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Water clustering on nanostructured iron oxide films

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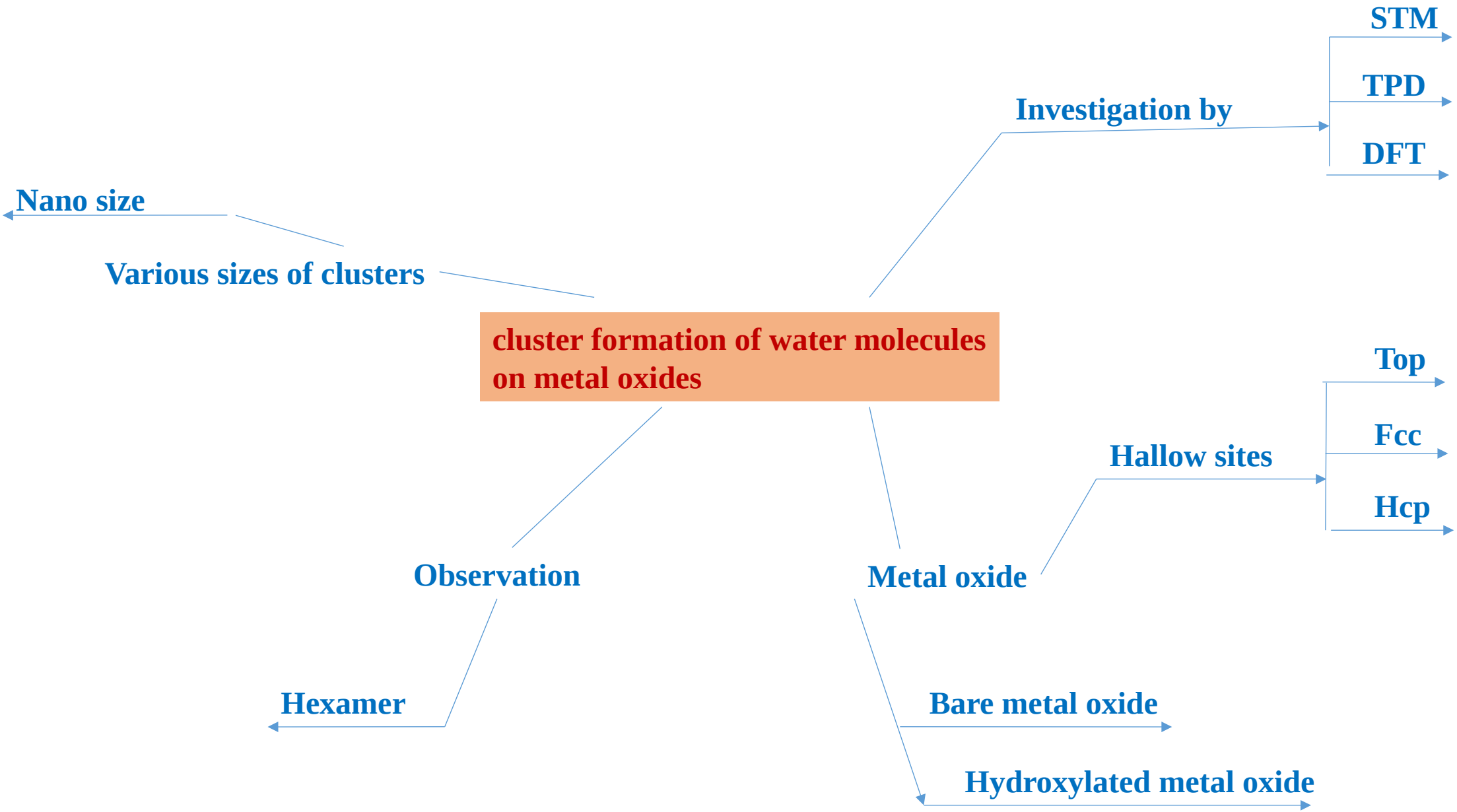
Introduction

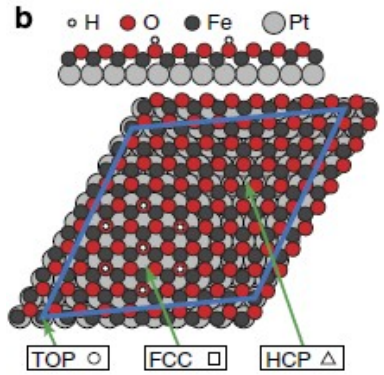
- Motivated by applications in diverse fields such as electrochemistry, geochemistry, atmospheric chemistry, corrosion and catalysis.
- The structure of water adsorbed on solid surfaces has been a topic of strong and sustained interest over the past decades.
- Hydroxyl groups form strong hydrogen bonds to water molecules and are known to substantially influence the wetting behavior of oxide surfaces, but it is not well-understood how these hydroxyl groups and their distribution on a surface affect the molecular-scale structure at the interface.
- Oxides add an additional level of complexity compared with metals, as water molecules can bond both to metal cations and oxide anions.
- STM studies, which allow direct visualization of hydrogen bonding networks.

