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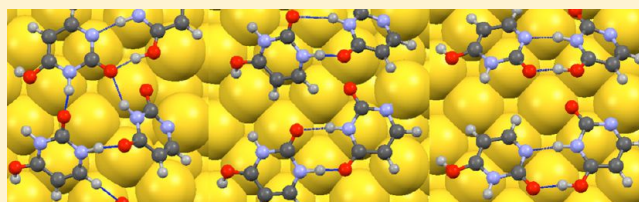
# The Role of Hydrogen Bonding and Proton Transfer in the Formation of Uracil Networks on the Gold (100) Surface: A Density Functional Theory Approach

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**ABSTRACT:** We have used density functional theory calculations, including a correction for the dispersive forces (DFT-D), to investigate the formation of a monolayer superstructure of uracil molecules adsorbed on the Au(100) surface. Our calculations provide insight into the interplay between lateral adsorbate–adsorbate and vertical adsorbate–substrate interactions, where we found that uracil adsorption to the surface is strongly dependent on the lateral interactions, particularly hydrogen bonding, although the first adsorbed molecule, before the formation of a uracil network, is covalently bonded to the surface. The self-assembly of the uracil network on the surface is mediated by proton transfer, and the ensuing charge separation stabilizes the geometry. Dispersive forces also play a role, and in particular, the introduction of a correction leads to flatter geometries with molecules lying parallel to the surface, thereby enhancing  $\pi$ – $\pi$  stacking and hydrogen-bonding.



## 1. INTRODUCTION

Gold is an active catalyst in several chemical processes, including the hydrogenation of carbonyl and nitro compounds.<sup>1,2</sup> Unlike platinum, palladium, or ruthenium, it has been shown to be highly chemoselective—achieving up to 90% conversion of  $\alpha,\beta$ -unsaturated carbonyl compounds to alcohols via selective hydrogenation—without any further modification.<sup>2</sup> This feature is particularly useful when many functional groups compete in a reaction. The selective reactivity of gold has been the subject of several studies:<sup>3</sup> for example, its use in the purification of alkene streams, in which it prevents poisoning through polymerization, which is otherwise obtained when a palladium catalyst is used instead,<sup>4</sup> and its role in the reduction of the nitro group in substituted nitro compounds to aromatic amines, which are important industrial intermediates.<sup>5</sup>

In the prebiotic world, solid substrates may have played a templating role in the self-assembly of amino-functional molecules (nucleobases and amino acids) upon their surface via hydrogen bonds and van der Waals (vdW) interactions.<sup>6</sup> Noncovalent interactions in nucleic acids and amino acids have been conjectured to be the driving forces in the origin of life from the “primeval soup”. This templating effect may make these heterogeneous systems relevant in a wide range of fields, including medicine, biochemistry, and biosensing.<sup>7</sup> In this work, the formation of a self-assembled network of the RNA base uracil on a gold surface has been investigated.

DNA, in which the genetic information is stored, and RNA are polymers made of nucleotide building blocks, formed by purine and pyrimidine nucleobases (cytosine, guanine, adenine, thymine, and uracil), a five-carbon sugar (ribose) and between one and three phosphate groups. The DNA and RNA structures are stabilized by hydrogen bonding (HB) between

nucleobases and by stacking interactions between base layers.<sup>8</sup> These noncovalent chemical interactions drive some of the most essential biofunctions capable of determining highly specific functions, that is, molecular recognition. A correct matching between base pairs ensures the information passage from the parent DNA strand to the daughter RNA strand, although eight other possible pairings lead to DNA mismatches that can result in the formation of tumors. Major influences on the structure and stability of DNA and RNA are the hydrogen bonds between two adjacent bases from opposite strands (i.e., forming a Watson–Crick pair), and the dispersive interactions (i.e., vdW,  $\pi$ – $\pi$  stacking) between two bases within each of the strands. Studies on nucleobases serve as models to investigate how the unique properties associated with these molecules, such as molecular recognition, translate to two-dimensional systems. In addition, the order of atoms in the molecules plays a significant role, adding a steric effect to these systems that can be used for chiral enantioselective catalysis, as well.<sup>9</sup> The aim of this work is to elucidate these interactions in a two-dimensional, self-assembled network.

Self-assembly can be directed by several noncovalent binding forces. Hydrogen bonding is particularly strong, and because it has a specific direction, it is an ideal control tool in the design of self-assembled compounds,<sup>10</sup> especially in biological systems, to reproduce the base-pairing of nucleic acids.<sup>11</sup> Strong and planar hydrogen bonding can activate a proton-transfer process by which an ionic compound is formed, resulting in an enhancement of the noncovalent interaction, in which the

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formation of the hydrogen bond can be interpreted as the first step in the proton-transfer reaction.<sup>12</sup> In addition, protonated products are stable and can be involved in mutagenic phenomena.<sup>13</sup>

The self-assembly of DNA/RNA nucleobases on solid substrates is a complex process that is still only partially understood and is preparatory to (poly)nucleotide self-assembly. Indeed, the challenge in harnessing self-assembled systems is in understanding the driving forces that induce the formation of the overlayer on the substrate. Often, many chemical scenarios are compatible with experimental data, but these can be illustrated and explained at the molecular level by computational techniques.

