
THE ADSORPTION OF SOME COMMON MOLECULAR GASES ON NEUTRAL NINE-ATOM GERMANIUM-PHENYL NANOCLUSTER: A DFT STUDY.

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ABSTRACT

The structural stability, adsorption energy and electronic property characteristics of CH_4 , CO , H_2S and NH_3 gases on neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster were studied using DFT at CAM-B3LYP method and Lan12dz basis set. These molecular gases adsorption on neutral nine-atom germanium-phenyl nanocluster were optimized at B3LYP/Lan12dz basis set. The structural stability of molecular gas adsorptions on [$Ge_9(C_6H_5)$] nanocluster were discussed in terms of calculated energy and dipole moment. The adsorption of CH_4 , CO , H_2S and NH_3 molecules on [$Ge_9(C_6H_5)$] nanocluster was studied using the above method and basis set. A number of possible different relative orientations of the gas interactions with the neutral nine-atom germanium-phenyl nanocluster were investigated. The adsorption energy of the stable structure $CO-[Ge_9(C_6H_5)]$, $NH_3-[Ge_9(C_6H_5)]$ and $H_2S-[Ge_9(C_6H_5)]$ were calculated to be -14.75, -17.52 and -19.32 eV respectively. This results suggest that the interaction between the molecular gases on [$Ge_9(C_6H_5)$] nanostructure surface are strong. Also, the electronic properties of the molecular gases on neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster was found to be affected by the adsorption of CH_4 , CO , H_2S and NH_3 gas. The density of state showed a decrease in the HOMO-LUMO band gap energy change ΔE_g of the nanostructure upon the adsorption of CH_4 , CO , H_2S and NH_3 gas molecules. Considering these changes in the HOMO-LUMO band gap energy that was calculated to occur during CH_4 , CO , H_2S and NH_3 adsorption, it is clear that [$Ge_9(C_6H_5)$] nanocluster is sensitive to CH_4 , CO , and NH_3 adsorption suggesting that [$Ge_9(C_6H_5)$] nanocluster has potential to act as sensor.

Keywords: Adsorption Energy, Sensor, First Principle Calculation, HOMO-LUMO, Nanostructure, Band gap, Germanium-phenyl.

INTRODUCTION

Presently, rapidly increasing environmental air pollution created by chemical gaseous pollutants from modernization, industrialization, increasing automobiles and human activities is a major concern for its adverse effects on human health, plants, animal life and the welfare of mankind. Some of these common chemical atmospheric gases include carbon monoxide (CO), methane (CH_4), Hydrogen sulfide (H_2S), ammonia (NH_3), carbon dioxide (CO_2), sulphur dioxide (SO_2), Hydrogen (H_2), oxygen (O_2), Ozone (O_3), water (H_2O) vapour, Argon (Ar), nitrogen (N_2) and nitrogen dioxide (NO_2). Typically, among these gaseous pollutants of interest are CH_4 , CO , H_2S and NH_3 that are most toxic gases having very harmful effects on human beings and animals as it inhibit the free consumption of oxygen by the body tissues and related effects (Torres *et al*, 2018; El-Barbary *et al*, 2015; Giselle *et al*, 2007). The entire atmospheric world that used to provide clean air is very polluted today due to rapid increase and release of these toxic gases into the environment beyond a certain concentration. For example, NH_3 , although a vital constituent in many industries such as fertilizers, plastics, petrochemicals, textiles, pesticides, dyes and related industries is quite hazardous to human health beyond a concentration of 25 ppm in air (Ullah *et al*, 2013). The need for detection of these harmful and toxic gases is of prime concern today and therefore it is necessary to check its emission from industrial plants, households, vehicle emissions and environmental monitoring. Historically, gas sensors were first primarily used in coal mines where accurate monitoring of hazardous gases were being investigated continually. Soon gas sensors were also beginning to appear in the chemical industry, in environmental pollution monitoring units and in the human health sector. But in light of increasing demand for security, environmental control, health improvement and so on, gas sensors are becoming more important and growing at a faster pace in this 21st century (Sze and Kwok, 2006). Semiconductor materials are generally good as sensors to various molecular gases and to humidity (Mackenzie and Brown, 2012). Samä *et al*, (2016) reports Ge nanowires as a humidity sensor, few works are found concerning the fabrication of a gas sensor based on germanium structured materials with semiconducting nine-atom germanium-phenyl clusters have not been previously investigated. Recently, germanium compounds have emerged as a critically important material in the fabrication of nanoelectronics, sensors and optics. Thus, the use of hybrid inorganic-organic materials as

