Effect of Size, Temperature, and Structure on the Vibrational Heat Capacity of Small Neutral Gold Clusters

Vishwanathan K*
Physical and Theoretical Chemistry, University of Saarland, Germany

Abstract

The vibrational heat capacity $C_{vib}$ of a re-optimized neutral gold cluster was investigated at temperatures 0.5-300 K. The vibrational frequency of an optimized cluster was revealed by small atomic displacements using a numerical finite-differentiation method. This method was implemented using density-functional tight-binding (DFTB) approach. The desired set of system Eigen frequencies (3N - 6) was obtained by diagonalization of the symmetric positive semi definite Hessian matrix. Our investigation revealed that the $C_{vib}$ curve is strongly influenced by temperature, size, and structure and bond-order dependency. The effect of the range of interatomic forces is studied; especially the lower frequencies make a significant contribution to the heat capacity at low temperatures. In addition to that, we have exactly predicted the vibrational frequencies ($\omega_{ij}$) which occur between 0.55 to 370.72 cm$^{-1}$, depending on the nanoparticle morphology at $T=0$ for small neutral gold clusters $Au_N=3$-$20$. This result has been proved and confirmed by the size effect values. It was found that beside the particle size, geometric shape, defect structure and an increase in asymmetry of nanoparticles effects on heat capacity. Surprisingly, the Boson peaks are typically ascribed to an excess density of vibrational states for the small clusters. Finally, temperature dependencies of the vibrational heat capacities of the re-optimized neutral gold clusters have been studied for the first time.

Keywords: Gold atomic clusters; Density-functional tight-binding (DFTB) approach; Finite-differentiation approximation; Force constants (FCs); Vibrational density of states (VDOS); Vibrational heat capacity ($C_{vib}$); Boson Peaks (BP)

Introduction

The study of nanostructured materials exhibiting novel properties is one of the most fascinating fields of current research. Small nanomaterial’s are of particular interest because of intriguing characteristics [1-3]. Nanoparticles with smaller dimensions may exhibit different properties in comparison with bulk material. The nanoparticles possess unique physic-chemical, optical and biological proper-ties which can be manipulated suitably for desired applications [4]. The advances in the field of nanoscience and nanotechnology has brought to fore the Nano sized inorganic and organic particles which are finding extensive applications as modifications in medicine and therapeutics, synthetic textiles and food packaging products [5]. The incorporation of engineered nanoparticles into household, personal care, consumer, and industrial products is increasing the exposure of humans and the ecosystems to these materials through production, transportation, storage, use, and disposal. Due to their small sizes, nano-materials (NMs) can enter into cells and interact with cell organelles and/or macromolecules and may thus disrupt the normal cellular functions [6-9]. Various NMs have been observed to show systemic effects when administered into systemic circulation, either intentionally for biomedical therapy or accidentally during environmental exposures, and may even cross the blood/brain barrier [6,8,10].

Clusters are well suited for a rapidly increasing number of applications and they have been an active eld of research for about a quarter of a century. Instead of reviewing all the literature, we refer the reader to the already existing review article by Baletto and Ferrando and also to the book by Wales [11,12]. Clusters can be viewed as solids at the Nano scale; yet molecular cluster chemistry and solid state chemistry have traditionally been considered as separate topics [13]. Nowadays, gold chemistry plays a very important role in Nano electronics and bio-nanoscience [14]. Particularly, gold clusters are of potential relevance to the Nano electronics industry and hence remain the subject of many experimental as well as theoretical studies. They contain edge atoms that have low coordination [15] and can adopt binding geometries that lead to a more reactive electronic structure [16]. Gold in the Nano regime, especially gold Nano crystals have shown size-sensitive reactive properties and are considered to be as promising chemical catalysts [17]. As one of the precious metals, gold has good corrosion resistance and extremely high stability and has been widely researched for biomedical applications [18].

The vibrational properties of clusters and small particles have been studied very intensively [19-26], and are vital for understanding and describing the atomic interactions in the cluster [27-32]. Thermal properties like heat capacity and thermal conductivity as well as many other material properties are strongly influenced by the vibrational density of states (VDOS). For this reason, a better understanding of the rules governing the vibrational properties of nanostructured materials is of high technological and must be given a high priority. The vibrational properties play a major role in structural stability [25,26,33].

The size-dependent properties of metallic clusters are currently of considerable interest, both experimentally [34] and theoretically [24,35]. Although the size effect on specific heat capacity has recently attracted much attention [36], many publications only focus on low temperature [37]. Some of the theoretical studies on the thermodynamic

*Corresponding author: Vishwanathan K, Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrucken, Germany, Tel: 496813020; E-mail: vishwanthan7@yahoo.com

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properties of clusters are based on molecular-dynamic simulations [11] from which the caloric curve, the heat capacity of clusters and the phase transitions can be determined. Nano clusters 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 [38]. 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 nanooptics [39] to applications in medicine and materials.

Reyes-Nava et al. [40] calculated the heat capacity for a few Na, systems using the simple many-body Gupta potential, which approximates the atomic interactions with an analytical description that does not explicitly include electronic degrees of freedom. It was found that solid-liquid phase transitions occurring over a certain temperature range depend critically on the size N of the system. Lee et al. [41] carried out accurate molecular dynamics simulations. From a literature search [42], one can see that only a very few theoretical studies attempt to calculate the thermodynamically properties of the clusters directly through de-termination of the partition function Z. Doye and Calvo calculated the partition function for Lennard-Jones systems using the simple many-body Gupta potential, which was calculated by Dong and Springborg [44]. The desired set of system Eigen frequencies (3N-6) is obtained by a diagonalization of the symmetric positive semi definite Hessian matrix. The effect of the range of interatomic forces has been studied. We found that the lower frequencies made an excellent contribution to the heat capacity (to be explored later) is obtained by a diagonalization of the symmetric positive semi definite Hessian matrix. The desired set of system Eigen frequencies (3N-6) is obtained by a diagonalization of the symmetric positive semi definite Hessian matrix. The effect of the range of interatomic forces has been studied. We found that the lower frequencies made an excellent contribution to the heat capacity (to be able to store significant heat energy) even at low temperatures (Figure 1). This novel and reliable methodology is constructed to explain the essence of the physical picture.

In our case, we are studying the finite-temperature behavior, which is sensitive to the size of the cluster [45] and the recent interest in planar gold clusters [46,47]. For example, according to Y. Dong and M. Springborg’s [44] results, the gold clusters with up to N = 6 have a two-dimensional structure, whereas from N=7, the gold clusters form three-dimensional structures. However, in some of the research studies, say that for the clusters with N=7-15, the structure can be either 2D or 3D or both. However, experimental and theoretical studies have found that planar structures are stable up to around 15 atoms [48,49].

In the present work, we shall at first remember our earlier results on Vibrational Heat Capacity of Gold Cluster AuN=14 at Low Temperatures [50]. As an extension of that work, we shall subsequently present new results devoted to the vibrational contributions to the thermodynamic low-temperature properties of the other clusters. Nevertheless, the purpose of the last part is to explore which kind of information can be obtained by studying the heat capacities of the AuN=14 cluster and, in particular, to see whether the heat capacities can be correlated to structural and/or energetic properties of the clusters.

