Spectroscopic Evidence for Neutral and Anionic Adsorption of (S)-Glutamic Acid on Ag(111)

M. Smerieri,‡,† L. Vattuone,‡,† M. Rocca,‡,† and L. Savio*,†

†IMEM-CNR, Via Dodecaneso 33, 16146 Genova, Italy
‡Dipartimento di Fisica dell’Università di Genova, Via Dodecaneso 33, 16146 Genova, Italy

ABSTRACT: We report here on a combined photoemission and vibrational spectroscopy investigation of (S)-glutamic acid adsorption on Ag(111). We show that, in the temperature range 250 K ≤ T ≤ 400 K, non-zwitterionic adsorption takes place and the anionic form prevails at nonvanishing coverage. Significant conformational changes of the self-assembled layer must occur above 300 K, corresponding to a substantial reduction of the sticking probability and a modification of the vibrational spectrum. The similarity of behavior with respect to glutamic acid adsorption on the previously investigated Ag(100) and Ag(110) surfaces is also discussed.

1. INTRODUCTION

A clear picture of the hybrid organic—inorganic interface and of the basic mechanisms governing it is essential for the success of both those applications which exploit the molecule—surface interaction and those which want to avoid it. In the former group we mention nanoelectronics,1 the design and fabrication of hybrid nano-objects2 and biosensors,3 as well as all issues related to biocompatibility. In the latter group we list fouling, hygiene, and biocorrosion. In fact the adsorption of peptides, proteins, and protein residues is a preliminary step for the further growth of biofilms on solid surfaces4 and it is often necessary to prevent it.

The great academic and practical interest in this field justified a huge experimental effort which, however, has been so far insufficient for a complete understanding of the biomolecule/surface interactions at the molecular level.5 Among the many possible molecules of biological interest, amino acids represent one of the most attracting categories. They have a simple enough structure to be assumed as a model for the chemisorption of biofunctional molecules but, at the same time, their self-organization in solid molecular crystals shows strong similarities to the native secondary structure of proteins as, e.g., α-helices or β-sheets. Moreover, their adsorption on metal and/or oxide surfaces has applications in surface functionalization,6 in emerging fields such as “green” corrosion inhibition7 or nanoparticle shape control8 and, being chiral molecules, in enantiomeric catalysis.6

The growing experimental and theoretical research effort on amino acid interaction with metal surfaces is witnessed by several review papers on the specific topic.5,9,10 Due to the complexity of these systems, a combination of different methods is often necessary to achieve a complete characterization of the molecular bonding and self-organization at the surface. Experimentally, scanning tunneling microscopy (STM) is usually employed to determine the morphology of the self-assembled layers,11–15 while the chemical nature of the molecules is mainly characterized by X-ray photoemission spectroscopy (XPS)15,16–21 or infrared spectroscopy.18,22 Additional surface science techniques such as low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS),20,21 high resolution electron energy loss spectroscopy (HREELS),17 and Raman Spectroscopy23 have also been exploited. The first studies concentrated on the simplest amino acids on Cu surfaces.9 The panorama of the investigated systems is, however, getting wider and wider, including S-containing amino acids (cysteine and methionine) at Au14,24–26 and Ag27–29 or at the chiral Cu(531) surface,30 as well as the use of more reactive substrates such as Pt(111)31 and Pd(111).21

Self-assembly of amino acids at metal surfaces is an interesting issue for the comprehension and control of supramolecular interactions. From the combination of experimental and theoretical analysis it is nowadays established that both anionic and zwitterionic adsorption are possible, as well as different degrees of interaction with the substrate. Strong molecule–substrate interaction may depend both on the surface and on the amino acid. A typical example is given by alanine adsorption on the reactive Cu(110) surface.32 Self-organization into chiral clusters of six or eight units separated by chiral channels exposing bare metal atoms allows release of the stress due to the lattice mismatch with the substrate. On the other hand, the molecule–surface interaction is reinforced in...
the presence of S-containing species. On the stepped Cu(531) substrate such amino acids may bind either in a three point triangular footprint or in a four point quadrangular footprint.30 On the less reactive Au(111)26 and Ag(111)11 adsorption occurs through the S-headgroup. On Ag(111) it was further demonstrated that an irreversible transition from a zwitterion α-phase to an anionic β-phase occurs above 393 K.

