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Structural, Magnetic and Optical Properties of $PtAu_n$ (n = 1-9) Clusters Using Density Functional Theory

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In this paper, we present a systematic computational study based on the density functional theory (DFT), which aims to shed light on the potential effects of doping gold Au clusters with platinum Pt atom, and to find new structural, magnetic and optical properties that platinum-doped gold clusters $PtAu_n$ (n = 1-9) will have, so that clusters with the lowest and most stable energy are selected from the rest of the isomers for each cluster size. Stable structures with lower energy reveal that they have three-dimensional structures starting with n = 6. The process of doping gold Au_n clusters with platinum Pt atom does not lead to an improvement in their stability, but we find that all the properties, whether magnetic or optical, changed for Au_n clusters after doping with platinum. All calculated properties were discussed and compared with similar previous studies, where the magnetic moment, absorption, reflectivity, optical conductivity, refractive index, and damping coefficient showed impressive results as a function of the cluster size. All properties computed by the generalized gradient density approximation (GGA) were compared with the local density approximation (LDA). In general, the results showed that doping Au_n clusters with platinum atom significantly changed their properties.

Keywords: Density functional theory (DFT), Doping, Cluster, Structural properties, Magnetic properties, Optical properties.

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1. INTRODUCTION

In the last few years, there has been a growing interest in the physics and chemistry of nanocluster science. The researchers' work focused on re-searching to find the unique properties of these clusters, whose unique structure between the molecule and the size (mass) was the main reason for theoretical researchers to delve into the understanding of the transition from atoms to clusters, molecules and finally to solid state.

For several years, great effort has been devoted to the study of the structural and chemical properties of mixed bimetallic clusters. This type of clusters is very important in its use thanks to the possibility of using it according to special requests.

Nano-sized bimetallic groups have received great attention due to their wide applications in many fields, including optics, magnetism and catalysis [1], and because they have physical and chemical properties that change with size as a result of the surface change with size. The nanoclusters made of noble metals, especially $PtAu_n$ nanoclusters, are attractive catalysts [2]. The physical and chemical properties of bimetallic clusters depend not only on the size and shape, but also on the atomic structure of two metallic elements [3]. Therefore, the researchers were interested in doing current studies to find new structural and electronic variables that the groups have due to their new size [4, 5].

Both particles of noble metals such as gold and platinum have wide applications, whether in organic chemistry, where they play an important role in protein delivery [6] or cancer treatment [7], the ability to resist fungi [8]. Because of their potential as optical sensors contributing to phototherapy, they generally play a broad role in sensor synthesis and biomedicine [9, 10]. Platinum particles are also included in the catalytic oxidation of blue carbon, as well as in the general electrochemical behavior of amino compounds, and generally in many applications in various fields [11, 12].

2. DETAILS OF CALCULATIONS

The electronic structure calculations of $PtAu_n$ (n = 1-9) clusters were performed using the density functional theory (DFT) [13], as implemented in the SIESTA program [14]. It is noted that this code uses norm-conserving Troullier-Martins nonlocal pseudopotentials [15], and, at the same time, as the researchers note, shares flexible basis sets of localized Gaussian-type atomic orbitals. The exchange correlation energy was evaluated using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernserh (PBE) [16] and local density approximation (LDA) [17]. The self-consistent field (SCF) calculations were carried out with convergence criterion of 1×10^{-4} a.u. for the total energy; we used a double ζ (DZ) basis with polarization function for Pt and Au atoms. For an energy shift parameter of 50 meV, the variation density was intended in a regular real-space grid with a cut-off energy of 170 Ry. The simulated clusters were positioned in a big cubic supercell with a parameter of 30 Å, including enough vacuums between neighboring clus-

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ters and periodic boundary conditions were executed. To sample the Brillouin zone, only a single k-point centered at Γ was used because of the extended size of the super cell. The conjugated gradient method within Hellmann-Feynman forces was used and all the forces after structural relaxation were less than 10^{-3} eV/Å.