Here, we have investigated the self-assembly of the RNA nucleobase uracil on a well-defined solid surface, Au(100), which although less stable than Au(111) is still found experimentally; for example, in stable nanoparticles from a wide size range. We have investigated the structure of a monolayer of uracil molecules adsorbed on the surface to provide insight into the interplay between lateral adsorbate–adsorbate and vertical adsorbate–substrate interactions. The self-assembly is directly influenced by covalent interactions as well as hydrogen-bonding, stacking, and vdW forces, and an accurate description is therefore essential to understand and, hence, achieve control of the process at the molecular level.<sup>14</sup> Consequently, we have performed an *ab initio* molecular modeling study employing periodic density functional theory (DFT) with a correction to include dispersive forces (DFT-D2).<sup>15</sup>

The application of full monolayer coverage allows us to understand the intermolecular interactions where the model can be used to calculate scanning tunneling microscopy (STM) images. Self-assembled monolayers of uracil on solid gold electrodes, Au(100), have been investigated experimentally via *in situ* STM studies showing a self-assembled uracil monolayer; the proposed model for the stable physisorbed phase consists of a flat sequence of molecules.<sup>16</sup> Comparison of our results with the experimental STM will enable interpretation of the experiment and quantification of the binding between the surface and the adsorbate and between adsorbate molecules.

## 2. COMPUTATIONAL METHODS

*Ab initio* geometry optimizations were performed using the VASP code<sup>17</sup>, version 5.2.11, with the additional DFT-D2 method of Grimme to take into account the dispersive forces.<sup>18</sup> Gold parameters were chosen from recent calculations using the same code;<sup>19</sup> hence, the scaling factor  $s_6$ , which depends on the Kohn–Sham functional, is 0.75, and we have included pair interactions up to a radius of 12 Å. Moreover, we have used a value of 40.62 J·nm<sup>6</sup>/mol for the  $C_6$  coefficient and 1.772 Å for the vdW radius of Au, as in ref 19. The generalized gradient approximation (GGA) was employed with the PW91 functional<sup>20</sup> and the spin interpolation formula of Vosko et al.<sup>21</sup> As recently reported,<sup>22</sup> a scaling factor of 0.75 for the PW91 functional provides acceptable results for both the dispersion forces and the hydrogen bonds. On the basis of these authors' results, we have applied a very similar methodology with the same scaling factor. Although hydrogen bonding (H-bonding) is overestimated by GGA-D2 functionals, in this work, we have compared energy differences of different conformations carried out with the same parameters, thereby minimizing any effects of the overestimation of the H-bonding in identifying the relevant trends in the adsorption behavior. The inner electrons have

been described by the projector augmented wave (PAW) method<sup>23</sup> and the KS valence states expanded in a plane-waves basis set with a cutoff at 500 eV for the kinetic energy. An energy threshold defining self-consistency of the electron density was set to 10<sup>−5</sup> eV. This high value for the cutoff energy ensured that no Pulay stresses occurred within the cell during relaxations. To improve the convergence of the Brillouin-zone integrations, the partial occupancies were determined using Gaussian smearing, with a set width for all calculations of 0.01 eV, which can be considered as a form of finite-temperature DFT;<sup>24</sup> however, the calculated energies were derived from SIGMA=0 to minimize the entropic contribution to the total energy. The optimization of the structures was conducted via a conjugate gradients technique, which uses the total energy and the Hellmann–Feynman forces on the atoms, with a convergence criterion of <0.03 eV/Å in the present study. Spin–orbit coupling was not taken into account. Calculations were carried out in the reciprocal space of the cell and were described by a Monkhorst–Pack grid<sup>25</sup> of 8 × 8 × 8 and 2 × 2 × 1 K-points for the bulk and surfaces, respectively, which ensures the electronic and ionic convergence. A higher number of K-points was tested, but the difference in energy was <0.01 eV.

We have used a slab model containing four atomic layers, in which the two lower layers were kept frozen at the optimized bulk positions, but the two uppermost layers were free to relax during the optimization. The slab used is a  $p(3 \times 3)$  supercell, resulting in 72 Au atoms exposing an area of 133.8 Å<sup>2</sup>. We have built an overlayer of uracil molecules, starting from the single uracil configuration on Au(100) determined previously<sup>26</sup> and adding up to four molecules per cell, repeating the geometry optimization after each addition to reproduce the fully covered surface and mimic the self-assembly. As is common usage in the experimental approach to express the coverage in molecules/nm<sup>2</sup>, we will use the following labels: 1 molecule on the surface corresponds to 0.75 molecules/nm<sup>2</sup>; 2 molecules' step is 1.50 molecules/nm<sup>2</sup>; 3 molecules on the surface is 2.25 molecules/nm<sup>2</sup>; and finally, 4 adsorbed uracil molecules gives a full coverage of 3 molecules/nm<sup>2</sup>.

We have calculated the adsorption energy per molecule as follows:

$$E_{\text{ads}} = [E(n\text{U}, \text{Au}) - n \cdot E(\text{U}) - E(\text{Au})]/n$$

where  $E(\text{U})$  and  $E(\text{Au})$  are the total electronic energies of the uracil molecule and the Au(100) surface, respectively, after separate geometry optimizations;  $E(n\text{U}, \text{Au})$  is the energy of the geometrically relaxed surface–adsorbate system; and  $n$  is the number of molecules.

The interaction and cohesion energies per molecule have also been calculated to discuss the interplay between transversal ( $E_{\text{int}}$ ) and lateral interactions ( $E_{\text{cohe}}$ ), as in refs 27 and 28, which are defined as

$$E_{\text{int}} = [E(n\text{U}, \text{Au}) - E(n\text{U}) - E(\text{Au})^*]/n$$

$$E_{\text{cohe}} = [E(n\text{U}) - nE(\text{U})]/n$$

where  $E(n\text{U})$  and  $E(\text{Au})^*$  are the energies of the uracil superstructure in the vacuum and the gold surface, calculated separately and kept in the same geometry as found in the adsorbate–surface calculation. Moreover, we have calculated the Bader population analysis<sup>29</sup> to investigate the nature of the bonding to the surface and between the molecules. All configurations were visualized with Mercury 3.0.<sup>30</sup>