gas sensors has proved efficient with improved sensing characteristics. Therefore, the discovery of gas sensors that are highly sensitive to detect CH_4 , CO , H_2S and NH_3 gases has long been an important research target. Van der Bossche *et al.*, (2017) reported the development of a low-cost sensor using a metal oxide that has suitability for detecting methane leaks. The detection of the sensor is in the range of 0.8–2.7 ppm. Mishra *et al.*, (2004) reported the detection of carbon monoxide at parts per billion (ppb) using polyaniline nanocomposites. Their results showed that carbon monoxide can be detected in the range 0.0006 to 0.3 ppb at room temperature. Zhongkang *et al.*, (2017) reported first-principle calculations based on DFT were performed to investigate the sensing properties of Boron Phosphide (BP) towards H_2S toxic gas. The adsorption energy and charge transfer were used to study the interaction strength between Boron Phosphide and H_2S . The results show that the adsorption energy between H_2S and pristine Boron Phosphide is small as well as the charge transfer. Mao *et al.*, (2018) have investigated the structure and electronic properties of toxic gas NH_3 , SO_2 , and NO_2 molecules adsorption on $GeSe$ monolayer using first-principle based DFT method. Their results showed that the adsorption energy, charge transfer and electron localization function of the $GeSe$ monolayer is sensitive to the gas molecules caused by the modification of the electronic structure.

To the best of our knowledge, the sensing of CH_4 , CO , H_2S and NH_3 toxic gas molecules by neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster has not been studied before, either theoretically or experimentally. We therefore felt that it was important to determine whether neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster can absorb CH_4 , CO , H_2S and NH_3 gases and thus whether [$Ge_9(C_6H_5)$] nanocluster could potentially be used as a practical CH_4 , CO , H_2S and NH_3 gas sensor. That work is the focus of the present paper. We investigated a number of possible orientations of the CH_4 , CO , H_2S and NH_3 gas molecules with respect to the neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster. We calculated the optimized molecular geometry, adsorption energies, HOMO, LUMO, band gap energy, binding energy, Gibb's free energy, enthalpy energy, and the density of states.

Theory of Computation

In this work, density functional theory has been used to calculate the adsorption and electronic properties of the neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster at CAM-B3LYP functional with LanI2dz basis set. Gaussian 09 software program has been used to perform these calculations. According to the DFT, the total energy can be written as:

$$E[\rho(r)] = \hat{T}[\rho(r)] + \frac{1}{2} \iint \frac{\rho(r)\rho(r^1)}{|r-r^1|} dr dr^1 + \int V_{ext}(r)\rho(r)dr + E_{xc}[\rho(r)] \quad (1)$$

where $\rho(\vec{r})$ is the electron density, $\hat{T}[\rho(r)]$ is the kinetic energy and $E_{xc}[\rho(r)]$ includes all many-body contribution to the total energy. The one-particle Schrodinger's equation for a non-interacting system is given by

$$H_{eff}(r)\Psi_i(r) = \left[-\frac{\nabla_i^2}{2} + V_{eff}(r) \right] \Psi_i(r) = \varepsilon_i \Psi_i(r) \quad (2)$$

where

$$V_{eff}(r) = V_{ext}(r) + \int \frac{\rho(r^1)}{|r-r^1|} dr + \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \quad (3)$$

$V_{eff}(r)$ is the effective external potential in which the non-interacting electrons are moving. The last term is called exchange-correlation potential.

$$V_{xc} = \frac{\delta E_{xc}[\rho(r)]}{\delta \rho(r)} \quad (4)$$

$V_{xc}(\vec{r})$ is the exchange-correlation potential, V_{xc} and $E_{xc}[\rho(r)]$ are functionals of the electron density, $\rho(\vec{r})$. For a normalized wave function $\Psi_i(r)$, the particle density is given by

$$\rho(r) = \sum_{i=1}^N |\Psi_i(r)|^2 \quad (5)$$

where the sum is over the N lowest eigen states. So, all the information about the system is incorporated in the electron density and the total energy of the system can be written as functional of the density:

$$E[\rho(r)] = T_{ni}[\rho(r)] + V_{ne}[\rho(r)] + V_{ee}[\rho(r)] + \Delta T[\rho(r)] + \Delta V_{xc}[\rho(r)] \quad (6)$$

By considering a system of non-interacting electrons, the expression for the kinetic energy is considerably simplified i.e.

