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Unravelling the GLY-PRO-GLU Tripeptide Induced Reconstruction of the Au(110) Surface at the Molecular Scale

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Abstract

The adsorption of GLY-PRO-GLU tri-peptide on Au(110) is investigated within the frame of all atom classical mechanics simulations and Density Functional Theory, focusing on the surface reconstruction. It is shown that the tri-peptide adsorption reorganizes and restructures the Au(110) surface. A mechanism for the surface restructuring is proposed for both the neutral and zwitterionic form of the peptide at room temperature in Ultra High Vacuum. Diverse residues may be involved in the Au atoms displacement, and in particular glutamic acid, triggering a double proton transfer and the formation of a zwitter ionic state, is found to be responsible for the triggering of the surface reconstruction.

Keywords: Amino acids, peptides, gold surface, DFT, Molecular Dynamics

Introduction

Understanding and controlling protein-surface interactions is of fundamental scientific interest, as a key step in medical, biological, biotechnology and environmental applications.¹ Since the 1990s the adsorption of amino acids (AA), as structural units of proteins, on metal surfaces under Ultra High Vacuum (UHV) has been extensively studied¹⁻² followed by their investigation using computational ab initio methods since the 2000s¹.

An transitional phase towards the challenging investigation of protein adsorption on surfaces, is the study of peptide adsorption under UHV conditions.³⁻⁸ Despite the characteristic difficulties encountered, surface scientist have succeeded to study assemblies of oligopeptides, as summarized in a recent review.¹

Surface science techniques, such as Reflection Absorption Infrared Spectroscopy (RAIRS), X-Ray Photoelectron Spectroscopy (XPS) and Scanning Tunneling Microscopy (STM), when used in combination with molecular modeling techniques, are the ideal methodology to describe, understand and predict molecular adsorption properties up to the molecular level. The fundamental information obtained under well controlled conditions helps the understanding of more complex systems, for instance at the liquid–solid interface.⁹

XPS and PM-RAIRS results¹⁰⁻¹³ showed that di- and tripeptides are adsorbed intact on gold and copper surfaces under two different ionic forms, the zwitterionic and the neutral ones. Their adsorption mode on gold, as well as the growth mechanism of the adsorbed layer, has been found to be very sensitive to the peptide sequence: both Gly-Pro-Glu and Gly-Pro, which differ only by the presence of a Glu fragment, strongly interact with gold surfaces.

In particular, on the Au (110) surface, at low coverage, both Gly-Pro-Glu and Gly-Pro organize in layers leading to the formation of relatively large aggregates¹⁴.

Adsorption of amino acids on metallic surfaces can induce surface faceting.¹⁵⁻¹⁶ This was often observed when the substrate was annealed to obtain a self-assembled adlayer of AA at the surface. To our knowledge, only two other examples of drastic substrate reconstruction, or surface faceting, have been reported at room temperature. In the first case, atomic diffusion and creation of triangular shape structures at step edges has been reported in the presence of a formate at low coverage on Cu(110).¹⁷⁻¹⁸ In the second example the adsorption of Gly-Pro-Glu on Au(111), induced an important mass transportation and thus the creation of “gold fingers”, composed of small aggregates of Gly-Pro-Glu molecules bound to Au atoms.¹⁹

In this work we want to provide a microscopic, atomistic characterization of the peptide-gold adsorption in the case of Gly-Pro-Glu adsorption on Au(110), in order to explain and interpret

recent surface experiments including Infrared Spectroscopy (IR), XPS, and Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM) (See ref.¹ and references therein), and to fill the gap between fundamental science and real applications. In order to interpret the experiments we have performed classical (force field-based) molecular dynamics simulations to explore the different binding conformations of GLY-PRO-GLU to Au(110).

Our study aims to correlate the modifications induced by the adsorbed layer to the gold surface ordering, and to investigate the molecular induced surface reconstruction, which is relevant to self-assembled monolayer applications in general.²⁰⁻²⁹

Computational Details

Calculation level

Molecular Dynamics (MD) simulations have been performed with the GROMACS package using the available CHARMM³⁰ force field in combination with the 12-6 Lennard-Jones description for the gold surface developed by H. Heinz and co-workers³¹. Such a force field has been extensively and successfully tested in biomolecular-inorganic interactions^{5, 31-35}.

The simulations were performed in gas phase conditions, corresponding to the ultrahigh vacuum (UHV) as utilized in RAIRS, STM, LEED and Photoemission experiments.⁹ The peptide was investigated in its neutral and zwitter ionic form. 10 trajectories, each of 10 ns, were sampled per species. The sampling was performed within the NVT ensemble at $T = 300$ K using a time steps $\delta t = 1$ fs.

