Global Journal of Advanced Engineering Technologies and Sciences

A THEORETICAL STUDY OF CHLORINE MOLECULE ADSORPTION ON Au CLUSTERS

Nkechi E. Ibisi*[12], Zhenyu Li[1], Anthony I. Onuchukwu[2], Jinlong Yang[1]
*[1]Hefei National Laboratory For Physical Sciences in Microscale, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China.
[2]College of Natural and Applied Sciences, Michael Okpara University of Agriculture Umudike. P. M. B 7267 Umuahia. Abia – State, Nigeria.

Abstract

Adsorption of chlorine molecule on cationic, neutral, and anionic Au_n (n=1−6) clusters have been studied using density functional theory to find the adsorption structure and energy, charge population, and vibrational frequency. Comparative results are obtained using the PW91 exchange-correlation functional and the B3LYP hybrid functional. Calculations show a pronounced sensitivity to cluster size and charge state. Adsorption energy of Cl_2 is above 0.2 eV on all clusters, indicating that the adsorption is energetically favorable. The adsorption energies of cationic clusters decrease as the cluster size increases. An even-odd oscillation of the adsorption energy is observed for neutral clusters, in which the odd clusters were observed to favor dissociative adsorption. Adsorption energy for the anionic clusters was found to be consistently high in the range of 2.4 - 4.5 eV with the exception of Au_3^- cluster. Effects of the strength of interaction between Cl_2 and Au_n on charge transfer and Cl-Cl stretching frequency are also discussed. In addition Au_3Cl_2 cluster showed an extraordinary stability amongst the studied clusters which was further explained based on structural planarity, binding energy of Cl_2 molecule on the clusters and energetics of its nearest neighbours. Our results demonstrate the possibility of electronic structure engineering by cluster size control.

Keywords: Au Clusters, Chlorine Molecule, Density functional theory(DFT), Adsorption

Introduction

Experimental and theoretical studies have been devoted to unveiling the catalytic mechanism of nanosized gold clusters. [1-7] Reports from these studies have shown compelling evidence that their chemical activity is hinged on their unique cluster size effect, contact structure, and support selection. These observations have made it a growing choice of catalytic materials.

Bulk gold is chemically inert and is generally regarded as a poor catalyst. Interestingly, it is found that gold clusters smaller than 3-4 nanometers catalyze various reactions with high efficiency even below room temperature. [8,1] Some of the properties of gold-based catalyst such as low operation temperature and high efficiency have potential for positive environmental and economic impact, especially in CO oxidation which served as a model reaction and application. [6] Furthermore, studies of supported clusters have found that the stoichiometry of metal oxide substrate has a significant effect on the CO oxidation, [9, 7, 10] suggesting that catalytic reactivity of gold cluster is influenced by the clusters' charge state.

Häkkinen and Landman [11] and Grönbeck and Andreoni [12] both conducted studies on neutral and anionic clusters using density functional theory to predict the ground-state structures of the clusters. Häkkinen and Landman[11] also reported the structural sensitivity of neutral and anionic clusters and the dominant planarity in which he noted that three dimensional structures (3D) are preferred for $N \geq 8$. As a further example, Gilb *et al.* performed ion mobility measurements and density functional calculations of small gold cluster cations (Au_n^+, n<14) with focus on ion mobility using density functional calculations to generate and probe the minimum energy isomers. [13] In fact, Nijamudheen and Datta [14] have shown the effect of charging on the structural and electronic properties of small gold clusters containing 2-20 atoms by partitioning the total energy into various components like nuclear-nuclear repulsion (ENN), electron-nuclear attraction (EEN), electron-electron repulsion (EEE), and kinetic energy (EKE).

Reactivity of free gold clusters (Au_n) and its dependence on both size and charge states of the clusters were studied both experimentally and theoretically. For example, Cox *et al.* [15] investigated the reactivity of small neutral, cationic and anionic gold clusters towards hydrogen, methane and oxygen. They found that hydrogen reacts readily with small gold cations whereas anionic clusters are reactive to oxygen. Wallace and Whetten [16] studied the pressure dependent adsorption activity of CO on Aun- (n=4-19) which showed a strong size dependence of both adsorption activity and saturation. Ding *et al*. performed a theoretical study on adsorption behavior of nitric oxide molecule on Aun clusters (n=1-6) [17] as well as molecular nitrogen adsorption on Aun clusters of the same number of atoms [18] using density functional theory calculations to predict the adsorption trends varying due to charge transfer.

In spite of the above mentioned studies there are still other challenges in gold catalysis and of a particular interest is the interaction of chlorine and gold. Chlorine adsorption on gold has been considered as an important gas-solid interaction system with an evolving focus on Au catalysis where both gold and chlorine are often involved. [19, 20] For example gold is found to be especially active towards catalytic oxidation of mercury by chlorine [19] and has shown potential commercial applications in environmental mercury removal. [21]

Gold chloride is used as homogeneous catalyst for a number of important organic reactions including intramolecular cyclizations and cross cycloisomerization reactions. [22, 23] Chlorine is also used as a lixiviate for gold and its adsorption on Au (111) electrode has been studied electrochemically. [24] Recently, Pinnaduwaje *et al.* [20] reported that there is increase in the selectivity for olefin epoxidation due to the presence of Cl on Au, which indicates that chlorine may be an effective promoter for enhancing the selectivity of Au-based catalyst used in heterogeneous epoxidation of olefins.

Despite these indications, the detail on how chlorine interacts with gold is still unclear. A number of experimental and theoretical studies have reported chlorine interaction with Au surface. Based on surface studies, potential binding sites of chlorine on gold surface includes flat terrace sites and different types of defect sites. [25]

Defects and under coordinated gold atoms are especially important to understand catalysis since these sites are thought to be more reactive and are often the active sites on a surface. [25] Having considered interaction of chlorine on a surface there is a lack of direct experimental and theoretical evidence on chlorine interaction on Au clusters. Clusters have low coordination and are less symmetric due to their limited sizes. This cluster characteristic affects the electronic properties of the atom and can lead to unusual chemical properties.

