Combined surface science and density functional theory approach towards
water ordered structures formation on magnetite

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Three different adsorbed water species were distinguished on Fe-terminated Fe_3O_4 multilayer films using thermal desorption spectroscopy (TDS), and ultraviolet photoelectron spectroscopy (UPS) measured under adsorption-desorption equilibrium conditions [1]. By means of density functional theory (DFT) calculations, the first species (γ-water) were confirmed to correspond to dissociative water adsorption with the resulting hydroxyl (OH) groups of water on the surface iron (Fe) sites, and the hydrogen (H) atoms adsorbed onto surface oxygen (O) sites. The DFT results for the γ-water structure are consistent with the two OH-stretch lines observed by infrared-reflection-absorption-spectroscopy (IRAS) [2], and the UPS study [1]. The DFT calculations confirm the subsequent formation of dimeric water structures (β-water) formed by H-bonded molecular water to the surface OH-groups on surface-Fe, and the H on the surface-O sites, respectively, as suggested by IRAS [2] and low energy electron diffraction (LEED) experiments [1]. The DFT results reveal that formation of the γ-water overlayer structure results from the diffusion of the mobile H-atoms from the initially molecular adsorbed water molecules on iron sites followed by formation of a transition structure with the H-atom adsorbed on nearest-neighboring oxygen sites, diffusing over the surface to adsorb on-top onto the next O-sites. This result is consistent with the proposed second-order kinetics of the recombinative adsorption process [1].

1. Y. Joseph et. al., J. Phys. Chem. B 104, 3224 (2000).
2. U. Leist et al., Phys. Chem. Chem. Phys. 5, 2435 (2003).