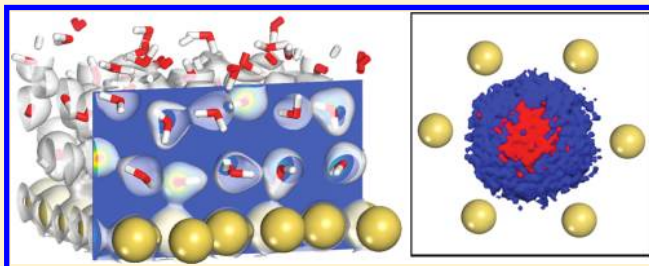


Anomalous Wetting Layer at the Au(111) Surface

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S Supporting Information

ABSTRACT: In this paper we present a microscopic picture of the interface between liquid water and a Au(111) surface at room temperature conditions, as obtained from ab initio molecular dynamics simulations. We find that the first wetting layer has peculiar structural and electronic features that can be revealed only by considering the dynamical evolution of the system. Surface phonons and molecular vibrations lead to instantaneous charge density distortions that are pivotal to explain the features of such an atypical wetting layer, and, in turn, the surface hydrophilicity.

SECTION: Surfaces, Interfaces, Catalysis

Understanding at a microscopic scale how liquid water wets metal surfaces is of fundamental relevance both at basic and applied research levels. From one side, it would be desirable to understand whether concepts as hydrophobicity/hydrophilicity still hold at the molecular level, and, in that case, it would be extremely relevant to identify the fingerprints of the resulting wetting layer. On the other side, on a more macroscopic scale, one would like to understand how the presence of the hydration layers influences the physical properties of the metal, when employed for example in electrochemical cells or in biosensors working in a liquid environment.

Hydrophobic/hydrophilic properties of materials strongly depend on the ability of the surface to establish hydrogen bonds with interfacial water molecules. For this reason wetting properties are usually tailored by appropriate surface modifications, which consist in linking to the surface specific functional groups or realizing self-assembled monolayers¹ with molecules of desired polarity and able to form hydrogen bonds with water. In this respect, predicting the wetting properties of clean flat metal surfaces is a quite compelling task because metal characteristics are determined by delocalized valence electrons, rather than local polarity, and their interactions with water cannot be classified exploiting the hydrogen bond paradigm.

Water/gold interface is a prototype system for this problem: notwithstanding the wide range of studies and applications of this noble metal, its coupling with liquid water is still a controversial issue. Indeed, gold fails to fit theoretical trends,² being supposed to behave as a hydrophobic substrate, in terms of interaction energy. On the other hand, most recently, experiments have evidenced that a clean Au(111) surface at room temperature is hydrophilic.³ Gold surfaces are extremely relevant for technological

fields, and Au(111) is the most stable gold surface. Therefore, understanding the behavior of the Au(111) surface in a wet environment is pivotal for applications such as nanoparticles for surface enhanced Raman spectroscopy (SERS) detection⁴ or imaging,⁵ molecular biomimetics⁶ and specific sensing.⁷ Previous ab initio works on the Au(111)–water interaction have been focused on the adsorption of single water molecules or ordered water layers at $T = 0$ K;^{2,8,9} the study of the liquid water/Au(111) interface has been limited so far to classical force field simulations.^{9–11}

In this work we focus on the water/Au(111) interface addressing the problem via extensive ab initio molecular dynamics (AIMD) simulations. Our results show that in the case of surfaces that do not contain any explicit hydrophilic group (such as $-\text{OH}$ or $-\text{NH}_2$), the macroscopic behavior of the surface/water interface in ambient conditions can hardly be inferred from the description of the metal/water interaction gained from ab initio calculations performed at $T = 0$ K.² Indeed much of the interaction in actual experiments may be related to thermally induced vibrations (such as surface phonons and bond stretching), which play an important role in dipole-mediated interactions. In the case of Au, we find not only that the interaction with water appears to be enhanced when room temperature dynamic is considered but also that the presence of the surface increases the H-bond strength between interfacial water molecules. Dynamics is relevant because the instantaneous surface corrugation induced by atomic motion (with bond and charge distortion) is responsible for the features of