$$T_{ni}[\rho(r)] = \sum_{i=1}^N \langle \psi_i | -\frac{\nabla_i^2}{2} | \psi_i \rangle \quad (7)$$

where $T_{ni}[\rho]$, $V_{ne}[\rho]$ and $E_{xc}[\rho]$ are the K.E of non-interacting electrons systems, classical coulomb energy and the exchange-correlation energy respectively. The form of the exchange-correlation function is not known, and an approximation must be provided as one of the inputs to a DFT calculation. According to B3LYP function, the exchange-correlation energy $E_{xc}[\rho(r)]$ is given by

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a_0(E_x^{HF} - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{LYP} - E_c^{LDA}) \quad (8)$$

The Ionization potential(IP) and the electron affinity(AE) of the nanocluster are calculated from the HOMO and LUMO energy in the framework of Koopman's theorem(Koopman, 1993).

$$IP = -\varepsilon_{HOMO}, AE = -\varepsilon_{LUMO} \quad (9)$$

Computational approach

Figure 1 represent the molecular structure of $CO-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ and $NH_3-[Ge_9(C_6H_5)]$ nanostructure . In this report, a computational analysis of CH_4, CO, H_2S and NH_3 gas molecules on the neutral nine-atom germanium-phenyl $[Ge_9(C_6H_5)]$ nanocluster were performed using Gaussian 09 software program package within DFT framework. PES scan was performed to predict the most stable molecular structure of the nine-atom germanium-phenyl nanostructure using DFT/MP2 method with CEP-31g basis set. Geometry optimization of the selected most stable molecular structure out of 37 conformers was run at DFT/B3LYP level using Lanl2dz basis set by the Berny algorithm as implemented in Gaussian 09 software in the framework of the unrestricted formalism UB3LYP. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minimum(no imaginary frequency). A number of possible different orientations of CH_4, CO, H_2S and NH_3 gas molecules with respect to the neutral nine-atom germanium-phenyl $[Ge_9(C_6H_5)]$ nanocluster were investigated. For each of the single gas adsorbate, only one adsorption site was considered, namely the top of a germanium atom. At each of the orientation, for each particular molecular gas the respective properties were obtained from the Gaussian 09 output file with all the necessary correction terms where applicable. Adsorbed energy, HOMO.,LUMO. energy gap(E_g), enthalpy energy and Gibb's free energy($\Delta H, \Delta G$), calculated energy of the different structures, Dipole moment and point group were calculated at CAM-

B3LYP method and Lan12dz basis sets. We aimed at investigating the sensitivity of nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster towards CH_4 , CO , H_2S and NH_3 toxic gas molecules. First-principle calculations based on DFT were performed using Gaussian 09 package. The Gauss Sum 3.0 program was also used to obtain density of state results (O'Boyle *et al*, 2008). The adsorption energy (E_{ads}), was calculated using the relation (Wei *et al*, 2018);

$$E_{ads} = E_{Ge-C_6H_5/gas} - E_{Ge-C_6H_5} - E_{gas} \quad (10)$$

where $E_{Ge-C_6H_5/gas}$ is the total energy of germanium-phenyl nanocluster of which the gas molecule is adsorbed, $E_{Ge-C_6H_5}$ is the energy of [$Ge_9(C_6H_5)$] nanocluster and E_{gas} is the energy of the gas molecule respectively. The more negative E_{ads} obtained after geometry optimization, the easier for the free gas molecule to be adsorbed on the $E_{Ge-C_6H_5}$ monolayer surface, indicating the adsorption system is more stable. In addition, the adsorption enthalpy change ΔH and Gibb's free energy ΔG were calculated using the relation (Nasser *et al*, 2015) at $T=298$ K, and $P=1$ atm.

$$\Delta H = H_{Ge-C_6H_5/gas} - H_{Ge-C_6H_5} - H_{gas} \quad (11)$$

$$\Delta G = G_{Ge-C_6H_5/gas} - G_{Ge-C_6H_5} - G_{gas} \quad (12)$$

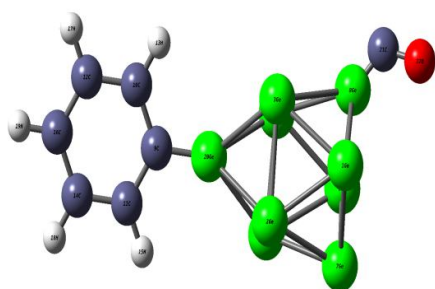
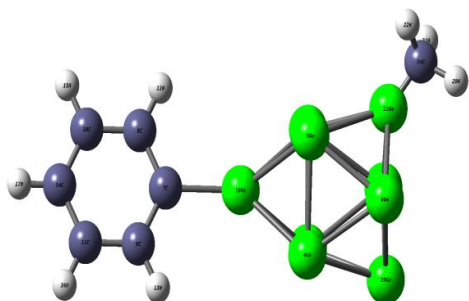
where $H_{Ge-C_6H_5/gas}$, $H_{Ge-C_6H_5}$ and H_{gas} are the sum of electronic and thermal enthalpies of $Ge_9C_6H_5/gas$, $Ge_9C_6H_5$ and the toxic gas molecules respectively as obtained from the frequency calculations. As we know, a negative value of ΔH will correspond to an exothermic adsorption. Gibb's free energy change (ΔG) also will be calculated similar to ΔH using the corresponding data at the same condition. Zero-point corrections are included in these data. The HOMO-LUMO energy gap (E_g) was calculated using the relation

