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INVESTIGATION OF N_2O ADSORPTION ON GALLIUM NITRIDE NANOTUBES – A COMPUTATIONAL STUDY

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Abstract

Quantum mechanical density functional theory (DFT) and molecular mechanics (MM) investigations have been used to investigate the interactions between armchair (4, 4) gallium nitride nanotube (GaNNT) and nitrous oxide (N_2O), commonly known as laughing gas or nitrous gas. All the structures have been optimized to a relaxed structure using B3LYP/6-31G (d,p) levels of theory using the Gaussian 09 simulation package. Adsorption energy of N_2O on the nanotube surface is -9.168 kJ/mol with the binding distance 3.520 Å of N_2O from GaNNT site. Mulliken charge, change in bond length, shortest binding distance and density of states (DOS) analysis suggests important insight of N_2O adsorbed on GaNNT.

Keywords: Density functional theory, Mulliken charges, Bandgap, Adsorption, GaNNT.

Introduction

Carbon nanotubes (CNTs) have been synthesized by Ijima (Iijima, 1991) brought interesting physical and chemical properties because of which it is used as a novel material (Besley et al., 2005; Noei et al., 2017). Following CNT, numerous investigations have been attempted to research on non-carbon based nanotubes, which show self-governing electronic, magnetic, optical and chemical properties. The interesting subject of studies are, boron nitride nanotubes (BNNTs), aluminium nitride nanotubes (AlNNTs) and gallium nitride nanotubes (GaNNTs) which are the neighboring elements of C in the Periodic Table (Seif et al., 2007; Baei et al., 2011). One dimensional nanostructures of group III-V with large surface to volume ratio, direct band gap, optical, and surface properties have drawn important interest in wide range of applications (Bae et al., 2002;

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Sahoo et al., 2011; Sahoo et al., 2010; Pimputkar, 2019). GaNNT has been found that the hollow nanotubes are robust, high performances, electrically and optically active and hence are exciting nanostructures for chemical and gas sensing, biochemical sensing, electronics and optoelectronics applications (Johnson et al., 2002; Waltereit et al., 2000; Kuykendall et al., 2007).

Nitrous oxide is a colourless gas with pleasant, sweetish scent and taste, which when inhaled produces insensibility to pain preceded by mild hysteria, sometimes laughter. Scientific reports demonstrate that N_2O has been perceived as an ecological toxin and a generally solid ozone harming substance (Iwamoto and Hamada, 1991). N_2O is likewise a noteworthy supporter of the destruction of the ozone layers in the stratosphere. At present, the N_2O focus in the environment is rising relatively 0.25% consistently (Trout et al., 1996; Boro et al., 2012). The adsorption of N_2O on BNNTs surfaces is investigated (Baei and Moradi, 2012; Esrafili and Saeidi, 2017) but it showed no suitable adsorption significances. 2D gallium nitride (GaN) has been investigated as gas sensors reported recently (Yong et al., 2017). However, It is very desirable to find suitable sensor for the detection of N_2O. Density functional theory has become an important theoretical method, because it gives fundamental parameters for small and even complex molecules at lower cost (Geerlings et al., 2010). In addition, MM simulations give information at the molecular level on the adsorption of the inhibitor molecules on receptor surface (John et al., 2013). As the lack of experimental and theoretical study have been reported on the adsorption of N_2O on GaNNT surfaces, the investigation of the physisorption of N_2O on GaNNT is important. In this study, we report the results of physisorption of N_2O molecule on armchair (4, 4) GaNNT surface.

Computational Details

Density functional theory (DFT) has been used for all geometry optimizations and quantum chemical calculations. The Becke's three parameter hybrid exchange functional using the Lee-Yang-Parr correlation functional theory B3LYP (Becke, 1993; Lecklider, 2011) was selected for the calculations. Calculations were done using the 6-31G (d,p) basis set in the gas phase at room temperature. Molecular properties estimated include the highest occupied molecular orbital (HOMO) energies, lowest unoccupied molecular orbital (LUMO) energies, Mulliken population, partial density of states (DOS), dipole moment and adsorption energy. All optimization calculations were done using the Gaussian 09 program (Frisch et al., 2009).