The electronic structure calculations have been performed with the *ab initio* plane-wave pseudopotential approach as implemented in the VASP code³⁶⁻³⁷. The Perdew-Burke-Ernzerhof (PBE) functional³⁸⁻³⁹ was chosen to perform the periodic DFT calculations. The valence electrons were treated explicitly and their interactions with the ionic cores described by the Projector Augmented-Wave method (PAW)⁴⁰⁻⁴¹, which allows to use a low energy cut off equal to 400 eV for the plane-wave basis. The integration over the Brillouin zone was performed on a $2 \times 5 \times 1$ k-point mesh.

In the geometry optimizations at 0 K, the positions of all atoms in the supercell have been relaxed in the potential energy determined by the full quantum mechanical electronic structure until the total energy differences between the loops is less than 10^{-4} eV.

In order to account for the dispersion interactions, DFT-D2 approach of Grimme⁴² and DFT-D3⁴³ were used, as implemented in VASP, which consists in adding a semi-empirical disper-

sion potential to the conventional Kohn-Sham DFT energy. In the original paper of Grimme (D2 correction) only the first two rows of the periodic table of elements are included - for gold we used a value of $40.62 \text{ J.nm}^6/\text{mol}$ for the dispersion coefficient C_6 and of 1.772 \AA for the van der Waals radius (R_0).⁴⁴⁻⁴⁵ For the D3 correction the default parameters were used.

Description of the models

The adsorption of the tripeptide GLY-PRO-GLU, (in one letter code: EPG), see **Fig. 1**, is studied on the Au(110) surface.

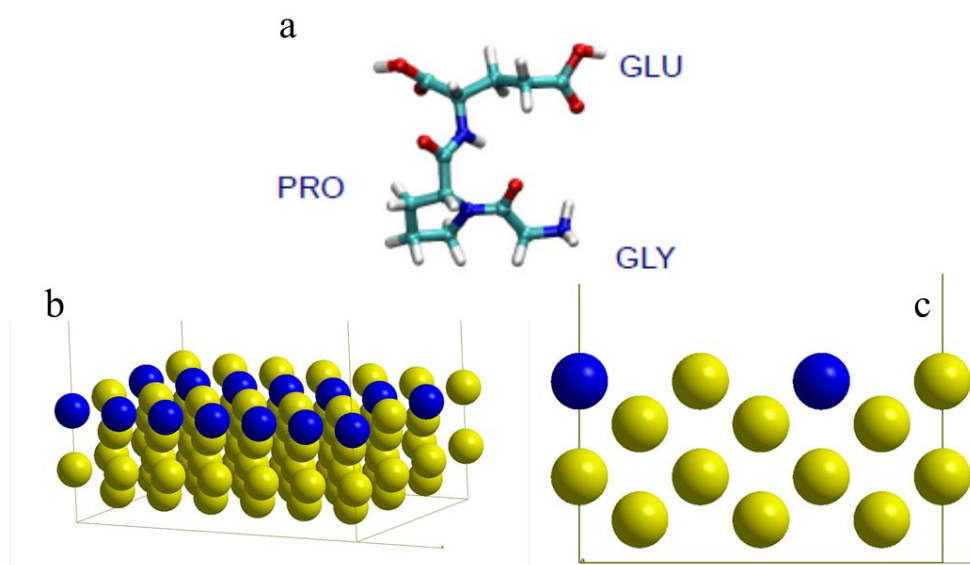


Figure 1. a. Schematic representation of the GLY-PRO-GLU peptide, showing the 3 amino acid residues. (turquoise = carbon, red = oxygen, blue = nitrogen, white = hydrogen), b and c. slab model of the Au(110) surface showing the missing row in blue.

The Au(110) surface⁴⁶ forms a (1×2) clean surface reconstruction⁴⁷ (See **Fig. 1**), called the Missing Row Reconstruction (MRR)^{48-49, 50}.

In the classical force field calculations the MRR Au (110) surface is modeled by a slab model consisting of 20 layers, with 546 Au atoms per layer. The super cell dimensions were: $8.10 \times 8.10 \times 16.44 \text{ nm}^3$. On the surface, 13 GLY-PRO-GLU peptides were placed, corresponding to a coverage of $0.2 \text{ GLY-PRO-GLU / nm}^2$.

The model used in the DFT calculations is smaller than the one used in the classical force field simulations. In the DFT calculations the Au(110) model slab consisted of four Au layers from which the top layer has one on two rows missing, accordingly to the MRR reconstruc-

tion, accounting for a total of 140 Au atoms. The two bottom layers of the slab were kept fixed during the geometry optimizations.