We first searched for the lowest-energy structures of pure Au_n clusters with 2-10 atoms. Second, the most stable ground state structures obtained for Au_n clusters were doped through substitution with one Pt atom. Then, the obtained Pt-Au_n clusters were optimized until reaching their ground states. In order to get lowest-energy structures of $PtAu_n$ clusters, several initial isomeric structures, including some high and low symmetries, were optimized by placing one Pt atom in different possible sites of the pure corresponding Au_n in order to get as close as possible to the low energy structure. Then, we cannot be sure that a more stable structure than those found in our calculations does not exist. The aim of our study is to highlight the variation of the properties of gold cage clusters due to the Pt doping atom. We hope that this work would be useful to understand the influence of the Pt atom on the properties of gold clusters and to provide some guidelines for the probable future experimental studies. The calculated study results were found to be consistent with the literature, confirming the reliability of the study protocol for simulating small Au clusters.

3. RESULTS AND DISCUSSION

3.1 Structural Properties of Au_{n+1} and $PtAu_n$ (n = 1-9) Clusters

The calculated structural properties of pure gold and platinum-doped gold clusters depend on the groups structure, in addition to the positions of the atoms and the average bond length between them; the DFT was chosen using GGA and LDA to reach the most stable structures with lower energy. In this work, we have come up with the electronic structures of the most stable groups using the application of annealing simulation (AS), which has gone through the following stages.

- The first stage: a random group of atoms is placed in the block simulation box.
- Stage 2: we raise the system temperature until it is about 1000 K in a total of 1000 iterations.
- Stage 3: the system temperature is stable at T = 1000 K for about 500 iterations.
- Stage 4: we gradually reduce the system temperature until t = 0 K in 1000 iterations.

Fig. 1 and Fig. 2 represent the most stable pure gold and platinum-doped groups, respectively.

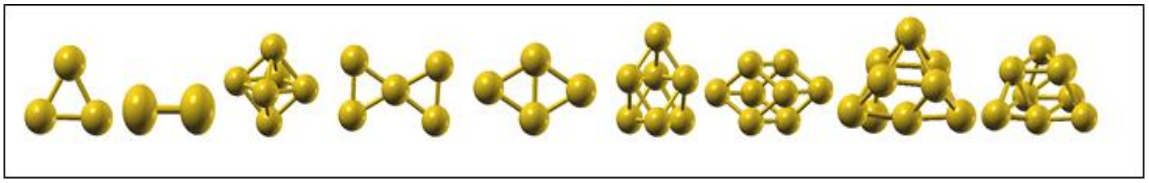


Fig. 1 – The most stable Au_n (n = 2-10) clusters

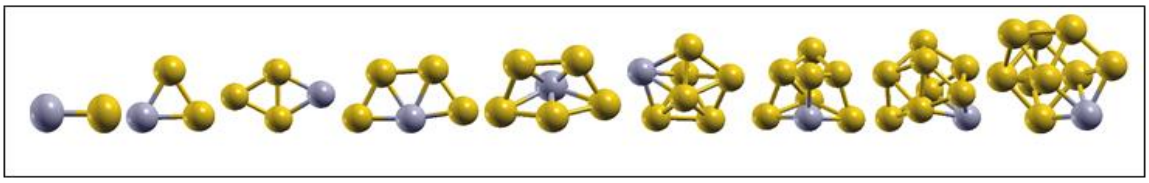
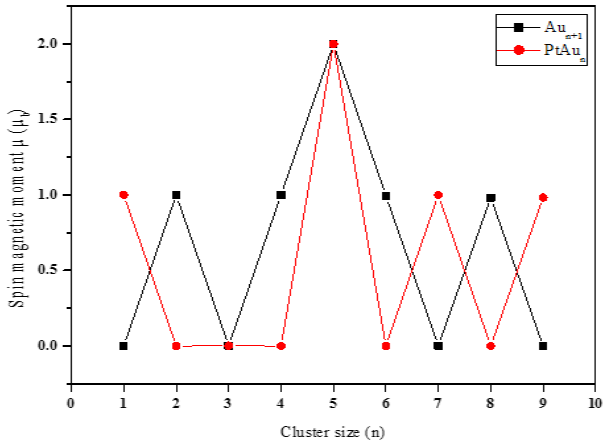


Fig. 2 – The most stable $PtAu_n$ (n = 1-9) clusters

3.2 Magnetic Properties

The magnetic moment is defined as the difference between the total number of spin-up electrons and the total number of spin-down electrons. All the calculated magnetic moment results for pure gold Au_{n+1} and platinum-doped gold $PtAu_n$ clusters are shown in Fig. 4a and Fig. 4b, respectively, where two figures represent the magnetic moments of Au_{n+1} and $PtAu_n$ clusters in terms of cluster size in both approximations used, GGA and LDA, respectively.