$$E_g = E_{LUMO} - E_{HOMO} \quad (13)$$

where E_{LUMO} and E_{HOMO} are energies of LUMO and HOMO respectively. The shift of the energy gap (E_g) due to sensor properties was calculated using the relation (Nasser *et al*, 2015)

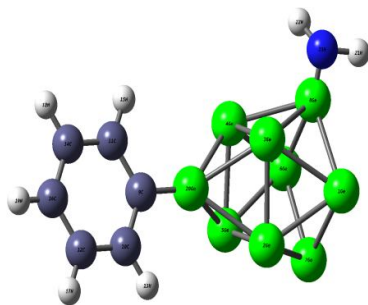
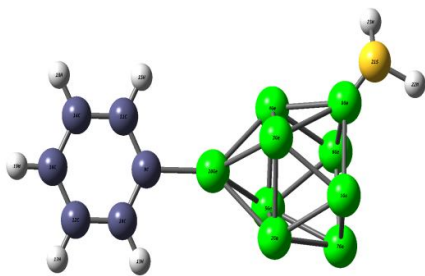
$$\Delta E_g = \left(\frac{E_{g2} - E_{g1}}{E_{g1}} \right) \times 100\% \quad (14)$$

where E_{g1} and E_{g2} are, respectively, the initial energy value E_{g1} and E_{g2} of the $[Ge_9(C_6H_5)]$ nanocluster and of $E_{Ge-C_6H_5/gas}$ at any passing time. All calculations in the present work were performed using Windows version of Gaussian 09 (Frisch *et al*, 2009) suit of ab initio quantum mechanical program. Only the results obtained with the DFT functional are reported in this work since the DFT method has proven to be one of the most accurate methods for the computation of the electronic structure of solids and most of the properties of some molecules.



a. $CH_3 - [Ge_9(C_6H_5)]$
 $CO - [Ge_9(C_6H_5)]$

b.



c. $H_2S-[Ge_9(C_6H_5)]$

d.

$NH_2-[Ge_9(C_6H_5)]$

Figure 1: Optimized Structures of $CO-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ and $NH_2-[Ge_9(C_6H_5)]$ nanostructures.

RESULTS AND DISCUSSION

Stability and Calculated Energies

The structural stability of the nine-atom germanium-phenyl $[Ge_9(C_6H_5)]$ nanostructure and all the molecular gases CH_4 , CO , H_2S and NH_3 are analyzed by calculating their energy, dipole moment and point group. As seen from Table 1, the calculated energy for pure $[Ge_9(C_6H_5)]$ nanostructure is about -7203.5eV. The calculated energies for $CO-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ and $NH_3-[Ge_9(C_6H_5)]$ are -10284.4, -8283.6, -7524.5 and -8727.9 eV respectively. It is observed that from the pure $[Ge_9(C_6H_5)]$ nanostructure, these energies are increasing with the highest being that of $CO-[Ge_9(C_6H_5)]$ nanostructure having value of -10284.4 eV which is more stable than the other structures. The structural stability of the nanostructure gradually increases with the increase in the number of atoms. Upon adding more atoms to the cluster, it becomes more stable, initially for a lower number of atoms i.e. pure $[Ge_9(C_6H_5)]$ nanocluster, the cluster is in the

premature stage; it attains its stability only on addition of atoms. Furthermore, these slight variations in the calculated energies arises from the change in the electronic configuration of the molecular gases. However, the stability of the defect structured cluster decreases owing to the removal of atoms from the regular structure. The dipole moment result from unequal charge distribution in the atoms of a cluster. As follow from the data in Table 1, $CO-[Ge_9(C_6H_5)]$ and $H_2S-[Ge_9(C_6H_5)]$ have dipole moments of 9.329 D and 8.300 D respectively with respect to pure $[Ge_9(C_6H_5)]$ nanocluster. This large values for the dipole moment suggest the unequal charge distribution on the coordinate axis, that is, more charge distribution in a particular axis than the other. In contrast, the values observed for $CH_3-[Ge_9(C_6H_5)]$ and $NH_3-[Ge_9(C_6H_5)]$ are low suggest an evenly distribution of charges in the respective coordinate axes. It is found that the dipole moment is maximum for $CO-[Ge_9(C_6H_5)]$ calculated to be 9.329 Debye due to asymmetry of the structure. All the nanostructures in the present study have C_1 point symmetry which exhibits only identity axis operation. Comparing the energies of different clusters it is inferred that increase in the number of atoms in the cluster leads to the stability of the cluster.

