Glutamic acid adsorbed on Ag(110): direct and indirect molecular interactions

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Abstract

First-principles calculations are used to rationalize the adsorption geometry and long-range order observed for (s)-glutamic acid rows adsorbed on Ag(110). Hydrogen bonds and van der Waals interactions are found to be important for the direct molecular interaction within the molecular rows. Adsorption induced charge-density waves in the substrate lead to an indirect interaction between the adsorbates, resulting in the formation of long-range order. Remarkably, structural relaxation effects also play a decisive role in the indirect interactions.

(Some figures in this article are in colour only in the electronic version)

The autonomous ordering and assembly of atoms and molecules on atomically well-defined surfaces appears as a very promising alternative route to even smaller functional systems with nanometer dimensions [1–4]. However, the mechanisms controlling the self-ordering phenomena need to be thoroughly understood in order to employ self-assembly and growth processes and to create tailor-made surface nanostructures. In this context, the detailed analysis of prototypical, well-defined model systems from first-principles calculations is a useful first step [5–11]. Here we present density functional theory (DFT) calculations on the adsorption of (s)-glutamic acid on Ag(110). As found by scanning tunneling microscopy (STM) [12], this system is interesting in the context of molecular self-assembly. Depending on the adsorption temperature and adlayer coverage, glutamic acid (cf figure 1) adsorbed on Ag(110) yields a variety of ordered overlayer structures. The (4 × 8) phase is particularly intriguing, since it is formed by highly ordered molecular chains running along the [$\bar{1}$10] direction that are separated by about 33 Å.

In order to rationalize this fascinating example of long-range interaction, we perform DFT calculations using the Vienna *ab initio* simulation package (VASP) [13] and the PW91 functional [14] to model the electron exchange and correlation within the generalized gradient approximation (GGA). The electron–ion interaction is described by the projector-augmented wave (PAW) method [15], which allows for an accurate treatment of the first-row elements as well as the Ag 4d electrons with a relatively moderate energy cutoff of 340 eV. The surface Brillouin zone is sampled using a 2 × 2 × 1
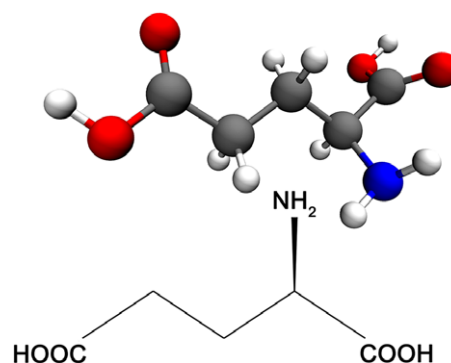

Figure 1. Schematic and ball and stick diagram showing the molecular structure of (s)-glutamic acid.