In this work, we report a comprehensive study based on DFT for the adsorption of chlorine molecule on Aun clusters, focusing on size of (n=1-6). We investigate the interaction by comparing the adsorption energy of chlorine molecule on neutral, cationic and anionic clusters. We observe that anionic clusters have a stronger interaction with chlorine molecule and the Cl-Cl bond length is greater than >2.4eV for all studied clusters. However, the neutral clusters prefer dissociation adsorption for odd numbered clusters while the adsorption energy decrease as the cluster size increases for cationic clusters. Besides the cluster size, we also considered the charge transfer interaction between Au cluster and chlorine and the weakening and elongation of Cl-Cl bond which are essential factors for adsorption.

Computational Details

The density functional theory (DFT) results were obtained with the Gaussian 03 package using the generalized gradient approximation (GGA) and the hybrid functional. [26] The Perdew-Wang parameterization (PW91) of the gradient corrected exchange-correlation energy was used in GGA,[27] while the Becke's three parameters hybrid functional (B3LYP) was used in the hybrid DFT.[28]

The basis set LANL2DZ and the corresponding Los Alamos relativistic effective core potential (RECP) were used to take into account the scalar relativistic effects including mass velocity and Darwin corrections for heavy gold atom,[29] while 6-311+G(3df) basis set was used for chlorine which includes polarization and diffuse functions.

Geometry optimizations of several isomeric structures were carried out until the gradient forces vanished with respect to the threshold value of 0.00045a.u, and all calculations performed with (75,302) pruned grid. Analysis of vibrational frequency was performed to ensure optimized geometries as minima not as transition structures. A scale factor of 0.9614 for B3LYP vibrational frequency was used as common. [30]

All adsorption energies were corrected taking into account the effects of basis set superposition error (BSSE) estimated by using the counterpoise corrections method [31] and the spin contamination was found negligible.

We used the natural population analysis (NPA) [32] to calculate the populations and information of whether the charge transfer exists in the adsorption process. [32, 33] Since the 6–311+G(3df) basis set used in the calculation involves polarization and diffuse functions, the NPA charge analysis is more appropriate than Mulliken population analysis. [34]

RESULTS

The optimized ground state structures of free Au_n cluster (n=1-6) were first considered which showed dominantly planar structures, this is attributed to strong relativistic bonding effects [35] that reduce the s – d energy gap thereby inducing the hybridization of the atomic 5d - 6s levels and causing overlap of the 5d shells of neighbouring atoms in the cluster. The planar structures is in good agreement with previous studies reported by Häkkinen and Landman [11], Grönbeck and Andreoni [12] and the lowest energy isomer cationic structures of Gilb *et al*. [13]. These results were further supported by Furke *et al.* who used ion mobility measurements and density functional calculations to find energetically favorable structures for anionic clusters. [36]

Some parameters of chlorine molecule such as electron affinity (EA), ionization potential (IP), bond length, dissociation energy (De) and vibrational frequency were investigated, we observed that theoretical results by both B3LYP and PW91 with 6 – 311+(3df) basis set are in good agreement with experimental results Ref. [38–40]. To check the accuracy of the computational methods used for this investigation, we have also performed the calculations for Au_2 and AuCl, which is of importance to the Au and chlorine interaction. The calculated Au_2 bond length with B3LYP and PW91 is 2.57Å and 2.55Å. These values are in excellent agreement with previous DFT studies with the same functional and basis set (B3LYP/LANL2DZ) by Sankaran *et al.* for Au2 (2.57Å) [41] and it also compared favorably with a higher level coupled cluster calculation by Wesendrup, Hunt and Schwerdtfeger Au2 (CCSD 2.517Å, CCSD(T) 2.512Å).[42] Our DFT Au_2 bond length is ~0.1Å above the experimental result 2.47Å [49],[52],[38].

For AuCl, the calculated bond length is 2.26 Å (B3LYP) and 2.24 Å (PW91) while the experimental value is 2.23 Å.[43]. We also compared our results with those based on coupled cluster calculation and MP2 method and it shows good agreement. For example Schulz and Hargittai reported AuCl bond length calculated with three different correlated theories: density functional with the B3LYP formalism, MP2 and CCSD(T) as follows: 2.293Å(B3LYP), 2.277Å(MP2), 2.293Å(CCSD(T)) [46] and it is in a good agreement with our results. The AuCl stretching frequency is calculated to be 333.7cm^{-1} for B3LYP and 344.7cm^{-1} for PW91, reasonably agreeing with the experimental value of 382.8cm^{-1}. Hargittai *et al.* (47) also carried out a B3LYP and MP2 level of calculation for this frequency, and they obtained 328 cm^{-1} for B3LYP and 353 cm^{-1} for MP2.

The dissociation energy for both Au_2 and AuCl compares favorably with experiment [45, 44] and previous high level theoretical studies. [46-47] These results are summarized in Table 1 and 2 together with the available experimental data.

Table 1. Bond lengths r, vibrational frequencies ω, dissociation energies D_e for neutral, anionic, and cationic Cl_2 molecule (designated as 0, –, + respectively). Electron affinities (EA) and ionization potentials (IP) of Cl_2 molecule are given in adiabatic values to compare with the available experimental data. (Units: r in Å, ω in cm^{-1} and energies in eV)

	B3LYP	PW91	EXPT.	Ref.
r0	2.011	2.008	1.988	[38]
r -	2.7071	2.6956	-	
r +	1.9087	1.9148	-	
ω0	540.5	533.5	559.7	[39]
ω-	203.2	196.6	-	
ω+	633.1	617.7	-	
De0	2.357	2.798	2.514	[38]
De -	1.152	1.786	-	
De +	6.156	6.815	-	
EA	2.84	2.67	2.38	[40]
IP	11.384	11.209	11.480	[39]

Table 2. Calculated Bond length R, Electron Affinity EA, Dissociation energy De and Frequency ω for Au2 and AuCl.

