H_2O Adsorption on Magnetite $Fe_3O_4(001)$

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Metal oxides are used in a wide range of applications and chemical processes such as the water-gas shift reaction [1]. The interaction of their surfaces with water and the balance between adsorbate/adsorbate and adsorbate/substrate interactions is of interest.

Recent studies of water on these surfaces have found significant complexity, with evidence for mixed-mode adsorption and coverage dependent hydrogen bonding [2]. Only recently, the study of water adsorption on TiO_2(110) and its controversy have been solved, showing the coexistence of molecular and dissociated water [3].

This study focuses on magnetite, one of the most studied iron oxides, and the interaction of its (001) surface with water. Experimental techniques such as temperature programmed desorption (TPD), combined with density functional theory (DFT) calculations, are used to gain insight in the process of adsorption/desorption of water on the previously determined surface [4]. The TPD spectra shows 4 distinct peaks between 150 K and 250 K corresponding to the desorption of the first monolayer of water, consisting in total of 9 molecules, determined using a calibrated molecular beam [5]. The most stable configurations of n molecules ($0 < n < 9$) have been calculated following a systematic approach based on DFT. Inspired by these configurations, the minimal energy path can be deduced and an energy profile composed of the succession of desorbing water molecules can be drawn, which is is agreement with the TPD. A micro-kinetic model is used to obtain the Gibbs free energies and based on transition state theory, an attempt to simulate a TPD spectra is made.

The combination of TPD and DFT allows to get insight in the adsorption/desorption process of water on magnetite, and to understand how exactly it occurs. Water molecules form a complex hydrogen-bond network with molecular and dissociated molecules, where a fraction is adsorbed by hydrogen-bonding only, showing the importance of adsorbate/adsorbate interactions. The atomic structure of the substrate provides the main adsorption sites and offers for example the environment for the dissociation process to occur, by allowing to store hydrogen on available surface oxygen atoms, which plays a crucial role when building the network.

References:
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