Adsorption of CH_4 , CO , H_2S and NH_3 on $[Ge_9(C_6H_5)]$ nanostructure.

As shown in **Table 1**, the adsorption energy E_b (calculated from equation 10) corresponding to the various configuration of molecular gases CH_4 , CO , H_2S and NH_3 adsorption on $[Ge_9(C_6H_5)]$ nanostructure particularly Ge(8) atom are examined. For comparison, the adsorption energies of gas molecules (CH_4 , CO , H_2S and NH_3) adsorption on $[Ge_9(C_6H_5)]$ nanostructure are also indicated. The adsorption energies E_b , of $CO-[Ge_9(C_6H_5)]$, $NH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ and $CH_3-[Ge_9(C_6H_5)]$ are -14.75(2.694), -17.52(6.204), -19.32(4.218) and 1.197(20.953) eV respectively. These results suggest that the interaction between the molecular gases on $[Ge_9(C_6H_5)]$ nanostructure surface are strong with the exception of $CH_3-[Ge_9(C_6H_5)]$. The adsorption energies with positive values suggest the interaction of the molecular gas with the $[Ge_9(C_6H_5)]$ nanostructure surface is weak and the particular orientation of the molecular gas is not stable, thus belong to endothermic specificity. The $H_2S-[Ge_9(C_6H_5)]$ complex have an adsorption energy value of -19.32 eV which is more negative than the adsorption energy values -14.75eV and -17.52 eV for $CO-[Ge_9(C_6H_5)]$ and $NH_3-[Ge_9(C_6H_5)]$. $H_2S-[Ge_9(C_6H_5)]$ is

the most stable with H_2S gas molecule located sideward of the germanium-phenyl nanostructure such that the sulphur atom of H_2S is located sideward of the Ge(8) atom in the germanium-phenyl nanostructure. For the stable configurations, $CO-[Ge_9(C_6H_5)]$ is weaker than $NH_3-[Ge_9(C_6H_5)]$. Carbon monoxide is oxygen rich yet with a reduced adsorption energy. The adsorption energy E_b for $NH_3-[Ge_9(C_6H_5)]$ is calculated to be about -17.52 eV that is large enough to form a hydrogen bond between NH_3 and germanium-phenyl nanostructure. A hydrogen bond is a weak interaction whose strength can be placed between the chemical bond and the Van der Waal force.

Table 1: Adsorbed energy, HOMO.LUMO. energy gap, enthalpy energy and Gibb's free energy($\Delta H, \Delta G$), Dipole moment and point group were calculated at CAM-B3LYP/LanI2dz basis sets.

nanostructure	Calc. Energy /eV	HOMO /eV	LUMO /eV	Energy gap /eV	ΔE_g /%	ΔH /eV	ΔG /eV	Dipole moment /D	Adsorbed energy E_b /eV
$CO - Ge_9(C_6H_5)$	-10275.2	-6.835	-3.236	3.599	34.9	-28.29	-28.29	9.329	2.694
$OC - Ge_9(C_6H_5)$	-10284.5	-6.075	-3.944	2.131	20.1	-14.69	-14.97	4.737	-14.748
$NH_2 - Ge_9(C_6H_5)$	-8727.9	-6.177	-3.674	2.503	06.5	-17.69	-17.96	3.724	-17.524
$H_2N - Ge_9(C_6H_5)$	-8722.8	-6.509	-3.944	2.565	03.9	-17.42	-17.42	5.867	6.204
$CH_3 - Ge_9(C_6H_5)$	-8283.6	-6.151	-3.589	2.562	04.0	1.09	0.82	4.284	1.197
$H_3C - Ge_9(C_6H_5)$	-8280.5	-6.555	-4.051	2.504	06.5	-11.43	-11.70	5.517	20.953
$H_2S - Ge_9(C_6H_5)$	-7524.5	-6.370	-3.381	2.989	12.1	-19.32	-19.59	8.300	-19.319
$SH_2 - Ge_9(C_6H_5)$	-7514.7	-6.000	-2.805	3.195	19.8	-14.97	-15.24	6.778	4.218
Pure $Ge_9(C_6H_5)$	-7203.5	-6.229	-3.563	2.666	-	-	-	7.771	-

All these simulated nanostructures have point group C_1 .