Out-line of the paper



Experimental Set-up

STM Measurements:



- **To made Monolayer FeO films Pt(111) surfaces**
  - Evaporation of Fe onto clean, sputtered and annealed Pt(111) surfaces.
  - Conditions at T=1,000 K ,P=1X10-6 mbar of oxygen.

- **Using a home-built variable-temperature Aarhus STM55**
  - Mounted in an ultra-high vacuum (UHV) chamber with a base pressure of P=1X10-10 mbar.
  - For water dosed onto the surface using 1ms pulses from a binary piezoelectric valve.

- **Calibration of water coverages**
  - 1 ML is defined here as the density of O atoms in the FeO film, 1.2X1015 cm-2.
  - A single pulse from the piezoelectric doser produced a water coverage of 0.02 ML on the surface.

- **STM image processing was conducted using the Gwyddion software package56**

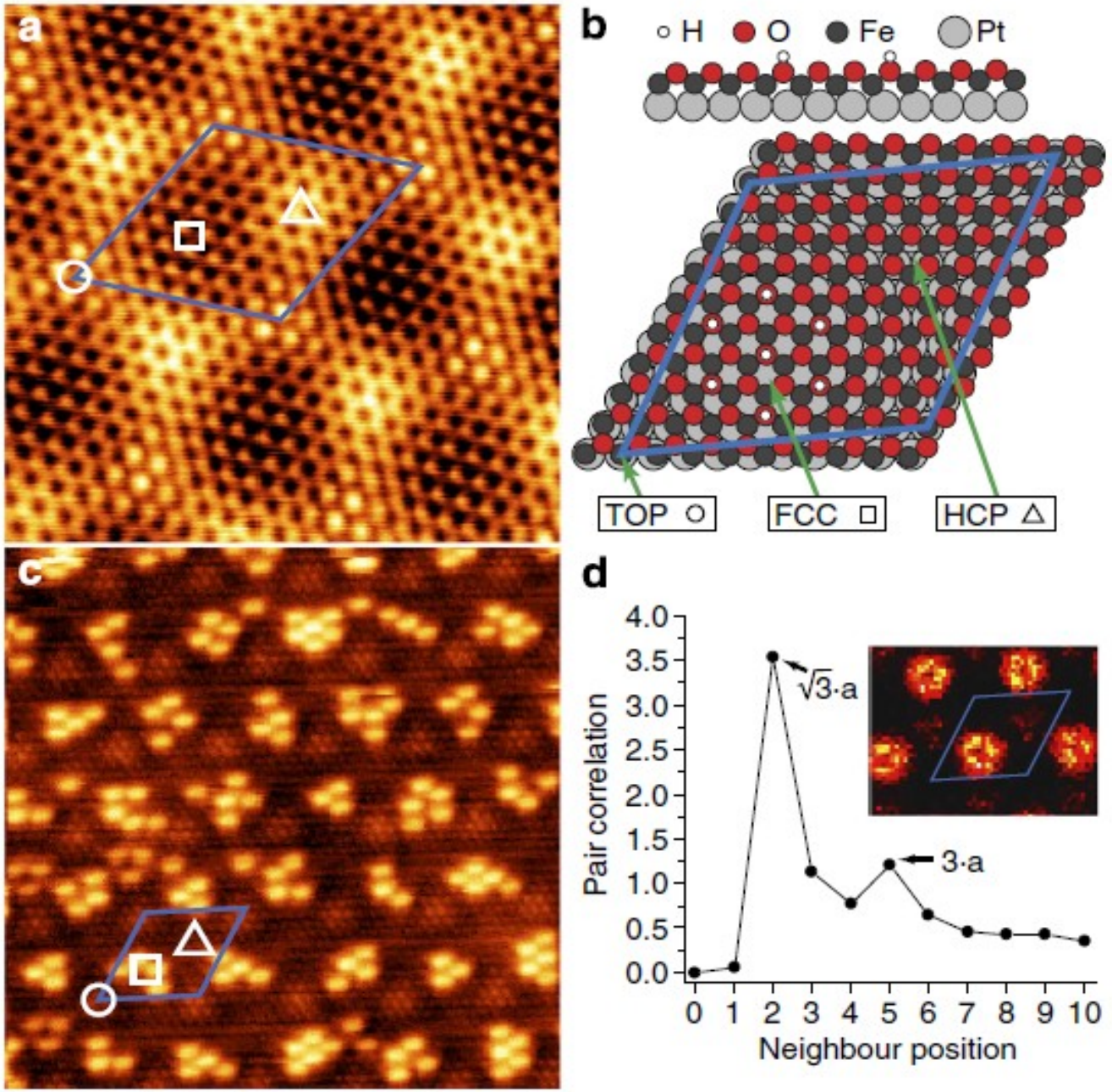
TPD Experiments

- **Using UHV surface analysis system (SPECS), equipped with a Hiden quadrupole mass spectrometer (QMS) fitted with a glass shroud with a 4-mm entrance aperture.**

