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1 Scientific Report : Quantum description of water sandwiched between metal surfaces.

The purpose of my visit at the Physics department of Stony Brook University was to focus on the quantum interactions of water sandwiched between metal surfaces. During these days, we tried to understand how water rearrange itself while confined between two metallic surfaces (here palladium $\langle 111 \rangle$.) We used ab-initio molecular dynamics (AIMD) simulations within density functional theory (DFT), [1, 2] to perform our calculations within the localized orbitals code SIESTA [3, 4].

While the chemisorption of water on top of metallic surfaces has already been deeply investigated [5, 6, 7, 8], confined water sandwiched between two surfaces remains a delicate subject to deal with.

First, the two descriptions of the localized orbitals of water and delocalized wave functions of the metal are still hard to define properly and accurately. Second, AIMD of many atom systems are very time and memory consuming and then it is not straightforward to obtain converged results (typically few ps).

It is known that a 2D rule can be stated [5] from the chemisorption of one layer of ice on top of a metal surface. The most stable configuration is formed by hexagonal structures with oxygen atoms at each angle and one and only one hydrogen between two oxygens (fig : 1). Such a constraint imposes only three different positions for water known as ; flat, up and down.

On order to respect the 2D rule, water has to chemisorb using these 3 orientations. Periodic boundary conditions impose that half of the total number of molecules need to be flat, and the other half can be either up or flat. However, the energy of chemisorption would differ from a flat molecule to an up or a down molecule. It appears that the energy of chemisorption of a flat molecule is a bit stronger than the chemisorption involving a down or up molecule. We also noticed that the distance between a molecule in flat position and the metal surface is slightly closer than between either a down or up molecule (fig : 2). From an electronic analysis it has been deduced that

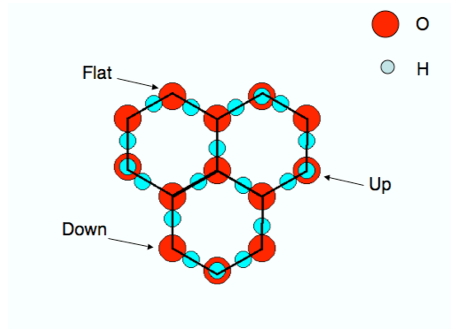


Figure 1: On this picture, the water molecules respect the 2D-water rule. Oxygens form hexagonal structure and only 1 hydrogen binds 2 oxygens. Only three space's orientations are possible for water ; one calls "flat" the molecule when it is parallel to the surface, "up" when a hydrogen of the molecule is pointing to the opposite side of the surface and "down" when a hydrogen is pointing towards the surface. The other hydrogen of the two last configurations lies parallel to the surface.

the electronic process involved in the chemisorption is not the same whether an oxygen or a hydrogen makes a bond with the metallic surface. Indeed, the oxygen atom tends to donate an electron to the surface, while the hydrogen atom is accepting an electron from the surface.

Water in bulk has also been studied carefully by scientists, and it remains that the water molecules would prefer to keep an tetrahedral orientation. It means that in average a water molecule has got 4 nearest neighbours. In our system (fig :1), we have observed that there is a competition for water between these 2 orientations ; the first layer connected to each surface has to be chemisorbed respecting the 2D rule, while the other layers tend to adopt a bulk behavior.

This competition has been studied for different water density and for different initial ionic velocities.

On the fig : 3, we plotted the histogram of the atom density (respectively O and H) as a function of Z, the coordinates perpendicular to the surfaces. The metallic surfaces are located at -1.5 \AA and at 16.5 \AA . From this graph, we can already deduce that a gap occurs between the chemisorbed layers and the bulk water. This clearly means that the two configurations of water (ie : water chemisorbed or in bulk) repulse each other because of strong interactions between atoms. It also appears from the analysis of the simulations that a

