

Cooperative Formation of Long-Range Ordering in Water Ad-layers on Fe₃O₄(111) Surfaces

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Abstract: The initial stages of water adsorption on magnetite Fe₃O₄(111) surface and the atomic structure of the water/oxide interface remain controversial. Herein, we provide experimental results obtained by infrared reflection-absorption spectroscopy (IRAS) and temperature-programmed desorption (TPD), corroborated by density functional theory (DFT) calculations showing that water readily dissociates on Fe_{tet} sites to form two hydroxo species. These act as an anchor for water molecules to form a dimer complex which self-assembles into an ordered (2×2) structure. Water ad-layer ordering is rationalized in terms of a cooperative effect induced by a hydrogen-bonding network.

Water interaction with oxide surfaces plays an important role in geology, electrochemistry, corrosion, water splitting, and catalysis.^[1] Iron oxides, in particular magnetite (Fe₃O₄), are some of the most studied oxides using a “surface science” approach.^[2] Herein we provide the first compelling experimental and theoretical evidence that on the Fe₃O₄(111) surface water adsorption leads to cooperative adsorption of dissociated and molecular water species, which induces the formation of an ordered water monolayer, monitored via structural and spectroscopic studies in combination with density functional theory (DFT) calculations.

While recent experimental and theoretical work on the structure of Fe₃O₄(001) single crystal surfaces suggest that it is well-understood,^[2b] the (111) surface remains controversial. On the basis of structural studies also corroborated by DFT calculations, a single metal (namely, Fe_{tet}) termination is considered as the most stable,^[3] whereas a double metal (Fe_{oct2}-Fe_{tet1}; “tet1” and “oct2” being commonly used nomenclature for this particular oxide structure) termination was favored on the basis of CO and water adsorption studies using

infrared reflection absorption spectroscopy (IRAS).^[4] Our recent study^[5] seems to have eliminated such a discrepancy by employing DFT calculations for CO adsorption. The combined experimental and theoretical results could only be rationalized in terms of the Fe_{tet1}-terminated Fe₃O₄(111) surface, although octahedrally coordinated iron ions as a minority species may be present at surface defects. Note that, in contrast to CO that adsorbs intact under ultrahigh vacuum (UHV)-based conditions and has, therefore, been used as a probe molecule for surface termination, water readily dissociates on the Fe₃O₄(111) surface,^[2a,6] thus rendering determination of the surface termination by water adsorption difficult. Indeed, it was generally accepted that a water molecule dissociates on Fe_{tet1}-terminated Fe₃O₄(111) ultimately forming two surface hydroxo species, that is, Fe-O_wH and O_sH (where O_w and O_s indicate oxygen atoms in water and on the oxide surface, respectively).^[6,7] However, this scenario was questioned by results presented in Ref. [4b] suggesting spontaneous formation of a complex composed of dissociated and non-dissociated water molecules (a so-called “half-dissociated” water dimer) based on the assumption, however, that the surface is Fe_{oct2}-terminated.

To provide a unified picture for the structure and adsorption properties of the Fe₃O₄(111) surface, herein we re-examined water adsorption models. Using well-characterized Fe₃O₄(111) thin film surfaces and taking careful precautions with respect to the film preparation and surface termination, we show that all experimental results agree well with the “classical” dissociation mechanism resulting in a terminal (Fe-O_wD) hydroxy and surface hydroxy (O_sD) species at the initial stage. Analysis of the previous studies on Fe₃O₄(111), both for single crystals and thin films, suggests that a certain controversy that exists in the literature may have resulted from the experimental difficulties of preparing well-defined, clean and uniform surfaces. In particular, single-crystal studies may suffer from having several surface structures coexisting. Although thin films grown on a metal substrate appear to be uniform, defect structures are still difficult to control and characterize. In addition, surface preparation and even vacuum conditions may play an important role as a result of adventitious adsorption of residual gases in the background. Finally, from a theoretical point of view, adsorption on the iron oxide systems needs careful consideration as far as electronic and magnetic properties are concerned (see Ref. [4c] and references therein).