In the DFT model only one GLY-PRO-GLU molecule was considered on a slab with a thickness of 4.29 Å (4 Au layers) and dimensions $20.65 \times 23.36 \text{ Å}^2$, resulting in a coverage of 0.2 molecules/nm², i.e. equal to the one used in the classical force field simulations.

Results and discussion

The first result of our simulations, is that it is possible to directly observe the MRR Au(110) reconstruction as consequence of the GLY-PRO-GLU adsorption on the gold surface as suggested in earlier experimental studies^{11, 25}. Moreover, the simulations can provide here an atomistic mechanism to explain the Au atom displacements induced by the tripeptide. Interestingly, the Au atom displacement and the surface reconstruction were confirmed for both the neutral and the zwitter ionic peptides, although with some important differences.

Adsorption of the neutral GLY-PRO-GLU peptide on MRR Au(110).

The MD trajectories for the GLY-PRO-GLU on the Au(110) surface are analyzed by dividing the different Au atom displacements (jumps) into 4 groups, i.e. Au jumps due to the: interaction with GLY, PRO, and GLU, respectively and spontaneous Au atom jumps (See **Table 1**). Spontaneous Au jumps are known and are responsible for surface reconstructions such as the herringbone reconstruction of the Au(111) surface and the MRR reconstruction of the Au(110) surface. These spontaneous jumps occur on average every 50 and 25 atoms for the Au(111) and Au(110), respectively. In the presented models, four of these spontaneous Au atom jumps, occurring without the interaction with the peptide, are observed.

Table 1. Run time of the simulation, interaction type, and number of Au atom jumps for 10 different MD runs of neutral GLY-PRO-GLU peptide on MRR Au(110).

Run (each of 10 ns)	Interaction via GLY	Interaction via PRO	Interaction via GLU	Au atom jump Spontaneously
1	0	1	1	0
2	0	0	0	0
3	0	1	0	1
4	2	1	0	1
5	0	0	0	0

6	0	1	0	0
7	0	1	1	0
8	0	0	0	1
9	1	1	1	0
10	0	1	0	1

The low reactivity (low number of Au jumps) of Au surface in the presence of the neutral tripeptide allows to identify a mechanism for each molecule and to associate it with the interaction with a specific amino acid residue.

The most common mechanism for the observed Au jumps, seven occurrences over ten trajectories, involves the PRO residue. In some cases, the PRO residue is assisted, in a second step, by a further interaction with the GLU or the GLY residues. If we follow one of the trajectories where the displacement occurs (e.g. run 7, **Table 1**) we see that the pyrrolidine group is in bridge position between two gold atoms and is the only group involved in the Au atom displacement. The width of the indent gold line varies from 5.6 to 5 Å and the width of the pyrrolidine group is around 4 Å. Based on these dimensions, for a non-charged system, steric interactions are expected to be the driving force behind the Au atom displacement. It is interesting to note that the peptide fits inside the indent creating tension in xy plane.

The Au atom displacement initiated by a GLY residue is less common, indeed is found only in two of the ten investigated trajectories. The displacement mechanism is described in **Fig. 2**. The amino group of GLY together with a coordinated movement involving the PRO residue acts as a lever to displace the Au atom (See **Fig. 3**).

