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Research Article

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A Medium-Sized Nanoclusters Au_{38} : A Numerical Finite-Difference Method with DFTB Approach

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Abstract

We present a vibrational spectrum analysis of Au_{38} cluster, with energy (-4.95 eV/atom) having a group symmetry C_1 . We have carried out DFTB calculation by using the numerical finite-difference method and extracted the required force constants. Our calculations have confirmed with the experimental results, that is, a thermodynamically very stable structure can not be crystalline, but having a high probability of amorphous. The lowest energy geometrical structures are being confirmed by comparison (of the nuclei coordination numbers) of the different axis of rotations at a standard orientation of crystal shape. Moreover, we have accurately predicted the vibrational frequency range from 1.62 to 298.53 cm^{-1} at $\Delta E = 0$. Significantly, the spectrum has shown 10 sets of double state degeneracy and the rest of the 88 spectrum's are having independent single state degeneracy. Amazingly, at NVM 101,102 that gives a pair of degeneracy {238.54, 238.89} cm^{-1} that has occurred within the range of Mid Infrared MIR, IR-C 3330-200 cm^{-1} . Nevertheless, our investigation has revealed that the vibrational spectrum strongly depends upon the size, shape, and structure, as well as, stretching and bending vibrations of the atoms.

Keywords: Gold Atomic Clusters, Density-Functional Tight-Binding (DFTB) approach, Finite-Difference Method, Force Constants (FCs) and Vibrational Spectrum.

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1 Introduction

In general, nanoclusters are interesting because their physical, optical and electronic characteristics are strongly size dependent. Often changing the size by only one atom can significantly alter the physical chemical properties of the system [1], for that reasons, many new periodic tables can thus be envisioned classifying differently-sized clusters of the same material as new elements. Potential applications are enormous, ranging from devices in nano-electronics and nano-optics [2] to applications in medicine and materials.

Gold colloids not only having some practical application recently, but also, have been used for centuries to stain glass which has been even used for the study of direct electrochemistry of proteins [3]. The main reasons are, gold is a soft metal and is usually alloyed to give it more strength. In addition to that gold is a good conductor of heat and electricity, and is unaffected by air and most reagents. Noble-metal (Cu, Ag, and Au) clusters have attracted much attention in scientific and technological fields because of their thermodynamic, electronic, optical and catalytic properties in nano-materials [4, 5].

The vibrational properties play a major role in structural stability [6, 7, 8, 9, 10, 11, 12, 13]. The structural determination of metal nanoparticles of their vibrational (phonon) density of states have been calculated by Huziel E. Saucedo and Ignacio L. Garzón [12]. Specific heat capacity is an important thermodynamic property and is directly related to the structural stability, identification and energy of substances. Most recently, Huziel E. Saucedo and Ignacio L. Garzón [10] calculated vibrational properties and specific heat of core-shell Ag-Au icosahedral nanoparticles.

Most recently, many researchers have observed that, beyond Au_{25}^{-1} , the low-symmetry core-shell structures dominate the low-energy clusters, and the hollow-cage structures are unlikely to exist in larger size due to the strong relativistic effects [14]. Chuanchuan Zhang *et al.*, [5], worked on the lowest-energy geometrical and electronic structures of Cu_{38}^{-1} clusters which are investigated by density functional calculations combined with a genetic algorithm based on a many body semi-empirical interatomic potential, the traditional FCC-truncated Octahedron (OH) and an incomplete-Mackay icosahedron (IMI) are recognized as the two lowest energy structures (energetically degenerate isomers) but with different electronic structures: a semiconductor-type with the energy-gap of 0.356 eV for the IMI and a metallic-type with negligible gap for the OH, which is in good agreement with the experimental results. The electron affinity and ionization potential of Cu_{38}^{-1} are also discussed and compared with the observations of the ultraviolet photoelectron spectroscopy experiments. The dynamical isomerization of the OH-like and IMI-like structures of Cu_{38}^{-1} is revealed to dominate the premelting stage

through the investigation by the molecular dynamics annealing simulations.

Above all, recent theoretical study of Au_{38}^{-1} , Luo *et al.*, also suggest a spindle-like structure of Au_{38}^{-1} , which contains a tetrahedral core [15]. The structures of gold clusters in the size regime between 36 and 54 atoms have not been confirmed experimentally. In search for such structural information, the questions are: Is the tetrahedral core so stable that it can be retained in Au clusters beyond the size Au_{36}^{-1} ? If it is, at what size of Au cluster would the tetrahedral core transform to a different core? Also, what would the next core structure look like? To answer some of these questions and to understand the structural growth pattern of medium-sized Au clusters, they have performed a global structure search of low-energy clusters of Au_{36}^{-1} to Au_{38}^{-1} by using the basin-hopping (BH) global optimization method [16] combined with DFT calculations. The most stable structures are identified by comparing the experimental PES spectra with the computed electronic density of states of all lowest-lying isomers [17, 18, 19].

