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Computational Modeling of Nanosensors Based on Graphene Nanoribbons Including Electron-Phonon Effects

Kirti Kant K. Paulla
Wright State University

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Computational Modeling of Nanosensors Based on

Graphene Nanoribbons Including Electron-Phonon Effects

A thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Engineering

By

Kirti Kant Paulla

M.S., Wright State University, 2012
B.E., Gandhi Institute of Technology And Management, 2006

2013

WRIGHT STATE UNIVERSITY
I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY Kirti Kant Paulla ENTITLED Computational Modeling of Nanosensors Based on Graphene Nanoribbons Including Electron-Phonon Effects BE ACCEPTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF Doctor of Philosophy in Engineering

Amir Farajian, Ph.D.
Thesis Director

Ramana V. Grandhi, Ph.D.
Director, Engineering Ph.D. Program

Dr. R. William Ayres
Interim Dean, Graduate School

Committee on Final Examination

Amir Farajian, Ph.D.

Raghavan Srinivasan, Ph.D

H. Daniel Young, Ph.D.

Yan Zhuang, Ph.D.

Vikram Kuppa, Ph.D.
Abstract


We investigate detection mechanisms of real time sensors, based on ultra-thin (single and bi-atomic layer thick) and ultra-narrow (~1nm) graphene nanoribbons (GNRs), using first principle based theoretical methods. In the first part of this study we study the electronic and magnetic structures of bilayer graphene nanoribbons (BGNRs) beyond the conventional AA and AB stackings, by using density functional theory within both local density and generalized gradient approximations (LDA and GGA). Our results show that, irrespective of the method chosen, stacking arrangements other than the conventional ones are most stable, and result in significant modification of BGNRs characteristics. The most stable bilayer armchair and zigzag structures with a width of ~1 nm are semiconducting with band gaps of 0.04 and 0.05 eV, respectively. We show shift evolution of magnetic states and emergence of magnetization upon deformation in bilayer zigzag GNRs. Band gap dependence on shift can be used to design accurate nanosensors.

In the second part of this study we study detection of CO and CO$_2$ gas molecules by change in quantum conductance of armchair graphene nanoribbons (AGNR) with a width of ~1 nm. Quantum conductance modulations are calculated by using second-order Møller-Plesset (MP2) method and density functional theory (DFT) for geometry optimization and a hybrid approach for electronic structure calculations. We determine stable and metastable physisorption orientations of gas molecules with varying
concentrations. Our MP2-calculated binding energies relate 8.33% and 16.33% surface coverages of CO and CO$_2$, respectively, to $1.72 \times 10^4$ and 497 parts per million (ppm).

With such concentrations molecules adsorption results in conductance characteristics shifts on the order of few meV. As the concentrations detected in experiments are much less, other mechanisms including substrate and/or carrier gas doping as well as adsorption on defects or electrodes may contribute toward gas sensing using graphene plates. We also discuss temperature effects and propose possible methods for improving gas detection by GNRs.

Next, we studied interactions of single and double NO$_2$ molecules with graphenenanoribbons using first principles, for nanoelectronic-based sensing of extremely low NO$_2$ concentrations. Adsorption geometries, energy barriers, and room temperature rate constants are determined to assess reaction kinetics. Resultant modulations of quantum transport are determined through Green’s function implementation of Landauer's formalism. We show that formation of hydrogen bonded NO$_2$ at edge and physisorbed NO$_2$ at center are processes without barriers, whereas chemisorptions at center or edge are activated processes. Detectable current decrease is predicted for higher concentration hydrogen bonded or for chemisorption cases. Nonbonding and weak $sp^3$ hybridization at the edge of AGNR are shown to be more favorable than center adsorptions, revealing increased edge reactivity compared to graphene. Raman spectra for NO$_2$ chemisorption cases are simulated and discussed with characterization and sensing point of view. We discuss possible measures to enhance sensitivity of GNRs for detecting nitrogen dioxide and similar molecules.
We also address the issue of room-temperature effects on electronic transport modulations in AGNR used as a gas sensor. Coherent (excluding electron-phonon interactions) and non-coherent (including electron-phonon interactions) transports are calculated using nonequilibrium Green's function formalism and Born approximation. While these calculations often are computationally demanding, we show that within nanosensor context with physisorbed molecules simple approximations can be made that significantly reduce the calculation time without affecting the results qualitatively. The non-coherent contributions arising from CO and CO$_2$ vibrations turn out to be a few order of magnitudes less than the coherent transmission, with low-energy molecular vibrons having a larger effect than that of high-energy ones. We discuss the contribution of each phonon mode to electron transmission, and assess the thermal stability of sensor response for AGNR-based CO and CO$_2$ nanosensors at various temperatures.
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beloved wife Divya Naidu. Without the encouragement from my family and friends, I would not have finished this degree.
Dedication

This dissertation is dedicated to my parents
1. Introduction and Literature Review

1.1. Introduction

Since its discovery in 2004\textsuperscript{1,2}, graphene has received much research attention and resulted in a noble prize for its discoverers on its way to becoming one of the most studies and researched materials, with more than 20,000 publication during the last decade. Because of its exceptional electronic, mechanical, optoelectronic and chemical properties, graphene has proved its potential for become an important material in next-generation electronic and energy applications. This thesis document is an attempt to study, discuss and model the sensing ability of graphene and its derivatives, especially Graphene Nano-Ribbon (GNR). Synthesis, properties, and potential applications of graphene, including electronic, sensor, energy, and display technologies, have been widely studied\textsuperscript{3}. Review of graphen.nano-science and technology offers valuable insight into the physics and chemistry of a unique two-dimensional material and its wide range of application.

Until 2004 graphene was deemed an “academic” material where its perfect monolayer structure of carbon atoms connected together with sp\textsuperscript{2} hybridized bonds was treated solely as a theoretical model for describing various idealized physical and chemical properties in different forms of carbon nanostructures like graphite, fullerenes and carbon nanotubes. Older studies\textsuperscript{4-6} on modeling of pristine two-dimensional (2-D) crystals, indicated graphene would be unstable in reality due to thermal fluctuations that
prevent long-range crystallinity at finite temperature. Their argument being that thermal fluctuations are expected to give rise to atomic displacements as large as inter-atomic distance, therefore 2-D materials should be unstable\textsuperscript{4,5}. This theoretical prediction was disproved by A. K. Giem and Novaslov\textsuperscript{1,2} with their experimental observation of single layer graphene by simply using a sticky tape. The effect of thermal fluctuations is still important at finite temperature and will be addressed in further detail in the succeeding sections. Existence of graphene is attributed to the existence of microscopic crumpling in the third dimension\textsuperscript{7}. The experimental observation of the strong electron–phonon (quantized particle of thermal vibration) coupling in graphene is just another demonstration of its richness in properties\textsuperscript{8} and suggests that other interesting phenomena may be observed. For example, the strong electron–phonon interaction in metals is related to the emergence of superconductivity, which indicates that even in graphene this phenomenon could occur.
Figure 1: (a) Graphene lattice with two atom unit cell and A, B sub-lattice atoms. (b) Armchair and Zigzag edge geometry with nanoribbon axis orientation. (c) Armchair graphene nanoribbon with width index N=7, counting carbons chains from one edge to the other.

A single infinite layer of graphene can be modeled by repeating two non-equivalent carbon atoms, often termed as A and B sub-lattices (Fig. 1) along with two translation vectors in a plane. This atomic structure is often used as a basic building block to theoretically construct other carbon based materials: fullerenes, nanotubes, and stacked
Graphite. All these carbon materials have been extensively perused in the past by researchers and still attract attention.

Graphene possesses remarkable transport properties. High carrier mobility of graphene promises ballistic devices having high switching speeds for application in nanoelectronics. Graphene also offers ultrathin body and excellent thermal conductivity for use in field effect transistors (FET)\(^1,3,9,10\). There is possibility of producing defect-free graphene films for electronic devices promises high integration potential with conventional fabrication processes. This is a significant advantage over carbon nanotubes (CNTs), which have also been studied extensively as a promising gas-sensing nanomaterial\(^11\). Two-dimensional graphene is a semi-metal without a band gap. A number of methods have been proposed to induce a band gap in graphene including doping, defects, substrate effects, magnetic and electric fields. One of the primary methods to introduce a band gap is by using a narrow graphenenanoribbon (GNR). All GNRs with widths less than 10 nm have experimentally been shown to possess an intrinsic band gap owing to edge effects\(^10\). It is expected that gas molecule adsorption will have a much smaller effect on modifying the electronic properties of a material with zero band gap (metallic) when compared to a semiconductor with small intrinsic band gap. This property makes GNRs more attractive for nanoelectronic-based sensor applications. Reliable, economical and large-scale production of defect-free, hydrogen-terminated GNRs with widths smaller than 10 nm near perfect edge geometries was attained in experiment\(^12\). Therefore such a GNR has been considered in this research. We study doubly stacked graphenenanoribbons of different edge geometry to demonstrate its application as a nano-electro-mechanical sensor. Many carbon based materials are
commonly used for nano-electro-mechanical sensors, specifically carbon nanotubes and graphene. This is mainly because of the useful properties of carbon based materials which have been briefly discussed earlier. The intrinsic coupling of mechanical properties of carbon (such as strain, stress) to its electrical properties like conduction and band-structure are fundamental to the nano-electro-mechanical sensor application, while the metallic to semiconductor and vise-versa transition of carbon based materials allow them to function as switches. Along with the benefits of using carbon based materials as sensors, the electrical properties of carbon nanotubes and graphene allow it to be used in many electrical components of nano-electro-mechanical systems (NEMS). We also study single layer GNR as a possible sensor of individual gas molecules at finite temperatures. The details are provided in subsequent sections.

1.2. **Introduction to a Nano-sensor**

In general a sensor converts a measurable physical or chemical quantity into a signal that can be detected by an observer or the apparatus. In short, a sensor is a device that reacts to a stimulus. So, there can be many categories of sensors such as, gas sensors for detecting gas molecules, accelerometers and gyros for sensing acceleration and angular velocity, actuators for measuring mechanical displacements etc. Several kinds of input signals can be detected, mostly but not always from the categories listed above and an electrical signal as output. A sensor is supposed to have two major properties.

1. Maximum response to whatever is to be detected - in other words: large sensitivity
2. No or very small response to all other inputs - in other words: very small cross-sensitivity or a high selectivity.

A sensor constitutes of a detector coupled with a device that modulates the signal upon detection. For example, if we have a mechanical input - pressure, acceleration, angular velocity, vibration, etc., the sensor will respond as a membrane bows according to pressure, a cantilever bends upon acceleration, a vibrating gyro mass starts to wobble when encountering angular velocity, and so on. Converting this movement to electrical signals can also be done in a number of ways.

One of the first working nanosensors was built by researchers at the Georgia Institute of Technology in 1999\textsuperscript{13}. It involved attaching a single particle onto the end of a carbon nanotube and measuring the vibrational frequency of the nanotube both with and without the particle. The difference between the two frequencies allowed the researchers to measure the mass of the attached particle. Chemical sensors have also been researched using nanotubes to detect various gaseous molecules. A more detailed analysis will be presented in the later sections.

1.3. Literature review for bilayer graphenenanoribbonnano-sensor

Graphene nanoribbon (GNR), a quasi-one dimensional system, possess unique electronic\textsuperscript{14–16}, magnetic\textsuperscript{17–21}, and optical\textsuperscript{20,21} properties. Chemical\textsuperscript{22,23}, photocatalitic\textsuperscript{24} and lithographic\textsuperscript{25,26} methods, as well as unzipping carbon nanotubes\textsuperscript{27,28}, are used for reliable production of graphenenanoribbons. Recently, sub-10 nm atomically precise
Graphenenanoribbons were produced through bottom-up fabrication of linear polyphenylenes by cyclodehydrogenation process\textsuperscript{12}. Geometrically, two main types of nanoribbons can be cut from a sheet of graphene: one with zigzag edges and another with armchair edges (Fig. 1(b)). In Figure 1(b), if the nanoribbon axis is from left to right, zigzag edge is obtained and top to bottom nanoribbon axis is representative of armchair geometry. Different types of ribbons are specified by their edge geometry and width (Fig. 1(c)). Armchair GNRs (AGNRs) exhibit semiconducting behavior coupled with an extremely low carrier effective mass, making them a potential candidate for novel channel materials in the next generation of field-effect-transistors\textsuperscript{14–16}. The edge states of zigzag GNRs (ZGNRs) have been of great interest due to their peculiar dispersion relation with almost flat edge bands near Fermi energy. When Coulomb interactions are taken into account, the existence of flat edge bands may lead to edge magnetism for various kinds of ribbon edges\textsuperscript{29,30}. It has been shown that ZGNRs are antiferromagnetic and can be used in applications involving quantum dots and resonant-tunneling-diodes\textsuperscript{1}. In addition, recent studies also investigated the unique properties of GNRs for applications such as magnetoresistive and spintronic devices\textsuperscript{10,31}. Edge magnetism in single layer GNRs, and its potential as a half-metallic material under a lateral electric field\textsuperscript{32}, has been studied within first-principles calculations.
Figure 2: Two general schemes of nano-electromechanical sensor made of bilayer graphene nanoribbons: (a) change in relative orientations of the two layers, and (b) bending of the bilayer nanoribbon.

Much research has been carried out on single layer structures, however, bilayer GNRs (BGNRs), with distinct advantages\(^{33,34}\), still pose challenge to researchers with nontrivial edge interactions, magnetism, and stacking stability. In fact, BGNRs can be used as nano-electromechanical sensors, where changes in their electronic transport properties are caused by deformations such as a change in the relative orientation of the two layers (Fig. 2(a)), or bending of the BGNR (Fig. 2(b)). Explicitly, we shown that different stacking orientations caused by deformation, result in altered band structures.
and band gaps. In such an electromechanical nanosensors the relative orientation of the BGNR layers, and therefore transport properties, could change owing to mechanical stretch and/or bending. These possibilities are schematically depicted in Fig. 2. In plane shifts, presumably caused by a change in the relative orientations of the two bulk materials attached to the two layers, and/or bending of the bulk materials will cause a detectable change in the transport properties of the BGNR, as is schematically shown in Fig. 2(a,b), respectively. These possibilities will be investigated in subsequent sections.

It is shown that the band gap of BGNRs can be controlled by doping or applying a gate bias. Although AGNRs are non-magnetic, ZGNRs have antiferromagnetic order between their edges. Therefore, to identify the edge states of bilayer ZGNRs (BZGNRs), it is crucial to understand both the magnetic and electronic properties of the system. Dependence of bilayer AGNRs (BAGNRs) energy gap on the interlayer distance and width was investigated using an ab initio method. Width-dependent bandgap in BAGNRs and BZGNRs, as well as magnetism in BZGNRs, were investigated using a first-principle method. Lima et al., using a model including van der Waals interactions, predicted that BZGNRs are nonmagnetic. A weak hybridization caused by edge atoms and small charge transfer were shown for BZGNRs with different layer widths. In all of these studies, and in the studies on nanodevices based on BGNRs, the relative orientation of the two nanoribbon layers plays a major role. Considering two parallel GNRs with fixed width that constitute a BGNR, two crucial parameters that affect the characteristics of the system are interlayer distance and relative shift $d$ of one layer with respect to the other. The relative orientations are depicted in Fig. 3, and schematics of
electro-mechanical sensors capable of detecting shifts in $x,y$ and $z$ directions, through modulation in electronic structures, are demonstrated in Fig. 2. Two common stacking configurations AA and AB (Bernal) are specified by $d=0$ and $d=\text{C-C bond length}$, respectively. Previous studies\textsuperscript{38,39,46} on BGNRs show that BAGNR is more stable when the shift is along the nanoribbon axis, while the shift perpendicular to the axis is energetically favored in the case of BZGNR. Usually, only the common AA and AB stackings are considered in research on BGNRs. However, recent theoretical works on coronene dimer\textsuperscript{47,48} and experimental work on BGNRs\textsuperscript{49} have indicated that other stacking arrangements are more stable for these systems. To clarify the effects of stacking arrangement and interlayer distance, in this work we study the electronic and magnetic structure of BAGNR and BZGNR with fixed ribbon widths but with various stacking types and interlayer distances. Our results show that stacking arrangements other than the conventional AA and AB are indeed more stable and result in significant modification of BGNRs' characteristics.
Figure 3: One unit cell of bilayer armchair and zigzag graphenenanoribbons (BAGNR and BZGNR). Left: BAGNR configuration in which the “top” layer is shifted by $d$ along the axis of the nanoribbon. Right: BZGNR in which the “top” layer is shifted by $d$, perpendicular.

