

Water agglomerates on $\text{Fe}_3\text{O}_4(001)$

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What is Agglomeration?

AGGLOMERATION – AGGREGATION

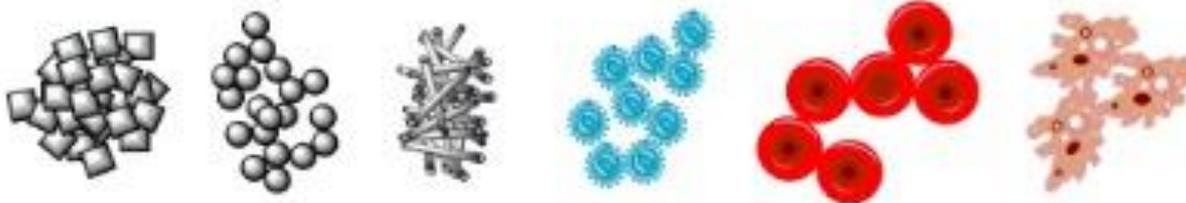
PRIMARY PARTICLES



PRIMARY PARTICLES



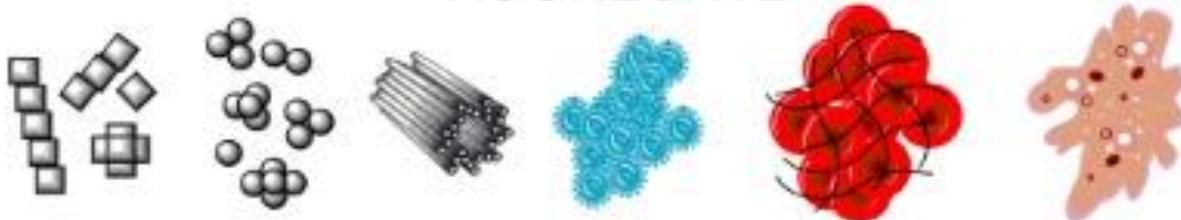
AGGLOMERATE



AGGLOMERATION:
Primary particles
loosely bound together

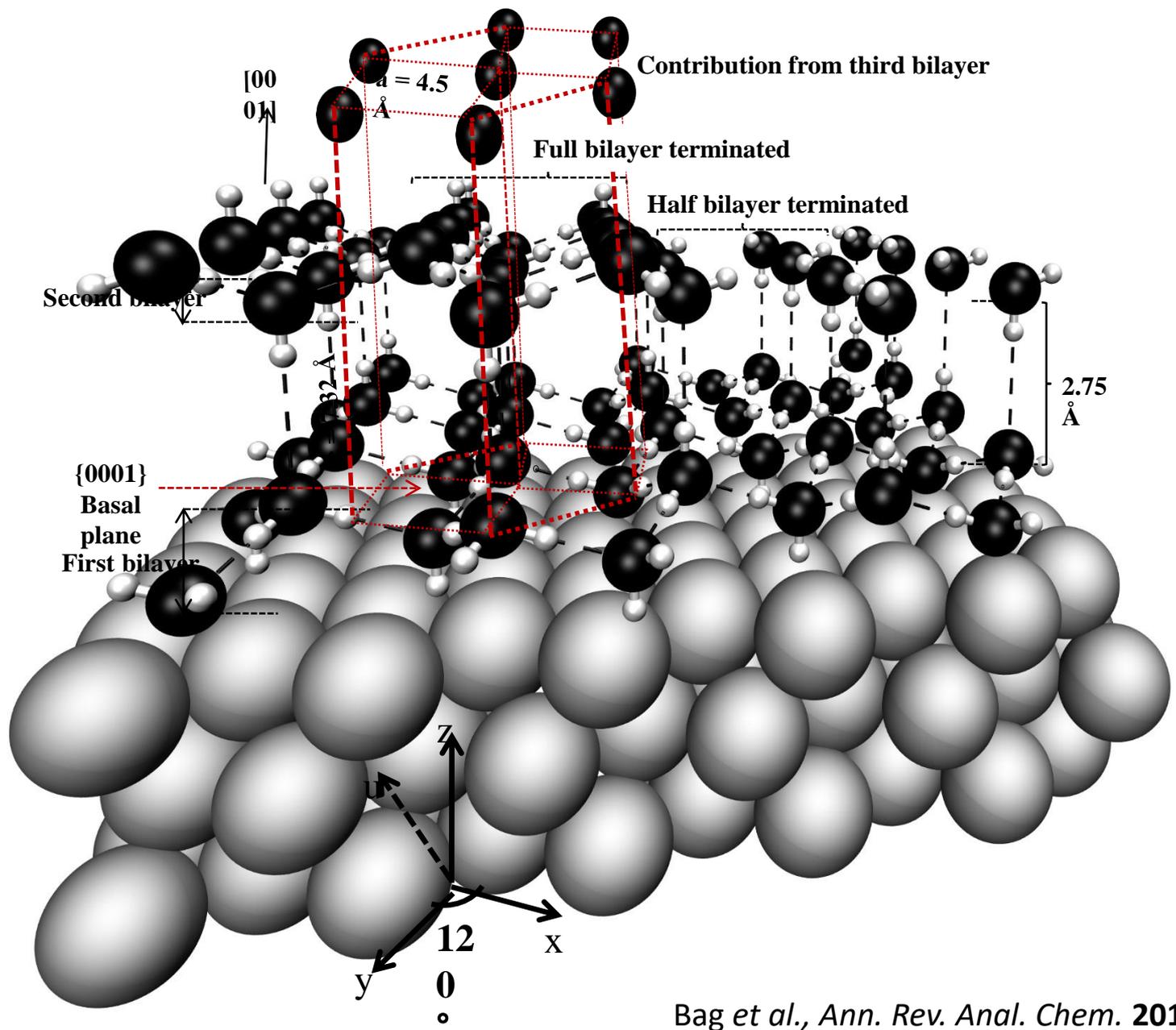


AGGREGATE



AGGREGATION:
Dense mass of fused or held
by strong forces particles
(new formed particles)