**Table 1.** Adsorption Energies, Charge Transfer and Distances from the Surface Calculated with DFT-D2 with vdW ( $E_{\text{ads}}$ ) and without vdW correction ( $E_{\text{ads}}^{\text{p}}$ )<sup>a</sup>

no. uracils (pairing)	+D, incl. dispersive forces			pure DFT		
	$E_{\text{ads}}^{\text{D}}$ (eV)	charge transfer ( $e^-$ )	$d_{\text{O}-\text{Au}}$ ( $d_{\text{N}-\text{Au}}$ ) (Å)	$E_{\text{ads}}^{\text{p}}$ (eV)	charge transfer ( $e^-$ )	$d_{\text{O}-\text{Au}}$ ( $d_{\text{N}-\text{Au}}$ ) (Å)
1	1.65	0.07	2.52 (2.50)	0.93	0.04	2.64 (3.05)
2 (A)*	2.21	0.10	2.39 (2.25)	1.08	0.14	2.47 (2.31)
2 (B)	2.17	0.10	2.55 (2.28)	1.01	0.13	2.74 (2.37)
3 (A)**	2.26	0.07	2.65 (2.22)	1.12	0.13	2.74 (3.30)
3 (Ax)*	1.89	0.10	2.35 (2.21)	0.95	0.01	2.42 (2.28)
3 (B)*	2.24	0.02	2.28 (2.23)	1.15	0.17	2.41 (2.29)
3 (Bx)	1.96	0.09	2.62 (2.22)	0.99	0.11	2.81 (2.34)
4 (AB)*	2.16	0.12	2.33 (2.19)	1.13	0.15	2.41 (2.31)
4 (AA)**	2.15	0.14	2.36–2.98 (2.22–2.23) <sup>b</sup>	1.05	0.14	2.47 (2.32)
4 (BB)	2.11	0.09	2.37–2.70 (2.28–2.30) <sup>b</sup>	0.93	0.12	2.65 (2.39)

<sup>a</sup>In several cases [2(A), 3(B), and 4(AB)], a hydrogen bond gives rise to a proton transfer, \* (or two proton transfers, \*\*, as illustrated in Figures 3,4,5 and in the text). <sup>b</sup>Interaction of two molecules with gold atoms: O–Au and N–Au.

The STM images are calculated using the Tersoff–Hamann formalism,<sup>28</sup> which states that the tunneling current in an STM experiment is proportional to the local density of states (LDOS) integrated from the Fermi level to the bias. To simulate an STM topographic image theoretically, we have integrated our DFT-based partial charge density from  $-3.0$  eV to  $E_{\text{F}}$  using Hive.<sup>31</sup> It is implemented in its most basic formulation, approximating the STM tip by an infinitely small point source. An STM in constant current mode follows a surface of constant current, which translates into a surface of constant integrated LDOS [ $\rho(x, y, z, \epsilon) = C$  where  $C$  is a real constant]. The constant  $C$  is chosen such that the isosurface has a height,  $z$ , for a certain distance (Å) above the highest atom of the surface or a constant charge level ( $e/\text{Å}^3$ ). This construction returns a height,  $z$ , as a function of the position ( $x, y$ ), and this height map is then mapped linearly onto a corresponding scale, as implemented in the Hive program.<sup>31</sup>

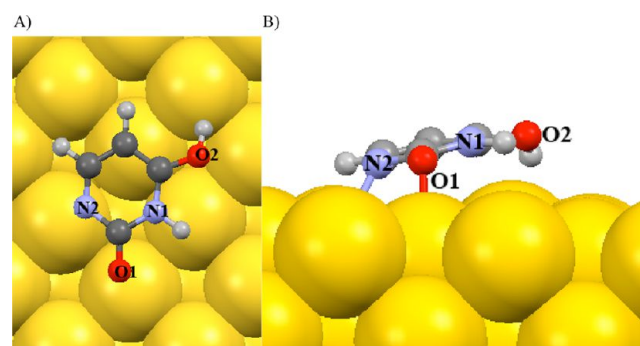
### 3. RESULTS AND DISCUSSION

**3.1. Effect of the Dispersive Forces.** In our previous work,<sup>26</sup> the structure of the single uracil molecule adsorbed on Au(100) was calculated using conventional DFT, and the resulting most stable configuration is a specific enol form lying flat on the surface and covalently bonded through the carbonylic oxygen ( $d_{\text{Au}-\text{O}} = 2.60$  Å) with a calculated adsorption energy of  $-0.93$  eV and a charge transfer of  $0.04 e^-$ .

In this work, we have included a correction to take into account the dispersive forces to calculate the adsorption modes and self-assembly steps of the uracil molecule. Inclusion of the dispersive forces now also considers van der Waals and  $\pi$ – $\pi$  interactions, and hence, we have obtained a stronger interaction between the molecule and the surface, resulting in shorter distances to gold atoms, higher charge transfers, and generally more flattened geometries (Table 1). Our DFT approach may still overestimate the H-bonding as well as the dispersive correction, which in this work is limited to pairwise interactions, as explained in the previous section. However, our calculations provide a comparison among relative energies, calculated with identical parameters, of several pairings, configurations, and coverages, and we consider that they will therefore be sufficiently accurate to provide insight into the complex scenario of the uracil self-assembly process.

We first calculated the single uracil on Au(100) again, including the vdW parametrization, leading to an almost identical flat configuration, interacting through both oxygen and

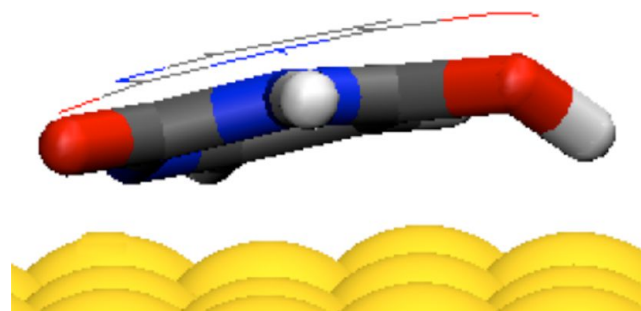
nitrogen but with shorter distances ( $\sim 15\%$ ),  $d_{\text{Au}-\text{O}} = 2.52$  Å and  $d_{\text{Au}-\text{N}} = 2.50$  Å. Moreover, the adsorption energy,  $E_{\text{ads}} = -1.65$  eV, is significantly larger. This structure is still the most stable configuration and is shown in Figure 1 (A, top down



**Figure 1.** Single uracil molecule adsorbed flat on gold surface Au(100) via carbonyl oxygen and heterocyclic nitrogen. C is gray, O is red, N is blue, and H is light gray.