mesh. The adsystem is modeled by periodically repeated slabs, containing six atomic Ag layers plus the adsorbed molecules and a vacuum region equivalent in thickness to about 14 atomic Ag layers. In order to estimate the H-bond strength within Bader's topological paradigm [16], we use a functional of the calculated charge density [17]. In the case of molecules weakly bonded to each other or to the surface, dispersion interaction — not accounted for in the GGA — may contribute a sizable percentage of the total interaction energy [9]. In order to assess at least approximately the influence of the van der Waals (vdW) interaction on the adsorption energetics, we present additional data that are obtained using a semiempirical approach based on the London dispersion formula to include the dispersion interaction [18]. Due to the limitations inherent in this approach, in particular if applied to metallic systems, it
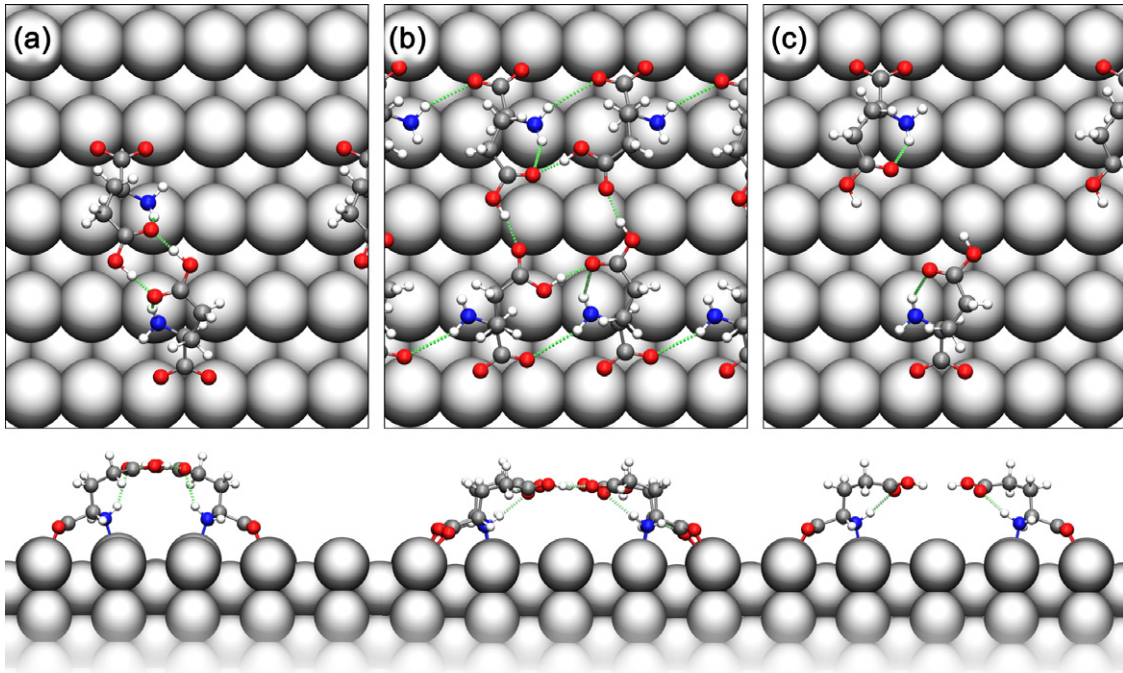
Figure 2. Adsorption structures of glutamic acid adsorbed at Ag(110) with lowest energy for (a) DFT–GGA and (b) DFT–GGA + VDW. Model (c) represents the structure proposed in [12]. Hydrogen bonds are indicated with dashed green lines.

should be considered as providing energetic trends rather than accurate results.

We start by determining the structure of the molecular rows within the (4 × 8) translational symmetry and assume the adsorption of the deprotonated species as observed experimentally [12]. Around 20 structural candidates for various coverages were probed. From this the starting positions were chosen by chemical intuition to optimize the interaction between the adsorbates on the one hand, and between the surface and the molecules on the other hand. The energetically most favored models within DFT, DFT + vdW and the structure proposed by the experimentalists [12] are shown in figure 2 (the further structural candidates probed computationally are at least 0.1 eV away from the energetically most favored models (a) and (b)). The DFT minimum energy model (model (a)) features a shorter molecule–molecule distance than the structure proposed in [12], model (c). This allows for hydrogen bonding between the molecules. H bonds also form for model (b), energetically most favored if van der Waals interactions are taken into account. In table 1 the adsorption energies per molecule, $E_{ads} = (E_{tot} - nE_{glu} - E_{subs} + 0.5nE_{H_2})/n$ are compared for models (a)–(c). Here E_{tot}, E_{subs}, E_{glu} and E_{H_2} refer to the energies of the total system, the silver substrate, the adsorbate (s)-glutamic acid, and hydrogen in gas phase, respectively. The number of molecules per surface unit cell is given by n. Irrespective of whether or not dispersion forces are included in the calculation, we find model (c) to be least favored.

Bader's topological paradigm allows access to the H-bond energy via a functional of the calculated charge density [16, 17]. Values of −2.78 (−1.39), −2.53 (−0.63),

Table 1. Adsorption energies per molecule in eV calculated in DFT–GGA and with semiempirical van der Waals contribution.