	R(Å)			**EA(eV)**			**De(eV)**			**ω(cm^{-1})**		
	B3lyp	Pw91	Expt.	B3lyp	Pw91	Expt.	B3lyp	Pw91	Expt.	B3lyp	Pw91	Expt.
Au_2	2.57	2.54	2.47[a]	1.94	2.12	2.02[e]	1.87	2.20	2.29[d]	162.2	168.9	190.9[a]
AuCl	2.26	2.24	2.23[b]				2.58	2.94	2.90±13[c]	333.7	344.7	382.8[a]

Ref: a [49][38],[52], b [43], c [44], d [45],[52], e[50]

GEOMETRIES

We optimized the geometries of $(Au_nCl2)^{+,-,0}$ (n=1-6) from as many started geometries including two and three dimensional structures in order to avoid trapping into local minima. We also performed the calculations with higher spin multiplicities to test the suitability of the spin multiplicity used in the calculation, and we confirmed that the lower spin multiplicities of 1 and 2 gave lower energies.

In all cases, 2D geometries are more stable than the 3D ones. Au atoms remain mostly in the Au plane except for few exceptions where the chlorine molecule departs from the Au plane. The preferred planarity of small gold clusters is attributed to relativistic effects which have been reported by Häkkinen *et al.* [48] and other previously published work. [35]

CATIONIC CLUSTERS

The optimized geometries of cationic Au_n clusters using B3LYP and PW91 functionals gave similar geometries as observed in Fig. 1 and Fig. 2 respectively. Structures of the free Au clusters were not distorted upon chlorine molecule adsorption except some variations of the bond lengths, dihedrals (internal co-ordinates changed). It is interesting that in the optimized geometries there is a bent angle of Au – Cl – Cl which is around 100° – 117° in all the clusters. The cationic geometric structure of Cl_2 on Au_n clusters (n = 1 – 6) is very similar to that observed for NO adsorbed on Au_n clusters. [17] This geometry is favorable for overlap between the $p\pi^*$ orbital of Cl_2 and $d\sigma + sp$ hybridized orbital of Au.

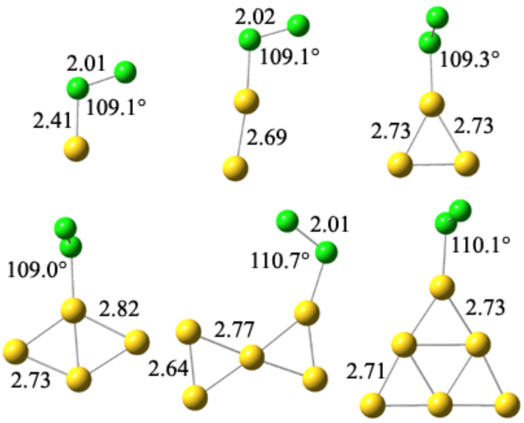


Fig.1 Optimized geometries of cationic Au_n clusters (n = 1 – 6) using B3LYP functional.

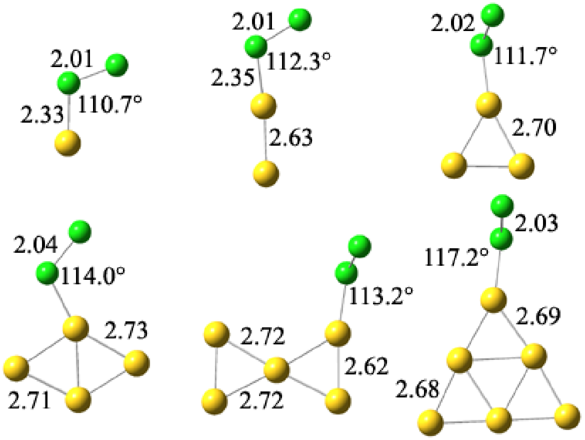


Fig. 2 Represents geometries of cationic Au_n clusters (n = 1 – 6) using PW91 functional

NEUTRAL CLUSTERS

Fig. 3 and 4 represents the optimized geometries of neutral Au_n clusters (n = 1 – 6) using B3LYP and PW91 functionals. For Au_3 and Au_5 clusters Cl_2 molecule dissociated into atoms instead of adsorbing as a molecule. When a molecule dissociates, the breaking species form a chemical bond per atom, which leads to stronger binding energy. The rest of the optimized geometries have a bent angle of Au – Cl – Cl which is between 103° – 157° with the exception of B3LYP Au_1 which has similar Au-Cl bond lengths of 2.27Å as Au_3 and Au_5.

We found two structures of Au_4Cl_2, with a Y shaped and rhombic gold structure. The latter had a slightly lower energy. One of the chlorine atoms caps at the side of the rhombus, showing a similar structure as that of the ground state geometry of free Au_5 cluster. The Au-Au bond lengths varies between 2.68 and 2.77Å while the expanded Au-Au bond length of rhombic structure after Cl_2 molecule attached is 3.49 Å.

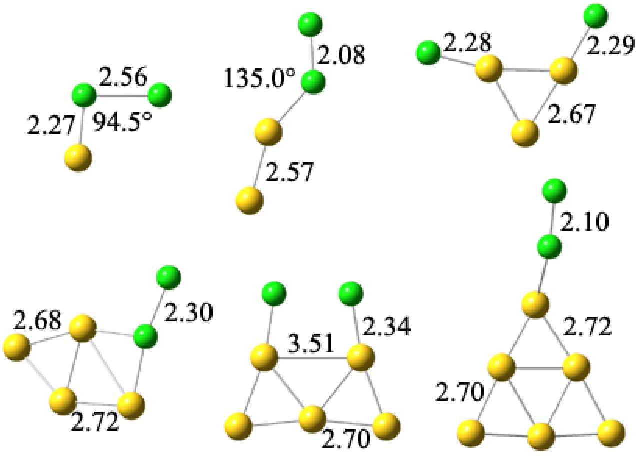


Fig. 3 Optimized geometries of neutral Au_n clusters (n = 1 – 6) using B3LYP functional.