HOMO-LUMO orbitals of adsorbed CH_4 , CO , H_2S and NH_3 gas molecules on $[Ge_9(C_6H_5)]$ nanocluster.

Molecular orbitals play an important role in the theoretical design of sensors. HOMO-LUMO gap of different clusters provides the insight for the electronic properties of clusters. The change in the energy band gap E_g , between the HOMO and LUMO upon shifting from pure isolated $[Ge_9(C_6H_5)]$ nanostructure to $CO-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ $NH_3-[Ge_9(C_6H_5)]$ gives the sensing aptitude of the nanocluster towards the molecular gases. As shown in Table 1, the HOMO and LUMO energy orbitals for $CO-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ and $NH_3-[Ge_9(C_6H_5)]$ are found to be (-6.075 eV, -3.944eV), (-6.151eV, -3.589 eV), (-6.370 eV, -3.381eV), and (-6.177eV, -3.674eV) respectively calculated according to equation (13). Comparing the HOMO-LUMO energies of the $[Ge_9(C_6H_5)]$ nanostructure with the ones after the adsorption of CH_4 , CO , H_2S and NH_3 gas molecules on the nanostructure complex, it is clear that the energy values are so close. Also, it is noticed that there is no any contribution from the gas molecules at the molecular orbitals since the electron density of HOMO and LUMO are distributed entirely over all the nine-atom germanium atoms. As it is observed, it is found that each complex has a different value of HOMO-LUMO energy gap when compared to pure isolated $[Ge_9(C_6H_5)]$ nanostructure. Pure isolated $[Ge_9(C_6H_5)]$ nanostructure is a semiconductor with a calculated band gap energy of 2.666 eV. Semiconductors have energy band gap between zero and 3 eV and materials with greater values than this are considered as insulators (Yu and Cardona, 1996). The complex $OC-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$, and $NH_3-[Ge_9(C_6H_5)]$ have band gap energy values of 2.131(3.599), 2.503(2.565), 2.562(2.504), 2.989(3.195) eV respectively. A high gap energy value of 3.599 eV, 2.989 eV and 3.195 eV are observed for $CO-[Ge_9(C_6H_5)]$ and $SH_2-[Ge_9(C_6H_5)]$ clusters relative to the neutral nine-atom germanium-phenyl $[Ge_9(C_6H_5)]$ nanostructure in which the electronic conduction is expected to be lower. This suggest that it requires more energy to lift electrons from the HOMO level to the LUMO level. The band gap energy E_g of adsorption of $OC-[Ge_9(C_6H_5)]$ nanocluster has significantly decreased from 2.666 eV to 2.131 eV, with respect to neutral nine-atom $[Ge_9(C_6H_5)]$ nanostructure upon adsorption of OC demonstrating a decrease of about 20.1% based

on equation (14) above . This decrease of the E_g with OC adsorption is attributable to increasing electron density in the LUMO. CO has been most frequently sensed than NH_3 , H_2S and CH_4 (MacDonel *et al*, 2013). CH_4 molecule is adsorbed on the neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster, its energy band gap E_g has decreased from 2.666 to 2.562 or 2.504 eV demonstrating a lower decrease of about 04.0% or 6.5% respectively upon the clustering process. Similarly, NH_3 molecule is adsorbed on the neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster, $NH_3 - [Ge_9(C_6H_5)]$ its energy band gap E_g has decreased from 2.666 to 2.503 or 2.565 eV demonstrating a lower decrease of about 6.5% or 3.9% respectively. These band gap energy changes ΔE_g are significant and the electrical conductivity of the nanoclusters will change notably. A chemical sensor works based on the electrical conductivity changes upon adsorption of an adsorbate. The electrical conductivity and the energy gap E_g , are related according to the relation (Peyghan *et al*, 2014):