**Theoretical and Computational Procedure**

The DFTB [51-55] is based on the density functional theory of Hohenberg and Kohn in the formulation of Kohn and Sham. In addition, the Kohn-Sham orbitals ψ(r) of the system of interest are expanded in terms of atom-centered basis functions {ψm(r)},

\[ ψ(r) = \sum c_m ψ_m(r), \quad m = j \]

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 \( c_m \). Index \( m \) describes the atom, where \( ψ_m \) is centered and it is angular as well as radially dependent. The \( ψ_m \) 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
\[ \sum_n c_{mn}(H_{nm} - \epsilon_n S_{mn}) = 0 \]  
(2)

Here, \( c_{mn} \)'s are expansion coe cients, \( H \) is for the single-particle energies (or where \( f \) 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
\[ H_{mn} = \langle \phi_m | H | \phi_n \rangle \]
\[ S_{mn} = \langle \phi_m | \phi_n \rangle \]  
(3)

They depend on the atomic positions and on a well-guessed density \( \rho(r) \). By solving the Kohn-Sham equations in an effective one particle potential, the Hamilton- 

\[ H_{ef}(r) = \epsilon_i \psi_i(r), H_{ef}(r) = \hat{T} + V_{ef}(r) \]  
(4)

To calculate the Hamiltonian matrix, the effective potential \( V_{ef}(r) \) has to be approximated. Here, \( \hat{T} \) being the kinetic-energy operator
\[ \sum_i (\hat{T} = -\frac{1}{2}\nabla^2) V_{ef}(r) \]  
(5)

\[ V_{ef}(r) \] is the Kohn-Sham potential of a neutral atom, \( r = r-R \) is an atomic position, and \( R \) being the coordinates of the \( j \)-th atom. 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,
\[ E_{tot} = \sum_i \epsilon_i - \frac{1}{2} \sum_i \sum_j U_{ij} (r_i - r_j) \]  
(6)

Here, the majority of the binding energy \( (I_j) \) is contained in the difference between the single-particle energies of the system of interest and the single-particle energies \( \epsilon_{fn} \) of the isolated atoms (atom index \( j \), orbital index \( m \)). \( U_{ij} (r_i - r_j) \) is determined as the difference between \( I_j \) and \( E_{SCF} \) for di-atomic molecules (with \( E_{SCF} \) 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 [53,55,56].

Re-optimization and numerical force constants (FCs)

The vibrational frequencies of the gold clusters were calculated within the harmonic approximation by diagonalization of the Hessian matrix. The finite-difference method has been implemented within DFTB approach for our calculation (a finite-difference approximation to calculate the force constants). We found a total energy over those gradients were extended for a small displacement \( ds = (\pm 0.01) \) a.u. within the equilibrium coordinates of a previously optimized structure (at \( T=0 \)) by Dong and Springborg [44]. However, the DFTB method has some difficulties to extract the force constants which are most important for our spectrum calculations. Mainly, to get one set of hessian matrix it is necessary to compute two times for both positive and negative gradients. It is a reasonable value and allowed us to discriminate between the translational, rotational motion (Zero-eigenvalues) and the vibrational motion (Non-Zero-eigenvalues).

In our case, we have calculated the numerical-first-order derivatives of the forces \( (F_{i,j} = f) \) 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,
and experimental results calculated by Bishea and Morse [64], Gruene et al., [65] Mancera [66], Molina et al. [67], and with Nose [68], for the vibrational spectrum of Au$_n$ at 0.1-3 K. The lowest and the highest frequency ranges are 0.55-34.18 cm$^{-1}$ and 165.46-370.72 cm$^{-1}$, respectively.

The relative importance of high and low frequencies naturally depends on the size, structure, and frequency spectra of the clusters. The size is super critical to the physiochemical properties of Au cluster. It is certainly affected by the ratios of dangling bond to overall bulk bonding number. Nanoparticles have a substantial fraction of their atoms on the surface. The surface energy is the (thermodynamically unfavorable) energy of making dangling bonds’ at the surface. Atoms at the surface are under-coordinated, and because breaking bonds results in a loss of energy, surface atoms always have higher energy than atoms in the bulk. It is surely expected that such a vibrational spectrum depends on the material, size, and shape of clusters and nanoparticles [22]. Most importantly, the vibrational properties of atomic clusters are a fingerprint of their structures and can be used to investigate their thermodynamic behavior at low temperatures [23].

Of course, there is an increasing amount literature illustrating the conceptual and practical relevance of two dimensional (2D) systems with long range interactions [69-71]. The vibrational frequency of FCs contributions comes from both the symmetric and the asymmetric stretch and bending modes. We believe that bond-stretching ($k_s$) and bond-bending ($k_b$) force constants depend on the nearest neighbor distance obtained from lattice vibrations [72]. It is important to note that the stretching modes moves to lower frequency (approaching zero), and the bending mode b moves to higher frequency. The low frequencies are probably due to the influence of large collective motions of atoms and the high frequencies due to localized motions of atoms [73], which diminish bond length fluctuations. The interatomic interaction that is responsible for the frequency ranges and the variation of the FCs led to a shift in the mode frequencies [74].

The vibrational heat capacity $C_{vib}$ for the lowest frequency $\omega_{\text{min}}$ at 0.1-30 K

Figure 2 has shown $C_{vib}$ for all the clusters. The frequency of the lowest vibrational state of a nanoparticle is $\omega_{\text{min}}$. The asymptotic behavior of heat capacity at low temperatures takes the form with respect to $\omega_{\text{min}}=T=0.1-3$ K. As a result, the effect of the lowest frequency modes is dominant for all the clusters. This is very clear evidence that shape of $C_{vib}$ curves differ with respect to the size and structure of the clusters.

Interestingly, for all the clusters the $C_{vib}$ starting at ranges (critical temperature, T) are within the temperature range of about $T=0.1-3$ K. As a result, the effect of the lowest frequency modes is dominant for all the clusters. This is very clear evidence that shape of $C_{vib}$ curves differ with respect to the size and structure of the clusters.

The clusters Au$_{N}$ (N=4, 5, 6, 8, 9, 11, 12, 15, 17, 18, 20) have extremely low $\omega_{\text{min}}$ frequencies between 0.55-9.83 cm$^{-1}$. Which is even lower than the range of Far Infrared FIR, IR-C 200-10 cm$^{-1}$! The starting at ranges are within the temperature range of about $T=0.1-0.7$ K. In the same manner, for the clusters Au$_{N}$ (N=3, 7, 10, 13, 14, 16, 19) the frequencies are in between 10.08-34.17 cm$^{-1}$. Which is within the range of Far Infrared FIR, IR-C 200-10 cm$^{-1}$. Due to this the starting at ranges are within the temperature range of about $T=0.7-3.0$ K.

In Figure 2, particularly the cluster Au$_{4}$ (black line) and Au$_{16}$ (blue line) both are very similar due to their $\omega_{\text{min}}$ values, 17.02 and 17.13 cm$^{-1}$. However, even though they have different sizes, they have the very same $C_v$ symmetry.

Moreover, the $C_{vib}$ curve shows the asymptotic behavior, rising smoothly and finally reaching a linear flat at temperatures above $T=15$ K for all Au$_N$ (N=3-20) clusters. This is scientifically significant with respect to the cluster size and shape. The minimum vibrational frequency $\omega_{\text{min}}$ plays an important role in determining the shape of the $C_{vib}$ curve at low temperature.