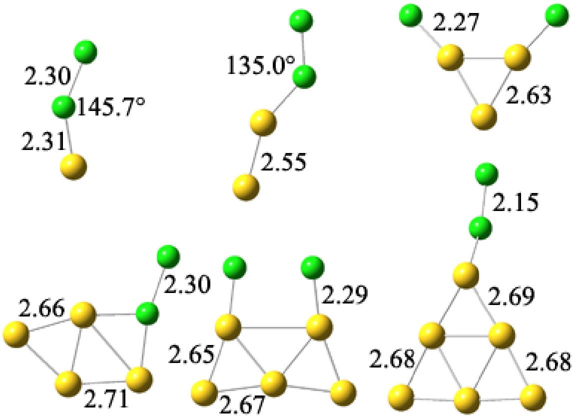


Fig. 4 Represents geometries of neutral Au_n clusters (n = 1 – 6) using PW91 functional

ANIONIC CLUSTERS

As shown in Fig. 5 and 6, the optimized geometries of anionic Au_n clusters (n = 1 – 6) have a bent angle for Au – Cl – Cl with n = 2 – 5 and a straight Au – Cl – Cl line with n =1. The distance between Au and the nearest Cl (D_{Cl-Au}) atom is between 2.53Å to 2.38Å and the distance between the Cl-Cl (D_{Cl-Cl}) is 2.65Å-2.94Å for all clusters with the exception of Au_3 which has a D_{Cl-Cl} of 2.42Å.

The anionic clusters have a stronger interaction with Cl_2 molecule and Cl-Cl bond length is greater than >2.40 even though it is a molecular adsorption. The additional electron in the anionic state of the clusters is strongly localized on Cl_2 molecule further activating the Cl-Cl bonding and decreasing the stretching frequencies, this alters the bond length significantly. A similar pattern is reported on interaction of O_2 with anionic gold clusters by Yoon *et al* [51].

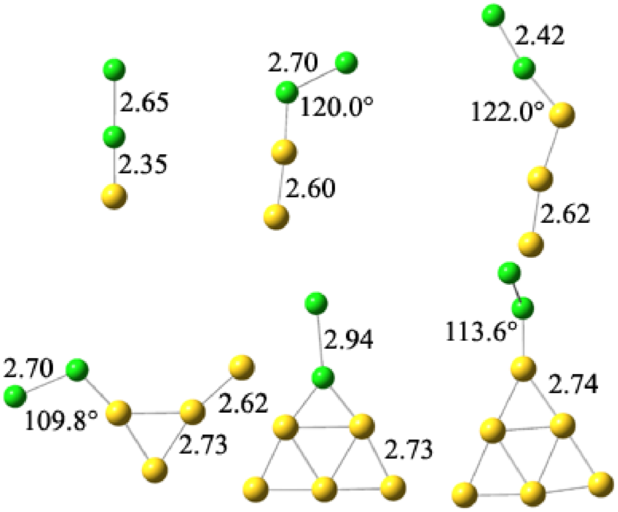


Fig. 5. Optimized geometries of anionic Au_n clusters (n = 1 – 6) using B3LYP functional.

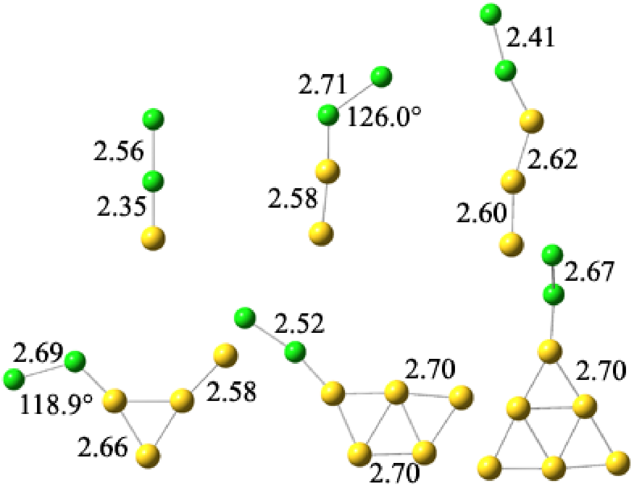


Fig. 6. Optimized geometries of anionic Au_n clusters (n = 1 – 6) using PW91 functional.

Table 3. The calculated results for Cl_2 adsorption on Au_n clusters (n = 1 - 6). Spin multiplicity S, Adsorption energy Ead, Cl_2 bond length r, NPA charge population on Cl_2 molecule qCl_2, Vibrational frequency of Cl_2, ωCl_2 are given. (Units: Ead in eV, r in Å and ω in cm^{-1})

	B3LYP					**PW91**				
$Au_nCl_2^+$	**S**	**Ead**	**R**	**qCl_2**	**ωCl_2**	**S**	**Ead**	**R**	**qCl_2**	**$^{\omega}Cl_2$**
1	1	1.23	2.012	0.20	511.473	1	1.62	2.010	0.24	496.423
2	2	0.77	2.016	0.16	514.243	2	1.05	2.014	0.21	490.805
3	1	0.65	2.017	0.15	515.587	1	0.89	2.023	0.16	489.411
4	2	0.62	2.015	0.20	520.249	2	0.88	2.038	0.19	442.247
5	1	0.46	2.020	0.12	511.179	1	0.74	2.029	0.13	476.714
6	2	0.44	2.014	0.14	519.698	2	0.65	2.026	0.16	473.268
Au_nCl_2										
1	2	2.34	2.755	-0.59	167.219	2	1.19	2.299	-0.56	199.350
2	1	0.38	2.084	-0.04	400.154	1	0.77	2.124	-0.09	371.525
3	2	6.38	-	-0.92	-	2	8.45	-	-0.80	-