- X-ray source and electron energy analyzer for X-ray photoelectron spectroscopy.
- For these experiments, a hat-shaped Pt(111) crystal 7mm in diameter and K thermocouple was used.
- Eurotherm temperature controller (linear heating ramp rate=2K/s for all measurements.
- To produce H atoms from H2 gas using thermal gas crackers.

- **DFT Calculations. All calculations were performed using the Vienna Ab.**

Results and Discussion



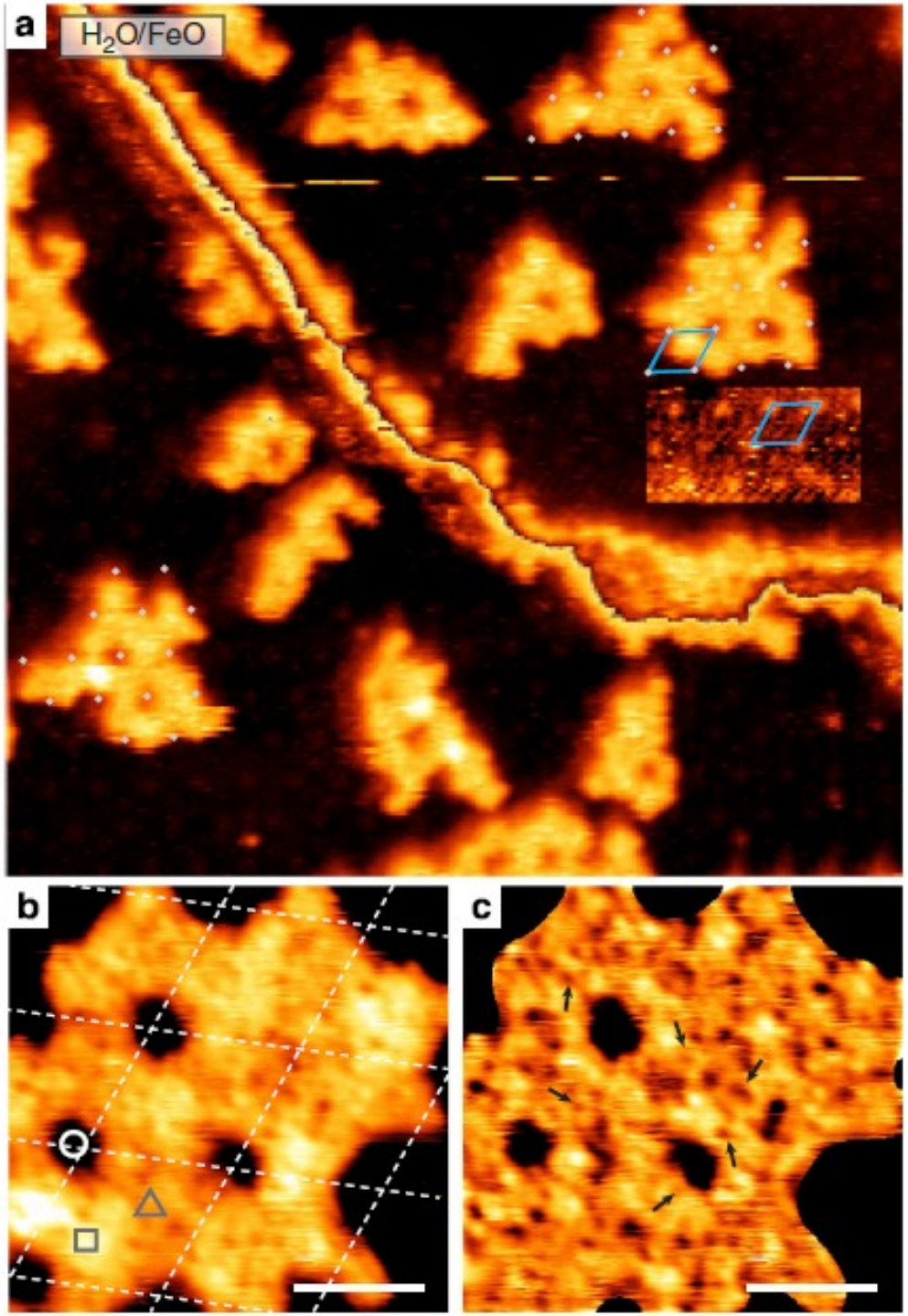
Bare and hydroxylated FeO films

Figure 1 | (a) STM image of the bare FeO/Pt(111) film (65X65Å2, 65mV, 3 nA).

