

Supporting information for:

Water-ice analogues of polycyclic aromatic hydrocarbons: Water nanoclusters on Cu(111)

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STM images of water at 5 K and after annealing to 25 K and 40 K

STM images were acquired for low coverages of water deposited onto Cu(111). The surface was held at ~ 5 K during dosing followed by STM imaging and then thermal annealing, which enabled the self-assembly of larger ordered clusters. The sample was then cooled back down to 5 K to acquire high-resolution images. In Fig. S1a the STM image before annealing is shown in which water monomers can be seen (4 water molecules are circled in white) as well as larger clusters like hexamers (2 hexamers are circled in white). After annealing to 25 K (Fig. S1b) a large number of ordered structures are observed, including some previously reported *i.e.* octamers ($n = 8$) and the larger structures presented in this study. Figure S1c shows an STM image taken after annealing at 40 K. The higher annealing temperature resulted in the onset of formation of larger aggregates (referred to as 3D clusters in the figure).

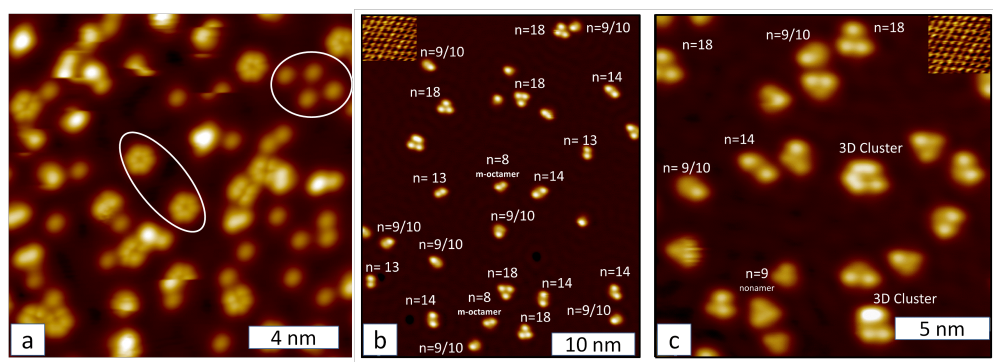


Figure S1: STM images of ~ 0.05 ML of H_2O on Cu(111) deposited at 5 K (a), annealed to 25 K (b), and 40 K (c). Imaging performed at 5 K.

DFT calculations of water clusters

Simulated STM images

The simulation of STM images within the Tersoff Hamann^{S1} approach as done here requires the choice of two parameters: the voltage, V , and the distance between the tip and the substrate, $d(\text{tip}/\text{Cu})$. In Fig. S2 we show the simulated STM image for the $n = 13$ ‘symmetric dimer’ at a range of voltages and distances from the surface. All values give qualitatively similar images, with two bright spots, corresponding to the two high-lying oxygens of the DAs, being the dominant feature. Therefore, the results presented in this work are not determined by the choice of voltage bias or tip/substrate distance.

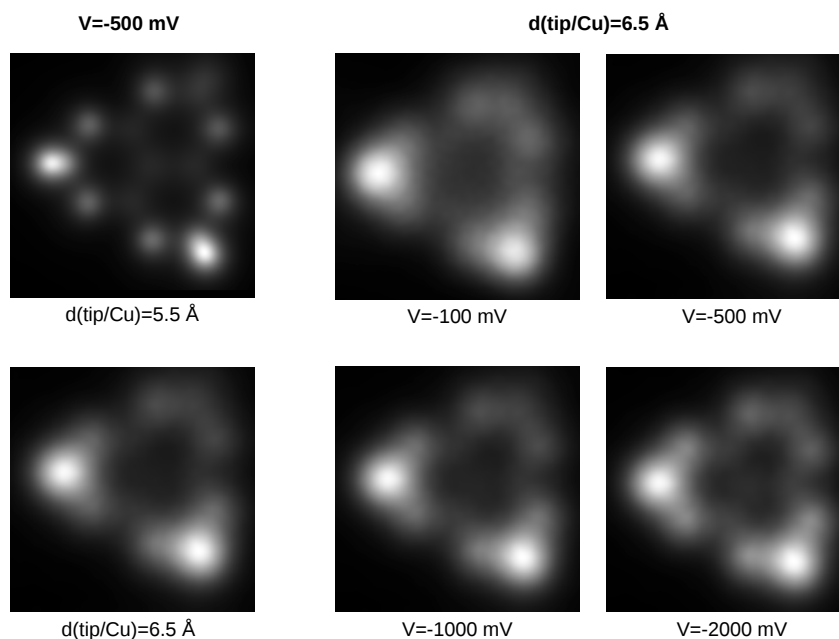


Figure S2: Simulated STM image of the $n = 13$ molecules cluster. Different values of the distance between the STM tip and the substrate, $d(\text{tip}/\text{Cu})$, and of the voltage, V , have been investigated. All values give the same qualitative result with two brighter spot visible, corresponding to the high-lying oxygens in the DAs.