In this study, we focus on the vibrational properties of gold clusters with sizes Au_{38} atoms. Some general information about global minima gold structures which have been calculated by the work of Springborg and Dong [20, 21]. The structures were found through a so called *genetic algorithm* (GA) in combination with *Density Functional Tight-Binding* (DFTB) energy calculations and a *steepest descent* algorithm permitting a local total energy minimization. Nevertheless, peculiarly, in our case, we use our numerical finite-difference approach [22] along with density functional tight-binding (DFTB) method and extracted the vibrational spectrums. Overall, for a better understanding and to visualize, the detailed information is discussed in the results and discussion section.

2 Theoretical and Computational Procedure

At first, the DFTB [23, 24, 25] is based on the density functional theory of Hohenberg and Kohn in the formulation of Kohn and Sham. In addition, the Kohn-Sham orbitals $\psi_i(\mathbf{r})$ of the system of interest are expanded in terms of atom-centered basis functions $\{\phi_m(\mathbf{r})\}$,

$$\psi_i(\mathbf{r}) = \sum_m c_{im} \phi_m(\mathbf{r}), \quad m = j. \quad (1)$$

While so far the variational parameters have been the real-space grid representations of the pseudo wave functions, it will now be the set of coefficients c_{im} . Index m describes the atom, where ϕ_m is centered and it is angular as well as radially dependant. The ϕ_m is determined by self-consistent DFT calculations on isolated atoms using large Slater-type basis sets.

In calculating the orbital energies, we need the Hamilton matrix elements and the overlap matrix elements. The above formula gives the secular equations

$$\sum_m c_{im}(H_{mn} - \epsilon_i S_{mn}) = 0. \quad (2)$$

Here, c_{im} 's are expansion coefficients, ϵ_i is for the single-particle energies (or where ϵ_i are the Kohn-Sham eigenvalues of the neutral), and the matrix elements of Hamiltonian H_{mn} and the overlap matrix elements S_{mn} are defined as

$$H_{mn} = \langle \phi_m | \hat{H} | \phi_n \rangle, \quad S_{mn} = \langle \phi_m | \phi_n \rangle. \quad (3)$$

They depend on the atomic positions and on a well-guessed density $\rho(\mathbf{r})$. By solving the Kohn-Sham equations in an effective one particle potential, the Hamiltonian $\hat{H}$ is defined as

$$\hat{H}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}), \quad \hat{H} = \hat{T} + V_{eff}(\mathbf{r}). \quad (4)$$

To calculate the Hamiltonian matrix, the effective potential V_{eff} has to be approximated. Here, $\hat{T}$ being the kinetic-energy operator $\sum(\hat{T} = -\frac{1}{2}\nabla^2)$ and $V_{eff}(\mathbf{r})$ being the effective Kohn-Sham potential, which is approximated as a simple superposition of the potentials of the neutral atoms,

$$V_{eff}(\mathbf{r}) = \sum_j V_j^0(|\mathbf{r} - \mathbf{R}_j|). \quad (5)$$

V_j^0 is the Kohn-Sham potential of a neutral atom, $\mathbf{r}_j = \mathbf{r} - \mathbf{R}_j$ is an atomic position, and $\mathbf{R}_j$ being the coordinates of the j -th atom.

Finally, the short-range interactions can be approximated by simple pair potentials, and the total energy of the compound of interest relative to that of the isolated atoms is then written as,

$$E_{tot} \simeq \sum_i \epsilon_i - \sum_j \sum_{m_j}^{occ} \epsilon_{jm_j} + \frac{1}{2} \sum_{j \neq j'} U_{jj'}(|\mathbf{R}_j - \mathbf{R}_{j'}|), \quad (6)$$

$$\epsilon_B \equiv \sum_i \epsilon_i - \sum_j \sum_{m_j}^{occ} \epsilon_{jm_j}$$

Here, the majority of the binding energy (ϵ_B) is contained in the difference between the single-particle energies ϵ_i of the system of interest and the single-particle energies ϵ_{jm_j} of the isolated atoms (atom index j , orbital index m_j), $U_{jj'}(|\mathbf{R}_j - \mathbf{R}_{j'}|)$ is determined as the difference between ϵ_B and ϵ_B^{SCF} for diatomic molecules (with E_B^{SCF} being the total energy from parameter-free density-functional calculations). In the present study, only the $5d$ and $6s$ electrons of the

gold atoms are explicitly included, whereas the rest are treated within a frozen-core approximation [23, 25, 26].