1.4. Literature review for Graphenenanoribbon based gas nano-sensor

Carbon forms two oxides that are in the gas phase at standard temperature and pressure: carbon monoxide and carbon dioxide. Carbon oxides are important components of the atmosphere and of concern in the petroleum industry and in medicine where their concentrations need to be monitored with utmost accuracy. Carbon monoxide is a carcinogen \(^{50}\) and toxic at high concentrations, whereas carbon dioxide is a greenhouse
gas and the major contributor to global warming. Detection of hazardous gas nitrogen dioxide (NO\textsubscript{2}) is an essential task in many fields such as chemical processing, environmental and emission monitoring, as well as detecting explosives. At concentrations higher than 1 ppm (parts per million) in air, NO\textsubscript{2} can cause irreversible damage to the human tissue and lungs, and is listed as a hazardous substance by The National Institute for Occupational Safety and Health (NIOSH), Environmental Protection Agency (EPA). Therefore, detecting this dangerous gas at concentrations lower than the 1 ppm range is important for human safety and also for aforementioned industry and environmental applications.

Effective detection systems, or sensors, are therefore required to measure the concentrations of CO, CO\textsubscript{2}, NO\textsubscript{2} and similar gas molecules. A good gas sensor should be reusable and stable, and posses high sensitivity and low response time. Nanosensors have attracted intensive research interest due to their applications in industry, environmental monitoring, biomedicine, etc. A general schematic of gas nano-sensor is shown in Fig. 4, which has components like, but not limited to, a substrate, cathode, anode, sensing films and detectors etc. With recent advances in nanotechnology there is huge potential to build highly sensitive, portable sensors with low power consumption and response time, at much lower costs\textsuperscript{51–55}. The exceptionally high surface area of carbon nano-materials is ideal for the adsorption of gas molecules. In particular, the recent discovery of graphene\textsuperscript{1,2} has fuelled the invention of gas sensors that exploit its unique surface area, geometry, and electronic properties. Upon exposure to certain gases, the changes in its electronic properties can be detected experimentally by measuring the sensor conductance or resistance\textsuperscript{56–60}. Graphene-based gas sensors have been widely studied
recently both in experiment\textsuperscript{56–62} and at various levels of theory\textsuperscript{63–67}. It is to be noted here that in experiment graphene-based gas sensors use graphene flakes, GNR films or graphene oxide as the sensing medium. The current study explores the possibility of using narrow GNRs as a possible replacement. Possible advantages of using GNRs are presence of varied band gaps and to provide high edge to surface area ratio. Edges might favor adsorption both enthalpically and entropically. This report provides detailed discussion on feasibility and possible advantages of using such 1-D structures for sensing application.

![Figure 4: Schematic representation of nano-sensor detecting gas molecules](image)

Following the success of the early graphene-based sensors, a considerable number of experimental and theoretical reports sought to understand how the adsorbing molecules alter the conductivity of graphene. Conduction at nanoscale is proportional to
density and mobility of the charge-carriers. There has been recent experimental and theoretical study exploring the role of each factor to conduction modulation. The efforts to isolate the contribution for each source have proved difficult, and different groups proposed different reasoning to account for conduction change. Quantum hall measurements by Schedin et. al showed an increase in charge carrier density upon gas adsorption. It is to be noted that graphene lattice will be induced with holes if the adsorbed gas is an acceptor (strong tendency to attract electron) and electrons are the major carrier when the gas molecule is of the donating type. This induced charges residing on the surface should contribute to scattering processes and in turn decrease carrier mobility. This phenomenon was not as prevalent in experiment observations for measuring carrier mobility, which shows a negligible increase. Hwang et.al showed that mobility of charge carriers in graphene lattice absorbing gas molecules (NO₂, NH₃) increased rapidly and then plateaued with time. Recent research has suggested that the main scattering mechanism that reduces carrier mobility in graphene sensors is the migration of charge impurities from the substrate.

Here we investigate a GNR-based nanosensor for detection of CO, CO₂ and NO₂ gas molecules. We use hybrid ab initio methods for relaxation of the weak adsorption structures (CO and CO₂), to account for the relatively weak van der Waals interaction between the gas molecules and the GNR. The interaction between NO₂ and graphenenanoribbons was studied using DFT. Non-equilibrium Green’s function (NEGF) formalism for the calculation of quantum conductance is subsequently used to reveal conductance changes upon gas molecule adsorption. Considering different possible
sources of conductance modulation, we investigate the effects of each source, and explain the dominant one that is responsible for the nanosensor functionality.

1.5. **Electron-phonon interaction and effect on molecular adsorption**

Recent advances in experimental synthesis and characterization techniques of nano-scale-materials have directed scientific research towards the understanding of thermal transport at the atomistic level/range. Topic of current interest is mainly semiconducting, half metallic and non-conducting systems, where phonon or lattice vibrations are the majority heat carriers. Phonons are termed as quantized particles of periodic lattice vibrations analogous to photons. The motion of electron waves is disrupted by phonons altering the precise regularity in crystal lattice.

There have been theoretical reports of ultra high thermal conductivity of graphene. Dispersion relation obtained from electrons and phonons in graphene was applied in the ballistic regime and dependence of thermal conduction on temperature and Fermi energy was calculated by Saito et. al. Although there have been a few theoretical reports on thermal properties of graphene, graphite, and carbon nanotubes, it was in 2008 that the pioneering work of Balandin and Gosh first measured the thermal conductivity experimentally using Raman spectroscopy. They obtained the thermal conductivity of single layer suspended graphene to be 5300 W/mK at 3000K and its dependence on graphene flake size. Later experimental observations by Gosh et.al. showed that thermal conductivity decreases by stacking layers of graphene one over the other and approaches bulk graphite limit.
The interaction between an electron, in a particular state described by a wave function and a phonon (lattice vibrations), described by a phonon eigen state or frequency forms an important part of device functionality, not to mention the application of these concepts in properties like super-conductivity and thermoelectric effect at the nanoscale. The basic idea is simple: Phonons causes atoms in the periodic lattice to deflect from their mean position. As an example if phonon vibrational mode is longitudinal, it will compress and expand the lattice at various points, causing a change in electrostatic potential acting on an electron, in turn affecting charge transport. Electrons can be scattered by adsorption or emission of phonons. Complexity arises when considering the effect of collective phonon modes on the electron cloud in the crystal lattice. Depending on the type of atom and the crystal lattice, electrons from a wave function around there rather stationary ion cores, if the effect of finite temperature is not considered. But, with the periodic motion of the ion cores, the electron cloud responds to the perturbation in electrostatic potential caused by oscillating ion cores. The electron cloud in this case is not static.

The effect of ion motion on electron cloud can generally be treated in two separate parts: 1. The dynamic change in charge density of electrons to negate the effect of the electrostatic field caused by mobile positively charged ion cores, 2. Scattering of electrons from one state to another using Born-Oppenheimer method. It can be proved that this separation is not spurious by introducing the adiabatic principle.

The Born-Oppenheimer method (named after its original inventors, Max Born and Robert Oppenheimer) takes into account the relative absolute rest masses of electrons and nuclei. A single proton is 1846 times heavier than an electron and the nucleus also contains
neutrons in addition to protons. In the dynamic sense electrons can be regarded as particles which follow nuclear motion adiabatically, \textit{i.e.} they are dragged along-side the nuclei without requiring a finite relaxation time. This of course is an approximation though there can be other non-adiabatic processes by which an electron can respond to nuclear motion. In many systems, the adiabatic separation is an excellent approximation of describing the relation between the electron and the nuclear motion. In most of the cases non-adiabatic effects can be neglected.

Having good understanding of the concepts of electron-phonon interaction, nano-sensor, and overview of properties of graphene based systems; we now can go head and state the objective of this research project.

\subsection*{1.6. Raman Spectroscopy, Surface Enhanced Raman spectroscopy (SERS) and Graphene Enhanced Raman Spectroscopy (GERS)}

Traditionally spectroscopic techniques (light-matter interactions) have been a valid tool for characterization of nanomaterials, whether it is determination of crystal structure, bonding type, chemical reactivity etc. Many forms of spectroscopic techniques are available today to study atoms, molecules and extended structures. One such characterization technique that has been prominently used is Raman spectroscopy. Historically, Raman spectroscopy has played an important role in structural characterization of carbon materials\textsuperscript{78,79}. The Raman spectra for different kinds of carbon materials are different from each other. Although the main Raman bands can be observed in the spectra in every graphitic form, their shape, position and intensity are different. For
example the G band around 1600 cm$^{-1}$ is a single peak for graphene and is formed due to in-plane longitudinal and transverse optical mode$^{80-82}$, but for single walled carbon nanotube (SWNT) the G band is composed of two peaks$^{93}$.

Raman spectroscopy in graphite has been used to probe the degree of disorder, making it possible to evaluate crystal size and also to measure the degree of stacking order of the graphene layers$^{84-86}$. In carbon nanotubes, Raman spectroscopy has been intensively used to characterize their diameters, environmental effects, defects and optical transition energies$^{83}$. The first Raman spectroscopy experiment on graphene came in 2006, when it was shown that Raman spectroscopy can be used as a characterization technique perfect tool for determining the number of graphene layers (from 1 to 5 layers)$^{80-82}$. Beyond that, Raman spectra of graphene provided a better knowledge about charge effects on the phonon energies$^{8,87-89}$, experimentally, estimate and monitor doping in graphene$^{90}$, and has also shown to be a good measure of electron-phonon interaction through shifts and broadening of characteristics peaks$^{88}$.

Over the years, this technique has evolved to accommodate nano-materials by overcoming one of its main limitations, low scattering cross section leading to weak Raman signals$^{91}$. One such modified version of Raman spectroscopy that has overcome this barrier is called Surface Enhanced Raman spectroscopy (SERS)$^{91}$. SERS is a surface-sensitive technique that could enhance Raman signal of molecules adsorbed, traditionally on rough surfaces, by up to 5-12 orders of magnitude. SERS is currently the only spectroscopic technique capable of detecting single molecules and providing their chemical fingerprint. Typically, precious metal (e.g. silver, gold) nanoparticles are used as SERS substrates. However, silver is easily oxidized and lacks biological compatibility.
Therefore, there is a need to develop new high-efficiency substrate materials for SERS applications. Recently graphene sheets have shown to be a high efficiency SERS surface materials, hence the term was coined graphene enhanced Raman spectroscopy (GERS, leading to enhancement up to 1-2 orders of magnitude). Graphenenanoribbons could also be used as substrate for SERS, as they possess similar qualities like graphene and might enhance Raman signal by accentuated charge transfers to/from the molecule compared to 2D graphene. Modeling Raman scattering of small molecules presents its own set of challenges. Previous studies have hinted that inclusion of polarized basis set results in improved results, whereas DFT methods are good enough for obtaining experimentally comparable results. The main conclusion was that basis set is probably more important than level of theory, and that C-H stretching vibrations are likely to be poorly computed due to their strongly an-harmonic nature of vibration. The present work is aimed at gaining proof of concept understanding of electron-phonon interactions in graphene like system, through modeling Raman scattering upon adsorption of NO₂.
2. Method

This section discusses the theory and application of atomistic computer simulations to model, understand and predict the properties of real materials. Specific goals include: energy models from first-principles approaches; density functional theory and the total-energy pseudopotential method; errors and accuracy of quantitative predictions based on two different approximations, inclusion of perturbative methods in weakly bound systems, coherent and non-coherent transport properties.

2.1. Bilayer GNR

Beside experimental existence of graphene, thin graphene strips have also been experimentally isolated. The name given to these confined graphene strips is graphenenano-ribbons (GNRs). Most of the physical properties of these GNRs are highly dependent on width and topology of these edge structures. There are two types of graphene edges that can be cut out from a two dimensional graphene sheet, referred to as Armchair (AGNR) and Zigzag (ZGNR) ribbon, as shown in Fig. 3, and their width is characterized by an index number “N”, that is the number of carbon dimer lines.

All GNR structures considered in this study are edge hydrogenated to eliminate dangling bond effects. GNRs with width indices (number of carbon chains) of N=8 for armchair
and N=5 for zigzag configuration, that have a width of ~1 nm, are considered. These nanoribbons are semiconducting\textsuperscript{30}. The electronic structure calculations were performed using spin-resolved density-functional theory (DFT) as implemented in the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) 2.0.2 code\textsuperscript{95,96}. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) and local density approximation (LDA) with parametrization done through Perdew-Wang-92 (PW92), were used for the exchange-correlation term, with a double-\(\xi\) basis with polarization orbitals (DZP) and a real-space grid cutoff of 200 Ry. Standard convergence checks were performed to ensure the reliability of calculation setup. The applicability and accuracy of GGA vs. LDA for describing exchange and correlation has been a point of discussion and has been debated in various previously conducted studies\textsuperscript{97–102}. It is widely accepted that GGA-DFT calculations usually underestimate the band gap of semiconductors and insulators\textsuperscript{100}. On the other hand Tranet. al. suggest through studies on bilayer graphene like systems, that LDA performs better on predicting the interlayer distance than GGA\textsuperscript{101}. Taking this into consideration, we perform electronic structure and energy calculations using both LDA and GGA methods. We considered a single layer armchair and a single layer zigzag GNR with one unit cell per super cell to perform relaxation. The structures were relaxed until the maximum forces were smaller than 0.005 eV/Å. Both single layer AGNR and ZGNR were found to be semiconducting, with bands gaps of 0.20 eV and 0.33 eV, respectively, and with ZGNR having magnetic edges, in good agreement with previous work using similar level of theory\textsuperscript{30,102} using LDA-DFT. We found a variance of less than 1% in bond lengths of nanoribbons when using LDA and GGA, so the GGA-relaxed nanoribbon geometries
were placed, one above the other, with varying shift and interlayer distances to obtain the bilayer structures depicted in Figure 3.

We considered various stacking configurations. When the top layer is placed exactly over the bottom layer, AA stacking is obtained in which $d=0$. AB stacking refers to graphite structure where $d=1.42$ Å. Recent studies\textsuperscript{48,49,103} have indicated that shifted structures are more stable for coronene dimer. Therefore, in addition to AA and AB, various other shifted structures were considered including $d=1.65$ Å, the minimum energy orientation of coronene dimer\textsuperscript{48}. Energy calculations were performed on BGNRs to obtain the energetically favored configurations at each interlayer distance. For these energy calculations, we did not relax the BGNR structures, as van der Waals forces were not explicitly included in the method that we used. The assumption was that BGNR structures based on relaxed single-layer configurations would provide a reasonable qualitative picture. By considering several different stackings, beyond AA and AB, that are normally neglected in the literature, we focus on a different aspect of BGNR characteristics. Three possible spin-polarized initial guesses were used for each energy calculation to obtain the ground state spin configuration. These were (i) antiferromagnetic (AF) inlayer and ferromagnetic (FF) interlayer (AF-FF), (ii) AF inlayer and interlayer (AF-AF), and (iii) FF inlayer and interlayer (FF-FF). Spin-nonpolarized initial guess was also considered. In addition to the equilibrium interlayer distance 3.335 Å\textsuperscript{104,105}, three other interlayer distances, namely 2.5 Å, 4.5 Å, and 6.0 Å, were considered to evaluate and compare the stability of bilayer magnetic states for varying inlayer and interlayer shifts and to check the viability of GGA and LDA functionals in this particular context.
2.2. Gaussian 03/09 and gas nanosensor

2.2.1. CO and CO$_2$ sensing

We consider narrow armchair GNR (AGNR) with the width indices $N=7,8$, i.e., having 7,8 carbon chains respectively between the two edges (Fig. 1(c)), which translated to a width of approximately 0.9 & 1.0 nm respectively. Hydrogenated AGNR with these widths have been experimentally obtained$^{12}$.