4	1	0.66	2.302	-0.40	261.192	1	1.04	2.298	-0.38	283.545
5	2	4.33	2.817	-0.65	152.383	2	4.58	2.994	-0.65	120.32
6	1	0.22	2.104	-0.17	375.721	1	0.59	2.154	-0.20	349.072
$Au_nCl_2^-$										
1	1	3.68	2.647	-1.00	133.385 263.275	1	3.57	2.556	-0.96	145.425 266.539
2	2	2.40	2.700	-0.76	252.578	2	2.50	2.709	-0.76	277.474
3	1	1.95	2.422	-0.71	262.582	1	2.22	2.405	-0.70	290.200
4	2	3.76	2.696	-0.87	195.230	2	3.74	2.695	-0.76	166.270
5	1	4.39	2.937	-1.20	93.431 264.470	1	3.92	2.937	-1.09	292.783
6	2	3.89	2.691	-0.80	193.705	2	3.73	2.672	-0.78	177.145

ADSORPTION ENERGY

The adsorption energies (Ead) of Cl_2 molecule adsorption on cationic, anionic and neutral Au_n clusters were calculated based on the optimized geometries and it is defined as the energy difference between the adsorption system with individual cluster and chlorine molecule which is represented as the following equation.

$$\mathbf{Ead = [E_{Au\ Cluster} + E_{Cl2}] - E_{Adsorption\ System}}$$

The results are listed on Table 3. Adsorption energy as a function of cluster size for $Au_nCl_2^{+,-,0}$ was plotted in Figs.7-9. For each charge state, the result of the calculation using B3LYP and PW91 exchange – correlation functionals are compared. PW91 typically gave a higher adsorption energy value. However the adsorption energies calculated with the two functionals show very similar behaviors as a function of cluster size. This suggests that adsorption trends should have been correctly predicted by both functionals. The adsorption energies of the cationic clusters decreased as the clusters size increased. As the cluster size increased the change in adsorption energy became increasingly smaller for cationic clusters.

For the neutral clusters there is an even and odd oscillation in which the odd numbered cluster favored a dissociative adsorption. The bond length of Au-Cl becomes very small and the interaction between Cl-Cl is greatly reduced as Au-Cl becomes stronger. The adsorption energy of anionic clusters is between 2.4 - 4.4eV with the exception of $Au_3Cl_2^-$ which is 1.95eV for B3LYP and 2.2eV for PW91. We observed that the anionic Au_3 cluster has the biggest electron affinity relative to the other anionic gold clusters as a result the adsorption energy is small.

There is relatively remarkable adsorption for the clusters of different charge states since none of the clusters had adsorption energy less than 0.2eV.

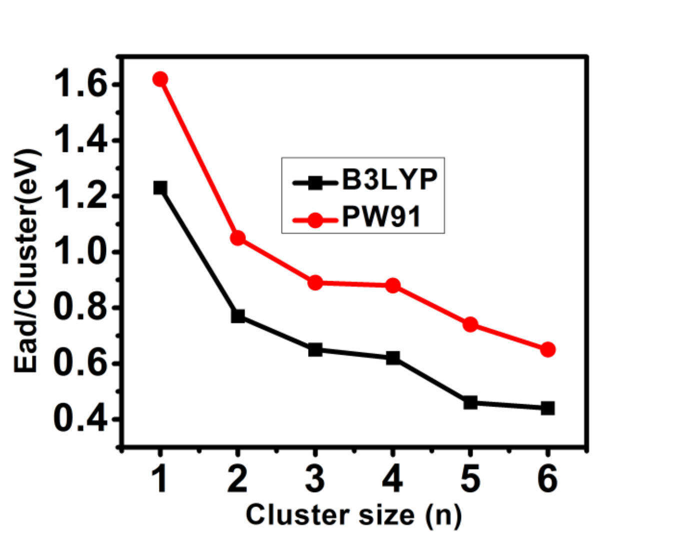


Fig. 7 Adsorption Energy of Cationic Au_nCl_2 Clusters (n=1-6)

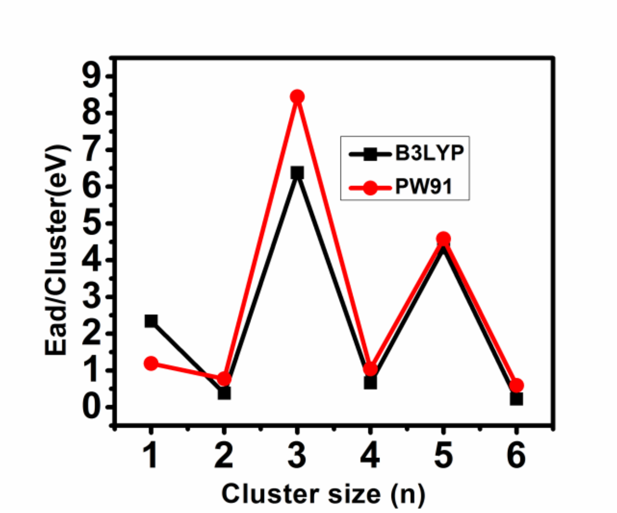


Fig. 8 Adsorption Energy of Neutral Au_nCl_2 Clusters (n=1-6).

