic form?
2. does the molecule bond to the surface through one or both O atoms and/or the N atom?
3. if a deprotonated glycinate is formed, what is the fate of the acid H atom that is removed?
4. what are the adsorption sites and chemisorption bondlengths, and does adsorption significantly modify the underlying structure of the  $\text{TiO}_2(110)$  surface?

Our results provide answers to all of these questions. First, the N 1s SXPS data provide clear evidence that while a zwitterionic form of glycine is present at high coverage, this is not true at lower coverage. Based on the thermal stability and attenuation of the substrate photoemission signal (fig. 2), it seems likely that this ‘high’ coverage regime corresponds to a multilayer (or at least second layer), while the ‘low’ coverage behaviour is characteristic of the first adsorbed layer. Secondly, the evidence from the PhD analysis, that a coadsorbed bridging OH species is formed, indicates that deprotonation of the chemisorbed species does occur, and identifies the adsorption site of the acid hydrogen as on the bridging oxygen atoms. In addition, the consistently weak modulations of the N 1s PhD data indicate that the N atoms is not directly bonded to the substrate. Finally, the PhD analysis also provides a more complete structure determination, identifying the local adsorption sites of both the glycinate and OH species and their associated bondlengths. While our analysis also formally provides information on the relaxation of the outermost substrate layer atoms, it is clear from Table 1 that the precision we achieve in these parameters it is insufficient to yield and significant new information. The magnitude and sign of near-surface layer relaxations of clean  $\text{TiO}_2(110)$  have been studied extensively in the last few years, and a PhD study has contributed to this topic [34], but the local character of the structural information intrinsic to this technique means PhD data from an adsorbate has limited sensitivity to these parameters. We might remark, though, that the earlier study of coadsorbed formate and hydroxyl on this surface [20] showed smaller relaxations than those of the clean surface, and this may also be inferred in the present study, consistent with the behaviour of metal surfaces that adsorbates commonly reduce

the magnitude of any clean surface relaxation.

Comparison of the Ti-O chemisorption bondlengths in the present study of glycine reaction, and in the earlier investigation of the formic acid reaction, shows a consistent picture. The precision of the present study is slightly lower, a consequence of the smaller useful PhD data set and thus the larger variance. Nevertheless, the Ti-O<sub>hydroxyl</sub> and Ti-O<sub>carboxylate</sub> bondlengths of the two systems agree within the precision estimates, while both studies show a significantly shorter value for the Ti-O<sub>hydroxyl</sub> bond.

Our investigation provides no explicit information on the molecular orientation which we assume, on the basis of the carboxylate-surface bonding, and the apparent absence of amino-surface bonding, to be 'standing-up' – but with no quantitative description. So far we have also not discussed the extent to which the PhD data could be consistent with some entirely different adsorption geometry. It seems clear, however, both from the qualitative discussion of the PhD spectra given above, and from the results of Fig. 3, that the chemically-shifted O emitter atoms must occupy some mixture of near-atop and bridging sites. Perhaps the only plausible alternative to the structure we have considered is that the glycinate species is bonded not in a bidentate fashion to two five-fold-coordinated surface Ti atom, but in a monodentate structure, with just one carboxylate oxygen atom bonded to a single Ti atom. This type of structure has been postulated to occur for both glycine and alanine on Cu(110) at certain coverages [9, 10]. In this case the three O atomic emitter atoms contributing to the PhD modulations would all have different local adsorption sites; bridging OH, atop O bonding to the surface, and the second carboxylate O atom substantially higher above the surface. Like the N atom in the 'standing-up' glycinate, this third O emitter site would be expected to lead to only very weak PhD modulations due to the lack of strongly-scattering near-neighbour atoms. We may anticipate, therefore, that the key difference relative to the bidentate structure that we have determined is that the overall PhD modulations would be weaker (due to the contribution of one O atoms with essentially no modulations) and that the relative amplitude of the PhD modulations from the hydroxyl and carboxylate O atom contributions will change from a ratio of 1:2 to 1:1. What is not clear, from this