Weaker molecule−substrate interaction as well as multilayer adsorption are characterized, in general, by molecules in the zwitterionic form, which is typical of amino acids in the solid phase. Intermolecular interactions, in general, are determined by H-bonds33,34 or by long-range order forces mediated by the substrate.35

In the study of amino acid adsorption at metal surfaces silver so far has played a minor role. The system is, nonetheless, of utmost interest: it is reactive enough to allow most amino acids to be adsorbed stably at room temperature (RT), but the interaction is so weak that intermolecular bonds are expected to prevail over molecule−substrate attraction. This may lead to a peculiar behavior with respect to Cu and to transition metals. In this context it is worth mentioning that the calculated adsorption energy of phenylalanine in its most stable configuration is −0.3 eV on Ag(111) and −0.5 eV and −1.3 eV on the corresponding Cu and Pt surfaces, respectively.36 Surface enhanced raman spectroscopy (SERS) on roughened Ag surfaces demonstrated that at RT a large variety of amino acid species adsorbs in the zwitterionic form from liquid solution,23 while glycine does not chemisorb on clean Ag at 300 K due to the inability of this substrate to deprotonate it into glycinate.37 Methionine and tyrosine are also weakly bound to Ag(111).29 They adsorb as zwitterions and form very similar linear structures. This lead the authors of ref 29 to propose that the observed zwitterionic noncovalent intermolecular bonding represents a general scheme for amino acid adsorption on weakly reactive, close-packed metal surfaces.

We have recently studied (S)-glutamic Acid (Glu) adsorption at Ag(110)22 and Ag(100)13,15 by microscopic, spectroscopic, and theoretical methods. We demonstrated that, in both cases and contrary to what is observed for more reactive substrates, the self-organization process is dominated by intermolecular interactions. The Ag surface, however, is not an inert spectator since the size and geometry of the Glu self-assembled layers depend not only on deposition temperature, but also on crystal face. Molecules are always in the non-zwitterionic (anionic or neutral) state, similarly to what was reported for amino acids on Cu(110)26 but contrary to the SERS results for deposition from
the liquid phase on roughened Ag.\textsuperscript{23} Two, almost isoenergetic, structures observed on Ag(100)\textsuperscript{15} can be fully resolved by DFT calculations and it was demonstrated that, at least for neutral molecules, self-organization is driven by the maximization of the number of H-bonds.\textsuperscript{13} This behavior is peculiar for a poorly reactive substrate, since on more reactive metals this interaction is of secondary importance with respect to the molecule–surface bond.

In this manuscript, we extend our investigation to the last low Miller Index Ag face, reporting on a combined XPS and HREELS investigation of the Glu/Ag(111) system in the temperature range $250 \leq T \leq 400$ K. Glu adsorption occurs in the non-zwitterionic form, coherently with what observed for Ag(110) and Ag(100), although with a reduced sticking probability related to the lower reactivity of the (111) plane. Therefore the system does not follow the general trend proposed in ref 29 and based on the common behavior of methionine and tyrosine. Two different molecular conformations, stable below and above room temperature, respectively, have been identified by vibrational spectroscopy.

2. EXPERIMENTAL SETUP

Experiments were carried out in an ultra high vacuum (UHV) apparatus hosting a conventional, nonmonochromatic X-ray source (DAR400, Omicron) and a hemispherical analyzer (EA125, Omicron) for photoemission spectroscopy and a HREEL spectrometer (Delta0.5, Specs) for vibrational analysis. In addition, the UHV chamber is equipped with a four degrees of freedom manipulator, a quadrupole mass spectrometer (QMS), an ion gun, valves for gas inlet, and all other typical vacuum facilities. The sample can be cooled down to a crystal temperature $T = 87$ K by liquid N$_2$ flux and heated to $T = 800$ K by electron bombardment. While annealing a Glu layer, however, only irradiative heating is employed since it was proven for Glu/Ag(100)\textsuperscript{15} that electron bombardment causes partial fragmentation of the admolecules.