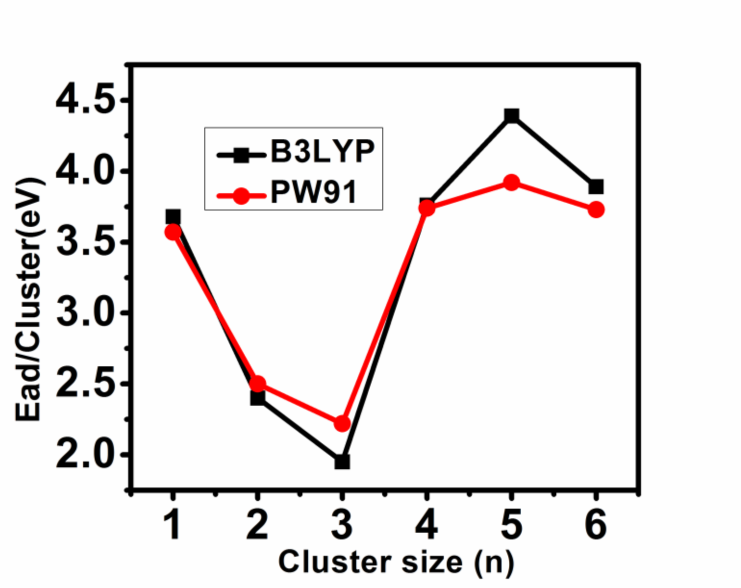


Fig. 9 Adsorption Energy of Anionic Au_nCl_2 Clusters (n=1-6)

CHARGE TRANSFER AND VIBRATIONAL FREQUENCY

Charge transfer is crucial for enhanced catalytic ability, it is also an essential factor to determine the Cl_2 molecule adsorption behavior on the ionic clusters such as Au_n cluster (n=1-6). When the charge transfer occurs, Pπ* antibonding orbital of Cl_2 will be filled by more electrons so the Cl-Cl bonding will be weakened as a result Cl_2 bond length will be elongated and vibrational frequency of Cl_2 bond will be decreased, this trend is observed on all charge states.

Vibrational modes can be divided into three classes, those involving Au and Cl ($AuCl_2$ mode), Cl – Cl stretch (Cl_2 mode) and Au modes which gave relatively small frequencies all less than 200cm^{-1}. The highest vibrational frequency (>500cm^{-1}) corresponds to the Cl_2 mode. When the interaction between Au atoms and Cl molecule is weak the vibration frequency is higher, and when it is strong the vibration frequency is lower. For the cationic clusters the Cl_2 bond lengths are between 2.01-2.02Ǻ and all there vibrational frequencies of Cl_2 bond are between 442.2 and 496.4cm^{-1} for PW91 calculations.

For neutral clusters, all the even numbered clusters had low Cl-Cl bond length below 2.3Ǻ and there vibrational frequencies are larger than 260cm^{-1} while the odd numbered clusters had elongated Cl-Cl bond lengths and

appreciably smaller vibrational frequency. The Au_3Cl_2 Cl-Cl bond length is peculiar because of the dissociative adsorption that took place and these accounts for the very strange value of the adsorption energy.
For anionic clusters with exception of $Au_3Cl_2^-$, all the Cl-Cl bond lengths are between 2.6-2.9 Å so their vibrational frequency is low. The $Au_3Cl_2^-$ also showed a peculiarity, the Cl-Cl bond length is 2.4Å, which gives a subsequently higher vibrational frequency. It is noteworthy to mention that two asymmetric Cl-Cl vibrational modes were observed for anionic $AuCl_2$ and Au_5Cl_2.

STRUCTURE AND RELATIVE STABILITY OF NEUTRAL Au_3Cl_2 CLUSTER

Binding energies of molecular chlorine on Au_2, Au_3 and Au_4 Clusters

The binding energy of nanostructures is very important for its structural and electronic properties. Thus the binding energies of the chlorine molecules to the neutral gold clusters Au_2, Au_3 and Au_4 has been calculated to evaluate the stability of Au_3 cluster. Stable clusters can be identified by a higher stability as compared to its nearest neighbors. Therefore the binding energies of molecular chlorine on Au_2, Au_3 and Au_4 clusters were determined by the following equation below and the results are summarized in Table 4.

$$BE = E[Au_n] + E[Cl_2] - 2E[Au_nCl_2]$$

Here n is equal to 2, 3, 4 whereas E[Au], $E[Cl_2]$ and $E[Au_nCl_2]$ represents the total energies of the most stable Au_n, Cl_2 and Au_nCl_2 respectively. If Cl_2 does not bind to a gold cluster as molecular chlorine, it can still bind as two separate chlorine atoms, as long as the reactants have sufficient energy to break the Cl–Cl bond. The values of our calculated results have shown that Au_3 has a higher binding energy value to chlorine molecule compared to Au_2 and Au_4 and the greater the binding energy, the more stable the nucleus. It has also been demonstrated by Li *et al* that the binding energy of bare gold clusters increases with an increase in the size of gold clusters [62]. Increasing binding energy means increasing stability due to enhanced core electron configurations. Whereas when molecular chlorine combines with Au_n (n=2-4), the binding energy of molecular chlorine on Au_2, Au_3 and Au_4 increases thus: $Au_2<Au_4<Au_3$ as can be noted from Table 4.

The Au_3Cl_2 cluster showed an unusual high stability in spite of having an odd number of electrons. The results suggest that the Cl_2 molecule incorporated into the bare Au_n changed the structural stability and it is worth noting that the binding energy of AuCl is greater than Au_2.The bond lengths are 2.57 and 2.23eV for Au-Au and Au-Cl, the shortening of bonds due to relativistic effects is especially pronounced in the monohalides of gold as observed in Au-Cl. This is due to the pronounced contraction of 6s orbital in the d^{10} electronic configuration of gold.