(b) Ball model of the FeO/Pt(111) film. The 25Å moire´ unit cell is indicated as are the three high symmetry domains.
OH groups are shown (with white dots for H atoms) in the preferred FCC domain of the moire´ unit cell

(c) STM image (140140Å2, 0.7V, 0.4 nA) of the hydroxylated FeO film with an OH coverage of 0.05 ML, acquired at 160 K after additionally dosing B0.02 ML water (not visible).

(d) Inset: distribution of OH groups within the moire ´ cell, showing the preference for occupation of FCC domains.



Water adsorption on bare FeO

Figure 2 | (a) STM image (480X480Å2) of water adsorbed on the bare FeO/Pt(111) film, acquired at 110 K. The moire´ unit cell is indicated in blue and the positions of TOP domains are indicated with grey dots.

The rectangular area shows enhanced contrast of the bare FeO film, where bright spots are seen corresponding to the TOP domains.

The image shows two terraces (higher terrace in the upper right) separated by a single-atomic height step in the Pt(111) substrate. A cyclic colour scale is used to improve contrast.

(b) High-magnification STM image of a H2O island on the bare FeO film Fig. 1b. Scale bar, 20Å.

(c) The same STM image as in b after subtraction of the long-range height variations. Arrows indicate some of the 4–5Å pores observed in the structure.

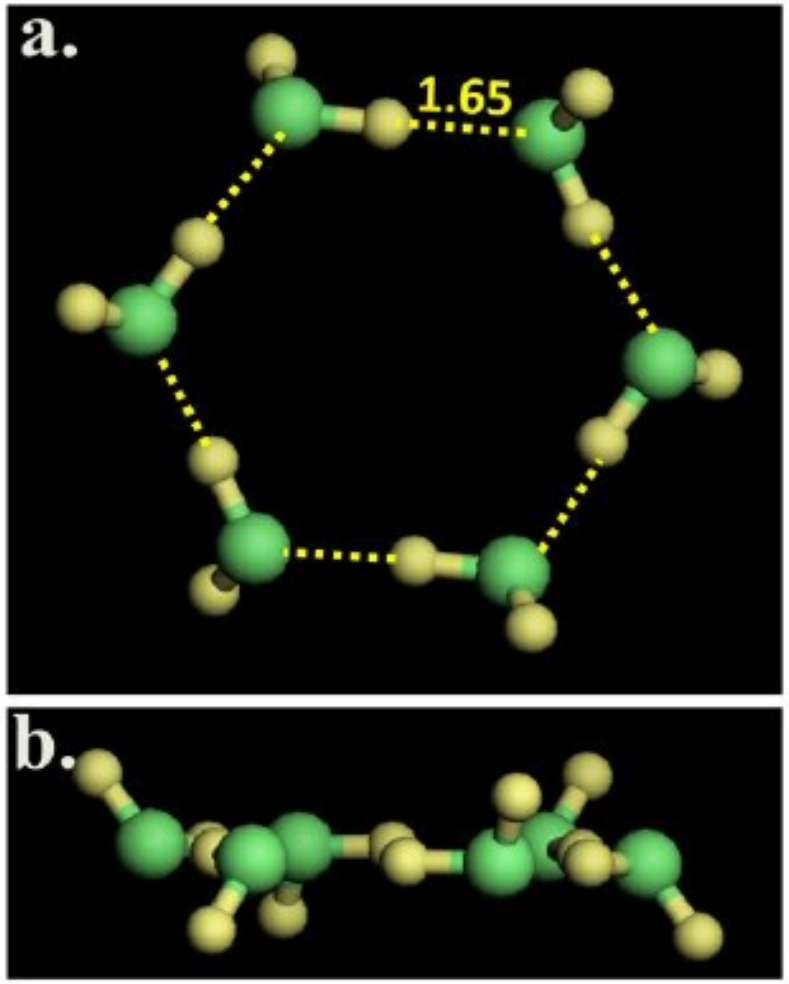


Figure 4. S_6 cyclic hexamer in the gas phase.

