

# Water Adsorption on O/Ru(0001): Dissociation and Cooperative Effects

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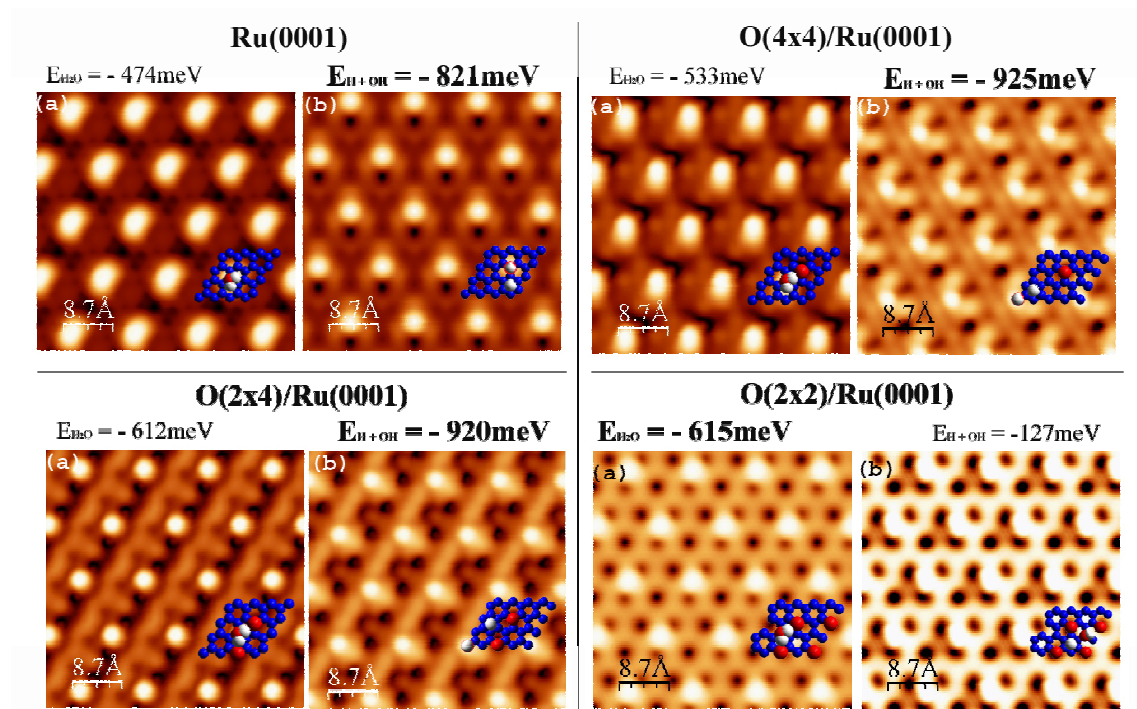
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Using density functional theory we found that, depending on coverage, co-adsorbed oxygen can act both as a promoter and as an inhibitor of the dissociation of water on Ru(0001), the transition between these two behaviours occurring at  $\sim 0.2$  ML. The factors determining this transition are (i) hydrogen bond between  $\text{H}_2\text{O} - \text{O}_{\text{ads}}$  and (ii) the adsorption energy of the reaction products, OH in particular (see Table I). The chemistry of this co-adsorbed system is dictated by the effective coordination of the Ru atoms that participate in the bonding of the different species. In particular, we observed that a low coverage of oxygen increases the adsorption energy of the OH fraction on the Ru surface. This surprising extra-stabilization of the OH with the co-adsorption of oxygen can be understood in the context of the metallic bonding and could well correspond to a general trend for the co-adsorption of electronegative species on metallic surfaces.<sup>1</sup> On the other hand, the cooperative adsorption of water on the metallic substrate reinforces significantly the intermolecular interaction. Here, we present a molecular-scale description of the dimer hydrogen bond strengthen induced by the formation of a bond between the donor water molecule and the Ru substrate. This strong hydrogen bond involves the weakening of the intramolecular OH bond of the donor molecule, which might facilitate the partial dissociation of water.<sup>2</sup>

**Table I.** Adsorption energies ( $E_{ads}$ ) of H, OH and H<sub>2</sub>O adsorbed on Ru(0001) at different  $\theta_{O}$ . The energy gained by dissociative adsorption,  $E_{H+OH}$ , defined by  $E_{H+OH} = E_{H} + E_{OH}$ ; where  $E_{H_2O} = 5.58$  eV is the required energy for partial dissociation of the water molecule in vacuum. The relative stability of dissociative versus molecular adsorption,  $\Delta E$ , is defined by  $\Delta E = E_{H+OH} - E_{H_2O}$ . Notice that positive values of  $\Delta E$  denote favoured dissociative over intact adsorption.

Surface	$E_{ads}^H$ (eV)	$E_{ads}^{OH}$ (eV)	$E_{ads}^{H_2O}$ (meV)	$E_{diss}^{H_2O}$ (meV)	$\Delta E$ (meV)
Ru(0001)	2.90 (fcc)	3.49 (fcc/hcp)	474	821	347
O(4x4)/ Ru(0001)	2.89 (fcc)	3.61 (hcp/fcc)	533	925	392
O(2x4)/ Ru(0001)	2.86 (fcc)	3.64 (hcp)	612	920	308
O(2x2)/ Ru(0001)	2.60 (fcc)	3.10 (top/hcp)	616	127	-489



**Figure 1.** Simulated STM images of the intact and dissociative adsorption of water on Ru(0001) surface previously exposed to different coverage of Oxygen.

- (1) Cabrera-Sanfeliix, P.; Arnau, A.; Mugarza, A.; Shimizu, T. K.; Salmeron, M.; Sanchez-Portal, D. *Physical Review B* **2008**, 78.
- (2) Cabrera-Sanfeliix, P.; Arnau, A.; Sanchez-Portal, D. *Submitted* **2009**.