In this work, we used well-ordered Fe₃O₄(111) thin films grown on Pt(111) (see Experimental Section in the Supporting Information). Prior to water adsorption, the films were

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characterized by CO adsorption in the same manner as described in Ref. [5] to ensure that the Fe_{tet} -termination dominates the surface. We first address temperature-programmed desorption (TPD) results. Figure 1a shows a series of TPD spectra as a function of water coverage obtained after D_2O dosing at 140 K and heating to 700 K in each run. Beyond the desorption peak at approximately 160 K assigned to the onset of the amorphous solid water (ASW) film formation, several desorption peaks are clearly resolved at 201, 223, and 255 K which are sequentially populated at increasing exposure. The peak positions are independent of water coverage, indicating a first order desorption kinetics. In contrast, a broad signal above 270 K shows typical behavior for second order kinetics expected for recombinative desorption of dissociated water.^[6c] Finally, a small signal at around 375 K, can safely be assigned to water adsorption on defect sites.

The desorption spectra can be transformed into coverage-dependent desorption energy plots using inversion analysis of the Polanyi–Wigner equation.^[8] For first order desorption kinetics this procedure yields the desorption energies (E) as a function of water coverage (θ) [Eq. (1)]

$$E(\theta) = -RT \ln \left(-\frac{d\theta/dT}{\beta \cdot \nu \cdot \theta} \right) \quad (1)$$

where β is a heating rate, and ν is a pre-factor. Figure 1b shows the results for $\nu = 10^{13} \text{ s}^{-1}$ commonly used. Although the absolute values depend on the pre-factor (increasing the pre-factor to 10^{15} s^{-1} leads to a shift of all energies towards higher (i.e. more exothermic) values by about 15 kJ mol^{-1}),

the results clearly show that the desorption energy considerably decreases with increasing coverage, most markedly in the low coverage regime ($\theta/\theta_{\text{max}} < 0.15$), in nice agreement with microcalorimetry results.^[4b]

To quantify water coverage, we made use of TPD spectra on the clean Pt(111) surface showing a characteristic desorption feature upon formation a well-ordered ice film.^[9] Since the measurements were performed with the same setup and on the same Pt crystal as used for the iron oxide film, all apparatus effects are self-cancelled. The results showed that the total amount of water adsorbed on $\text{Fe}_3\text{O}_4(111)$ before the ASW film starts to grow, corresponds to $2.3 \pm 0.2 \text{ ML}$ (ML = monolayer; 1 ML is defined as $3.2 \times 10^{14} \text{ cm}^{-2}$, that is, one water molecule per $\text{Fe}_3\text{O}_4(111)$ unit cell). This value agrees fairly well with the model of a half-dissociated water dimer (i.e. two H_2O per unit cell) forming at increasing water coverage, previously put forward by Joseph et al.^[6a] However, their TPD spectra (see also Refs. [6c, 7b]) showed, in essence, featureless desorption traces in the 200–300 K region. Such a picture is often attributed to surface heterogeneity and/or reorganization of ad-species during the TPD run, thus broadening and smearing desorption features. In contrast, the presence of well-resolved peaks in our spectra favor the model where each desorption peak showing first order kinetics is associated with individual desorption of water molecules having discrete binding energies. In principle, this could be the case when several adsorption sites coexist on the surface, from which water desorbs independently. Such an explanation was essentially provided in Refs. [7c, 10] reporting TPD peaks of water on the $\text{Fe}_3\text{O}_4(111)$ selvedge surface of a hematite $\text{Fe}_2\text{O}_3(0001)$ natural crystal, since different surface