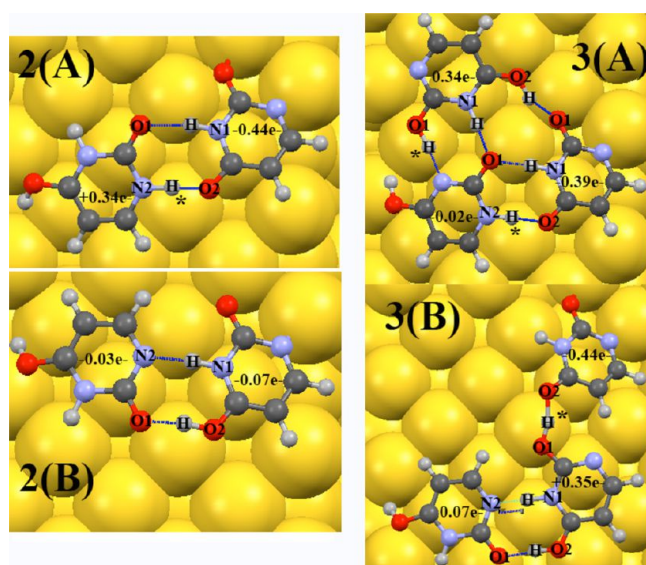
view, and B, side view). In Figure 2, we present a comparison with the corresponding structure from the previous calculation, without the dispersion correction,<sup>25</sup> to illustrate the contraction of the surface–molecule distance.

In all the geometries studied hereafter, we note (see Table 1 and Figures 3–5) that the introduction of the dispersive forces component induces a contraction of the molecular overlayer



**Figure 2.** Comparison between the single uracil on the surface calculated without (thin lines) and with (thick lines) vdW correction. Introducing a correction to the system to take account of the dispersive forces leads to a stronger interaction.





**Figure 3.** Self-assembly of uracil: configurations A and B for two and three molecules on the surface. Charge transfer labels are shown and have been calculated from the Bader populations.

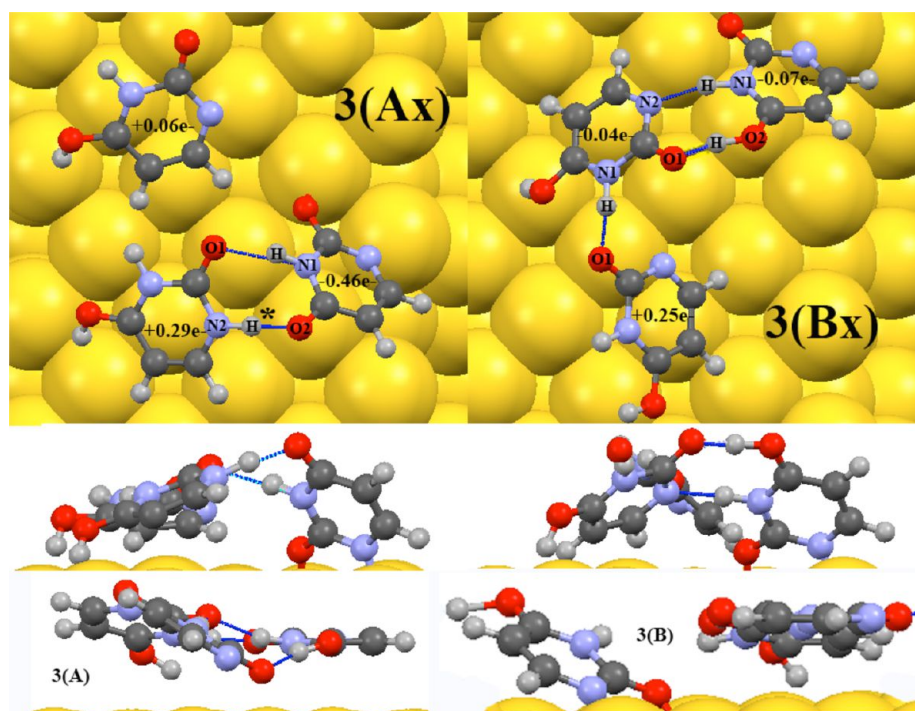
toward the metal surface of  $\sim 5$ – $15^\circ$  and a reduction of the tilt angle of  $10$ – $20^\circ$ . In addition, the interaction energies and the cohesion energies, presented in Table 2, illustrate, respectively, the balance between the interaction to the surface and among the uracil molecules. Indeed, with the inclusion of the dispersion forces in the calculations, the interaction to the surface has increased by approximately  $1$  eV ( $\sim 100$  kJ mol $^{-1}$ ) per uracil, compared with the pure DFT calculation, indicating that dispersive forces are fundamental in the description of the adsorption to gold. Moreover, uracil molecules are closer to each other, and flat geometries induce stronger H-bonding,

with angles closer to  $180^\circ$ , thereby potentially activating proton transfer and, consequently, a charge separation.<sup>32</sup> Indeed, the increase in cohesion energies by  $\sim 5$ – $10\%$  points to a stronger H-bond network. Table 3 reports structural information of the hydrogen bonds for all the configurations investigated in this paper.

