Chapter 7

Molecular Dynamics Study Of
Icosahedral $Au_{32}$ Cluster

Abstract

Relativistic Density Functional Theory (DFT) based molecular dynamical simulations are performed on $Au_{32}$ golden fullerene with an aim of understanding its thermal stability. Various conformations being populated at different temperatures of a cluster have been analyzed. The chapter shows that the icosahedral conformation is stable only up to 300 K and structure remains in a hollow conformation only up to 400 K. This clearly explains the reasons for failure by experimentalists in trapping the unique fullerene conformation in spite of the theoretical predictions of it being a very stable one.
7.1 Introduction

During the last decade new class of Au nano clusters have resulted in a substantial excitement in both experimental and theoretical chemists. Apart from the tetrahedral Au$_{19}$ and Au$_{20}$ clusters,[1] new class of golden cages[2] have been proposed using both experimental and theoretical methods. In addition several state of art theoretical studies have shown plausible existence of golden fullerenes.[3–7] Au$_{32}$,[3, 4] Au$_{50}$[5, 6] and Au$_{72}$[7] are the sizes with fullerene structure as the ground state geometry at relativistic Density Functional Theory (DFT) methods.

The fact metal clusters can have hollow fullerene structural orientations has led to a lot of excitement. Among the three sizes, Au$_{32}$ has been most intriguing cluster. It started with a report by Johansson and co-workers[3] that ground state geometry of Au$_{32}$ is a icosahedral golden fullerene. The report shows as to how the spherically hollow Au$_{32}$ conformation with nearly 0.9 nm diameter is structurally similar to C$_{60}$. In addition to its shape uniqueness, the theoretical studies also revealed a record value of magnetic shielding at the center of the cage indicative of induced ring currents in the molecule. In other words, the ground state Au$_{32}$ geometry has been proposed to be aromatic in nature.

The hollow nature combined with the ring currents in the center of Au$_{32}$ can find use in distributing pharmaceuticals. However, the bottle neck in its practical application is the failure by the experimental methods to trap this conformation in spite of its high stability as predicted by theoretical methods. It has been proposed that maintaining the spherical aromaticity is critical in trapping the fullerene Au$_{32}$ conformation experimentally.[8] Other reports propose that a C$_1$ is more stable conformation[4, 9]. Motivated by these findings, we in the present work report a finite temperature study in Au$_{32}$ to evaluate its stability as a function of temperature.

The chapter is organized as follows. In Section 7.2, we discuss the computational methodology and clusters for which the simulations were carried out. In Section
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7.3, we note the results and observations from the simulation studies. We conclude in brief the chapter in Section 7.4.

7.2 Computational Details

All calculations are performed in the framework of Density Functional Theory (DFT), using a linear combination of Gaussian orbitals as implemented in \textit{de-Mon2k} code.\cite{10} About 50 conformations are generated and optimized using the Perdew-Burke-Ernzerhof (PBE) exchange and correlation functional\cite{11} with 1997 Stuttgart-Dresden Relativistic Effective Core Potential’s (RECP)’s\cite{12} as the basis set for the valence electrons. 5s, 5p, 5d and 6s electrons are considered to constitute the valence electrons. We note that these ECP’s are now documented for accurate prediction of structure as well as spectroscopic properties of Au clusters.\cite{13, 14} No additional polarization functions are added. The A2 auxiliary functions are set to fit the charge density.\cite{15} The convergence of the geometries is based on gradient and displacement criteria with a threshold value of $10^{-5}$ au and the criteria for convergence of SCF cycles was set to $10^{-9}$. Only the lowest spin state is considered for all the Au clusters. The spin multiplicities for even electron (even number of Au atoms) clusters are singlets and doublets for odd electron (odd number of Au atoms) clusters. It has also been reported in an earlier literature that Au clusters prefer to be in their lowest spin state.\cite{16} Following the geometry optimization, harmonic vibrational frequencies are computed for various conformations. All of the frequencies are found to be positive, thereby, indicating the conformations to be a local minima.

