Combined Surface Science and Density Functional Theory Approach towards Water Ordered Structures Formation on Magnetite

Maria E. Grillo *1), Wolfgang Ranke 2), Carsten Menke 1)

1) Accelrys, GmbH (Accelrys), Inselkammerstr.1, Unterhaching D-82008, Germany
2) Max-Planck-Gesellschaft, Fritz-Haber-Institut, Faradayweg 4-6, Berlin D-14195, Germany

Corresponding author: e-mail mariag@accelrys.com

Abstract:

The interaction of water with iron oxide surfaces is relevant for several processes of practical interests. Three different adsorbed water species were distinguished on Fe-terminated Fe₃O₄ 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 H-atoms adsorbed onto surface oxygen (O) sites. The DFT result for the γ-water structure is consistent with the two OH-stretch lines observed by infrared-reflection-adsorption-spectroscopy (IRAS) [2], and the UPS study [1]. The DFT calculations confirm the subsequent formation of mixed molecular- and dissociated-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 the IRAS [2] and LEED experiments [2]. 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 on iron sites followed by formation of a transition structure with the H-atom adsorbed the nearest-neighboring oxygen sites, diffusing over the surface to adsorb on-top onto the next O-sites.