In the background



Probing equilibrium of molecular and deprotonated water on TiO₂(110)

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Wang *et al.*, *Proc. Natl. Acad. Sci. U.S.A* **2014**, *117*, 1801-1805

J. Phys. Chem. C **2010**, *114*, 11157–11161

Water Adsorption on ZnO(0001): Transition from Triangular Surface Structures to a Disordered Hydroxyl Terminated phase



Structural motifs of water on metal oxide surfaces

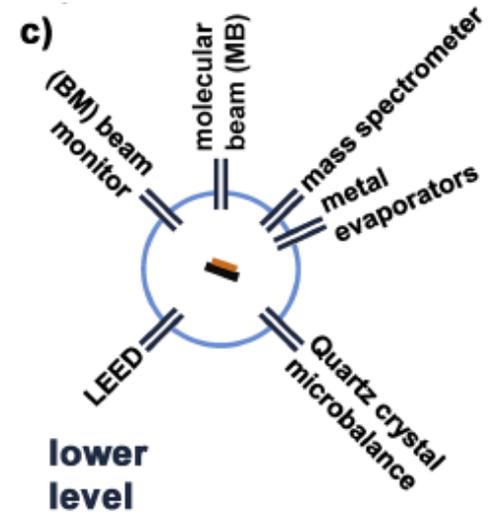
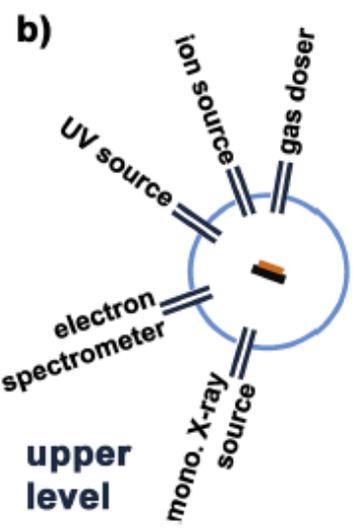
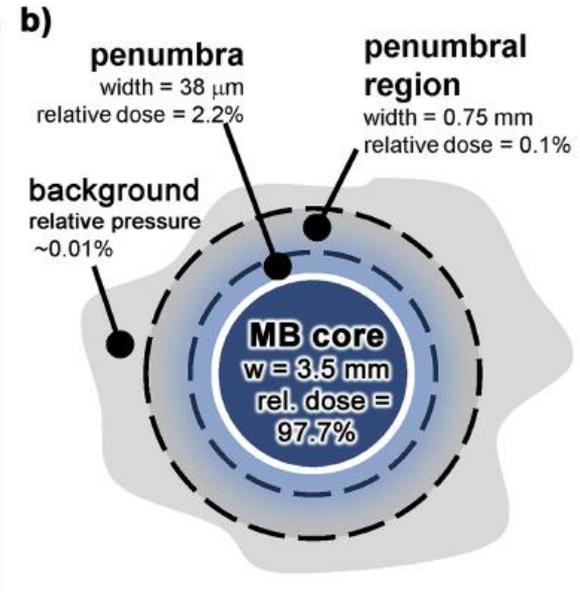
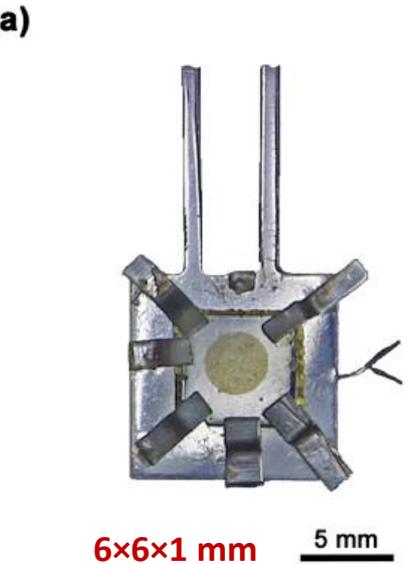
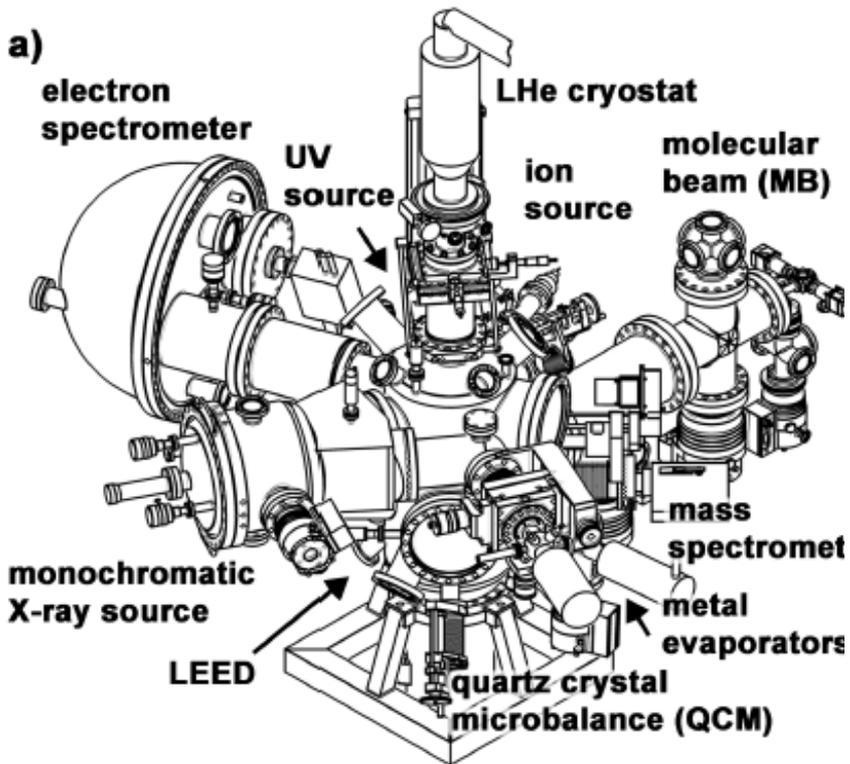
Rentao Mu,^a Zhi-jian Zhao,^a Zdenek Dohnálek^b and Jinlong Gong^{*a}

