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Exploring structures, electronic and reactivity properties of Au_6H_n (n = 1–12) clusters: A DFT approach

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ABSTRACT

Density functional calculations at the PBE/DNP level have been carried out to investigate the structures, electronic and reactivity properties of Au_6H_n (n = 1–12) clusters. Adsorption of hydrogen atoms stabilizes the Au_6 cluster indicated by the high binding energies. The adsorption of H atoms till Au_6H_6 retains the planar triangular structure of Au_6. However, the triangular structure is distorted on further addition of H atoms till Au_6H_9. In clusters Au_6H_{10}, Au_6H_{11} and Au_6H_{12}, though the triangular structure is restored but the structures are non-planar. The averaged Hirshfeld atomic charges indicate the H atoms to be negatively charged in all the clusters. Odd–even alternation in HOMO–LUMO gap, chemical hardness, vertical ionization potential, adiabatic ionization potential and binding energy is observed with the clusters having even number of H atoms possessing higher values and are observed to be more stable than their congeners with odd number of H atoms. DFT based reactivity descriptors indicate that in Au_6, the Au atoms forming the vertices of the outer triangle have higher relative electrophilicity value while those forming the vertices of the inner triangle have higher relative nucleophilicity value. However, in Au_6H_6, two nearby Au sites forming the vertices of the inner and outer triangle have the highest relative electrophilicity and relative nucleophilicity values. In Au_6H_{12}, these are located in the inner triangle.

1. Introduction

Bulk gold is noble; however, when the size is reduced to nanometer range, it exhibits striking reactive behavior [1–4]. A number of both experimental [5–11] and theoretical [12–31] methods have been made on gold nanoparticles and clusters that possess unique physical and chemical properties. The potential application of gold nanoparticles and clusters as building blocks for functional nanostructured materials, electronic devices and nanocatalysts [32–35] has motivated the recent surge of research activity in the area of their physical and chemical properties.

Gold with a singly filled s-shell with an atomic configuration [Xe] $4f^{14}$ $5d^{10}$ $6s^1$ exhibits properties similar to alkali metals. However, it possess significant relativistic effect which is larger than any other element with $Z < 100$ in the periodic table. Presence of relativistic effect reduces the s–d energy gap thus inducing hybridization of the atomic 5d–6s energy levels and causing an overlap of the 5d shells of the neighboring atoms in the cluster [36]. For instance, presence of relativistic effect has led to the uniqueness of gold in having stable planar 2D clusters up to n = 12 [37,38].

Hydrogen has an atomic configuration of $1s^1$ similar to gold that makes it interesting to study the interaction of small gold clusters with hydrogen atoms, both H and Au having single valence s electron. Gold hydrides have attracted considerable attention as they serve as important intermediates in gold catalyzed reactions [39,40] such as hydrogenation [41], hydrosilylation [42], C–H bond activation [43], and aerobic oxidation of alcohols [44]. The study of gold hydride clusters is important to understand the adsorption of hydrogen onto metal surfaces. Moreover, the gold hydrides serve as archetype to study the relativistic effects. The chemistry of gold has been demonstrated by several theoretical and experimental works [45,46] to have significant resemblance to that of the hydrogen atom. In 1978, *ab initio* studies were performed by Hay et al. [47] on diatomic gold hydride using relativistic effective core potentials. A number of experimental and theoretical studies have been reported about the interaction of the gold clusters with hydrogen [48–51]. Phala performed DFT calculation to study the interaction of small Au_n (n = 1–13) clusters with H and CO [52]. Buckart et al. [46] in 2003 presented that the spectra of Au_n^- and $Au_{n-1}H^-$ showed identical features for $n > 2$ in their photoelectron spectra; thus suggesting that hydrogen behaved as protonated species. Even though a large number of studies have been done on gold cluster hydrides involving a single hydrogen atom, but a very rare amount of study has been done on multi-hydrogen atom interaction [53]. Apart from the interaction between hydrogen and gold cluster, insight into the reactivity of Au cluster and the reacting sites within them is also important. The ability to withdraw (electrophilicity) or donate (nucleophilicity) electrons of the various sites in a cluster is closely related to its catalytic activ-

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ity. However, exploring the reactive sites in hydrogen adsorbed gold clusters is still lacking behind.

A planar triangular structure with D_{3h} symmetry has been assigned to Au_6 [54]. Based on this structure, we aim to study multi-hydrogen adsorption on Au_6 and try to reveal the

(i) structure and stability of Au_6H_n (n = 1–12) clusters,
(ii) electronic and reactivity properties of the Au_6H_n clusters.

The paper is outlined as follows. Section 2 summarizes the computational methods. The following section (Section 3) shows the results obtained from the calculations. Finally, Section 4 gives the summary of the present study.

2. Computational methods

Density Functional Theory (DFT) calculations are carried out using DMol^3 [55] package utilizing PBE functional [56] incorporating the Perdew, Burke, Ernzerhof correlation at the generalized gradient approximation (GGA) level. The DNP numerical basis set is the highest quality set available in DMol^3 and has been chosen for our calculations. DNP basis functions are the double numerical sets containing a polarization d-function on heavy atoms and polarization p-function on hydrogen. Although the size is comparable to 6-31G** basis set but the numerical basis set of given size are much more accurate than Gaussian basis set of same size. Relativistic calculations in gold are important and are performed with scalar relativistic corrections to valence orbitals relevant to atomic bonding properties via a local pseudopotential (VPSR) [57]. For matrix integrations fine grid mesh points are employed. Convergence criterion of 10^{-6} a.u. has been used for self consistent field procedures on energy and electron density. To justify the level of calculation employed in the present work, we have compared the calculated values of bond length (R_e), dissociation energy (D_e) and vibrational frequency (ω_e) of Au_2 at different levels of theory (VWN, BLYP, PW91, PBE functional and DNP basis set) with the experimental values (Table 1).