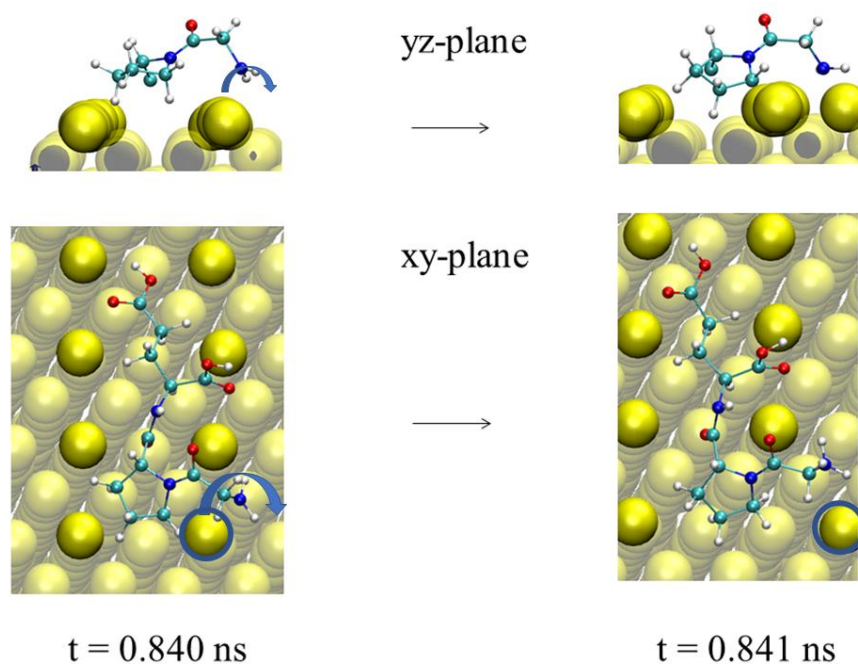


Figure 2. Snap shot of the Au atom displacement on MRR Au(110) initiated by the GLY residue of the GLY-PRO-GLU tripeptide at $t = 0.840 \text{ ns}$. Only GLY and Pro represented for the zy plane representation. (Au = yellow, turquoise = carbon, red = oxygen, blue = nitrogen, white = hydrogen)

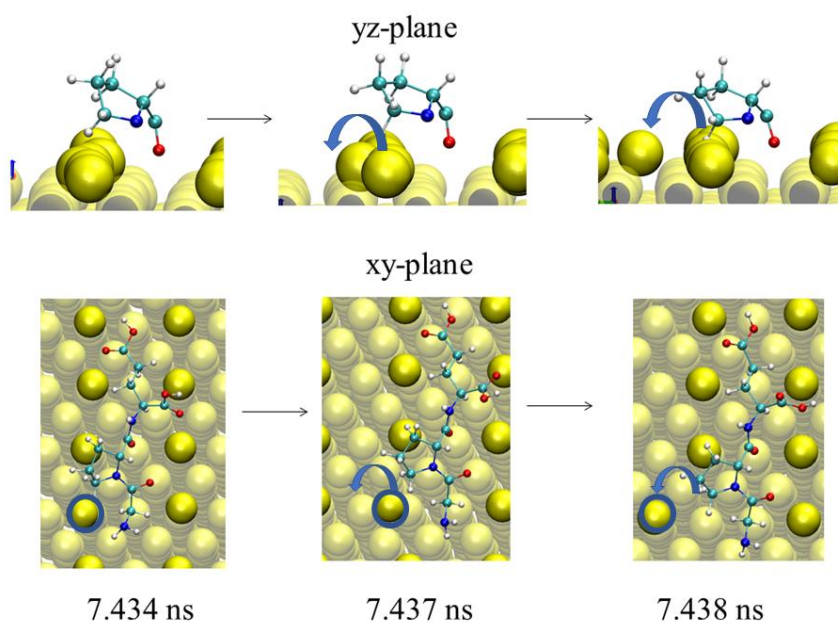


Figure 3. Snap shot of the Au atom displacement on MRR Au(110) initiated by the PRO residue of the GLY-PRO-GLU tripeptide at $t = 7.43 \text{ ns}$. (Au = yellow, turquoise = carbon, red = oxygen, blue = nitrogen, white = hydrogen)

The third possible mechanism for an Au atom displacement is the one initiated by the GLU residue (See **Table 1**, run 1, 7, and 9). This reaction is observed 2 times over the 10 trajectories. The GLY residue fits well in the indentation of the MRR Au(110) reconstruction, allowing a strong interaction with the second Au layer.

The torsion of the dihedral allows the GLU residue to form an intra-molecular H-bond with the carboxyl group of GLY. Interestingly another Au atom jump can be observed next to the PRO residue (See **Fig. 4** at the left side).