The lowest energy conformation is found to be of icosahedral (I\textsubscript{h}) symmetry. Finite temperature study was carried out on this cluster in order to evaluate its thermal stability. The finite temperature simulation is carried out using Born-Oppenheimer Molecular Dynamics (BOMD). The simulations are carried out between 200 K to
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2000 K. For each temperature, the cluster is equilibrated for a time period of 10 ps followed by a simulation time of 30 ps. The temperature of the cluster is maintained using the Berendsen’s thermostat ($\tau = 0.5$ ps) in the NVT ensemble. The nuclear positions are updated with the velocity Verlet algorithm with a time step of 1 fs. The atomic positions and bond length punctuations of atoms are analyzed using traditional parameters such as root mean squared bond length fluctuations ($\delta_{\text{rms}}$) and the Mean Squared ionic Displacements (MSD)'s[17, 18].

$\delta_{\text{rms}}$ is defined as

$$\delta_{\text{rms}} = \frac{2}{N(N-1)} \sum_{i<j} \sqrt{\langle R_{ij}^2 \rangle_t - \langle R_{ij} \rangle_t^2} \quad \text{(7.1)}$$

where, N is the number of particles in the system, $r_{ij}$ is the distance between the $i^{th}$ and $j^{th}$ particles in the system and $\langle ... \rangle_t$ denotes a time average over the entire trajectory. The MSD of an individual atom is defined as,

$$\langle R_i^2 \rangle = \frac{1}{M} \sum_{M-1} [R_i(t_{0m} + t) - R_i(t_{0m})]^2 \quad \text{(7.2)}$$

where, $R_i(t_{0m})$ is the instantaneous position of atom i at $t_0$ and $R_i(t_{0m} + t)$ is the corresponding position of atom i after a time interval t.

7.3 Results and Discussion

Figure 7.3 gives the root mean square displacement of Au$_{32}$ as a function of various temperatures. It is clearly seen from the Figure that the structure undergoes systematic structural variations from 600 K onwards. The $\delta_{\text{rms}}$ around 300 and 400 K is minimal and is 0.03 and 0.04 respectively. However, around 600 K it jumps to a value 0.08 and around 700 K the value reaches to 0.1 indicate of significant displacements of atoms around 600 K onwards. Around 1200 K, the value reaches nearly 0.3. Several research works have by now established that
clusters at finite temperature undergo a transformation from solid-like state to a liquid-like state. At low temperatures, the atoms in a cluster vibrate around their equilibrium positions as in case of a bulk solid (and hence the name solid-like state). As the temperature increases, the atoms within the cluster reorient their positions. As they reorient, the cluster transits into other local minima through diffusive motion of atoms. Finally, at very high temperatures, clusters transit through several conformations within few femto seconds. These conformational reorientation’s/isomerization increases dramatically beyond a temperature specific to each cluster and resembles a liquid droplet (and hence the name liquid-like state). This phenomenon has been very widely explored experimentally as well as theoretically in several clusters such as silicon,[19] gallium,[20] aluminum,[21] tin,[22] sodium,[23] and gold[24] experimentally and/or theoretically. A δ_{rms} value of 0.3 is indicative of a nearly liquid like state of the cluster.[24] In other words, Au_{32} is in a nearly liquid like state around 1200 K.
Figure 7.1: Root Mean Square displacement of Au\textsubscript{32} as function of temperature.
Figure 7.2: One of the space filling conformations seen at 500 K.
To get a more detailed insight, we have analyzed the ionic motions of the atoms. The analysis reveals that the cluster remains in the ground state icosahedral state up to 300 K. Around 400 K we note that the cluster oscillates between icosahedron and other hollow conformation which is of $C_1$ symmetry. Around 500 K, the cluster transits into other space filling conformations (see Figure 7.2). The atomic motions increase beyond 500 K and the cluster begins to resemble a liquid droplet by 1200 K.

### 7.4 Conclusions

Born Oppenheimer molecular dynamical simulations on Au$_{32}$ reveal that the fullerene conformation is unstable beyond 300 K. This conformation gives way to other hollow conformations around 400 K. Space filling conformations dominate trajectories from 500 K. Clearly other factors such as capping agents are needed for stabilizing the much needed fullerene Au$_{32}$ conformation.

### 7.5 Future Scope

In the future we plan to address the general stability of hollow cages, viz. Au$_{18}$ at different temperatures with traditional molecular dynamics parameters. In addition to that, electron Localization Function (ELF) are to be calculated for Au$_{32}$ clusters for various conformations in order to describe the nature of bonding within the Au clusters in critical manner.