Geometry, chemical reactivity and Raman spectra of gold clusters

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Abstract: Structures, stability, and chemical reactivity of Au\textsubscript{n} (n = 2-10) clusters are investigated using density functional theory (DFT). We have studied the reactivity parameters of the clusters in terms of relevant electronic structure principles. It is observed that stability and properties are strongly dependent on the cluster size. Clusters with an even number of atoms are found to be energetically and chemically more stable than odd-numbered clusters. Electronic structure of clusters has been investigated using partial density of states (PDOS). PDOS analysis clearly shows that energy states of highest occupied molecular orbital and lowest unoccupied molecular orbital are predominantly contributed by s orbital. From time-dependent DFT calculations, it is shown that absorption spectra of even-numbered clusters are more intense and are observed at lower wavelength region than the odd-sized gold clusters.

Subjects: Chemical Physics; Computational and Theoretical Chemistry; Computational Physics; Materials Chemistry

Keywords: cluster; stability; chemical reactivity; density functional theory; Raman intensity; absorption spectra

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PUBLIC INTEREST STATEMENT
Clusters are aggregates of few atoms which exhibit unusual electronic, chemical and optical properties different from those of bulk materials and constituent atoms. They can play important role as building blocks in nano-scale electronic, nanocatalytic systems, optical and magnetic diagnostic devices. Generally, bulk gold is chemically inert but when reduced to nanometer size, they become reactive. Particularly, gold nanoparticles show high catalytic activity towards the oxidation of CO and hence they are of great importance to the industrial and scientific communities. Also, gold has been shown to exhibit surprising mechanical properties in nanoscale. These remarkable physical and chemical properties of gold come only in the reduced dimensions and they depend on the structure (size and shape) of the cluster. Experimental determination of cluster structure is quite difficult. Theoretical calculations help in determining the equilibrium geometries. It also helps in analyzing raw experimental data and sometimes, verifies experimental results.
1. Introduction
Gold clusters have been analyzed in various theoretical and experimental studies in recent years because of their important role as building blocks in nanoscale electronic (Fan & Bard, 1997; Häkkinen, Barnett, & Landman, 1999), nanocatalytic systems (Sanchez et al., 1999; Valden, Lai, & Goodman, 1998), optical and magnetic diagnostic devices (Claussen, Franklin, ul Haque, Porterfield, & Fisher, 2009; Sudeep, Joseph, & Thomas, 2005). Gold has been shown to exhibit surprising mechanical properties in nanoscale by forming stable nanowires and nanobridges with quantized electrical conductivity, which has great relevance in understanding atomic junctions (Agraït, Yeyati, & Ruitenbeek, 2003). As gold clusters can efficiently catalyze the CO oxidation reaction at low temperature, they are of great importance to the industrial and scientific communities (Chen, Crawford, & Hu, 2007; Lopez et al., 2004; Molina & Hammer, 2003). Moreover, it is reported that one can design gold clusters with tunable optical properties by simply changing their size (Zheng, Nicovich, & Dickson, 2007). The possibility of tuning cluster properties as a function of charge states has also been reported (Chaves, Rondina, Piotrowski, Tereshchuk, & Da Silva, 2014). Gold clusters also exhibit significant promise for the direct conversion of solar to chemical energy using photocatalysts (Linic, Christopher, & Ingram, 2011).

Since the remarkable properties of clusters come only in the reduced dimensions and also as these properties depend on the size and shape of the clusters (Singh, Bhattacharya, & Sarkar, 2013; Singh & Sarkar, 2014a, 2014b; Sarkar & Blundell, 2009), one has to understand their structure and their functionalities in quantum mechanical level. Small Au clusters have a tendency to form planar structures. Gas-phase mobility experiments indicate that Au cluster up to \( n = 12 \) have planar structure (Furche et al., 2002). Theoretical calculation predicted the two-dimensional structure of \( \text{Au}_n \) cluster up to \( n = 13 \) (Fernindez, Soler, Garzon, & Balbas, 2004; Weis, Bierweiler, Gilb, & Kappes, 2002). In comparison, other noble metal clusters become three-dimensional at lower cluster size (Baletto & Ferrando, 2005; Jug, Zimmermann, Calaminici, & Köster, 2002).

To study the cluster properties, one needs to have a good understanding of stability and electronic as well as geometrical configurations of the clusters. Knowledge of the reactivity property which is most vital for the catalytic applications of clusters is also required. Since there is no direct experimental method to observe atomic arrangements in cluster, alternative method is employed for determining cluster structures. Experimental measurements such as frequencies for Raman and IR spectra are compared with theoretically calculated frequencies for candidate structures. This method has been extremely helpful for determining gold cluster geometries (Claes et al., 2013; Gruene et al., 2008). This approach of structure determination can only be successful if we can accurately calculate and predict IR and Raman intensities for the clusters.

