Theoretical Characterization of Molecular Metal Oxides. Challenging Cases

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The characterization and understanding of molecular physico-chemical properties is one of the primary goals of computational techniques, which has revealed very useful in the search of general patterns and trends on families of chemical compunds. Also, when experimental data are hardly accessible, limited or incomplete, calculations can provide crucial information for unravelling the electronic structure and related phenomena, reaction paths, spectra, etc. The present talk sketches mostly DFT studies performed on several properties of Polyoxometalates.[1] This is a structurally and chemically rich family of molecular transition-metal (TM) oxides with a numerous scientific community and interesting applications in many fields. Several molecules of increasing structural complexity are discussed, ranging from medium systems such as the decavanadate ($V_{10}O_{28}^{6-}$) and Wells-Dawson ($P_2W_{18}O_{62}^{6-}$) anions to a recently characterized nanoscopic 48 TM-containing compound. As the systems become larger (more complex), the calculations become more challenging and added-value. Almost all the cases discussed feature a common characteristic, namely the presence of some metallic valence electrons with different degrees of localization, sometimes conferring the molecule special properties related to redox processes, stability or magnetism.[2] From the theoretical point of view, this feature represents both an additional difficulty and an exciting characteristic. The properties that are presented in this talk, selected from works performed in the Quantum Chemistry Group (URV) in the last years, are mainly electrochemistry, NMR[3] and magnetism[4] with allusions to protonation and cation encapsulation.[5]

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