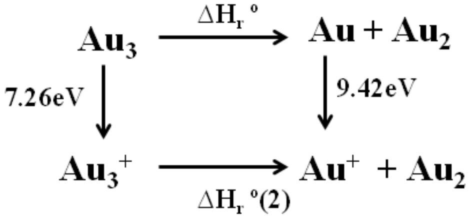
The minimum energy structure of Au_3Cl_2 has two Au-Cl bonds and this would likely have contributed to the enhanced stability of the structure while Au_2Cl_2 and Au_4Cl_2 have one Au-Cl bond each in the geometric structure. This is because stable isomers as observed in Au_3Cl_2 tend to equally delocalize valence electrons of the constituent atoms over the entire structure and maximize the number of Au-Cl bonds in the structure.

Energetics of gas phase gold clusters of Au_2, Au_3 and Au_4

On this basis we first determined the atomization energies of Au_2[1.87(B3lyp),2.20(Pw91)] and Au_3[2.75(B3lyp),3.41(Pw91)], by combining values of these results one can easily obtain the enthalpy of reaction for Au_3.

$Au_3 = Au_2 + Au$

$\Delta H_r{}^o$= Enthalpy of reaction



From our results we obtained 1.21eV (PW91) for the enthalpy of reaction ($\Delta H_r{}^{o}$) as compared to the experimental value of 1.51 ± 0.13eV[61] and the ionization energies of Au_3 and Au are 7.26eV and 9.42eV respectively while the experimental results are 7.27 ± 0.15eV and 9.26 ± 0.1eV[59].

Table 4. Binding energies (BE) of Cl_2 on Au_2, Au_3, Au_4 in the neutral clusters Au_2Cl_2, Au_3Cl_2, and Au_4Cl_2, Electron affinities (EA), Ionization energies (IE) and Atomization energies (AE) of Au_2, Au_3 and Au_4 in (eV).

	B3lyp	**Pw91**	**B3lyp**	**Pw91**	**Expt.**	**B3lyp**	**Pw91**	**Expt.**	**B3lyp**	**Pw91**	**Expt.**
	BE		**AE**			**IE**			**EA**		
Au_2	0.38	0.77	1.87	2.20	2.29 ± 0.02^{c}	9.43	9.59	9.5 ± 0.3^{e}	1.94	2.12	2.02^{i}
Au_3	2.49	3.03	2.75	3.41	3.80 ± 0.13^{d}	7.26	7.37	7.27 ± 0.15^{f}	3.68	3.78	3.9^{a} $3.4 - 3.95^{b}$
Au_4	0.66	1.05	4.66	5.81	-	7.94	8.11	8.6^{g}	2.62	2.86	2.58^{h}

c[54], d[55], e[60] f[59] g[56] h[60] a[57] b[60] i[50]

CONCLUSION

In conclusion using DFT with both GGA and hybrid functional, we have given a systematic theoretical study of chlorine molecule adsorption on gold clusters($(Au_nCl_2)^{+,-,0}$ (n=1-6). Based on the carefully optimized geometries, we have calculated the adsorption energies and analyzed the corresponding adsorption possibilities. Charge transfer between Au clusters and chlorine molecule and also the corresponding weakening and elongation of Cl-Cl bond have been observed. The results show that by controlling the size of the clusters one can also control the property of materials to some degree.

In particular Au_3Cl_2 cluster showed an extraordinary stability amongst the studied clusters which was further explained based on the structural planarity, binding energy of Cl_2 molecule on the clusters and energetics of its nearest neighbors. Stable isomers as observed in Au_3Cl_2 tend to equally delocalize valence electrons of the constituent atoms over the entire structure and it also maximized the number of Au-Cl bonds in the structure.

In particular Au_3Cl_2 cluster showed an extraordinary stability amongst the studied clusters which was further explained based on the structural planarity, binding energy of Cl_2 molecule on the clusters and energetics of its nearest neighbours.

Acknowledgment

This work is partially supported by MOST (2011CB921404), NSFC (21121003 and 91021004), and by USTCSCC, SCCAS, and Shanghai Supercomputer Centers.

References

1. M. Valden, X. Lai, D.W. Goodman, Science 281, 1647 (1998)
2. W. T. Wallace, R. W. Whetten, J. Am. Chem. Soc. 124, 7499 (2002)
3. H. Häkkinen, U. Landman, J. Am. Chem. Soc. 123, 9704 (2001)
4. M. Haruta, Catal. Today 36, 153 (1997)
5. F. Boccuzzi, A. Chiorino, J. Phy. Chem. B, 104, 5414 (2000)
6. A. Sanchez, S. Abbet, U. Heiz, W. D. Schneider, H. Häkkinen, R. N. Barnett, and U. Landman, J. Phys. Chem. A 103, 9573 (1999)
7. H. Over and A.P. Seitsonen, Science 297, 55892003 (2002)
8. M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon, J. Catal. 144,175 (1993)
9. J. D. Grunwaldt, A. Baiker, J. Phys. Chem. B 103, 1002 (1999)
10. T. T. Magkoev, D. Rosenthal, S. L. M. Schroder, K. Christmann, Tech. Phys. Lett. 26, 894 (2000)
11. H. Häkkinen and U. Landman, Phys. Rev. B 62, R2287 (2000)
12. H. Grönbeck and W. Andreoni, Chem. Phys. 262, 1 (2000)
13. S. Gilb, P. Weis, F. Furche, R. Ahlrichs, and M. M. Kappes, J. Chem. Phys. 116, 4094 (2002)
14. A.Nijamudheen and Ayan Datta in *Proceedings of the International Conference on NanoScience, Technology and Societal Implications (NSTSI11) Bhubaneswar, India. 2011*, pp 1-5
15. D. M. Cox, R. Brickman, K. Greegan, A. Z. Kaldor, Z. Phys. D 19, 353 (1991)
16. W. T. Wallace, R. L. Whetten, J. Phys. Chem. B 104, 10964 (2000)
17. X. Ding, Z. Li, J. Yang, J. G. Hou, Q. Zhu, J. Chem. Phys. 121, 2558 (2004)