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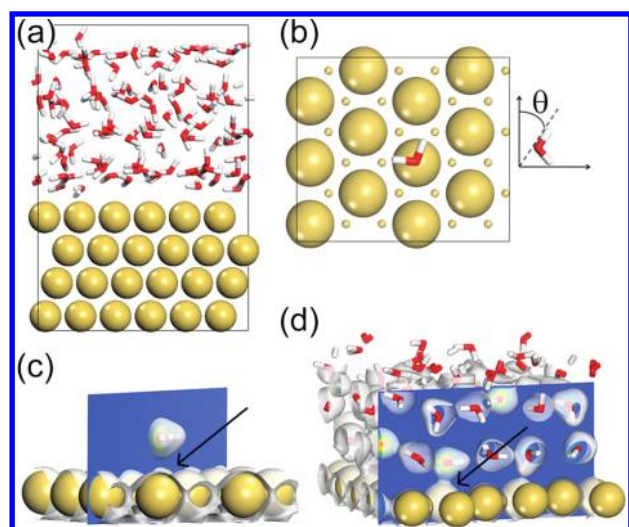


Figure 1. (a) Side view of starting configuration for the total liquid water/gold system in the simulated unit cell. (b) Top view of single H_2O molecule on a $\text{Au}(111)$ surface ($\text{H}_2\text{O}@Au$). Large (small) spheres represent atoms of the first (second and third) $\text{Au}(111)$ layer. Inset defines the θ angle, described in the text. Isosurface plots of the total charge density for (c) the $\text{H}_2\text{O}@Au$ system and (d) the total water/ $\text{Au}(111)$ interface, taken from a representative snapshot from the AIMD trajectory. In panels c and d, a charge slicer passing through the O atom and perpendicular to the surface is superimposed for clarity.

the wetting layer, driving a better agreement with experimental behavior.³ This is a genuine effect of the AIMD simulation, as it is correlated to the capability of producing a comprehensive description of both the electronic structure and the oscillating dipoles associated with vibrating systems. Thus, it cannot simply be predicted either by ground-state ab initio calculations (i.e., no temperature) or by standard classical force field molecular dynamics (i.e., no electrons).

We used density functional theory (DFT),¹² in the generalized gradient corrected approximation (PBE),¹³ and Car–Parrinello¹⁴ molecular dynamics (CPMD), as implemented in the Quantum-ESPRESSO package.¹⁵ Test calculations including London dispersion (DFT-D) have been performed with the parametrization proposed in refs 16 and 17: the results confirm and strengthen our conclusions about the features of the surface wetting layer on $\text{Au}(111)$ surfaces (see the Supporting Information for detailed results). We employed ultrasoft pseudopotentials,^{18,19} the electronic wave functions (charge density) were expanded in plane waves, with energy cutoffs up to 25 (200) Ry, and the integration over the Brillouin zone was performed with the Γ point of the supercell. The numerical integration of the ion equations of motion was carried out with a time step of 7 au; an electronic mass of 450 au was employed as in previous CPMD calculations of water.^{20,21} The starting configuration for the first principle simulations was obtained by performing preliminary classical MD simulations (NVT) with the SPC potential for water and using the force field for water–gold interactions proposed in ref 22. In our water/gold system (Figure 1), the cell dimensions in the (x,y) plane were fixed and determined by the size of a relaxed Au slab composed of four atomic layers with $3\sqrt{3} \times 5$ surface periodicity. In the z direction, the cell dimension was varied, while keeping the number of water molecules constant (104), until the stress along this direction yielded a pressure equal to an atmospheric one.²³ In the first-principle calculations, the atomic configuration resulting