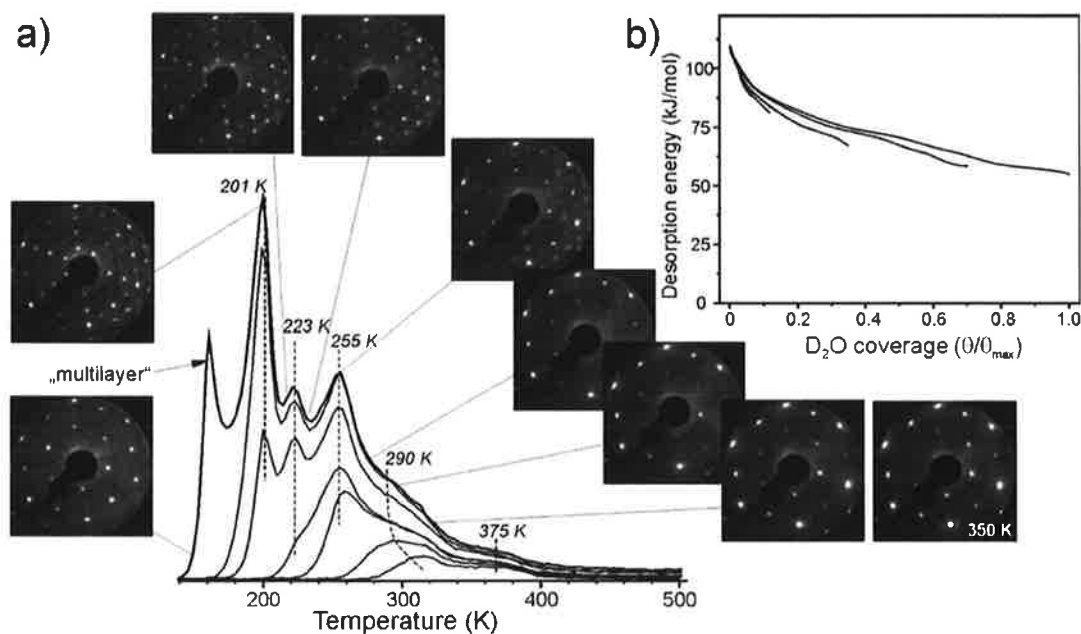


Figure 1. a) TPD spectra of D_2O adsorbed at 140 K at increasing exposures. The spectra are cut at 500 K, for clarity. At the highest exposure, the formation of “multilayer” (ASW) film sets in. The heating rate is 3 K s^{-1} . Snapshots from the LEED ($E = 64 \text{ eV}$) movie recorded while heating the sample covered by the ASW film at 140 K synchronized with a TPD spectrum. b) Desorption energy as a function of water coverage, normalized to the total coverage (θ_{max}) measured before ASW formation, obtained by inversion analysis of the Polanyi–Wigner equation applied to each spectrum shown in (a), see text.

phases are inevitably formed during surface preparation. This is clearly not the case for our films exposing a single termination.

Under the assumption that the TPD signal at high temperatures above 270 K is associated with dissociated water, the observation of three distinct desorption peaks at 200–255 K is difficult to rationalize within a simple dimer model having only one non-dissociated water molecule per unit cell. Therefore, this finding suggests the formation of water oligomers larger than a dimer (e.g. trimer and tetramer). Alternatively, three-dimensional water clusters are formed, from which water molecules desorb in a one-by-one manner. Sharp desorption signals imply species desorbing almost simultaneously, suggesting, in turn, a certain degree of ordering at the surface.

To examine whether water forms ordered structures on $\text{Fe}_3\text{O}_4(111)$ we employed low energy electron diffraction (LEED). Certainly, careful precautions had to be taken to minimize electron beam damaging effects. Figure 1a displays snapshots from the LEED movie recorded upon heating of the ASW film (formed by 1.5 L; $1 \text{ L} = 10^{-6} \text{ Torr} \times \text{s}$) of D_2O at 140 K) to synchronize with the thermal desorption. Additional spots clearly identified as of $\text{Fe}_3\text{O}_4(111)-(2 \times 2)$ appear upon desorption of the ASW film and attenuates above about 260 K. The formation of the (2×2) structure depends on the water coverage and not on the adsorption temperature (140 K vs. 250 K).

This finding indicates that ordering is thermodynamically driven and not kinetically limited. Note also, that the (2×2) spots appear in LEED immediately upon electron beam exposure and showed no intensity attenuation in time, at least, on the scale of a minute. Rapidly changing the spot position for sampling also showed no effect on the LEED spots intensity. Therefore, we can safely rule out beam effects on water ordering.

There are only a few examples in the literature of water/oxide interfaces which exhibited an ordered water ad-layer.^[11] Water adsorption on the $\text{MgO}(001)$ surface is likely the most intensively studied system (Ref. [12] and references therein) that showed $c(4 \times 2)$ and $p(3 \times 2)$ structures in LEED.^[13] Using a genetic algorithm, DFT calculations predicted two stable structures. At low temperature, a $c(4 \times 2)$ structure is stable that contains ten water molecules in the cell thus leading to a nominal coverage 1.25 H_2O per $\text{MgO}(001)$ unit cell. A $p(3 \times 2)$ structure containing six water molecules per cell (1 H_2O per surface cell) is more stable at high temperature. Both structures feature surface hydroxy groups resulting from the dissociation of water molecules. However, the way these structures form on $\text{MgO}(001)$ remains poorly understood. In the case of adsorption on $\text{ZnO}(10\bar{1}0)$,^[11a] the dissociation only occurs when two molecules occupy adjacent adsorption sites thus resulting in a half-dissociated dimer forming a (2×1) superstructure.