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In this paper

- Determining the structure of water on metal oxide surfaces is a key step toward a molecular-level understanding of dissolution, corrosion, geochemistry, and catalysis, but hydrogen bonding and large, complex unit cells present a major challenge to it.
- The evolution of water agglomerates on $\text{Fe}_3\text{O}_4(001)$; a complex mineral surface relevant in both modern technology and the natural environment was studied.
- Quantitative temperature programmed desorption (TPD) revealed the coverage of stable structures, monochromatic X-ray photoelectron spectroscopy (XPS) shows the extent of partial dissociation.
- Noncontact atomic force microscopy (AFM) using a CO-functionalized tip and STM provided a direct view of the agglomerate structure.
- An ordered array of partially dissociated water agglomerates was found to form at low coverage, and these serve to anchor a hydrogen-bonded network.

Experimental method



- The sample was prepared by consecutive cycles of 1 keV Ne⁺ sputtering at 300 K. It was followed by annealing to 900 K for 20 min in a partial pressure of 1 × 10⁻⁶ mbar of O₂, which results in the growth of a new Fe₃O₄(001) surface. A sharp (√2×√2)R45° pattern was observed in LEED.
- D₂O was adsorbed directly onto a 3.5 mm diameter spot in the center of the sample surface using an effusive molecular beam source with calibrated flux (9.2 ± 0.5 × 10¹² D₂O molecules/cm²·s)

Deposition using molecular beam (MB)

