Electronic Supplementary Information For Nucleobases Tagged to Gold Nanocluster Cause a Mechanistic Crossover in the Oxidation of CO

Sandhya Rai,† Masahiro Ehara,‡ and U. Deva Priyakumar*,†

Center for Computational Natural Science and Bioinformatics, International Institute of Information Technology, Hyderabad, India, and Research Center for Computational Science, Institute for Molecular Science, 38 Nishigo-Naka, Myodaiji, Okazaki 444-8585, Japan

E-mail: deva@iiit.ac.in

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*To whom correspondence should be addressed

†IIIT-H

‡IMS Japan

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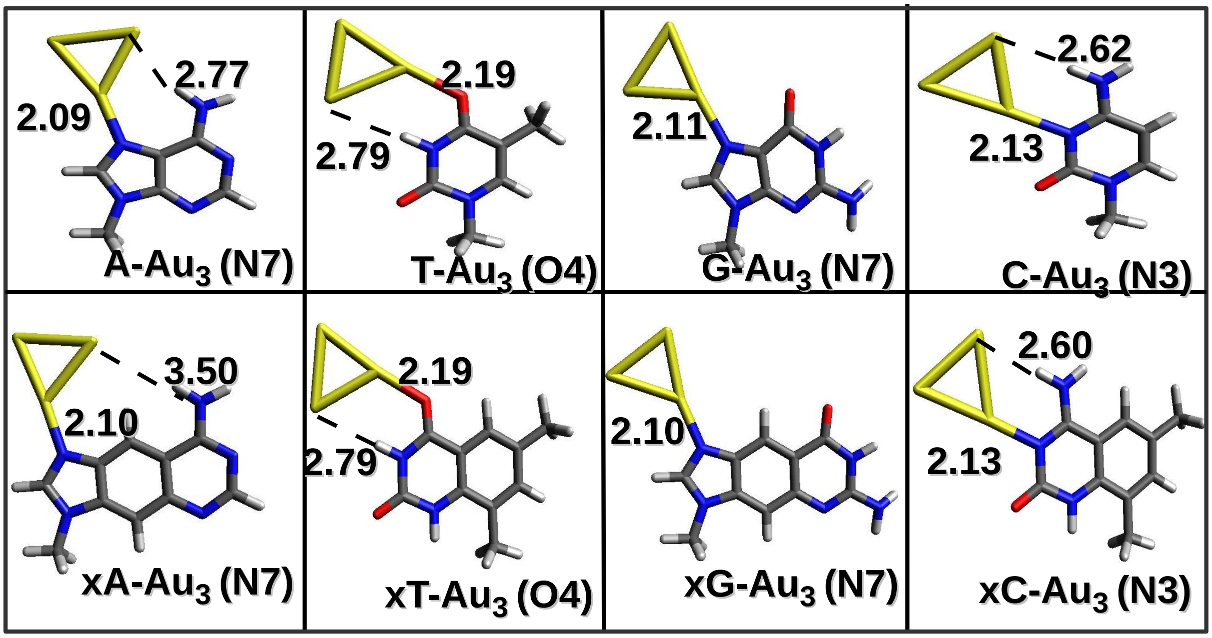

Figure S1: Geometries of the nucleobase-gold complexes optimized at PBE0/SDD∪6-31++G(d,p) level of theory.

Adsorption of reactants on the catalyst surface

It is known that O_2 has low affinity towards gold surface and the adsorption mechanism is mainly physisorption. Thus, in order to understand the reaction mechanism, it is imperative to see how the ER and LH mechanisms facilitate the adsorption of the reactants on their surface.