To shed light on the atomic structure of the water ad-layer on $\text{Fe}_3\text{O}_4(111)$, we performed IRAS measurements. Full

analysis will be presented elsewhere;^[14] here we only highlight key observations. Figure 2a shows a series of spectra obtained at the saturating exposure at the sample temperature as indicated. A sharp OD band at 2680 cm^{-1} appears at 350 K and almost doubles intensity upon water dosing at 320 and

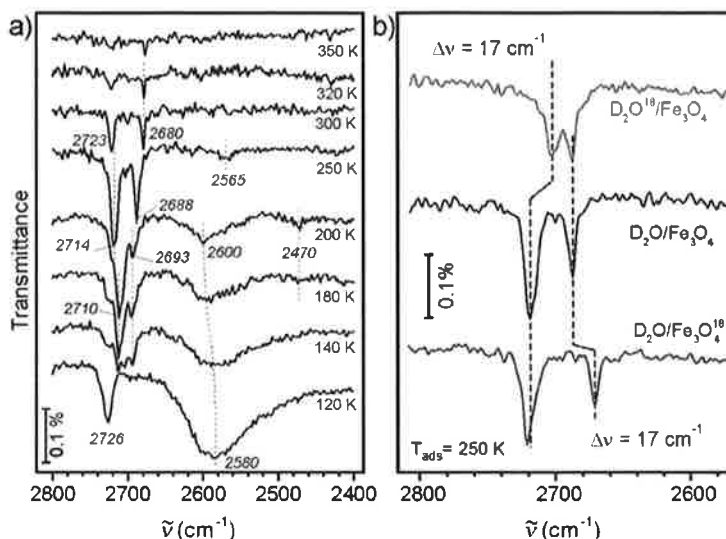


Figure 2. a) IR spectra obtained at the saturating exposure at the sample temperature as indicated (see text). b) IR spectra obtained at 250 K for ^{18}O -labelled water (top) and oxide film (bottom) for comparison with results on $\text{D}_2\text{O}/\text{Fe}_3\text{O}_4(111)$ (middle) shown in panel (a).

300 K. At increasing coverage achieved by water exposure at 250 K, the band at 2723 cm^{-1} signal gains considerable intensity, and the peak shifts to 2714 cm^{-1} . Concomitantly, a new band at 2688 cm^{-1} grows, whereas the band at 2680 cm^{-1} disappears. In addition, a weak band shows up at 2565 cm^{-1} which falls in the range of hydrogen-bonded OD vibrations. At 200 K, two bands, at 2710 and 2693 cm^{-1} , start to dominate the spectrum in this region, while very broad signals develop in the $2650\text{--}2450 \text{ cm}^{-1}$ region indicating the formation of a hydrogen-bonding network, culminating in the formation of the ASW film at 120 K. The ASW film shows a well-established band at 2726 cm^{-1} assigned to a “dangling” OD vibration at the water surface and a broad band centered at 2580 cm^{-1} of hydrogen-bonded OD species in the bulk.

The band around 2720 cm^{-1} falls in the range calculated by DFT^[4b,c] for stretching vibrations of terminal O_wD hydroxy formed by dissociation of a single water molecule on both surface terminations, that is, 2754 cm^{-1} on $\text{Fe}_{\text{oc}12^-}$ and 2729 cm^{-1} on $\text{Fe}_{\text{te}1^-}$ -terminated surfaces, when scaled using observed fundamentals of the water molecule (see Ref. [4b]). However, computed frequencies for surface hydroxy groups (O_wD) considerably differ and are expected to show up at approximately 2440 cm^{-1} and 2705 cm^{-1} , for the $\text{Fe}_{\text{oc}2^-}$ and $\text{Fe}_{\text{te}1^-}$ termination, respectively. To further identify the nature of the observed sharp bands in the $2720\text{--}2680 \text{ cm}^{-1}$ region with the help of isotopic labelling, we performed adsorption experiments with D_2^{18}O water on the same film. In addition, “normal” D_2O water was exposed to the oxide film prepared

with ^{18}O . The results of adsorption at 250 K are summarized in Figure 3b for direct comparison with $\text{D}_2\text{O}/\text{Fe}_3\text{O}_4(111)$. Clearly, only the band at 2714 cm^{-1} red-shifts upon D_2^{18}O adsorption, whereas the 2688 cm^{-1} band only shifts upon ^{18}O labeling in the oxide, both shifts being about 17 cm^{-1} .