(S)-Glutamic acid (C$_5$H$_9$NO$_4^-$ – see inset of Figure 1) is an amino acid formed by a five C atom long chain. Each end terminates with a carboxylic group, while the amino group is bonded to the fourth C atom ($\alpha$-C), determining the chirality of the molecule. High purity Glu is evaporated from a glass crucible resistively heated to 405 K. The crucible is separated from the UHV chamber by a valve and it is differentially pumped through a bypass to the turbomolecular pump, so that the amino acid powder can be carefully outgassed before each preparation.

The Ag(111) surface is cleaned by sputtering followed by annealing to 740 K. After Glu deposition at a fixed temperature the sample is
The XPS data are fitted with Gaussian peaks after subtracting a linear background, using the IGOR software package. The N1s and C1s regions were reproduced with one and four components, respectively. Most of the O1s spectra were fitted with a doublet; in those corresponding to the largest exposures at 250 and 300 K, however, a third component around 534 eV had to be added to account for the high energy tail most probably caused by a small degree of water/OH contamination.

3. RESULTS AND DISCUSSION

3.1. XPS Analysis: Adsorption Probability and Chemical State of the Adsorbate. Figure 1 reports representative XPS spectra of the Ag3d, O1s, C1s, and N1s regions after deposition of Glu on Ag(111) at sample temperature 250 K ≤ T ≤ 390 K. Figure 2 shows a typical uptake experiment performed at 250 K and followed by annealing of the Glu layer.

The intensity of the O1s, C1s, and N1s signals decreases with increasing T, indicating a strong temperature dependence of the sticking coefficient. This is the same behavior already observed for Glu/Ag(100), but the effect is even more pronounced in the present case and could not be entirely compensated by a prolonged exposure time. For all preparations a single feature is present in the O1s and N1s regions, while a doublet is observed for C1s. The O1s binding energy ranges from 531.5 to 532.6 eV, the lower values corresponding to higher temperature and smaller coverage. The O1s peak consists indeed of two components related to the nonequivalent oxygen atoms of the carboxylic groups, as discussed in the following. The N1s photoemission peak is always found around 400.0 eV except for the 250 K layer, for which it moves to 400.4 eV for the longest Glu dose. The value of 400 eV is characteristic of non-zwitterionic adsorption, as will be discussed in the following. The C1s region shows peaks in the E_b ranges [285.2, 286.2] eV and [288.0, 288.9] eV, respectively. Also in this case, E_b slightly upshifts with coverage.

Upon annealing the 250 K layer to 300, 350, and 400 K (see Figure 2) the intensity of the photoemission peaks decreases with respect to that of the original layer, indicating partial desorption of the adsorbates. At the same time the binding energy of the O1s, C1s, and N1s peaks shift toward lower values, by amounts depending on the reduction of coverage. The resulting spectra are qualitatively similar to those observed upon deposition at that T. As it was the case for Glu/Ag(100), it is therefore reasonable that Glu molecules are arranged in different configurations, corresponding to local energy minima, and they can switch from one conformation to a more stable one when thermal energy is available. However, the final intensity observed upon annealing at 350 K and at 400 K is larger than that measured after prolonged exposure at the same T. This underlines the nonequivalence of the two processes and suggests a precursor mediated adsorption mechanism, as discussed in the following.