We have neglected solvent and charge effects in all of our simulations. MM simulation with the universal force field of the interaction between gas molecules and the tube surface was carried out using adsorption locator (Reynolds, 2010).

The adsorption energies (E_{ads}) of the N_2O adsorbed on GaNNT structures have been calculated by the following equations:

$$E_{ads} = E_{(GaNNT+N_2O)} - (E_{GaNNT} + E_{N_2O}) \quad (1)$$

where $E_{(GaNNT+N_2O)}$ is the energy of the surface with the gas molecule, and E_{GaNNT} and E_{N_2O} are the energy of the GaNNT and N_2O molecule respectively.

Results and Discussions

The optimized structures of N_2O, GaNNT and N_2O adsorbed on the GaNNT have been shown in Fig. 1. We have chosen single N_2O and armchair (4, 4) gallium nitride nanotube having tube length of 10.263 Å. The empty hands of the gallium in the tube have been adjusted by hydrogen atoms. To understand the tube and adsorption top view and side view of the complex system have been shown in Fig. 1 (c) and (d). The selected bond lengths and bond angles of the atoms in the individual molecules and complex system have been noted in Table 1. The simulation was carried for 5 cycle and each cycle contains 50000 steps. Fig. 2 shows the energy fluctuation curves for the equilibrium adsorption of N_2O on GaNNT. Then we observed a most stable structure of the GaNNT. From Fig. 1 and Table 1 it is clear that the bond lengths and bond angles between atoms of the individual molecules have been increased in the complex system after interaction.

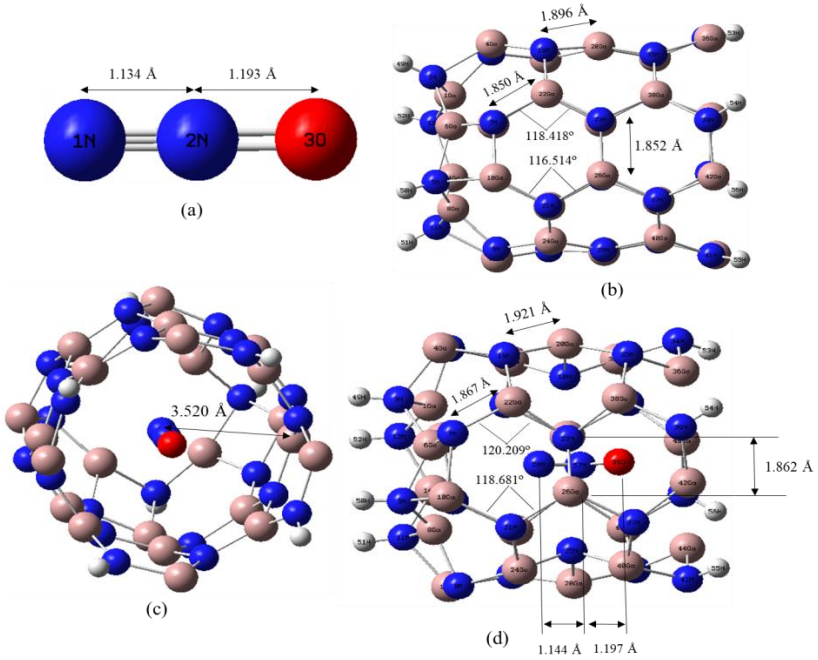

Fig. 1. Optimized structures and selected bond lengths of (a) N_2O, (b) GaNNT, (c) N_2O + GaNNT system (top view) and (d) N_2O + GaNNT system (side view). Here the blue, red, gray and white colours indicate the nitrogen, oxygen, gallium and hydrogen atom respectively.

Table 1. Selected bond lengths (in angstroms) and bond angles (in degrees) of N_2O, GaNNT and N_2O + GaNNT system calculated using B3LYP/6-31G (d,p) level.