In this paper, we attempt to critically analyze various properties of \( \text{Au}_n \) clusters using density functional theory (DFT). DFT is one of the most common choices for the theoretical study of clusters since it has the best performance/cost ratio for systems with hundreds of valence electrons. Different exchange-correlation functionals and basis sets within the framework of DFT have been employed. We hope that our results will be helpful for other larger and similar clusters for their optimal utilization in many technological applications.

2. Theoretical background
Chemical reactivity and stability of atoms, molecules, and clusters can be successfully described using DFT. Within DFT framework, the ionization potential (IP) and electron affinity (EA) can be obtained from the total electronic energy calculations on the \( N - 1 \), \( N \), and \( N + 1 \) electron systems as

\[
\text{IP} = E(N - 1) - E(N) \tag{1}
\]

and

\[
\text{EA} = E(N) - E(N + 1) \tag{2}
\]
Chemical potential ($\mu$) (Parr & Yang, 1989) and chemical hardness ($\eta$) (Parr & Pearson, 1983) are determined in terms of IP and EA as

$$\mu = -\frac{\text{IP} + \text{EA}}{2}$$

(3)

$$\eta = \text{IP} - \text{EA}$$

(4)

Parr, Szentpaly, and Liu (1999) defined electrophilicity index ($\omega$) as

$$\omega = \frac{\mu^2}{2\eta}$$

(5)

The static electric dipole polarizability ($\alpha$) is a measure of the linear response of the electronic cloud of a chemical species to a weak external electric field. It represents a second-order variation of energy ($E$) with respect to the applied electric field ($F$) and is defined as

$$\alpha_{a,b} = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right); \quad a, b = x, y, z$$

and the static dipole polarizability is computed as the trace of the polarizability tensor as follows

$$<\alpha> = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

(7)

The cohesive energy is calculated as

$$E_{\text{coh}}(\text{Au}_n) = \frac{nE[\text{Au}] - E[\text{Au}_n]}{n}$$

(8)

The fragmentation energy is calculated as

$$\Delta E_1(\text{Au}_n) = E[\text{Au}_n] - E[\text{Au}_{n-1}] - E[\text{Au}]$$

(9)

To analyze the relative stability, the stability function is measured as

$$\Delta E_2(\text{Au}_n) = E[\text{Au}_{n+1}] + E[\text{Au}_{n-1}] - 2E[\text{Au}_n]$$

(10)

Raman intensity ($I_i$) of the clusters are calculated using the relationship (Krishnakumar, Keresztury, Sundius, & Ramasamy, 2004)

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i^4 \left[1 - \exp \left(-\frac{h v_i}{kT}\right)\right]}$$

(11)

where $v_i$ is the exciting frequency (in cm$^{-1}$ units), $v_i$ is the vibrational wave number of the $i$th normal mode, $S_i$ is the calculated Raman activities, $f$ is the normalization factor, and $T$ is the temperature. $h$, $c$, and $k$ are the Planck’s constant, speed of light, and Boltzmann constant, respectively.

### 3. Computational method

In cluster study, possibility of locating global minima geometry depends on the choice of initial structures. All possible initial structures should be considered to ensure that the true minimum is not missed. However, as the cluster grows in size the number of possible geometries becomes very large. It becomes quite difficult to search all the possible initial geometries for larger clusters. In this concern, commonly adopted approach includes genetic algorithm (Hartke, 1993; Heiles & Johnston, 2013), basin-hopping (Heiles & Johnston, 2013; Wales & Doye, 1997) and *ab-initio* molecular dynamics (Shah...
& Kanhere, 1996; Singh & Sarkar, 2014a, 2014b; St-Amant & Salahub, 1990)-based search for the possible candidate structures. Our choice of initial structure is based on two approaches. First, we have considered gold structures reported in previous studies (Assadollahzadeh & Schwerdtfeger, 2009; Baishya & Deka, 2011; Bhattacharjee, Mishra, & Deka, 2014; Fernindez et al., 2004; Grönbeck & Andreoni, 2000; Lee, Ge, Sahu, Tarakeshwar, & Kim, 2003; Li, Wang, Yang, Zhu, & Tang, 2007; Neogrády, Kellő, Urban, & Sadlej, 1997; Sárosi, Petrar, & King, 2013; Wang, Wan, & Zhao, 2002; Weis et al., 2002; Wells, Delgass, & Thomson, 2002; Wesendrup, Hunt, & Schwerdtfeger, 2000; Zanti & Peeters, 2010). In the second approach, we subjected initial cluster structures to constant-temperature 
ab-initio molecular dynamics run near the melting temperature of bulk gold. During molecular dynamics simulation, cluster evolves through various structural transformations. Based on low-energy criteria, some of these geometries having different structures are recorded. Ab-initio molecular dynamics simulation is performed using SIESTA 3.2 (Soler et al., 2002). Simulation is carried out in the NVT ensemble at 1,200 K and temperature is controlled using Nose thermostat. Newton’s equations of motion are integrated using Verlet algorithm and simulation is carried out for 5,000 fs (with a time step of 1.0 fs).