Adsorption of CO on the catalyst in ER mechanism: For ER mechanism to be followed, CO adsorption on the catalyst surface takes place prior to the nucleophilic attack by O_2. Our studies reveal that CO has a strong affinity for Au surface. CO adsorbs on the Au_3 cluster in an end-on fashion with a significant adsorption energy of -34.49 kcal/mol. In order to investigate the adsorption property of CO on the base tagged catalytic surface, the structure of CO complexed to different base-gold complexes were optimized. The struc-

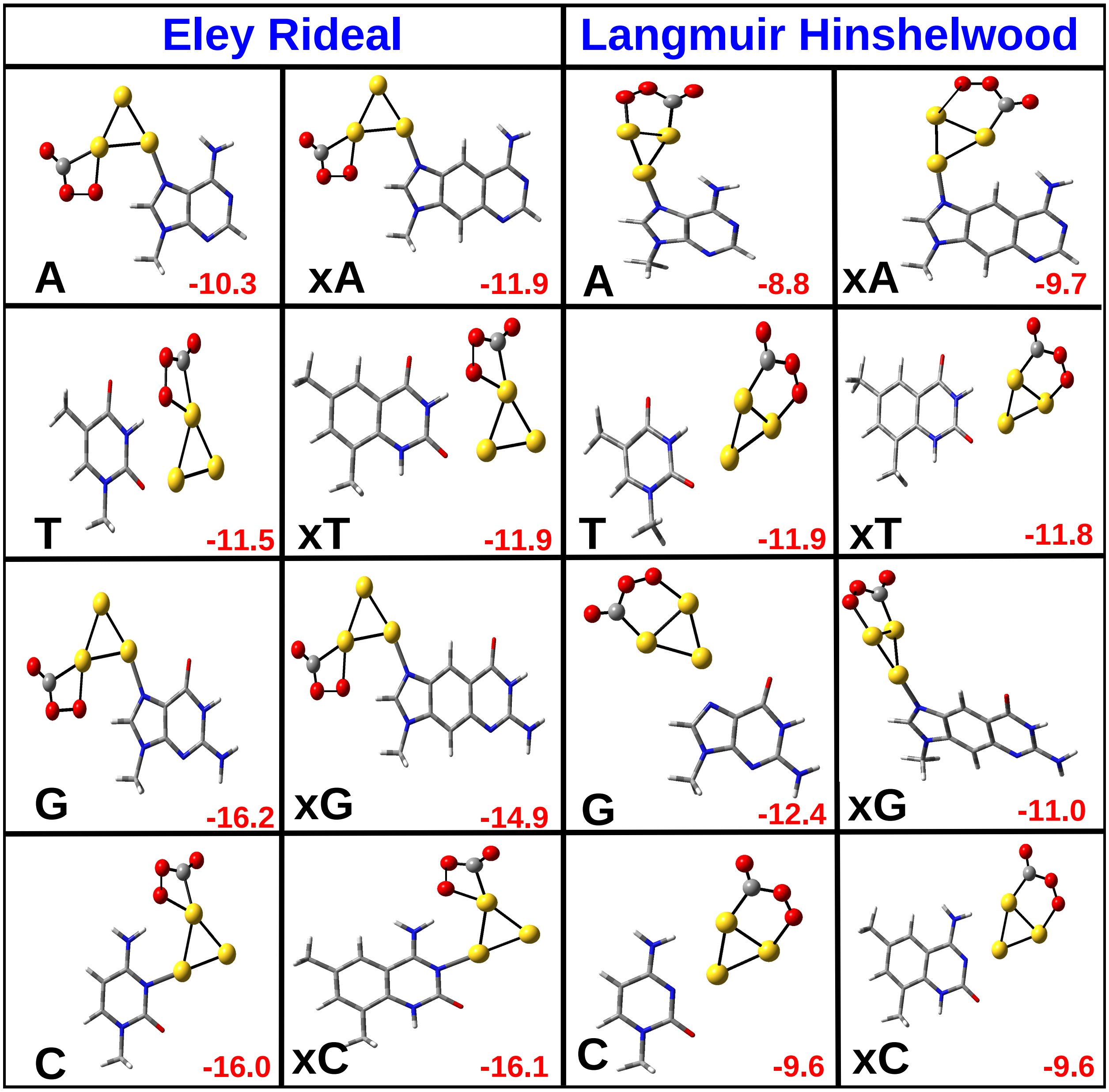

Figure S2: Optimized geometries of transition states obtained at PBE0/SDD∪6-31++G(d,p) level of theory. The relative stabilization energies are calculated with respect to uncomplexed reactants and are reported in kcal/mol.