qualitative discussion, is whether this combination of effects can lead to a comparable level of agreement with the experimental PhD spectra. However, full calculations show that this monodentate O bonding of the glycinate to the surface does lead to a substantially inferior fit to the data. A number of different models were tested including two azimuthal orientations of the carboxylate component in the [001] or  $[\bar{1}\bar{1}0]$  directions, two different tilts of the molecule within the carboxylate plane, and calculations with and without the coadsorbed hydroxyl species. The models assuming no hydroxyl species would correspond to monodentate adsorption of an intact glycine molecule but, like the preferred bidentate model in the absence of OH, these models gave very poor fits to the experimental data ( $R \sim 1.0$ ), particularly for the  $40^\circ$  PhD spectrum (see Fig. 5). With the carboxylate in the [001] azimuth the best-fit structure (Fig. 5) is still very substantially inferior to that for the bidentate glycinate + OH model, with  $R=0.41$ . In fact a slightly lower  $R$ -factor value of 0.38 was obtained with the carboxylate in the  $[\bar{1}\bar{1}0]$  azimuth but this is still well outside the variance (0.05) of the value (0.21) for the best-fit bidentate structure. We may also remark that this location of the glycinate would be very difficult to reconcile with the published STM images.

Our study therefore shows the bonding site, bond lengths and molecular orientation of coadsorbed glycinate and hydroxyl on  $\text{TiO}_2(110)$ , resulting from interaction with glycine, are almost identical to that of coadsorbed formate and hydroxyl species on the same surface. In particular, our results specifically exclude the suggestion, based on total energy calculations, that the glycine bonds to the surface in a zwitterionic form.

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**Table 1.** Summary of the main structural parameter values obtained for the structure of coadsorbed glycinate and hydroxyl species on TiO<sub>2</sub>(110) as determined in this study. Comparable values from an earlier study of coadsorbed formate and hydroxyl species are included. A negative value for the outermost Ti atom relaxation indicates an inwards shift towards the bulk relative to an ideal bulk-terminated structure.

parameter	(2x1) formic acid-reacted surface (Å) [20]	glycine-reacted surface (Å) (this work)
Ti-O <sub>carboxylate</sub> layer spacing	2.06±0.03	2.12±0.05
O <sub>carboxylate</sub> offset from atop	0.25±0.15	0.34±0.08
Ti-O <sub>carboxylate</sub> bondlength	2.08±0.03	2.14±0.05
Ti-O <sub>hydroxyl</sub> layer spacing	1.42±0.05	1.36±0.04
Ti-O <sub>hydroxyl</sub> bondlength	2.02±0.05	2.01±0.03
Six-fold-coordinated Ti atom relaxation	-0.08±0.06	0.00±0.09
Five-fold-coordinated Ti atom relaxation	-0.07±0.06	-0.10±0.14



## Figure Captions

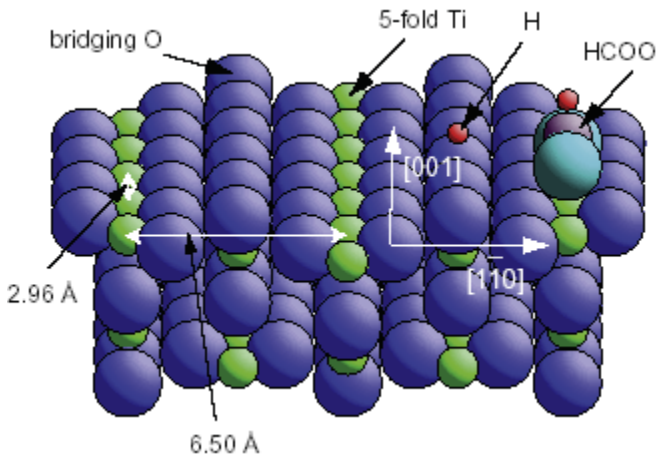


Fig. 1 Schematic diagram of the TiO<sub>2</sub>(110) surface showing the dimensions of the unit mesh, the principle surface azimuthal directions, and the local adsorption geometry of the formate species (HCOO) and the coadsorbed H resulting from interaction with formic acid. O atoms are shown with larger atomic radii (blue) than the Ti atoms (green).