For the structure optimization, two unit cells of AGNR were hydrogenated at the edges and relaxed using Møller-Plesset perturbation theory (MP2) method and 3-21G basis using GAUSSIAN 03/09 program$^{106}$. MP2 improves on the Hartree–Fock (HF) method by adding Møller-Plesset correlation-energy correction$^{107,108}$, truncated at second order$^{108–111}$. The MP2 method is therefore successful in investigating the influence of the dispersion interaction on molecular adsorption phenomena and is best suited for modeling the physisorption of small molecules, despite being computationally expensive, as is evident from the previous works on similar systems$^{64,112}$. These advantages make MP2 more accurate than density functional theory (DFT) for physisorption relaxations.

To determine the preferred positions of the physisorbed gas molecules (CO and CO$_2$), they were placed at different sites on the central hexagon of the AGNR patch, including on top of a carbon atom, above the center of a C-C bond, and above the center of the hexagon, as input orientations. Parallel and perpendicular orientations of the gas molecules with respect to the plane of AGNR were considered to obtain the metastable (local minimum) and most stable (global minimum) structures, if present. These input
structures were fully relaxed using the method and basis stated above. Binding energies were calculated by using the equation

\[ E_b = E_{\text{total}} - (E_{\text{AGNR}} + E_{\text{molecule}}), \tag{1} \]

where \( E_{\text{AGNR}} \) and \( E_{\text{molecule}} \) correspond to the total energies of the optimized pristine two-unit-cell AGNR patch and the isolated molecule under consideration (CO or CO\(_2\)), respectively, and \( E_{\text{total}} \) represents the total energy of the optimized AGNR with the molecule adsorbed.

We also consider a five-unit cell AGNR structure similar to the seven-unit cell structure for calculating the molecular vibrational data like frequencies, eigen vectors and force constants. From this seven-unit cell structure, we extract the necessary data like Hamiltonian and overlap matrices assuming two central principal layers\(^ {113,114} \) of two-unit cell each as junction part and 1.5 cells on either side as redundant parts. ONIOM\(^ {115,116} \) methodology with MP2/HF methods was used to treat the interaction between CO/CO\(_2\) molecule and the GNR lattice. A similar methodology was used to treat the vibration properties of the five-unit cell cluster.

### 2.2.2. NO\(_2\) sensing

The interaction between NO\(_2\) and graphenenanoribbons was studied using DFT. The geometry of the reactants and products was fully optimized using the hybrid functional B3LYP\(^ {117-119} \) and 6-31G basis set. The method and basis have resulted in predictions in reasonable agreement with experiments\(^ {63,93,94,120-127} \). Verified properties
include stable geometries, binding energy, activation barrier heights and vibration spectra. The atomic spin densities were estimated by the Mulliken population method to analyze the charge transfer to/from NO$_2$ molecule in various adsorption configurations. As NO$_2$ contains an unpaired electron, the unrestricted formalism UB3LYP/6-31G was used. All computations were unconstrained and carried out using the quantum chemistry package, Gaussian 09$^{106}$. Quadratic convergence was applied wherever tight/linear convergence failed. All transition states were verified to be of the first order with emergence of one and only one imaginary frequency. Potential energy curves provided an initial estimate of energy barrier and reaction pathways were calculated from fully optimized transition states. Reaction rate and energy barriers are calculated for the 5 unit cell systems that represent the junction regions of the 13 unit cell system. Reaction rate was determined using transition state theory approximation$^{128}$ and following equation

$$R = \frac{k_B T}{c \hbar} e^{-\Delta G/k_B T}, \quad (2)$$

where $R$ is the reaction rate in number of reactions/sec, $k_B$ is the Boltzmann constant, $T$ is the temperature, $\Delta G$ is the change in Gibbs free energy and concentration $C$ is assume to be 1. Change in Gibbs free energy is calculated as the difference between the sums of electronic and thermal free energies of reactant and transition state at room temperature.

### 2.2.3. Raman spectroscopy

It has been well known that accurate computation of IR and Raman intensities is difficult because of their dependence on dipole moment and polarizability derivatives. Although the computation of absolute intensities is important, in practice the major use of quantum-
mechanical spectra simulation is predicting assignment of characteristic bands and origin and shift of these bands in medium-sized molecules. In such a situation, it is invariably the relative, rather than absolute, intensities that are useful. All the calculations are carried out using Gaussian 09 suite. B3LYP method and 631G basis are used to calculate the Raman activates analytically. Though it is required that polarized basis set be used for accurate calculation of Raman spectra, a recent research on poly-aromatic hydrocarbons shows promising results using BLYP/6-31G method/basis\textsuperscript{127}. Raman activity ($S_k$) as computed by Gaussian, is given by\textsuperscript{93}

$$S_k = \left\{ \frac{45(a'_k)^2 + 7(\gamma'_k)^2}{45} \right\}, \quad (3)$$

Where $a'$ and $\gamma'$ are the mean polarizability and anisotropy of the $k$th Raman tensor, respectively\textsuperscript{126}.

In order to compare the computed Raman spectra with experiment, the activities have to be converted to intensities. We are limiting our scope to relative intensities ($I_k$), which can be calculated as\textsuperscript{93,129}

$$I_k = S_k \left( \frac{(\nu_o - \nu_k)^4}{\nu_k \left[ 1 - e^{-\frac{\hbar\nu_k}{kT}} \right]} \right), \quad (4)$$
Where $\nu_0$ is the exciting laser wavenumber, $\nu_k$ is the wavenumber of the $k$th vibrational mode, $c$ is the speed of light, $h$ and $k_B$ are Planck’s and Boltzmann’s constants, $T$ is the temperature.

2.3. Coherent transport

For coherent conductance calculations, we used our program TARABORD$^{113,114,130}$. First we consider CO and CO$_2$ adsorption. To prepare the necessary input data for TARABORD, seven unit cells of AGNR with all dangling bonds saturated with hydrogen were relaxed using method/basis HF/3-21G. This cluster size was chosen based on the previous results on carbon nanotube-based sensor$^{131}$, and allows us to consider “principal layers”$^{113,114}$ including two unit cells of the AGNR. A principle layer includes the minimum number of unit cells such that each principle layer interacts only with its nearest neighboring principle layers. To model NO$_2$ adsorption on AGNR geometry, three model systems of hydrogen terminated armchair-edge graphenenanoribbons of width index seven (AGNR7) were used in this study. The width index indicates seven carbon chains across the 9.27 Å width. The three systems contained 2, 5 and 13 unit cells, corresponding to 9.65, 22.23, and 56.67 Å lengths, and were used for initial structure optimizations, reaction rate calculations, and conductance calculations, respectively. Quantum conductance and density of states (DOS) (not reported in this study) were simulated for the 13 unit cell systems. The central 5 units are treated as molecular junction, 2 units to the left and right of the molecular junction served
as the first unit cells of semi-infinite contacts and the 2 unit cells at the either ends were assumed redundant to eliminate finite boundary effects.

Subsequently, in order to obtain the necessary Hamiltonian and overlap matrices, electronic structure calculations were carried out using the BLYP$^{119,132}$ method. BLYP uses all “gradient-corrected” functional. It is obtained by adding gradient corrections to the local density approximation (LDA) method, specifically the exchange correction of Becke and the correlation function of Lee, Yang and Parr$^{119,132}$. The basis set assumed for solving the quantum mechanical equations within the GAUSSIAN program was 3-21G. This method/basis combination was previously shown to produce results in agreement with other works on carbon nanotube electronic structures$^{131}$. As is shown shortly, for GNR’s, too, our results agree with other studies based on different methods.

We consider an adsorption density of one molecule per two unit cells of the AGNR. The relaxed GNR geometries obtained from MP2 calculations of molecule adsorption were embedded within the relaxed seven-unit cell structure, taking into account the local deformation that is caused due to the interaction of the molecule with the GNR lattice. This served as an initial guess for the next set of geometry optimization – ONIOM$^{115,116}$ which is implemented in GAUSSIAN program. ONIOM stands for Our own N-layered Integrated molecular Orbital and molecular Mechanics. This computational technique models large molecules by defining two or three layers within the structure that are treated at different levels of accuracy (e.g., quantum mechanical and molecular mechanics). We considered two layers, one layer constituted of the molecule
and the hexagon(s) directly under it being treated with high accuracy MP2 method whereas the rest of the system was treated with HF method. Therefore through ONIOM we treat the entire structure with ab-initio-based methods MP2/HF.

These steps are necessary, as performing a full MP2 relaxation on the larger (i.e., seven-unit cell) GNR patch, used for electronic structure and conductance calculations, is prohibitively time-consuming. To further validate our results, band structures were calculated for all the systems considered by using two unit cells of AGNR with adsorbed molecules and periodic boundary conditions (PBC). To compare the accuracy of our results we also relaxed the entire larger (i.e., seven-unit cell) GNR patch with GGA-PBE method implemented in GAUSSIAN. Binding energy, band structures, and conductance were calculated for these GGA-PBE relaxed systems using electronic structure calculated through BLYP methodology.
We calculate the transmission coefficient of the systems under consideration at zero temperature and infinitesimal bias. TARABORD uses the (non-)equilibrium Green's function in order to calculate the conductance of an open system that contains a general finite system like the GNR molecular cluster described in Fig. 5. The starting point of the transport calculation is obtaining the necessary Hamiltonian and overlap matrices. The transport calculation is independent of the particular electronic structure calculation (ESC) procedure, employed for obtaining the Hamiltonian and overlap matrices. The only requirement of the ESC is that the Hamiltonian and overlap matrices should be

**Figure 5:** Flow chart of coherent conductance calculation
available in some spatially localized basis. In this study we utilize linear combination of atomic orbitals (LCAO) based ab-initio descriptions as described earlier, to obtain the necessary inputs. Details of the conductance calculation are provided in Ref. [113, 131] and references therein. Figure 5 shows in a flow chart scheme the entire process to attain these transmission coefficients.

In summary, the transmission coefficient \( t(E) \) which is the conductance of a nanoribbon is given by

\[
t(E) = \frac{2q^2}{\hbar} (f_L - f_R) T(E), \tag{5}
\]

where \( q \) is the carrier (here, electron) charge, \( h \) is the Planck constant, and \( T(E) \) is the transmission probability. \( f_L \) and \( f_R \) are the Fermi-Dirac distribution functions of the left and right contacts. The function \( T(E) \) is the transmission probability for a charge carrier to start from “source-left contact” (after being injected by a macroscopic contact), pass through “junction”, and end up in “drain-right contact” (where it would be collected by another macroscopic contact). For pristine GNR’s considered here, the left contact, junction, and right contact parts of the system are the same; i.e., the same GNR either with or without the adsorbed molecules, as we consider the conductance characteristics of infinite nanoribbons.

The total retarded Green's function \( G' \) of the system projected onto the junction region is given by

\[
G' = (zS - H - \Sigma^r)^{-1}, \tag{6}
\]
$H$ and $S$ are the junction Hamiltonian and overlap matrices, respectively, and $z$ is the complex energy. $\Sigma^r$ is the retarded self-energy of the junction part and is calculated as the sum of the retarded self-energies of the corresponding left and right contacts.

$$\Sigma^r = \Sigma^r_L + \Sigma^r_R,$$  \hspace{1cm} (7)

where $\Sigma^r_L$ and $\Sigma^r_R$ are the retarded self energies of left and right contacts. These quantities can be independently calculated using the Hamiltonian and Overlap matrices of the left and right contact.

$$\Sigma^r_{L/R} = (H_{L/R} - zS_{L/R})^\dagger G^S_{L/R} (H_{L/R} - zS_{L/R}),$$  \hspace{1cm} (8)

$G^S_{L/R}$ are the surface Green's functions of left/right contacts. The advanced Green's function $G^a$ and total advanced self-energy $\Sigma^a$ are the Hermitian conjugates of the retarded Green's function and self-energy matrices.

$$G^a = [G^r]^\dagger,$$  \hspace{1cm} (9)

$$\Sigma^a = [\Sigma^r]^\dagger,$$  \hspace{1cm} (10)

The coupling functions of the left and the right contact are given as

$$\Gamma_{L/R} = i[\Sigma^r_{L/R} + \Sigma^a_{L/R}],$$  \hspace{1cm} (11)

Using Eq. (3-8), the transmission probability $T(E)$ can be calculated as

$$T(E) = Tr[\Gamma_L G^r \Gamma_R G^a],$$  \hspace{1cm} (12)
2.4. Non-coherent transport

\[ t_n(E) = Tr[\sum L G^> - \sum L G^<] \]

\[ \Sigma_{L(R)}^{\Gamma} = -i \Gamma_{L(R)} (1 - f_{L(R)}(E)) \]

\[ G^{<\langle>} = G^r \sum L(G^a) \]

\[ \Sigma_{L(R)}^{\langle>} = i \Gamma_{L(R)} f_{L(R)}(E) \]

\[ \Sigma_{e-ph}^{\langle>}(E) = \sum_k \int d\omega \gamma_k D_k^{\langle>}(\omega) G^{\langle>} (E - \omega) \gamma_k \]

\[ D_k^{\langle>}(\omega) = -2\pi \left[ (N_k + 1) \delta(\omega \pm \omega_k) + N_k \delta(\omega \mp \omega_k) \right] \]

\[ N_k = \left( e^{\frac{\hbar \omega_k}{kT}} - 1 \right)^{-1} \]

\[ \gamma_k = \sqrt{\frac{\hbar}{2\omega_k M}} \sum \frac{\partial S}{\partial R_i} \sum \frac{\partial S}{\partial R_i} S^{-1} H - \sum HS^{-1} \frac{\partial S}{\partial R_i} \chi_{ik} \]

**Figure 6**: Chart of non-coherent conductance calculation procedure

33
To incorporate the effect of electron-phonon (e-ph) interaction in our systems, we consider each region of scattering (where electron interacts with lattice vibration) as an additional contact, assuming that the interaction to be local, i.e. weak electron-phonon interaction. We indicate the self-energy of this additional contact as $\Sigma_{e-ph}'$ and is added to the self-energies of the left and right contacts from the coherent calculations part. The total retarded self-energy can now be calculated as follows:

$$\Sigma_{r,<} = \Sigma_{L, <} + \Sigma_{R, <} + \Sigma_{e-ph}'$$

(13)

$\Sigma_{e-ph}'$ can be calculated using the relation

$$\text{Im}\{\Sigma_{e-ph}'\} = \frac{1}{2} \left( \Sigma_{e-ph}^< - \Sigma_{e-ph}^> \right)$$

(14)

Where $\Sigma_{e-ph}^<$ and $\Sigma_{e-ph}^>$ are lesser and greater self-energies of the electron-phonon calculation\textsuperscript{133}.

We use first order Born approximation\textsuperscript{133-135} to compute the $\Sigma_{e-ph}^{<,>}$ terms which are given as follows:

$$\Sigma_{e-ph}^{<,>}(E) = \sum_k \int d\omega \gamma_k D_k^{<,>}(E - \omega) \gamma_k$$

(15)

Here $D_k^{<,>}$ and $\gamma_k$ are the phonon correlation function and phonon coupling respectively. $G^{<,>}$ are the lesser and greater Green’s function and are calculated using the following formula.

$$G^{<,>} = G^r \Sigma^{<,>} G^a$$

(16)

We include the effect of electron-phonon interaction up to first order in $G^{<,>}$ (Fig. 6). Here $G^a$ and $G^r$ are the advanced and retarded Green’s function calculated using Eqs. (3) and (6). Total lesser and greater self energies ($\Sigma^{<,>}$) initially don’t contain the electron-
phonon iteration and are calculated from the data obtained from the coherent part of the calculation as follows:

\[
\Sigma_{L(R)}^{<} = i\Gamma_{L(R)} f_{L(R)}(E) \tag{17}
\]

\[
\Sigma_{L(R)}^{>} = -i\Gamma_{L(R)} (1 - f_{L(R)}(E)) \tag{18}
\]

The phonon correlation function (\(D^{<()}\)) and phonon coupling (\(\gamma_k\)) are independently calculated using the following relations

\[
D_k^{<()}(\omega) = -2\pi i [(N_k + 1)\delta(\omega \pm \omega_k) + N_k \delta(\omega \mp \omega_k)] \tag{19}
\]

\[
N_k = (e^{\frac{\hbar \omega_k}{kT}} - 1)^{-1} \tag{20}
\]

Where \(N_k\) is the occupation number, \(\omega_k\) is the \(k^{th}\) eigen frequency, \(T\) is the absolute temperature and \(\delta\) is Dirac delta function.

