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Citation: AIP Conference Proceedings **1731**, 090039 (2016); doi: 10.1063/1.4948003
View online: http://dx.doi.org/10.1063/1.4948003
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1731?ver=pdfcov
Published by the AIP Publishing

Stability, Structural and Electronic Properties of Benzene Molecule Adsorbed on Free Standing Au Layer

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Abstract. We report stability and electronic properties of benzene molecule adsorbed on the Au atomic layer within the framework of density function theory (DFT). Horizontal configuration of benzene on the top site of Au monolayer prefers energetically over other studied configurations. On the adsorption of benzene, the ballistic conductance of Au monolayer is found to decrease from $4G_0$ to $2G_0$ suggesting its applications for the fabrications of organic sensor devices based on the Au atomic layers.

Keywords: DFT, Electronic Structure, Ballistic conductance.
PACS: 31.15.v- 71.20.-b 73.22.-f 77.22.ch

INTRODUCTION

Two dimensional (2D) materials have generated lots of interest due to their numerous technological applications [1]. Among these materials, group-IV elements and transition-metal chalcogenides compounds possess unique properties as compared to their three dimensional (3D) bulk counterpart [2-6] leading to novel applications.

Lately, noble-metals in two dimensional structures emerged as promising materials with exotic behavior e.g. multilayers of Au have been found to show Dirac-cone like features that are important for high performance electronic applications [7-8]. The exploration of the properties of free standing noble metal layers is the need of hour.

On the other hand, the adsorption of organic molecules on metal surface has promising applications in electronics and catalysis [9-10]. The benzene molecule can be regarded as a building block for many organic compounds. A systematic study of benzene adsorbed on 2D layers still lacks, therefore, in the present work we explore the structural stability and electronic properties of benzene adsorbed on monoatomic graphene like layer of gold (Figure 1).

COMPUTATIONAL DETAILS

First principle calculations have been performed within the framework of density functional theory using SIESTA code [11]. Troullier Martin, norm conserving, relativistic pseudo-potentials in fully separable Kleinman and Bylander form have been used to treat the electron-ion interactions. The exchange and correlation energies were treated within the generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof (PBE) [12] parameterization. A 4x4x1 supercell has been used to model monoatomic gold layer. A Vacuum of ~ 25 Å along the z-direction has been introduced to minimize the interaction between the periodic images of the 2D model. The structural optimization of the pristine gold monolayer and benzene were carried out using standard conjugate-gradient (CG) technique. Throughout geometry optimization, confinement energy of numerical pseudo-atomic orbital is taken as 0.01 Ry. A 200 Ry mesh cut off has been used for the reciprocal space expansion of the total charge density. Structure was relaxed until the forces on each atom were less than 0.01eV/Å. A 8x8x1 Monkhorst-Pack grid of k points was used for Brillouin Zone integration.

DAE Solid State Physics Symposium 2015
AIP Conf. Proc. 1731, 090039-1–090039-3; doi: 10.1063/1.4948003
Published by AIP Publishing. 978-0-7354-1378-8/$30.00

RESULTS AND DISCUSSIONS

Structural Properties

The lattice constant of 2D Au layer in hexagonal lattice is calculated as 4.61 Å. To find the most stable adsorption site of benzene on Au monolayer, we have considered two different configurations namely: horizontal and vertical with different adsorption sites as shown in Figure 1. Note that 4 × 4 supercell of Au atoms is used to remove artificial interactions between the benzene molecules in the periodic lattice in x-y direction (Figure 1).

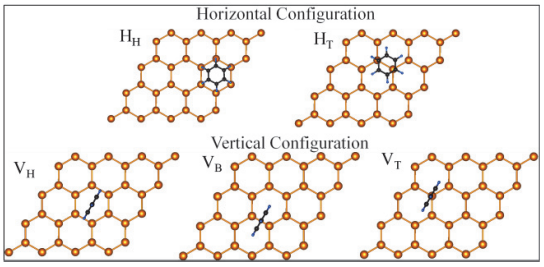

FIGURE 1. Ball and stick model with top and side view of benzene adsorbed on gold sheet in Horizontal: hollow (H_H) and top (H_T) sites (a-b) and vertical: hollow (V_H), bond (V_B), and top (V_T) site configurations (c-e).

To identify the most stable configuration, we have calculated adsorption energy as:

$$E_{ads} = E_{Au-moleucule} - E_{Au} - E_{molecule}$$

Where $E_{Au\text{-}molecule}$ is the total energy of Au layer/benzene composite system, E_{Au} and $E_{molecule}$ are the total energy of pristine Au layer and molecule (organic molecule benzene, C_6H_6) respectively. Note that the negative value of adsorption energy indicates the stability of benzene molecule on monolayer. The variation of adsorption energy with layer-molecule separation is depicted in Figure 2. The calculated adsorption energy values for the considered adsorption sites at the optimized benzene-molecule separation ($R_{benzene\text{-}monolayer}$) have been tabulated in Table 1.

It has been found that top site adsorption in horizontal configuration (H_T) is most stable as compared to other adsorption sites in considered configurations. The adsorption energy value is -0.21 eV for H_T configuration (Table 1) suggests benzene to be physisorbed on gold monolayer with vertical spacing of 3.4 Å.