**Anomalous behavior of neutral gold clusters:** In Figure 2, we have noticed some anomalous behavior in the shoulder of the heat capacity $C_{vib}$ curves between the clusters Au$_N$ (N=10-19). And the same behavior is exhibited between the clusters Au$_{16}$ (N=4-5), which is due to the size and structure de-pendency of the clusters. The data reveal an anomalous contribution to the heat capacity at low temperatures. It was identified that this anomaly in heat capacity is caused by the effect of disorder in the cluster size and structure. Probably, gold nanostructures exhibit anomalous thermal behavior such as the shape transformation of Nano rods, generation of nanoparticles by heating a mesh etc., at extremely low temperature [75]. The results of our work within the numerical model caused us to consider the intrinsic relation between normal (anomalous) particle diffusion and normal (anomalous) heat conduction, along with size dependent thermal conductivity.

The vibrational heat capacity $C_{vib}$ for the highest frequency $\omega_{\text{max}}$ at 10-1000 K

Figure 3 has shown $C_{vib}$ for all the clusters. The frequency of the highest vibrational state of a nanoparticle is $\omega_{\text{max}}$. The asymptotic behavior of heat capacity at low temperatures takes the form with respect to $\omega_{\text{max}}=T$ of eqn. (8). The $\omega_{\text{max}}$ value is determined by the size, shape, and defect structure of the nanoparticle.

Here at $C_{vib}$ curve, we did not see much of a difference on the shoulder (asymptotic curve) that means they are very much closer to each other. Of course, here we do not see anomalous behavior as we have observed in the case of low frequency (Figure 2). The reasons are, the high frequencies do contribute to the heat capacity when the temperature increases from 100 to 300 K ($C_{vib}$ increases from 0.04 $k_B$ atom to 0.11 $k_B$/atom). Most importantly, as this takes place, vibrational modes with lower frequencies give larger contribution to the heat capacity at ambient temperatures. However, the high frequencies do not generate large $C_{vib}$ differences when comparing different cluster sizes (Figures 2 and 3). The increase in heat capacity depends on the particle size, shape and the clusters perfection.

In Figure 3 you can see $C_{vib}$ for all the clusters, and, most importantly, you can see that $C_{vib}$ starting at ranges are within the temperature range of about $T=10-37$ K, where the effect of the highest frequency modes are dominant for all the clusters. It is evident, that, the starting points varies with respect to the critical temperature $T$, from which the $C_{vib}$ curve raises either suddenly or smoothly. The overall temperature ranges are 10-1000 K. The maximum high frequency falls within the range of Mid Infrared MIR, IR-C 3330-200 cm$^{-1}$ for the corresponding harmonic frequency ranges of 165.46-370.72 cm$^{-1}$, with the one exception of the frequency 165.46 cm$^{-1}$ which is for the Au$_N$ (N=4) cluster.

**Comparison:** The intensity of the enhancement of the specific heat
capacity for the lowest vibrational frequency comes in the temperature range of 0.1-15 K (Figure 2) but for the highest vibrational frequency it covers the temperature span 10-500 K (Figure 3). In both of these cases, above these maximum temperatures it gets saturated. Nevertheless, the vibrational heat capacity $C_{vib}(min)$ and $C_{vib}(max)$ is zero at $T=0$ but there are variations in the at ranges which is only because of the first mode of the vibrational frequencies, and it nally asymptotes towards $0.125\ k_B/\text{atom}$ at high temperatures.

**Superposition of the lowest, the middle and the highest frequencies**

The ESI shows the frequency ranges for all the clusters, $Au_N$ ($N=3-20$). Figures 4-7 shows how $C_v$ varies with cluster size, structure and temperature. These results show that $C_{vib}(min)$ curve for the lowest frequency, by that we mean very low frequency shoulder, varies for different clusters with respect to their size and structure. It is almost identical with the middle $C_{vib(mid)}$ and the high frequency $C_{vib(max)}$ curve. These results will be important to describe heat transfer at Nano scale as well as Casimi-Lifshitz forces between clusters due to thermal quantum fluctuations [76].

**The lowest frequency**

Figure 4 shows the very beginning of the low and the high frequencies, $Au (N=5)$, 0.55 cm$^{-1}$ and $Au (N=10)$, 34.18 cm$^{-1}$. However, both the frequency values are only for the lowest frequency range. Here, one of the frequency ranges is not within the Far Region of IR (Far Infrared FIR, IR-C), 200-10 cm$^{-1}$.

A very interesting observation that $Au (N=5)$ has very high heat capacities ($C_{vib(min)}\approx 0.125\ k_B/\text{atom}$ at 5 K), whereas $Au (N=10)$ has low heat capacities ($C_{vib(min)}\leq 0.01\ k_B/\text{atom}$ at 5 K). Comparisons of the relative low-frequency modes which were produced at close and distant locations for departures and arrivals at $C_{vib(max)}$. The effects of temperature on the low-frequency vibrational spectrum and local structural arrangements, and the low-frequency density of states distributions reveal that increasingly transverse atoms motions play a dominant role in controlling the band corresponding to the bending or transverse oscillations of the nano-particles at low temperatures.

The exact middle frequency (only possible for the odd sized clusters): Figure 5 shows that the exact middle frequencies ($\omega_{mid}$) as a function of cluster size ($N$), $Au_{N=3,5,7,9,11,13,15,17,19}$ [odd number of clusters] at $T=0$ K, and the respective modes are 2.5,8,11,14,17,20,23,26. The lowest middle frequency ($\omega_{min}$) 79.22 cm$^{-1}$ of $Au (N = 19)$, and the highest middle frequency ($\omega_{max}$) 106.38 cm$^{-1}$ of $Au (N=7)$. 

Figure 3: $Au_N$ ($N=3-20$) cluster: $C_{vib}$ per atom (for the highest frequency $\omega_{max}$ in cm$^{-1}$) as a function of temperature at 10-1000 K.

Figure 4: $Au_{5,10}$ cluster: $C_{vib}$ per atom as a function of temperature at 0.5-300 K. It is a superposition and the contributions from the $\omega_{min}$ and $\omega_{max}$ vibrational modes.

Figure 5: Only for the exact middle frequency ($\omega_{mid}$) as a function of cluster size ($N$), $Au_{N=3,5,7,9,11,13,15,17,19}$ [odd number of clusters] at $T=0$ K, and the respective modes are 2.5,8,11,14,17,20,23,26. The lowest middle frequency ($\omega_{min}$) 79.22 cm$^{-1}$ of $Au (N = 19)$, and the highest middle frequency ($\omega_{max}$) 106.38 cm$^{-1}$ of $Au (N=7)$. 

**Figure 3:**

- **Ground State:** $C_{vib}(min)$ per atom (for the lowest frequency) as a function of temperature at 0.1-15 K.
- **Upper State:** $C_{vib}(max)$ per atom (for the highest frequency) as a function of temperature at 10-500 K.

**Figure 4:**

- **Ground State:** $C_{vib}(min)$ per atom as a function of temperature at 0.05-300 K.
- **Upper State:** $C_{vib}(max)$ per atom as a function of temperature at 0.5-300 K.

**Figure 5:**

- **Ground State:** $C_{vib}(min)$ per atom as a function of odd cluster size ($N$) at $T=0$ K.
- **Upper State:** $C_{vib}(max)$ per atom as a function of odd cluster size ($N$) at $T=0$ K.
number of clusters, \( \text{Au}_{3,5,7,9,11,13,15,17,19} \), out of which \( \text{Au} (N=19) \), has the lowest middle frequency, 79.22 cm\(^{-1}\) and \( \text{Au} (N=7) \), has the highest middle frequency, 106.38 cm\(^{-1}\) which is the frequency range and the rest of the odd number of clusters which falls within this range (Figures 5 and 6). Here, the frequency ranges are within the Far Region of IR (Far Infrared FIR, IR-C), 200-10 cm\(^{-1}\).