The theoretical study of gold clusters has been done using DFT. We have adopted B3LYP (Becke, 1993; Lee, Yang, & Parr, 1988) and B3PW91 (Becke, 1993; Perdew, 1986) exchange-correlation hybrid functional. B3LYP functional give consistent result for other transition metal clusters (German, Efremenko, & Sheintuch, 2001; Lacaze-Dufaure et al., 2011; Singh & Sarkar, 2014a, 2014b; Zacarias, Castro, Tour, & Seminario, 1999) and gold clusters (Baishya & Deka, 2011; Grönbeck & Andreoni, 2000; Wells et al., 2002). B3PW91 functional has also been reported to give accurate results for gold clusters (Assadollahzadeh & Schwerdtfeger, 2009; Neogrády et al., 1997; Sárosi et al., 2013; Wesendrup et al., 2000).

Appropriate choice of basis set is of prime importance in first principle treatment of metal clusters. The basis set should be capable of describing electronic properties accurately and at the same time provide affordable computational cost (i.e. time taken for computational calculation should not be too long). The number of electrons being treated explicitly should be limited to possible minimum level without compromising with accuracy of calculation. As we all know, relativistic corrections are also required for describing the inner core electrons for heavy transition metal like gold. LANL2DZ (Hay & Wadt, 1985) basis set is the most widely used and also proven to be appropriate for investigating transition metal clusters (including gold clusters) (Baishya & Deka, 2011; Grönbeck & Andreoni, 2000; Wells et al., 2002). B3PW91 functional also has been reported to give accurate results for gold clusters (Assadollahzadeh & Schwerdtfeger, 2009; Neogrády et al., 1997; Sárosi et al., 2013; Wesendrup et al., 2000).

The LANL2DZ explicitly deals with 19 valence electrons (5s² 5p⁶ 5d¹⁰ 6s¹) per Au atom through a split valence double-ζ polarized basis set. The remaining core electrons are taken into consideration through effective core potential (ECP) with relativistic corrections. The mass–velocity and Darwin relativistic corrections are incorporated to the potential through the method developed by Hay and Wadt (1985) in the Los Alamos National Laboratory. We have also considered another relevant basis set LAN2MB (Hay & Wadt, 1985; Wadt & Hay, 1985) which also treats valence electrons explicitly through a minimum basis set and core electrons through ECP with relativistic corrections. CAM-B3LYP functional (Yanai, Tew, & Handy, 2004) (which is Handy and co-workers’ long range corrected hybrid exchange-correlation functional using the Coulomb-attenuating method) has also been checked for its accuracy. CAM-B3LYP functional does not significantly alter cluster properties obtained from other functionals. The trend of property evolution with size remains the same. The results obtained with CAM-B3LYP functional are included in the supplementary material. Time-dependent density functional theory (TD-DFT) calculations are performed on the optimized geometry using the same functional and basis set. Using TD-DFT, excitations to 20 lowest transition states have been determined. DFT and TD-DFT calculations have been performed using Gaussian 09 program package (Frisch et al., 2010). For all the peaks in absorption spectra, we have taken a full-width at half maximum value of 1,000 cm⁻¹. For the calculation of Raman intensity, we have used GaussSum 3.0 (O’boyle, Tenderholt, & Langner, 2008).

4. Results and discussion
In order to test reliability of the methodology, we have calculated IP and EA of Au atom. The calculated IP values at different levels are 9.39 (B3LYP/LANL2DZ), 9.34 (B3LYP/LANL2MB), 9.35 (B3PW91/
LANL2DZ), and 9.31 eV (B3PW91/LANL2DZ). Calculated EA values are 2.17 (B3LYP/LANL2DZ), 1.63 (B3LYP/LANL2MB), 2.09 (B3PW91/LANL2DZ), and 1.57 eV (B3PW91/LANL2MB). We compare the calculated results with experimental IP value of 9.22 eV (Kittle, 1996) and EA value of 2.31 eV (Huheey, Keiter, & Keiter, 1993) for Au atom. Even though B3LYP/LANL2DZ slightly overestimates the IP value, the EA value calculated at this level of theory is closest to the experimental value. CAM-B3LYP/LANL2DZ calculation gives 9.25 (IP) and 1.95 eV (EA), while CAM-B3LYP/LANL2MB calculation gives these values as 9.19 (IP) and 1.47 eV (EA). It is seen that IP obtained using CAM-B3LYP functional is in close agreement with experimental value, but the EA values are underestimated from experiment. In the following sections, the reported structures and properties are calculated at B3LYP/LANL2DZ method if the method is not specifically mentioned.

