

# Theoretical study of $\text{Au}_8\text{O}_2$ , $\text{Au}_8\text{O}_2^+$ and $\text{Au}_8\text{O}_2^-$ nanoclusters



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## Abstract

The present work deals with the preliminary theoretical study of  $\text{Au}_8$  clusters (neutral, cationic, anionic) and oxygen molecule separately and then the interaction of oxygen molecule with  $\text{Au}_8$  clusters (neutral, cationic, anionic) using different DFT functionals. It is evident from the results that the formation of  $\text{Au}_8\text{O}_2^-$ , anionic complex having one unpaired electron is more favorable as compared to its cationic or neutral counterparts. Furthermore, frequency calculations of O-O bond show that vibrational frequency is least for  $\text{Au}_8\text{O}_2^-$ , anionic complex having one unpaired electron. It reveals that there is effective activation of oxygen and thus it can be very useful in CO oxidation reaction which is a very important reaction for reducing environmental pollution.

**Keywords:** Gold Nanoclusters, Density Functional Theory, CO Oxidation.

## Introduction

Several interesting phenomena involving nanomaterials have been mentioned during the past decade due to their unique structural, mechanical, and electrical properties. The increasing availability of extremely sophisticated experimental techniques coupled with the high-quality electronic structure calculation programs has improved the understanding of the complex nature of these nanomaterials and properties. One of the most recent observations is that of gold based catalysis at the nanoscale. It is well known that while the bulk phase of the gold is inert, the gold nanoparticles of size around 1-5 nm has been found to be an excellent catalyst for many organic and inorganic reactions. Among these chemical reactions, the interesting catalytic reactions are the oxidation of carbon monoxide at 200 K and the activation of oxygen molecules. The adsorption of atoms or molecules on small metal clusters in the gas phase is an active area of experimental and theoretical investigation.

Although bulk phase Gold has long been known as the chemically inert metal, it was the report of Haruta et al.<sup>1</sup> that showed that nanosized gold clusters can be catalytically active. A wide variety of chemical reactions, e.g. CO oxidation<sup>2</sup>, epoxidation<sup>3, 4</sup>, C-C bond formation<sup>5</sup>, water gas shift<sup>6</sup> and selective hydrogenation/reduction<sup>7</sup> are reported to be catalysed by supported gold clusters. Especially, the most notable is the environmentally important reaction of oxidation of CO to  $\text{CO}_2$  at temperatures far below room temperature.

## Review of Literature

Whetten's group<sup>8</sup> who studied  $\text{O}_2$  adsorption on  $\text{Au}_n^-$  clusters found that  $\text{Au}_n^-$  clusters with odd  $n$  do not adsorb  $\text{O}_2$  and that  $\text{Au}_n^-$  clusters with even  $n$  will only adsorb one  $\text{O}_2$  molecule. They postulated that the adsorption of an  $\text{O}_2$  molecule requires the formation of a chemisorbed  $\text{O}_2^-$  species; this charge transfer occurs readily only when the  $\text{Au}_n^-$  cluster has an unpaired electron. Since an Au atom has 11 valence electrons, the cluster  $\text{Au}_n^-$  has an unpaired electron only when  $n$  is even. Thus, only anionic clusters with even  $n$  will adsorb  $\text{O}_2$ . The interest in oxygen chemistry on  $\text{Au}_n$  clusters is increased by the recent finding that very small Au clusters are good oxidation catalysts<sup>2</sup>.

The direct vapor-phase epoxidation of propene to propene oxide in the presence of molecular oxygen and hydrogen over gold catalysts supported on Ti-incorporated silica materials prepared by different methods have been reported by A.K. Sinha et al.<sup>3</sup>

The properties of the alkali metal clusters have been investigated by K. R. S. Chandrakumar's group<sup>9, 10</sup> using ab initio electronic structure calculations, with special reference to their structural evolution and the size dependence of several reactivity descriptors.

In the past two decades, high attention has been given for the direct synthesis of  $H_2O_2$  from  $H_2$  and  $O_2$  with Pd and Au-based catalysts.<sup>11-15</sup> Olivera et al.<sup>14</sup> predicted that gold would be a better catalyst for the direct synthesis of  $H_2O_2$  than Pd, Pt, and Ag. Subsequent experiments did show that highly dispersed Au nanoparticles are very selective and active for the synthesis reaction.<sup>15, 16</sup> Theoretical investigation of the formation of hydrogen peroxide from  $H_2$  and  $O_2$  over anionic gold clusters  $Au_n^-$  ( $n = 1-4$ ) has been proposed by Fang Wang et al.<sup>17</sup>

Structure, bonding, and linear optical properties of a series of silver and gold nanorod clusters whose structures are of cigar-type has been performed by Meng-Sheng Liao et al.<sup>18</sup> using DFT/TDDFT.