Top **(a)** and side **(b)** views of the optimized structure of a S_6

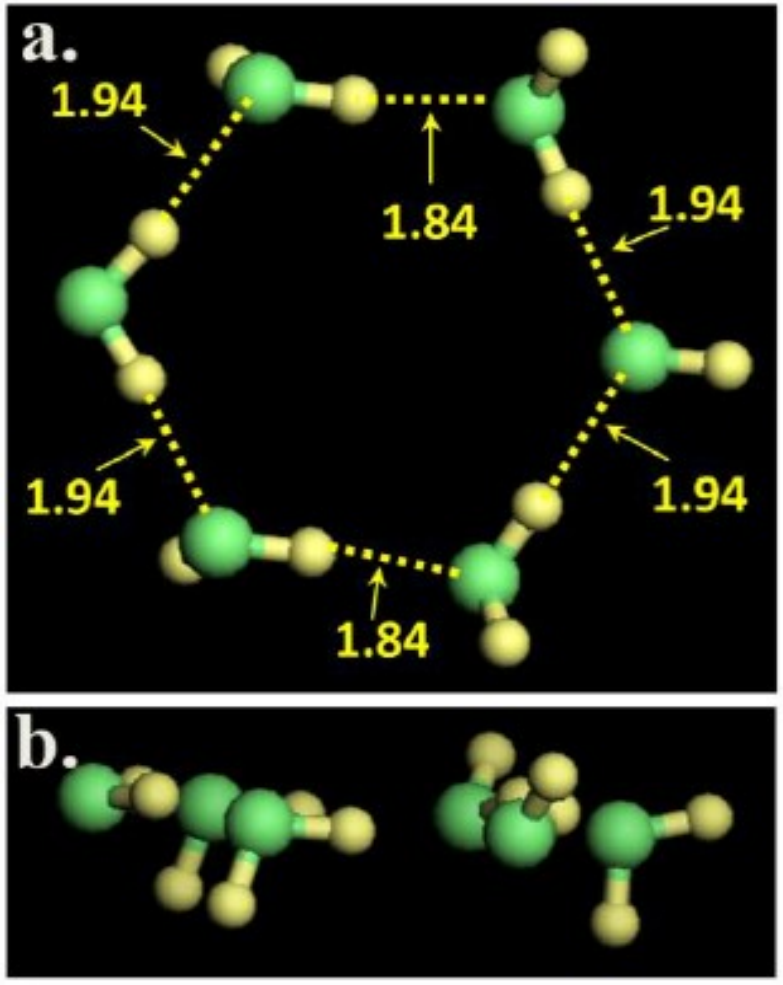
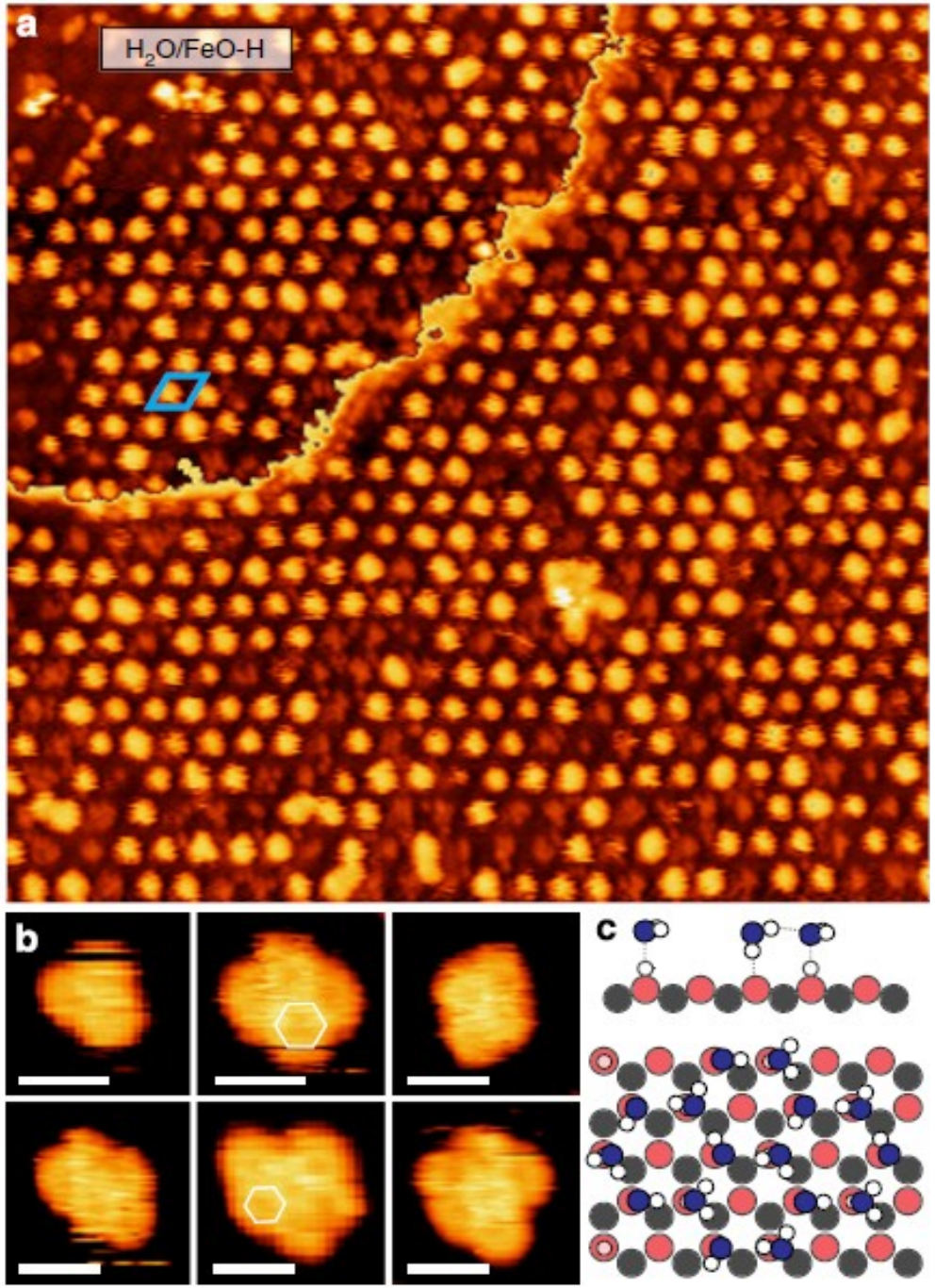