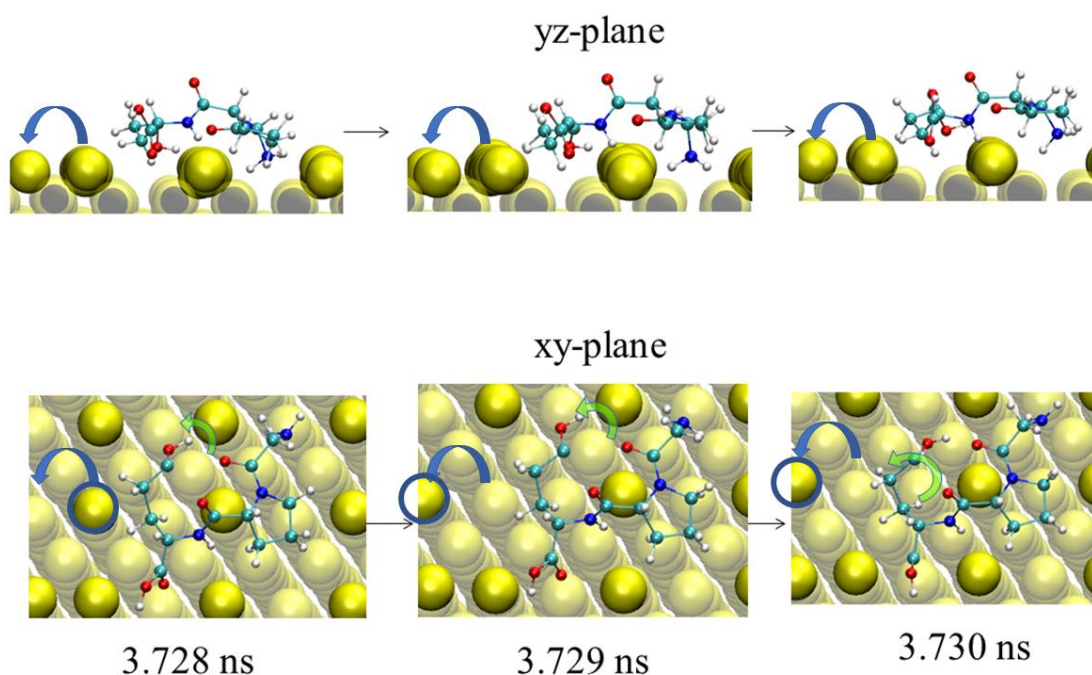


Figure 4. Snap shot of the Au atom displacement on MRR Au(110) initiated by the GLU residue of the GLY-PRO-GLU tripeptide at $t = 3.72$ ns. (Au = yellow, turquoise = carbon, red = oxygen, blue = nitrogen, white = hydrogen)

Adsorption of the zwitter ionic GLY-PRO-GLU peptide on MRR Au(110).

The zwitter ionic peptide behaves differently from its neutral state. Indeed, at odd with what observed in the neutral state, the zwitter ionic peptides interact strongly with each other forming dimers, already at the investigated coverage (i.e. the same as for the neutral peptide: 0.2 nm^{-2}). In particular $\text{NH}_3^+/\text{COO}^-$ interactions do not only occur between different molecules but also as intra-molecular interactions, changing the peptide flexibility and having an important impact on the binding of the sidechain groups to surface. Also in the case of the zwitterionic peptides we have divided the possible jumping events in four categories according to the involved residues (See **Table 2**).

Table 2. Run time of the simulation, interaction type, and number of Au atom jumps for 10 different MD runs of zwitter ionic GLY-PRO-GLU peptide on MRR Au(110).

Run (each of 10 ns)	Interaction via GLY	Interaction via PRO	Interaction via GLU	Au atom jump Spontaneously
1	1	4	3	1
2	2	3	2	0
3	0	1	1	2
4	1	1	3	1
5	2	0	1	0
6	1	2	3	0
7	2	2	2	0
8	1	2	2	0
9	3	0	4	0
10	1	3	2	0

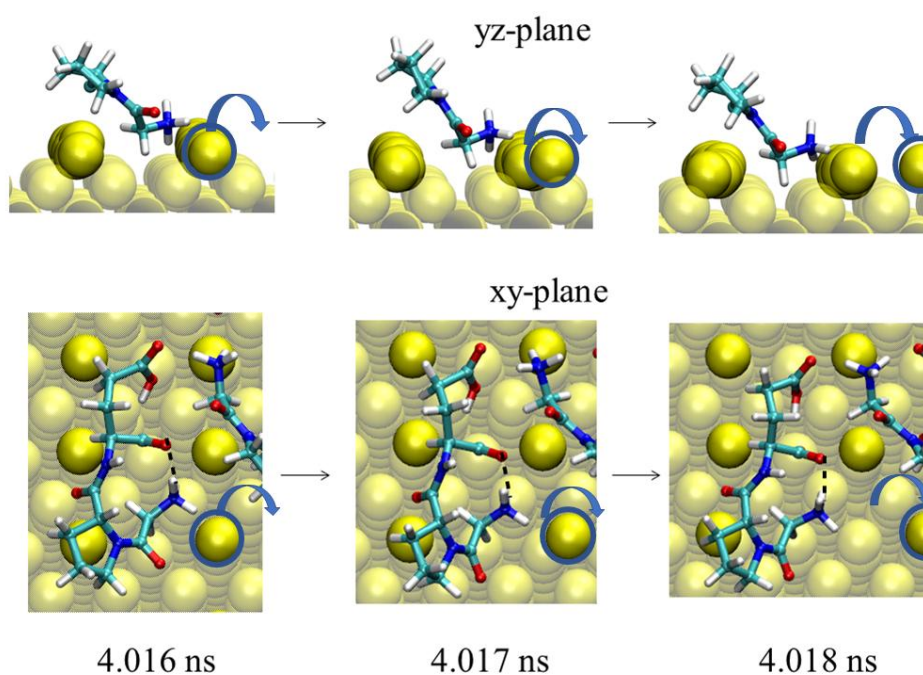


Figure 5. Snap shot of the Au atom displacement on MRR Au(110) initiated by the GLY residue of the zwitter ionic GLY-PRO-GLU tripeptide at $t = 4.01$ ns. Only GLY and Pro represented for the zy axis, and H-bond depicted by a black dashed line. (Au = yellow, turquoise = carbon, red = oxygen, blue = nitrogen, white = hydrogen)