We note that Au_{n+1} clusters have magnetic moments except for Au_4, Au_8 and Au_{10} clusters, while we find that platinum-doped gold $PtAu_n$ clusters also have magnetic moment values except for n = 2, 3, 4, 6, and 8 clusters, which are zero magnetic moment. Also, the magnetic moment values recorded for all studied clusters range from (1-2) $\mu\beta$, our results are also fairly close to the results of [18].



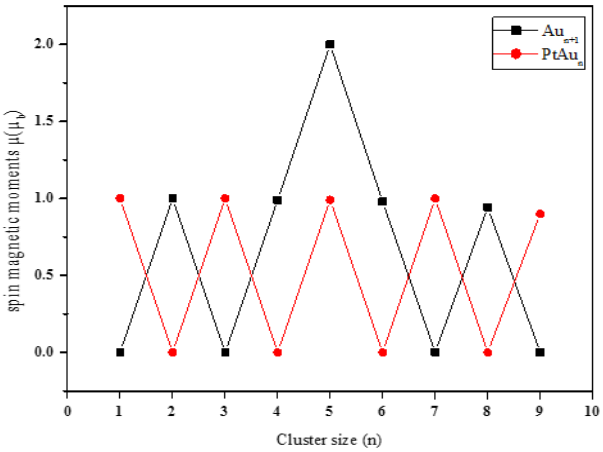


Fig. 3 – Magnetic moments of Au_{n+1} and $PtAu_n$ clusters in: (a) GGA and (b) LDA approximations

3.3 Optical Properties

3.3.1 Absorbance

Absorption occurs when electromagnetic radiation falls on a material and the energy of photons is converted into internal energy. The absorption coefficient α is defined as the percentage of decrease in radiation energy per unit distance in the direction of propagation within the medium [18]. It is calculated as follows:

$$\alpha = 4\pi k/\lambda, \quad (1)$$

where λ is the wavelength (cm^{-1}), k is the coefficient of extinction.

Fig. 4 represents the absorbance in terms of energy changes for Au_2 and PtAu clusters.

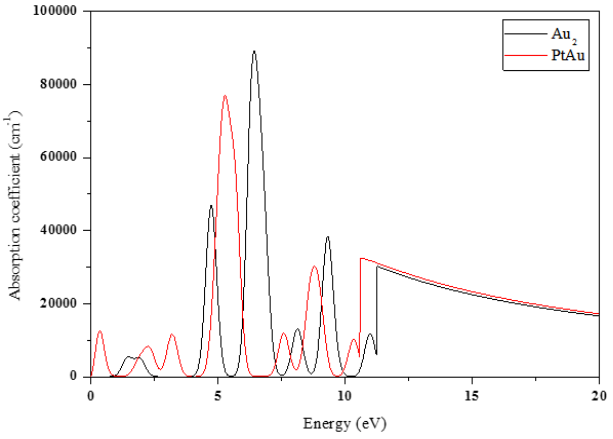


Fig. 4 – Absorbance of Au_2 and PtAu clusters

Light absorption occurs, that is, there is a value for the upper and lower limits of the energy gap estimated at 0.9 eV, which means that no direct electronic transitions occur from the valence band to the conduction band.

As for fields [0.9-2.5] eV, [7.5-8.55] eV, [10.8-11.5] eV which correspond to [0-5000] cm^{-1}, [0-12000] cm^{-1}, [0-11000] cm^{-1}, respectively, we recorded low absorption. Except for these areas, we recorded peaks with high absorption, where the highest peak of 90000 cm^{-1} was recorded at 7 eV energy.

For the PtAu cluster, we notice that when the cluster is exposed to minimum energy values, absorption occurs at 12000 cm^{-1} and then decreases to notice its increase and decrease at other times to record its highest value at an energy of 5.5 eV with a value estimated at 78000 cm^{-1} followed by two peaks of lowest intensity corresponding to energies of 8.5 eV and 11 eV with values estimated at 30000 cm^{-1} and 35000 cm^{-1}, respectively. It is also seen that the two absorption coefficients in Fig. 4 are identical based on an energy of 11.25 eV. Finally, we conclude that the Au_2 cluster is characterized by high absorbance in the field of [4.5-7.5] eV.