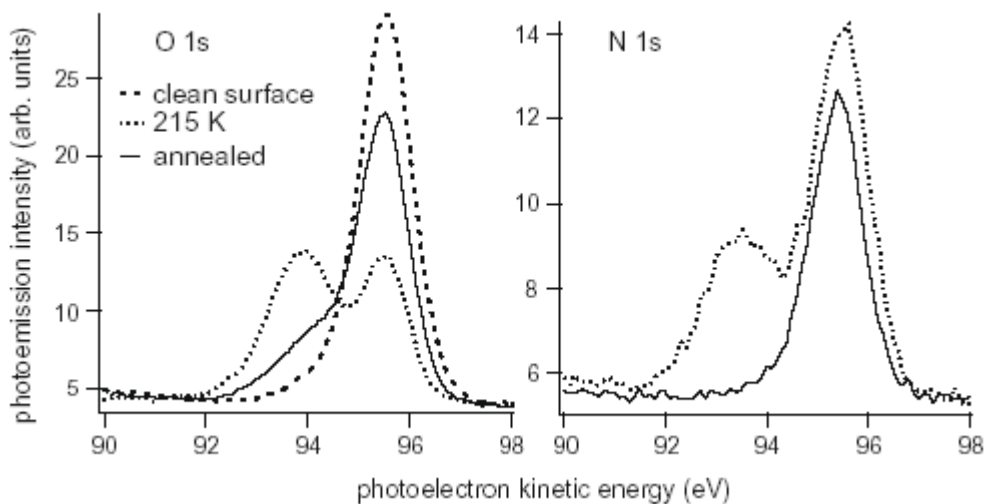


Fig. 2 O 1s and N 1s SXPS spectra recorded from the clean TiO<sub>2</sub>(110) surface, after deposition of glycine at ~215 K, and after subsequent annealing to ~325 K. Photon energies of 630 eV and 500 eV respectively were used, yielding similar photoelectron kinetic energies.

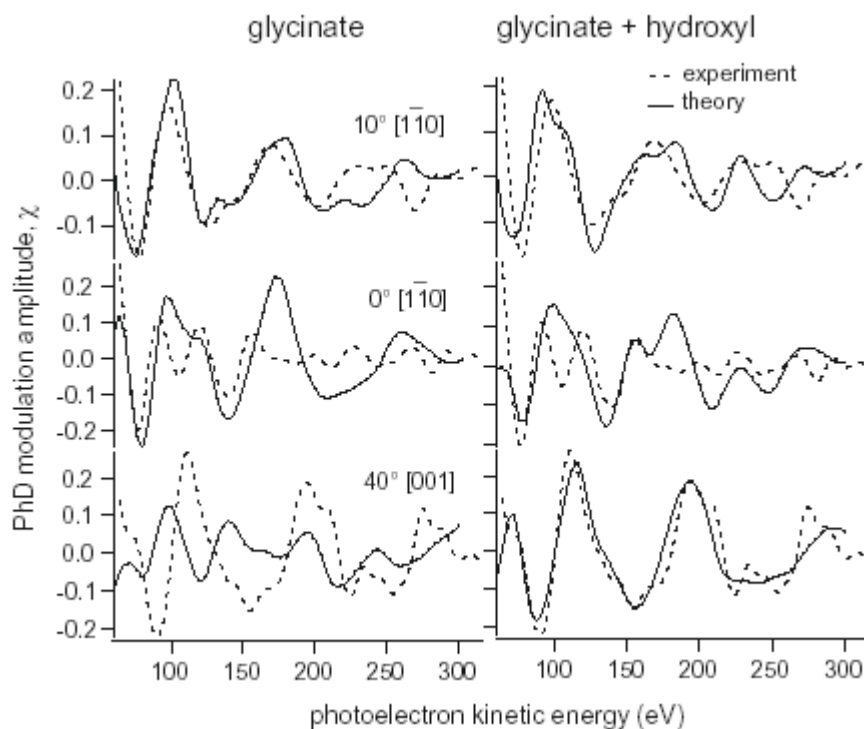


Fig. 3 Comparison of the experimental O 1s PhD spectra from the adsorbed species with the results of theoretical simulations for the best-fit structural models of adsorbed glycinate alone, and of coadsorbed glycinate and hydroxyl species, on  $\text{TiO}_2(110)$ .