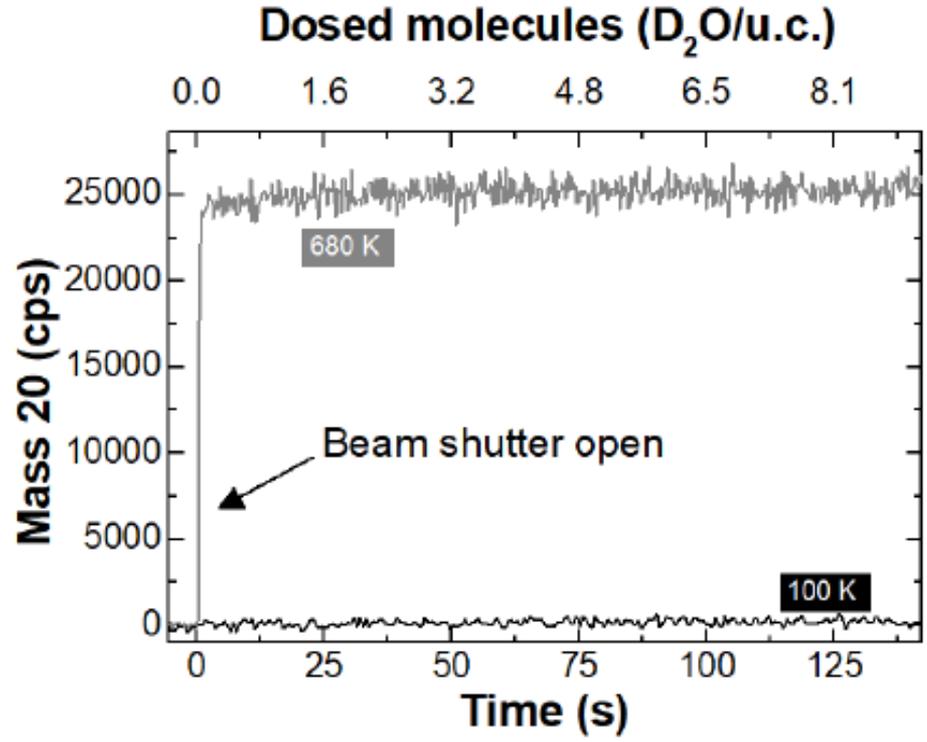


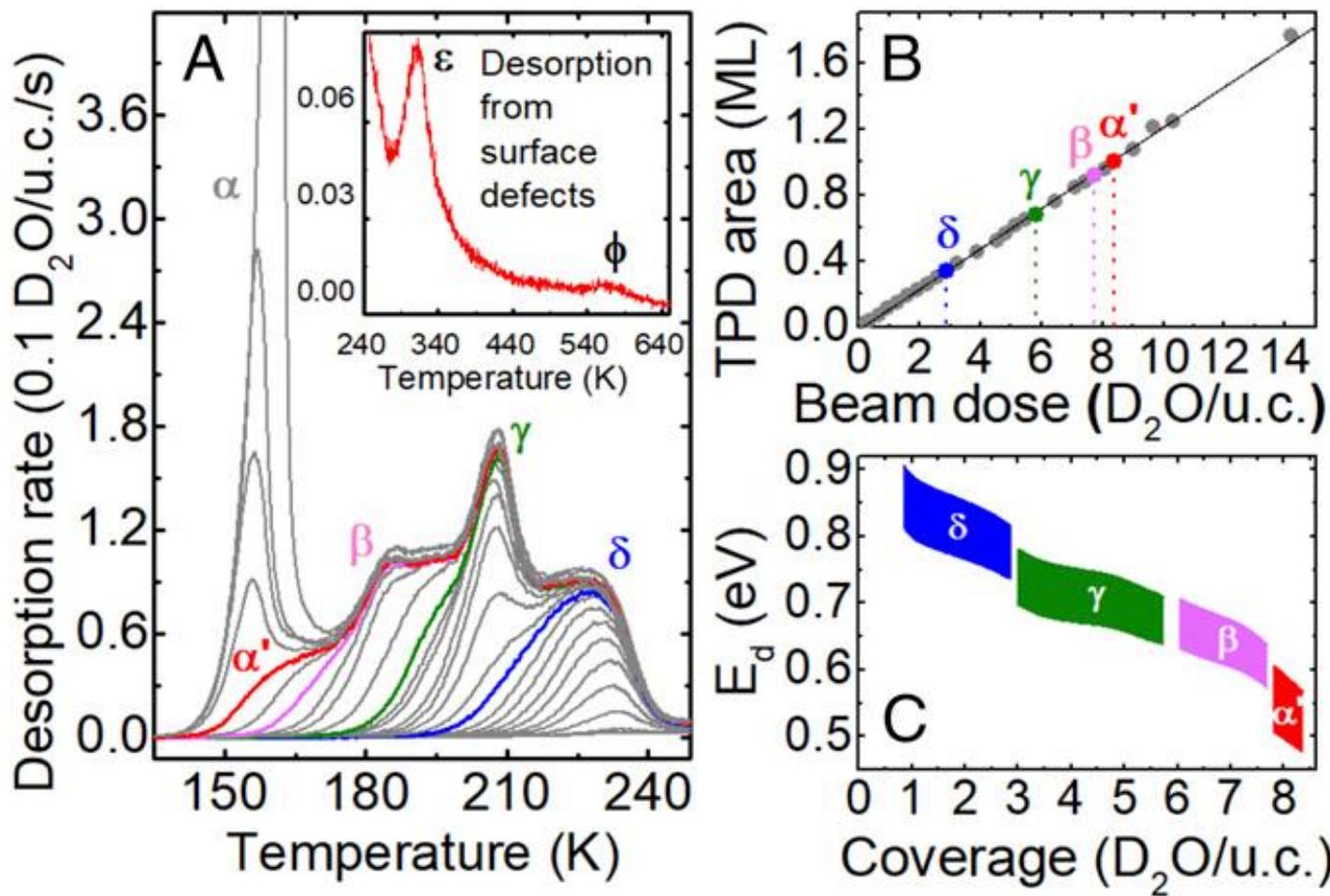
Fig. S1: D₂O signal measured while dosing by molecular beam for a sample temperature of 100 K (black curve) and 680 K (gray curve), molecular beam intensity = 0.065 D₂O/u.c. per second.

$$I(T) \sim -\frac{d\theta}{dt} = \nu(\theta, T) \cdot \theta^n \cdot \exp\left(\frac{-E_{des}(\theta, T)}{k_B T}\right)$$

- ν Frequency factor
- θ Instantaneous coverage
- n Kinetic desorption order ($0 \leq n \leq 2$)
- E_{des} Activation energy to desorption

Polanyi-Wigner Equation

The water coverage is defined in H₂O molecules per (√2×√2)R45° unit cell (H₂O/u.c.), where 1 H₂O/u.c. is a coverage of 1.42 × 10¹⁴ cm⁻².



For TPD, the sample is exposed to water at 100 K, and then heated with a linear ramp of 1 K/s.

Fig. 1. Quantification of water adsorbed on $\text{Fe}_3\text{O}_4(001)$ by TPD. **(A)** Experimental TPD spectra obtained for initial D_2O coverages ranging from 0 to 14 molecules per $\text{Fe}_3\text{O}_4(001)-(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ unit cell (Inset: higher temperature range showing desorption peaks ϵ and ϕ , which originate from surface defects). The colored curves indicate the coverages for which a particular desorption feature (labeled α' , β , γ , and δ) saturates, α marks the multilayer desorption peak. **(B)** Plot of the integrated TPD peak areas as a function of beam exposure. The colored data points correspond to the colored curves in A. Based on these data, we conclude the β , γ , and δ peaks saturate at coverages of eight, six, and three molecules per $(\sqrt{2} \times \sqrt{2})\text{R}45^\circ$ unit cell, respectively. **(C)** Inversion analysis of the TPD data for D_2O on $\text{Fe}_3\text{O}_4(001)$ for the different peaks. The filled area marks the uncertainty range of the coverage-dependent desorption energies for each peak.