tures of these complexes are shown in Figure S3 along with their adsorption energies, which clearly indicate that, CO can be adsorbed on the nucleobase-cluster complex with different, albeit significant, adsorption energy depending the nucleobase attached. Interestingly, CO adsorbed on the bare cluster has larger adsorption energy. Also, Au_3 tagged to thymine

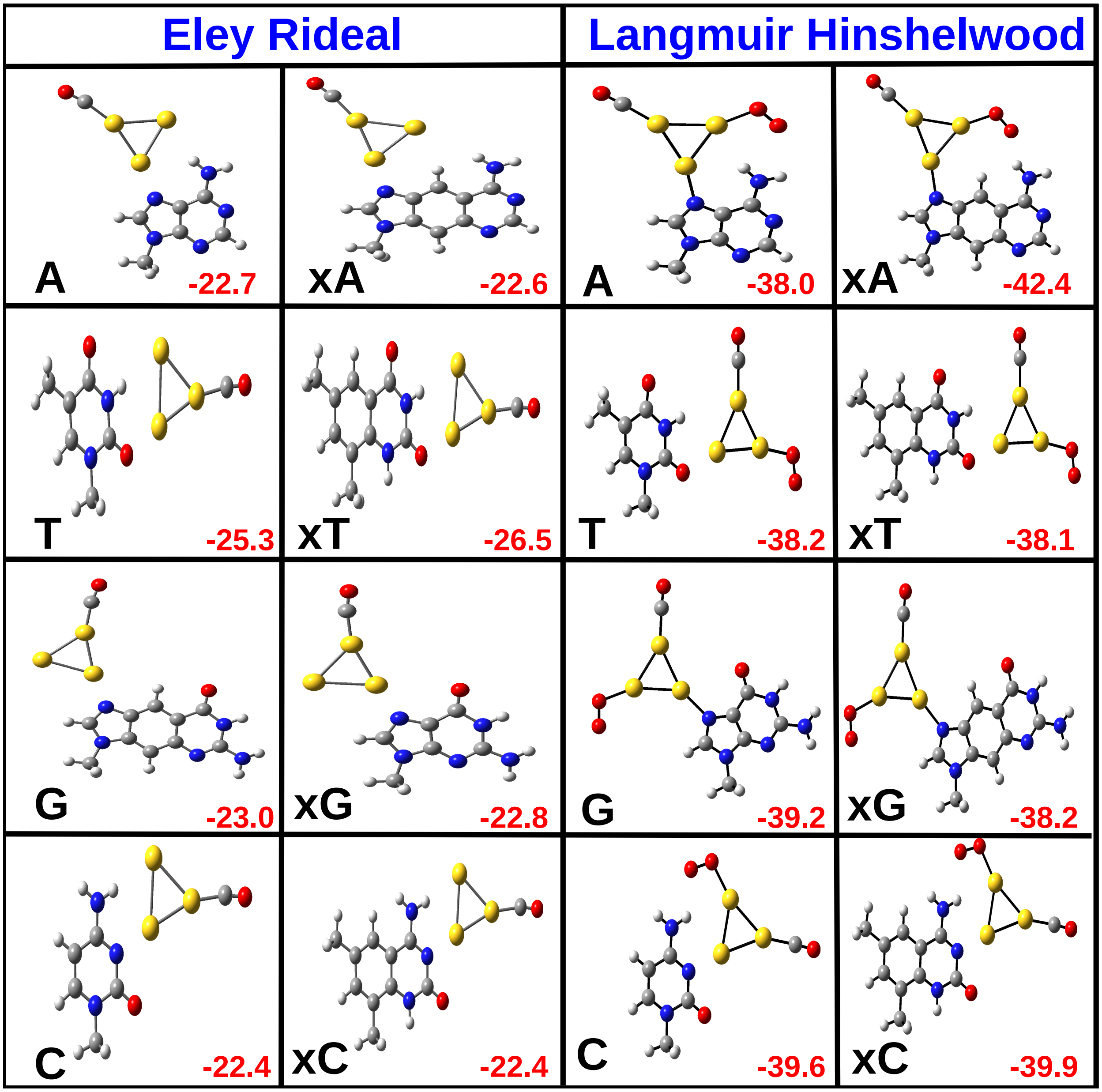

Figure S3: Relaxed structures of CO on different catalysts optimized at PBE0/SDD∪6-31++G(d,p). Blue color refers to N, grey represents C, red represents O, yellow represents Au and white represents H. The adsorption energies are calculated with respect to uncomplexed reactants and are reported in kcal/mol.

shows a larger adsorption energy (Figure S3), but has least charge transfer from base to gold. It can be predicted on the basis of these observations that anionic gold clusters are repelled by the π electron cloud of CO which is more susceptible to a nucleophile.

Understanding the nature of adsorption of CO on the catalyst surface can lead to interesting facts responsible for catalyzing the reaction. For Au_3–base complex, there are two potential Au atoms that can interact with CO, since one Au atom is involved in interaction with the base. We have considered the site showing higher affinity towards CO adsorption. Structural analysis of these complexes suggests that, on adsorption of CO on the catalyst surface, (i) the Au–C bond length varies between 1.95 Å to 1.98 Å and (ii) C–O bond length increases from 1.13 Å (in free CO) to 1.14 Å, without interrupting the the