

**Ability of density functional theory methods to accurately model the
reaction energy pathways of the oxidation of CO on gold cluster: A
benchmark study**

by

Saumya Gurtu, Sandhya Rai, Masahiro Ehara, U Deva Priyakumar

in

Theoretical Chemistry Accounts

Report No: IIIT/TR/2016/-1



Centre for Computational Natural Sciences and Bioinformatics
International Institute of Information Technology
Hyderabad - 500 032, INDIA
February 2016

Ability of Density Functional Theory Methods to Accurately Model the Reaction Energy Pathways of the Oxidation of CO on Gold Cluster: A Benchmark Study

Saumya Gurtu^a, Sandhya Rai^a, Masahiro Ehara^b, U. Deva Priyakumar^a

^a Center for Computational Natural Science and Bioinformatics, International Institute of Information Technology, Hyderabad, India.

^b Research Center for Computational Science, Institute for Molecular Science, Myodaiji, Japan.

Gold clusters are currently regarded as new generation catalysts owing to their exceptional efficiency in accelerating several classes of reactions. Density functional theory (DFT) is the method of choice for the investigation of energy pathways of reactions assisted by metal nanoparticles due to their computational efficiency. However, the reliability of such theoretical studies depends to a large extent on the choice of the DFT functional used. In the present work, the performance of a series of DFT based functionals to accurately model the prototypical CO oxidation reaction catalyzed by a Au₃ cluster has been examined by comparing the results with those obtained from high level ab initio CCSD(T) method. This comparison study has been carried along the two possible pathways (Eley–Rideal (ER) and the Langmuir–Hinshelwood (LH)). No significant differences among the DFT functionals were observed in terms of obtaining the geometries of stationary points including the transition states with minor exceptions. However, the adsorption energies, barrier heights and reaction energies calculated using the DFT methods lie in a wide range with some methods showing high deviations from the CCSD(T) results. Our calculations suggest that the adsorption energy values are sensitive to the inclusion of long range correction and dispersion correction, whereas the barrier heights do not show much dependence on the inclusion of dispersion effects. The percentage of Hartree-Fock exchange included in the DFT functional also plays a crucial role in predicting the correct pathway. Based on this extensive benchmark study, it is suggested that the computationally less expensive hybrid density functionals, PBE0, B3PW91 and B3P86, are better suited for accurate modeling of this class of reactions.