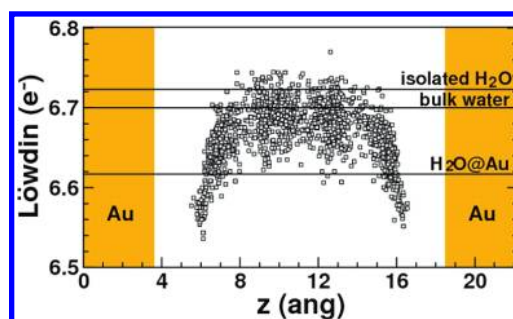


Figure 2. Distribution of the Löwdin net atomic charges for oxygen atoms along the direction normal to the surface (shaded area), obtained by sampling the electronic structure during the AIMD simulation. Black lines mark the Löwdin charge values for reference systems.

from classical MD was first thermalized at $T = 400$ K for 3.0 ps with a Nosé–Hoover thermostat. The equilibration was followed by ~ 16 ps of production run. Since the purpose of the present investigation was to compare the properties of interfacial water with those of bulk water, we considered the temperature (400 K) at which DFT using PBE and CP dynamics yielded results in good agreement with experiment for structural and diffusion properties of liquid water at ambient conditions.^{24,25} The dipole moments of water molecules are calculated through the evaluation of the maximally localized Wannier functions²⁶ (WanT code²⁷), obtained by transforming the DFT electronic orbitals of selected snapshots along the trajectory into localized states in real space.

Before analyzing the results obtained for the Au/liquid water interface we first discuss the interaction of a single water molecule with the $\text{Au}(111)$ surface ($\text{H}_2\text{O}@Au$) at zero temperature. In agreement with previous calculations,² our results show that the molecule prefers to adsorb with its oxygen atom at on-top sites with the molecular plane almost parallel to the surface (Figure 1b). In this configuration the equilibrium $\text{Au} \cdots \text{O}$ distance is about 2.8 Å, the angle between the molecular plane and the surface normal is 85° , and the interaction energy is -120 meV. The adsorption energy is almost insensitive to the azimuthal H_2O rotation and minimal Au –water electronic hybridization is observed. Previous studies^{28,29} have described this weak interaction in terms of electron donation occurring between the water molecule (electron donor) and a surface atom (electron acceptor); in other words, water acts as a weak Lewis base pointing one of its lone pairs toward a surface gold atom. In fact, Löwdin charge analysis shows that upon $\text{Au} \cdots \text{O}$ interaction, a small charge donation occurs from the oxygen to the gold atom with the gold atom gaining ~ 0.02 electrons, in agreement with experimental results.³ The comparison with Löwdin charges for the isolated H_2O molecule and liquid bulk water (Figure 2) clearly evidences an oxygen charge depletion induced by the presence of the metal surface. This issue is also highlighted by the total electron charge density of the interface, which exhibits a partial polarization along the $\text{Au} \cdots \text{O}$ direction (see arrow of Figure 1c). As we will comment in the following, this interaction markedly affects the way liquid water meets the Au surface, despite being weaker than typical hydrogen bond energy (the latter being about 0.25 eV²⁸); yet, from the above analysis it is hard to conclude whether gold would behave as a hydrophobic or hydrophilic surface.

In the case of the liquid water/Au interface, we calculated how the water density changes in the direction perpendicular to the