geometry of catalyst. Previous studies have shown that such elongation is a result of the charge transfer from Au atom to CO. Bonding of Au–C can be explained on the basis of Dewar–Chatt–Duncanson model. The complex involves charge transfer from the Au to the antibonding π^* orbital of CO donation and backdonation to the Au from the CO bonding σ orbital. The occupied antibonding π^* orbital of CO results in the elongation of CO bond length. This suggests that the charge is transferred from Au to CO resulting in chemisorption rather than physisorption.

Coadsorption of CO and O_2 on the catalyst in LH mechanism: However, for the LH mechanism to be followed a coadsorption on CO and O_2 is studied. The two reactants can attach to the catalytic surface in several ways. We present here the ones which are energetically most favorable. It is evident from Figure S3 that the adsorption energies vary with the supporting base involved. This difference can be accounted for on the basis of the difference in the charge density over the cluster on interaction with different bases. On comparing the coadsorption energies with the adsorption energy of CO, we find an increase of $\sim$15 kcal/mol for all Au_3 based catalysts. This suggests that the presence of preadsorbed CO on neighboring Au atoms notably enhances the binding of O_2 to the catalyst. These results clearly indicate that coadsorption can enhance the binding of $[CO+O_2]$ on the catalytic surface. The possible reason for the same could be the change in charge density over the cluster due to the presence of CO in its vicinity.

