

Does the Boson Peaks Exist in Small Neutral Gold Clusters?

Vishwanathan K*

Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrucken, Germany

Abstract

The Boson peaks are typically ascribed to an excess density of vibrational states for the small clusters. A well resolved boson peak is observed in the low-frequency portion of the spectrum. A starting point for our discussion is the behaviour of the boson peak, derived from the vibrational density of states and the temperature dependencies of the vibrational heat capacities of the re-optimized neutral gold clusters. This Boson peak is associated with the existence of intermediate range order (IRO) in the arrangements of atoms. The low frequency (Far Infrared FIR, IR-C 200-10 cm^{-1}) containing this dominant spectral line (Boson peak) is interpreted in terms of its relationship to the amplitude and extent of the density fluctuations in atoms and is, thereby, considered a measure of the intermediate range order in these atoms. We found a systematic relation among the boson peak energy, the boson peak intensity per atom, and the zigzag-bond density; the peak energy decreases and the peak intensity increases as zigzag-bond density decreases.

Keywords: Gold atomic clusters; Density-functional tight-binding approach; Boson peaks; Spectral lines

Introduction

The study of nanostructured materials exhibiting novel properties is one of the most fascinating fields of current research. Small nanomaterials are of particular-interest because of intriguing characteristics [1-4]. Nanoparticles with smaller dimensions may exhibit different properties in comparison with bulk material. The nanoparticles possess unique physico-chemical, optical and biological properties which can be manipulated suitably for desired applications [5]. Particular, gold chemistry plays a very important role in nanoelectronics and bionano-sciences [6].

Nanotechnology and nano-sensors are broad, interdisciplinary areas that encompass (bio)chemistry, physics, biology, materials science, electrical engineering and more. Nanomaterials are at the leading edge of the rapidly developing field of nanotechnology. Their unique size-dependent properties make these materials superior and indispensable in many areas of human activity. Gold nanoparticles are one of the most potentially useful nanoparticles. This is especially true in cancer therapeutics because of their photothermal properties. Gold nanoparticles are readily synthesised structures that absorb light strongly to generate thermal energy which induces photothermal destruction of malignant tissue [7-9].

Noble metals and their compounds have a long and distinguished history as therapeutic agents in medicine. Recent years have seen tremendous progress in the design and study of nanomaterials geared towards biological and biomedical applications. Particularly gold nanoparticles have attracted intensive interest, because they are easily prepared, have low toxicity and can be readily attached to molecules of biological interest. The gold nanoparticles have become more precious than pretty gold because of their wide use and applications [10].

The use of gold compounds in medicine, and many experts still consider gold to be among the most effective drugs for reducing inflammation in joints, thus reducing the symptoms of pain and stiffness. Several forms of gold are available, but usually one of the injectable forms of gold salt (e.g., gold sodium thiomalate [Myochrysine] or aurothioglucose [Solgana] is used. An oral tablet containing gold, called auranofin (Radaura), is also available. As diseases evolve, so too does the need for this robust and versatile metal to aid in the treatment of a range of conditions, now and into the future. That is why gold nanoparticles are medically more precious than pretty gold [10]. The Boson peak is usually studied in glasses [11-13], where enhancement of heat capacity is induced by disorder. The modelling of clusters may be important for understanding the mechanism which lead to this effect. In glasses, there are different local configurations 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 [14,15]. A corresponding lowtemperature peak is observed in the temperature dependence of the specific heat if plotted as $Cvib(T)/T^3$.

Zhang and Douglas [16,17] usually study the Boson peak from the velocity autocorrelation function, but they are both concerned about an "excess" contribution to the vibrational density of states. This feature has been observed in metal nanoparticles and zeolites (see: Greaves) 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 [18] also studied the perspectives on zeoliteen capsulated metal nanoparticles and their applications in catalysis.

In the present work, only an in-depth study on the behavior of the Boson peaks which are linked to the vibrational spectrum [19,20], which are existed in small neutral gold clusters at low-temperatures.