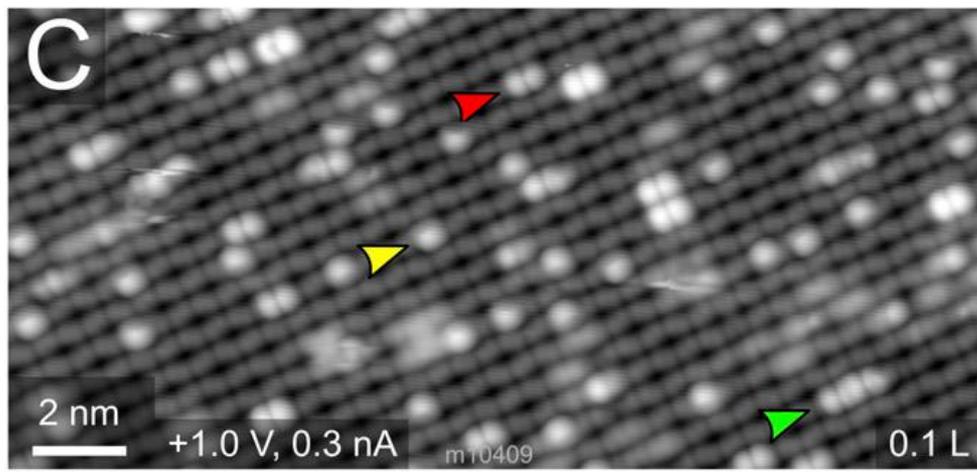
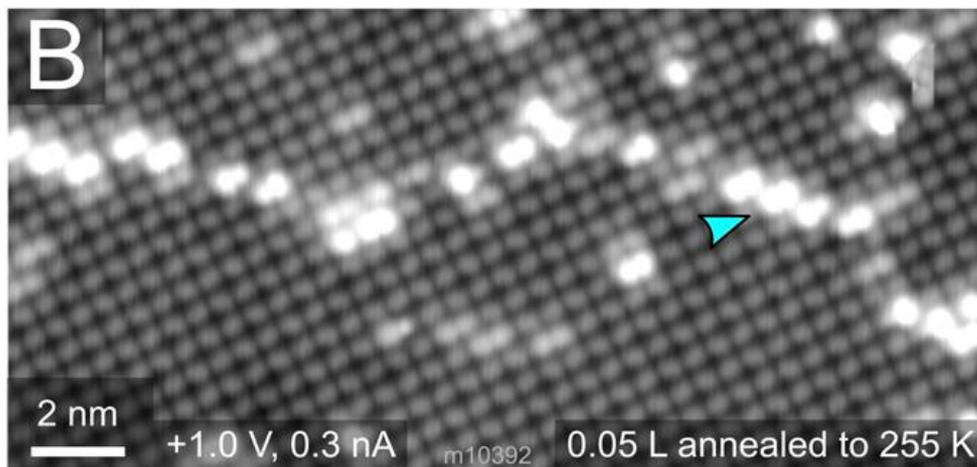
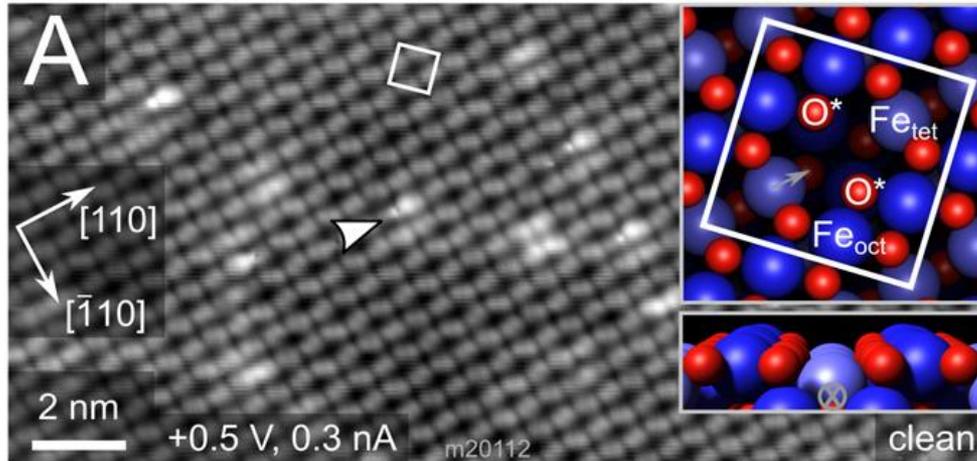


Fig. 2. Water monomers, dimers, and multiple neighboring protrusions on the Fe₃O₄(001) surface imaged by low-temperature (78 K) STM. **(A)** The as-prepared Fe₃O₄(001) surface. The ($\sqrt{2}\times\sqrt{2}$)R45° periodicity is indicated by the white square, and the white arrow highlights an O*H group. (Inset) Top and side views of the Fe₃O₄(001)–($\sqrt{2}\times\sqrt{2}$)R45° surface structure with the SCV structure (the top view is aligned with the STM image, and the gray vector indicates the viewing direction to locate the side view). Only the Fe_{oct} atoms are imaged in STM. **(B)** STM image acquired after 0.05 L of water was adsorbed and heated to 255 K. The surface is clean, except for protrusions located at surface defects including antiphase domain boundaries in the ($\sqrt{2}\times\sqrt{2}$)R45° reconstruction (cyan arrow). **(C)** STM image following adsorption of 0.1 L of water at 120 K. Isolated single protrusions (yellow arrow), double protrusions (red arrow), and multiple neighboring protrusions (green arrow) are due to water molecules adsorbed on the Fe_{oct} rows.