The highest frequency: In the same manner, Figure 7 shows mainly only the very end of low and high frequencies, \( \text{Au} (N=4) \), 165.46 cm\(^{-1}\) and \( \text{Au} (N=20) \), 370.72 cm\(^{-1}\). However, both the frequency values are only for the highest frequency range. Here, the frequency ranges are within the Far Region of IR (Far Infrared FIR, IR-C), 200-10 cm\(^{-1}\) and also within the Middle Region of IR (Mid Infrared MIR, IR-C), 3330-200 cm\(^{-1}\). From the Figures 4-7, we certainly confirmed that the low frequency contributions are much higher than the middle and the high frequency contributions to the heat capacity, \( C_{\text{vib}} \). Amazingly, \( C_{\text{vib}} \) curves differ significantly with respect to the low/middle/high frequency as a result of temperature as well as size and structure of the clusters.

The vibrational spectrum (\( \omega \)) of \( \text{Au}_{N=3} \) and the reliability of our model

Bishea and Morse [64] did research on the spectrum of \( \text{Au}_2 \). For example, they found that the totally symmetric breathing mode in the excited electronic state had a frequency of 182.9 cm\(^{-1}\). We should expect the totally symmetric breathing mode in the ground state will have a somewhat higher frequency, perhaps around 200-250 cm\(^{-1}\). The gold trimer, \( \text{Au}_3 \) has three normal modes, two of which may be degenerate, depending on the symmetry. Moreover, additional modes may be in other experiments. In our case, after the re-optimization the vibrational frequencies were found to be 19.21, 87.47 and, 246.21 cm\(^{-1}\).

Throughout our calculated vibrational frequencies, we assume that the ground state of \( \text{Au}3 \) must have either \( C_{\text{vib}} \) or \( C_{\theta} \) geometry. We consider the various possible ways that we can arrange the three atoms in \( \text{Au}_3 \), as the Jahn-Teller distortion will drive it away from the equilateral \( D_{3h} \) configuration [77-79]. For example, \( \text{Au}_3 \) without the spin-orbit coupling (SOC) effects exhibits a Jahn-Teller distortion towards the \( C_{2v} \) symmetry; however, with spin-orbit coupling it recovers the \( D_{3h} \) symmetry.

An important point: The very low frequency mode 19.21 cm\(^{-1}\) (Figure 1), corresponds to a motion that is not well-approximated as a harmonic motion, since motion on the potential energy surface along this coordinate converts the molecule from one equivalent isosceles triangle to another. As we move along this coordinate, the potential energy goes up (initially quadratically), then becomes anharmonic, then reaches a maximum, then descends into a different minimum where a different gold atom lies at the apex of the isosceles triangle. This will have implications for the heat capacity (\( C_{\theta} \)) (Figure 8), which we have modeled as a pure harmonic oscillator.

With this confirmation of \( \text{Au}_3 \) vibrational modes, and with the help of Gatedit package [80]. Tolerance for principal axis classiﬁcation: 0.00500 in angstrom (A) and Precision for atom position: 0.00399 in angstrom (A) we went back to the total energies, structures and then veriﬁed their symmetry of global structure optimization which were predicted by Dong and Springborg [44]. As a result, some of those \( \text{Au}_3 \) clusters symmetries were differed (For example, \( \text{Au}_{4} (D_{3d}), \text{Au}_{6} (D_{3d}/D_{5d}), \text{Au}_{10} (D_{3d}), \text{Au}_{11} (C_{3v}), \text{Au}_{12} (C_{3v}), \text{Au}_{13} (C_{3v}), \text{Au}_{16} (C_{2v}), \text{Au}_{17} (C_{2v}), \text{Au}_{19} (C_{2v}), \text{Au}_{20} (C_{2v}) \)) (Figures 1-6 and 9-14).

The discrepancy at the frequency modes: For the global minimum energy structure, if the \( \theta > 90^\circ \) then the modes are 24.7, 127.0, 183.1 cm\(^{-1}\) and if the \( \theta > 60^\circ \) with acute structure the modes are 69.0, 89.3.
167.1 cm$^{-1}$ again, and if the $<60^\circ$ with acute structure the modes are 5.3, 109.2, 168.6 cm$^{-1}$, which are Harmonic frequencies for various isomers of Au$_n$ calculated using PBE/VDB by Mancera and Benoit [66]. So this gives a confirmation that the vibrational modes varies with respect to the bond angle and isomers. Even for the experimental values [64] the modes are 61.9, no value (silent) and 179.9 cm$^{-1}$ as well as, in another experimental calculation [81], no value (silent), 118 and 172 cm$^{-1}$.

**The vibrational heat capacity $C_{vib}$ of gold neutral clusters**

Figures 15-17 shows $C_{vib}$ as a function of temperature for different cluster sizes. Out of Au$_n=3$-20 cluster we have selected some of the 14 special clusters which display different interesting properties. The vibrational heat capacity $C_{vib}$ has been plotted with respect to $\alpha = \omega / T$ and $\alpha = \omega / (0.6950356^* T)$ of eqn. (8) at temperature, $T=0.5$-300 K.

The $C_{vib}$ curve is a sum of $C_{vib}$ curves, one for each normal mode of
Vibrational heat capacity, $C_{vib}$, is a measure of the energy required to increase the temperature of a system by one degree. The $C_{vib}$ curves for different clusters exhibit an S-shaped pattern, with inflection points where the slope changes direction. These inflection points correspond to the vibrational frequencies of the clusters. The temperature at which the inflection point occurs is proportional to the vibrational frequency for that cluster.

**Figure 13:** Corrected and predicted minima of the global structure optimization of Au$_{18}$ ($D_1$) and Au$_{19}$ ($C_1$) (from top to bottom) at $T=0$ K.

**Figure 14:** Corrected and predicted minima of the global structure optimization of Au$_{19}$ ($C_1$) at $T=0$ K.

The temperature at which the inflection point occurs can be calculated using the equation $\alpha_i = \frac{\omega_i}{(0.6950356 \times T)}$ for eqn. (8) and the corresponding Boson peak $C_{vib} = T^3$ vs. $T$.

**Figure 15:** Au$_{6,7,8}$ $C_{vib}$ per atom as a function of temperature at 0.5-300 K. $\alpha_i = \frac{\omega_i}{(0.6950356 \times T)}$ of eqn. (8) and the corresponding Boson peak $C_{vib} = T^3$ vs. $T$.

**Figure 16:** Au$_{9,10,13,14,15,18,20}$ $C_{vib}$ per atom as a function of temperature at 0.5-300 K. $\alpha_i = \frac{\omega_i}{(0.6950356 \times T)}$ of eqn. (8) and the corresponding Boson peak $C_{vib} = T^3$ vs. $T$.

**Figure 17:** Au$_{5,6,9,12}$ $C_{vib}$ per atom as a function of temperature at 0.5-300 K. $\alpha_i = \frac{\omega_i}{(0.6950356 \times T)}$ of eqn. (8) and the corresponding Boson peak $C_{vib} = T^3$ vs. $T$. 