Phonon coupling function is given by,

\[
\gamma_k = \sqrt{\frac{\hbar}{2\omega_k M}} \left[ \sum \frac{\partial H}{\partial R_i} - \sum \frac{\partial S}{\partial R_i} S^{-1} H - \sum H S^{-1} \frac{\partial S}{\partial R_i} \right] \chi_{ik} \tag{21}
\]

Here \(M\) is the mass of the atom, \(\chi_{ik}\) is the \(k^{th}\) eigen vector of the atom index “i”. Partial derivate terms are with respect to atomic coordinated \(R_i\).

Having obtained all the quantities necessary to calculate \(\Sigma^{<()}_{e-ph}\) we now obtain total lesser and greater self energies (\(\Sigma^{<()}\)), which includes electron-phonon interaction up to the first order. Of course this loop can be solved for self-consistency as is termed self-consistent Born approximation (SCBA) (Fig. 6). SCBA is computationally very expensive and is very time-consuming for such large systems treated with first principle
methods. So we currently consider first order Born approximation which should be adequate for initial analysis of the systems in consideration. Phonon dependent electron transport was earlier studied using tight binding approximation\textsuperscript{137} in carbon chain applying similar methodology which showed promising results using Non-Equilibrium Green’s Function (NEGF)\textsuperscript{138} methodology.

Finally after obtaining the lesser and greater Green’s functions $G^{(<)}$ which included electron-phonon interactions using equation (13), we can now calculate the transmission function for non-coherent transport as follows:

$$t_n(E) = Tr[\Sigma^<_L G^> - \Sigma^>_L G^<] \quad (22)$$

Where $\Sigma^{(<)}_L$ are from the calculations in coherent transport section and do not contain electron-phonon interactions. Using this methodology we can isolate the effect of each phonon mode on electron transmission, and we are able to calculate the cumulative effect of lattice vibrations on non-coherent transmission.
3. Results and Discussion

3.1. Bilayer GNR

3.1.1. Bilayer armchair graphenenanoribbons (BAGNR)

Our calculations show that BAGNR structures are non-magnetic at every stacking type and every interlayer distance. Irrespective of the method used, at the equilibrium interlayer distance 3.335 Å, Fig. 7 (a) and (c) reveal that \( d = 1.65 \) Å is a relatively stable stacking type, with energy \( \sim 100 \) meV per unit cell lower than the energy at \( d = 0.71 \) Å (almost half of the C-C bond length). For BAGNR, both \( d = 0.71 \) Å and \( d = 1.65 \) Å stackings are more stable than AA (\( d = 0 \)), and \( d = 1.65 \) Å is more stable than AB (\( d = 1.42 \) Å). Same trend is observed using both LDA and GGA. This is in contrast to the common assumption that AB (Bernal type) stacking of BGNRs is the stable stacking. According to the results depicted in Fig. 7 (a,c), the stacking energy of BAGNR shows a minimum-energy plateau (with a tolerance of \( \sim 7 \) meV) for shifts between \( d = 1.65 \) Å and \( d = 2.25 \) Å. The latter shift value corresponds to the lowest energy and is almost 1.5 times the C-C bond length, i.e. half of the AGNR lattice constant. Owing to symmetry, therefore, the energy curve in Fig. 7 (a,c) for shift values \( d \) between 1.5 and 3 C-C bond lengths will be the mirror image of the curve for shift values between 0 and 1.5 C-C bond lengths. The lattice constant for BAGNR is 4.26 Å as obtained from single layer periodic relaxation. Here we observe that both LDA and GGA approaches lead to the same result and similar energy trends for lateral shifts of BAGNR.
3.1.2. Bilayer zigzag graphenenanoribbons (BZGNR)

As for BZGNR at equilibrium interlayer distance 3.335 Å, Fig. 7 (b,d), the LDA and GGA results do not agree for all shift distances \( d \), primarily because exchange and correlation energy calculated through LDA is dependent on electron density, whereas GGA functional depends on both electron density and its gradient. GGA shows that the most stable state occurs at \( d = 0.71 \) Å and is magnetic with inlayer and interlayer antiferromagnetic spin couplings (AF-AF). The net spin charge of this state turns out to be 0.16 |e|/edge carbon atom. For BZGNR at equilibrium interlayer distance, the AF-AF initial spin guess leads to ground state for all stacking types (i.e., for all shift distances \( d \)). In fact, the AF-AF state together with the "no-spin" state are the only initial guesses that remain the same for all shift distances after electronic structure optimization. The other magnetic initial guesses, namely AF-FF and FF-FF, result in non-magnetized (i.e., no-spin) state upon electronic structure optimization for shift distances between 0 and 0.76 Å, and have the same energy [Fig. 7 (b)]. At \( d = 0.81 \) Å, both AF-FF and FF-FF initial guesses result in FF-FF magnetization whose energy starts to rise above the no-spin energy curve. For \( d > 0.81 \) Å, AF-FF and FF-FF initial guesses remain intact upon electronic structure optimization, with AF-FF state being more stable. For \( d > 0.81 \) Å, all edge spin charge values are almost the same as that of single-layer ZGNR (~0.25 |e|/edge carbon atom).

Contrary to these GGA results for BZGNR, the LDA method predicts non-magnetic ground state for all the shift distances considered between 0.00 Å (AA) and 1.42 Å (AB). This non-magnetic LDA ground state of BZGNR is similar to the one obtained by Sahu et al. 38 who only investigated AB stacking arrangement. Here we
observe that for shift distances more than 1.42 Å, LDA predicts magnetic ground states that are energetically less stable than the non-magnetic ground state which occurs at a shift distance of 0.61 Å [Fig. 7 (d)]. The difference in energy between the shift distances of 0.61 Å (ground state prediction using LDA) and 0.71 (ground state prediction using GGA) is less than 2 meV. Considering the advantage of LDA over GGA in calculating interlayer distance for the interlayer distance in graphite\textsuperscript{38,101}, as was explained earlier, we could conclude that the shift distance $d=0.61$ Å is the most stable and the ground state is non-magnetic. However, the difference between GGA and LDA ground state energy values is smaller than, or comparable to, the precision of our calculations.
**Figure 7:** GGA energy variation at optimum interlayer distance 3.335 Å in (a) BAGNR with varying shift distances, and (b) BZGNR with varying shift distances and initial spin orientations. (c) and (d) show the corresponding LDA results.

To understand the resemblance of Figs. 7 (a) and 7 (c) but the striking difference between Figs. 7 (b) and 7 (c), we note that BAGNR does not possess edge magnetization while BZGNR does. The nonmagnetic nature of BAGNR is confirmed by both LDA and GGA calculations at all shift distances. For BZGNR, GGA and LDA predict magnetic states for all and some shift distances, respectively. It is known that GGA predicts stronger edge magnetization in ZGNR as compared to LDA owing to inclusion of non-local exchange interactions. It could therefore be expected that stronger interactions, i.e. larger energy differences, would exist between the edge-magnetized states where GGA predicts stronger magnetization compared to the LDA prediction. The striking difference between Figs. 7 (b) and 7 (c) for shift distances $d > 0.81$ Å could therefore indicate more pronounced non-local exchange interactions. It is important, however, to note that, within our energy precision limit, the GGA magnetic ground state is indistinguishable from GGA non-magnetic states, and that both of these happen almost at the same shift distance as the one predicted for LDA ground state.

The stacking types with minimum energy for BAGNR ($d= 1.65-2.25$ Å) and BZNGR ($d= 0.61$ Å) are different from those found in previous studies. Comparing only AA and AB stackings in a BZGNR with width index N=16 carbon chains, Ref. found that AB is more stable by 3 meV/atom by using LDA, and performing structure
relaxation. This is in contrast to our results depicted in Fig. 7(b), and can be due to different nanoribbon widths (N=16 vs. N=5) or the fact that structure relaxation was not carried out for bilayer systems in our study. For the case of coronene dimer, Podeszwa has recently shown\textsuperscript{48} that $d = 1.65$ Å stacking results in minimum energy configuration (for interlayer distance 3.5 Å). This was interpreted\textsuperscript{48} in terms of reduced exchange repulsion caused by decreased overlap, and was extrapolated to graphene-graphene interaction. Our results, however, show that for the case of graphene nanoribbons, the open edges and their magnetic states further affect the shift distance $d$ that correspond to the minimum energy. It should be mentioned that in another recent work on coronene dimer\textsuperscript{47}, the shift distance $d = 1.76$ Å was shown to result in minimum energy (for interlayer distance 3.32 Å).
Table 1: Characteristics of most stable states of bilayer zigzag graphene nanoribbon (BZGNR) at various interlayer distances obtained by using GGA and LDA (bold face values denote LDA results). The equilibrium interlayer distance is 3.335 Å. Net spin charge is defined for each edge atom of each ribbon. For interlayer distance 2.5 Å, the GGA net spin charges on the edge atoms of the same ribbon are unequal. Ground state energies are normalized using different energy scales for GGA and LDA methods at equilibrium interlayer distance. (* The energy difference between AF-AF and AF-FF spin configurations at interlayer distance 4.5 Å is less than 4 meV. ** The energy difference among all shift distances at interlayer distance 4.5 Å is less than 4 meV.)

| Interlayer distance (Å) | Relative Energy (eV) | Stable spin configuration | Stable shift distance (Å) | Band Gap (eV) | Net spin charge (|e| /C-atom) |
|------------------------|----------------------|--------------------------|--------------------------|---------------|-----------------------------|
| 4.5                    | 0.74 /1.16           | AF-AF/AF-AF*             | 0.00/0.00**              | 0.60 /0.36    | 0.26/0.22                   |
| 3.335                  | 0.00 /0.00           | AF-AF/no-spin            | 0.71/0.61                | 0.25 /0.05    | 0.16/0.00                   |
| 2.5                    | 1.71 /1.10           | FF-AF/no-spin            | 1.42/0.71                | 0.70 /0.68    | 0.093/0.039/0.00            |
BZGNR characteristics at different interlayer distances obtained by using GGA and LDA are shown in Table 1. GGA predicts a net spin charge on edge carbon atoms that decreases with decreasing interlayer distance. At interlayer distance 2.5 Å, BZGNR with \( d = 1.65 \) Å configuration (not the most stable structure, and therefore not shown in Table 1) leads to nonmagnetic ground state from all initial spin guesses. The other stacking types, however, develop a net spin magnetization with AF interlayer spin order and different values of spin at the two edges of each layer (Table 1). Small interlayer distance enhances the interlayer coupling and leads to spin rearrangement. In fact, when the interlayer distance is 2.5 Å the interlayer edge interactions are stronger than the inlayer ones, as in the latter case the distance between the edges of the same layer (i.e., the width of nanoribbon) is \( \sim 10 \) Å. The BZGNR in this case behaves like a single layer, developing net magnetic moments on the edges with unequal net spin charge on the top and bottom carbon atoms of the same "combined edge" \(^{46}\). When the interlayer distance increases to 4.5 Å and beyond, the interlayer interactions diminish, and the two layers behave almost like two individual non-interacting single layer ZGNRs. As a result, different stacking arrangements corresponding to different shift distance \( d \) do not affect the system's energy, and AF-AF and AF-FF spin configurations are energetically indistinguishable. This GGA result is in agreement with LDA calculations that show a similar trend. But at interlayer distance of 3.335 Å and 2.5 Å non-magnetic ground states are obtained at lateral shift distances of 0.61 and 0.71 Å, respectively. We also see that GGA band gaps are larger than the LDA ones and this trend is seen throughout lateral
and longitudinal shifts of the BGNRs. Considering the previously mentioned advantage of LDA in this context, here we only report the band structures obtained by using LDA.

Figure 8: LDA band structures of BAGNR at optimum interlayer distance 3.335 Å with different stacking types: (a) AA, (b) AB, (c) d= 1.65 Å, and (d) d= 2.25 Å. Fermi energy is shifted to zero.
Figure 9: LDA band structures of BZGNR for most stable spin configurations, at optimum interlayer distance 3.335 Å, with different stacking types: (a) AA, (b) AB, (c) d= 0.61 Å, and (d) d= 1.65 Å. The spin configuration in (d) is AF-AF, with a difference of 5 meV between the up- and down band gaps. Fermi energy is shifted to zero.

Band structure results for BAGNR and BZGNR are depicted in Figs. 8 and 9, respectively. Figure 8 reveals that AA stacked BAGNR and the ground state ($d= 2.25$ Å) are semiconductors with a band gap of 0.07 and 0.04 eV, respectively. The band gap of AB stacked BAGNR is 0.23 eV that is in good agreement with previous results$^{38}$. For
BZGNR, as mentioned above, the LDA ground state (at $d = 0.61 \, \text{Å}$) shows no spin polarization at the edges. The same is true for the AA and AB stacking configurations. The band structures of these stacking configurations are depicted in Fig. 9, together with the band structure for the state with minimum energy at $d = 1.65 \, \text{Å}$. This latter state does have AF-AF edge magnetization, as is seen from Fig 7(d), with net spin charge $0.14 |e|$ per edge C-atom. The most stable arrangement, $d = 0.61 \, \text{Å}$, has a band gap of 0.05 eV. The stacking types AB and $d = 1.65 \, \text{Å}$ have larger band gaps of 0.16 and 0.17 eV, respectively. For BZGNR we see that the band gap increases with increase in the lateral shift distance. BZGNRs have four (almost) flat bands occurring near Fermi energy, a consequence of two families of edge states localized on each edge\textsuperscript{140}. Although the magnetic polarization of $\pi$ states in hydrogen-terminated GNRs is less than that of dangling bonds, the magnetic tails of edge-localized $\pi$-orbital give rise to the inlayer and interlayer interactions\textsuperscript{141,142}. At 1 nm width, the inter-edge interaction plays an important role in defining the most stable electronic structure and magnetic ordering\textsuperscript{143,144}. These four bands are observed for the relatively stable stacking AA and the ground state ($d = 0.61 \, \text{Å}$) in Fig. 9 (a) and (c) as two sets of coinciding flat bands. For the other, less stable, stacking arrangements in Fig. 9 (b) and (d), however, the overlap of one set is not as precise.

