The Abdus Salam
International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA International Atomic Energy Agency

WORKSHOP ON NEW MATERIALS FOR RENEWABLE ENERGY
17 - 21 October 2011, ICTP, Trieste

AB-INITIO MODELING OF Ru-BASED HOMOGENEOUS CATALYSTS FOR WATER OXIDATION

Simone PICCININ
S.I.S.S.A. Scuola Internazionale Superiore di Studi Avanzati
Trieste, Italy

ABSTRACT 1I:

Splitting water to produce molecular oxygen and hydrogen is a promising way to convert and store solar energy in the form of chemical fuels [1]. Efficient catalysts are needed to promote this electrochemical reaction, which, especially on the oxidation side, is extremely challenging, requiring the loss of four electrons and four protons and the creation of the O-O bond. For this semi-reaction several catalysts have been proposed in the past three decades, both heterogeneous (metals and metal oxide surfaces) and homogeneous (transition metals with organic ligands). In this talk I will present the results of our first-principles Density Functional Theory calculations on the reaction mechanism promoted by an all-inorganic tetraruthenium-polyoxometalate homogeneous catalyst, able to efficiently oxidize water at a low overpotential (~ 0.35 V) [2,3]. We show how state-of-the-art theoretical methods help to shed light on the complex mechanism of this reaction. In particular, we combine hybrid functional calculations for the energetics of the intermediates [4] and metadynamics to explore the free energy surface in the space of a few collective variables. We find that the mechanism proposed in the literature for this system needs to be critically re-examined and we propose an alternative reaction pathway.

[1] V. Balzani, A. Credi, M. Ventura, ChemSusChem 1, 26 (2008)
[2] A. Sartorel et al., J. Am. Chem. Soc. 130, 5006 (2008)
[3] Y. Geletti et al., Angew. Chem. Int. Ed. 47, 3896 (2008)
[4] S. Piccinin and S. Fabris, PCCP 13, 7666 (2011)