Vibration. Each of these individual $C_{vib}$ curves is S-shaped, but with the inflection points (where the curve changes from concave up to concave down) occurring at different temperatures. The temperature of the inflection point is proportional to the vibrational frequency for that...
particular normal mode. Since each individual \( C_{\text{vib}} \) curve is S-shaped, the sum must be S-shaped (to a degree) also. However, because our molecules/clusters have some normal modes of vibration with extremely low vibrational frequencies, some of the individual curves being summed to give the total \( C_{\text{vib}} \) curve will have their inflection points at extremely low temperatures. If we examined the \( C_{\text{vib}} \) curve at extremely low temperatures (perhaps lower than we have calculated, at \( 0.4 \text{ K} \rightarrow 0 \text{ K} \)), we would see that they start out at with \( C_{\text{vib}}=0 \), then rise from \( C_{\text{vib}}=0 \) (concave up), then go through an inflection point at a low temperature. All of this follows logically from the fact that the overall \( C_{\text{vib}} \) curve for a single molecule/cluster is a sum of \( C_{\text{vib}} \) curves for each vibrational mode.

\( \text{Au}_3 \) (a planar-triangular \( C_3 \)): In fact, under careful observation, in the \( C_{\text{vib}} \) curve, there is a minute \( \chi \text{e}r k/b e n d i n g \), in between 0.15 and 0.25 \( k_b \)/atom at the temperature range about 0.5 to 10 K (Figure 8). Thus, there seems to be a strong correlation between the atom located coordination numbers and the bond angle, which result in a huge variation, due to the fact that the normal mode energy intervals (19.21; 87.47 and; 246.21 \( \text{cm}^{-1} \)) are so large which has a great influence on the stability of the cluster.

\( \text{Au}_4 \) (a planar-triangular \( D_n \)), \( \text{Au}_5 \) (a decahedron \( D_n \)) and \( \text{Au}_6 \) (a tetrahedron \( T \)):

In Figure 15, the \( C_{\text{vib}} \) curve starts with the temperature at 0.6 K, and makes a hump-like shape which is an a fascinating phenomenon to observe. Most importantly, \( N=6 \) is a much more rapidly increasing function of \( T \) at low temperature than in the cases of the other cluster sizes (but still \( C_{\text{vib}} \) rises smoothly and reaches the size effect value). However, it has more energy stored at low temperature, but the \( C_{\text{vib}} \) curve crosses over at about 40 K of the \( \text{Au} \) \((N=8)\) and 50 K of the \( \text{Au} \) \((N=7)\) clusters which demonstrates its rapidness. Nevertheless, the main reason could be, the minimum frequency start with degenerate, followed by a double state degenerate, followed again double state degenerate and some single state degenerates and finally end with double state degeneracy, which also provides another confirmation that atoms are located in a periodic and zigzag arrangements with respect to the nearest neighboring atoms coordination. In the case of \( \text{Au}_4 \) and \( \text{Au}8 \) both \( C_{\text{vib}} \) starts at 0.5 K and rises smoothly with asymptotic behavior, and these are the only clusters which have more double state degeneracy and triplet state degeneracy, respectively. So the structural dependency of heat capacity is being confirmed with the triple, double and single state degeneracies.

Interatomic interactions in the clusters reflect a frequency distribution with a high degree of degeneracy due to the high symmetry of their lowest energy configurations (the potential energy with respect to the atomic coordinates). No degeneracy was obtained for the other gold clusters (except \( \text{Au}_{11}(N=6, 7, 8) \)) due to the absence of symmetry in their minimum energy.

\( \text{Au}_5 \) (\( D_n \)); \( \text{Au}_6 \) (\( S \)); \( \text{Au}_7 \) (\( C \)); and \( \text{Au}_8 \) (\( C \)):

In Figure 16, it is shown that the \( C_{\text{vib}} \) curve heat capacity goes sharply up from zero, without the small region where the heat capacity is very close to zero. The very low frequency modes begin contributing to the heat capacity at lower temperatures. It is possible to have very low lying excited electronic states that can be thermally excited at low temperatures. If that is the case, there will be an additional contribution to the heat capacity due to electronic excitation. The heat capacity of the real substance would be higher than what we have calculated. However, no experimental data is available for comparison. Surprisingly, for each size \( C_{\text{vib}} \) there is a monotonously increasing function of \( T \) (which tends asymptotically). The temperature dependence of the individual modes (Figures 4-7) led to the total vibrational heat capacity for all the clusters.

The calculated heat capacity curve remains near zero at the lowest temperatures, then begins monotonically rising near 1.75 K. Similar behavior is reflected in all of the clusters that were studied, although the precise location of the transition from near-zero values to the monotonic increase varies. The existence of this low-temperature, near-zero heat capacity regions arises because all of these clusters have a lowest vibrational frequency. The heat capacity only begins to deviate significantly from zero when the thermal energy, \( kT \), has a significant likelihood of exciting the lowest frequency vibrational mode. This behavior is in effect a quantum size effect, resulting from the sparse vibrational density of states.

In addition at low temperatures it is the lowest-energy (lowest-frequency) vibrational states that mainly contribute to heat capacity. Indeed, if the frequency of the lowest vibrational state of a nanoparticle is at a minimum, the asymptotic behavior of heat capacity at low temperatures arises. This is a region \( T=0.5-1.75 \text{ K} \) where the effect of the lowest frequency internal modes are dominant for all the clusters.

\( \text{Au}_{14} \) (\( C \)):

In our case, \( \text{Au}_{14} \) has \( C \) symmetric structure and indeed of low symmetry [44]. The vibrational spectrum in structures spans the range from 17.02 up to 240.20 \( \text{cm}^{-1} \). The \( C_{\text{vib}} \) spectrum includes several low-frequency modes. However, the frequencies are not necessarily all distinct due to degenerations state; i.e., some of the roots of the secular equation may occur more than once. In Figure 16, we show the heat capacity \( C_{\text{vib}} \) as a function of \( T \), for \( N=14 \) cluster size. As shown by this figure, at very low temperatures (\( T>1.75-0.5 \text{ K} \)) the \( C_{\text{vib}} \) curve falls off to zero. Surprisingly, at lower temperatures (1.75-0.5 K) the value of \( C_{\text{vib}} \) is very small and close to zero. This shows that some of the modes of vibration of the cluster are frequencies which cannot be accessed at low temperatures.

Figure 16 also shows that interatomic vibrations in heat capacity can be neglected around (1.75-0.5 K) and the \( C_{\text{vib}} \) curve rises gradually with temperature, which is an exact signature of the vibrational changes. The smooth change, especially pronounced at low temperatures (1.75-25 K), is even more interesting.

It is due to the energy increase of the system. For a given size, the reduction of the heat capacity is more significant at lower temperatures. As the temperature is raised, the difference between the vibrational energies becomes progressively more conspicuous. There can never be any method which explains the difference as long as we retain a simple harmonic oscillator. However, the \( C_{\text{vib}} \) curve gives a confirmation that is temperature dependent. In the quantum limit, \( T(1.75-0.5 \text{ K}) \rightarrow 0 \), the \( C_{\text{vib}} \) curve approaches zero, while in the classical limit, \( T(300 \text{ K}) \rightarrow \text{high temperature} \rightarrow \text{size effect} \), the curve moves towards a value of \( C_{\text{vib}}=2.50 \text{ \( k_b \)/atom} \), which clearly indicates a temperature influenced size effect/dependency.