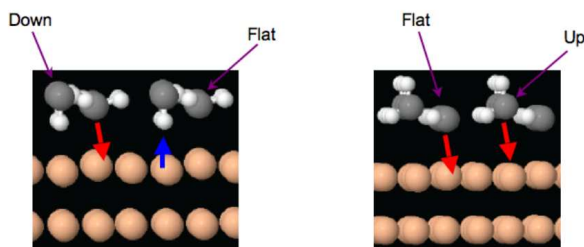


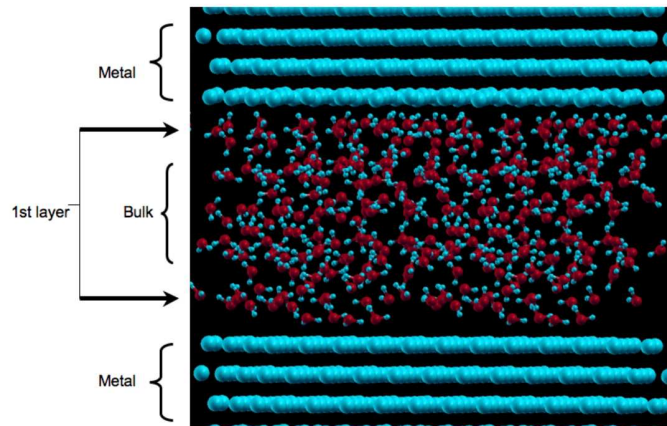
Figure 2: Those are 2 different configurations for the chemisorption of water on top of a palladium surface. On the left picture the flat molecule is donating an electron, while the down molecule is accepting an electron through the hydrogen. On the right one, both of the molecules are donating electron to the surface. On each plot, the flat molecule is slightly closer from the surface than the up or down molecule.

broken spontaneous symmetry occurs in the system ; depending on the side of the sandwich, the chemisorption of water molecules will tend to prefer one position instead of others. For example, we can see from the histogram by looking at the distances between the chemisorbed molecules and the surfaces that one there are more down molecules on the right side while there are more flat molecules on the left side. This has for effect to introduce more charge in a side of the slab than in the other. This could mean that the metal is polarizing.

However a deeper investigation of the electronic interactions in the system is required before making any conclusion. Indeed, we need to implement in our code the maximally localized Wannier function in order to define accurately the water's orbitals in term of bonding. The work already provided would yield to a publication relating the geometry properties of water confined between two metallic slabs. We will also keep working on the electronic structure of water, by trying to find a relevant tool to describe orbitals.

References

- [1] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864, (1964).
- [2] W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133, (1965).
- [3] P. Ordejón, E. Artacho and J. M. Soler, Phys. Rev. B **53**, R10441, (1996).



- [4] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, *J. Phys.: Condens. Matter* **14**, 2745 (2002); see also <http://www.uam.es/siesta/>
- [5] J. Cerdá, A. Michaelides, M.-L. Bocquet, Peter J. Feibelman, T. Mitsui, M. Rose, E. Fomin and M. Salmeron, *Phy. Rev. Lett.* **93**, 116101, (2004)
- [6] H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelmenchikov, L. G. M. Pettersson and A. Nilsson, *Phys. Rev. Lett.* **89**, 276102, (2002)
- [7] V. A. Ranea, A. Michaelides, R. Ramírez, P. L. de Andres, J. A. Verg'es and D. A. King, *Phys. Rev. Lett.* **92**, 136104, (2004)
- [8] Peter J. Feibelman, *Science* **295**, 99, (2002)

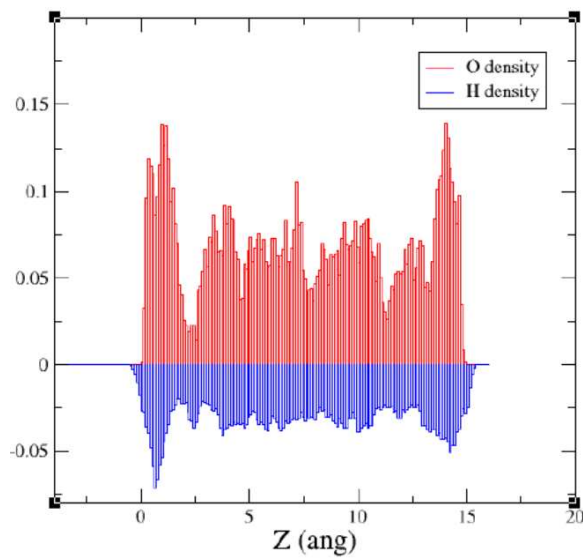


Figure 3: Histogram of the density of oxygen atoms (in red) and hydrogen atoms (blue) as a function of the Z coordinate, perpendicular to the surfaces. We observe the two behavior of water ; the layer of water chemisorbed, respectively at 1 \AA and 14 \AA and the water in bulk (between 2 \AA and 13 \AA). An important gap occurs between chemisorbed water and water in bulk, which tells us that there are strong repulsive interactions between atoms.