Greg Mills<sup>19</sup> used density functional theory to examine the binding of  $O_2$  to  $Au_n$  and  $Au_n^-$  clusters ( $n = 2-5$ ).

Theoretical investigation on the structure and electronic properties of hydrogen- and alkali-metal-doped gold clusters and their interaction with CO, an enhanced reactivity of hydrogen-doped gold clusters has been reported recently by Naresh K. Jena et al.<sup>20</sup>

Ab initio studies on the electronic structure and properties of Aluminum hydrides viz., *closo* ( $Al_nH_{n+2}$ ), *nido* ( $Al_nH_{n+4}$ ), and *arachno* ( $Al_nH_{n+6}$ ) that are analogues of boron hydrides has been done by K. Srinivasu et al.<sup>21</sup>

The doping of H-atom in a gold cluster can lead to a significant increase in its reactivity. The H-doped gold cluster decreases the barrier height for the environmentally important CO oxidation reaction as compared to the pristine cluster.<sup>22</sup>

Rhitankar Pal et al.<sup>23</sup> reported spectroscopic evidence of two modes of  $O_2$  activation by the small even-sized  $Au_n^-$  clusters, superoxo and peroxy chemisorption. Their work shows that there is a superoxo to peroxy chemisorption transition of  $O_2$  on gold clusters at  $Au_8^-$ ,  $O_2Au_n^-$  ( $n = 2, 4, 6$ ) involves superoxo binding and  $n = 10, 12, 14, 18$  involves peroxy binding, whereas the superoxo binding re-emerges at  $n = 20$  due to the high symmetry tetrahedral structure of  $Au_{20}$ , which has a very low electron affinity.

Density functional theory study of the adsorption of nitrogen and sulfur atoms on gold (111), (100), and (211) surfaces has been reported by April D. Daigle and Joseph J. BelBruno.<sup>24</sup>

H. M. Lu and X. K. Meng<sup>25</sup> proposed a theoretical model to calculate catalytic activation energies of platinum nanoparticles of Different sizes and shapes.

Recently, Naresh K. Jena et al.<sup>26</sup> reported Density functional theory (DFT) based study that investigates the possibilities of using complexes of DNA bases.

Following these initial reports of the reactivity of gold nanoparticles, the platform has been well set for the investigation of nanoscale gold catalysis leading to an upsurge of activities on structural

features, electronic properties of gold clusters, and their possible uses in nanocatalysis.<sup>27-49</sup>

#### Aim of the Study

The present work deals with the study of  $Au_8$  clusters (neutral, cationic, anionic) and oxygen molecule separately and then interaction of oxygen molecule with  $Au_8$  clusters (neutral, cationic, anionic) using different DFT functionals.

#### Computational details

We prepared the raw geometries of  $Au_8$  clusters using Gabedit software and then optimized the geometries of neutral, cationic and anionic nanoclusters using computational chemistry package TURBOMOLE<sup>50</sup>. Then added one oxygen molecule to the  $Au_8$  cluster and optimized the whole structure again. We used a large number of initial positions for binding oxygen molecule to the cluster and observed several minima but considering here only those corresponding to the lowest energy.

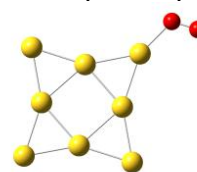
The calculations are done by DFT-R1 (def2-TZVP basis set) using three different functionals i.e. b-p, tpss and b3-lyp.

#### Results and discussion

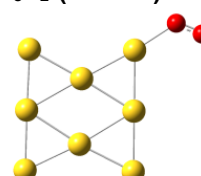
Figure 1 represents the optimized geometries of  $Au_8O_2$ ,  $Au_8O_2^+$ ,  $Au_8O_2^-$  complexes. We have calculated the energy of  $Au_8O_2$ ,  $Au_8O_2^+$ ,  $Au_8O_2^-$  complexes considering  $O_2$  as singlet and triplet.