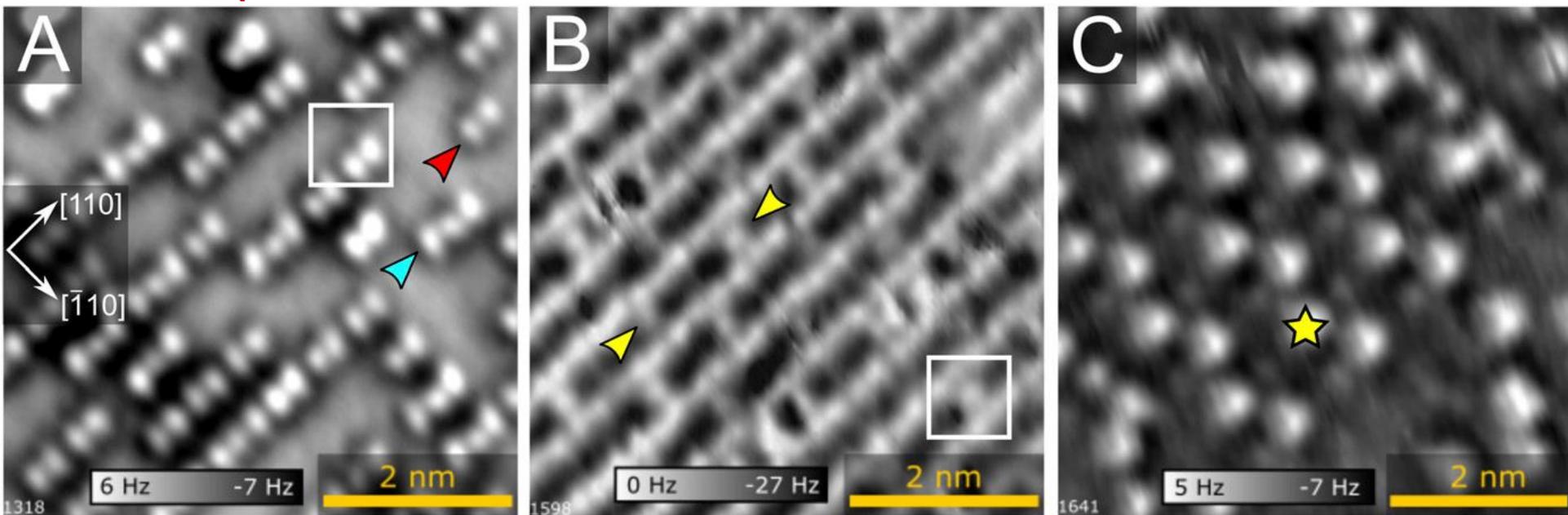
δ peak **γ peak** **β peak**

Fig. 3. Imaging water agglomerates on $\text{Fe}_3\text{O}_4(001)$ with nc-AFM using a CO-functionalized tip. nc-AFM images obtained after exposing the as-prepared $\text{Fe}_3\text{O}_4(001)$ surface to **(A)** $2.5 \pm 0.5 \text{ H}_2\text{O/u.c.}$, **(B)** $\sim 6 \text{ H}_2\text{O/u.c.}$, and **(C)** $\sim 8 \text{ H}_2\text{O/u.c.}$ The Q+ oscillation amplitudes were **(A)** 45 pm, **(B)** 110 pm, and **(C)** 65 pm, and the bias was set to 0 V in all images. In each case, water was dosed at 105 K, and the sample preheated to $\sim 155 \text{ K}$ before imaging at 78 K. The coverages in A–C correspond roughly to the partial populations of the δ , γ , and β peaks in TPD, respectively. Partially dissociated water dimers and trimers on the Fe_{oct} rows are indicated by red and cyan arrows in A, respectively, and yellow arrows highlight protrusions bridging the Fe_{oct} rows in B. Additional water deposited on the surface appears as bright protrusions (yellow star), suggesting it protrudes significantly above the surface and the previously adsorbed molecules (C). The $(\sqrt{2} \times \sqrt{2})R45^\circ$ surface unit cell is shown by a white square.