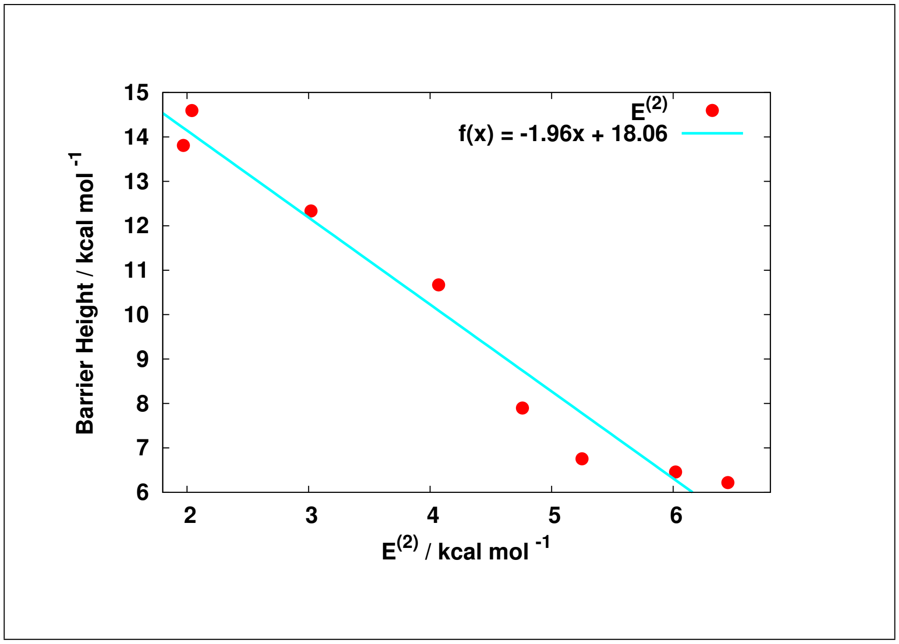

Figure S4: Correlation plot between the $E^{(2)}$ and the barrier height corresponding to the first step of the reaction via the ER mechanism.

Adsorption of CO on the [O] activated catalyst surface

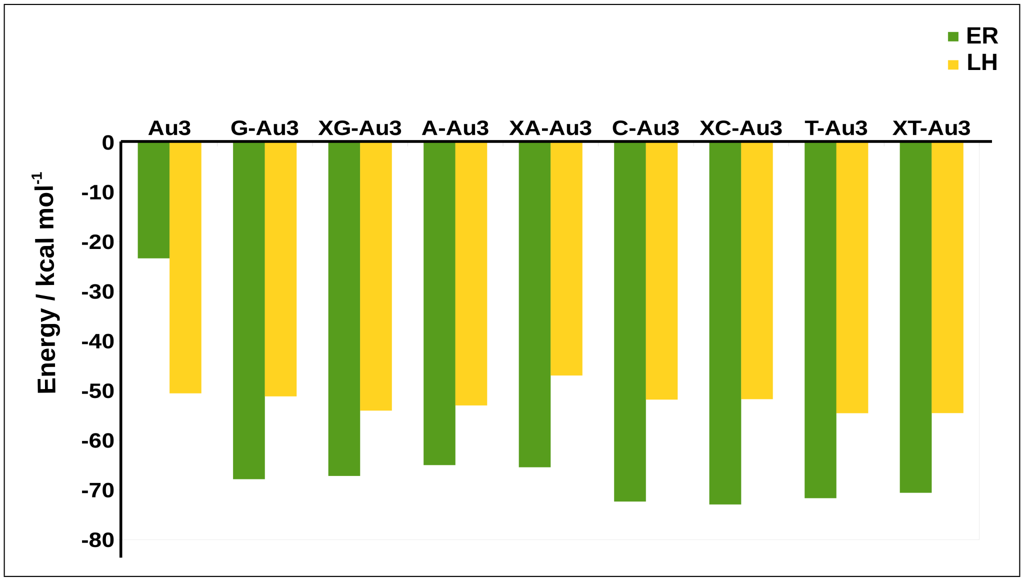

Figure S5: Energy difference between the reactant and Int. 2 in the presence of different catalysts for ER and LH mechanisms.

Transition state NBO data

Table 1: Second order perturbation theory analysis in NBO Basis for the transition state corresponding to ER mechanism involving particularly the charge transfer from the gold cluster to the π^* orbital of CO. All calculations were performed at PBE0/SDD∪6-31++G(d,p) level of theory.

System	Donor	Acceptor	$E^{(2)}$ (kcal/mol)
G-Au_3	n_{Au}	π^*_{CO}	24.82
xG-Au_3	n_{Au}	π^*_{CO}	24.82
A-Au_3	n_{Au}	π^*_{CO}	22.17
xA-Au_3	n_{Au}	π^*_{CO}	22.48
C-Au_3	n_{Au}	π^*_{CO}	24.95
xC-Au_3	n_{Au}	π^*_{CO}	25.27
T-Au_3	n_{Au}	π^*_{CO}	18.64
xT-Au_3	n_{Au}	π^*_{CO}	18.28