Structure of water hexamer and nonamer

Previous work on small water clusters adsorbed on Cu(111) reported the observation of a number of structures formed by up to nine H₂O molecules which were imaged with high-resolution STM and further studied by means of DFT.^{S2} The water hexamer and nonamer are among these structures and they are shown in Fig. S3. Two arrangements are possible

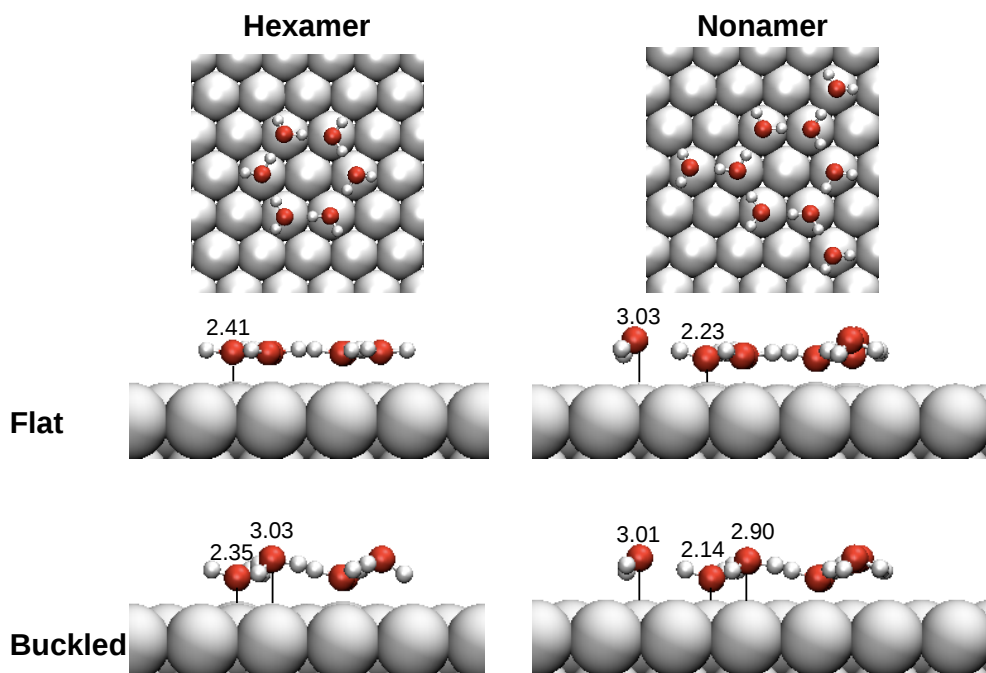


Figure S3: DFT-calculated (with optB86b-vdW) adsorption structures for a hexamer (left hand side) and a nonamer (right hand side) of water on Cu(111). The top view is shown in the top figures, side views for the flat and buckled configurations are shown in the middle and bottom panels, respectively. O atoms are shown in red, H in white and Cu in grey. Selected O/Cu distances are shown in the side view panels.

for the water molecules in each cluster, one where the central hexamer is flat (middle panel) and one where it is buckled. In the calculations in Ref. S2, performed without the inclusion of van der Waals interactions, the buckled structure is the most stable in both cases. In the present work, calculations are performed with a van der Waals-inclusive functional and the buckled hexamer is still the most stable (by $\Delta E_{\text{ads}} = E_{\text{ads}}^{\text{flat}} - E_{\text{ads}}^{\text{buckled}} = 16$ meV). However, the two configurations for the nonamer are isoenergetic within the accuracy limits of our

calculations ($\Delta E_{\text{ads}} = -4 \text{ meV}$).