The lowest energy structures for Au\(^n\) (\(n = 2–10\)) clusters are shown in Figure 1. All the lowest energy structures shown here have zero imaginary frequency, suggesting that they correspond to the minimum energy states in the potential energy surface. The geometry and electronic properties are sensitive to the exchange-correlation functional and basis set used. For Au\(_2\) dimer, the calculated bond lengths at different methods are 2.57 Å (B3LYP/LANL2DZ), 2.67 Å (B3LYP/LANL2MB), 2.54 Å (B3PW91/LANL2DZ), and 2.65 Å (B3PW91/LANL2MB). The experimental bond length of gold dimer is 2.47 Å (Weast, 1974). The bond lengths are overestimated in all the calculation methods. The bond length calculated at B3PW91/LANL2MB method is closest to the experimental value.

For Au\(_3\) trimer, the isomer with lowest energy is an obtuse angle triangle with C\(_{2v}\) symmetry. The bond angle and bond lengths of Au\(_3\) trimer are 140.72°, 2.64 Å (B3LYP/LANL2DZ), 140.55°, 2.73 Å (B3LYP/LANL2MB), 140.65°, 2.61 Å (B3PW91/LANL2DZ), 137.43°, and 2.72 Å (B3PW91/LANL2MB). Similar structure was observed for Au\(_3\) in other studies (Fernández et al., 2004; Lee et al., 2003).

The lowest energy structure for Au\(_4\) tetramer is a capped triangle with C\(_{2v}\) symmetry. Zanti and Peeters (2010) also found capped triangle is lower in energy than the trapezoid structure using B3LYP/LANL2DZ, and use of another functional like PW91 revert the order. In the present study, capped triangle geometry has 0.07 eV (B3LYP/LANL2DZ), 0.17 eV (B3LYP/LANL2MB), 0.02 eV (B3PW91/LANL2DZ), and 0.19 eV (B3PW91/LANL2MB) lower energies than the trapezoid. For Au\(_n\), the structure with lowest energy is W-shaped with C\(_{n}\) symmetry at all levels of calculations. This obtained structure is consistent with other DFT calculations (Grönbeck & Andreoni, 2000; Wang et al., 2002; Zanti & Peeters, 2010). The most stable structure for Au\(_5\) is a planar triangle with D\(_{3h}\) symmetry as is the case in most of the DFT studies (Wang et al., 2002; Zanti & Peeters, 2010). For Au\(_n\), the lowest energy structure is a side-capped triangle. The structure can be seen as the adsorption of Au atom on triangle planar
structure of Au$_6$. In the case of Au$_8$, the ground state structure is a capped planar rhombus with D$_{4h}$ symmetry. The most stable structure for Au$_9$ is a planar bicapped hexagon having C$_{2v}$ symmetry. The transition from two dimensional to three-dimensional structures occurs at $n > 9$. The tendency of gold clusters to adopt planar structures up to a large cluster size may be attributed to the relativistic effects (Hakkinen, Moseler, & Landman, 2002). Strong hybridization of 5$d$ and 6$s$ orbitals due to relativistic effects allows 5$d$ electrons to easily participate in bonding (Hakkinen et al., 2002). This feature leads to planar geometry of gold clusters (Hakkinen et al., 2002).

In Figure 2, the cohesive energy of Au$_n$ clusters is displayed. Generally, the LANL2MB basis set gives 0.2–0.3 eV lower $E_{coh}$ than LAN2DZ. The experimental cohesive energy for gold dimer is 1.10 eV (Billings & Gray, 1972). In this study, B3PW91/LANL2DZ method gives 0.96 eV, while other calculation methods further underestimate the cohesive energy value of Au$_2$. In general, larger clusters have higher cohesive energy, suggesting greater delocalization (conjugation) of the electrons (Nijamudheen & Datta, 2010). The fragmentation energy ($\Delta_1E$) is shown in Figure 3(a) and $\Delta_1E$ is sensitive to the relative stabilities. A cluster with local minima (higher negative value) of $\Delta_1E$ is more stable than its neighbor. The observed pattern suggest that even-numbered clusters are relatively more stable than their neighboring odd-numbered clusters. Another very sensitive quantity to measure relative stability of cluster is the stability function, $\Delta_2E$. Figure 3(b) displays the calculated $\Delta_2E$ values. It also show even–odd oscillations, and suggest that even-numbered clusters are relatively more stable than their neighboring odd-numbered clusters. Since Au atom has half-filled 6$s^1$ orbital, the higher stability of even-numbered clusters can be understood in terms of the spin pairing effect (Nijamudheen & Datta, 2010). An electron can be more easily accommodated in the singly occupied highest occupied molecular orbital (HOMO) of the odd-numbered cluster than in the doubly occupied HOMO of odd-sized clusters. Among the cluster, Au$_6$ cluster has the lowest $\Delta_1E$ value and highest $\Delta_2E$ value indicating it is relatively most stable than other clusters in the size range of the present study. Also from Figure 2, we see that $E_{coh}$ of Au$_6$ is a local maximum. The enhanced stability of Au$_6$ is attributed to the two-dimensional d-orbital aromaticity (Wannere et al., 2005).