2.1 Structural re-optimization process

In our case, we have calculated the numerical first-order derivatives of the forces ($\mathbf{F}_{i\alpha}, \mathbf{F}_{j\beta}$) instead of the numerical-second-order derivatives of the total energy (E_{tot}). In principle, there is no difference, but numerically the approach of using the forces is more accurate [22],

$$\frac{1}{M} \frac{\partial^2 E_{tot}}{\partial \mathbf{R}_{i\alpha} \partial \mathbf{R}_{j\beta}} = \frac{1}{M} \frac{1}{2ds} \left[\frac{\partial}{\partial \mathbf{R}_{i\alpha}} (-\mathbf{F}_{j\beta}) + \frac{\partial}{\partial \mathbf{R}_{j\beta}} (-\mathbf{F}_{i\alpha}) \right] \quad (7)$$

Here, $\mathbf{F}$ is a restoring forces which is acting upon the atoms, ds is a differentiation step-size and M represents the atomic mass, for homonuclear case. The complete list of these force constants (FCs) is called the Hessian H , which is a $(3N \times 3N)$ matrix. Here, i is the component of $(x, y \text{ or } z)$ of the force on the j 'th atom, so we get $3N$.

2.1.1 The Hessian Matrix

Briefly, this method is described as follows: The Hessian matrix is represented in an orthonormal basis consisting of the five or six eigenvectors of the Hessian matrix which span its kernel and of $(3N-5)$ or $(3N-6)$ arbitrarily chosen mutually orthonormal basis vectors, which are orthogonal to the kernel-eigenvectors. When represented in this basis, the Hessian should be partially diagonal. The diagonal part is now cut away and the remaining Hessian is diagonalized to reveal the eigenfrequencies of the clusters normal modes.

The Hessian matrix is the matrix of second derivatives of the energy with respect to geometry which is quite sensitive to its geometry. Energy second derivatives are evaluated numerically. The mass-weighted Hessian matrix is obtained by numerical differentiation of the analytical first derivatives, calculated at geometries obtained by incrementing in turn each of the $3N$ nuclear coordinates by a small amount ds with respect to the equilibrium geometry. The introduction of the Hessian matrix and its diagonalization ultimately leads to the eigen-frequencies of the system and its eigenvectors, describing the harmonic motion of the clusters atoms. In order to obtain the matrix elements H_{ij} of the Hessian matrix which are needed if one wishes to investigate the clusters thermodynamic properties and one should obtain the derivatives of potential energy surface (**PES**) [21, 27].

3 Results and Discussion

3.1 The optimized structure of the cluster Au_{38}

We present a vibrational spectrum analysis of re-optimized Au_{38} cluster, having energy (-4.95 eV/atom) with a group symmetry C_1 at $\Delta E = 0$. Initially, the structures were found through a so called *genetic algorithm* (GA) in combination with *Density Functional Tight-Binding* (DFTB) energy calculations and a *steepest descent* algorithm permitting a local total energy minimization [20] .

In our case, we have accurately predicted that the vibrational frequencies of the clusters are very strongly depend on the size, structure and shape of the clusters, as well as, mainly influenced by the stretching and the bending mode vibrations of the atoms that is due to a changes on the bond length fluctuations for a small step-size $ds = \pm 0.01$ a.u. on the PES of equilibrium coordinates. The detailed information can be found below.

3.2 The vibrational frequency (ω_i) range of the cluster Au_{38} at $\Delta E = 0$

Table 1 shows that the low (at the least) and the high (at the most) frequency range of cluster Au_{38} . The lowest and the highest frequency range in between 1.62 cm^{-1} to 298.53 cm^{-1} .

Firstly, the cluster has some low frequencies (ω_{min}) in between $1.62\text{-}9.81 \text{ cm}^{-1}$, that is only for the very first 8 NVM, which comes even below the scale of Far Infrared FIR, IR-C 200-10 cm^{-1} .

Secondly, for the 9-92 NVM, the frequency ranges are occurred in between $11.98\text{-}199.43 \text{ cm}^{-1}$, which comes within the range of Far Infrared FIR, IR-C 200-10 cm^{-1} .

