A Density Functional Study of Molecular Oxygen Adsorption and Reaction Barrier on Pu (100) Surface

M.N. HUDA, A.K. RAY, Department of Physics, University of Texas at Arlington, Arlington, Texas 76019 — Oxygen molecule adsorptions on a Pu (100) surface have been studied in detail, using the generalized gradient approximation to density functional theory and the DMol3 suite of programs [1]. Dissociative adsorption with a layer by layer alternate spin arrangement of the plutonium layer is found to be energetically more favorable compared to molecular adsorption. Hor2 approach on a bridge site without spin polarization was found to the highest chemisorbed site with an energy of 8.787eV among all the cases studied. The second highest chemisorption energy of 8.236eV, is the spin-polarized Hor2 or Ver approach at center site. Inclusion of spin polarization affects the chemisorption processes significantly, non-spin-polarized chemisorption energies being typically higher. We also find that the 5f electrons to be more localized in spin-polarized cases. The ionic part of O-Pu bonding plays a significant role, while the Pu 5f-O 2p hybridization is rather weak. Adsorptions of oxygen push the top of 5f band away from the Fermi level, indicating further bonding by the 5f orbitals might be less probable. [1] B. Delley, J. Chem. Phys. 92, 508 (1990); J. Chem. Phys. 113, 7756 (2000).

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