Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary material for the manuscript:

Water adsorption and O-defect formation on Fe_2O_3 (0001) surfaces

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Content:

1. FIG. S1: Stability diagrams within PBE+U, PW91, HSE and HSE(12%) approaches.
2. FIG. S2: Top and side views of the adsorption structure of molecular water on the pristine hematite (0001) surface obtained with different force thresholds at the ionic relaxation step.
3. FIG. S3: Calculated constant-current STM images of the pristine α-Fe_2O_3(0001).

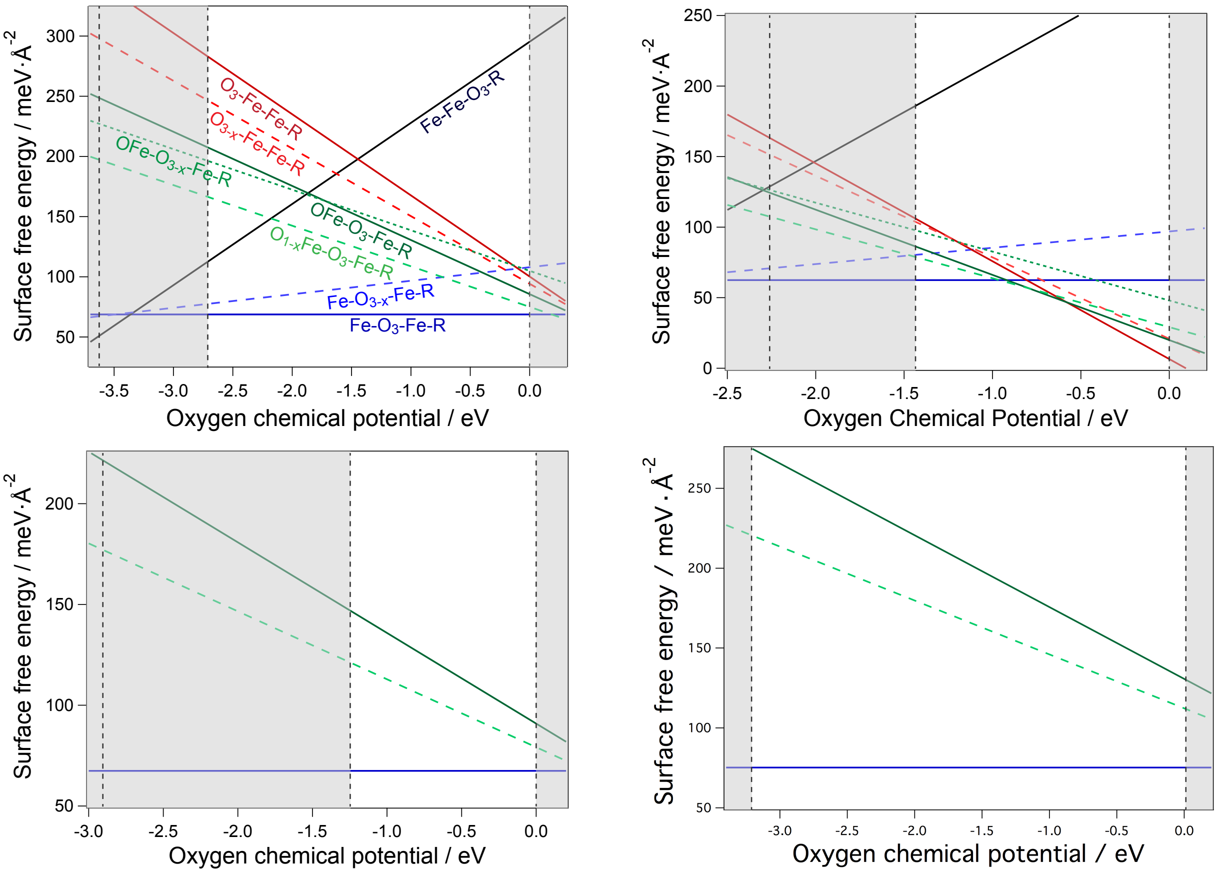

FIG. S1: Stability diagrams within the different levels of approximation: PBE+U (top-left), PW91 (top-right), HSE(bottom-right) and HSE(12%) (bottom-left). Bright area marks oxygen chemical potential region where terminations are in thermodynamic equilibrium with the bulk hematite phase. On the left of bright region, terminations are in equilibrium with bulk magnetite and then with bulk iron, respectively. Note, for HSE functional only transition between hematite and metallic iron phases is shown. On the right of bright region, oxygen molecules start to condensate on the surface. The colour code is identical at all plots.