Theoretical and Computational Procedure

The DFTB [21-23] 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 { $\phi_m(\mathbf{r})$ },

*Corresponding author: Vishwanathan K, Department of Physical and Theoretical Chemistry, University of Saarland, 66123 Saarbrucken, Germany, Tel: +49015163119680; E-mail: Vishwa_nathan_7@yahoo.com

Received September 06, 2017; Accepted September 15, 2017; Published September 22, 2017

Citation: Vishwanathan K (2017) Does the Boson Peaks Exist in Small Neutral Gold Clusters? J Develop Drugs 6: 178. doi:10.4172/2329-6631.1000178

Copyright: © 2017 Vishwanathan K. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

$$\sum_{m} c_{im} \left(H_{mn} - \epsilon_{i} S_{mn} \right) = 0 \tag{1}$$

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 dependent. 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:

$$\sum_{m} c_{im} \left(H_{mn} - \epsilon_i S_{mn} \right) = 0 \tag{2}$$

Here, c_{im} 's are expansion coefficients, \in_i is for the single-particle energies (or where \in_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:

$$H_{mn} = \left\langle \phi_m \left| \hat{H} \right| \phi_n \right\rangle, S_{mn} = \left\langle \phi_m \left| \phi_n \right\rangle$$
(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 $\hat{\mathbf{H}}$ is defined as:

$$H\psi_{i}(\mathbf{r}) = \epsilon_{i}\psi_{i}(r), H = T + V_{eff}(r)$$
(4)

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

$$\mathbf{V}_{\text{eff}}(\mathbf{r}) = \sum_{j} V_{j}^{0} \left(|\mathbf{r} - \mathbf{R}_{j}| \right)$$
(5)

 V_j^0 is the Kohn-Sham potential of a neutral atom, $r_j=r-R_j$ is an atomic position, and R_ibeing 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:

$$\mathbf{E}_{\text{tot}} \Box \sum_{i} \epsilon_{i} - \sum_{j} \sum_{m_{j}}^{\text{acc}} \epsilon_{jm_{j}} + \frac{1}{2} \sum_{j \neq j'} U_{jj'} \left(|\mathbf{R}_{j} - \mathbf{R}_{j'}| \right), \epsilon_{B} \equiv \sum_{i}^{\text{acc}} \epsilon_{i} - \sum_{j} \sum_{m_{j}}^{\text{acc}} \epsilon_{jm_{j}} \left(6 \right)$$

Here, the majority of the binding energy (\in_B) is contained in the difference between the single-particle energies \in_i of the system of interest and the singleparticle 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 \in_B and ϵ_B^{scr} for diatomic molecules (with ϵ_B^{scr} being the total energy from parameter-free density functional calculations). In the present study, only the 5*d* and 6*s* electrons of the gold atoms are explicitly included, whereas the rest are treated within a frozen-core approximation [21,23,24].

Calculation of vibrational heat capacity

Finally, from the calculated vibrational frequencies and with the use of Boltzmann statistics [25-27], we can get the formula to investigate size, structure and temperature effects on the vibrational heat capacity of clusters,

$$C_{\rm vib} = \frac{1}{N} \sum_{i=1}^{3N-6} \frac{\alpha_i^2 e^{\alpha_i}}{\left(e^{\alpha_i} - 1\right)^2}, with \, \alpha_i = \frac{\hbar \omega_i}{k_B T}; \frac{C_{\rm vib}(T)}{T^3}$$
(7)

J Develop Drugs ISSN: 2329-6631 JDD an open access journal Here, *N* is the total number of atoms in a cluster, \hbar is the reduced Planck's constant, ω_i is vibrational frequencies (low(min), high(max)), k_B is Boltzmann's constant and *T* is the absolute temperature. In this study, we focus only on the vibrational part of the heat capacity, i.e., on C_{vib} and the Boson Peaks, $C_{vib}(T)/T^3$.

Results and Discussion

In this article, we present only an in-depth study on the behavior of the Boson peaks are thermally activated as well as the local atomic arrangements (within a cluster or group of strongly correlated atoms) but still are constrained by surrounding atoms [28]. This is an interesting point and may shed light on the enhancement of the heat conductance process mentioned in Ref. [29] and Ref. [30].

The Boson Peaks (BP) C_{vib}/T^3 vs. T of the neutral gold clusters

As shown in Figures 1-3, with respect to the eqn. (7) and the corresponding Boson peaks C_{vib}/T^3 vs. *T* were plotted at temperature within the range *T*=0.5-30 K.

Au₃(**C**_{2ν}): Figure 1 shows that the increase in Boson peak curve C_{vil} /*T*³ from 00.00035 $k_{B}/atom$ [violet line] for $\alpha_{i}=\omega_{i}/T$ and 0-0.001 $k_{B}/atom$ [green line (Aquamarine 4)] for $\alpha_{i}=\omega_{i}/(0.6950356*T)$ found for *T* → 0 → high temperature, 30K, and the maximum deviation at 6.00 K and 4.9 K, respectively, are due to a strong disorderly nature in the cluster. In addition to that confirmed with the parameter dependency.