In the case of the Au atom displacement by a GLY-residue, the tilting of the proline residue is

observed and associated with the “pushing” movement on the displaced Au atom (See **Figure 5**). Although, this mechanism is the least frequent, it still occurs 14 times during the 10 MD runs of 10 ns (See **Table 2**).

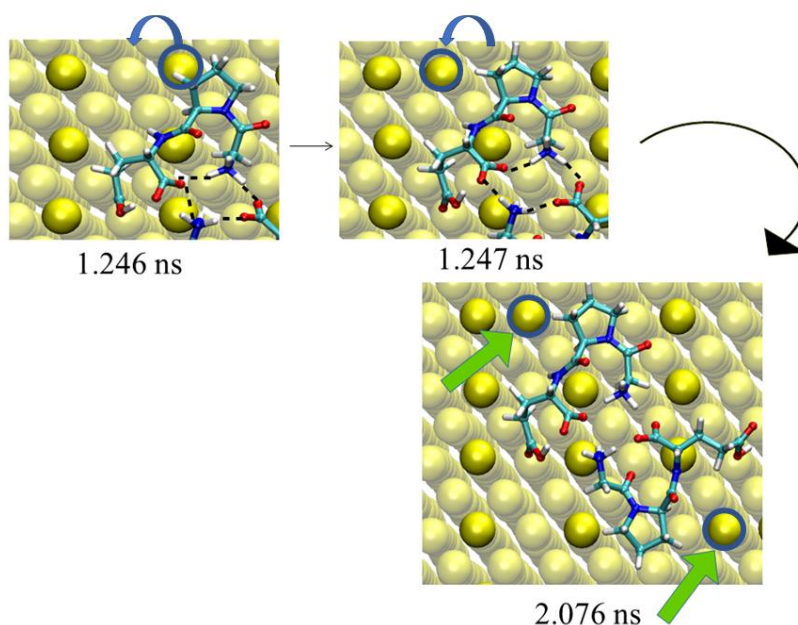


Figure 6. Snap shot of the Au atom displacement on MRR Au(110) initiated by the PRO residue of the zwitter ionic GLY-PRO-GLU tripeptide at $t = 2.07$ ns. The green arrows show the displaced surface Au atoms. (Au = yellow, turquoise = carbon, red = oxygen, blue = nitrogen, white = hydrogen)

The zwitter ionic peptide tends to form dimers via intermolecular H-bonds. The planar dimer displaces a first Au atom after 1.24 ns, with the help of the PRO residue. The second peptide displaces another Au atom after 2.07 ns (See **Figure 6**). The geometry of the adsorption complex shows mirror symmetry. The peptide dimerization enhances the displacement of the Au surface atoms and thus the surface reconstruction. The described mechanism is observed in several different simulations (18 times during the 10 simulations, See **Table 2**).