**Figure 1: Optimized Geometries of  $Au_8O_2$  Neutral, Cationic and Anionic Complexes**

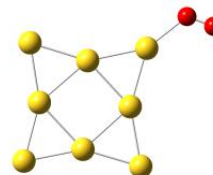
**$Au_8O_2$  (doublet)**



**$Au_8O_2^+$  (doublet)**



**$Au_8O_2$  (triplet)**



It is evident from Table 1, 3 & 5 that, when functional b-p is used,  $Au_8$ -Anion is more stable by 67.8731 kcal/mol than its neutral counterpart while  $Au_8$ -Cation has least stability. Similarly, for b3lyp and tpss functionals,  $Au_8$ -Anion is more stable by 59.6943 kcal/mole & 61.1432 kcal/mole than  $Au_8$ -Neutral.

**Table 1: Energy calculated using DFT-RI (def2-TZVP basis set) and functional b-p**

	Au <sub>8</sub> -Neutral (singlet)	Au <sub>8</sub> -Cation (doublet)	Au <sub>8</sub> -Anion (doublet)	O <sub>2</sub> Molecule (triplet)
Energy (kcal/mol)	-682380.0028	-682200.9509	-682447.8759	-94383.17118

**Table 2: Properties calculated using DFT-RI (def2-TZVP basis set) and functional b-p**

		Au <sub>8</sub> O <sub>2</sub> Neutral (singlet)	Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (doublet)	Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (doublet)
singlet oxygen	E (kcal/mol)	-776749.1058	-776592.3722	-776847.8833
	q <sub>O2</sub>	0.322	0.173	0.478
	d <sub>o-o</sub> (Å)	1.26989	1.23406	1.29257
	B.E. (kcal/mol)	14.06813872	-8.250145493	-16.83617469
triplet oxygen		Au <sub>8</sub> O <sub>2</sub> Neutral (triplet)	Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (quintet)	Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (quintet)
	E (kcal/mol)	-776767.2493	-776588.8973	-776832.6573
	q <sub>O2</sub>	0.132	0.180	0.242
	d <sub>o-o</sub> (Å)	1.24258	1.22866	1.25381
	B.E. (kcal/mol)	-4.075332131	-4.775184622	-1.6102162

**Table 3: Energy calculated using DFT-RI (def2-TZVP basis set) and functional b3-lyp**

	Au <sub>8</sub> -Neutral (singlet)	Au <sub>8</sub> -Cation (doublet)	Au <sub>8</sub> -Anion (doublet)	Oxygen Molecule (triplet)
Energy (kcal/mol)	-681470.9492	-681294.1365	-681530.6435	-94333.4879

Table 2, 4 & 6 shows various parameters i.e. Energy, the charge on oxygen, Oxygen-Oxygen bond distance and binding energy of various complexes calculated using def2-TZVP basis set and different

functional at DFT level. Charge on oxygen is found maximum in Au<sub>8</sub>O<sub>2</sub><sup>-</sup> (doublet) for all functional. While O-O bond distance is found to be 1.29257 Å, 1.2892 Å and 1.30 Å for b-p, b3lyp and tpss respectively.

**Table 4: Properties calculated using DFT-RI (def2-TZVP basis set) and functional b3-lyp**

		Au <sub>8</sub> O <sub>2</sub> Neutral (singlet)	Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (doublet)	Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (doublet)
singlet oxygen	E (kcal/mol)	-775774.661	-775631.0658	-775874.8016
	q <sub>O2</sub>	-0.255	0.014	-0.567
	d <sub>o-o</sub> (Å)	1.2415	1.2064	1.2892
	B.E. (kcal/mol)	29.77610973	-3.441401951	-10.67023055
triplet oxygen		Au <sub>8</sub> O <sub>2</sub> Neutral (triplet)	Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (quintet)	Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (quintet)
	E (kcal/mol)	-775805.099	-775630.0641	-775864.1344
	q <sub>O2</sub>	-0.002	0.022	-0.0005
	d <sub>o-o</sub> (Å)	1.20617	1.20532	1.20460
	B.E. (kcal/mol)	-0.661929865	-2.439734093	-0.00308076

**Table 5: Energy calculated using DFT-RI (def2-TZVP basis set) and functional tpss**

	Au <sub>8</sub> -Neutral (singlet)	Au <sub>8</sub> -Cation (doublet)	Au <sub>8</sub> -Anion (doublet)	Oxygen Molecule (triplet)
Energy (kcal/mol)	-681450.5434	-681278.9776	-681511.6866	-94385.19808