Thirdly, for the rest of the 93-108 NVM, are having the maximum high frequencies, which are (ω_i) - $205.14\text{-}298.53 \text{ cm}^{-1}$) falling within the range of Mid Infrared MIR, IR-C 3330-200 cm^{-1} .

3.3 The double and the single state degeneracy of the cluster Au_{38} at $\Delta E = 0$

First of all, the vibrational spectra of eigenvalues were found in the region between 1.62 and 298.53 cm^{-1} . Mainly, we have observed the most of the eigenvalues (90) are non-degenerate (single state) vibrations. Moreover, 20 out of 108 (NVM of (3N-6)) has 10 pairs of double-fold degeneracy (see Table 1). This gives a very strong confirmation of the energy can be observed and be released with the same

Figure 1: Au_{38} (C_1); Style (Wireframe): View along the a-axis, b-axis and c-axis (from top to bottom) at $\Delta E = 0$.

amount that corresponds to a certain local bond length re-arrangements. Very interestingly, at NVM 101, 102 that gives a pair of degeneracy $\{238.54, 238.89\} \text{ cm}^{-1}$ that has occurred within the range of Mid Infrared MIR, IR-C $3330\text{-}200 \text{ cm}^{-1}$. Surely, such kind of spectrum could be highly possible to observe in the experimental calculations. The other extreme case, NVM 5, 6 gives a pair of degeneracy $\{7.13, 7.67\} \text{ cm}^{-1}$ which has occurred even below the scale of Far Infrared FIR, IR-C $200\text{-}10 \text{ cm}^{-1}$, the most probably this could be silent in the experimental case. Finally, the consecutive pairs are: NVM 15, 16 $\rightarrow \{16.31, 16.80\} \text{ cm}^{-1}$ and NVM 17, 18 $\rightarrow \{18.54, 18.97\} \text{ cm}^{-1}$, which has occurred within the scale of Far Infrared FIR, IR-C $200\text{-}10 \text{ cm}^{-1}$, it reveals openly and gives a confirmation of four-edged core-level atoms are moving equally having with the same bond lengths on the clusters, additionally, this also can be observable in the experimental way of calculations.

Figure 2: Au_{38} (C_1) ; Style (Wireframe): View along the a^* -axis, b^* -axis and c^* -axis (from top to bottom) at $\Delta E = 0$.

Mainly, on the clusters, the degree of degeneracy is being released due to the bond length fluctuation of the symmetric as well as anti-symmetric move of the atoms. Additionally, for understanding and describing the atomic interactions in the cluster [28, 29, 30, 31, 32, 33], one must have the basic knowledge of, if the energy absorbed when bond breaks, at the same time, the energy released when bond forms. When increase the bond length then bond strength will become weaker but if we bring closer the bond length to each other, as a result, the bond strength will become stronger. We can observe attraction with a shared electrons as well as repulsion due to nuclei and electron shell. In addition to that due to the degree of degeneracy [which are being composed by] that gives a deep interpretation about the elliptical motion but that could be a single motion.

Figure 3: Au_{38} (C_1); Style (Wireframe, Polyhedral): The lowest energy geometrical structures of Au_{38} cluster. Standard orientation of crystal shape at $\Delta E = 0$.

3.4 Structural view of the shapeless structures:

When two atoms come very close, the force between them is always repulsive, because the electrons stay outside and the nuclei repel each other. Unless both atoms are ions of the same charge (e.g., both negative) the forces between atoms is always attractive at large internuclear distances r . Since the force is repulsive at small r , and attractive at small r , there is a distance at which the force is zero. This is the equilibrium distance at which the atoms prefer to stay. The interaction energy is the potential energy between the atoms. It is negative if the atoms are bound and positive if they can move away from each other. The interaction energy is the integral of the force over the separation distance, so these two quantities are directly related. The interaction energy is a minimum at the equilibrium position. This value of the energy is called the bond energy, and is the energy needed to

Figure 4: Au_{38} (C_1); Style (Wireframe): Rotate around the x axis (upward direction [above] and downward direction [below]) at $\Delta E = 0$.

separate completely to infinity (the work that needs to be done to overcome the attractive force.) The strongest the bond energy, the hardest is to move the atoms, for instance the hardest it is to melt the solid, or to evaporate its atoms. As a result, this makes a complete structure for those collection of the atoms.