\( \text{Au}_{14} \) and \( \text{Au}_{15} \):

For Au clusters, Koskinen et al., [51] calculated above the ground states of \( N=11, 12, 13, \) and 14, respectively, corresponding roughly to \( T=1000 \text{ K} \). Particularly, they have shown \( \text{Au}_{14} \) as an example to demonstrate the features of a novel liquid-liquid coexistence (LLC), for \( \text{Au}_{14} \) the LLC ends at \( E_{\text{tot}} \sim 2 \text{ eV} \) followed by a 3D-liquid-3D-solid coexistence for \( E_{\text{tot}}<1.1 \text{ eV} \) corresponding roughly to temperatures around 300 K (Figure 3c) for the partial caloric curves \( T(E_{\text{tot}}) \) of both dimensionalities [51]). The planar clusters form the hot, low-potential energy phase. The 3D liquid phase has the heat capacity of \( C_{\text{vib}}=4.05 \text{ K} \) and the 3D solid phase \( C_{\text{vib}}=3.06 \text{ K} \) per atom, which
are greater than our estimated value \( C_{\text{vib}} \approx 2.50 \text{ kJ/mol at 300 K} \), for neutral cluster \( \text{Au}_n \).

Moreover, the expected absolute value \( C_{\text{vib}} \) should be \( 2.57 \text{ kJ/mol} \). In our case, the difference is only \( 0.07 \text{ kJ/mol} \), which are reasonable within the numerical accuracy. Nevertheless, \( C_{\text{vib}} \) has been achieved almost an accurate value, \( 2.56(39) \text{ kJ/mol} \) when the temperature is high enough, \( 950 \text{ K} \). But in the Koskinen et al., [51] case, the errors were higher \( 1.48 \) and \( 0.49 \text{ kJ/mol} \) than the expected absolute value for both 3D liquid and 3D solid phases. This discrepancy is due to the minimum energy difference of the anionic [51] and neutral clusters (which are more stable) [44]. So we conclude that the 2D planar structure is preferential over the 3D Structure.

\[ \text{Au}_{n}(D_3h) \text{: In our case, } \text{Au}_{n}(D_3h) \text{ has } D_3 \text{ symmetry and indeed of low symmetry} [44]. \text{ The vibrational spectra of eigenvalues were found in the region between } 8.07 \text{ and } 232.46 \text{ cm}^{-1}. \text{ In a recent study, Bulusu et al.,} [82] \text{ found that hollow gold cages exist for } \text{Au} \text{ with } N=16-18 \text{ both according to experimental and theoretical results. In the study of Dong and Springborg} [44], \text{ they found many AuN} \text{ clusters with } N=7-20 \text{ to have cage-like structures. We found that the } C_{\text{vib}} \text{ curve of a neutral gold cluster increases smoothly towards the high temperatures and approaches a constant value of about } C_{\text{vib}}=2.59, \text{ in } \text{kJ/mol} \text{ at } 300 \text{ K}, \text{ essentially becoming at.} \]

Moreover, the expected absolute value (for size-dependent) should be \( C_{\text{vib}}=2.67 \text{ kJ/mol} \) for neutral cluster \( \text{Au}_{n} \). In our case, the difference is \( 0.08 \text{ kJ/mol} \) from the expected value. Again, nevertheless, \( C_{\text{vib}} \) has been achieved almost an accurate value, \( 2.65(895) \text{ kJ/mol} \) when the temperature is high enough, \( 950 \text{ K} \). With this we can be sure that the structure can be \( D1 \) for \( \text{Au}_{n} \). However, the \( C_{\text{vib}} \) curve shows that the heat capacity goes sharply up from zero, excluding the small region where the heat capacity is very close to zero, at \( T=0.5-1.25 \text{ K} \). The rest of the clusters size effect has been addressed well.

The acoustic vibrations are more important at low temperatures, because they dominate the heat capacity [20-26]. Low-frequency modes of harmonic systems can be related to the small amplitude of acoustic waves, which are experimentally observed in all elastic bodies. This implies that, at low temperatures, the specific heat is largely determined by the low frequency part of the vibrational spectrum and it is only at high temperatures that a substantial portion of the spectrum comes into play.

The vibrational (Phonon) density of states has been calculated by Saucedo and Garzon [25]. Eigenvectors of normal modes are associated with low and high frequency vibrations. This behavior is caused by the stiffening of the bonds (i.e., the frequency shifts to a higher value as the strength increases). Such a local stiffening of the diagonal terms of the FCs matrix is known to lead to the formation of localized oscillation modes [83]. The nature of the bond is most readily interpreted through the eigenvectors and eigenvalues of this FCs Hessian matrix. The most important contribution is a short-range order in the disordered state of the cluster. FCs (stretching and bending modes) matrices, independent of symmetry and magnitudes, are strongly correlated with the bond lengths. A small change in bond length upon disordering can have a large effect on FCs and vibrational entropy. The general increase in the bond angle in this series indicates an increasing repulsion between the bonds and this is consistent with the increasing bond order.

The contribution of the vibrational free energy is related to the disorder in the FCs. In general, gold clusters are not so strongly disordered, having only minor positional disorder. Whereas the zigzag structure (for nonlinear clusters) has lower energy, in contrast, the zigzag structure within the clusters readily changes into 2D or 3D structures with its nearest neighbors towards better stabilization by multi-coordination [84]. We must remember that each normal mode acts like a simple harmonic oscillator, with a concert motion of many atoms. The center of mass does not move. All atoms pass through their equilibrium positions simultaneously and normal modes are independent; they do not interact. This means that normal modes do not exchange energy. This is only true in the absence of harmonic terms, which is a theoretical approximation that is never achieved in reality.

Thus, in these \( \text{Au}_{n} \) (\( N=3-20 \)) cases, frequencies are low and the curve is squeezed so that this point on the curve falls at a low temperature. If the frequencies are much higher, the same point on the curve will fall at a much higher temperature. The heat capacity remains significantly above zero at lower temperatures. This is because the neutral gold cluster has much lower vibrational frequencies than most molecules have. Nevertheless, our investigation revealed, the vibrational heat capacity curve shows a very strong influence of size, temperature, structure and bond-length (stretching, bending) dependency (Figure 18).

The Boson peak (BP) \( C_{\text{vib}}/T^2 \) vs. T of the neutral gold clusters: As shown.
in Figures 8, 15-17, with respect to the eqn. (8) and the corresponding Boson peak \( C^{\text{Vib}}_\text{Vol}/T^3 \) vs. \( T \) were plotted at temperature within the range \( T=0.5-30 \) K. Truly, we are surprised by our observation of a Boson peak in our nanoparticles. Hao Zhang and Jack F. Douglas [85,86] usually study the Boson peak from the velocity autocorrelation function, but they are both concerned about a ‘ excess’ contribution to the vibrational density of states. This feature has been observed in metal nanoparticles and zeolites and attributed to the coordinated harmonic motions of groups of atoms in the boundary region of the particle. There are similarities here to a glass because the surface of a nanoparticle has many features in common with this class of materials. In cases where the modes have been resolved, the Boson peak has corresponded to a ring of oscillating particles, the relatively low mass being related to the relatively high mass of these modes. Farrusseng and Tuel [87] also studied the perspectives on zeolite-encapsulated metal nanoparticles and their applications in catalysis.