Figure 6. C_s cyclic hexamer in the gas phase.

Top **(a)** and side **(b)** views of the optimized structure of a C_s

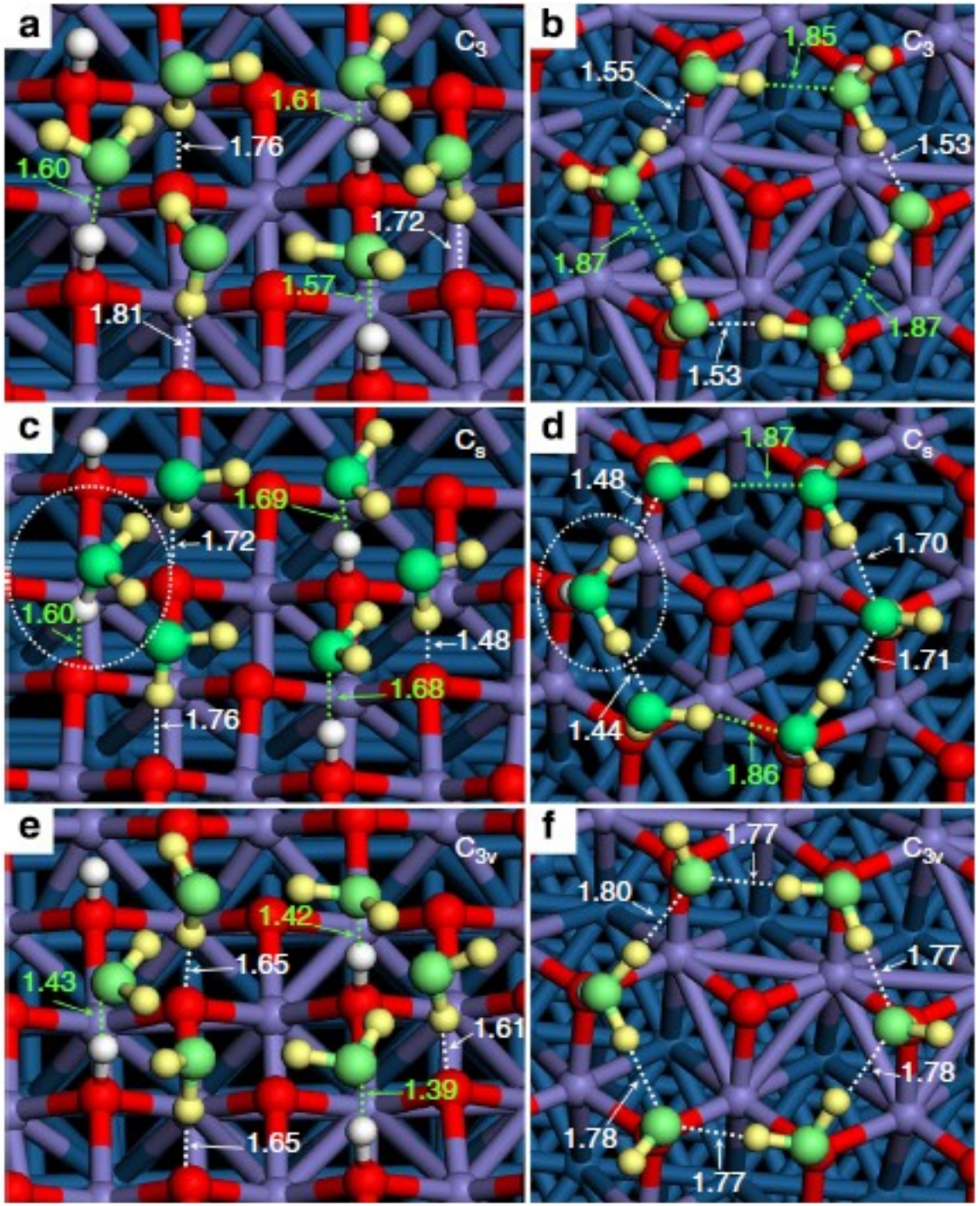


Water adsorption on hydroxylated FeO

Figure 3 | (a) STM image (600X600Å2)of water adsorbed on a hydroxylated FeO film with an OH coverage of 0.05 ML, acquired at 110 K. The image shows two terraces (higher terrace in the upper left).