The calculated HOMO–LUMO gaps of the clusters are shown in Figure 4(a) and Table S1 of supplementary material. It is considered to be one of the important parameter to study electronic stability of small clusters. A large HOMO–LUMO gap indicates high field strength is required to perturb the electronic structure. The HOMO–LUMO gap for Au$_6$ is highest among the clusters, which indicates it is chemically more inert than other clusters and is related to its high stability. It can be seen from Figure 4 that even-numbered clusters have higher HOMO–LUMO gap than odd-numbered clusters. Thus, even-number clusters have relatively higher chemical stability than their neighboring odd-numbered clusters.
The calculated values of IPs as obtained with different methods are plotted in Figure 4(b), which reflects the size-dependent evolution of electronic structure. One important point which is worth mentioning is the observation of prominent even–odd oscillation of IP in all the methods. The even-numbered clusters have higher IP values than odd-numbered clusters. This can be understood from the spin pairing effect as explained above. Even-numbered clusters are more stable and higher energy is required to remove electrons from such clusters as compared to odd-numbered clusters. The calculated electron affinities (EA) at different methods and experimental values (Häkkinen et al., 2003; Taylor, Pettiette-Hall, Cheshnovsky, & Smalley, 1992) are presented in Table 1. In general, good agreement between calculated and experimental results is observed for B3LYP/LANL2DZ method. The EA also shows odd–even oscillation pattern, in which clusters with odd-numbered atoms have higher EA values than even-numbered clusters. The observed pattern is in opposite to the even–odd oscillation that we have seen for IP, HOMO–LUMO gap, and ΔE.

Electrophilicity measures the power of a system to soak up electrons (Chattaraj, Sarkar, Parthasarathi, & Subramanian, 2005; Chattaraj, Sarkar, & Roy, 2006; Elango et al., 2005; Parr et al., 1999; Parthasarathi et al., 2006; Sarkar, Padmanabhan, Parthasarathi, Subramanian, & Chattaraj, 2006; Sarkar et al., 2005). Though electrophilicity is basically a kinetic concept but thermodynamic information is also inherited in it (Chattaraj et al., 2006). The calculated electrophilicity index values are tabulated in Table 2. Stable systems are less prone to acquire additional electrons from surrounding and as a result, they are...
expected to have low electrophilicity index values. The even–odd alternation is also seen for the calculated electrophilicity index, with even-numbered clusters having lower values than neighboring odd-numbered clusters, which again confirms the higher stability of clusters with even number atoms. It may be pointed here that Au6 has the lowest value of electrophilicity index among the cluster sizes of our study, suggesting it has relatively high stability in the size range of the present study. Chemical hardness is used to describe relative chemical stability of molecules/clusters. The calculated chemical hardness values show even–odd oscillation behavior. From the maximum hardness principle (Pan, Solà, & Chattaraj, 2013; Parr & Chattaraj, 1991; Pearson, 1987) which states that, “There seems to be a rule of nature that molecules arrange themselves so as to be hard as possible,” it can be inferred that even-numbered clusters with higher chemical hardness values are chemically more stable than their neighboring odd-numbered clusters.

The static polarizability is an important parameter in cluster study as they are very sensitive to the electronic structures and delocalization of valence electrons. The static polarizability is given in Table 2 and static polarizability per atom is presented in Figure 5. The static polarizability of gold clusters increases monotonically with increasing cluster size. The static polarizability per atom also displays even–odd oscillation behavior except for Au4 cluster. From the minimum polarizability principle (Chattaraj & Sengupta, 1996) which is stated as, “The natural direction of evolution of any system is towards a state of minimum polarizability,” it can be inferred that even-numbered clusters with lower static polarizability per atom values are chemically more stable than their neighboring even-numbered clusters.

### Table 1. EA of gold clusters in units of eV

| Au_n | Electron affinity |
|------|------------------|
|      | Experiment | Calculated B3LYP/LANL2DZ | Calculated B3LYP/LANL2MB | Calculated B3PW91/LANL2DZ | Calculated B3PW91/LANL2MB |
| Au_2 | 1.92       | 1.94               | 1.92             | 1.91               | 1.90             |
| Au_4 | 2.70       | 2.73               | 2.70             | 2.68               | 2.68             |
| Au_6 | 2.06       | 2.04               | 2.02             | 2.00               | 1.93             |
| Au_8 | 3.40       | 3.26               | 3.20             | 3.19               | 3.07             |
| Au_10| 2.73       | 2.67               | 2.60             | 2.63               | 2.59             |
| Au_12| 2.89       | 2.21               | 2.30             | 2.13               | 2.22             |

Source: Experimental values are from Taylor et al. (1992) and Häkkinen et al. (2003).