One of the universal features of disordered glasses is the “Boson peak”, which is observed in neutron and Raman scattering experiments. The Boson peak is typically ascribed to an excess density of vibrational states. Shintani and Tanaka [88] studied the nature of the Boson peak, using numerical simulations of several glass-forming systems. They have discovered evidence suggestive of the equality of the Boson peak frequency to the 1/e-Regel limit for “transverse” phonons, above which transverse phonons no longer propagate. Their results indicate a possibility that the origin of the Boson peak is transverse vibrational modes associated with defective soft structures in the disordered state. Furthermore, they suggest a possible link between slow structural relaxation and fast Boson peak dynamics in glass-forming systems.

However, Malinovsky and Sokolov [89] found that the form of a low-frequency Boson peak in Raman scattering is universal for glasses of varying chemical composition. They have shown that from the shape of the Boson peak one can determine the structural correlation function, i.e., the character of violations of ordered arrangement of atoms within several coordination spheres in non-crystalline solids. Most importantly, very recently Milkus and Zaccone found [90] that bond-orientation order is not so important for the Boson peak. Whereas a much more important parameter is the local breaking of inversion symmetry.

Indeed, there is similar behavior of heat capacity in glasses and clusters at low temperatures. Glasses have some distribution of interatomic distances and modification of atomic coordination induced by disorder, compared to periodic crystals [91]. In clusters or nanoparticles, it is caused by the reduced atomic coordination of the surface atoms. Because the ratio of surface to volume is large, the number of atoms with reduced coordination is significant. The vibrations of surface atoms enhance the VDOS at low energies and the heat capacity increases.

The Boson peak is usually studied in glasses, where enhancement of heat capacity is induced by disorder. The modeling of clusters may be important for understanding the mechanism which lead to this effect. In glasses, there are different local con gurations of atoms that may be simulated by isolated clusters. In particular, it was found that the vibrational density of states (VDOS) exhibit an excessively low-frequency contribution. A corresponding low-temperature peak is observed in the temperature dependence of the specific heat if plotted as \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \).

\( \text{Au}^{(C)}(N_\text{Au}) \): Figure 8 shows that the increase in Boson peak curve \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) from 0-0.00035 \( k_B \) /atom [violet line] for \( T=0 \) and 0-0.001 \( k_B \) /atom [green line (Aqua-marine 4)] for \( T=0 \) to high temperature; 30K, and the maximum deviation at 6.0 K and 4.9 K, respectively, are due to a strong disorderly nature in the cluster. In addition to that conformed with the parameter dependency.

\( \text{Au}^{(C)}(N_\text{Au}) \): Figure 17 shows that the calculated \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) for \( N_\text{Au}=5; 6; 9; 12 \) in the temperature 0.5-10 K range. The increase in Boson peak \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) from 0.88503 \( k_B \) /atom (the maximum deviation with higher amplitude at 0.6 K, \( \text{Au}_5 \). Nevertheless, with the lesser amplitude the deviation occurs at 0.6 at 0.6 K for the other clusters, \( \text{Au}_5, \text{Au}_6, \text{Au}_9, \text{Au}_{12} \) found for \( T \to 0 \) to higher temperature, the rest of the clusters are in the interval between 0.5 to 4 K.

However, Figure 16 also shows the calculated \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) vs. \( T \) for \( N_\text{Au}=(10; 14; 18; 20) \) in the temperature 0.5-30 K range. The detailed confirmation is given below.

\( \text{Au}^{(C)}(S_\text{Au}) \): There is strong evidence that the maximum deviation of the Boson peak \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) is 6.88469 \( \times 10^{-3} \) \( k_B \) /atom at 12 K, is lesser amplitude than the all other clusters, which is only because of their large number of high frequency modes.

\( \text{Au}^{(C)}(N_\text{Au}) \): Based on the experimental observations, the maximum in silica glass is placed at about 10 K and 8.5 K for neutral gold cluster (Figure 16 and Richet et al., [92,93]), and the maximum deviation \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) attains \( 2.4 \times 10^{-4} \) (molK) for silica glass and 0.0004 \( k_B \) /atom for gold cluster, respectively. Please notice that the units are not the same.

\( \text{Au}^{(D)}(N_\text{Au}) \): The \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) deviation is 0.00178 \( k_B \) /atom found for \( T \to 3.7 \) K temperature. It shows the disorder nature of the cluster.

\( \text{Au}^{(C)}(N_\text{Au}) \): The \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) deviation with a higher amplitude and the intervals in between 5.31 \( k_B \) /atom at 1-1.5 K, which has a large number of high frequencies modes.

To be noticed: Let us remember the Figure 2, and the vibrational heat capacity \( C^{\text{Vib}}_{\text{atom}} \) at above 30 K, that at high temperatures it gets saturated 0.12 \( k_B \) /atom (as a linear). Similarly, in the Boson peak, \( C^{\text{Vib}}_{\text{Vol}}(T)/T^3 \) also gets saturated (a linear) at above 30 K, but here it is towards zero values (0 \( k_B \) /atom). The lower frequencies certainly make a larger contribution to heat capacity. Nevertheless, the Boson peaks are highly visible, i.e., and the strength of the peaks strongly depends on the atomic coordination number. There are several origins, most of them related to the thermal fluctuations. If the atomic coordination is low, a single negative force constant renders the atomic arrangement much closer to an unstable situation than in the highly coordinated case [60].

The size effect of the gold neutral cluster \( \text{Au}^{(3-20)} \)

Interestingly, from the Figure 18, the clusters \( \text{Au}_{16} \) possess the most significant and stable cluster of all other clusters which have \( \text{C} \) and \( \text{C} \) symmetry (comparable with \( \text{Au}_{20} \) tetragonal cluster). In fact, the cluster \( \text{Au}_{16} \) has a greater number of single state degeneracy modes.

\( \text{Au}^{(C)}(T) \): For the size effect at about temperature 950/950* K, the \( C^{\text{Vib}}_{\text{Vol}} \) curve reached 2.62/2.61 \( k_B \) /atom but for the absolute value it should be 2.63 \( k_B \) /atom. So there is a minute difference on both \( C^{\text{Vib}}_{\text{Vol}} \) values which is 0.01/0.02 \( k_B \) /atom.

\( \text{Au}^{(C)}(T) \): For the size effect at about temperature 950/950* K, the \( C^{\text{Vib}}_{\text{Vol}} \) curve reached 2.70/2.69 \( k_B \) /atom. However, here the absolute value should be 2.70 \( k_B \) /atom. However, only at \( T=950^\circ K \), there is a minute difference 0.01 \( k_B \) /atom.

However, this minute differences are also clearly seen at temperature 300/300 K* for the rest of the clusters. The size effect on
the heat capacity should be very sensitive to the accuracy because the absolute differences are small as shown in Figure 18.

**Physical parameters influence at the C\textsubscript{vib} curves and its shapes**

If one carefully observes in Figures 2-8 and 15-17 they shows very clearly that the shape of the C\textsubscript{vib} curves are not only dependent upon the low and high frequency ranges, but also with respect to the physical parameters (\(b, \tilde{k}\)). However, along with this we have noticed that the size dependency values of C\textsubscript{vib} vary a little bit. Nevertheless, with high temperature at 950 K/950 K\*, our calculated C\textsubscript{vib} values are overlapping with the absolute values of C\textsubscript{vib}.

This confirms the accuracy of the size dependency (Figure 18, violet, blue and red line curve). Nevertheless, near to the room temperature at about 300 K/300 K\*, the C\textsubscript{vib} values are still very close to the absolute values.