Before proceeding with a more detailed analysis of the XPS results, we believe that some considerations on the coverage regime are helpful. Since a direct calibration of the Glu coverage is not available, we tried to estimate it by cross-checking two indirect methods. First, we compared the O1s/Ag3d intensity ratio for the present preparations and for the “comb” structure forming on Ag(100) at 300 K. It was demonstrated that at saturation coverage the comb structure fully covers the Ag(100) surface and the Glu coverage of the corresponding empirical model is Θ_{Glu} ∼ 0.09 ML (in ML of Ag). Assuming this as calibration coverage, we obtain Θ_{Glu} ∼ 0.07 ML and Θ_{Glu} ∼ 0.14 ML for the largest exposures at 300 and 250 K, respectively. Assuming a 5% error on the area of each XPS peak, these coverage values are easily affected by a 20% error. In a second step we calculated Θ_{Glu} from the ratio of the total C1s and Ag3d_{3/2} intensities, weighted by the corresponding cross sections (corrected considering the doublet nature of the Ag3d photoemission feature) and taking into account the attenuation due to Ag layers closer to the surface and to the Glu layer. Using this approach we estimate a maximum Glu coverage of 0.16 and 0.34 ML for the 300 and 250 K preparations, respectively (with an error of ±10%). However, since the formula is valid mainly for multilayer adsorption, it is not very precise in the submonolayer regime and might overestimate the coverage. Although the two independent estimates of Θ_{Glu} are at the limit of compatibility, they clarify that the data we are presenting here correspond to Glu adsorption in the monolayer regime, with a local coverage comparable to those detected on Ag(100).

For a more detailed analysis of the peak intensities and for their correct attribution, the XPS spectra were fitted with a Gaussian shape plus linear background. A typical analysis is reported in Figure 3 for XPS spectra of the O1s, N1s, and C1s regions, respectively. The O1s peak results from the superposition of two contributions, indicated as O531 and O533 in the following. The N1s region shows only one peak. Four components, corresponding to the four nonequivalent C atoms of the Glu molecule, are found in the C1s spectra. The total O1s and N1s photoemission signals calculated from uptake experiments at different T are reported in Figure 4. At all T, Θ_{Glu} (proportional to the total XPS area), increases with Glu dose. The total amount of adsorbed Glu, on the contrary, changes strongly with temperature. The available N1s series (the signal of the 350 K preparation was too weak to be fitted) are in good agreement with O1s data and confirm the validity of our analysis. The inset of the O1s panel shows a signal proportional to the Glu/Ag(111) sticking probability (S) vs T. It is calculated as the ratio of the O1s area vs exposure for the shortest Glu dose at each temperature and it is therefore reported in arbitrary units. S decreases with increasing T, with a drop above 300 K which is even higher than the one observed for Glu/Ag(100) (empty symbols -- shown for comparison). The observed behavior is indicative of precursor mediated adsorption: with increasing T the shorter residence time of the Glu molecule in a precursor state reduces the probability that it diffuses to an already existing island or that it finds another molecule to start a stable nucleus of a new self-assembled structure before desorption takes place. The lower sticking probability of Glu(111) with respect to Glu(100) may depend on a lower residence time on the compact surface, possibly indicative of the lower adsorption energy or a higher
diffusion barrier. Alternatively, it may be related to the smaller interatomic distance of the Ag(111) face. Assuming that the adsorption and diffusion barriers for Glu on Ag(111) and Ag(100) are comparable, two molecules landing at the same distance on the two surfaces must indeed perform a higher number of hops on Ag(111) than on Ag(100) before they can meet and thus stick on the surface as a new island.

The most direct information provided by XPS is on the chemical nature of the adsorbed Glu molecules. In fact the zwitterionic and nonzwitterionic forms of an amino acid can be distinguished by the N1s photoemission signal, which is expected to be around 400 eV if the amino group is neutral (–NH₂) and at or above 401 eV if it is charged (–NH₃⁺). Some of us have demonstrated previously that adsorption of Glu on Ag(110) and Ag(100) is non-zwitterionic. Here we show that the same is true for Glu/Ag(111), since 399.8 eV ≤ Eb(N1s) ≤ 400.4 eV for all dosing conditions. This is at variance with what was observed for other amino acids deposited on the same substrate and disproves the proposed hypothesis that the zwitterionic form represents a somehow universal condition for amino acid adsorption at the poorly reactive Ag(111) surface. The different behavior can be related to the significantly different structure of Glu (acidic) with respect to methionine (S terminated) and tyrosine (aromatic). This difference is reflected both in the Koolman and in the Timberlake classification schemes, which sort the three molecules in separate groups.