Analysis of the adsorption of water clusters

The H-bond strength between the H_2O molecules in the cluster and between the cluster and the substrate have been analyzed to examine why clusters tend to flatten on $\text{Cu}(111)$ as they become larger. The H-bond strength is computed as:

$$E_{\text{HB}} = \left(E_{n \times \text{H}_2\text{O}}^{\text{gas}} - \sum_n E_{\text{H}_2\text{O}} \right) / n \quad (1)$$

where $E_{n \times \text{H}_2\text{O}}^{\text{gas}}$ is the total energy of a cluster of n water molecules in the gas phase and $E_{\text{H}_2\text{O}}$ of a single H_2O in the gas phase. The interaction between the water molecules and the substrate is estimated as:

$$E_{\text{int}} = \left(E_{\text{H}_2\text{O}/\text{Cu}(111)} - E_{\text{Cu}(111)}^{\text{sp}} - E_{n \times \text{H}_2\text{O}}^{\text{gas}} \right) / n \quad (2)$$

where $E_{\text{H}_2\text{O}/\text{Cu}(111)}$, $E_{\text{Cu}(111)}^{\text{sp}}$ and $E_{n \times \text{H}_2\text{O}}^{\text{sp}}$ are total energies of the whole system and of the unrelaxed substrate and water cluster in the gas phase, respectively. As with energy decompositions in general, this decomposition is somewhat arbitrary but has proved useful in the past in obtaining a semi-quantitative description of the balance of water-substrate and hydrogen bonding interactions for water on metals.^{S3}

The values of these two quantities for clusters from the hexamer ($n = 6$) to the tri-lobed structure ($n = 18$) are shown in Fig. S4. Calculations were performed on both optB86b-vdW- and PBE-optimized structures. To an increase in size of the cluster, a decrease in H-bond strength and an increase in water/surface interaction also follow. This trend applies to both functionals, although the water-surface interaction calculated with PBE is systematically weaker, as expected. Conversely, the H-bond strength is very similar with both functionals. Indeed, the average H-bond strength in the cluster reduces linearly with N from $E_{\text{HB}} = -325 \text{ meV}$ in the hexamer to $E_{\text{HB}} = -199 \text{ meV}$ in the tri-lobed structure. Conversely,

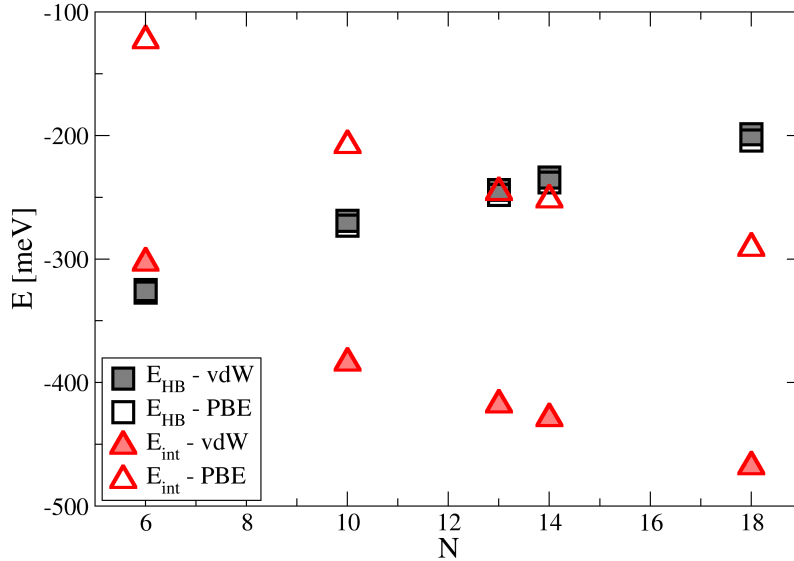


Figure S4: H-bond strength, E_{HB} , and surface/cluster interaction, E_{int} , for structures from the hexamer ($n = 6$) to the tri-lobed structure ($n = 18$). Shaded symbols correspond to values calculated with the optB86b-vdW functional, open symbols with the PBE functional. E_{HB} was calculated according to Eq. 1 and E_{int} according to Eq. 2.

the cluster/surface interaction increases from $E_{\text{int}} = -303$ meV in the hexamer to $E_{\text{int}} = -468$ meV in the tri-lobed structure. This weakening of the H-bonding network and the increased interaction with the surface thus explain the smaller $\text{H}_2\text{O}/\text{Cu}(111)$ separation and the subsequent flattening of the structure. However, the flattening is only partial because of other constraints in the water ring: indeed, double acceptors are at equilibrium at ~ 3.20 Å away from Cu(111), and the molecules bonded to them at ~ 3.00 Å and this does not change whether the rest of the structure is flat or buckled.

References

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- (S2) Michaelides, A.; Morgenstern, K. *Nat. Mater.* **2007**, *6*, 597.

(S3) Michaelides, A.; Alavi, A.; King, D. A. *Phys. Rev. B* **2004**, *69*, 113404.