### Table 2. Chemical hardness, electrophilicity and static polarizability of gold clusters

| Au_n | Chemical hardness (eV) | Electrophilicity (eV) | Static polarizability (a.u.) |
|------|------------------------|-----------------------|-----------------------------|
| Au_2 | 3.17                   | 4.33                  | 78.86                       |
| Au_4 | 2.52                   | 7.05                  | 143.08                      |
| Au_6 | 2.74                   | 5.46                  | 167.35                      |
| Au_8 | 2.23                   | 6.33                  | 204.79                      |
| Au_10| 3.24                   | 4.29                  | 234.62                      |
| Au_12| 2.01                   | 6.91                  | 298.50                      |
| Au_14| 2.72                   | 5.33                  | 317.34                      |
| Au_16| 1.84                   | 7.64                  | 396.71                      |
| Au_18| 2.81                   | 4.49                  | 420.76                      |

Note: The reported values are obtained using B3LYP/LANL2DZ level of theory.
odd-numbered clusters. $Au_n$ has the lowest values of static polarizability per atom among the clusters which suggest its highest stability compared to other clusters involved in this study.

As we have mentioned earlier, comparison of calculated IR spectra with experiment helps in structural assignment for clusters (Gruene, Butschke, Lyon, Rayner, & Fielicke, 2014; Gruene et al., 2008). The frequencies and IR intensities for IR active modes of gold clusters are presented in Table 3 along with available experimental data. No IR-active mode is found in $Au_2$ while for $Au_3$, there is no experimental data to compare with our calculated result. Gruene et al. (2014) have shown that IR multiple photon dissociation (IR-MPD) spectra of $Au_4$ have bands at 76 and 158 cm$^{-1}$. These bands are in agreement with our calculated frequency modes at 77.60 and 156.80 cm$^{-1}$. The calculated spectra for $Au_5$ show absorption bands in the range between 51.20 and 171.60 cm$^{-1}$. Our calculated mode at 51.20 cm$^{-1}$ fits with the experimental absorption at 53 cm$^{-1}$. Experimental results are not available for $Au_6$ to compare with the calculated IR spectra. IR spectra of $Au_6$ exhibit absorption bands in the frequency range from 32.40–176.00 cm$^{-1}$, with the highest intensity peak at 176.00 cm$^{-1}$. Gruene et al. (2008) reported that IR-MPD spectra of $Au_7$ have intensity peaks at 165, 186, and 201 cm$^{-1}$. The experimental peak positions at 165 and 186 cm$^{-1}$ are in agreement with our calculated modes at 165.20 and 180.40 cm$^{-1}$, respectively. However, the band at 201 cm$^{-1}$ is not observed in our calculation. The IR spectra of $Au_8$ exhibit bands in the frequency range from 31.86 to 172.11 cm$^{-1}$. Intensity peaks at 46, 113, and 193 cm$^{-1}$ observed in the IR-MPD spectra of $Au_8Kr_3$ (Gruene et al., 2014) could not be matched with our calculated frequency modes. This may be due to the presence of three Kr atoms in the IR-MPD spectra of $Au_8$ as reported by Gruene et al. (2014). It can be noted here that for other clusters ($Au_n$, $n = 2$–7), the spectra contain only one Kr atom (Gruene et al., 2008, 2014). The spectra of $Au_9$ have absorption bands in the range from 17.20 to 182.40 cm$^{-1}$; and $Au_{10}$ show absorption modes in the frequency range between 8.80 and 170.90 cm$^{-1}$. Comparison with experiment is not possible as experimental IR spectra for $Au_9$ and $Au_{10}$ are not available.

Calculated Raman spectra of $Au_n$ clusters at B3LYP/LANL2DZ level of DFT theory are displayed in Figure 6. Table 4 presents frequencies for the Raman intensity peaks of the $Au_n$ clusters. The Raman intensity of the clusters is simulated by the incident light of excitation wavelength 785 nm and at temperature 293.15 K. Raman spectrum of $Au_2$ cluster has only one peak corresponding Au–Au stretching mode at frequency 174.00 cm$^{-1}$ and $Au_3$ cluster has three peaks. The highest peak for the breathing mode is at frequency 18.80 cm$^{-1}$ and the other low intensity peak at 119.20 cm$^{-1}$ is for the symmetric stretching. The asymmetric stretching mode at 150.60 cm$^{-1}$ is found to have very low intensity. The highest peak in the Raman spectrum of $Au_4$ cluster is observed at frequency
15.60 cm⁻¹ which is for the breathing mode. Other low intensity peaks are presented in Table 4. Raman spectrum of Au₃ cluster has highest peak for the breathing mode at frequency 87.60 cm⁻¹ and another prominent peak is observed at 51.20 cm⁻¹ which corresponds to the asymmetric stretching. Intensity peak for the symmetric stretching is observed at 136.80 cm⁻¹. The most intense