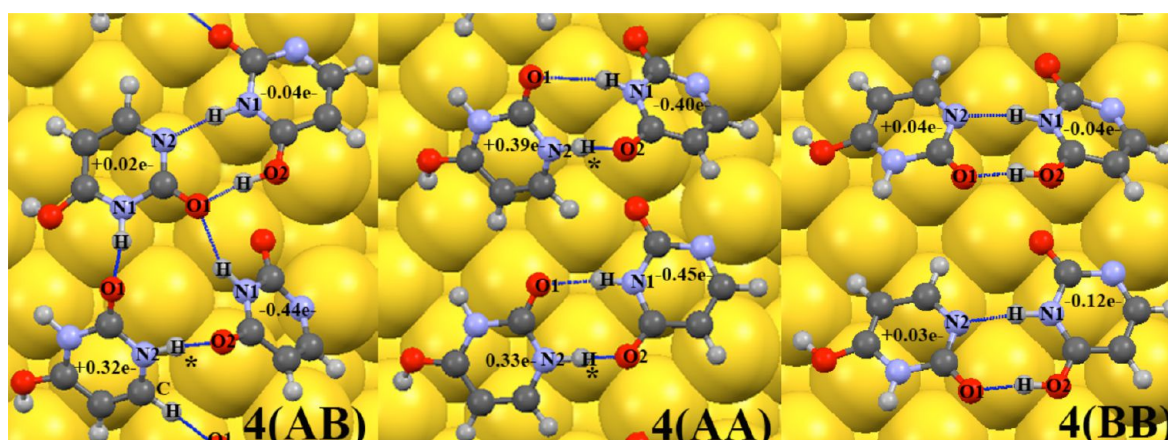
**3.2. Adsorption Configurations of Uracil Molecules on Au(100).** The enol form in Figure 1, as adsorbed on the surface in these calculations, has a hydroxyl group that potentially enables proton transfer between this group and a neighboring molecule's nitrogen. During the geometry optimization, spontaneous proton transfer has been observed in some configurations. Proton transfer induces charge separation between the two molecules involved, and the interaction between the two newly formed ions can stabilize the final configuration. In the following paragraphs, we will discuss this process in detail for each geometry.

Several configurations have been simulated to reproduce the uracils' self-assembly. The results are illustrated in Figures 3, 4, and 5 for a number of stable low-energy adsorption configurations resulting from the geometry optimization with DFT-D2. In Tables 1 and 2, we have illustrated the adsorption, interaction, and cohesion energies obtained with and without the dispersive correction. As previously noted, we observe that the cohesion energy is highly enhanced by the inclusion of this parametrization. However, we have also observed spontaneous proton transfer with the pure DFT approach, but the dispersive correction leads to a magnification of the lateral interaction, and configurations 3(A) and 4(AA) therefore undergo only one proton transfer with the pure DFT, but two proton transfers with DFT-D2.

**3.2.1. Uracil Network Growth: Two Molecules.** Positioning two equivalent uracil molecules on the surface, bound as shown in Figure 1, implies a choice in the pairing of the H-bonding.<sup>33</sup>



**Figure 4.** Two alternative configurations, 3(Ax) and 3(Bx), in which a third molecule is added to a surface-bound pair. The two less-stable adsorbing modes are significantly less flat than 3(A) and 3(B) (bottom), indicating an effect on the adsorption energy due to the  $\pi$ – $\pi$  interactions.



**Figure 5.** Configurations 4(AB), 4(AA), and 4(BB), in which uracils are coupled following pairings of AA and BB pairs. Bader charges are indicated on the molecules as well as the hydrogen bonds.

**Table 2. Interaction and Cohesion Energies**

	+D incl. dispersion forces		pure DFT	
	$E_{\text{int}}$ (eV)	$E_{\text{cohe}}$ (eV)	$E_{\text{int}}$ (eV)	$E_{\text{cohe}}$ (eV)
2A	−2.10	−0.32	−0.89	−0.24
2B	−1.63	−0.70	−0.41	−0.63
3A	−1.32	−1.05	−0.14	−0.98
3Ax	−1.60	−0.41	−0.66	−0.32
3B	−1.58	−0.73	−0.57	−0.60
3Bx	−1.79	−0.60	−0.39	−0.63
4AB	−1.72	−0.63	−0.61	−0.55
4AA	−1.86	−0.46	−0.58	−0.49
4BB	−1.65	−0.62	−0.33	−0.63

This step is particularly meaningful, since these interactions are primarily responsible for the molecular recognition and, therefore, pivotal to the networking. We have calculated the two possible pairings with uracil in the energetically preferred enol form (Figure 3). We have found a small, but still significant, difference in the adsorption energies of the two configurations,  $\Delta E_{\text{ads}}^{2(\text{A})-2(\text{B})} = 0.04$  eV, which could be due to the charge separation found in 2(A) (Figure 3), in which one hydrogen bond has induced proton transfer. Adsorption seems to favor an interaction similar to the Watson and Crick type (WC) via proton transfer. The initial state in 2(A) has two identical enols, as in Figure 1, but one uracil  $\text{—OH}$  donates a proton to the  $\text{—N}$  in the other molecule to form a second  $\text{N—H}\cdots\text{O}$  hydrogen bond, inducing a charge separation from the Bader population analysis of  $+0.34$  and  $-0.44$   $e^-$ . The final configuration therefore has a symmetrical  $\text{H-bonded}$  setup in which  $\text{N—H}\cdots\text{O}$  is one of the two pairing types in the traditional DNA/RNA WC structure (adenine–thymine). This proton transfer can be explained first by the resonance structures that can be conjectured for the final state in the enol–keto pair, and second, it leads to the formation of a stable symmetric  $\text{H-bond ring}$ .<sup>32</sup>