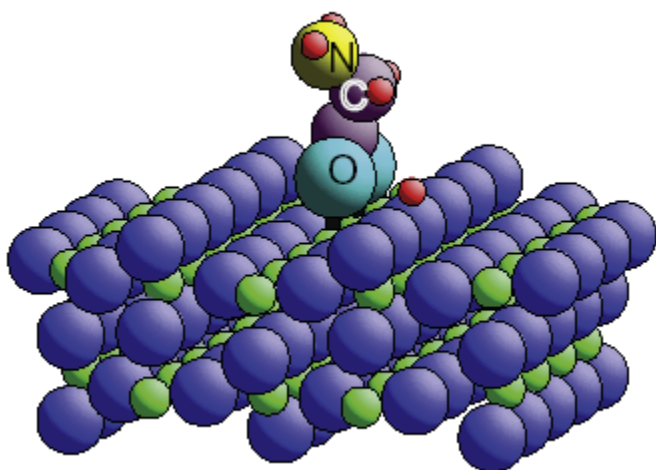


Fig. 4 Ball model of the optimised structure for glycinate on  $\text{TiO}_2(110)$  based on the determined positions of the carboxylate O atoms and the implication from our results that the molecule is 'standing up'; the positions of the C, N and H atoms are schematic only, and were not determined explicitly in this investigation.

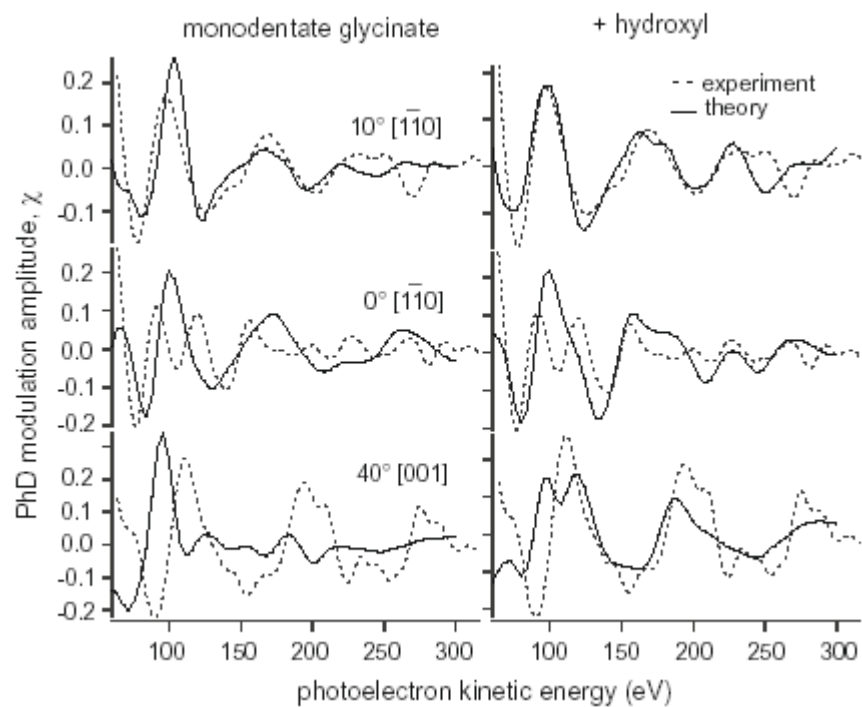


Fig. 5 Comparison of the experimental O 1s PhD spectra from the adsorbed species with the results of theoretical simulations for alternative models based on adsorbed glycinate bonded in a monodentate fashion either alone, or coadsorbed with hydroxyl species, on  $\text{TiO}_2(110)$ .

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