Calculated structural parameters for the stable site in the horizontal configuration are: the bond length and

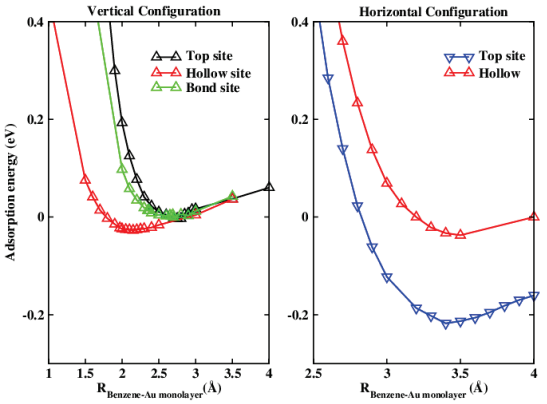

FIGURE 2. Variation of adsorption energy as a function of layer-molecule separation for vertical and horizontal configurations.

bond angles ($d_{Au\text{-}Au}$) and ($\Theta_{Au\text{-}Au\text{-}Au}$) of functionalized Au monolayer are 2.66 Å and 120.35^0 respectively, for benzene the bond lengths and bond angles between atoms are ($d_{C\text{-}C}$), ($d_{C\text{-}H}$) and ($\Theta_{C\text{-}C\text{-}C}$), ($\Theta_{C\text{-}C\text{-}H}$) and ($\Theta_{H\text{-}C\text{-}C}$) are 1.42 Å, 1.11 Å and 120.01^0, 120.02^0 and 119.95^0 respectively. HOMO and LUMO of the pristine benzene molecule are -6.44 eV and -1.46 eV respectively.

TABLE 1. Calculated adsorption energies (E_{ads}) at equilibrium distance between benzene-monolayer ($R_{Benzene\text{-}monolayer}$) for different adsorption sites.

Adsorption Sites	$R_{Benzene\text{-}monolayer}$ (eV)	E_{ads} (eV)
Horizontal Hollow (H_H)	3.50	-0.04
Horizontal Top (H_T)	3.40	-0.21
Vertical Hollow (V_H)	2.15	-0.03
Vertical Bond (V_B)	2.70	-0.001
Vertical Top (V_T)	2.70	-0.003

Electronic Properties

For the stable configuration horizontal top site (H_T), the electronic band structure of organic molecule adsorbed gold monolayer has been calculated along the direction of high symmetry point Γ-M-K-Γ (Figure 3). Electronic band structure of pristine monolayer of Au show metallic character. For pristine benzene the difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is calculated as ~ 5 eV. The pristine gold monolayer remains metallic on adsorption of benzene but there are some modulations in bands' dispersion upon adsorption (inset Figure 3(b)). The number of bands crossing the Fermi level is found to be changing

on functionalization. Considering that the intrinsic quantum ballistic conductance of a given system can

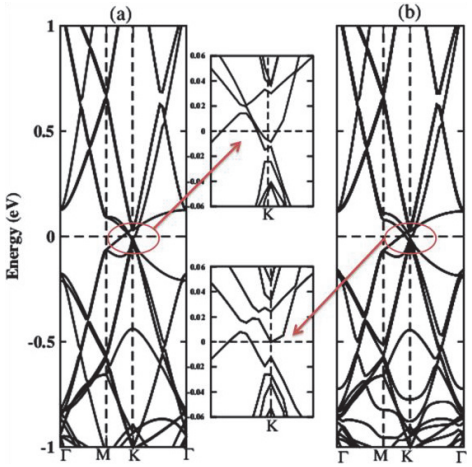

FIGURE 3. Electronic band structure for (a) pristine Au monolayer and (b) functionalized Au monolayer. The number of bands crossing the Fermi energy is shown in inset. Fermi level is set at 0 eV.

be estimated by number of bands crossing the Fermi level. We found that in pristine gold layer, four bands are crossing the Fermi level resulting in conductance of $4G_0$ (inset Figure 3 (a)), while in case of benzene adsorbed gold layer at stable site, two bands are crossing Fermi level give rise to decrease in conductance to $2G_0$ (inset Figure 3(b)). This decrease in the quantum ballistic conductance on benzene adsorption by 50% offers a possibility for sensing application of organic molecules.

CONCLUSIONS

In summary, first principle calculations have been performed to investigate the stability and electronic properties of benzene on Au monolayers. Top site adsorption of benzene on Au monolayer in horizontal configuration is found to be most favorable. Quantum ballistic conductance decreases by 50% on the adsorption of benzene molecule. Our findings may guide the experimentalist for the realization of organic sensors based on gold atomic layers.

ACKNOWLEDGMENTS

The authors wish to acknowledge SIESTA team for the code. Pooja Kapoor wishes to acknowledge the financial support from UGC New Delhi in the form of UGC-BSR Junior Research Fellowship. Munish Sharma wishes to acknowledge DST New Delhi for providing financial support in the form of INSPIRE-Fellowship. CVRAMAN, high performance computing cluster at Department of Physics, Himachal Pradesh University was used for obtaining the results in the present study.

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