Parameters		N_2O	GaNNT	N_2O + GaNNT
Bond Lengths	1N-2N	1.134	-	1.144
	2N-3O	1.193	-	1.197
	19N-20Ga	-	1.896	1.921
	23N-26Ga	-	1.850	1.867
	7N-22Ga	-	1.852	1.862
Bond Angles	7N-22Ga-23N	-	118.418	120.209
	10Ga-21N-26Ga	-	116.514	118.681

From the Mulliken charge distribution various electronic properties have been investigated which help to analyze the total charge transferred and the molecular interactions in a molecular system. The stability and structural properties of the molecular system can be predicted (Castro Neto et al., 2009; Shokuhi Rad et al., 2016; Rad, 2016; Rad et al., 2016). Bond lengths of the distinctive particles inside the atomic frameworks are specifically influenced by charge distribution of the system (Pauling, 1960).

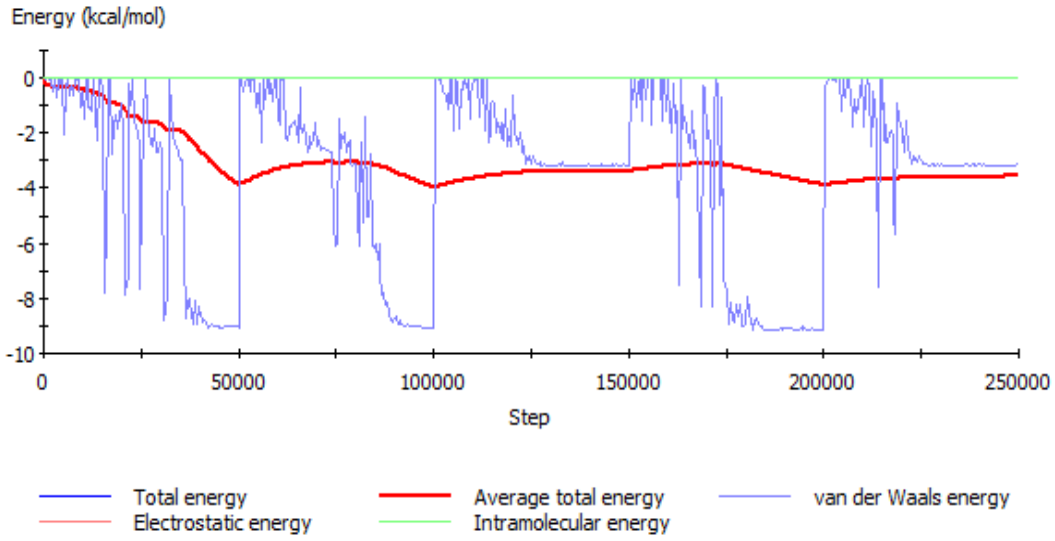

Fig. 2. Energy fluctuation curves for the equilibrium adsorption of N_2O on GaNNT.

Fig. 3. (a), (b) and (c) show the Mulliken charge distributions and the molecular electrostatic potential map of N_2O, GaNNT and N_2O (red colour is negative charge and blue colour is positive charge) respectively. It is clear from Fig. 3(a) that the one N atom carries slightly neutral charges and another N atoms carries high positive charges. From Fig. 3(b) the N atoms carry positive charges and Ga atoms carry negative charges. Fig. 3(c) shows that all the atoms are slightly neutral charge or partially charged. Thus it is clear that the two molecules have many possible reactive centers.

The nature of charge can also be apprehended from the colour scales, where red ones are electron acceptors and green ones are donors. The partial charges occur because shared electrons oscillate between the bonded atoms (Atkins and Paula, 2009). This phenomena occurs due to the difference of electronegativity between the molecules (IUPAC, 2014). From Fig. 3(c), we have observed that due to interaction between N_2O and GaNNT molecules the whole system gets almost neutral charge. This occurred due to the combined effect of charge distribution of atoms. In Fig. 3(c), after adsorption of N_2O on GaNNT, the bond lengths have been observed to increase significantly for being the similar charge effect.

