An STM study of Water clustering on Pd(111): Experiment and Theory

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The early stages of water clustering on Pd(111) has been studied by means of low temperature (40 K) Scanning Tunneling Microscopy (STM) experiments [1]. At the lowest coverages, individual water molecules diffuse around the metal surface. Upon collision, they form dimers, trimers, tetramers, pentamers and cyclic hexamers, the latter showing the largest stability (see Figure 1.a).
As the coverage is further increased, islands presenting a commensurate hexagonal honeycomb structure relative to the Pd(111) substrate are formed (Figure 1.b). After some time, the island edges end up decorated by bright features (Figure 1.c). Next, heating up the sample to 70 K leads to a restructuring of the islands (Fig. 1.d), now adopting more regular shapes which resemble either a rosette pattern (Figure 2.c) or a lace-type pattern (Figure 2.e).

In order to understand the experimentally observed water clustering mechanism, we have performed first-principles total energy calculations[2] and STM simulations[3] for different proposed models. First, we find the stable geometry for each model, and next we simulate its associated STM image and compare it against the experimental image.

Our main result is that the water structures are not based on ice bilayer models, as it has always been assumed in the past[4]. Even the case of half-dissociated bilayers, recently proposed for water on Ru(0001)[5], can be ruled out. Instead, the characteristic honeycomb pattern is attributed to hexamers consisting of flat molecules (F) which are H-bonded to similar adjacent hexamers in an sp2 type bond arrangement. However, simple geometrical arguments force any adjacent hexamer to have at least one non-flat molecule. The simulations show that these non-flat molecules (D) adopt an sp3 type configuration, with one H pointing towards the surface and the other pointing away. The orientation of the D molecules does not favour H-bonding to other F molecules and therefore, they are expected to be present at the island edges. Following this simple rule, both the rosette and the lace type structures shown in Figures 2.e and 2.c, respectively, can be rationalized from the models drawn in Figures 2.d and 2.a. The associated STM simulations (Figures 2.d and 2.b) show a very good agreement against the experiment for both models.

As for the low T image of Figure 1.c, we again find that the honeycomb features present in the internal part of the islands correspond to flat hexamers, whereas the bright edges stem from second layer water molecules H-bonded to the D molecules.

In summary, our results show a novel water clustering mechanism which markedly deviates from the usual ice bilayer model.

References

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Figure1

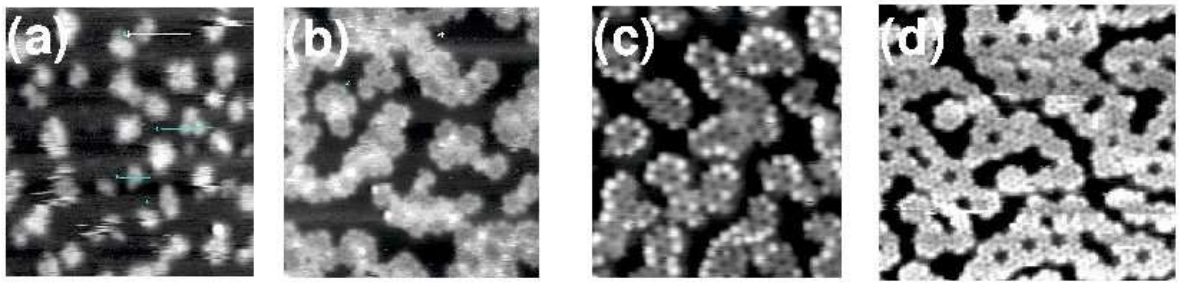

Figure 2