Model	DFT–GGA	DFT–GGA + vdW
(a)	−1.05	−1.74
(b)	−1.01	−1.91
(c)	−0.78	−1.44

and −0.30 (−0.15) eV per surface unit cell (per molecule) are determined for models (a)–(c). It is interesting to note that the larger number of hydrogen bonds formed in model (b) (cf dashed lines in figure 2) is overcompensated in energy by the contribution of the two very strong H bonds characteristic for model (a). Comparing the DFT–GGA energy difference between model (a) and (c) with the difference of the calculated dissociation energies shows a significant deviation, which is maybe related to various points: (i) the calculated dissociation energy is based on an empirical expression, (ii) the carboxyl groups have a net negative charge due to the deprotonated state, leading to a higher repulsive electrostatic interaction in model (a) and (iii) there might be a repulsive part due to higher deformation of the molecules in model (a). Within DFT–GGA, the adsorption energy per atom is slightly lower for model (b) than for model (a), indicating a repulsive interaction between the surface adsorbed (s)-glutamic acid molecules. This trend reverses, however, if vdW contributions are approximately included in the calculations. While the energetical arguments thus allow one to rule out the structure proposed in [12], i.e., model (c), they do not give a clear-cut indication for the model that actually corresponds to the experiments.
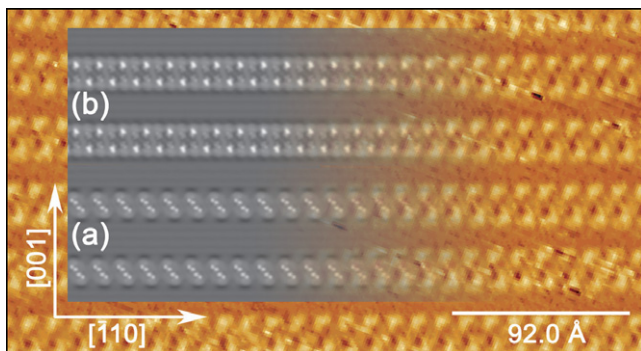
Figure 3. Comparison of the calculated (for model (a) and (b), see the text) and experimental STM images [12] of the (4 × 8) phase of glutamic acid adsorbed on the Ag(110) surface.

Therefore we focus in the following on the spectral fingerprints of models (a) and (b), and compare the simulated and experimental data. In figure 3 STM images simulated according to the Tersoff–Hamann approach [19] for a bias of −0.67 V are compared with the micrographs measured at the same voltage. Obviously, neither model perfectly describes the experimental finding. In particular the row width appears smaller than measured. Altogether, model (b) seems in better agreement with the measured data than model (a). However, given the methodological problems [20, 21] in simulating the complex (and partially unknown, e.g., tip geometry) physics in modeling STM data, any conclusion drawn from figure 3 should be considered with caution. The measured vibrational frequencies of the adsorbate [12] allow for a more decisive comparison between the structural candidates. We calculated the vibrational modes using the frozen phonon approximation [22]. Due to the significant mass difference between adsorbate and substrate atoms and the corresponding effective decoupling of the respective vibrations, we only include the uppermost two substrate layers in the phonon calculations. A comparison of measured and calculated frequencies is shown in table 2. As can be seen, both model (a) and (b) account well for the data assigned to the scissoring mode $\delta_{\mathrm{siss}}(\mathrm{NH_2})$ and the symmetric stretch mode $v_{\mathrm{sym}}(\mathrm{OCO^-})$. Thereby the slight underestimation of the calculated $v_{\mathrm{sym}}(\mathrm{OCO^-})$ frequencies are related to the small number of substrate layers in the calculations resulting in an overestimation of the bond strength. The $v(\mathrm{C=O})^{\mathrm{acid}}$ mode, however, is suitable for discrimination between the model (a) and (b). Only the latter is capable of explaining the measured splitting symmetric stretching mode into two pronounced peaks. Structure (a), in contrast, shows only one stretching mode instead of the measured two. In addition, the frequency calculated is around 25 cm^{-1} lower than measured. This is likely to be related to the very strong hydrogen bonding between the two molecules that shifts down the frequency of the double bond vibration. In contrast, model (b) reproduces the experimental findings very well. Compared to the respective gas-phase vibrations, all modes shift down upon adsorption due to the inter-molecular bonding. In conjunction with the higher adsorption energy upon inclusion of dispersion interaction and the slightly better description of
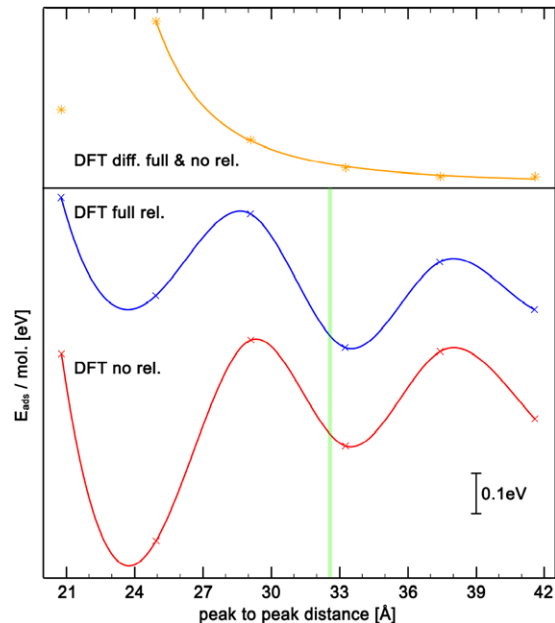

Figure 4. Adsorption energy per molecule in dependence on the peak to peak distance with and without relaxing the structure as well as the difference between the two curves. Here, a fit $E \sim A/x^3$ is used to guide the eye. The experimental determined distance is indicated by the green vertical line [12].