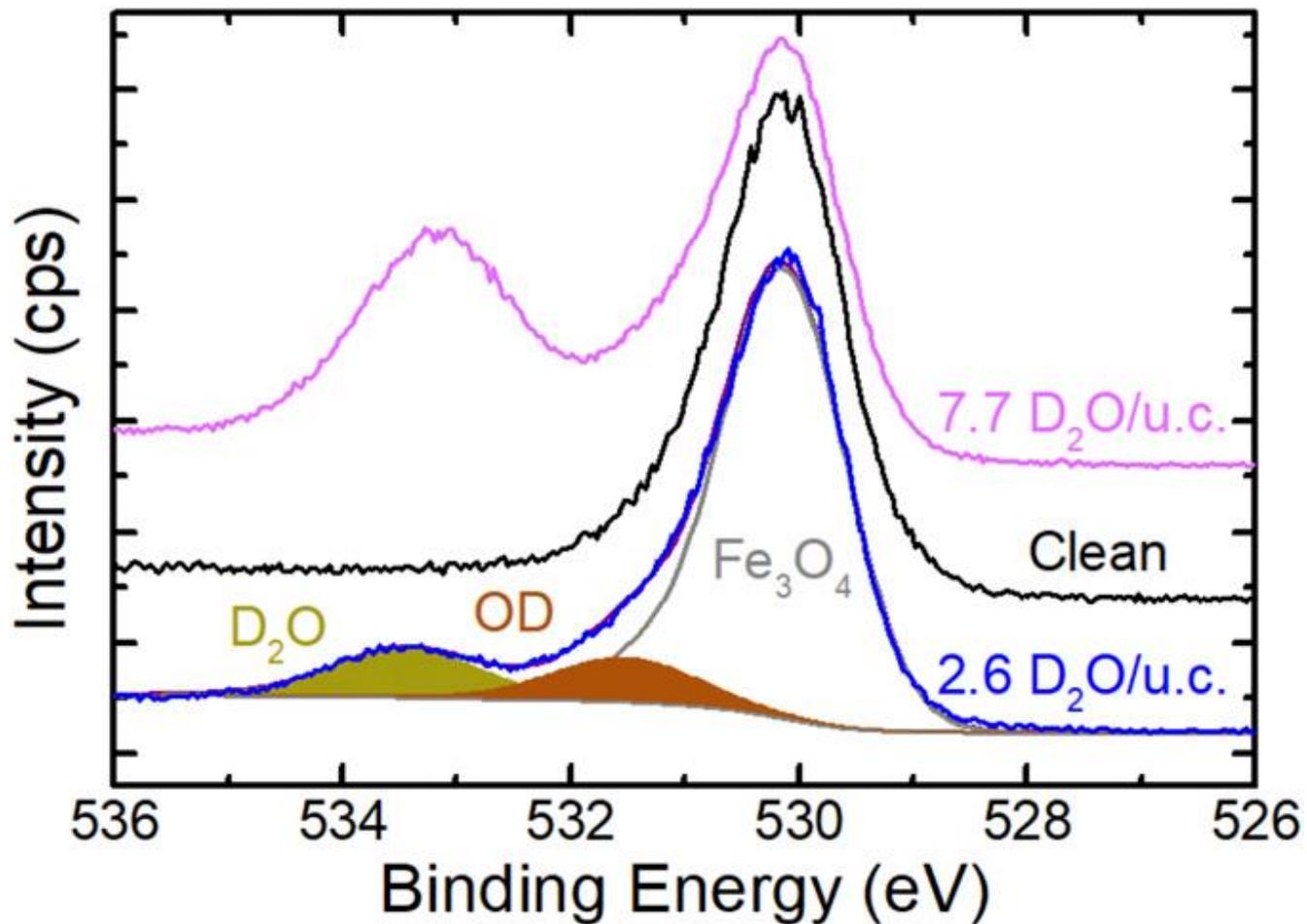


Fig. 4. O 1s XPS data showing that the water agglomerates formed on Fe₃O₄(001) are partially dissociated. The as-prepared surface exhibits a single peak at 530.1 eV due to the lattice oxygen atoms. The 2.6 D₂O/u.c. data should be compared with the surface shown in Fig. 3A and show roughly equal contributions from OD and D₂O, consistent with one dissociated molecule per water dimer/trimer. Most of the additional water adsorbed at a coverage of 7.7 H₂O/u.c. is molecular. Data were measured at 95 K, with monochromatic Al K α radiation and at a grazing exit of 80° for the emitted photoelectrons.

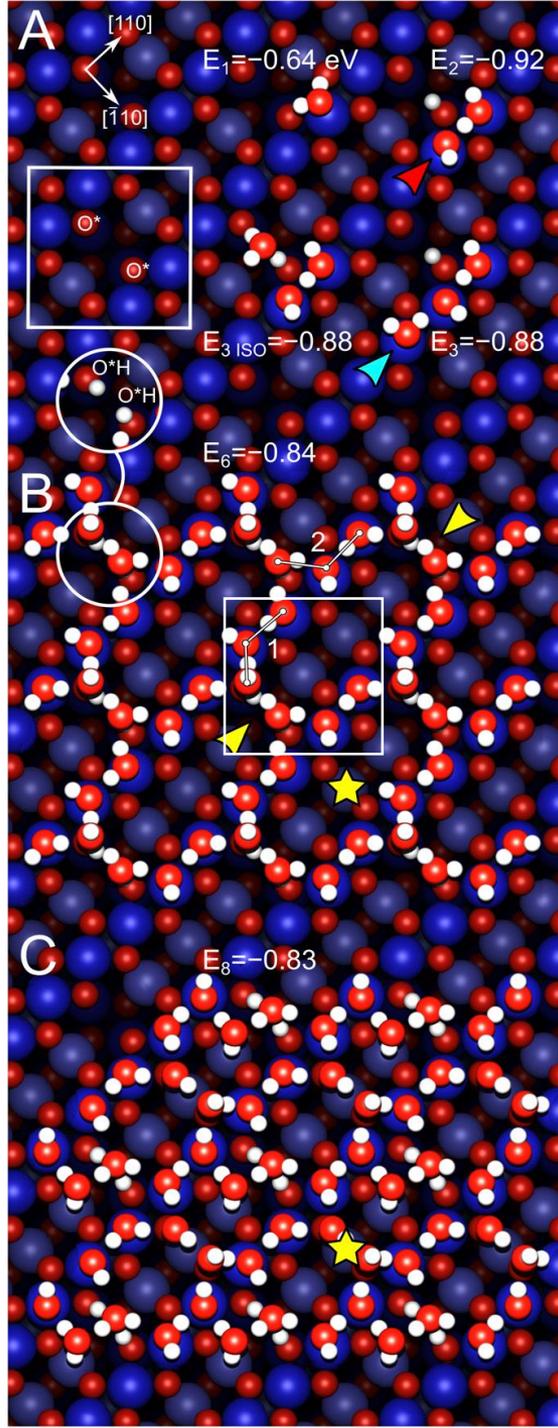


Fig. 5. Top view of the minimum-energy structures determined by DFT for water coverages of 1, 2, 3, 6, and 8 H₂O/u.c. Fe atoms are blue, O are red, and H are white. **(A)** An isolated molecule adsorbs intact, but partially dissociated water dimers and trimers are energetically preferred. Two partially dissociated trimer structures are calculated to be energetically degenerate. The ($\sqrt{2} \times \sqrt{2}$)R45° unit cell and both O* are highlighted. DFT-based model at 6 H₂O/u.c. showing a **(B)** ring-like structure based on full occupation of the Fe_{oct} rows with OH or H₂O, and water molecules bridging the O* sites. These bridging molecules are adsorbed partly through H bonds to surface O*H groups. The O*H groups beneath the adsorbed molecules are shown in the topmost white circle. Alternatively, the structure can be viewed as based on a pair of H₂O–OH–H₂O trimers (labeled 1 and 2). **(C)** DFT-based model at 8 H₂O/u.c. showing a complex structure utilizing dangling bonds in the 6 H₂O/u.c. structure to form a second bridge in the region of the yellow star. All adsorption energies are given in electronvolts.