$Au_5(C_{2v})$, $Au_6(D_{3h})$, $Au_9(C_s)$ and $Au_{12}(C_1)$: Figure 2 shows that







Page 2 of 4



the calculated C_{vib}/T^3 vs. *T* for Au_N (*N*=5, 6, 9, 12) in the temperature 0.5-10 K range. The increase in Boson peak C_{vib}/T^3 from 0.88503 $k_B/atom$ (the maximum deviation with a higher amplitude at 0.6 K, Au₅. Nevertheless, with the lesser amplitude the deviation occurs at 0.6 at 0.6 K for the other clusters, Au₆, Au₉ and Au₁₂) found for $T \rightarrow 0$ to higher temperature, the rest of the clusters are in the interval between 0.5 to 4 K.

Howsoever, Figure 3 also shows the calculated C_{vib}/T^3 vs. *T* for Au_N (*N*=10, 14, 18, 20) in the temperature 0.5-30 K range. The detailed confirmation is given below.

 $Au_{10}(S_8)$: There is strong evidence that the maximum deviation of the Boson peak $C_{vib'}/T^3$ is 6.88469 × 10⁻⁵ $k_{B'}/atom$ at 12 K, is lesser amplitude than the all other clusters, which is only because of their large number of high frequency modes.

 $Au_{14}(C_s)$: Based on the experimental observations, the maximum in silica glass is placed at about 10 K and 8.5 K for neutral gold cluster (see Figure 3 and Richet et al. [31,32]), and the maximum deviation C_{vib}/T^3 attains $2.4 \times 10^{-4} J/(molK)$ for silica glass and $0.0004 k_B/atom$ for gold cluster, respectively. Please notice that the units are not the same.

 $Au_{18}(D_1)$: The C_{vib}/T^3 deviation is 0.00178 $k_B/atom$ found for *T* → 3.7 K temperature. It shows the disorder nature of the cluster.

 $Au_{20}(C_1)$: The C_{vib}/T^3 deviation with a higher amplitude and the intervals in between $5.31 \times 10^{-3} \cdot 4.97 \times 10^{-3} k_g/atom$ at 1-1.5 K, which has a large number of high frequencies modes.

Most importantly, the Boson peaks, C_{vib}/T^3 are getting saturated that is towards closer to zero values (0 $k_B/atom$) at about 10 to 30 K above ranges. 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 [28].

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 Figure 3; Au_N (N=3, 4, 10, 13, 14, 15, 18, 20): C_{vib} per atom as a function of temperature at 0.5-300 K. $\alpha_i = \omega_i^{/}$ (0.6950356**T*) of eqn. (7) and the corresponding Boson peaks C_{vib} T^3 vs. *T*. atomic clusters (Au_{N=3-20}). Especially, the vibrational modes with lower frequencies are given a significant contribution to the heat capacity at low temperatures. The vibrational heat capacity is a strong function of cluster size and temperature, particularly in the low temperature regime which is clearly seen at the Boson peaks. Overall, the Boson peaks shows the disorder nature of the clusters within the atomic coordination, as a zig-zag arrangement.

Dedication

Dedicated to Professor Prasanta Kumar Panigrahi, IISER, Kolkata, on the occasion of his 60th birthday, and Professor Kwang S Kim, UNIST, on the occasion of his 67th birthday.

Acknowledgements

A part of this work was supported by the German Research Council (DFG) through project Sp 439/23-1. We gratefully acknowledge their very generous support.