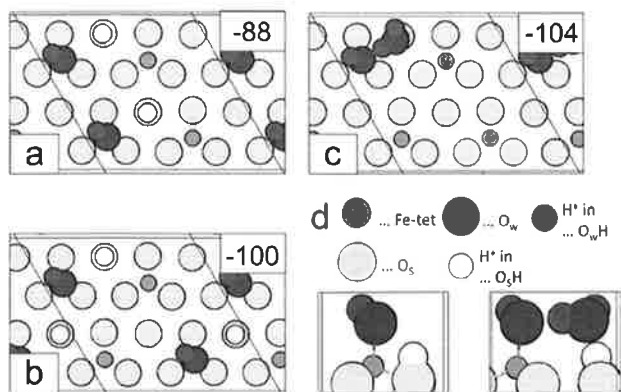


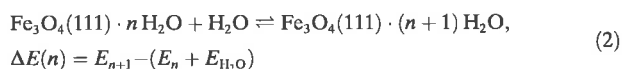
Figure 3. a)–c) Top views of several computed structures containing two water molecules in the (2×2) cell. The calculated ΔE energies in kJ mol^{-1} are shown in the top right corner. Side views of a “monomer” and a “dimer” are shown in (d).

Therefore, the high frequency bands above 2710 cm^{-1} must be associated with terminal $\text{Fe-O}_w\text{D}$, and the bands below 2695 cm^{-1} with the surface hydroxy groups O_sD , in agreement with the “classical” adsorption model involving dissociation of a single water molecule on a cation–anion pair resulting in two hydroxy groups as observed. However, these results are at variance with those reported in Ref. [4b] showing that the bands (at 2720 and 2695 cm^{-1} in that case) are originating from water and do not involve surface oxygen. To validate our current bands assignment, we performed additional IRAS experiments in another UHV setup on several identically prepared samples which fully reproduced the isotopic shifts as in Figure 2b. To investigate such a discrepancy, we analyzed experimental details in both studies which revealed a critical role of the surface preparation and vacuum conditions on water adsorption results especially at low coverages (only presented in Ref. [4b]). It is found that UHV annealing at high temperatures (above 750 K) is important for the formation of a uniform Fe_{tet} -terminated surface as highlighted in the LEED I/V study^[3c] and also in our most recent IRAS/DFT study of CO adsorption.^[5] Unfortunately, this condition was not carefully controlled in the previous water adsorption study.^[4b]

The evolution of the spectra shown in Figure 2a is rather complex and suggests a rearrangement of water species upon increasing coverage up to the critical point where long-range ordering takes place as judged by LEED. In principle, two scenarios could be envisioned. In the first one, water molecules dissociate and give rise to hydroxy species which form a (2×2) array as a template which is maintained upon adding further water molecules. It is more plausible, however, that the formation of a (2×2) structure only occurs upon molecular-water adsorption. Indeed, water ordering is not

observed by LEED at 300 K , that is, in relative abundance of dissociated water species. On the other hand, it cannot be ruled out that the high coverage, only reached at low temperatures, is needed for detection by conventional LEED which requires ordered structures in areas larger than $5\text{--}10\text{ nm}$.

The formation of the (2×2) ordered structure was further analyzed on the basis of DFT calculations henceforth using a $\text{Fe}_3\text{O}_4(111)\text{--}(2 \times 2)$ supercell. Equation (2) describes the chemical reaction of sequential water adsorption:



As previously observed for the (1×1) slabs, the first water molecule strongly adsorbs and readily dissociates ($\Delta E = -123\text{ kJ mol}^{-1}$). The second water molecule in the cell (i.e. 0.5 ML coverage) may either dissociate on available empty Fe-O sites or anchor to the preformed hydroxy groups to form a dimer (Figure 3). Although, according to calculated energies, both processes are equally possible (-100 vs. -104 kJ mol^{-1} per water molecule), the energy gain is considerably smaller than for monomer formation on the clean surface (-123 kJ mol^{-1}).