Although it is quite significant information, non-zwitterionic adsorption is not a complete definition of the chemical state of the molecules. Indeed it indicates that the amino group remains neutral, which fits for adsorption both in the neutral and in the anionic form. To distinguish between them on the basis of XPS results is not straightforward. Some reports base this assignment on a quantitative analysis of the O1s spectra. The O533 component is ascribed to O atoms involved in OH groups and the O531 one to O atoms double bonded to C (C=O) or in carboxylate groups (COO⁻); the neutral or anionic nature of the amino acid layers is then deduced from the O533/O531 ratio. Considering the structure of Glu (inset of Figure 1 for the neutral form) and applying this strict model, we should expect a 1:1 ratio for adsorption in the neutral form (two oxygen atoms involved in OH bonds and two involved in C=O bonds) and a 1:3 ratio for adsorption in the anionic form.
(one oxygen atom involved in an OH bond, one in a COO$^-$ group and two in C–O bonds). The results of this analysis are summarized in Figure 5. Panel A shows the uptake curves for the O531 and O533 peaks parametric in deposition temperature; the inset represents their ratio vs the total area of the photoemission signal. In panel B we plot the behavior of the binding energy of O1s peaks vs total area of the photoemission signal. Full and empty symbols refer to the O531 and O533 peaks, respectively.

Figure 6. (A) Area of the O531 and O533 components vs exposure time. Full and empty symbols refer to the O531 and O533 peaks, respectively. Inset: Ratio between the peak areas of the O533 and O531 components vs total area of the photoemission signal. (B) Binding energy of the O1s peaks vs total area of the photoemission signal. Full and empty symbols refer to the O531 and O533 peaks, respectively.

Further mention that the term “anionic” may not fully explain the complexity of the possible reactions occurring on the surface and leading to the deprotonated species. It is not known whether the COOH decomposition is homolytic (generating a radical and an H atom) or heterolytic (generating an anion and a proton). As suggested for Glu/Ag(100),$^{15}$ a very plausible mechanism could be that coadsorbed neighboring neutral species decompose into two Glu radicals with H$_2$ desorption from the surface. Subsequent electron transfer from the metal surface to the radical is also possible and leads to the stabilization of an anionic state. Unfortunately these remain reasonable hypotheses in absence of a thorough DFT analysis of the system.

Figure 5B shows the upshift of the O531 and O533 binding energies with coverage. A similar behavior is observed also for Eb(N1s) and for all the four components of the Cls peaks. The phenomenon is common to other amino acid/metal systems, such as Glu/Ag(100),$^{15}$ Ala/Pd(111),$^{21}$ and Gly/Pr(111),$^{31}$ and has been reported up to coverages of several layers. It was ascribed to relaxation and/or chemical shifts. Slight positive shifts of Eb(N1s) observed experimentally for NH$_3$ mono- and multilayer formation on metal surfaces have been attributed by theoretical studies to H bonding networks of NH$_3$ layer(s).$^{43}$ Since our data are limited to the submonolayer regime, a chemical origin for the effect is most probable.