References

- Smit RHM, Untiedt C, Yanson AI, Van Ruitenbeek JM (2001) Common origin for surface reconstruction and the formation of chains of metal atoms. Physical Review Letters 87: 266102.
- Rodrigues V, Bettini J, Silva PC, Ugarte D (2003) Evidence for spontaneous spin-polarized transport in magnetic nanowires. Physical Review Letters 91: 096801.
- Choi YC, Lee HM, Kim WY, Kwon SK, Nautiyal T, et al. (2007) How can we make stable linear monoatomic chains? Gold-cesium binary subnanowires as an example of a charge-transfer-driven approach to alloying. Physical Review Letters 98: 076101.
- Wales D (2003) Energy landscapes: Applications to clusters, biomolecules and glasses. Cambridge University Press.
- 5. Feynman R (1991) There's plenty of room at the bottom. Science 254: 1300-1301.
- Pyykkö P (1997) Strong closed-shell interactions in inorganic chemistry. Chemical Reviews 97: 597-636.
- Dykman LA, Khlebtsov NG (2011) Gold nanoparticles in biology and medicine: recent advances and prospects. Acta Naturae 3: 34-55.
- Giljohann DA, Seferos DS, Daniel WL, Massich MD, Patel PC, et al. (2010). Gold nanoparticles for biology and medicine. Angewandte Chemie International Edition 49: 3280-3294.
- Salata OV (2004) Applications of nanoparticles in biology and medicine. Journal of Nanobiotechnology 2: 3.
- Giasuddin ASM, Jhuma KA, Mujibul HA (2012) Use of Gold Nanoparticles in Diagnostics, Surgery and Medicine: A Review.
- McIntosh C, Toulouse J, Tick P (1997) The Boson peak in alkali silicate glasses. Journal of Non-Crystalline Solids 222: 335-341.
- Chumakov AI, Monaco G, Monaco A, Crichton WA, Bosak A, et al. (2011) Equivalence of the boson peak in glasses to the transverse acoustic van hove singularity in crystals. Physical Review Letters 106: 225501.
- Ciliberti S, Grigera TS, Martín-Mayor V, Parisi G, Verrocchio P (2004) The Boson peak and the phonons in glasses. AIP Conference Proceedings 708: 565-570.
- Kantelhardt JW, Russ S, Bunde A (2002) Vibrational models for the Boson peak. Journal of Non-Crystalline Solids 307: 96-102.
- Xu N, Wyart M, Liu AJ, Nagel SR (2007) Excess vibrational modes and the boson peak in model glasses. Physical Review Letters 98: 175502.
- Zhang H, Douglas JF (2013) Glassy interfacial dynamics of Ni nanoparticles: Part II Discrete breathers as an explanation of two-level energy fluctuations. Soft Matter 9: 1266-1280.
- Zhang H, Kalvapalle P, Douglas JF (2010) String-like collective atomic motion in the interfacial dynamics of nanoparticles. Soft Matter 6: 5944-5955.
- Farrusseng D, Tuel A (2016) Perspectives on zeolite-encapsulated metal nanoparticles and their applications in catalysis. New Journal of Chemistry 40: 3933-3949.

- Vishwanathan K (2016) Vibrational Heat Capacity of Gold Cluster AuN=14 at Low Temperatures. J Phys Chem Biophys 6: 232.
- Vishwanathan K (2017) Eect of Size, Temperature, and Structure on the Vibrational Heat Capacity of Small Neutral Gold Clusters. J Material Sci Eng 6: 325.
- Porezag D, Frauenheim T, Köhler T, Seifert G, Kaschner R (1995) Construction of tight-binding-like potentials on the basis of density-functional theory: Application to carbon. Physical Review B 51: 12947.
- Seifert G, Schmidt R (1992) Molecular dynamics and trajectory calculations: the application of an LCAO-LDA scheme for simulatins of cluster-cluster collisions. New Journal of Chemistry 16: 1145-1147.
- Seifert G, Porezag D, Frauenheim T (1996) Calculations of molecules, clusters, and solids with a simplified LCAO-DFT-LDA scheme. International Journal of Quantum Chemistry 58: 185-192.
- 24. Seifert G (2007) Tight-Binding Density Functional Theory: An Approximate Kohn-Sham DFT Scheme. The Journal of Physical Chemistry A 111: 5609-5613.
- 25. McQuarrie DA (1975) Statistical mechanics. New York: Harper Row.

- 26. Landsberg PT (1990) Thermodynamics and statistical mechanics. Oxford University Press, New York: Dover.
- 27. Waldram JR (1985) The theory of thermodynamics. The Theory of Thermodynamics. In: Waldram JR (ed.), Cambridge, UK: Cambridge University Press.
- Luo P, Li YZ, Bai HY, Wen P, Wang WH (2016) Memory Effect Manifested by a Boson Peak in Metallic Glass. Physical Review Letters 116: 175901.
- Pérez-Madrid A, Lapas LC, Rubí JM (2009) Heat exchange between two interacting nanoparticles beyond the fluctuation-dissipation regime. Physical Review Letters 103: 048301.
- 30. Pérez-Madrid A, Lapas LC, Rubí JM (2013) A thermokinetic approach to radiative heat transfer at the nanoscale. PLoS ONE 8: e58770.
- Richet NF (2009) Heat capacity and low-frequency vibrational density of states. Inferences for the boson peak of silica and alkali silicate glasses. Physica B: Condensed Matter 404: 3799-3806.
- 32. Richet NF, Kawaji H, Rouxel T (2010) The boson peak of silicate glasses: The role of Si-O, Al-O, and Si-N bonds. The Journal of Chemical Physics 133: 044510.