Configuration 2(B), however, presents a  $\text{N—H}\cdots\text{N}$  and an  $\text{O—H}\cdots\text{O}$   $\text{H-bonding}$  ring that stabilizes the enol–enol form, without proton transfer, in which both molecules donate charge to the surface (Table 1). In addition, we observe a significant gain in adsorption energy compared with the single molecule in Figure 1:  $\Delta E_{\text{ads}}^{2(\text{A})-1} = 0.55$  and  $\Delta E_{\text{ads}}^{2(\text{B})-1} = 0.51$  eV. At this coverage ( $0.75$  molecules/ $\text{nm}^2$ ), the effect of inclusion of the dispersive forces seems to affect more the transversal

component of the adsorption (interaction energy), which is doubled, rather than the cohesion ( $+10 \div 30\%$ ), and the most stable configuration is the one interacting more closely with the surface. However, both configurations have only one molecule covalently bonded to the surface gold atoms, whereas the second uracil interacts solely by lateral interactions with the bound uracil molecule. This indicates that the first step in the assembly is directed by lateral interactions in which  $\text{H-bonding}$ , inducing proton transfer, is the energetically preferred process.

**3.2.2. Uracil Network Growth: Three Molecules.** On the basis of these uracil pairs, we have continued the network by adding a third molecule to the previous two configurations, where the most stable networks formed are indicated as 3(A) and 3(B) in Figure 2 and Table 1. The 3(A) network, which is grown from the preoptimized 2(A) geometry, is dominated by hydrogen motifs of several types, with two proton transfers forming a different enol form on the surface (from  $\text{N2O2H}$  to  $\text{N1O2H}$  with  $-0.02$   $e^-$ ) and two ions ( $+0.34$   $e^-$  and  $-0.39$   $e^-$ ). The formation of this network affects the interaction to the surface, increasing the total adsorption energy of the three uracil molecules to  $E_{\text{ads}} = -2.26$  eV, where Bader population analysis confirms charge transfer and a high cohesion energy in 3(A) of  $E_{\text{cohe}} = -1.05$  eV, the highest of the calculated configurations.

Configuration 3(B), grown from 2(B), has a lower adsorption energy by a difference of only  $\Delta E_{\text{ads}}^{3(\text{A})-3(\text{B})} = 0.02$  eV. In this case, charge separation occurs again, and we can observe one proton transfer between  $\text{O—H}\cdots\text{O}$ , leaving a charge of  $0.44$   $e^-$  on the uracil molecule whose oxygen and nitrogen are bound to the surface, which results in a shortening of the bond distances and a higher interaction energy ( $E_{\text{int}} = -1.58$  eV) than in 3(A) ( $E_{\text{int}} = -1.32$  eV). This stronger interaction to the surface balances the stabilization due to extensive  $\text{H-bond}$  and proton-transfer networks formed in configuration 3(A), leading to very similar adsorption energies (Table 1). Interestingly, if we do not take into account the vdW correction in the calculation, the adsorption energies for the two configurations would be in reverse order, with  $E_{\text{ads}}^{3(\text{A})} = -1.12$  eV and  $E_{\text{ads}}^{3(\text{B})} = -1.15$  eV, indicating that in 3(A), the second and third molecule interact almost exclusively by dispersive forces to the surface, which adds stability to the poor covalent bonding. This favors the flat geometry and enhances the  $\text{H-bond}$  strength. Indeed, in pure DFT, that is, without the



Table 3. Hydrogen Bonding Structural Information<sup>a</sup>

molecules (pairing type)	D–H...A (Å)	+D, incl. dispersive forces			pure DFT		
		H...A (Å)	D...A (Å)	angle (deg) D...H...A	H...A (Å)	D...A (Å)	angle (deg) D...H...A
2 (A)	N1...H...O1	1.95	2.97	167	2.12	3.15	177
	N2...H...O2*	1.45	2.56	175	1.42	2.55	160
2 (B)	N1...H...N2	1.70	2.77	174	1.66	2.73	172
	O2...H...O1 <sup>b</sup>	1.48	2.52	171	1.50	2.54	171
3 (A)	O2...H...O1	1.53	2.51	155	1.56	2.59	163
	N1...H...O1* <sup>b</sup>	1.43	2.60	170	1.64	2.68	175
	N2...H...O2* <sup>b</sup>	1.52	2.61	177	1.41	2.54	174
	N1...H...O1(i)	1.63	2.68	170	1.60	2.66	176
3 (Ax)	N1...H...O1(i)	1.67	2.70	169	1.72	2.77	164
	N1...H...O1	1.90	2.93	164	2.06	3.09	169
	N2...H...O2* <sup>b</sup>	1.11	2.59	174	1.09	2.63	158
	N1...H...N2 <sup>b</sup>	1.55	2.65	178	1.75	2.90	162
3 (B)	O2...H...O1	1.60	2.63	173	1.52	2.56	170
	O2...H...O1* <sup>b</sup>	1.35	2.45	165	1.35	2.46	164
	N1...H...N2	1.78	2.84	165	1.84	2.90	160
	O2...H...O1 <sup>b</sup>	1.34	2.45	168	1.39	2.48	168
3 (Bx)	N1...H...O1	1.62	2.69	172	1.61	2.67	176
	N2...H...O2* <sup>b</sup>	1.50	2.59	169	1.52	2.52	165
	N2...H...O1	1.69	2.71	166	1.78	2.82	174
	O2...H...O1(i)	1.54	2.57	170	1.53	2.57	167
4 (AB)	N2...H...N1	1.71	2.77	171	1.85	2.90	166
	N2...H...O1 <sup>c</sup> (i)	2.04	3.00	155			
	C...H...O1 <sup>c</sup>	1.96	3.01	160			
	N1...H...O1	1.87	2.89	170	1.50	2.51	171
4 (AA)	N2...H...O2* <sup>b</sup>	1.44	2.56	177	1.56	2.62	175
	N2...H...O2* <sup>b</sup>	1.47	2.58	171	1.92	2.96	172
	N1...H...O1	2.29	3.27	161	2.39	3.35	157
	N1...H...N2	1.72	2.79	175	1.78	2.83	170
4 (BB)	O2...H...O1 <sup>b</sup>	1.46	2.51	171	1.63	2.65	169
	N1...H...N2	1.65	2.72	174	1.81	2.86	169
	O2...H...O1	1.60	2.62	173	1.57	2.60	171

<sup>a</sup>(i) = bifurcation. <sup>b</sup>Strong H-bond. <sup>c</sup>Weak.

dispersive forces correction, only one proton transfer has been observed in the 3(A) geometry optimization.