In order to understand the bonding capabilities of N_2O onto GaNNT surface at the atomic level, quantum chemical calculations were employed to obtained some electronic properties and orbital information. The optimized structure, HOMO and LUMO orbitals of N_2O, GaNNT and their complex system are shown in Fig. 4.

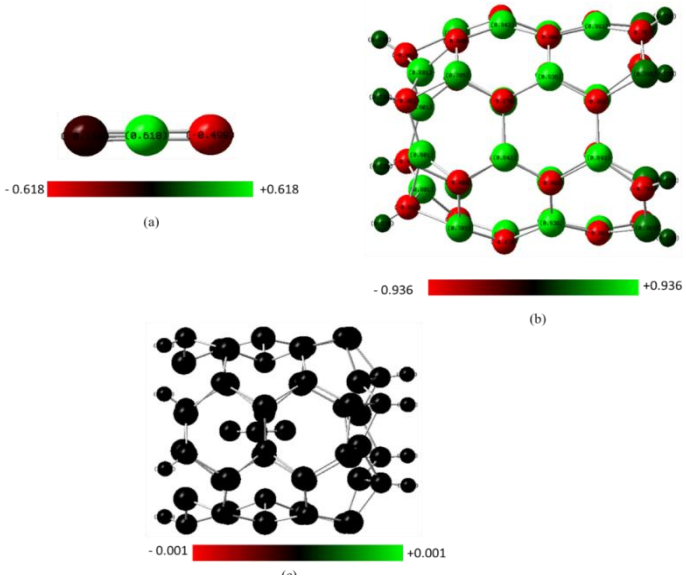

Fig. 3. Charge distribution and electrostatic potential map of (a) N_2O, (b) GaNNT and (c) N_2O + GaNNT system.

Similarly, the calculated quantum chemical properties and electronic properties of N_2O, GaNNT and their complex system for the most stable conformations are presented in Table 2. The energy gap ΔE, which is the difference between HOMO and LUMO energies, is an important parameter which specifies the binding ability between molecules. The HOMO and LUMO energy and ΔE have been analyzed from the density of states (DOS) which have been depicted in Fig. 5. As ΔE decreases, the binding ability of the molecule increases leading to an increase in adsorption onto a system surface. As well as, a molecule is more polarizable if the energy gap is low, and is generally associated with high chemical reactivity and low kinetic stability.

Table 2. Calculated quantum chemical properties for the most stable conformations of N_2O, GaNNT and N_2O + GaNNT system calculated using B3LYP/6-31G (d,p) level.

Molecules	Total Energy (Ha)	E_{HOMO} (eV)	E_{LUMO} (eV)	Bandgap ΔE (eV)	μ_D (Debye)	E_{ads} KJ/mol
N_2O	-184.660	-9.337	-0.096	9.241	0.0172	-
GaNNT	-47470.723	-4.003	-3.051	0.952	20.8281	-
N_2O+GaNNT	-47655.428	-4.122	-3.463	0.659	21.5414	-9.168

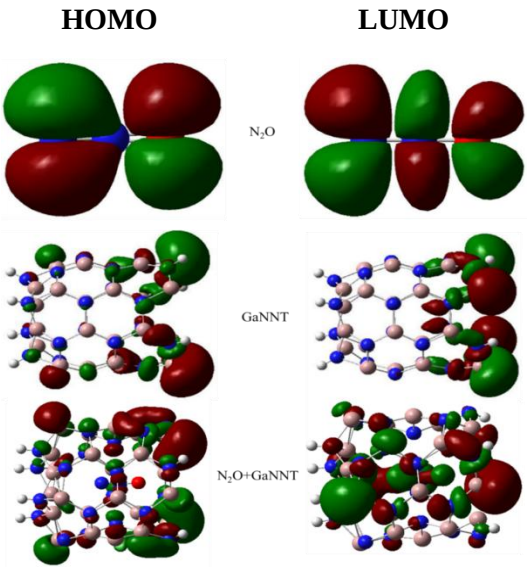

Fig. 4. The HOMO and LUMO molecular orbitals for relaxed structures of N_2O, GaNNT and N_2O + GaNNT complex system.