**Table 6: Properties calculated using DFT-RI (def2-TZVP basis set) and functional tpss**

		Au <sub>8</sub> O <sub>2</sub> Neutral (singlet)	Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (doublet)	Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (doublet)
singlet oxygen	E (kcal/mol)	-775822.3857	-775672.4477	-775915.5818
	q <sub>O2</sub>	-0.34	-0.07	-0.50
	d <sub>o-o</sub> (Å)	1.27498	1.23564	1.30
	B.E. (kcal/mol)	13.35568112	-8.27197437	-18.69717137
triplet oxygen		Au <sub>8</sub> O <sub>2</sub> Neutral (triplet)	Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (quintet)	Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (quintet)
	E (kcal/mol)	-775840.175	-775669.1289	-775899.3448
	q <sub>O2</sub>	-0.153	-0.02	-0.293
	d <sub>o-o</sub> (Å)	1.24452	1.22857	1.26095
	B.E. (kcal/mol)	-4.433554686	-4.953225838	-2.460176298

Table 7: Comparison of Binding Energies from table 2

Species	No. of unpaired electrons	B.E. (kcal/mol) by functional b-p	B.E. (kcal/mol) by functional b3-lyp	B.E. (kcal/mol) by functional tpss
Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (doublet)	1	-16.83617469	-10.67023055	-18.69717137
Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (doublet)	1	-8.250145493	-3.441401951	-8.27197437
Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (quintet)	3	-4.775184622	-2.439734093	-4.953225838
Au <sub>8</sub> O <sub>2</sub> (triplet)	2	-4.075332131	-0.661929865	-4.433554686
Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (quintet)	3	-1.6102162	-0.00308076	-2.460176298
Au <sub>8</sub> O <sub>2</sub> (singlet)	0	14.06813872	29.77610973	13.35568112

Table 7 represents the comparison of binding energies of various species. It is evident from the table that Au<sub>8</sub>O<sub>2</sub><sup>-</sup> anionic complex having one unpaired electron is showing about 30 kcal/mole (b-p functional) more favorable binding with Oxygen molecule than neutral species having no unpaired electron. Similar results are also reported by the calculations based on b3lyp (about 40 kcal/mole) and tpss (about 32 kcal/mole) functional.

Table 8 shows the calculated frequencies for O-O bond, which is least 1180.94 cm<sup>-1</sup> for the Au<sub>8</sub>O<sub>2</sub><sup>-</sup> (doublet) complex calculated using b-p functional while it is 1156.85 cm<sup>-1</sup> and 1153.29 cm<sup>-1</sup> for b3-lyp and tpss respectively.

Table 8: Frequency calculations with different DFT functionals

DFT func.	Au <sub>8</sub> O <sub>2</sub> (triplet)	Au <sub>8</sub> O <sub>2</sub> <sup>+</sup> (doublet)	Au <sub>8</sub> O <sub>2</sub> <sup>-</sup> (doublet)
$\nu_{O-O}$ (cm <sup>-1</sup> ) b-p	1368.44	1383.67	1180.94
$\nu_{O-O}$ (cm <sup>-1</sup> ) b3-lyp	1604.51	1578.91	1156.85
$\nu_{O-O}$ (cm <sup>-1</sup> ) tpss	1353.91	1376.88	1153.29

### Conclusion

From the above results, it is evident that the formation of Au<sub>8</sub>O<sub>2</sub><sup>-</sup>, anionic complex having one unpaired electron is more favorable as compared to its cationic or neutral counterparts. Similarly, Au<sub>8</sub>O<sub>2</sub>, neutral complex having no unpaired electron is least stable as compared to others. The O-O bond length is found to be maximum (1.30 Å) in Au<sub>8</sub>O<sub>2</sub><sup>-</sup>, anionic complex having one unpaired electron using tpss functional, which suggests that there is maximum charge transfer to O<sub>2</sub> in this case. If electron transfer accompanies the binding of O<sub>2</sub> to the Au cluster, the bond of the adsorbed O<sub>2</sub> will be longer than that of gaseous O<sub>2</sub>. The experimental value of O<sub>2</sub> bond length is 1.207 Å<sup>51</sup>. So we assume that the more extensive the electron transfers to O<sub>2</sub>, the longer the O-O bond of the adsorbed molecule. Furthermore, frequency calculations of O-O bond show that it is least for Au<sub>8</sub>O<sub>2</sub><sup>-</sup>, anionic complex having one unpaired electron. It means that there is effective activation of oxygen and thus Au<sub>8</sub>O<sub>2</sub><sup>-</sup>, anionic complex having one unpaired electron can be very useful in nanocatalysis of CO oxidation reaction. The results seem to act as a motivation for further theoretical and experimental studies.

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### End Notes

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