As observed from Figs. 8 and 9, different stacking orientations result in altered band structures and band gaps. This property could be employed in designing accurate electromechanical nanosensors in which the relative orientation of the BGNR layers, and therefore transport properties, change owing to mechanical stretch and/or bending. These possibilities are depicted in Fig. 2. In Fig. 2(a), a shift of the upper layer in the y-z plane,
presumably caused by a change in the relative orientations of the two bulk materials attached to the two layers, will cause a detectable change in the transport properties of the BGNR. Bending of the bulk materials as is schematically shown in Fig. 2(b) can cause a similar change in relative orientations and can be sensed. Furthermore Fig. 7(d) shows that for shift distances beyond \(d=1.42 \text{ Å}\), BZGNR develops AF-AF edge magnetization. Similarly, stable spin configurations at different interlayer distances in Table 1 show that edge magnetization could emerge upon increasing interlayer distance.
3.2.  CO and CO$_2$nanosensor

3.2.1.  CO and CO$_2$ adsorption based on MP2 and MP2/HF ONIOM simulations

The results of structural optimizations of CO and CO$_2$physisorption on a two-unit-cell AGNR patch are presented in Fig. 10. For CO, all parallel input initial guesses relaxed to the same output structure shown in Fig. 1(a), where CO remains parallel to the plane of the GNR. The oxygen atom in CO sits at approximately the center of the hexagon while the carbon atom occupies the bridge site (above C-C bond). The binding energy of CO in parallel position (CO-PRL) is -252 meV. The distance from the CO molecule to the AGNR plane is 2.99 Å. Perpendicular initial guesses with "C-down" orientation relaxed to a geometry depicted in Fig. 10(b) with carbon closer to the GNR lattice (than the oxygen) at a distance of 3.20 Å. Binding energy of CO in perpendicular orientation (CO-PRP) is -236 meV whose absolute value is slightly smaller than that for the parallel structure. In addition to the CO-PRP case presented in Fig. 10(b) with C-down orientation, we also considered "O-down" orientation that resulted in a binding energy of -245 meV. As the binding energy differences are smaller than the thermal energy required for activation of molecule's vibration and rotation with respect to the GNR lattice, estimated each as $k_B T=26$ meV with $k_B$ being the Boltzmann constant and $T=300$ K, we can expect to encounter all of these adsorption geometries at room temperature. It should be mentioned that the patch structures depicted in Fig. 10(a-c) are bi-radicals$^{145}$, as there are two edge CH$_2$ groups each of them producing an unpaired electron. This is owing to the selected way of cutting the patch from the AGNR, which becomes a bi-radical with a multiplicity equal to three. We checked that the aromatic versions resulted in the same adsorption geometries
and energies. While earlier published work indicate most stable orientation of CO on graphitic structures to be parallel\textsuperscript{146–148}, the binding energies were obtained by using density functional theory (DFT) that is less accurate than MP2 for treating physisorption. A recent study using plane wave basis set and local density approximation (LDA) method suggested perpendicular orientation of CO to be most stable structure\textsuperscript{149}. 
Figure 10: Top (inset) and side views of most stable (full MP2 relaxation output) orientation for each gas molecule on AGNR7 two unit cell patch: carbon monoxide in parallel orientation (a), carbon monoxide in perpendicular orientation (b), and carbon dioxide in parallel orientation (c). Top (inset) and side views of most stable (ONIOM relaxation output) orientation for each gas molecule taken from AGNR7 seven unit cell patch ((d)-(n)). Second/third row shows molecule adsorbed at the center/edge: carbon monoxide with initial parallel orientation that relaxed to "tilted" structure (d,g), carbon monoxide with initial perpendicular orientation (e,h), and carbon dioxide in parallel orientation (f,i). Fourth row shows two molecules of CO/CO$_2$ adsorbed per principal layer: metastable (l) and stable (m) CO orientations, respectively, and CO$_2$ adsorption (n).

As shown in Fig. 10(c), carbon dioxide relaxed on top of a C-C bond of the AGNR patch with oxygen atoms occupying hollow sites of the adjacent underlying hexagons. Optimized position of the CO$_2$ molecule turned out to be at a distance of 2.97 Å from the plane of the AGNR. Our results are in good agreement with previous results$^{150-152}$ and also with results obtained with incorporation of dispersive interactions for the case of CO$_2$ on polyaromatic hydrocarbons$^{155}$. According to our calculations, binding energy of CO$_2$ is -350 meV, which is higher than those reported in previously published works$^{150-153}$ due to the use of DFT methods or different substrate models in the latter cases. Initial guesses with perpendicular orientations of the CO$_2$ molecule relaxed to the same ground state in parallel position, therefore no metastable orientation was found in the case of CO$_2$, contrary to CO. The binding energies and the optimized orientation geometries suggest physisorption (physical adsorption without formation of chemical bond) for both of the
molecules. Binding energy and optimized geometry was corrected for basis set superposition error (BSSE), using the counterpoise (CP) correction scheme within the GAUSSIAN program, for the 2 unit cell patch using same method and basis set. For binding energy and perpendicular height, maximum corrections were found to be 15% and 20%, respectively. Since our main results are based on ONIOM geometry optimization, which is incompatible with CP, to maintain uniformity, we provide all the results without correction for the BSSE.

Since we see that both the CO and CO$_2$ are physisorbed on the two unit cell AGNR path, we used ONIOM method as described earlier to relax the molecules with surface coverage of one and two molecules per two unit cells on the 7 unit cell patch of AGNR7 at edge and center hexagons to evaluate the difference in adsorption energy and thus determine the most stable absorption sites. Initial input for all the ONIOM geometry optimizations were taken to be the embedded structure obtained by replacing the corresponding hexagon(s) in the HF-relaxed 7 unit cell patches with the molecule and the underlying hexagon(s) from the fully relaxed MP2 patch. Figure 10(d,e,f) show the optimized geometry of one CO/CO$_2$ molecules on the 7 unit cell patch using ONIOM considering center adsorption, and Fig 10(g,h,i) show edge adsorption. Analyzing the optimized geometries and binding energy values from Table 1 we determine that CO is most stable at center of the AGNR (Fig. 10(d)) with binding energy of -186 meV, where initial parallel orientation results in the "tilted" molecule adsorption depicted in Fig. 10(d). For edge adsorption, both parallel and perpendicular initial guesses lead to the same optimized structure for CO (Fig. 10(g,h)) which is a metastable state (second
highest absolute binding energy). CO adsorbed at the central site in perpendicular orientation is the least stable optimized structure (Fig. 10(e)). In this orientation carbon from CO is closer to the AGNR lattice unlike the stable and metastable cases where CO is oriented at a tilt angle (32.2°) to the AGNR plane with oxygen atom nearer the AGNR. The initial O-down perpendicular orientations relaxed to the same "tilted" output, as that of the initial parallel orientation. CO₂ is more stable at the edge (Fig. 10(i)) than at the center but the energy difference in only 1 meV (less than 0.4% difference), so we can assume that CO₂ is equally stable at center (Fig. 10(f)) and at the edge. AGNR8 was also considered and the structures were optimized using the same scheme, with CO/CO₂ adsorbed at the center of the patch with parallel and perpendicular alignment of adsorbates. Again, CO in tilted position is more stable than CO in perpendicular orientation. From Table 2, we notice an overall decrease in absolute binding energy of the molecules when comparing adsorption over AGNR7 and AGNR8. This trend of decrease in absolute adsorption energy with decrease in surface coverage of the adsorbate on GNRs can be compared with lack of significant change in interaction energy of CO₂ and H₂O molecules with poly-aromatic hydrocarbons reported previously.\textsuperscript{153}

The trend is carried over to the double surface coverage cases (two molecules per two unit cells of AGNR) as well. The ONIOM relaxed geometries for seven unit cell cases are shown in Fig. 10 (l,m,n). We see in Fig. 10 (l) that one CO is absorbed in perpendicular orientation atop the central hexagon, whereas the other CO adsorbs atop the edge carbon atom with an average binding energy of -100 meV/molecule. As can be seen from Fig. 10 (l), this adsorption configuration is asymmetric as the arrangement of
the two CO molecules on the left and right unit cells are different (the principal layer contains two unit cells, and the inset in Fig. 10(l) shows the right one). This asymmetric configuration is higher in energy compared to the most stable geometry (for two CO molecule adsorption) as shown in Fig. 10 (m) that is symmetric. Here both CO molecules orient themselves above the center of the edge hexagons at a tilt angle to the plane of the GNR with an average binding energy of -111 meV/molecule. It is to be noted here that in the two cases discussed above, the oxygen atom in the CO molecule is always closer to the GNR lattice unlike the perpendicular adsorption of CO on 2- and 7-unit cell patch (Fig. 10(b,e)). The average binding energy of 2 CO₂ adsorbed per principal layer (Fig. 1(n)) is -153 meV/molecule.
Table 2: Binding energy and molecular charge of single CO/CO$_2$ adsorbed on AGNR-N (where N=7,8 is the width index) at the edge and center locations. Molecular charge values are obtained from MP2/HF ONIOM molecular orientations translated to the HF relaxed periodically repeated two-cell GNR structure. Binding energy is obtained directly from ONIOM calculation relative to the relaxed GNR structures. PRL and PRP refer to parallel and perpendicular initial molecule orientations, respectively.

<table>
<thead>
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<th>Input Orientation</th>
<th>AGNR-7</th>
<th>AGNR-8</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Center</td>
<td>Edge</td>
</tr>
<tr>
<td>CO- PRL</td>
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</tr>
<tr>
<td>CO- PRP</td>
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<td>-157</td>
</tr>
<tr>
<td>CO$_2$ PRL</td>
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</tr>
<tr>
<td>CO$_2$ PRP</td>
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<td>-54</td>
</tr>
<tr>
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<td>)</td>
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<td>-0.003</td>
<td>0.001</td>
</tr>
</tbody>
</table>
3.2.2. Quantum conductance with one and two adsorbed molecules per principal layer

To exclude the effect of using two different methods (MP2 vs. HF) on the same pristine AGNR system, we only present here the conductance graphs of the system where the GNR lattice is fully relaxed with HF method and the adsorbed molecules are translated onto the relaxed GNR lattice according to the optimized geometries obtained from ONIOM calculation. This process of translation eliminates the artifact that is present due to small changes in C-C bond lengths caused by using two different methods for optimization of lattice and enables us to position the molecule accurately according to the MP2/HF ONIOM calculation.

Figure 11 (a,b) shows the quantum conductance curves for the most stable CO and CO$_2$ adsorption cases considered for single molecule coverage per principal layer, CO tilted and CO$_2$ in parallel orientations, with the molecules adsorbed at the center of the AGNR7 lattice. The conductance of pristine AGNR7 (PRS) is also shown for comparison. Comparing the band gaps, we do not observe any significant deviation upon molecular adsorption. According to our calculations, the band gaps of pristine AGNR of width index $N=7$ and 8 are 1.756 and 0.220 eV, respectively, which are in good agreement with previously published results$^{30,154}$. Figures 11 (b) shows shifts of the edges of conductance bands after CO and CO$_2$ adsorption as compared to the conductance characteristics of pristine nanoribbon. For one CO and one CO$_2$ adsorptions, the shifts are ~2 and ~20 meV, respectively. Figure 11 (d) shows that the shift values increase to ~40 and ~45 meV, respectively when there are two molecules adsorbed per principal layer. These shifts can in principal be detected as they change the on/off gate bias threshold in a
GNR-based field effect transistor (FET) after molecule adsorption, similar to the case of carbon-nanotube-based FET [36]. As the shift is increased for higher surface coverage, detection in these cases will be more feasible. Including the corresponding shifts for carrier energies below Fermi energy (Figs. 11 (a) and (c)), we noticed that upon CO adsorption the pseudo gap increases by 4 meV for double adsorption case and no change was observed for the single adsorption case, as compared to the pristine case. For CO₂ in parallel orientation, with one and two molecules adsorbed per principal layer of the AGNR7 lattice (Fig. 11), we find band gap increase of 3 meV for the double molecule adsorption, whereas single molecule adsorption resulted in the same band gap as that of the pristine case. Pseudo gap reduces by 7 meV in case of double CO₂ adsorption, compared to 2 meV for the single adsorption case. Similar to the CO case, higher surface coverages of CO₂ will result in more feasible detection as the shift values are larger.
Figure 11: Comparison of various quantum conduction curves. One CO$_2$ molecule adsorbed per principal layer on AGNR7 (green), one CO adsorbed per principal layer in tilted orientation (red) and pristine AGNR7 (PRS) (blue), at negative (a) and positive (b) carrier energies. Two CO (blue) and two CO$_2$ (red) molecules adsorbed per principal layer of AGNR7 for negative (c) and positive (d) carrier energies. Molecule orientations are the most stable ones based on ONIOM relaxation. Middle of the gap of the pristine AGNR is set to zero.

The difference between the conductance curves for one CO and one CO$_2$ adsorption cases in Figs. 11 (a) and (b) arise from the fact that the distance between the
molecule and the GNR lattice is only about three times larger than the inter-atomic distances in CO and CO$_2$ molecules. As a result, the Coulomb monopole fields of negatively charged oxygen atoms and those of the positively charged carbon atoms from the adsorbed molecules do not completely cancel each other at the underlying GNR atoms. Therefore, there are localized effective fields, with opposite directions, acting on the GNR lattice. The net effect would be a shift in conductance curves that will depend on the number of monopoles per principal layer and the distance between them. This is just a qualitative explanation, and indicates why for the cases of two-molecule adsorptions, depicted in Figs. 11 (c) and (d) the conductance curves are shifted more than the cases of one-molecule adsorptions (Figs. 10 (a) and (b)).

By performing Mulliken population analysis of the structures with adsorbed molecules and comparing to the pristine two-unit-cell periodically repeated AGNR, we observe that there is very small amount of charge transfer to/from the molecule from/to the GNR lattice. From Table 2, we see that for CO in parallel orientation, CO in perpendicular orientation, and CO$_2$ (in parallel orientation), the net charge transfers to the molecules are 0.005 |$e$|, -0.004 |$e$|, and -0.003 |$e$|, respectively, for adsorption at the center of AGNRM=7, and 0.001 |$e$|, 0.001 |$e$|, and 0.002 |$e$|, respectively, for adsorption at the edge. It is worth mentioning that in case of CO$_2$ a recent theoretical study conducted on molecular adsorption on linear polyaromatic hydrocarbon (LPAH) suggests the charge on CO$_2$ to be mainly 0.001 or -0.001 |$e$| depending on the location of the adsorbed molecule$^{153}$. The same study shows the CO$_2$ charge for the case of adsorption on small aromatic patches to be between -0.002 and 0.006 |$e$|. As Mulliken population analysis does not normally determine electron distribution at this level of accuracy (on the order
of 0.001 $|e|$), our charge transfer analysis gives a qualitative representation of electron/hole doping by molecule physisorption, in addition to providing comparison with other published results.

Experimental work on CO and CO$_2$ adsorption on graphene suggest that both molecules act as electron donors$^{57,60}$. From the charge values in Table 2 we noticed that in the most stable center and edge adsorptions, CO acts as a donor, while CO$_2$ acts as a donor at the edge and as an acceptor at the center. There might be some other interactions that might come into play. Some of them are metal-contact/graphene interactions, adsorption of molecules on contact, which are usually metals like gold, silver or platinum, and also presence of defects in the GNR lattice. Effect of molecular adsorption on metal electrodes, used to apply bias to and carry current to/from the graphene-based sensor, and contact-graphene interactions are not taken into consideration in present work and would be an extensive research in itself. Contrary to the physisorption on GNR, molecules may chemisorb on metal to form chemical bonds with the metal contacts present in the experimental setup, which results in more significant charge transfer. The disagreement between the CO$_2$ center adsorption results and experimental data may therefore arise from any one or more of the effects stated above.

We next study the effect of local strain on conductance, separating it from the effect of the charge transfer. In other words we consider the pristine AGNR system without the adsorbed molecule, treated with similar ONIOM scheme i.e. MP2 treatment of (underlying) hexagon(s). By comparing these structures to the corresponding ONIOM-relaxed systems with molecule adsorbed, we could isolate the deformation caused only by molecular adsorption. We observe that physisorption of adsorbate molecules do not
alter the bond lengths of the underlying hexagons, which further justified the translation of molecules onto the separately relaxed GNR lattice for conductance calculations. To verify and characterize the quantum conductance graphs, band structure calculations (Fig. 12) were performed using periodic units including two unit cells of the AGNR. Band structure results, obtained through GAUSSIAN PBC calculations are shown in Fig. 12 and agree very well with the conductance curves obtained from TARABORD (depicted in Fig. 11), upon assigning two quantum units of conduction ($q^2/h$) to each band.
**Figure 12:** Band structures of CO$_2$ adsorbed on AGNR N=7 (a) and on AGNR N=8 (b), as well as CO adsorbed on AGNR N=7 (c) and AGNR N=8 (d). Fermi energy is set at zero.

### 3.2.3. Quantum conductance with more than two adsorbed molecules per principal layer

Since upon doubling the number of gas molecules we see a difference in the conduction properties of AGNR, we presume that yet higher concentration of gases can cause significant alteration in electronic properties of these narrow GNR’s. To check this presumption, we consider higher surface coverages, namely 3, 4 and 5 CO molecules as well as 3 CO$_2$ molecules per principal layer, and investigate the effect of collective gas molecule adsorption on electronic structure and conduction. It should be noted that high surface coverage of CO on graphite, equivalent to 4 molecules physisorbed per principal layer on AGNR7 studied here, was achieved and identified by X-ray diffraction$^{155}$ and low-energy electron diffraction (LEED)$^{156}$ in low temperature (at 10 and < 25 K, respectively) experiments.