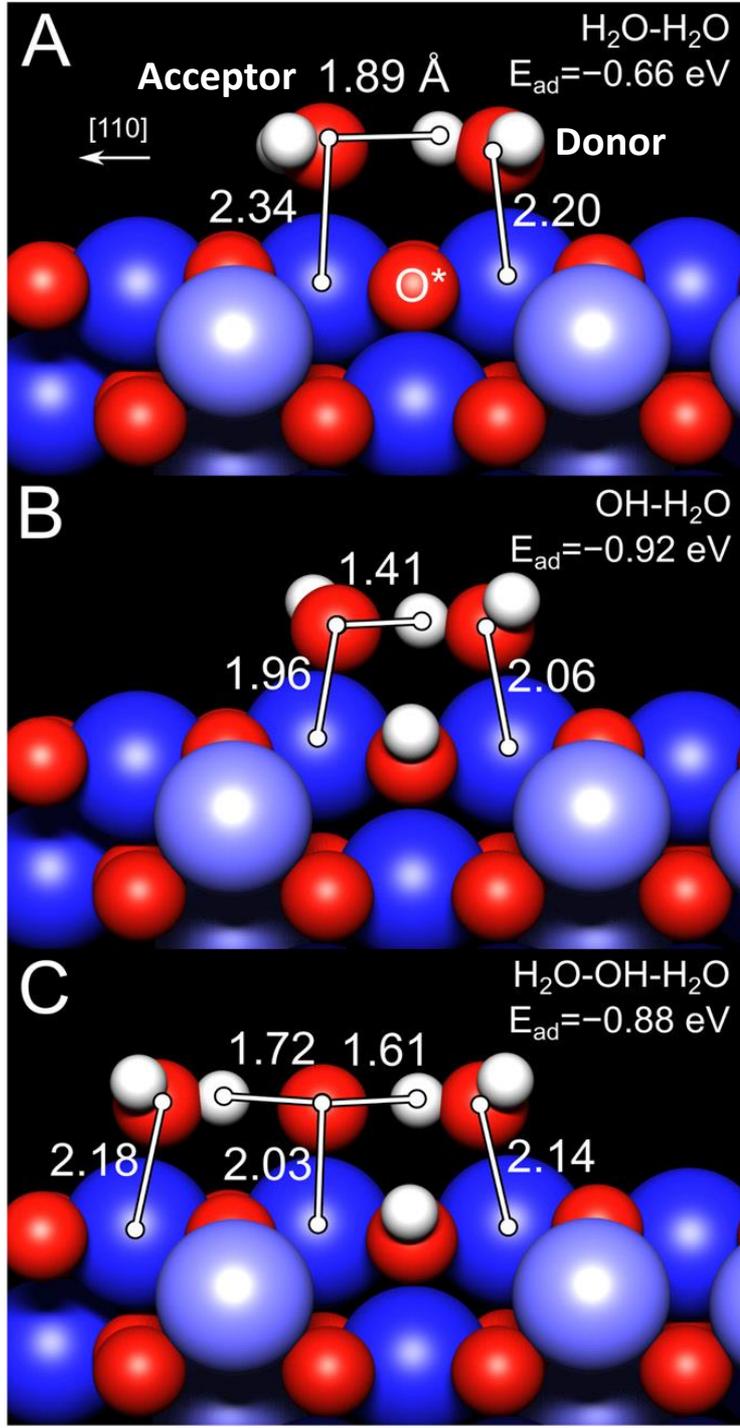


Fig. 6. The geometry of partially dissociated water dimers and trimers reveals a cooperative binding effect. **(A)** A molecular water dimer exhibits a relatively long intermolecular H bond, and the H-bond acceptor has a weakened interaction with the surface compared with an isolated molecule. **(B)** The partially dissociated water dimer exhibits a strong intermolecular H bond, and the H-bond-donating water molecule binds more strongly to the substrate. **(C)** In the partially dissociated water trimer, the second water molecule donates an H bond to the OH group, further weakening its bond to the substrate. All bond lengths are given in angstroms, and energies are in electronvolts.

Conclusion

- In conclusion, partially dissociated water dimers are the most stable species on the $\text{Fe}_3\text{O}_4(001)$ surface, closely followed by structurally related, partially dissociated water trimers.
- The nc-AFM images clearly show the adsorbed dimers and trimers, and XPS spectra reveal them to be partially dissociated.
- Moreover, the theoretically determined adsorption energies agree remarkably well with the E_d values obtained from an inversion analysis of the δ -peak, and the highly constrained adsorption geometry predicted by DFT is consistent with the high preexponential factor.
- Clearly, the $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstruction plays a crucial role in the adsorption behavior. At low coverages, the partially dissociated water dimers and trimers order with $(\sqrt{2}\times\sqrt{2})R45^\circ$ symmetry, while at high coverages the structure of the H-bonded network also belies the periodicity of the underlying substrate.

Thank
you!