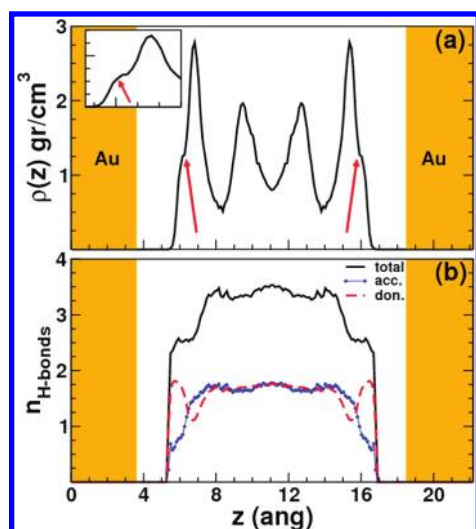


Figure 3. (a) Density of water molecules computed along the direction perpendicular to the Au(111) surfaces indicated by the shaded area. Inset zooms on the shoulder are marked by the left arrow. (b) Number of H-bond donors (dashed red line) and acceptors (dotted blue line) for each water molecule; the total number of hydrogen bonds per molecule is also reported as a solid black line. As proposed in previous works,³² we choose the following geometric criterion to define a hydrogen bond: O...O distance shorter than 3.5 Å and O...HO angle larger than 140°.

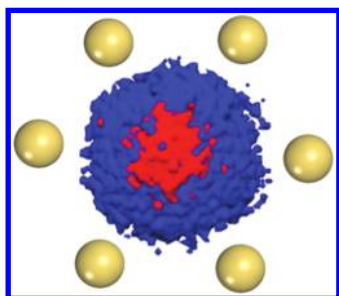


Figure 4. Oxygen (red isosurface) and hydrogen (blue isosurface) SDF of water molecules within 2.6 Å from gold atoms at the surface (yellow spheres represent gold atoms at the surface).

surface (Figure 3a), as it results from the AIMD trajectory: a layering effect, typical of water/solid interfaces,^{30–33} is evident. The first high-density peak of oxygen²³ is at 3.2 Å from the surface atoms: a larger distance with respect to the single H₂O@Au at $T = 0$ K. This peak has yet a prominent shoulder (red arrow and inset in Figure 3a) at an average distance of 2.6 Å. By inspection of the spatial distribution function (SDF),³⁴ it is possible to highlight specific binding mechanisms or preferred adsorption sites. Figure 4 shows the calculated oxygen (red) and hydrogen (blue) SDF in a sphere of 2.6 Å radius centered on a surface gold atom: while the oxygen species preferentially resides at on-top Au(111) sites, the hydrogen atoms are uniformly distributed around them. An analysis of the orientation of the water molecules in terms of tilt of the OH bonds with respect to the surface normal reveals that interfacial water ($d < 2.8$ Å) has also preferential orientations: both OH bonds are tilted at about the same angle (in the range 60–80° wrt the surface normal), and one oxygen lone-pair is directed toward the surface. This orientation backs up the dative-like bond picture presented above.

Moreover, this interaction is responsible for an oxygen-to-gold charge transfer (Figure 2), which favors a dynamical attractive coupling between the metal and the first wetting layer. We also highlight that the orientation with one of the OH bonds pointing toward the surface, which is typical of many hydrophobic surfaces (see, e.g., refs 33, 35, and 36), is not a preferred orientation for the molecules directly interacting with gold atoms but rather of the molecules at 3.2 Å.

The above discussion evidences that some features characterizing single molecule adsorption on a gold surface at $T = 0$ K can be still identified in the case of the Au/liquid interface at ambient conditions. Indeed, the same (on-top) adsorption site, similar Au–O distances and consistent water molecule orientations are observed for interfacial water. The uniform distribution of the H atoms around the O atoms shown by the SDF is also consistent with the independence of the adsorption energy (at $T = 0$ K) on the azimuthal rotation of the molecule. Yet, our AIMD trajectory points at an enhancement of the interaction between water and gold when vibrations induced by room temperature conditions are considered; indeed the average Au...O distance is shorter than that reported for a single molecule in the ground state. We ascribe this effect to thermal effects neglected at 0 K: surface phonons and molecular vibrations induce charge distortions that favor the interaction of water molecules with the surface atoms. This statement is supported by the results of an ab initio MD simulation of gold exposed to one monolayer of water molecules at ambient temperature. We found that, although most of the molecules tend to evaporate, some of them clearly interact with the oscillating gold atoms through their lone pair and are found at distances in the range 2.4–2.9 Å. During the MD simulations the Au atoms of the outer layer are characterized by displacements in the direction perpendicular to the surface of about ± 0.3 Å, and this corrugation causes an increase of the Au/H₂O interaction of about 20 meV.³⁷