For higher concentrations “association energy” ($E_{A-E}$) is defined as

$$E_{A-E} = E_{n-mol} - n \ast E_{mol} \quad , (5)$$

where $E_{n-mol}$ is the energy of $n$ molecules arranged according to the most stable physisorbed orientation on the GNR but without including the GNR in energy calculation.
and $E_{mol}$ is the energy of an isolated molecule. Association energy is the measure of interaction between the molecules when the concentration increases and there is collective adsorption. Association energy for the one molecule per principle layer cases is -0.5 and -0.2 meV for most stable cases of CO and CO$_2$ respectively. But for the double coverage case the association energies are -68 and 24 meV (based on ONIOM relaxation) for CO and CO$_2$ cases respectively. We do not report association energy values for higher concentration (3 and 5 molecules adsorption) cases as the structures are not relaxed, but for the arrangement considered, perpendicular orientation of CO leads to less repulsion and thus lower association energy values. Negative sign of the association energy indicates that the collective adsorption of gas molecules is favored and the molecules interact constructively between each other to lower the internal energy. The adsorbed gas molecules can be stabilized by the association energy, provided that the association energy is negative. This phenomenon was earlier reported for the case of C$_{60}$, benzene and pentacene molecules on metal surfaces$^{157-159}$. The associative stabilization occurs due to the interaction of (induced) dipoles in adsorbed molecules. Stabilization of high density coverage is more effective at low temperatures, as shown for, e.g., the CO case in Refs.$^{155,156}$.

To investigate the changes in conduction upon high-density molecular adsorption, we positioned 2, 3 and 5 CO (in parallel and C-down perpendicular orientation) and 3 CO$_2$ molecules, on the seven unit cell pristine AGNR7 according to the MP2 relaxed patch structures. We indicate molecular adsorption cases with $n$, the number of molecules per principal layer (2, 3 or 5), and PRL or PRP that represent parallel and perpendicular
cases as in Fig. 1(a,b). For example, 2CO-PRL would represent two CO molecules in parallel orientation per principal layer.

Conductance characteristics for 3 and 5 CO as well as 3 CO₂ per principal layer are shown in Fig. 13. Conductance characteristics for 2 CO molecules per principal layer are also given for comparison. The overall structure of the nanosensor is not relaxed for all the cases with adsorbed molecules in Fig. 13, but each adsorbed molecule is placed at the most stable physisorbed orientation based on full MP2 relaxation of one molecule on the GNR patch that was explained earlier. Figure 13(a) shows quantum conductance of 2CO parallel and C-down perpendicular cases near Fermi energy. Their band gap and pseudo gaps match those of the ONIOM relaxed cases (Fig. 11(c,d)), in which CO molecules were tilted (Fig. 10(l,m)). Quantum conductance of 3 and 5 CO adsorbed cases are shown in Fig. 13 (b, c). The most obvious changes are the emergence of narrow conducting energy intervals at 0.667 and 0.189 eV measured from the center of the gap for the pristine GNR, for 3 and 5 CO-PRP cases respectively. These narrow conducting energy ranges correspond to creation of impurity states localized mainly on the gas molecules, as will be discussed shortly. As a result, for C-down 3CO-PRP case we see a band gap change of 214 meV as compared to the 3CO-PRL case which shows no change in its band gap and pseudo gap (except for an overall shift of the conductance curve). Rotating the molecules and considering O-down 3CO-PRP case, we found that the conductance characteristics (not shown in Fig. 13) were the same as those for C-down 3CO-PRP case. For 5CO-PRP case we see further reduction in band gap by 773 meV. This is attributed to the movement of the narrow conducting region from 0.667 eV in 3CO-PRP case to 0.189 eV in 5CO-PRP case. The pseudo gap of the 5CO-PRP case is
also altered by 0.089 eV owing to a conduction jump of 2 units at 0.916 eV (Fig. 13(c)). Three CO₂ adsorbed case does not show a significant change in band gap or pseudo gap values compared to the pristine case (Fig 13(d)). Overall we see for 3/5CO-PRP adsorption cases, reduction in band gap is due to the emergence and shift of the narrow 1-unit conductance region. This is not the case for parallel oriented 3/5CO or 3CO₂ molecule adsorptions.

**Figure 13:** Comparison of AGNR’s quantum conductance curves with different numbers of CO and CO₂ molecules positioned on the HF-relaxed seven unit-cell AGNR patch according to the fully relaxed two unit cell MP2 optimization: Two CO molecules absorbed per principal layer in parallel (blue) and perpendicular (red) orientation (a), three CO molecules absorbed per principal layer in parallel (blue) and perpendicular (red)
orientation (b), five CO molecules absorbed per principal layer in parallel (blue) and perpendicular (red) orientation (c), and three CO$_2$ molecules absorbed per principal layer in parallel (blue) orientation as well as pristine (PRS) AGNR7 (red) (d). Middle of the gap of the pristine AGNR is set to zero. PRP and PRL refer to perpendicular and parallel adsorption orientations, respectively.

**Table 3:** Highest energy of highest occupied band (HOB) and lowest energy of the lowest unoccupied band (LUB) for adsorption cases with different densities based on MP2 relaxed orientation of the molecules on 2 unit cell patch. All values are relative to the center of the gap for the pristine (PRS) case, and are based on the band structures for periodic systems.

<table>
<thead>
<tr>
<th></th>
<th>PRS</th>
<th>Parallel</th>
<th>Perpendicular</th>
<th>3-CO$_2$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2-CO</td>
<td>3-CO</td>
<td>5-CO</td>
</tr>
<tr>
<td>HOB</td>
<td></td>
<td>-0.877</td>
<td>-0.924</td>
<td>-0.940</td>
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<tr>
<td>(eV)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>LUB</td>
<td></td>
<td>0.877</td>
<td>0.819</td>
<td>0.795</td>
</tr>
<tr>
<td>(eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Band-gap</td>
<td></td>
<td>1.754</td>
<td>1.743</td>
<td>1.735</td>
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<tr>
<td>(eV)</td>
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</table>
In Table 3 we summarize the energy values corresponding to the edges of the gap for the systems with various adsorption densities. We notice a systematic decrease in highest energy of highest occupied band (HOB) and lowest energy of lowest unoccupied band (LUB) values for CO$_2$ and CO in parallel adsorptions, compared to the pristine (PRS) case. Therefore, for these systems the band gaps do not change significantly. For CO in C-down perpendicular adsorption, however, there is a net reduction of the gap as compared to the pristine case. The O-down perpendicular adsorption results (not shown in Table 3) were the same as the results for C-down perpendicular cases. The main cause of the gap reduction is the emergence of LUB flat bands that are localized on the adsorbed molecules, as we will discuss in the next sub-section.

3.2.4. Emergence of impurity states

To investigate the characteristics of emerging flat bands and to clarify the role of perpendicular dipole moment of CO-PRP cases on the electronic structure of the combined system, we examined the band structures of the periodic systems. HOB and LUB results are depicted in Fig 14. We can clearly infer that for 3- and 5-CO-PRP cases the LUB has mainly localized on the CO molecules. This charge localization induces nearly flat impurity bands near the edge of the conduction band (Fig. 3(b,c)). Experiments suggest the dipole moment of CO to be 0.122 D$^{160}$, as compared to our calculated value of 0.154 and 0.571 D using MP2 optimization/BLYP electronic structure calculation and MP2 optimization/electronic structure calculation, respectively, with 3-
21g basis set. Improving the computational value of dipole moment will require 10s9p4d2f1g basis set (160 basis functions) and CCSD(T) methods\textsuperscript{161}, which are prohibitively time-consuming. We notice that LUB localization occurs when 3 or more molecules adsorb in perpendicular orientation, which means a net dipole movement of 0.462 D (based on our computational estimate) causes the emergence of impurity state. For 2CO-PRP and 2CO-PRL cases we find that the flat impurity bands occur at 2.2 and 2.5 eV above the center of the gap, respectively. Upon increasing surface coverage of perpendicular CO adsorption, these flat bands shift closer to the center of the gap. As for CO-PRL cases the z-component of dipole movement is very small, which keeps these localized states away from the center of the gap. In all these cases the HOB and nearby states with lower energy remain relatively intact by CO or CO\textsubscript{2} adsorption. If we consider the same periodic molecular configuration as in, e.g., 5CO-PRP case but without the GNR lattice, we obtain a band gap of ~4 eV. Including the lattice, results in a band gap of ~1 eV (Table 3). More importantly, the particular arrangement of CO molecules with perpendicular adsorption orientation would not be stable without the GNR lattice and application of perpendicular electric field (as discussed shortly).
**Figure 14:** Highest occupied band (HOB) and lowest unoccupied band (LUB) of 2, 3 and 5 CO molecules absorbed in parallel and perpendicular orientations on two unit cells of AGNR7 periodic structure. Carbon atoms are in gray and the oxygen atoms in are red (pink and mustard indicate positive and negative isosurfaces of the wave function). Wave functions are shown at 20% of the maximum value. PRL and PRP refer to parallel and perpendicular adsorption orientations, respectively.

<table>
<thead>
<tr>
<th>Number of CO molecules Adsorbed</th>
<th>AGNR-7</th>
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<tbody>
<tr>
<td></td>
<td>CO-PRL</td>
<td>CO-PRP</td>
<td>CO-PRL</td>
</tr>
<tr>
<td></td>
<td>HOB</td>
<td>LUB</td>
<td>HOB</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="HOB LUB Image" /></td>
<td><img src="image" alt="HOB LUB Image" /></td>
<td><img src="image" alt="HOB LUB Image" /></td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="HOB LUB Image" /></td>
<td><img src="image" alt="HOB LUB Image" /></td>
<td><img src="image" alt="HOB LUB Image" /></td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="HOB LUB Image" /></td>
<td><img src="image" alt="HOB LUB Image" /></td>
<td><img src="image" alt="HOB LUB Image" /></td>
</tr>
</tbody>
</table>

Since carbon monoxide is a polar molecule with net electric dipole moment, electric field can be applied normal to the GNR lattice to orient CO perpendicularly. It would then be possible to detect the concentration of CO by the band gap change. For C_{60}, benzene, and pentacene molecules adsorbed on metal surfaces with 100% coverage, the formation of the gas monolayer and introduction of “induced density of interface
states (IDIS)” were observed \(^{158,159}\). Though there is no actual charge transfer, the formation of the gas monolayer induces a potential, through the arrangement of dipoles acting collectively (interacting with each other and with the GNR lattice), thus inducing the localized states.

A typical electric field value used in experiments is 0.33 V/nm [Ref.\(^1\)], based on the applied gate bias and thickness of insulating layer. In order to test possible stabilization of perpendicular adsorption upon applying electric field, we considered a two-unit cell GNR patch with CO adsorbed based on MP2/3-21g method/basis set calculation. We applied electric field perpendicular to the lattice and performed single-point energy calculations for various adsorption heights. Applying an electric field of 0.514 V/nm, we found that the binding energies remained basically intact. Applying an electric field of 5.140 V/nm, however, the minimum energy values for molecular dipole oriented parallel, antiparallel, and perpendicular (with respect to applied field) were 137, 83, and 104 meV lower (i.e., more stable) than the corresponding values for zero electric field, respectively. The energy reductions for antiparallel and perpendicular molecular dipole orientations under stronger electric field are counter-intuitive, and are attributed to the presence of GNR patch and the change in charge transfer between the patch and the adsorbed molecule under electric field. Comparing to the binding energies at zero electric field, we note that an electric field of the order of 5 V/nm results in stabilization of CO adsorption perpendicular to the GNR surface of the order of ~20 meV, comparable to the thermal rotation/vibration energy of 26 meV at 300 K. Therefore, electric field greater than 5 V/nm would be required to stabilize molecular adsorption perpendicular to the lattice. Also, since other atmospheric gases like O\(_2\) and N\(_2\) have no net dipole moment,
adsorption of such gases might not be affected by application of such strong electric fields.

The 3 and 5 adsorption cases presented in Fig. 14 have CO molecules clusterized above the principal layer. We also considered 4 adsorbed molecules per principal layer where the molecules form a continuous line along the nanoribbon. As can be seen from Fig.15(a,b), the HOB and LUB are still localized mainly on the nanoribbon and the adsorbed molecules, respectively. However the band structure and conductance characteristics include unique features not observed for the clusterized cases. Specifically, in addition to the flat impurity band (LUB) above the center of the gap, there are non-flat bands LUB+1 and LUB+3 (Fig.15(c)) which emerge upon the adsorption the CO line and do not exist in the pristine nanoribbon case. These non-flat bands are also absent in the clusterized cases. The presence of these LUB+1 and LUB+3 states causes conductance increase to three quantum units (Fig. 15(d)) that is not observed for the conductance characteristics depicted in Fig. 13 for clusterized cases.
Figure 15: Localization of HOB (a) and LUB (b), as well as band structure and quantum conductance for 4CO-PRP. The CO molecules in this case form a continuous line along the nanoribbon, unlike the clusterized cases presented in Fig. 4. In (c) and (d), zero energy is the center of the gap for pristine AGNR.

3.2.5. Effects of surrounding gas density and temperature

The total number of adsorbed molecules depends on the concentration of the gas that is to be detected, and is thus a good measure of the sensitivity of a gas sensor. As partial pressure is directly proportional to the gas concentration, in a non-interacting gas mixture at constant temperature and volume, the detectable gas concentration can be obtained from the number of adsorbed molecules or surface coverage $\theta$. We define the
surface coverage as the total number of molecules adsorbed per hexagon\textsuperscript{131}. The surface coverage considered for AGNR\textsuperscript{7} cases are 8.33\% for single molecule adsorption and 16.66 \% for two gas molecules adsorbed per principal layer (2 unit cells). The pressure and surface coverage of a weakly interacting gas, at constant temperature, can be approximately described by the relation\textsuperscript{130,162}.

$$\theta = \frac{p}{\nu_0 \sqrt{2 \pi m k_B T}} e^{-E_b/k_B T},$$  \hspace{1cm} (23)$$

where $\theta$ is the surface coverage, $P$ is the pressure, $\nu_0 = 10^{12} \text{ s}^{-1}$ is the attempt frequency, $T$ is the temperature, $m$ is the mass of the molecule, and $E_b$ is the binding energy of the molecule. This relation is strictly valid for non-interacting adsorbates at low concentration. We calculate the pressure of CO and CO\textsubscript{2} at $\theta = 8.33\%$ to be $1.78 \times 10^3$ Pa and $5.04 \times 10^1$ Pa, respectively, at 300 K using the MP2 binding energies calculated for molecule adsorption on GNR patch. Given the pressure of the detected gas, concentration (partial pressure) can be calculated assuming the gas mixture is at standard pressure (1 atmosphere). The concentration of detected CO is $1.72 \times 10^4$ parts per million (ppm) and that of detected CO\textsubscript{2} is 497 ppm. For high surface coverages observed in low temperature experiments\textsuperscript{155,156}, the corresponding number of molecules per GNR principal layer that we consider is four. As we showed above, such high surface coverages can result in conductance changes that are more significant than the changes for one molecule per principle layer. The high surface coverages, however, are possible only at extremely low temperatures (~ 10-25 K) and are not likely to be observed at room temperature.
For comparison, exposure of graphene-based nanosensors to CO at 1 ppm$^{57}$ and 100 ppm$^{57,61}$, and to CO$_2$ at 100 ppm$^{60}$ resulted in detectable increase in electrical resistance at room temperature. The carrier gas that is used in, e.g., Ref. $^{[57]}$ is N$_2$ and He. For N$_2$, the ab initio MP2 binding energy is estimated to be 17.7 kJ/mol (0.183 eV)$^{165}$, that results in a surface coverage of 13.17% at atmospheric pressure used in experiments. If N$_2$ is part of (synthetic) air at ambient pressure$^{60,61}$, the surface coverage will be 11.53%. For O$_2$ the binding energy is estimated to be 6.3 Kcal/mol (0.273 eV)$^{164}$. Therefore surface coverage for oxygen as part of (synthetic) air at ambient pressure$^{60,61}$ is 109.78%. These surface coverages correspond to 1.85, 1.38, and 13.17 molecules per principal layer of AGNR$^7$, respectively. So at STP, surrounding gases with binding energy higher than or equal to that of CO and CO$_2$ will cover most of the surface area, however, applying electric field can orient and increase binding energy of molecules such as CO, as discussed before.