In one case, from the Figs. 1, 2; we are looking down the direct space a, b, or c axis and in the other case we are looking down the reciprocal space a^* , b^* and c^* axes. Since the axis of Cartesian coordinates does not have any changes, because it is not a crystal structure.

Fig 3. clearly shows the standard orientation of crystal shape of $Au_{38}(C_1)$ cluster at $\Delta E = 0$ (the lowest energy geometrical structure). Nevertheless, to see the perspective view, we have plotted with a two different style (Wireframe, Polyhedral).

Above all, from the Figs. 4, 5 and 6 we are able to see the minute detailed

information of all different kinds of rotations that help us to visualize as well as to understand the orientation of the structures. Example: the structures are being rotated around the X-axis, the Y-axis and the Z-axis [See the number of faces, vertices and edges]. Over all, in the perspective view the shell-like structures are found. It is suggested that the ability of gold to form strong binding in low-coordinated systems is the reason for the occurrence of shell-like structures. This cluster is composed of two shells surrounding a central atom.

Nan Shao *et al.* [34] reported a joint experimental and theoretical study of the structural evolution of medium-sized gold clusters. They found that the most stable structures of Au_{36}^{-1} to Au_{38}^{-1} exhibit core-shell type structures all with a highly robust tetrahedral four-atom core. All of their three clusters are observed to possess two coexisting isomers in the cluster beam. The appearance of a fragment of the face centered cubic (FCC) bulk gold, that is, the pyramidal Au_{20}^{-1} , at the size of Au_{38}^{-1} implies that the cluster-to-bulk transformation starts to emerge at the medium size range. It is expected that larger pyramidal like intermediates may emerge in later medium-to large-sized Au clusters beyond Au_{38}^{-1} .

Surely, the ab initio calculations performed within this study confirm the theoretical and the experimental results: The most stable configuration of the cluster is not crystalline but with a high probability this cluster is a shapeless. This cluster was composed of two shells surrounding a central atom. Furthermore, a shell structure should not be considered as a kind of ordering in the context of small nanoparticles. Even the random arrangement of gold atoms, used as starting condition for some of the calculations, shows such a shell structure. We conclude that, the highest probability of the lowest energy structure for can be amorphous (as non-crystalline), which is an excellent agreement with the conclusion of the known results [34, 35, 36, 37].

4 Conclusion

We have calculated the vibrational frequency (at $\Delta E = 0$) of a medium size cluster the shell-like structure (of course, they are part of the family of so-called full-shell clusters). Last but not least, our present study gives an additional support to the prediction of the existence of shapeless stable structures in metal clusters. The appearance of such structures will always depend on the range of the n-body interaction responsible for the metallic cohesion in these systems. As a consequence, the existence of amorphous clusters does not depend on the use of any specific model potential but on the range and screening of the collective interaction between nuclei and electrons.

Figure 5: Au_{38} (C_1); Style (Wireframe): Rotate around the y axis (LHS direction [above] and RHS direction [below]) at $\Delta E = 0$.

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6 Availability of data and materials

The author declares that all data supporting the findings of this study are available within the paper (Table 1).

Figure 6: Au_{38} (C_1); Style (Wireframe): Rotate around the z axis (clockwise (CW) direction [above] and anti-clockwise (ACW) direction [below]) at $\Delta E = 0$.

7 Competing interests

The corresponding author declares, there are no conflicts to declare.

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9 Author's Contributions

All the work has been carried by the corresponding author.

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Figures

Figure 1

Au₃₈ (C1); Style (Wireframe): View along the a-axis, b-axis and c-axis (from top to bottom) at $\Delta E = 0$.

Figure 2

Au₃₈ (C1) ; Style (Wireframe): View along the a^* -axis, b^* -axis and c^* -axis (from top to bottom) at $\Delta E = 0$.

Figure 3

Au₃₈ (C1); Style (Wireframe, Polyhedral): The lowest energy geometrical structures of Au₃₈ cluster. Standard orientation of crystal shape at $\Delta E = 0$.

Figure 4

Au₃₈ (C1); Style (Wireframe): Rotate around the x axis (upward direction [above] and downward direction [below]) at $\Delta E = 0$.

Figure 5

Au₃₈ (C1); Style (Wireframe): Rotate around the y axis (LHS direction [above] and RHS direction [below]) at $\Delta E = 0$.

Figure 6

Au₃₈ (C₁); Style (Wireframe): Rotate around the z axis (clockwise (CW) direction [above] and anti-clockwise (ACW) direction [below]) at $\Delta E = 0$.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Au38AuTable1.pdf](#)