Most importantly, at both the above mentioned temperatures, smoothness and the asymptotic behavior of heat capacity C\textsubscript{vib} for \(\alpha = \omega / T\), looks like much better than \(\alpha = \omega / (0.6950356\times T)\) of eqn. (8) (Figures 2, 3 and 8). In addition to that, the changes at the shape of the C\textsubscript{vib} curves are only due to existing some single state modes, but many double or triple state degree of degeneracies modes, and they are the contributing factors at C\textsubscript{vib}. See for example, cluster sizes Au\(_{N=7,9}\) at T=0 K (Figure 19). So with this in view, we can confidently say that our new methodology is a trustworthy and a successful model, with which one can take one further in making more accurate experimental calculations.

**Comparison with the theoretical and experimental results**

The spectral frequencies are the most recent studies covering neutral clusters are reported using far-infrared multiphoton-dissociation spectroscopy (FIR-MPD) for Au\(_{N=10,15}\) [94] and for Au\(_{N=15,20}\) [65]. In closing we would like to comment on a trend in the experimentally observed low-frequency vibrational spectra which was realized recently by Gruene et al. [65]. This work experimentally investigated neutral gold clusters (Au\(_{N=7-20}\)) in the gas phase by means of vibrational spectroscopy, which is inherently sensitive to structure. However, before they performed experiments, they used Gaussian package with DFT calculation.

The gold cluster, Au\(_{N=15,20}\) has 15, 51, 54 normal vibrational modes (NVM) respectively, some of which may be degenerate, depending on the symmetry. Moreover, some modes may appear in one or another experiment. We calculated the normal modes based on the structures which were predicted by Dong and Springborg [44]. However, after re-optimization the vibrational frequencies were found as mentioned in the Figures 2-19. Our calculated spectrum ranges are the peculiar values, which are in excellent agreement with the theoretical (DFT) and experimental results calculated for gold clusters by Gruene et al. [65]. Their visible modes at IR absorption coefficients, and the (\(\omega\)) frequencies are Au\(_{8} \) (148 cm\(^{-1}\)), Au\(_{9} \) (149 and 166 cm\(^{-1}\)), and for Au\(_{10}\) (165, 186 and 201 cm\(^{-1}\)). These values are in excellent agreement with our calculated value of Au\(_{10}\) (148.64 cm\(^{-1}\)) and for Au\(_{15}\) (within 144.15, 152.87 158.47, 165.28 cm\(^{-1}\)) (Figure 19).

However, they have only predicted vibrational frequencies in between 47 and 220 cm\(^{-1}\) wavenumbers. We have calculated even lower (3.99 cm\(^{-1}\)) and higher (370.72 cm\(^{-1}\)) wavenumbers than those. This is because in infrared (IR) absorption spectroscopy the number of allowed transitions is restricted by selection rules, and thus directly reflects the symmetry of the particle.

Overall for cluster Au\(_{N=10,20}\) certainly and in particularly, our lowest minimum frequency value of Au\(_{8}\) cluster is 4.66 cm\(^{-1}\) closer to the harmonic frequency of the Au8 cluster which was calculated by Mancera and Benoit [66]. Their harmonic frequency is 6.9 cm\(^{-1}\), as a minimum. Additionally, our highest maximum frequency values are comparable with Nose S calculated (\(\omega=221\) cm\(^{-1}\)) as a highest frequency for Au\(_{20}\) clusters. Their ranges for BLYP and BP86 are 26.42-162.22 cm\(^{-1}\) (BLYP) and 29.13-172.35 cm\(^{-1}\) (BP86), respectively. Certainly, the most stable structure for Au20 was found through frequency calculations for the (T\(_{b}\)) Au\(_{20}\) structure by Jun Li, Xi Li, Hua-Jin Zhai, and Lai-Sheng Wang [95,96].

The harmonic frequencies (\(\omega\)) for the global minimum energy structure of Au\(_{14}\) calculated using PBE/VDB, in cm\(^{-1}\) are being reported by Mancera and Benoit [66], which are in good agreement with some of our calculated normal modes of Au\(_{14}\) (a planar rhombus D\(_{4h}\)): 165.46 (167.2) cm\(^{-1}\); 147.12 (152.2) cm\(^{-1}\); 98.00 (96.5) cm\(^{-1}\) and 31.63 (34.5) cm\(^{-1}\), as well as, Au\(_{9}\) (a planar trapezoid C\(_{2v}\)): 132.74 (137.5) cm\(^{-1}\); 47.70 (47.6) cm\(^{-1}\) and 43.25 (47.6) cm\(^{-1}\).

Moreover, our verified symmetry and calculated vibrational frequency modes of Au\(_{N=5-6,8}\) clusters are almost in complete agreement with Mancera and Benoit [66].

\(\text{Au}_{N=5-8}\) Double and Triple state degeneracy at T= 0

These clusters are unique among the other clusters, due to their nature. Very strong and visible evidence of the vibrational heat capacity
$C_v$ per atom as a function of temperature is shown in Figure 15.

$\text{Au}_{N=6}$ ($D_3h$): The harmonic frequencies for the $\text{Au}_N$ cluster are in the range of 2.44 cm$^{-1}$ to 282.99 cm$^{-1}$, and there are 3 doubled and 1 tripled degenerate frequencies. 12 normal modes are represented as the following, one mode with degeneracy 3, three modes with degeneracy 2, and three single modes with non-degeneracy.

$\text{Au}_{N=7}$ ($D_{5h}$): The harmonic frequencies for the $\text{Au}_N$ cluster the range of 20.48 cm$^{-1}$ to 235.19 cm$^{-1}$, and there are only 6 doubly degenerate frequencies, which is an exceptional case of all other clusters. Out of 15 normal modes, 12 of these modes are twofold-degenerate and the remaining 3 are non-degenerate.

$\text{Au}_{N=8}$ ($T_d$): The harmonic frequencies for the $\text{Au}_N$ cluster are in the range of 4.66 cm$^{-1}$ to 215.08 cm$^{-1}$, there are 2 doubly and 4 triply degenerate frequencies. Out of 18 modes, 4 threefold, 2 double fold and 2 non-degenerate normal frequencies occurred.

Conclusions with Perspective

We have extracted vibrational frequencies at $T$=0 K, and investigated the vibrational heat capacities at a temperature range 0.5-300 K, of the re-optimized gold atomic clusters ($\text{Au}_N$). Especially, the vibrational modes with lower frequencies are given a significant contribution to the heat capacity at low temperatures. The $C_v$ is a monotonous function that tends asymptotically. The vibrational heat capacity is a strong function of cluster size and temperature, particularly in the low temperature regime.

Our first step towards the understanding of the so-called finite temperature effects was to take into account the vibrations of clusters. We focused our interest on the cluster size and temperature dependence of the heat capacities and the free energies of the clusters. Finally, we have studied vibrational and thermodynamic properties of the clusters in order to explore the interaction between stability, structure, and heat capacities of clusters. Our approach is worthy of further investigation and would pave a way in realizing numerical values which would allow for an experimental vibrational spectrum and heat capacity, which would prove crucial in development of Nano electronic devices. Nevertheless, our work gives a possible cause for the size, temperature, and structures effect of Au atomic clusters.

Supplementary Material

Details about the harmonic frequencies and the predicted minima of the global structure optimization of $\text{Au}_N$ clusters can be found in the supplementary material (see the ESI).

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