Inclusion of the dispersive forces leads to flat geometries, which reinforce hydrogen bonding and encourage proton transfer, thereby inducing a stabilizing charge separation and forming low-energy adsorption configurations. To illustrate the importance of a flat geometry to stabilize the self-assembly, we have also analyzed the less stable adsorption configurations 3(Ax) and 3(Bx), shown in Figure 4. Both configurations have strong hydrogen bonds: three in 3(Bx) and two in 3(Ax). In 3(Ax), an H-bond has led to a proton transfer (\*), inducing a charge separation. 3(Ax) and 3(Bx) have  $E_{\text{ads}} = -1.89$  and  $-1.96$  eV, respectively. The lower stabilities of 3(Ax) and 3(Bx) compared with 3(A) of  $\Delta E_{\text{ads}}^{3(\text{A})-3(\text{Ax})} = 0.37$  eV and  $\Delta E_{\text{ads}}^{3(\text{B})-3(\text{Bx})} = 0.30$  eV could be explained by observing the tilted geometries, as shown by the lateral view in the lower panel of Figure 4. In this figure, the lateral view is compared with the 3(A) and 3(B) configurations to emphasize the flatter geometry of the lower energy configurations. A tilted geometry reduces the  $\pi$ - $\pi$  stacking with the surface, and flat networks are therefore favored.

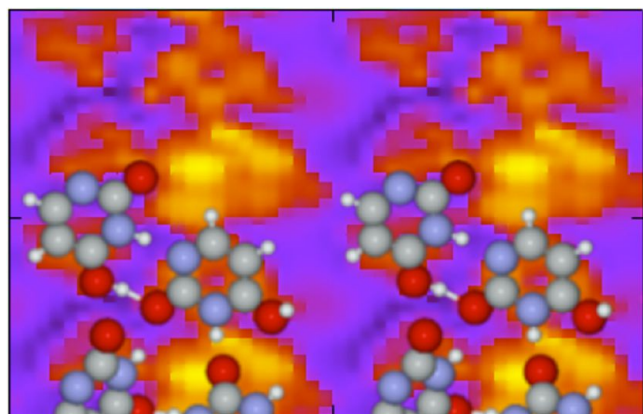
In Table 2, interaction and cohesion energies show that the lowest-energy configuration, 3(A), has an interaction energy of only  $-0.14$  eV with pure DFT. Adding the dispersive correction leads to an increase in the 3(A) transversal interaction energy to  $-1.32$  eV, whereas the cohesion energies are very close. The

3(A) configuration clearly has a strong cohesion energy due to the double proton transfer, but it also results in a very stable geometry as a result of both the covalent and dispersive transversal bonds to the surface. Dispersive forces appear to be significant in all the configurations, with a coverage of  $1.50$  molecules/nm<sup>2</sup> both in the interaction to the surface and in the molecule–molecule interactions, although whereas the former is translated in an evident increase in the interaction energy, the latter is interpreted in view of proton transfer. In these four configurations, proton transfer appears to be the primary force because 3(A) has the lower interaction energy but the higher cohesion energy (due to the double proton transfer), resulting in the lower-energy adsorption configuration.

**3.2.3. Uracil Network, Full Coverage: Four Molecules.** A network of four molecules on the surface aims to reproduce full coverage ( $3.00$  molecules/nm<sup>2</sup>). In this complete monolayer, the 4(AB) and 4(AA) configurations (Figure 5) are almost equally stable ( $\Delta E_{\text{ads}}^{4(\text{AB})-4(\text{AA})} = 0.01$  eV), at about the same adsorption energy as 2(B), but less than 2(A) and 3(A/B). In 4(AB) mode, two uracil pairs are placed on the surface with the pairings reflecting both A and B configurations. The rearrangement upon optimization leads to the formation of six hydrogen bonds, with one continuing to proton transfer, oxygen forming a bifurcated H-bond, and another weak H-bond between C–H...O. N–H...N and O–H...O are very strong H-bonds, and the bifurcation also adds an extra stabilization.<sup>32</sup> There is charge

separation in both uracil pairs. Again, this network seems to be strongly stabilized, mostly by lateral interactions, as only one molecule is bonding to the surface ( $-0.44\text{ eV}$ ), whereas the others are interacting laterally via H-bonds. Configurations 4(AA) and 4(BB) lead to  $E_{\text{ads}} = -2.15$  and  $-2.11\text{ eV}$ , respectively. In both networks, we can observe four hydrogen bonds each; charge separation is induced in three out of four interactions, and in 4(AA), there is proton transfer (\*), which could explain the stronger stabilization already mentioned before ( $\Delta E_{\text{ads}}^{4(\text{AA})-4(\text{BB})} = 0.04\text{ eV}$ ). Because of the small energy differences between these configurations, we expect that they are all likely to occur on the surface, particularly at room temperature. They also have similar interaction/cohesion energies, although 4(AA) has a stronger interaction energy but weaker cohesion than 4(AB). The full coverage description may benefit from an improvement in the methodology, particularly in the  $\pi$ - $\pi$  stacking to the surface, although the high number of hydrogen bonds is also not visible in the cohesion term.