| Cluster | Frequencies (cm⁻¹) | IR intensity (KM/mole) | Experimental frequency |
|---------|-------------------|------------------------|------------------------|
| Au₃     | 150.60            | 0.44                   |                        |
|         | 15.60             | 0.22                   | 76                     |
|         | 32.40             | 0.33                   | 158                    |
|         | 77.60             | 0.08                   |                        |
|         | 83.20             | 0.46                   |                        |
|         | 156.80            | 0.67                   |                        |
|         | 188.40            | 4.85                   |                        |
| Au₄     | 51.20             | 0.06                   | 53                     |
|         | 63.60             | 0.24                   | 100                    |
|         | 87.60             | 0.15                   | 192                    |
|         | 124.00            | 0.05                   |                        |
|         | 136.80            | 0.33                   |                        |
|         | 171.60            | 3.95                   |                        |
| Au₅     | 32.40             | 0.36                   |                        |
|         | 57.60             | 0.13                   |                        |
|         | 78.80             | 0.51                   |                        |
|         | 104.80            | 0.47                   |                        |
|         | 176.00            | 7.37                   |                        |
| Au₆     | 34.80             | 0.24                   | 165                    |
|         | 61.60             | 0.33                   |                        |
|         | 75.60             | 0.37                   | 186                    |
|         | 83.60             | 0.10                   | 201                    |
|         | 104.00            | 0.01                   |                        |
|         | 111.60            | 0.33                   |                        |
|         | 144.00            | 0.75                   |                        |
|         | 165.20            | 6.22                   |                        |
|         | 180.40            | 4.79                   |                        |
| Au₇     | 31.86             | 0.64                   | 66                     |
|         | 58.09             | 0.15                   | 113                    |
|         | 97.71             | 0.61                   | 193                    |
|         | 172.11            | 10.42                  |                        |
| Au₈     | 17.20             | 0.04                   |                        |
|         | 29.46             | 0.20                   |                        |
|         | 53.60             | 0.08                   |                        |
|         | 95.20             | 0.84                   |                        |
|         | 142.40            | 0.41                   |                        |
|         | 162.80            | 6.19                   |                        |
|         | 166.40            | 4.87                   |                        |
|         | 182.40            | 0.93                   |                        |

(Continued)
peak of \( \text{Au}_6 \) cluster is observed at 78.80 cm\(^{-1} \) which is for the breathing mode. Two other high peaks are seen at 104.80 and 120 cm\(^{-1} \) which are due to the symmetric and asymmetric stretching, respectively. The highest peak of \( \text{Au}_7 \) occurs for the breathing mode at 61.60 cm\(^{-1} \). Other lower intensity peaks are also observed which are listed in Table 4. The highest peak for \( \text{Au}_8, \text{Au}_9, \) and \( \text{Au}_{10} \) cluster are observed at 119.60, 104.80, and 8.80 cm\(^{-1} \), respectively. We observed that the frequency of the maximum Raman intensity moves toward low-frequency regions (or redshifts) upon going from \( \text{Au}_2 \) to \( \text{Au}_4, \text{Au}_5 \) to \( \text{Au}_7 \), and \( \text{Au}_8 \) to \( \text{Au}_{10} \).

The reactivity and optical properties of clusters are dependent on the electron arrangement and density of states (DOS) can provide detail information of the electronic structure. Partial density of states (PDOS) for \( \text{Au}_n \) clusters are shown in Figure 7. Here, only the energy states close to HOMO and

### Table 3. (Continued)

| Cluster  | Frequencies (cm\(^{-1} \)) | IR intensity (KM/mole) | Experimental frequency |
|----------|----------------------------|------------------------|------------------------|
| \( \text{Au}_{10} \) | 8.80 | 0.04 | |
| | 63.60 | 0.39 | |
| | 84.20 | 3.21 | |
| | 120.00 | 0.13 | |
| | 138.56 | 11.80 | |
| | 170.88 | 6.34 | |
| | 170.90 | 6.30 | |