Finally, we observe that a careful fitting of the doublet present in the Cls region allows resolution of four components at $E_b \sim 285.3$ eV, 286.6 eV, 288.3 eV, and 289.3 eV, respectively (see bottom panel of Figure 3). Since Glu in its neutral form contains three nonequivalent C atoms (C in carboxyl groups, α-C, and aliphatic C), we must conclude that an additional C species is present in our case because of the deprotonated carboxylic group. This information is coherent with what was provided by analysis of the O1s region and further supports our conclusions about the chemical nature of the adsorbate. For comparison with our previous results on Glu/Ag(100)$^{15}$ and with literature data on amino acid adsorption at metal (Cys/Cu(110),$^{18}$ Cys/Ag(111)$^{17}$) and oxide surfaces (Pro/TiO$_2$(110),$^{16}$ Al,$^{10}$ZnO(10–10)$^{16}$) we can safely assign the C species at $E_b \sim 289.3$, ~288.3, ~286.6, and ~285.3 eV to C atoms in the protonated and deprotonated carboxylic groups, to α-C, and to aliphatic C, respectively.

3.2. Vibrational Spectra and Conformation of the Glu Molecules. The outcome of HREELS experiments is reported in Figures 6 and 7. Figure 6 shows the energy loss spectra recorded after 2 min of Glu exposure on Ag(111) at T = 250, 290, and 314 K. A 20 min exposure was necessary to obtain a detectable signal at T = 357 K. Figure 7, on the contrary, follows the evolution of a Glu layer deposited at 250 K and annealed to increasing temperature. The peak assignment (summarized in Table 1) is performed by comparison with our previous results on other low Miller Index Ag faces,$^{15,22}$ with spectroscopic data reported in the literature for other amino acids on (111) metal surfaces (Cys/Au(111),$^{17}$ Gly/Cu(111)$^{46}$) and with theoretical calculations of the vibrational modes of isolated Glu molecules in the zwitterionic and nonzwitterionic form.$^{47,48}$ We can deduce the following information on the conformation of the molecules at different temperatures: (a) No OH stretch is visible in the 400–450 meV range. Since this mode is dipole active, and hence should be visible under in-specular conditions, our data suggest that the OH bonds lie flat on the surface. This statement remains valid also if we consider the possibility that the OH stretch
energy has downshifted below 400 meV due to strong H-bonding and thus is hidden in the tail of the 366 meV peak. As the difference in electronegativity between O and H is larger than between C and H, a rule of thumb implies that the dipolar intensity of the OH mode, when active, should be higher than that of the CH stretch. Therefore, a possible very weak intensity of the OH vibrational mode is compatible with a Glu/Ag related mode. Indeed, a weak feature around 110 meV was present in RAIRS spectra upon deposition of Glu on Ag(110) at 373 K. Peaks in the same energy range are detected for Gly/Cu(111), for Gly/Si(111)-7×7, and for polypeptides in liquid solution. These vibrations are proposed to originate from the combination of the C–C stretch and of the CH2 rocking motions, an assignment which is compatible with the values predicted for isolated Glu molecules if the usual energy downshift related to the interaction with the surface is taken into account.

The reduction of the 111–114 and 214 meV peaks occurs in the same temperature range of the drop in sticking probability observed by XPS and confirmed by inspection of the HREELS intensities. Therefore, a significant conformational change of the Glu-layer must occur above 300 K in association with the already discussed partial desorption of the organic layer. The disappearance of the ν(CO), ν(CC) and r(CH2) peaks indicates that in the high T conformation the dynamic dipole moment of these modes is screened, i.e. that these bonds are oriented (nearly) parallel to surface. So we propose that, similarly to the case of Glu/Ag(100), the Glu units on Ag(111) rearrange in a less dense structure in which they can lie almost flat on the surface.

The final picture we are able to draw is the following: at very low coverage and at all investigated temperatures Glu adsorbs on Ag(111) both in neutral and anionic forms; the latter becomes dominant with increasing coverage reasonably as a consequence of the enhanced intermolecular interactions. The interaction with the surface is made mainly by the COOH and/or COO− groups, either in monodentate or bidentate configuration. Although a microscopic analysis would be required, we are confident that in our experimental conditions the molecules self-assemble in monolayer islands, as they do on the other Ag faces and as it is common for amino acids in general. For T \leq 300 K denser structures form, with the molecules assuming possibly a bent or partially upstanding conformation. At higher T, on the contrary, Glu units are likely to sit in a flat conformation, with a reduced local density.