**3.3. STM of Full Coverage.** The topographical STM image in Figure 6 provides information about the spatial distribution



**Figure 6.** STM images of a 4(AB)  $p(2 \times 2)$  supercell obtained using a bias of 1 eV. We also represent the uracil superstructure in the sites corresponding to the STM signal. C is grey, O is red, N is blue, and H is white.

of the valence band states in the vicinity of the Fermi energy ( $E_F$ ), which is particularly useful for systems in which the molecules of interest can interact with the surface in many different orientations. Direct comparison with experiment is possible by means of calculated STM images, which do not suffer from external perturbations, like the electric field of an STM experimental tip, which can influence the position and orientation of molecules adsorbed on a surface.<sup>16</sup>

We have tested different potentials with respect to the Fermi energy, and we can conclude that a bias of +1 eV is enough to obtain a clear STM image using the methodology described in section 2. The STM images in Table 4 are calculated for uracil adsorption at high coverage on Au(100): 4(AB), 4(BB), and 4(AA). The temperature at which the STM experiment is performed has a strong effect, as the energy difference among the several possible configurations is very small; thus, room temperature experiments are expected to lead to a mix of configurations. Here, the STM images shown represent the lowest-energy superstructures that the uracil molecules would adopt at 0 K.

**Table 4.** STM Images Obtained at 1 eV over Fermi Energy for 4(AB), 4(BB), and 4(AA) Systems; Density and Tip Distance Is also Indicated<sup>a</sup>

4(AB) +1 eV
$0.001\text{ e/\AA}^3 \rightarrow 0.644\text{ \AA}$
4(BB) +1 eV
$0.001\text{ e/\AA}^3 \rightarrow 0.016\text{ \AA}$
4(AA) +1 eV
$0.0001\text{ e/\AA}^3 \rightarrow 0.160\text{ \AA}$

<sup>a</sup>All pictures represent a  $p(5 \times 5)$  supercell. Inset is a molecule representation by balls and sticks: C is grey, O is red, N is blue, and H is white.

Figure 6 shows the calculated STM of a  $p(2 \times 2)$  supercell and the self-assembled 4(AB) uracil structure. In addition to the adsorption energies and molecule distributions discussed above, the structure named 4(AB) (Figure 5 and Table 4) clearly shows a chain structure built by the uracil self-assembly through long-range interactions. The atomic positions are difficult to assign from the STM image alone because of the partial charges of some atoms that are not fully expressed in the image. Comparing our STM images with the experiments in ref 16, we can observe that all monolayer configurations are, indeed, compatible with the experimental images, although they do not correspond to the model proposed in that paper. Our structures, however, are based on a configurational energy minimization by state-of-the-art ab initio methodology, and we therefore propose them as models for the physisorption phase, assumed to be a combination of all three. The use of STM to discern the uracil self-assembly is thus not conclusive on its own, and other techniques, including computation, may be required to obtain a full experimental picture of the self-assembled uracil networks on gold.



## 4. CONCLUSIONS

Self-assembly on metals is driven by several intermolecular and surface interactions. In this work, we have illustrated these forces through the network formation of uracil on a gold surface, Au(100). We have elucidated the interplay between transversal and lateral interaction as well as electrostatic and dispersive interactions. This system interacts by one molecule adsorbed by covalent bonding to the surface, where the influence of dispersive forces is significant, as witnessed by the change in energy of configurations 3(A) and 3(B) when the van der Waals correction is included. Moreover, we note that flatter geometries can enhance  $\pi$ - $\pi$  stacking, favoring, for example, 3(A/B) configurations versus 3(Ax/Bx).

On the basis of our calculations, we can conclude that lateral interactions direct the molecular assembly after the first covalent adsorption of a single molecule. The following molecules interact by hydrogen bonding, often followed by proton transfer. Indeed, these lateral forces appear to influence the self-assembly more significantly than the covalent bonding to the gold surface, which is absent in the second and further molecules (excluding 4AA and 4BB). Often, proton transfer leads to a more stable configuration of the ion-ion interaction (all geometries apart from 3(Ax)) as a result of the stabilization effect. Dispersive forces are significant in the transversal interaction to the surface, as witnessed by the increase in the interaction energy when a correction is included.

In addition, the role of the lateral interactions can also be observed in geometries in which the interaction to gold is similar in terms of either the total charge transfer or the distance to the surface, but which have significantly different adsorption energies.

However, the results shown here are at the limit of this approach. Indeed, the full monolayer coverage of uracil on the surface is underestimated in our calculations. The rich hydrogen-bonded network, proton transfer, and charge separation we observe does not translate into a higher adsorption energy and may not fully justify the experimentally determined long-range self-assembly. One reason could be the small space available to the molecules on the slab, generating an excessively tilted geometry and possibly lowering the  $\pi$ - $\pi$  interaction to the surface, whereas a second issue may be an insufficient description of these latter forces. Moreover, the cohesion energies of the networks are excessively low, considering the number of H-bonds presents.

On the basis of our calculations, however, we can conclude that uracil adsorption is strongly dependent on the lateral interactions, particularly hydrogen bonding. The self-assembly is mediated by proton transfer, and the ensuing charge separation stabilizes the geometry. Dispersive forces also play a role, and in particular, the introduction of a correction leads to flatter geometries with molecules lying parallel to the surface, thereby enhancing H-bonds and, potentially,  $\pi$ - $\pi$  stacking. These flat configurations permit stronger hydrogen bonds with angles over  $160^\circ$ , facilitating proton transfer and charge separation. At this stage, we can conclude that hydrogen bonding among molecules, plus dispersive interactions to the surface, appear to be the main interactions in the adsorbed self-assembled networks, with geometries in good agreement with experimental STM images.<sup>16</sup>

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### Notes

The authors declare no competing financial interest.

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