Source: Experimental values for all the clusters except \( \text{Au}_7 \) are from Gruene et al. (2014) and Experimental values for \( \text{Au}_7 \) is from Gruene et al. (2008).
Table 4. Frequencies (cm\(^{-1}\)) of the Raman intensity peaks for Au\(_n\) clusters at B3LYP/LANL2DZ level

| Cluster | Frequencies (cm\(^{-1}\)) |
|---------|---------------------------|
| Au\(_2\) | 174.00                    |
| Au\(_3\) | 18.80, 119.20, 150.60     |
| Au\(_4\) | 15.60, 32.40, 77.60, 83.20, 156.80, 188.40 |
| Au\(_5\) | 51.20, 63.60, 87.60, 124.00, 136.80, 171.60 |
| Au\(_6\) | 32.40, 57.60, 78.80, 104.80, 120.00, 176.00 |
| Au\(_7\) | 11.60, 30.80, 35.60, 48.40, 61.60, 75.60, 83.60, 104.00, 111.60, 144.00, 165.20, 180.40 |
| Au\(_8\) | 23.20, 34.80, 51.20, 79.20, 88.00, 119.60, 192.80 |
| Au\(_9\) | 17.20, 32.80, 48.40, 53.60, 72.40, 80.80, 95.20, 104.80, 120.40, 142.40, 162.80, 182.40 |
| Au\(_{10}\) | 8.80, 12.80, 44.80, 63.60, 67.60, 95.20, 120.00 |

Figure 7. PDOS for Au\(_n\) clusters.
lowest unoccupied molecular orbital (LUMO) levels are shown as they have significant influence on the cluster reactivity and optical properties. It can be seen that energy states at HOMO and LUMO are predominantly contributed by s orbital. At HOMO level, a small contribution comes from d orbital, and the contribution from d orbital becomes dominant in the energy states below HOMO level. Contribution of p orbital to energy states at HOMO level and below HOMO is negligible. Significant

Figure 8. Absorption spectra of Auₙ clusters.

| Cluster | Excitation energy (eV) | λemax (nm) | Oscillator strength (f) | Major transition |
|---------|------------------------|------------|------------------------|-----------------|
| Au₂     | 2.930                  | 423.122    | 0.200                  | HOMO→LUMO       |
| Au₃     | 2.753                  | 450.324    | 0.293                  | HOMO→LUMO       |
| Au₄     | 2.826                  | 438.739    | 0.199                  | HOMO→LUMO+1     |
| Au₅     | 1.792                  | 630.285    | 0.028                  | HOMO-2→LUMO     |
| Au₆     | 3.047                  | 406.903    | 0.146                  | HOMO→LUMO       |
| Au₇     | 2.399                  | 516.640    | 0.059                  | HOMO-9→LUMO     |
| Au₈     | 3.122                  | 397.153    | 0.068                  | HOMO-5→LUMO     |
| Au₉     | 1.906                  | 650.626    | 0.026                  | HOMO→LUMO+1     |
| Au₁₀    | 3.091                  | 401.098    | 0.405                  | HOMO→LUMO+4     |
orbs. Small contribution from structures. Energy states at HOMO and LUMO are dominated by 
active modes and experiment is seen. DOS analysis gives a clear picture of the cluster electronic 
analyzed with IR and Raman spectra. Good agreement between our calculated frequencies of IR 
as maximum hardness principle and minimum polarizability principle. Vibrational properties are 
be chemically most inert. The reactivity of the clusters is described in terms of related principles such 
-orbital aromaticity and it is also found to 
contribution from 

5. Optical properties
The optical properties of materials are governed by their electronic structure and electronic struc-
ture in turn varies with cluster size. The optical absorption spectra of Auₙ clusters are presented in 
Figure 8 and in Table 5, we have tabulated excitation energy, wavelength, and oscillator strength 
corresponding to most intense peak positions. The most intense peaks for odd-numbered clusters 
are observed at higher wavelength region than the even-numbered clusters. Absorption spectra of 
Au₅ and Au₉ are extended up to near IR region. Absorption spectra of even-numbered clusters are 
observed to be more intense (higher absorption coefficient and higher oscillator strengths) than 
odd-numbered clusters, except for Au₃ cluster. Thus, the optical properties of gold clusters are very 
sensitive to the size. The optical properties can be effectively tuned by changing size of the cluster.

6. Conclusion
We have studied structural, electronic, and chemical reactivity properties of gold clusters using DFT. 
Gold clusters are observed to prefer planar structures with stability showing even–odd oscillation. 
Even-numbered cluster having higher stability is due to the spin pairing effect. Even–odd oscillation 
is also seen for other properties of gold clusters. Au₆ has highest stability among the clusters range 
of the present study. The high stability of Au₆ is due to its d-orbital aromaticity and it is also found to 
be chemically most inert. The reactivity of the clusters is described in terms of related principles such 
as maximum hardness principle and minimum polarizability principle. Vibrational properties are 
analyzed with IR and Raman spectra. Good agreement between our calculated frequencies of IR 
active modes and experiment is seen. DOS analysis gives a clear picture of the cluster electronic 
structures. Energy states at HOMO and LUMO are dominated by s orbital. Small contribution from d 
orbital is seen at the HOMO region. Absorption spectra of even-numbered clusters are more intense 
and are observed at lower wavelength region than the odd-numbered clusters.

Supplementary material
Supplementary material for this article can be accessed here http://dx.doi.org/10.1080/23312009.2015.1076713.

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