

Water Adsorption on Clean and Oxygen Decorated Metal Substrates

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Water growth on metal surfaces has been a topic of debate during many years. Nowadays, it is still unclear what are the growth mechanisms and the structures for water layers on many substrates. An important ingredient to understand the self-organization of water in metallic surfaces is the competition between inter-molecular and metal-substrate interactions. This competition determines whether the molecules (i) cluster in a 3D-phase, (ii) wet the surface following a well-ordered 2D-adlayer or even, in a more complicated scenario, (iii) a significant fraction of water molecules in the layer undergo partial dissociation (thus, decomposing into H and OH).^[1-3]

Both, the inter-molecular and metal-substrate interactions, are strongly influenced by the substrate itself and by co-adsorbing other adsorbates.^[4] In this work we have explored both types of interaction in the adsorption of water on clean Cu(110) and oxygen decorated Ru(0001) surfaces using Density Functional Theory (DFT) calculations motivated by recent scanning tunneling microscopy experiments.

The wetting of Cu(110) has been recently reported. Experimental results showed that at low temperature and coverage water forms one dimensional arrays of side-sharing pentagons on Cu(110).^[5, 6] These pentagon row structures can evolve to hexagon row structures as the coverage of water increases beyond 0.2 layers, according to the experimental evidence.^[6] It is then proposed that this transformation is mediated by the formation of lobe structure (LS) clusters made of n pentagons connected to a central hexagonal ring (n -LS). These cluster configurations are characterized by the appearance of additional bright spots in the experimental STM images (see Figure 1). The most frequent LS configurations are the 4-LS and they are believed to act as a catalyst for the propagation of H-bond re-orientation along the chain of pentagons and thus, they could be considered the precursors of the transformation to the hexagonal row structure. Using DFT calculations, we compare the structures and energetics of pentagon and hexagon infinite row structures and explore the possible structures for the isolated 4-LS, depending merely on the molecules orientation. Finally, we present the several 4-LS “defects” into the pentagon row structure.^[7]

We also present results on the wetting of the oxygen decorated Ru(0001) surface at 0.5 ML oxygen coverage, consistent with the O(2x1)/Ru(0001) surface. We found that the adsorption of water causes a shift of half of the chemisorbed oxygen atoms from hcp sites to fcc sites, creating a (2x2) honeycomb structure. Our calculations show that the energy cost of reconstructing the oxygen overlayer is more than compensated by the adsorption of water on the newly created unbounded Ru atoms. The STM images reveal a (4x2) water super structure, which is due to the existence of two relative orientations of the water molecules. Interestingly, the oxygen honeycomb structure induced by the adsorption of water remains metastable after

water desorption and does not revert to the stable linear 2x1 structure until after temperatures close to 300K.^[8]

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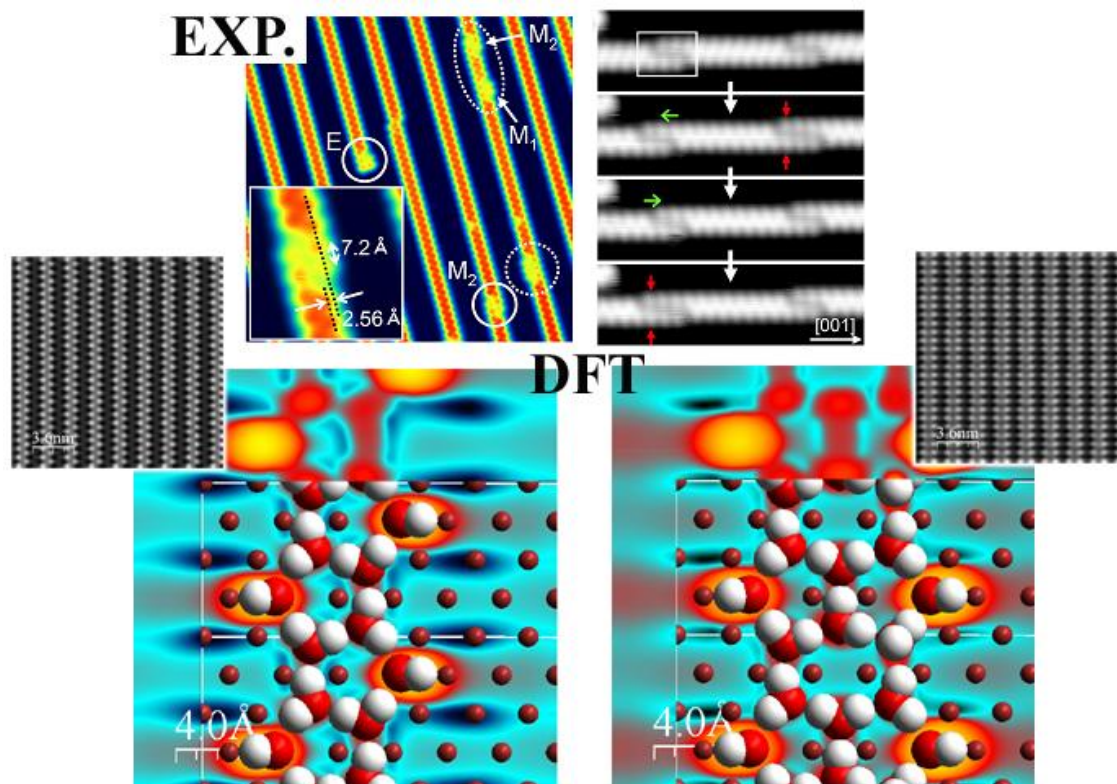


Figure 1. Upper panels correspond to experimental images: on the left STM images (30nm × 30nm) of the Cu(110) surface covered by 0.2 ML water after annealing to 120 K. The peculiar structures (named n-LS) are found in various locations: isolated (I), at the end of chains (E) and in the middle of chains (M₁ and M₂). On the right STM images (5nm × 15nm) of a chain composed of three segments offset by one lattice constant. The first image was obtained at 0.1V and 30pA followed by three successive images at the same bias but higher tunnel current (80, 100 and 120pA). The 4-LS can be displaced right and left along the zigzag chain (green arrows). Downward panels correspond to DFT images for pentagonal row structure, on the left, and, on the right, the proposed hexagonal row structured based on the propagation of 4-LS clusters.