(b) High-magnification images of H2O clusters on hydroxylated FeO showing a hexagonal ring structure. Scale bars, 10 Å.

(c) Schematic model of the hexagonal ring structure on hydroxylated FeO inferred from STM measurements.



Atomic structures of water clusters on hydroxylated FeO

Figure 4 | Tilted side (a,c,e) and top (b,d,f) views of three cyclic water hexamers, differing in the orientations of the molecules.

All numerical values for bond lengths are in Å.

Note: the transfer of one H+ ion from the surface to one water molecule, forming a hydronium (H3O+) ion, in the Cs structure,

highlighted by dashed white ovals in c,d. Blue, purple, red and white spheres indicate Pt, Fe, O and H atoms, respectively.

H and O atoms in H2O are highlighted by yellow and green spheres, respectively.

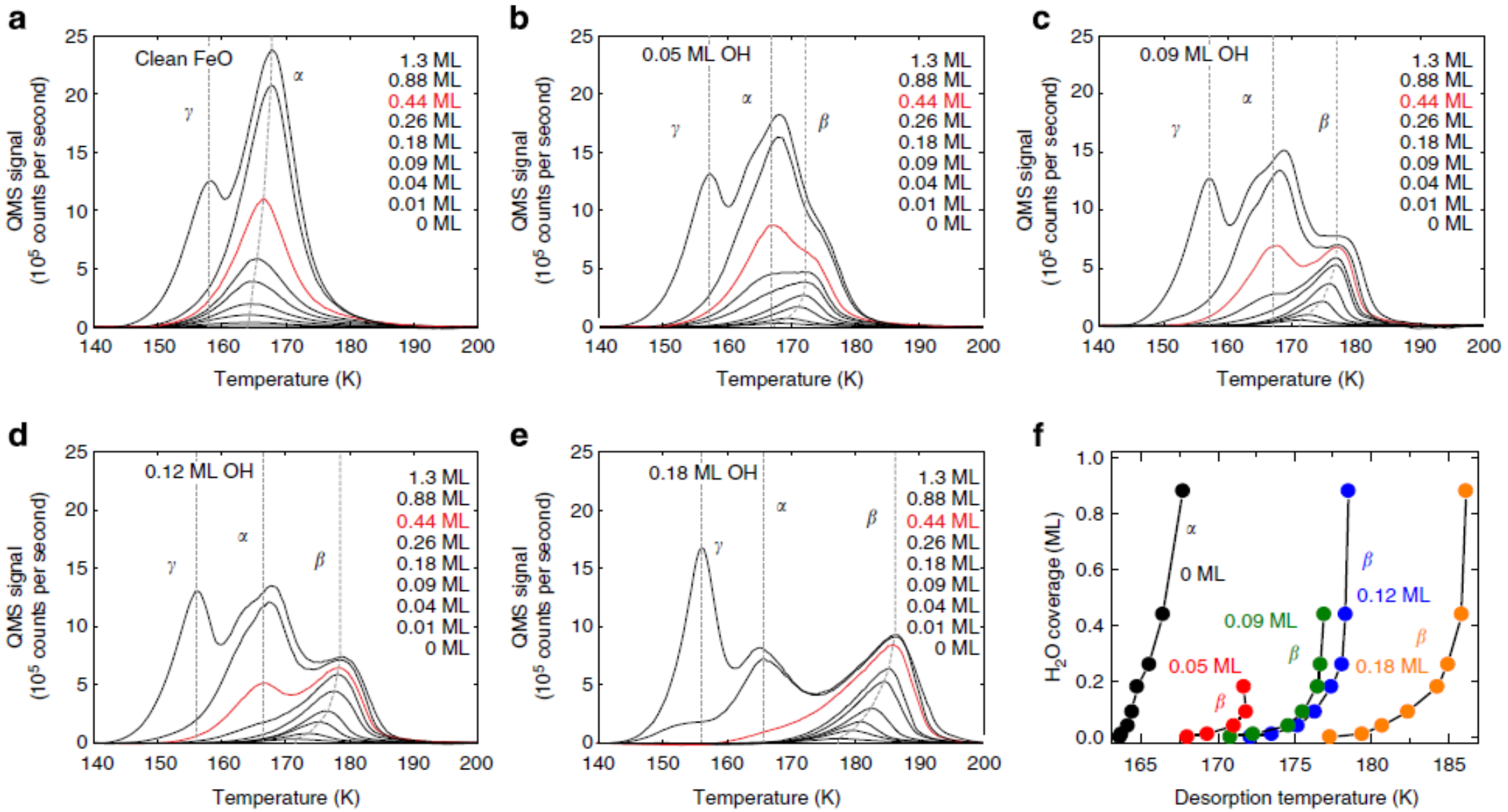


Figure 5 | Effect of hydroxylation on H2O desorption kinetics. TPD measurements (2 K s1 linear ramp) of H2O from **(a)** bare FeO/Pt(111), and hydroxylated FeO films with OH coverages of **(b)** 0.05 ML, **(c)** 0.09 ML, **(d)** 0.12 ML, **(e)** 0.18 ML.

Effects of OH and H2O coverage's

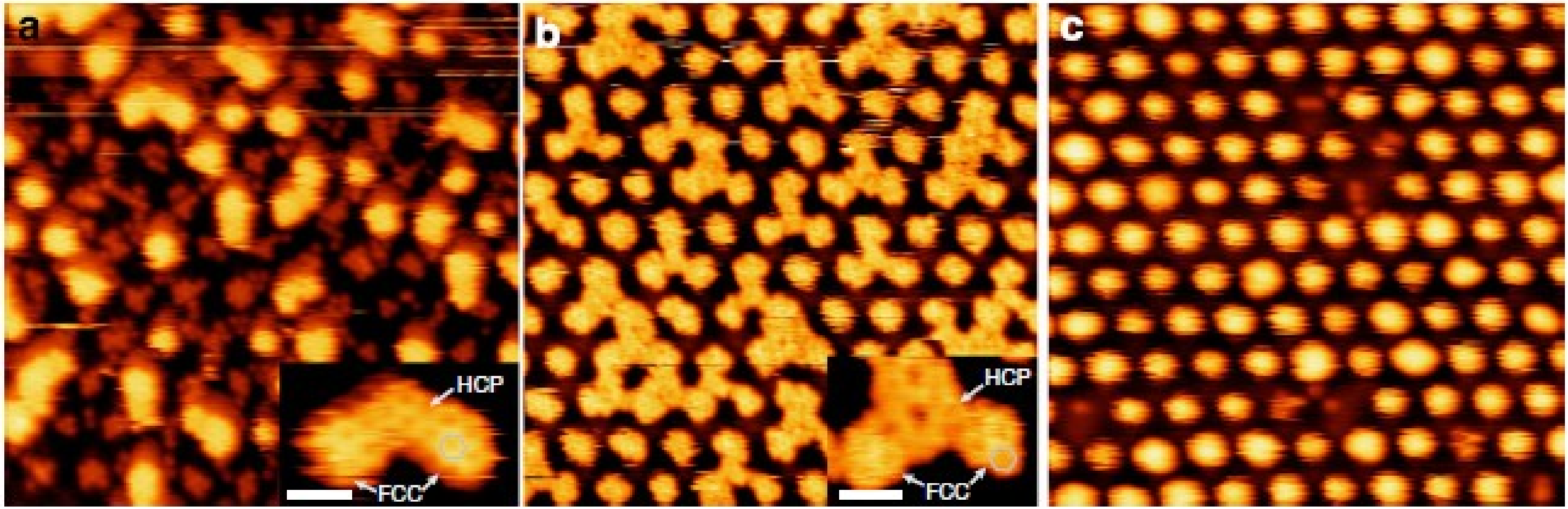