Table 2. Calculated vibrational modes compared to the experiment. Gas-phase frequencies of the nonzwitterionic molecule are also listed. All values in cm^{-1}.

Assignment	Exp. [12]	Model (a)	Model (b)	Gas phase
$v(\mathrm{C=O})^{\mathrm{acid}}$	1704	—	1710	1759
			1699	1756
	1664	1639	1675	—
			1659	
$\delta_{\mathrm{siss}}(\mathrm{NH_2})$	1577	1575	1565	1576
$v_{\mathrm{sym}}(\mathrm{OCO^-})$	1384	1361	1364	—

the STM findings, model (b) seems to be a plausible geometry for the intra-row structure.

On the basis of this model we will now try to understand the large and reproducible separation between the glutamic acid molecular rows found experimentally. In principle, two mechanisms could conceivably cause the large spacing between the glutamic acid rows of the (4 × 8) phase of the glutamic acid adsorbed Ag(110) surface, substrate-mediated interactions via long-range strain fields [23] or adsorption induced Friedel oscillations of the electron density at the metal surface [25, 24, 26, 27]. By performing calculations where the substrate atoms are either frozen at ideal bulk positions or fully relaxed according to the adsorption induced forces, one can assess the magnitude of strain and charge-density related spatial modulations of the adsorption energy. At first, we neglect strain effects and vary the distance between the molecular rows without taking structural relaxations into account. To this end total energy calculations for model (b) are performed within a (4 × n) surface periodicity, where $n = 5 \ldots 10$. The corresponding adsorption energies are shown in figure 4. They show a damped oscillation behavior.

The wavelength and the magnitude of these oscillations is very similar to that obtained in recent calculations for Cu(110) adsorbed adenine and phenylglycine molecules [27]. In this case the modulation of the adsorption energies was explicitly shown to be Friedel-oscillation related. Here the situation is more complex. While the experimentally determined inter-row distance of 32.6 Å corresponds to a local minimum of these oscillations, the calculated global minimum occurs at around 25 Å. This shows that the indirect interaction between the glutamic acid molecules cannot be explained completely in terms of purely electronic interactions [24].

Therefore we include in the second step the effects of structural relaxation. If the structural degrees of freedom of both adsorbate and substrate are completely relaxed, one obtains similar positions for the local minima of the adsorption energy, but the global minimum now occurs at about 33 Å. The structural relaxation causes strong shifts of substrate atoms close to the admolecules. The difference of the adsorption energy calculated with and without structural relaxation allows one to extract the strain interaction, as shown in the upper panel of figure 4. Excluding the lowest peak-to-peak distance, which indeed includes direct molecular interactions, a $E \sim d^{-3}$ distance dependence is found. This fits well with the elastic-interaction contribution due to the distortion of the substrate lattice caused by the adsorption process [28].

To conclude, we performed density functional calculations in order to rationalize the formation of long-range ordered structures of (s)-glutamic acid adsorbed on Ag(110) surfaces. By means of total energy calculations and the comparison of calculated and measured spectroscopic fingerprints we arrive at a structural model for the geometry of the molecular rows that extend in the $[\bar{1}10]$ direction. The interaction between the molecules within the row is determined by hydrogen bonds and dispersion forces. In addition, indirect interactions between the molecular rows determine the unit cell size in the [001] direction. Two effects are found to be important in the indirect interactions. Pure electronic interactions lead to adsorption energy oscillations with wavelengths of about 10 Å, similar to many more examples of long-range molecular ordering, e.g., the adsorption of adenine and phenylglycine on Cu(110) [4]. In contrast to the latter case, however, where strain effects in the indirect interaction are almost negligible [27], we find the structural relaxation to be very important for the correct reproduction of the measured glutamic acid row distance in the calculations. This could possibly be related to the different chain orientation of the glutamic and the phenylglycine rows with respect to the anisotropic substrate. The calculations presented here illustrate the complexity of the driving forces that may come together to determine molecular adsorption structures.

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