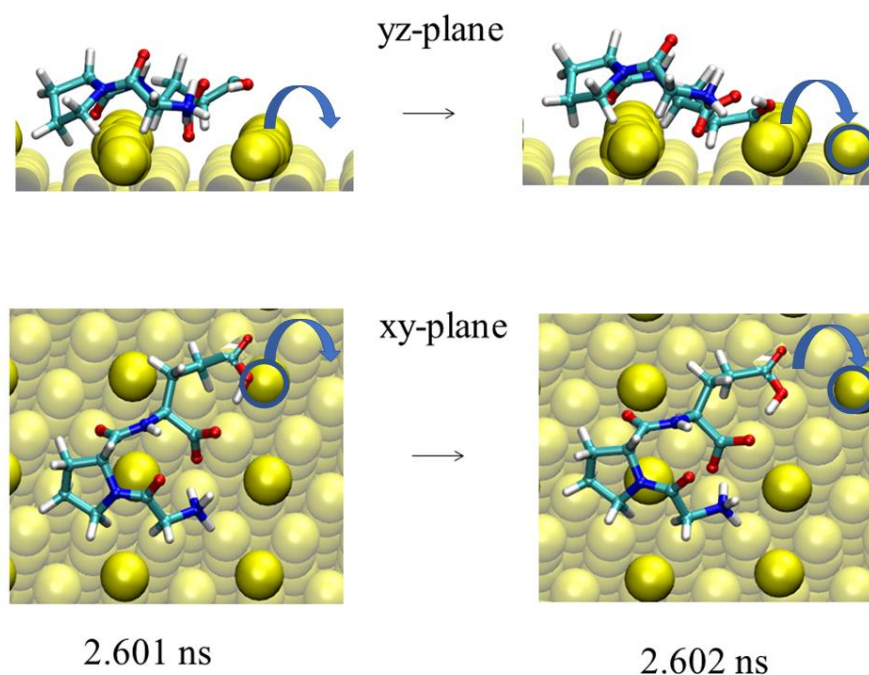


Figure 7. Snap shot of the Au atom displacement on MRR Au(110) initiated by the GLU residue of the zwitter ionic GLY-PRO-GLU tripeptide at $t = 2.60$ ns. (Au = yellow, turquoise = carbon, red = oxygen, blue = nitrogen, white = hydrogen)

Finally, the mechanism involving the GLU residue is the most common, as it was already observed in the case of the neutral peptide. In 23 events over the 10 trajectories the peptide (See **Table 2**) succeed to induce an Au atom displacement after 2.6 ns, on the MRR Au(110) surface. When this mechanism is at play (See **Figure 7**) the intramolecular interactions make the peptide more rigid, and orientate the GLU carboxylate-group, allowing an interaction with the Au atoms and to dislocate them.

Adsorption energies and complexes stability

In the classical simulations the gold surface is strictly neutral and its interaction with the peptide is taken into account via LJ parameters. Although such a description has been widely tested⁵¹, it still neglect important effects such as the electronic polarization of the metal, which could play an additional role in the stabilization of the binding of charged residues to the metal surface. In order to obtain accurate values for the peptide binding energies, as well to provide a further characterization of the surface reconstruction the MD simulations have been complemented by DFT calculations. In particular, starting from the MD trajectories, the most stable configurations for both the neutral and the zwitter ionic state have been identified and optimized at the DFT-D level. Both the configurations before and after the Au atom

displacement were considered and compared.

The models were resized in order to fit the calculation level, maintaining the same surface and environment (See method section above for the model description).

The adsorption energy was calculated for the models shown in **Figure 8**. It is interesting to note that the neutral state of the peptide forms spontaneously a zwitter ion. This leads us to propose that the proton transfer, which we observe and describe in **Figure 8b** is part of the adsorption and restructuration mechanism at the simulation conditions, i.e. $T = 300\text{ K}$ and $0.2\text{ molecules nm}^{-2}$. The whole adsorption process is expected to occur as follows. The tripeptide adsorbs on the surface and the GLU residue undergoes a rotation (See **Figure 8a**). This configuration enables a proton shift from the GLU terminal COOH group to the NH_2 end group mediated by the GLU sidechain group (See **Figure 8b**). This double proton transfer promotes the displacement of the Au atom situated next to the tail COO^- group of the peptide (See **Figure 8c**).

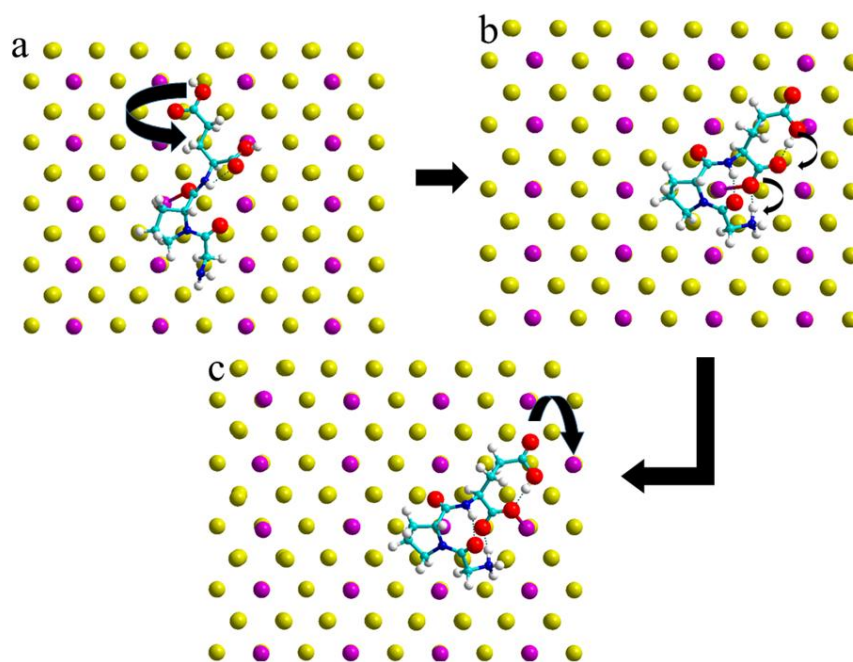


Figure 8. Selected Au hopping mechanism induced by IGF adsorption based on the DFT energetics.