$$\sigma \propto \exp\left(\frac{-\Delta E_g}{2K_B T}\right) \quad (15)$$

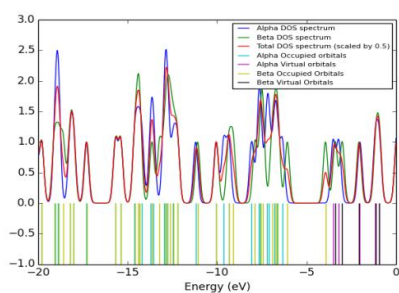
where σ is the electrical conductivity and K_B is Boltzmann's constant. From this equation, small values of ΔE_g i.e. 03.90%, 04.0%, 06.5% and 20.1% will result to higher electrical conductivity at a given temperature for NH_3 , CH_4 and OC molecular gas adsorption on the nanocluster surface. Therefore it seems that the electrical conductivity is affected by the interaction between the neutral nine-atom germanium-phenyl [$Ge_9(C_6H_5)$] nanocluster and the gas molecules, and the higher decrease band gap energy change ΔE_g of $OC - [Ge_9(C_6H_5)]$ complex cluster mainly results from clustering of OC cluster. It can be concluded that neutral nine-atom germanium [$Ge_9(C_6H_5)$] nanocluster is an appropriate chemical gas sensor for NH_3 , CH_4 and OC molecules. . It can therefore be deduced that pure [$Ge_9(C_6H_5)$] may transform the presence of NH_3 , CH_4 and OC into an electrical signal. On the other hand $H_2S - [Ge_9(C_6H_5)]$ have E_g value of 2.989 eV, which increases with H_2S adsorption on [$Ge_9(C_6H_5)$] nanostructure surface due to decreasing electron density, thus electrical conductivity is low.

As observed from Table 1, the predicted enthalpy ΔH and Gibb's free energy ΔG at 298 K were calculated according to equation(11) and (12) for $CO-[Ge_9(C_6H_5)]$, $NH_3-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$ and $H_2S-[Ge_9(C_6H_5)]$ nanoclusters to be about -28.29(-14.69) eV, -17.69(-17.42) eV, -11.43 eV, -19.32(-14.97) eV and -28.29(-14.97) eV, -17.96(-17.42) eV, -11.70 eV, -19.59(-15.24) eV respectively. The energies are all negative and suggest that adsorption of gas molecules on $[Ge_9(C_6H_5)]$ nanocluster surface. Although the results of ΔH are all negative for $OC-[Ge_9(C_6H_5)]$ and $CO-[Ge_9(C_6H_5)]$ nanoclusters, it indicates that adsorption of OC - from C head is more favorable for enthalpy than CO gas molecules but unfavorable for entropy. The carbon atom point towards Ge whereas the oxygen atom point away from the $[Ge_9(C_6H_5)]$ nanostructure surface. The adsorption energy is less lower and exothermic relative to -28.29 eV. This high adsorption energy leads to strong bond between the molecular gas and $[Ge_9(C_6H_5)]$ nanostructure surface. The calculated Gibb's free energy ΔG are also negative and favorable for adsorption of molecular gases CH_4 , CO , H_2S and NH_3 . In the case of $CH_3-[Ge_9(C_6H_5)]$, the hydrogen(H) atom in CH_3 points towards Ge atom in $[Ge_9(C_6H_5)]$ nanocluster and carbon atoms point away from the nanostructure surface, the enthalpy change ΔH and the free Gibb's energy ΔG are both positive, 1.09 and 0.82 eV respectively. This suggest the combination form is endothermic, leading to a weak interaction between hydrogen in CH_3 and $[Ge_9(C_6H_5)]$ nanostructure surface. However, $H_3C-Ge_9(C_6H_5)$ nanostructure is different, the carbon atom in H_3C points towards Ge atom in $[Ge_9(C_6H_5)]$ whereas the hydrogen(H) atom points away from the nanostructure surface. The enthalpy change ΔH and free Gibb's energy ΔG are both negative, thus there is a strong interaction between H_3C and $[Ge_9(C_6H_5)]$ nanostructure surface. Therefore, H_3C is adsorbed on the $[Ge_9(C_6H_5)]$ nanostructure surface. For H_2S on $[Ge_9(C_6H_5)]$ nanostructure surface, it is observed that ΔH and ΔG are both highly negative, suggesting a strong bond between the gas and the nanostructure surface. A similar trend is observed for NH_3 on $[Ge_9(C_6H_5)]$ nanostructure surface.

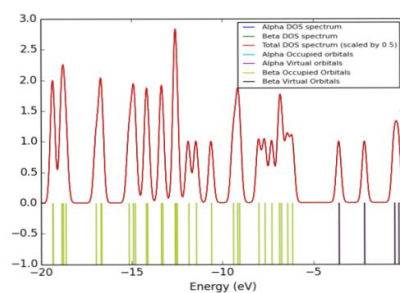
Density of states(DOS) of CH_4 , CO , H_2S and NH_3 complexes

The density of states (DOS) spectrum provides the information about the presence of the charges in a cluster. Figure 2 represent the density of