3.3.2 Optical Conductivity

It is an electrical phenomenon in which a material becomes more electrically conductive as a result of absorbing electromagnetic radiation such as light, and thus increasing electron gaps; this was achieved by the relationship:

$$\sigma(\omega) = \frac{J(\omega)}{E(\omega)}, \quad (2)$$

where σ is the optical conductivity (Sm/m), J is the current density (A/m^2) and E is the electric field (N/C).

Fig. 5 represents the changes in the optical conductivity value of Au_2 and PtAu clusters in terms of the energy applied to them.

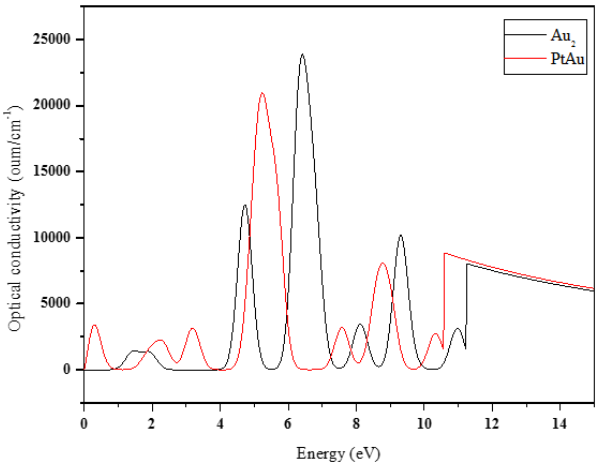


Fig. 5 – Optical conductivity of Au_2 and PtAu clusters

Fig. 5 shows that in the energy field 0-0.9 eV there is no optical conductivity for the pure gold Au_2 cluster, while the opposite is recorded for PtAu with a small peak of 27,000 Ω/cm^{-1} at 0.5 eV. As for the Au_2 cluster, the photoconductivity experiences either increase or decrease, starting from 0.9 eV, where the optical conductivity registers the highest intensity with a peak at 22500 Ω/cm^{-1} at an energy of 6.5 eV, followed by the two least intense peaks within this field estimated at 200 Ω/cm^{-1} and 9500 Ω/cm^{-1}, respectively, while the PtAu cluster recorded the highest intensity of the optical conductivity value estimated at 20000 Ω/cm^{-1}.

Starting from an energy of 11.3 eV, it is observed that the optical conductivity curves of both clusters are similar.

3.3.3. Refraction Index

The refractive index n_0 is defined as the change in the path of light rays from one transparent medium to another [20]:

$$n_0 = \left[\left(\frac{1+R}{1-R}\right)^2 - (k_0^2 + 1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R}, \quad (3)$$

where k_0^2 is the damping coefficient.

The following Fig. 6 represents the spectra of light refractive index in terms of photon energy for Au_2 and PtAu clusters.

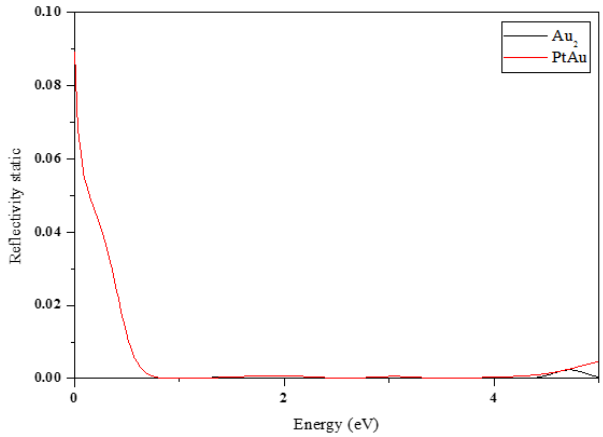


Fig. 6 – Refractive index of Au_2 and PtAu clusters

It can be seen from the figure that, as the energy of photons incident on it increases, the refractive index of the Au_2 cluster remains almost constant at the value (1.0), except for some changes in the value at energies of 4.8 eV and 6.4 eV, where a very slight increase in the value of the refractive index is seen. As for the PtAu cluster, at an energy of 0.1 eV, the refractive index had the highest value, estimated at about (1.8) to start decreasing, to reach a value of (0.89), and this is within the energy range [0-0.5] eV.

The value of the refractive index gradually increases due to the increase in the photon energy, reaching a less intense peak than the previous one, estimated at (1.1), and, starting from 7 eV, fluctuations of the refractive index around the value of 1 are observed for both clusters.