So far we have not discussed the role of hydrogen bonds, which are a significant element to be considered when dealing with biological molecules at surfaces. H-bonds have an intra- or intermolecular nature and their weight with respect to the molecule-surface bond becomes more relevant for weakly bound molecules. E.g. H-bonding was demonstrated to be the unresolved contributions of the NH3 in-plane bending and of the COO− asymmetric stretch. In infrared experiments the δ(NH3) frequency is considered as evidence of the zwitterionic or nonzwitterionic state of the molecule. The same does not hold for the present experiments, since the expected separation between the δ(NH3) and δ(NH3+) modes (~2 meV) is smaller than HREELS resolution. Moreover, the intensity of the δ(NH3) mode should correlate to the presence of the NH3 stretch around 400 meV. Since the latter is absent, we can guess an almost flat orientation of the NH3 vibrational plane and hence that the ν(COO−) mode is the dominant component of the 205 meV peak. (d) The peaks at 111–114 meV and at 214 meV disappear or are strongly reduced upon exposure/annealing above room temperature. The higher frequency mode is due to a C=O stretch with a possible contribution of the COOH stretch. The lower frequency one was observed at 118 meV on Glu/Ag(100) only in the 250 K preparation. On that occasion it was assigned to a possible contaminant, but in view of the present data we can safely classify it as a Glu/Ag related mode. Indeed, a weak feature around 110 meV was present in RRAIR spectra upon deposition of Glu on Ag(110) at 373 K. Peaks in the same energy range are detected for Gly/Cu(111), for Gly/Si(111)-7×7, and for polypeptides in liquid solution. These vibrations are proposed to originate from the combination of the C–C stretch and of the CH2 rocking motions, an assignment which is compatible with the values predicted for isolated Glu molecules if the usual energy downshift related to the interaction with the surface is taken into account.

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driving force for self-assembly of neutral Glu physisorbed on Ag(100).13 H-bonds are certainly present also for Glu/Ag(111) and, reasonably, they play a significant role in the determination of the molecular conformation and of the overall self-assembled structure. The increase of the anionic fraction with coverage in such a way to make deprotonation thermodynamically allowed. We suggest that the energetic gain provided by intermolecular interactions might indeed compensate for the energy cost of the deprotonation needed to access the anionic form. We remark however that a detailed investigation in this direction is not possible with our spectroscopic means; it would require a full DFT characterization of the system which is not available at the moment. 

Vibrational modes of Glu molecule: \( \nu \) = stretching; \( \delta \) = in-plane bending; \( \gamma \) = out-of-plane bending; \( t \) = twisting, \( w \) = wagging; \( r \) = rocking. Vibrational energies are expressed in meV for coherence with Figures 6 and 7.

### 4. CONCLUSIONS

In the present paper we have reported a complete HREELS and XPS study of the Glu/Ag(111) system in the temperature range between 250 and 400 K and we have discussed the results in comparison to what previously reported for other low Miller Index Ag faces.

Glu adsorbs in the non-zwitterionic form in all tested conditions, in agreement with that observed on Ag(100) and Ag(110) and at variance with what was reported for other amino acids on the same substrate. The adsorption probability is lower that for Ag(100), the difference growing with increasing temperature. Vibrational spectroscopy indicates the presence of at least two different conformations, stable below and above RT, respectively.

### REFERENCES


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**Table 1. Assignment of the Glu/Ag(111) Vibrational Peaks, Performed from Comparison with Previous Spectroscopic Measurements on Other Amino Acid/Metal Systems\(^{15,17,22,46}\) and with Calculations on Isolated Glu Molecules in the Zwitterionic\(^{47}\) and Non-Zwitterionic\(^{48}\) Forms\(^{a}\)**