The neutral peptide adsorbs to the surface (**Fig. 8a**) with a binding energy of -1.85 eV . The rotation of the GLU residue with the spontaneous double proton shift (**Fig. 8b**) stabilizes the adsorption by further 0.71 eV . The peptide adsorption liberates surface tension and allows an Au atom to jump from one position to another on the Au(110) surface. This last step occurs

almost without additional energy cost (0.04 eV), leading to a final adsorption configuration (**Fig. 8c**) which has a binding energy of -2.60 eV. This almost barrier less surface reaction is thus easily possible at room temperature, as observed in our simulation and in the experiment^{9, 25}.

Comparison with experiment

In earlier experimental investigations^{12, 14}, the coexistence of intact zwitter ionic and neural species were observed, however, it was difficult to quantify their relative amounts. It was also concluded that IGF adsorbed strongly to the surface.

In our models, both zwitter ionic and neutral IGF were investigated, and a strong interaction with the gold surface was calculated for IGF after proton shifts (-2.60 eV).

After increasing the coverage it was found experimentally that the 2D organization as well as the initial MRR reconstruction of the substrate vanished, as a consequence of displaced gold atoms by IGF molecules (i.e. the overall surface was found to become mobile). This phenomenon was recovered by the MD simulations, by observing the displacement of individual gold atoms on the surface. The surface reconstruction was found to be important between the substrate and IGF, however to a lesser extent compared with the denser and more stable Au(111) surface¹⁹. The strong interaction of IGF was experimentally concluded to be likely via the COOH and NH₂ groups if the geometry permits it. This point was unraveled in our study and found to be consisting of different adsorption configurations including proton shifts.

4. Conclusions

The GLY-PRO-GLU tripeptide adsorption on the reconstructed Au(110) surface was investigated using a combination of classical molecular dynamics simulations and DFT. A mechanism for the peptide interaction with the Au surface promoting the dislocation of Au atoms, is proposed.

The tripeptide adsorption was studied in both its neutral and zwitter ionic state. In its neutral state the main mechanism is the dislocation of a Au atom, possibly driven by the steric interaction between the “bulky” proline ring and the topmost gold atoms.

In its zwitterionic state the PRO driven mechanism is still present, but the most common one is the one involving the GLU residue. In particular an intramolecular hydrogen bond network, a 10-membered ring, involving the carboxyl group of the GLU sidechain and the GLY amino

group is formed as a consequence of a double proton shift allowing the terminal carboxyl group to act on a gold atom of the surface ridge.

It was also observed that, in the zwitterionic form, most of the peptides form dimers, which optimizes the H-bond interaction between the oppositely charged groups.

In the neutral state the peptide always lays parallel to the surface, while in the zwitter ionic state the peptide plane (defined by the pyrrole ring) can form a larger angle with the gold surface plane. So, both parallel and almost perpendicular dimers are observed in the simulations.

The mechanism involving the GLU residue is the most probable one and induces a jump of a Au atom on the MRR Au(110) surface. The intramolecular interactions, involving a double proton transfer, make the peptide more rigid and orientate the GLU carboxylate-group, allowing the GLU carboxylate-group to interact with the Au atoms and dislocate it. The energy barriers associated to these reaction paths are very small, and are compatible with the spontaneous experimental observation of atoms displacement at room temperature.

The next steps would be to investigate and calculate spectroscopic properties for the identified complexes and compare them with the experimental data, possibly also addressing the role of the surface coverage on the Au surface reconstruction.

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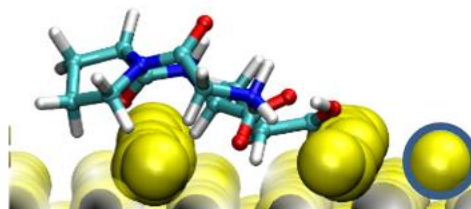
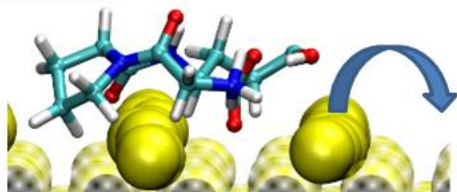
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TOC Figure

Au atom displacement on MRR Au(110) initiated the zwitter ionic GLYPROGLU tripeptide

XZ-plane



XY-plane