3.3.4 Damping Coefficient

The damping coefficient K is defined as the amount of energy of photons of the incident radiation absorbed by the electrons of the material [19] and is determined by the relationship:

$$k_0 = \alpha\lambda/4\pi. \quad (4)$$

Fig. 7 represents the changes of the damping coefficient in terms of energy for Au_2 and PtAu clusters.

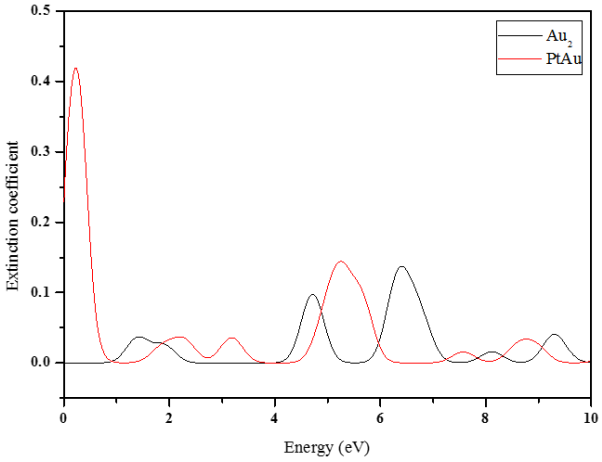


Fig. 7 – Damping coefficient of Au_2 and PtAu clusters

We note from Fig. 8, that for the PtAu cluster recorded in the range [0-0.9] eV, the highest peak reached by the damping coefficient, which is 0.43, corresponds to 0.4 eV, while in the range [0.9-10] eV, fluctuations are observed in the spectrum of the damping coefficient, except for its peak at 5.2 eV, corresponding to 0.15. From the comparison of the curves in the figure, we notice that the damping coefficient is inversely proportional to the absorption spectra of PtAu clusters.

From Fig. 8, no spectrum of the damping coefficient was recorded for the Au_2 cluster in the field [0-0.9] eV, since there is no absorption spectrum, but in the fields [0.9-2.2] eV, [4.2-5.2] eV, [5.8-7.2] eV, [8.8-9.8] eV, four peaks were recorded with values of 0.04, 0.1, 0.14, 0.05 corresponding to the energies of 1.4, – 4.8, – 6.4, 9.3 eV, respectively. From it, we conclude that the spectra of the damping coefficient correspond to the spectra of the absorption.

4. CONCLUSIONS

In present work, the structural, magnetic and optical properties of Au_{n+1} and PtAu clusters with n = 1-9 were investigated by density functional calculations with generalized gradient approximation (GGA) and local gradient approximation (LDA). Clusters with a total number of atoms up to five were found to have planar structures. The results show that new structures are obtained for each cluster size compared to those reported in the literature. The results of the magnetic moment reveal that gold clusters Au_{n+1} have this property to a greater extent than $PtAu_n$ (n = 1-9) clusters, the calculated optical properties clearly show the field of use of these clusters.

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Вивчення структурних, магнітних та оптичних властивостей кластерів $PtAu_n$ (n = 1-9) з використанням теорії функціоналу густини

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У статті ми представляємо систематичне обчислювальне дослідження, засноване на теорії функціоналу густини (DFT), метою якого є пролити світло на потенційні ефекти легування золотих Au кластерів атомом платини Pt, а також установити нові структурні, магнітні та оптичні властивості, які будуть мати леговані платиною золоті кластери $PtAu_n$ (n = 1-9), так що кластери з найнижчою та найбільш стабільною енергією вибираються з решти ізомерів для кожного розміру кластера. Стабільні структури з нижчою енергією показують, що вони мають тривимірні структури, починаючи з $n = 6$. Процес легування золотих кластерів Au_n атомом платини Pt не призводить до покращення їх стабільності, але ми виявили, що всі властивості, будь то магнітні або оптичні, змінилися для кластерів Au_n після легування атомами Pt. Усі розраховані властивості були обговорені та порівняні з аналогічними попередніми дослідженнями, де магнітний момент, поглинання, відбивна здатність, оптична провідність, показник заломлення та коефіцієнт загасання, які залежать від розміру кластера. Усі властивості, обчислені за допомогою наближення узагальненої градієнтної густини (GGA), порівнювали з наближенням локальної густини (LDA). Загалом результати показали, що легування кластерів Au_n атомами Pt помітно змінило їхні властивості.

Ключові слова: Теорія функціоналу густини (DFT), Легування, Кластер, Структурні властивості, Магнітні властивості, Оптичні властивості.