From Table 2 it has been seen that the bandgap of N_2O and GaNNT are 9.241 eV and 0.952 eV respectively. In the complex configuration the bandgap is 0.659 eV which is smaller than the individual molecules. So the complex system becomes more metallic and chemically reactive than the individual system. This confirms that the N_2O adsorbed on GaNNT.

From Table 2 the calculated adsorption energy using equation (1) which is -9.168 KJ/mol for the binding distance of N_2O from GaNNT is 3.520 Å which has been depicted in Fig. 1 (c).

We have also investigated the different possible binding sites of N_2O on GaNNT which were inside, outside and terminal of the GaNNT. But the most stable and strong bonded site for N_2O adsorption on GaNNT is inside the tube.

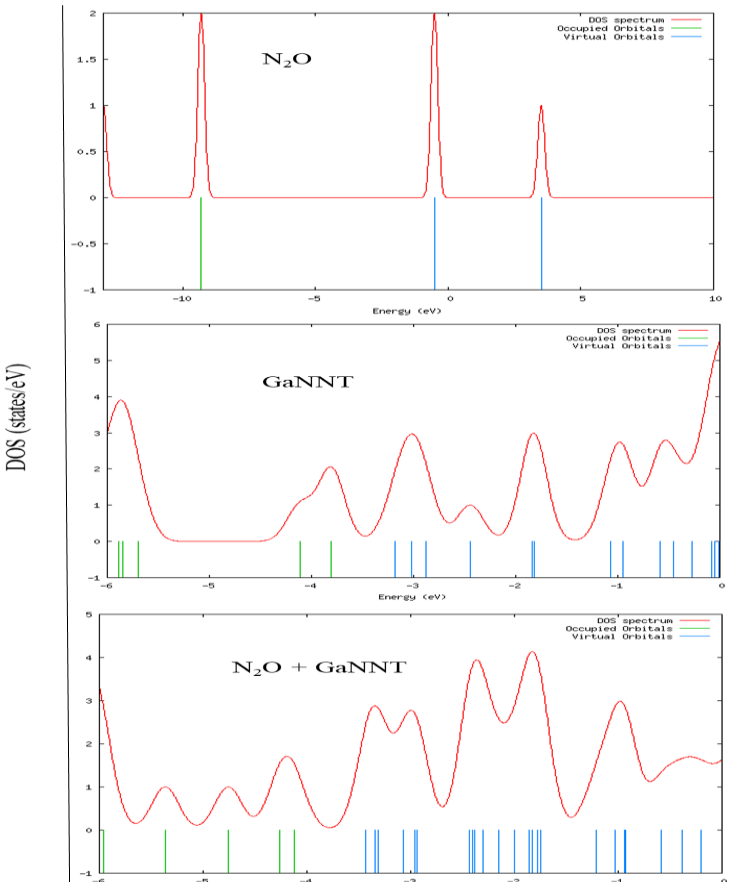

Fig. 5. The band structures and density of states versus Energy (eV) profile of N_2O, GaNNT and N_2O + GaNNT complex system.

Conclusion

In conclusion, using density functional theory (DFT), the adsorption of gas molecule N_2O on the GaNNT have been investigated. We have obtained the adsorption geometries, adsorption energies and electronic properties of gas molecule on the GaNNT. It is found that gas molecule N_2O is physically adsorbed on the GaNNT. After the adsorption of N_2O molecule, the electronic properties of the GaNNT present dramatic changes, especially regarding their bandgap and shortest binding distance. Based on the investigations of electrical properties changes due to surface-gas interaction, the GaNNT can be used as a N_2O gas sensor. This study has provided an important insight that will help in designing GaNNT novel sensors for the N_2O gas molecule.

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