Owing to the presence of a band gap in the nanoribbons considered here, the conductance at zero gate bias is zero. In the experiments$^{57,60,61}$, graphene plates are used that have zero gap, i.e. non-zero conductance at negligible bias. Despite this difference, the changes in conductance characteristics that we calculated at 1.72×10$^4$ and 497 ppm for CO and CO$_2$ indicate shifts of valance and conduction bands of the order of a few meV (5 meV for CO and 12 meV for CO$_2$). These shifts are expected to be yet smaller at lower concentrations. Such small shifts of the conduction characteristics are unlikely to cause the resistance changes reported for 1-100 ppm in experiments. The reason is that for pristine and undoped graphene platelets under no bias, band-structure/conduction shifts of the order of half of graphene’s pseudo gap is necessary to cause conductance
change. As graphene’s pseudo gap is \(~ 5-6 \text{ eV}^{104,165}\), shifts of the order of few meV are too small to create significant conduction change. It is therefore possible that other mechanisms in addition to direct interaction between physisorbed carbon oxides and pristine GNR may be responsible for experimental detection of these gas molecules. These mechanisms include adsorption on defect sites including unsaturated edges and adsorption on metallic contacts, as well as substrate and carrier gas dopings. The latter effect can position the Fermi energy in a region of density of states where even a change of the order of few meV can cause detectable conduction change. In fact, our estimated surface coverages for N\(_2\) and O\(_2\), typical carrier gases used in experiments\(^{57,60,61}\), given above, indicate possibility of doping by these molecules. A similar effect was observed in experiments in which doping of graphene films by adsorbed water or NH\(_3\) caused the peak of Hall resistance to move away from zero gate bias, indicating p- and n-doping, respectively\(^1\).

3.3. NO\(_2\) nanosensor

3.3.1. Energetics and stability of NO\(_2\) adsorption

Several initial guesses were considered for modeling NO\(_2\) adsorption on the 2 unit cell AGNR, which included adsorption on the A and B sub-lattice carbon atoms at the center and the edge, with either nitrogen or oxygen atom from NO\(_2\) closer to the AGNR lattice. The parallel molecular orientations where nitrogen and oxygen atoms reside at the same distance from GNR were considered as well. The relaxed geometries of the 2 unit
cell structures served as initial guesses for the 5 and 13 unit cell optimizations, whose results are used to calculate the reaction rates and conductance curves. In 2 unit cell structures there is spin polarization effect on the carbon atoms due to the comparable lengths of the zigzag and armchair edges, which is nullified in the larger patches due to larger armchair edge lengths. It is to be noted that zigzag edges are predicted to be spin polarized with opposite spin on the edge carbon atoms of either side. We obtained in total five relaxed geometries:

![Figure 16](image)

**Figure 16:** Stable geometries of NO2 adsorption on 2 unit cell patch (a-e), 5 unit cell patch (f-j), and 13 unit cell patch (k-o). Adsorption geometries are labeled by the observed type of bonding: (a,f,k) Hydrogen bonding (HB), (b,g,l) Physisorption (PHY), (c,h,m) chemisorption on the edge carbon atom through nitrogen atom (nitrogen-"down")
at the edge; NDE), (d,i,n) chemisorption on the edge carbon atom through oxygen atom (oxygen-"down" at the edge; ODE), (e,f,o) chemisorption on the central carbon atom through oxygen atom (oxygen-"down" at the center; ODC).

### 3.3.2. Hydrogen Bonding

The most favorable adsorption of NO$_2$ on AGNR occurs at the edge, where the NO$_2$ molecule and AGNR lie in the same plane (Fig. 16 (a,f,k)). The binding energy (hydrogen bond energy) observed here depends on the length of the AGNR edge, with which NO$_2$ bonds. A binding energy of -0.800 eV (-18.437 kcal/mol) is obtained for the 5 unit cell case, but considering 13 unit cell AGNR cluster single and double molecule adsorption, the binding energy reduces to -0.148 eV (-3.411 kcal/mol) per molecule. This is attributed to eigenstate changes and will be discussed shortly. These binding energies correspond to the formation of hydrogen bonds between the two oxygen atoms of NO$_2$ and three hydrogen atoms at the AGNR's edge, with energies comparable to the typical hydrogen bond energies$^{166}$. For 5 unit cell cases (Fig. 16 (f)), Mulliken analysis estimates a net negative charge of -0.32|e| on the NO$_2$ molecule, as shown in Table 4, accompanied by a net positive charge (compared to the pristine case) on the hydrogen atoms from the AGNR edge.

Usually the strength of hydrogen bond (in terms of binding energy) lies in between van der Waals interaction energy (lower limit) and weak covalent bond
formation energy (higher limit). It is well known that the ability of a C-H group to donate electron depends on the carbon hybridization, and is of the following order C(sp)-H > C(sp<sup>2</sup>)-H > C(sp<sup>3</sup>)-H<sup>167</sup>. Conceptually, the hydrogen bonds formed by the C-H groups are generally weaker than the classical hydrogen bonds formed by O-H and N-H groups, due to large electro-negativity difference<sup>167</sup>.

Unlike the hydrogen saturated zigzag edge where all edge hydrogen atoms are equidistant, inter-hydrogen atom distance at the armchair edge changes between a larger value and a smaller value, due to the chair geometry of carbon atoms at the edge. One of the two oxygen atoms from NO<sub>2</sub> has more net negative charge on it, due to donation of electron from two adjacent hydrogen atoms at the edge, with small inter-hydrogen distance. This oxygen atom is also closer to the two hydrogen atoms with an average hydrogen bond distance of 2.35 Å, compared to the other oxygen with hydrogen bond distance of 2.60 Å. The other oxygen atom, which shows less charge accumulation and larger hydrogen bond lengths, faces the two hydrogen atoms which are farther apart from each other. These three hydrogen atoms which are closer to the NO<sub>2</sub> molecule show a net increase in positive charge on them. It should be noted that zigzag edge of GNR, with high density of states near Fermi energy, is more chemically reactive and thus might favor chemisorption. However, in experiment it has not yet been possible to synthesize hydrogen terminated zigzag GNR (ZGNR) with ~ 1 nm width. Due to this high chemical reactivity, the zigzag edge is easily functionalized with oxygen or NH group<sup>168</sup>. Such single sided functionalization has been shown to stabilize ZGNR assemblies thorough
strong hydrogen bonds with a high binding energy of -1.3 eV and bond length of 1.55 Å.

**Table 4:** Binding energy and net molecular charge of NO2 adsorbed on AGNR7 cluster of two, five unit cells with one, and thirteen unit cells with one and two molecules adsorbed.

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<td>-0.32 eV</td>
<td>1.251 eV</td>
<td>-0.32 eV</td>
</tr>
</tbody>
</table>

### 3.3.3. Physisorption of NO2 (PHY)

The next most stable structure is physisorption of NO2, perpendicular to the plane of the AGNR patch. In this orientation, nitrogen from NO2 is closer to the AGNR lattice with a perpendicular distance of 3.00 Å. The two oxygen atoms are facing upwards as shown in Figure 16(b,g,l). For 5 unit cell system, the binding energy and net charge of NO2 are -0.588 eV and -0.14|e|, respectively. For single and double sided adsorption on
the longer 13 unit cell cases, binding energy and charge transfer values reduce. This is attributed to an increase in energy gap between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 13 unit cell case compared to the 5 unit cell case, that are 0.35 and 1.50 eV, respectively. Beta LUMO of NO$_2$ is well below (0.69 eV) the HOMO of 5 unit cell AGNR, enabling electron transfer from AGNR to NO$_2$. This results in stabilization and a relatively high binding energy. However, LUMO of NO$_2$ is only slightly lower (0.11 eV) than the HOMO of 13 unit cell AGNR that results in small electron transfer and less binding energy. This can be compared to NO$_2$ adsorption on graphene where the charge transfer predictions was estimated$^{169}$ (by considering large (> 1000 atoms) unit cell of graphene lattice) to be -1.0 |e| and the beta LUMO of NO$_2$ to be 0.4 eV lower than the Dirac point$^{169,170}$. For comparison, the calculated binding energy of NO$_2$ on 2-D graphene sheet is -0.17 to -0.19 eV, using LDSA$^{170,171}$ and -0.05 to -0.09 eV using GGA$^{148,170}$, respectively. The perpendicular distances are of the range 2.50-3.00 Å using LSDA$^{170,171}$ and 3.4-3.93 Å using GGA$^{148,170}$, respectively.

3.3.4. **N-down and O-down chemisorptions at the edge (NDE and ODE)**

Hydrogen terminated $sp^2$ hybridized armchair edges provide a suitable site for chemisorption of NO$_2$ with two different adsorption geometries. In one orientation (NDE), nitrogen is closer to and forms a bond with the edge carbon, as shown in Figure 1(c,h,m). The carbon-nitrogen bond length is 1.65 Å, with the carbon showing $sp^3$ character. The edge hydrogen atom is pushed down and the $sp^3$ hybridized carbon atom is
slightly raised. In another orientation (ODE), NO₂ chemisorbs at the edge with one oxygen atom forming a bond with an edge carbon atom as shown in Figure 16(d,i,n). O-C bond length is 1.55 Å which is slightly shorter than N-C bond length in NDE orientation. In ODE, the distance between nitrogen and oxygen bonded to carbon increases by 0.21 Å from its equilibrium value. This suggests that oxygen is strongly bonded to the carbon atom and less strongly to NO. The C-C-C angles having at their tips the carbon atom bonded to N and O in NDE and ODE orientations are between 111° and 116°, compared to 109.5° and 120° for \( sp^3 \) and \( sp^2 \) hybridizations. The corresponding C-C-N and C-C-O angles are between 97° and 107°. This suggests hybridization between \( sp^2 \) and \( sp^3 \), and can be called weak \( sp^3 \). This case is similar to chemisorption of radicals\(^{172}\), hydrogen\(^{173}\) and ozone\(^{174}\) on graphene with similar weak \( sp^3 \) adsorption, which is otherwise expected to form standard \( sp^3 \) bonds. Both NDE and ODE adsorptions involve conversion of edge carbon from \( sp^2 \) to weak \( sp^3 \) hybridization, resulting in bending/twisting of the AGNR. NDE adsorption energy on 2 and 5 unit cell structures is -0.369 eV and -0.097 eV, respectively. The ODE case shows larger deformation upon NO₂ adsorption, that is endothermic, with a corresponding positive adsorption energy on 5 unit cell AGNR equal to 0.020 eV (Table 4). For both NDE and ODE and all system sizes the charge transfer to the NO₂ molecule is approximately one third of electron charge (-0.33|e|). Comparison with other works is possible for NO₂ adsorption on AGNRs with dangling bond edge defect, where the binding energy is -2.70 eV and charge transfer is -0.55|e|\(^{63}\). In this case NO₂ bonds via nitrogen atom with a C-N bond distance of 1.48 Å. Due to the presence of unsaturated carbon (dangling bond) NO₂ bonds strongly and AGNR may not be
retrievable to its pristine state, making this case not suitable for use as sensor. Dangling bond defects would be undesirable while using AGNRs as (NO\textsubscript{2}) sensor.

### 3.3.5. O-down central chemisorption (ODC)

NO\textsubscript{2} also chemisorbs at the center of AGNR through one of its oxygen atoms as shown in Fig. 16 (e,j,o). The geometry of NO\textsubscript{2} is similar to ODE case with O-C bond length of 1.63 Å and N-O bond length stretch of 0.22 Å. Oxygen down central adsorption (ODC) involves conversion of the central carbon atom to weak \textit{sp}\textsuperscript{3} hybridization. The deformation involves curling along the width and bending along the axis of AGNR (Fig. 16 (e,j,o)). The curling is due to the change from planar \textit{sp}\textsuperscript{2} to weak \textit{sp}\textsuperscript{3} tetrahedral geometry and reduction of in-plane C-C-C angels in the middle of the AGNR patch. ODC adsorption is more endothermic, with positive binding energy of 0.313 eV for 5 unit cell system, than ODE and NDE adsorptions because ODC involves bending and curling while ODE and NDE involve only bending of AGNR. The ODC adsorption results in an average charge transfer to molecule of -0.33 |e| per molecule. Previous results available for ODC adsorption on 2-dimensional (2D) graphene report a similar final geometry. LDA predicts a binding energy of 0.19 eV, O-C bond length of 1.54 Å and charge transfer of -0.06 |e|\textsuperscript{171}. Other computational studies also support the endotherm nature of the reaction\textsuperscript{175,176}. On the other hand experimental Raman measurements suggest that NO\textsubscript{2} physisorbs on the surface of NO\textsubscript{2} at high concentrations with a binding energy of 0.4 eV\textsuperscript{177,178}. Here maximum surface coverage corresponds to
1.2 NO\textsubscript{2} molecules per every 100 carbon atoms of graphene. A net charge transfer of one electron from graphene to NO\textsubscript{2} was reported through hall resistivity measurements\textsuperscript{57}, which is not in accordance to a theoretical prediction that was mentioned earlier\textsuperscript{171}. Here we notice that chemisorption of NO\textsubscript{2} on GNR (center or edge), causes a transfer of one third of electron charge to the NO\textsubscript{2} molecule that could be verified by measuring hall resistivity. In addition to AGNR7 we also considered AGNR6 and AGNR8 for which we found no correlation of chemisorption of NO\textsubscript{2} with varying width, and found similar adsorption geometries and charge transfers. Adsorption energies on these AGNRs depend on width and location of adsorption (edge/center). The width dependence of adsorption energy comes from the energy gain/loss due to deformation of AGNR caused by deviation from planar structure of GNR, and depends on the location of adsorption and symmetry of deformation.

3.3.6. Reaction kinetics and rate constant calculation

Potential energy surface (PES) and force constant calculations were carried out for adsorption of NO\textsubscript{2} on 5 unit cell AGNR7 systems, to assess the kinetics of reaction and confirm stability of adsorption at edge/center of AGNR. HB and PHY adsorptions were found to be processes without barriers that can occur spontaneously. Therefore, HB and PHY are the main adsorption possibilities for NO\textsubscript{2} on GNR.

To understand the energetics of chemisorption possibilities, and their formation dynamics, the binding energies of NDE, ODE, and ODC cases are depicted in Fig. 2 and
compared with the binding energies of HB and PHY cases. For the three chemisorption cases, we define the reaction coordinate to be the bond length between the active atom of NO$_2$ (O or N) and the carbon at the edge (Ce) or at the center (Cc) of the AGNR lattice. For edge adsorption cases, Fig. 17 (a) and (b) depict the energies of the nitrogen-down and oxygen-down cases (NDE and ODE) together with the energies of hydrogen bond (HB) state and the transition state (TS) that occurs at an intermediate reaction coordinate. The energies of center adsorption case (ODC), physisorption PHY state, and the corresponding transition state, are depicted in Fig. 17 (c). TS is verified by observation of single large imaginary frequency. Zero energy in Fig. 17 is chosen as the energy of the isolated state where NO$_2$ and GNR are separated and have negligible interaction. The energy barrier heights that are the energy differences between transition states and HB or PHY state are 0.759, 1.101 and 0.940 eV, which need to be overcome in order to form NDE, ODE and ODC structures, respectively, from HB or PHY state. Energy is required to break the aromaticity of stable $sp^2$ hybridized carbon atoms and generate weak $sp^3$ hybridization at the center and edge of AGNR. For cases where bonding is achieved through the oxygen atom (ODE and ODC), energy is also required to stretch the N-O bond by about 0.2 Å. This energy is about 0.25 eV. This is also the energy difference between the energy barriers of NDE and ODE/ODC cases. Gibbs free energies of the reaction at room temperature starting from HB and PHY states leading to chemisorption are calculated to be 0.883, 1.111 and 1.154 eV for the NDE, ODE and ODC structures, respectively. The corresponding reaction rates predictions, based on transition state theory, are $7.05 \times 10^{-2}$, $9.66 \times 10^{-6}$ and $1.87 \times 10^{-6}$ reactions/second for unit concentration, respectively. As can be seen from Fig. 17, the chemisorption states (NDE, ODE, and
ODC) have less absolute binding energies than HB and PHY states that occur at larger reaction coordinates. Considering the fact that formations of HB and PHY from the isolated state have no energy barrier, one can conclude that the NO$_2$ molecules that approach AGNR adsorb according to either HB or PHY configurations. The chemisorbed states are much less likely to be formed according to the calculated low formation rates starting from the more probable HB and PHY states. The NDE state, however, is more probable than ODE and ODC owing to smaller energy barrier of formation from the HB state. It is worth mentioning that the energy barrier for chemisorption of NO$_2$ via formation of epoxide structure on graphene sheet was calculated to be 37.1 kcal/mol (1.61 eV)$^{175}$. Adsorption of NO$_2$ through the O atom is similar to chemisorption of ozone on graphene with energy barrier of 0.72 eV and similar adsorption geometry$^{174}$.