The stability and the electronic properties of the clusters have been determined from the binding energy per atom, binding energy per H-atom, the vertical ionization potential and the chemical hardness values. For a given cluster, the binding energy is a measure of its thermodynamic stability. We calculate the average binding energies using the following formulas:

$$E_b = [6E(\mathrm{Au}) + nE(\mathrm{H}) - E(\mathrm{Au_6H_n})]/(n+6) \quad (1)$$

$$E_b^a = [E(\mathrm{Au_6}) + nE(\mathrm{H}) - E(\mathrm{Au_6H_n})]/(n) \quad (2)$$

where E_b is the binding energy per atom, E_b^a is the binding energy per H-atom, E(Au) and E(H) are the energies of Au and H atoms respectively, $E(\mathrm{Au_6})$ and $E(\mathrm{Au_6H_n})$ are the energies of Au_6 and Au_6H_n clusters respectively and n is the number of H atoms in a given cluster.

Table 1
Comparison of the performance of different functional for bond length (Å), dissociation energy (eV) and vibrational frequency (cm^{-1}) of Au_2 with the experimental values. The basis set used for the calculations is the DNP basis set.

System	Property	Experimental	Method
Au_2	R_e (Å)	2.47	2.44 (VWN)
			2.53 (BLYP)
			2.49 (PW91)
			2.49 (PBE)
	D_e (eV)	2.30	2.97 (VWN)
			2.14 (BLYP)
			2.43 (PW91)
			2.40 (PBE)
	ω_e (cm^{-1})	191	169.6 (BLYP)
			184.0 (PBE)

The vertical ionization potential (VIP) is calculated as:

$$\mathrm{VIP} = E(\mathrm{Au_6H_n})^+ - E(\mathrm{Au_6H_n}) \quad (3)$$

where $E(\mathrm{Au_6H_n})^+$ is the energy of the cationic cluster at the optimized geometry of the neutral cluster. Generally, larger vertical ionization potential implies deeper HOMO energy level leading to lesser reactivity or higher chemical stability.

A useful parameter for examining the kinetic stability of the clusters is the HOMO–LUMO gap (HLG).

$$\mathrm{HLG} = E(\mathrm{LUMO}) - E(\mathrm{HOMO}) \quad (4)$$

Larger HOMO–LUMO gap corresponds to higher energy for perturbing the electronic structure thus indicating higher stability of electronic structure.

The reactivity of a system can be described in terms of its chemical hardness. The second derivative of energy (E) with respect to the number of electrons (N) at constant external potential, $v(\vec{r})$ defines hardness, η.

$$\eta = 1/2(\partial^2 E/\partial N^2)_{v(\vec{r})} = 1/2(\partial\mu/\partial N)_{v(\vec{r})} \quad (5)$$

where μ is the chemical potential of the system.

Applying three point finite difference approximation, hardness can be approximated as:

$$\eta = (IP - EA)/2 \quad (6)$$

where IP is the ionization potential and EA is the electron affinity of the system.

Within the framework of Density Functional Theory, applying Koopmans approximation, hardness can be expressed as:

$$\eta = (E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}})/2 \quad (7)$$

Condensed Fukui functions in a finite difference approximation have been proposed by Yang et al. [58] to describe the site reactivity or site selectivity and are given as:

$$f^+ = q(N+1) - q(N); \quad \text{for nucleophilic attack} \quad (8a)$$

$$f^- = q(N) - q(N-1); \quad \text{for electrophilic attack} \quad (8b)$$

$$f^0 = 1/2[q(N+1) - q(N-1)]; \quad \text{for radical attack} \quad (8c)$$

$q(N)$, $q(N+1)$, $q(N-1)$ are the electronic populations for atoms with (N), ($N+1$) and ($N-1$) electrons respectively.

Roy et al. [59] proposed relative nucleophilicity as:

$$f_{\mathrm{nu}} = f^-/f^+ \quad (9a)$$

and relative electrophilicity as:

$$f_{\mathrm{ele}} = f^+/f^- \quad (9b)$$

These are useful to identify the reactive site at which the reaction shall take place. Within the same molecule $f_{\mathrm{nu}}/f_{\mathrm{ele}}$ is important to compare the reactivity. For a site, if $f_{\mathrm{nu}} \gg f_{\mathrm{ele}}$, then the site is favorable for an electrophilic attack and favorable for nucleophilic attack if $f_{\mathrm{ele}} \gg f_{\mathrm{nu}}$. A site for which f_{nu} is almost equal to f_{ele} is said to be an amphiphilic site.

3. Results and discussion

3.1. Geometric structure and electronic properties

The planar triangular structure with D_{3h} symmetry for Au_6 cluster has been concluded to be the lowest energy structure from our previous work [54] and the present work utilizes this stable