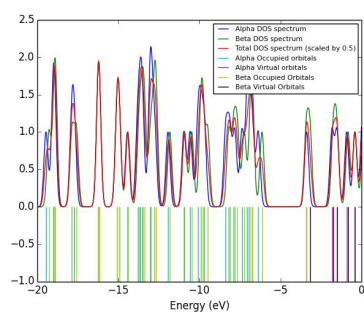
states spectrum of $OC-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ and $NH_3-[Ge_9(C_6H_5)]$ nanoclusters. From the DOS spectrum it is clearly inferred that the adsorption of CH_4 , CO , H_2S and NH_3 on to $[Ge_9(C_6H_5)]$ nanostructure leads to change in DOS spectrum compared with isolated pure $[Ge_9(C_6H_5)]$ nanostructure. In the DOS spectrum alpha as well as beta orbitals are observed. The alpha orbitals arise due to spin up electrons and beta orbitals due to spin down electrons. The presence of alpha and beta orbitals confirms the adsorption of CH_4 , CO , H_2S and NH_3 on $[Ge_9(C_6H_5)]$ nanostructure surface. Moreover more peak maximums are observed both in occupied and virtual orbitals. In the case of $OC-[Ge_9(C_6H_5)]$ nanostructure, it is clearly seen from the DOS spectrum that in the occupied orbitals there is an even distribution charges, a higher electron density and unequal number of elements present in nanocluster giving rise to overlapping while in the virtual orbital there are less charge density with few maximum peaks which indicate that charges can move to the virtual orbital, a narrow gap energy which favors electronic conduction. Many more peaks is observed in the occupied orbitals. Observing the DOS spectrum of $CH_3-[Ge_9(C_6H_5)]$, the charge density is more in the occupied orbitals than in the virtual orbitals, few number of peaks where electronic conduction is less favored. The same trend is observed in the case of $H_2S-[Ge_9(C_6H_5)]$ nanostructure, charge density is higher in the occupied orbital than virtual orbital, few peaks in the virtual orbital, a wide gap energy consequently electronic transition is less favorable. For $NH_3-[Ge_9(C_6H_5)]$ nanostructure, many peaks are observed in both occupied and virtual orbitals, no overlapping and no alpha and beta orbitals, thus electronic conduction is favored.



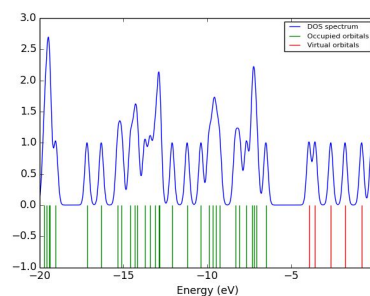
a. OC DOS Spectrum



b. CH_4 DOS Spectrum



c. H_2S DOS Spectrum



d. NH_3 DOS Spectrum

Figure 2: DOS Spectrum and HOMO-LUMO gap of $OC-[Ge_9(C_6H_5)]$, $CH_3-[Ge_9(C_6H_5)]$, $H_2S-[Ge_9(C_6H_5)]$ and $NH_3-[Ge_9(C_6H_5)]$ nanoclusters.

CONCLUSION

Using DFT method, structural stability, adsorption and electronic properties of pure neutral nine-atom germanium-phenyl $[Ge_9(C_6H_5)]$ nanostructure, CH_4 , CO , H_2S and NH_3 molecular gases on $[Ge_9(C_6H_5)]$ were studied. The structural stability is analyzed using the calculated energy and dipole moment. It is found that the dipole moment is maximum for $CO-[Ge_9(C_6H_5)]$ with value 9.329 Debye due to asymmetry of the structure. A number of possible different relative orientations of the gas interactions with the neutral nine-atom germanium-phenyl nanocluster were investigated. The adsorption energy of the stable structure $CO-[Ge_9(C_6H_5)]$, $NH_3-[Ge_9(C_6H_5)]$ and $H_2S-[Ge_9(C_6H_5)]$ were calculated to be -14.75, -17.52 and -19.32 eV respectively. This results suggest that the interaction between the molecular gases on $[Ge_9(C_6H_5)]$ nanostructure surface are strong. Also, the electronic properties of the molecular gases on neutral nine-atom germanium-phenyl $[Ge_9(C_6H_5)]$

nanocluster was found to be affected by the adsorption of CH_4 , CO , H_2S and NH_3 gas . The density of state showed a decrease in the HOMO-LUMO band gap energy change ΔE_g of the nanostructure upon the adsorption of CH_4 , CO , H_2S and NH_3 gas molecules. Considering these changes in the HOMO-LUMO band gap energy that was calculated to occur during CH_4 , CO , H_2S and NH_3 adsorption, it is clear that $[Ge_9(C_6H_5)]$ nanocluster is sensitive to CH_4 , CO , and NH_3 adsorption suggesting that $[Ge_9(C_6H_5)]$ nanocluster has potential to act as sensor.

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