<table>
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<th>Vibrational mode</th>
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<th>Glu/Ag(110) (anionic(^{22}))</th>
<th>Cys/Au(111) (zwitt.(^{15}))</th>
<th>Gly/Cu(111) (anionic(^{46}))</th>
<th>Glu (zwitt.(^{15}))</th>
<th>Glu (non-zwitt.(^{48}))</th>
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<td>176</td>
<td></td>
</tr>
<tr>
<td>( \delta (\text{NH}_3^-) )</td>
<td>183</td>
<td>189</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>( \nu (\text{CO}) )</td>
<td>171–177</td>
<td>173</td>
<td>181</td>
<td>179, 187</td>
<td>185–188</td>
<td></td>
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</tr>
<tr>
<td>( \nu (\text{COO}^-) )</td>
<td>205</td>
<td>202–210</td>
<td></td>
<td>199</td>
<td>204</td>
<td>201</td>
<td></td>
</tr>
<tr>
<td>( \nu (\text{NH}_2) )</td>
<td>202–210</td>
<td>213</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu (\text{COOH}) )</td>
<td>214</td>
<td>213</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu (\text{CO}) )</td>
<td>214 (202–210)</td>
<td>205, 210, 214</td>
<td></td>
<td></td>
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<tr>
<td>( \nu (\text{CH}_2) )</td>
<td>358 366–369</td>
<td>367</td>
<td>366</td>
<td>354</td>
<td>365–366</td>
<td>369</td>
<td></td>
</tr>
<tr>
<td>( \nu (\text{CH}) )</td>
<td>383</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \nu (\text{NH}_2) )</td>
<td>383</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>( \nu (\text{NH}) )</td>
<td>390–392</td>
<td></td>
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</tr>
</tbody>
</table>

\( ^{a} \) Vibrational modes of Glu molecule: \( \nu \) = stretching; \( \delta \) = in-plane bending; \( \gamma \) = out-of-plane bending; \( t \) = twisting, \( w \) = wagging; \( r \) = rocking.
the photoemission angle. Since the Ag3d_{3/2} intensity has been determined experimentally, the total intensity due to Ag, I_{Ag} is $5/3$ of $I_{Ag3d_{3/2}}$ due to the degeneracies of the 3/2 and 5/2 sublevels. We did not correct for the analyzer transmission function since the Ag3d and C1s photoemitted electrons have similar kinetic energies. This formula allows us to estimate the total C coverage and to deduce \( \Theta_{Ag} \) by dividing for the number of C atoms/molecule. Finally, we corrected for the attenuation factor due to the presence of the Glu layer, $e^{-d/\lambda_{Gl}} \approx 0.57$, assuming an average Glu thickness $d = 4 \text{Å}$ and a mean free path typical for amino acids.


(39) To obtain an absolute estimate of the Glu coverage from the ratio of the C1s and Ag3d intensities we applied the formula

$$
\Theta = \frac{I_{C}}{I_{Ag}} \frac{\sigma_{Ag}}{\sigma_{C}} \left( 1 - e^{-d/\lambda_{Gl}} \right)
$$

where \( \Theta \) is the C coverage; \( I_{C} / I_{Ag} \) and \( \sigma_{Ag} / \sigma_{C} \) are the total photoemitted intensity and cross section of the C (Ag) species, respectively; \( d \) is the Ag interlayer spacing, \( \lambda \) the mean free path, and \( \theta \) the photoemission angle. Since the Ag3d_{3/2} intensity has been determined experimentally, the total intensity due to Ag, I_{Ag} is $5/3$ of I_{Ag3d_{3/2}} due to the degeneracies of the 3/2 and 5/2 sublevels. We did not correct for the analyzer transmission function since the Ag3d and C1s photoemitted electrons have similar kinetic energies. This formula allows us to estimate the total C coverage and to deduce \( \Theta_{Ag} \) by dividing for the number of C atoms/molecule. Finally, we corrected for the attenuation factor due to the presence of the Glu layer, $e^{-d/\lambda_{Gl}} \approx 0.57$, assuming an average Glu thickness \( d = 4 \text{Å} \) and a mean free path typical for amino acids.