Therefore, at coverages close to 1 ML (i.e. four H_2O molecules in the cell), the oxide surface is predicted to be covered primarily by hydroxy groups, although dimers can also be found. To model structures at higher coverages, we performed calculations by adding water molecules one-by-one to a surface fully covered by monomers ($=1\text{ ML}$). Clearly, the first additional water molecule anchors to one of the monomers to form a dimer (not shown). The optimized structures and reaction energies ΔE for the case of 6, 7, and 8 molecules per (2×2) cell are shown in Figure 4. Note that zero point vibrational energy corrections per H_2O molecule only cause a constant shift upon calculation of reaction energies for each of the (2×2) structures considered (see Table 1 in Supporting Information). Therefore, only PBE + U total energies are used for discussion. For six H_2O molecules per cell (1.5 ML), the structure consisting of a trimer (the “clustered” structure, 6^{cl}) is more stable than of that of a hydrogen-bonded dimer and a monomer (6^{n}). However,

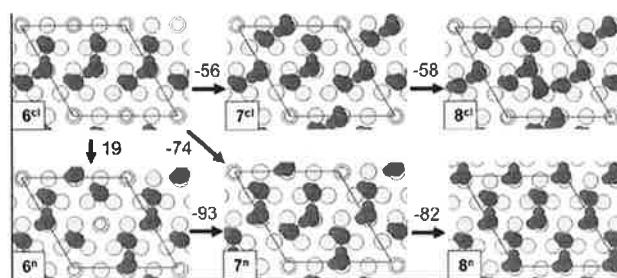


Figure 4. Top and side views of several computed structures containing 6, 7 and 8 water molecules in a $\text{Fe}_3\text{O}_4(111)\text{--}(2 \times 2)$ cell. The top panel depicts the formation of cluster-like water oligomers (6^{cl} , 7^{cl} , 8^{cl}), and the bottom panel shows development of the hydrogen bonding 2D-network (see text). Reaction energies upon adding one H_2O are given in kJ mol^{-1} . Shading as in Figure 3.

adding one H₂O to the structure 6^d yields $\Delta E = -56 \text{ kJ mol}^{-1}$, whereas a more exothermic reaction ($\Delta E = -74 \text{ kJ mol}^{-1}$) is obtained by the formation of the “network” structure 7ⁿ, where dimers start to build a 2D network by maximizing hydrogen bonds. This reaction pathway further dominates for the case of 8 H₂O molecules per cell, basically following the Bernal-Fowler rules.^[15] Thus, the formation of the 2D water network is thermodynamically favored. Moreover, the structure 8ⁿ features a (1 × 1) symmetry that is in good agreement with LEED data (Figure 1) showing a sharp (1 × 1) pattern at 140 K before the (2 × 2) structure develops. Although there is no direct proof (e.g. by scanning tunneling microscopy) for the atomic structure of the unit cell in the network, the proposed scenario is consistent with the experimental findings.

In summary, the presented results of water adsorption on Fe₃O₄(111) at the initial stages, that is, before the formation of amorphous solid water (or “ice”) sets in, show that water readily dissociates on the surface Fe_{tet}-O cation–anion pair to form two hydroxy species. These act as anchors for molecular-water adsorption resulting in dimer complexes which self-assemble into a (2 × 2) ordered structure. The formation of a long-range ordered water ad-layer is thermodynamically driven and includes cooperative formation of a hydrogen bonding network. The results further manifest a delicate balance that exists between water–surface and water–water interaction that determines stability of water species on oxide surfaces as recently demonstrated for the Cu₂O(111) surface solely on theoretical grounds.^[16]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: density functional theory · iron oxides · magnetite · surface structures · water adsorption

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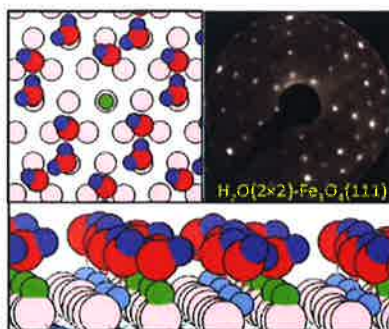
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Cooperative Formation of Long-Range
Ordering in Water Ad-layers on
 $\text{Fe}_3\text{O}_4(111)$ Surfaces



Surface water: Experimental and theoretical results show that water readily dissociates on Fe_{tet} sites of an $\text{Fe}_3\text{O}_4(111)$ surface to form two hydroxo species which act as an anchor for water molecules which self-assemble into an ordered (2×2) structure. Water ad-layer ordering is rationalized in terms of a cooperative effect induced by a hydrogen-bonding network.