Manuscript Number: TCAC-D-16-00028
Article Title: Ability of density functional theory methods to accurately model the reaction energy pathways of the oxidation of CO on gold cluster: A benchmark study
Journal Title: Theoretical Chemistry Accounts

Dear Dr. Priyakumar,

We are pleased to tell you that your work has now been accepted for publication in Theoretical Chemistry Accounts.

Thank you for submitting your work to this journal.

With kind regards,
Ilaria Ciofini & Prof. Carlo Adamo
Editor-in-Chief
Theoretical Chemistry Accounts

COMMENTS TO THE AUTHOR:

Reviewer #1: In this manuscript, the authors examined the applicability of currently available DFT functionals in a model reaction Au3 + CO + O2. All comparison data are very useful for readers who use DFT calculations. The functionals are enough widely collected and carefully compared. The model reaction and reaction path are also carefully prepared. But the authors' conclusion is obtained in a special case, so it is not general. The calculation method is simple and straightforward and at the level of daily work. Worrying about the above points, I think, nevertheless this manuscript seems to be worth publishing.
Before publishing, I have one comment. I don't agree with the authors' classification in Table 1. For example, LC-BLYP and LC-wPBE may not belong to pure DFT. I recommend the authors to re-consider this point.

Reviewer #2: Recommendation: This paper is publishable subject to a major revisions noted.
Major comment:
This is an interesting and useful work detailing differences in ability of DFT methods to model aerobic CO oxidation on Au3 cluster, with both the two possible pathways ER and LH.
In general the work is well structured and written and I believe that the information given and the conclusions reached can be of interest for a significant part of the theoreticians community.
However, a major revision need to be addressed:
The authors completly neglect the procedure to determine the most stable spin state configuration of all the analyzed systems.
In my opinion, this issue is very crucial and a computational study of CO oxidation on gold cluster must include some considerations on spin state configuration (see for example DOI:10.1002/chem.201202957), especially if there are adducts in which O2 and/or atomic oxygen are absorbed on a metallic cluster.
In these cases the potential energy surface crossing so-called two state reactivity may need to be considered (see for example DOI: 10.1016/j.theochem.2009.01.016 and DOI: 10.1021/ar990028j).
In conclusion, the article is certainly publishable in TCAC, but clarifying discussions, about the spin state configurations, have to be added.
Minor comment: about figure 1, some numerical values on the energy scale should be added.