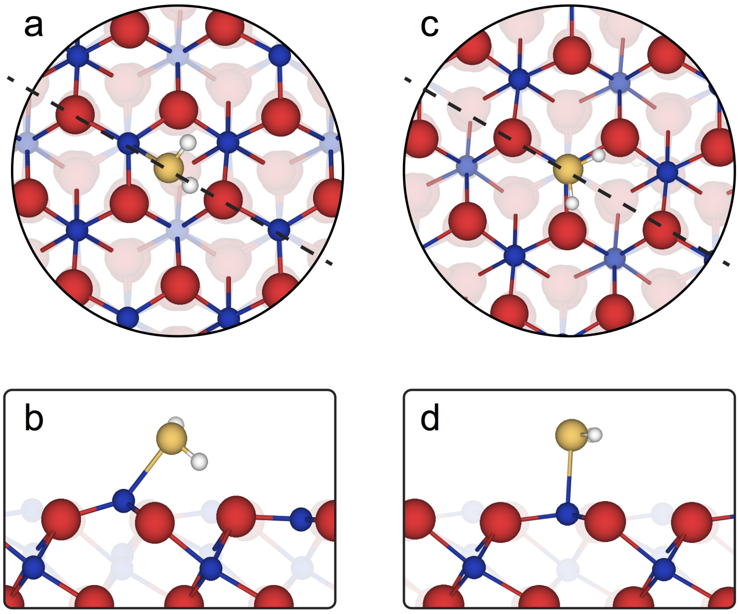

FIG. S2: Top (a,c) and side (b,d) views of the molecular adsorption structure on the pristine Fe$-$O$_3$$-Fe-$R termination with two different force thresholds for ionic relaxation: 0.01 eV/Å (left) and 0.03 eV/Å (right). The cuts in case of side views are made perpendicular to the surface through the dashed line as shown in (a,c), respectively. The strong dependence of water shifting and tilting on force threshold is clearly seen without any significant changes in bond length between surface iron and water oxygen (2.16 and 2.15 Å for the left and right figures, respectively). However, being closely to the surface water molecule on the left-side structures forms hydrogen bond with the surface oxygen ion, it is directed to. The presented structures have been obtained with the PBE+U functional but such behaviour does not depend on the used functional (we observed this with PW91/PBE+U and PW91/PBE+U+D2).

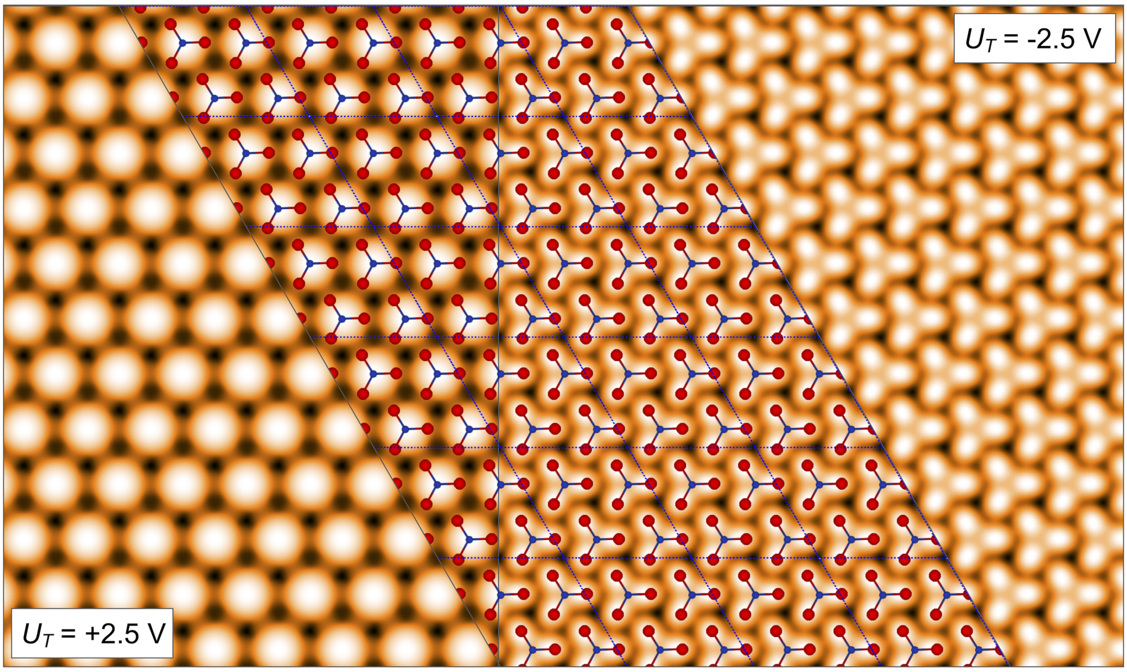

FIG. S3: Calculated constant-current STM images of the pristine α-Fe_2O_3(0001) obtained at $+2.5\,V$ (left) and $-2.5\,V$ (right) of the bias voltage. The central area is superimposed with the lattice structure of the upper surface layer. The STM images are calculated using the Tersoff-Hamann formalism [J. Tersoff, and D. Hamann, *Phys. Rev. B*, 1985, **31**, 805–813]. In these simulations the constant current condition was fulfilled that leads to the decreasing of the distance between the sample and a tip from 2.93 Å for $U_T = +2.5\,V$ to 1.91 Å for $UT = -2.5\,V$. The corresponding constant density is $3.86\,e{\cdot}\text{Å}^{-3}$.