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Water splitting for energy storage: first principles insights into the reaction mechanism of Ru-based homogeneous catalysts SIMONE PICCININ, CRN-INFM DEMOCRITOS, Trieste (Italy), STEFANO FABRIS, CNR-INFM DEMOCRITOS, Trieste (Italy) — Water oxidation has been recognized as the key bottleneck toward the development of artificial photosynthesis, where the goal is to use solar energy to produce chemicals for energy conversion and storage. This reaction requires the loss of four electrons and four protons and has a standard reduction potential of 1.23 V (pH=0, NHE). The recent development of an all-inorganic tetra-ruthenium polyoxometallate homogeneous catalyst [1,2] that oxidizes water at a low overpotential ($\sim$ 0.2 V) is a breakthrough in this field, since it combines the stability of inorganic compounds and the high activity of homogeneous catalysts. Here we report the results of a first-principles DFT study of the properties of this catalyst and the mechanism it promotes. We focus on the analysis of the thermodynamics of the water oxidation cycle, considering the relative stability of different candidate intermediates as a function of the external bias that drives the reaction. The comparison with available cyclic voltammetry allows to shed some light on the possible oxidation states of the Ru centers involved in the catalytic mechanism. [1] A. Sartorel et al. J. Am. Chem. Soc. 130, 5006 (2008) [2] Y. Geletti et al. Angew. Chem. Int. Ed. 47, 3896 (2008)

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