18. X. Ding, J. Yang, J. G. Hou, Q. Zhu, J. Mol. Struct. Theochem 755, 9 (2005)
19. Y. X. Zhao, M. D. Mann, J. H. Pavlish, B. A. F. Mibeck, G. E. Dunham, E. S. Olson, Environ. Sci. Technol. 40, 1603 (2006)
20. D. S. Pinnaduwage, L. Zhou, W. Gao, C. M. Friend, J. Am. Chem. Soc. 129, 1872 (2007)
21. R. Burks, Chem Eng. News 85, 87 (2007)
22. A. S. K. Hashmi, T. M. Frost, J. W. Bats, J. Am. Chem. Soc. 122, 11553 (2000)
23. A. S. K. Hashmi, L. Schwarz, J. H. Choi , T. M. Frost, Angew. Chem. Int. Ed. 39, 2285 (2000)
24. Z. C. Shi, S. J. Wu, J. Lipkowski, J. Electroanal. Chem. 384, 171 (1995)
25. T. A. Baker, C. M. Friend, E. Kaxiras, J. Chem. Phys. 129, 104702. (2008)
26. M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al* Gaussian 03, Revision B.04, (Gaussian, Inc., Pittsburgh PA. 2003).
27. J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46, 6671 (1992)
28. A. D. Becke, J. Chem. Phys. 98, 5648 (1993)
29. P. J. Hay, W.R. Wadt, J. Chem. Phys. 82, 270 (1985)
30. A. P. Scott, L. Radom, J. Phys. Chem. 100, 16502 (1996)
31. S. F. Boys, F. Bernadi, Mol. Phys. 10, 553 (1970)
32. E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, in *NBO Version 3.1* (Theoretical Chemistry Institute, University of Wisconsin – Madison. 1995)
33. A. E. Reed, L. A. Curtiss, F. Weinhold, Chem. Rev. 88, 899 (1988)
34. A. E. Reed, R. B. Weinstock, F. Weinhold, J. Chem. Phys. 83, 735 (1985)
35. P. Pyykkö, Chem. Rev. 88, 563 (1988)
36. F. Furche, R. Ahlrich, P. Weis, C. Jacob, S. Gilb, T. Bienweiler, and M. Kappes, J. Chem. Phys. 117, 6982 (2002)
37. H. Häkkinen, B. Yoon, U. Landman, X. Li, H.J. Zhai, L.S. Wang, J. Phys. Chem. A 107, 6168 (2003).
38. K. P. Huber, G. Herzberg, in *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules*, (Van Nostrand Reinhold, New York, 1979)
39. D. R. Lide, in *CRC Handbook of chemistry and Physics*, 86th edn. (CRC Press, Cleveland, OH. 2005)
40. P. S. Drzaic, J. Marks, J. I. Brauman, in *In Gas Phase Ion Chemistry*, edited by M. T. Bowers, (Academic Press, Orlando, 1984) pp 167.
41. M. Sankaran, B. Viswanathan, Bulletin of the Catalysis Society of India, 5, 26 (2006)
42. R. Wesendrup, T. Hunt, and P. Schwerdtfeger, J. Chem. Phys. 112, 9356 (2000)
43. E. S. Clark, D. H. Templeton, and C. H. MacGillavry, Acta Cryst. 11, 284 (1958)
44. Y.R. Luo, in *Comprehensive Handbook of Chemical Bond Energies*, (CRC Press, Boca Raton, Florida, 2007) pp 64-69
45. T. L. Cottrell, in *The Strengths of Chemical bonds*, 2d edn. (Butterworth, London 1958)
46. A. Schulz, M. Hargittai, Chem. Eur. J. 7, 3657 (2001)
47. M. Hargittai, A. Schulz, B. Réffy, M. Kolonits, J. Am. Chem. Soc. 123,1449 (2001)
48. H. Häkkinen, M. Moseler, U. Landman, Phys. Rev. lett. 89, 033401 (2002)
49. B. Simard, P. A. Hackett, J. Mol. Spectros., 142, 310 (1990)
50. K.J. Taylor, C.L. Pettiette-Hall, O. Cheshnovsky, R.E. Smalley, J. Chem. Phys. 96, 3319 (1992)
51. *B***.** *Yoon***,** *H***.** *Häkkinen***,** and U. Landman, J. Phys. Chem. A 107, 4066 (2003)
52. M. D. Morse, Chem. Rev. Washington, D.C. 86, 1049 (1986)
53. G. A. Bishea and M. D. Morse, J. Chem. Phys., 95, 5646 (1991)
54. K. A. Gingerich, Far. Symp. Chem. SOC. 14, 109 (1980)
55. K. Hilpert and K. A. Gingerich, Ber. Bunsenges. Phys. Chem. 84,739 (1980)
56. a) O. Chesnovsky, C. L. Pettiette, R. E. Smalley, Ion and Cluster Ion Spectroscopy and Structure (Ed.: J. P. Maier), Elsevier, Amsterdam, 1988; b) C. Jackschath, I. Rabin, W. Schulze, Ber. Bunsen-Ges. 96, 1200 (1992)
57. C. W. Bauschlicher, Jr., S. R. Langhoff, and H. Partridge, J. Chem. Phys. 91, 2412 (1989); C. W. Bauschlicher, *Ir.,* Chem. Phys. Lett. 156, 91 (1989).
58. M. A. Cheesman and J. R. Eyler, J. Phys. Chem. 96, 1082 (1992)
59. J. Ho, K. M. Ervin, and W. C. Lineberger, J. Chem. Phys. 93, 6987 (1990)
60. S. V. Kuzenetsov, Rapid Communications in Mass Spectrometry, 9, 191 (1995)
61. X. Li, H. Wang, X. Yang, Z. Zhu, Y. Tang, J. Chem. Phys. 126, 084505 (2007)