A relevant feature of interfacial water molecules is that upon interaction with surface gold atoms, their ability to establish hydrogen bonds with the surrounding molecules is markedly affected. This is evidenced by an analysis of the bottom panel of Figure 3, where the average number of hydrogen bonds (HBs) per water molecule is reported as a function of the distance from the surface.²³ Although at further distances from the surface (beyond 4 Å) the average number of H-bonds is the one observed for water in the liquid phase (with an equal number of H-bond acceptors and donors), the situation is different for the molecules of the surface hydration layer. These molecules have only one-half of their hydration shell and, for this reason, form a smaller number of H-bonds; yet, it is surprising to notice that at distances < 2.8 Å from the surface, water molecules persistently behave as H-bond donors: their average number of donated H-bonds is even slightly larger than what is found far from the surface (i.e., for liquid water). This feature has not been observed in other water/solid surfaces such as graphene or hydroxylated SiC;^{32,33} our tests on a few water–Au(111) force fields (based on simple non-bonded potentials) demonstrated that further force field developments are needed to correctly reproduce this feature^{22,37,38} (see Supporting Information). To analyze whether the interaction with gold is responsible for this enhanced H-bond formation, we have calculated the H-bond strength for a water dimer when the H-bond donor is interacting through its lone pair with a surface gold atom (on-top site) and then without the surface. Consistently with ref 8, our results indicate that the H-bond is stronger in the presence of the gold surface of about

0.2 eV. In other words, interfacial water molecules, due to their interaction with the gold surface, appear more acidic and keener on donating H-bonds that are stronger than those in the liquid phase. These unique features have been recently discussed in terms of the role that interfacial water has in mediating protein/gold interaction.²¹ The average number of hydrogen bonds that a water molecule forms determines its dipole moment. In particular, the dipole increases passing from the gas phase 1.87 D (no H bonds), to the liquid 2.88 D (about 3.6 H bonds), and to the solid phase 3.00 D (4 H bonds). Interfacial water molecules may have different dipoles depending on the hydrophobicity of the surface. At hydrophobic surfaces, molecules have a number of H bonds smaller than that in liquid, and for this reason have smaller dipoles (see, e.g., ref 33), while in the case of a hydrophilic surface, the molecules have dipoles similar to that found in liquid water.³² In the case of the Au surface, we found that the average dipole of the interfacial water molecules is unchanged with respect to the liquid value, and this is thus consistent with a surface of hydrophilic character.

In conclusion, we have revealed that the first water wetting layer at the Au(111) surface (the first high liquid density peak) is characterized by the presence of two types of water molecules: one interacting with the surface atoms, and the other not in contact with the gold surface. These molecules show markedly different features both in terms of structure and in their ability to form hydrogen bonds. Surprisingly, the water molecules closer to the gold atoms form hydrogen bonds with the surrounding molecules that are stronger than the average H-bond strength of liquid water. This effect appears to impart a hydrophilic character to the gold surface together with its wetting layer. The hydrophilicity of a surface is usually related to the ability of a surface to establish hydrogen bonds with water. In the case of Au, it is rather the surface together with its hydration layer that has a hydrophilic character.

Finally, our study highlights the importance of correctly describing vibrations and the corresponding oscillating dipoles to study interfacial solid/liquid systems and the difficulty of addressing the wetting properties of a surface based only on minimum energy structures calculated at zero temperature. Indeed, although the interaction of a single water molecule with gold is weak, this interaction appears to be enhanced when thermal effects (vibrations) are considered and its features can still be identified at the solid/liquid interface.

■ ASSOCIATED CONTENT

S Supporting Information. Classical force field and PBE-D tests and an AIMD run for gold exposed to water in the gas phase. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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