Figure 6 | STM images (250250Å2) of H2O adsorbed on hydroxylated FeO with various OH coverages and H2O exposures. **(a)** 0.1 ML H2O, 0.12 ML OH, **(b)** 0.25 ML H2O, 0.05 ML OH, **(c)** 0.1 ML H2O, 0.05 ML OH. Insets in a and b are high-resolution images of H2O clusters on the respective surfaces. Scale bars, 10 Å.

Conclusions

- STM, DFT and TPD studies addressing water clustering highly localized hydrophilic domains are formed upon hydroxylation of a moire structured FeO monolayer on Pt(111).
- The adsorbed water forms nanometre-sized clusters on hydroxylated metal oxide.
- The water clusters exhibit a hexameric ring structure stabilized by hydrogen bonding with surface OH groups.
- The larger islands on the bare surface which exhibit an amorphous structure.
- The STM and DFT results suggest that within the hexagonal structure, half of the water molecules accept H bonds from surface OH groups while the other half donate H-bonds to surface O ions, resulting in an H2O:OH ratio of 2:1. This 2:1 ratio is supported by TPD measurements.

Future plans

- STM studies, for direct visualization of oxygen bonding networks in arsenic oxyanions adsorbed on metal oxides.
- **To observe the arsenic species on metal oxides.**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