**Figure 17:** Potential energy scan results of chemisorbed systems. NDE (a), ODE (b), and ODC (c). X-axis represents the reaction coordinate which is defined to be the bond length between the active atom of NO$_2$ (O or N) and the carbon at the edge (Ce) or at the center (Cc) of the GNR lattice. Corresponding transition states (TS) structures, verified by observation of single large imaginary frequency, are shown as insets. Zero energy is
chosen as the energy of the isolated state where NO$_2$ and GNR are separated and have negligible interaction.

One measure of strength/stability of the weak $sp^3$ bond formed during chemisorption is the depths of the energy wells where the bonded structures lie. These are also the energies needed to overcome for dissociation of the chemisorbed states. The dissociation energies are 0.056, 0.190 and 0.039 eV for NDE, ODE and ODC cases, respectively. This shows that, although the energy barrier for the formation of ODE is high, it is more stable than NDE and ODC which are prone to dissociation. When a catalyst (SiO$_2$ or MgO) is present, NO$_2$ can be adsorbed at the edge via removal of a hydrogen as is a common practice for many polyaromatic hydrocarbons (PAH). ODC adsorption shows a very shallow potential energy well of 39 meV. Since the energies required for dissociation of the chemisorbed states are of the order of thermal fluctuation at room temperature (25.6 meV), we expect the residence time to be in the range of inverse of attempt frequency. We estimate the attempt frequency to be on the order of $10^{11}$ sec$^{-1}$, through fitting a second order polynomial at the minima of potential energy profiles of the three chemisorbed states.

The ODC formation reaction can proceed further by reduction of NO$_2$ to NO and generation of epoxide group (C-O-C) on the C-C bridge of graphene lattice. This process has a higher energy barrier than the energy barrier for chemisorption via epoxide formation, and such reaction are reported on activated graphite systems only, which include defects and additional functional groups. We observe a reduction in
energy barrier comparing ODC cases of GNR (calculated here) and graphene\textsuperscript{175} which may be attributed to 1-D structure and open edges of GNR, which provides freedom of deformation along the edge. This demonstrates increased chemical reactivity of GNRs compared to graphene. Reduction in energy barrier is observed upon reducing the dimensionality (compared to graphene) and freeing up the graphene lattice along the edges of GNR to deformation. The larger binding energy of HB adsorption at the edge than that of PHY adsorption at the center further manifests this effect.

As shown here, chemisorption of NO\textsubscript{2} and other molecules like ozone and hydrogen are accompanied by formation of weak \textit{sp}\textsuperscript{3} bond and lattice deformation. The strain caused by deformation and non-planarity are eased off in one direction of AGNR, whereas for 2-D graphene there are no edges to provide such a possibility. However, ripples are intrinsic to 2-D graphene\textsuperscript{172,173,182} and can be generated and altered in GNRs as well\textsuperscript{183}. The carbon atoms at the crest of these ripples or folds have a slight \textit{sp}\textsuperscript{3} character and are favorable chemisorption sites. Thus chemisorption energy barrier will be reduced in such circumstances as the deformation required for chemisorption is pre-provided. We expect to observe more adsorption-desorption phenomenon on such ripples compared to the planar sheet or ribbon.

\subsection{3.3.7. Transport calculation of Single NO\textsubscript{2} adsorption}

The influence of one NO\textsubscript{2} molecule adsorption on electronic transport properties of AGNR\textsuperscript{7} is studied via quantum conductance modulation analysis and is reported in
Fig. 18, for all the five configurations considered, compared to the pristine case (PRS) that is presented in Fig 18(a). Pristine AGNR7 shows a band gap of 1.546 eV using B3LYP/6-31G relaxation and BLYP/3-21G electronic structure\textsuperscript{131}, which is in accordance with recent theoretical predictions\textsuperscript{30}. As shown in Figure 18 (b), quantum conductance characteristics of NO\textsubscript{2} adsorbed via hydrogen bond (HB) only results in slight rounding of conductance steps. Similarly, physisorption of NO\textsubscript{2} (Figure 18. (c)) on AGNR shows small change. At carrier energies of ~-1.5 and 1.0 eV, there is a sharp dip in conductance from 2 units to lower values, contributed by the alpha electron. We observed similar drop while discussing NO\textsubscript{2} adsorption on CNT, and was attributed to existence of van Hove singularity in density of states\textsuperscript{131}. Analysis of density of states (DOS) for the corresponding systems (PHY and HB) indicate that rounding of conduction steps is caused by emergence of localized impurity states, which hamper electron transmission though scattering. The resulting changes in current at infinitesimal bias, calculated as the area under conductance curves, would hardly be detectable in experiment for one NO\textsubscript{2} adsorbed in HB and PHY cases.
Figure 18: Comparison of various quantum conduction curves for one NO$_2$ molecule adsorbed on AGNR7: Pristine (PRS) (a), hydrogen bonded (HB) (b), physisorbed (PHY) (c), chemisorbed at edge via nitrogen atom (NDE) (d), chemisorbed at edge via oxygen atom (ODE) (e), and chemisorbed at center via oxygen atom (ODC). Red and blue curves represent conductance contributions for alpha and beta electrons (two spin configurations). Middle of the gap of the pristine AGNR is set to zero.

Quantum conduction of chemisorption cases name NDE, ODE and ODC (Fig. 18(d,e,f)), show significant overall reduction in conduction. Maximum reduction of conduction below the Fermi energy is shown by ODC case. In general for chemisorbed cases, pseudo band gap widens from the 2.1 eV for pristine case. For chemisorbed cases the DOS curves are reshaped owing to lattice deformation and electron transfer to NO$_2$. The band gap, however, does not alter. The Bloch waves are scattered by localized non-conducting states, disrupting conducting channels, and directly resulting in conductance
drop above and below Fermi energy. From Fig. 18 (d,e,f) it is clear that even one NO\textsubscript{2} adsorption in the chemisorbed cases, if present, results in significant conductance (and current) reduction presumably detectable in experiment. However, as discussed before, chemisorbed cases are much less likely to be formed compared to HB and PHY cases.

### 3.3.8. Effect of NO\textsubscript{2} concentration on electron transport

To address the effect of NO\textsubscript{2} concentration on AGNR, we calculated quantum conductance of two molecules adsorbed on the AGRN lattice (Fig. 19 (b-f)). Quantum conductance of two NO\textsubscript{2} hydrogen bonded system shows further reduction in conductance, both below and above the Fermi energy (Fig. 19 b), that is much more pronounced than the reduction in single NO\textsubscript{2} HB case. Hydrogen bonding involves charge transfer from the valance band of the lattice to the conduction band of the molecule. Since charge is transferred from the lattice to the molecule we can expect to see further reduction in conductance at even higher concentrations. Physisorption of two NO\textsubscript{2} does not alter the conduction significantly (Fig. 19 c), as compared against the single molecule physisorbed case. The only difference occurs at carrier energies of +1.0 eV, where spin splitting is observed giving rise to recognizable difference in conduction caused by alpha (blue) and beta (red) electrons. By comparing two NO\textsubscript{2} adsorbed in HB and PHY configurations, we see that conductance change is more pronounced for the former. This is a result of larger charge transfer to the molecule in HB case than in PHY case (Table 4), and the fact that the two NO\textsubscript{2} molecules are located at the same place along the nanoribbon that enhances their local disruption effect. The two NO\textsubscript{2} chemisorbed cases (Fig. 19(d,e,f)) show further decrease in conductance at all carrier energies accompanied by band-gap expansion. For two NO\textsubscript{2} adsorbed at center location
(ODC) (Fig. 19 (f)) the band gap becomes 2.1 eV. This clearly demonstrated that chemisorption of NO\textsubscript{2} at center causes more change to conductance as compared to edge chemisorption, although in both cases there is a net charge transfer of one third of an electron to NO\textsubscript{2}. For two NO\textsubscript{2} adsorbed at the edge (Fig. 19(d,e)), we also observed spin splitting giving rise to different conductance curves for alpha and beta electrons.

![Figure 19: Comparison of various quantum conduction curves for two NO\textsubscript{2} molecules adsorbed on AGNR7: Pristene (PRS) (a), hydrogen bonded (HB) (b), physisorbed (PHY) (c), chemisorbed at either edge via nitrogen atom (NDE) (d), chemisorbed at either edge via oxygen atom (ODC). Red and blue curves represent conductance contributions for alpha and beta electrons (two spin configurations). Middle of the gap of the pristine AGNR is set to zero.](image)

Figure 19: Comparison of various quantum conduction curves for two NO\textsubscript{2} molecules adsorbed on AGNR7: Pristene (PRS) (a), hydrogen bonded (HB) (b), physisorbed (PHY) (c), chemisorbed at either edge via nitrogen atom (NDE) (d), chemisorbed at either edge via oxygen atom (ODC). Red and blue curves represent conductance contributions for alpha and beta electrons (two spin configurations). Middle of the gap of the pristine AGNR is set to zero.
A side effect of electron transfer to/from the molecule from/to the lattice is possible shift of Fermi energy. The Fermi energy can in principle be shifted to energies where significant conductance change is observed. For example, in the case of NO$_2$ physisorption, if the Fermi energy is shifted to ±1.0 eV there is conduction drop of one unit. A more detectable change can be observed for two NO$_2$ adsorbed in HB configuration, if Fermi energy is shifted to the right of the gap. This effect will be more prominent for GNRs with small band gaps (e.g. AGRNs with width index $N= 3p$ and $3p+2$, where $p$ is an integer, or AGNRs with larger widths), or for graphene sheets. In case of NO$_2$ adsorption on graphene, it was shown by analysis of partial DOS (PDOS) that spin down unoccupied component of NO$_2$ is 0.4 eV below the Dirac point in adsorbed configuration leading to transfer of one electron from graphene at an extremely low concentration$^{169,170}$. Therefore GRNs with band gaps around this range (0.4 eV) can show electron transfer by filing of this unoccupied state. This also indicates that sensing of NO$_2$ can be achieved even in the presence of weakly interacting atmospheric gases like O$_2$, N$_2$, CO and CO$_2$$^{57}$ that can contribute to sensing by carrier gas doping and sifting Fermi energy to where more significant changes are produced upon NO$_2$ adsorption$^{184}$.

We also observed that chemisorption of NO$_2$ at center and edge results in formation of weak $sp^3$ bond with significant energy barriers and charge transfers. The strength of the weak $sp^3$ bond is less than the normal $sp^3$ bond. This may be one of the reasons that Raman spectra of NO$_2$ adsorbed graphene do not show any D band, but shows significant shifts of the G bands indicating strong charge transfer$^{185}$. Also the existence of energy barriers of few eV required for formation of chemisorbed NO$_2$ may inhibit larger surface area coverage of chemisorbed NO$_2$ which is essential for Raman
spectra as only a small fraction (one in a million) of photons are inelastically scattered\textsuperscript{91}. This point was proved recently where adsorption of aromatic molecules like phthalocyanine (Pc), rhodamine 6G (R6G), protoporphyrin IX (PPP), and crystal violet (CV) was studied on graphene\textsuperscript{91}. Significant charge transfer was found to/from the molecule but the main cause of Raman effect enhancement was attributed to the vibration coupling of \(\pi-\pi\) stacked molecule and graphene, and not chemisorption, even though some molecules were adsorbed at a distance of 1 \(\text{Å}\) from the surface of graphene. Such Raman signal enhancement effect is not yet studied for free standing (suspended) GNR substrates and can be a novel method for sensing NO\textsubscript{2} gas. External stimulation methods like introduction of artificial ripples\textsuperscript{182} and folds can reduce the energy barrier to chemisorption and enhance sensing. It is also necessary to use free standing GNR (GNR on a trench) as sensor to exploit sensing by hydrogen bond. NO\textsubscript{2} charge transfer to/from graphene\textsuperscript{171} and CNT\textsuperscript{186} can be modulated by external electric fields\textsuperscript{184}.

3.4. Non-coherent transport calculations

CO and CO\textsubscript{2} molecules relaxed with MP2 method are used to calculate vibrational characteristics (eigen values of the force constant matrix) and are tabulated in Tables 5 and 6. Sample vibrational motion of both molecules is shown in Fig. 20 (a) and (b). As discussed earlier, the five unit cell structure was utilized to calculate vibrational frequencies (eigen values). In an experimental setting we would expect that GNR to be sandwiched between two electrodes on two sides of a substrate, when it is used for
sensing gas molecules. It is expected that the vibrations of GNR lattice atoms that are supported by the electrostatic potential from the atoms of the substrate, are small when compared to the vibrations of the molecule. So we assume in our non-coherent transport calculations that the atoms of the underlying graphene lattice are fixed. To validate this assumption, we compare the frequencies of these three cases (i) isolated gas molecules (Table 5) (ii) absorbed molecule free to move but the entire underlying lattice fixed (Table 5) (iii) absorbed molecule and the underlying hexagon/s free to move but the rest of the GNR lattice fixed (Table 6). After analyzing the corresponding frequencies of cases (i), (ii) and (iii), we see that the frequencies in cases (ii) and (iii) are essentially identical with a variance of less than 1%. Hence we see that the vibrations of the lattice do not significantly affect the vibrational frequencies of the molecule. Another argument to support this reasoning is that both molecules are physisorbed on the GNR lattice (there is no strong chemical bond with molecule to influence its motion), thus the vibration of the molecule should not be significantly affected by the vibration of the atoms in the GNR lattice. It is to be noted that the vibrations of the atoms in the GNR lattice will significantly affect the transmission of the electrons as these atoms are bound together with $sp^2$ hybridized bonds, but they do not contribute to the sensing effect. We will address the issue of non-coherent transport in GNRs with lattice atoms vibrating at a later stage in this research.
**Figure 20:** Visualization of vibrational sample modes of isolated CO (a) and CO$_2$ (b) molecules at specified frequencies with displacement vectors shown as black arrows.

**Table 5:** All the frequencies for adsorbed molecule (CO/CO2) with underlying GNR lattice atoms fixed, and without the GNR. Bold face frequencies are used to show similar frequencies in both the cases.

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Figure 21: Visualization of highest and lowest vibrational frequencies of CO in parallel adsorption (a,b), CO in perpendicular adsorption (c,d), and CO$_2$ adsorption (e,f) on the GNR lattice while fixing the GNR lattice atoms, with displacement vectors shown as black arrows. Only gas molecules are allowed to move.
**Table 6:** Frequencies of vibration when the adsorbed molecule (CO/CO\(_2\)) and the underlying hexagon atoms are free to move, while the remaining GNR lattice atoms are fixed. Bold face frequencies are used to show similar frequencies as compared to isolated molecules. Underlined and italic face numerical formats are to show gas molecule movements similar to the values in Table 5.
Figure 22: Visualization of vibrational frequencies of CO in parallel (a,b) CO in perpendicular (c,d), and CO\textsubscript{2} (e,f) adsorptions with displacement vectors shows as black arrows at specified frequencies. Gas molecules and the underlying hexagon atoms are free to move while the remaining GNR lattice GNR lattice atoms are fixed.

For non-coherent transport, we investigated two different nano-sensor systems (with CO and CO\textsubscript{2}) at a temperature of 300K and at a bias of 0.04V, in addition to
calculating coherent transport transmission. Coherent transmission coefficients are shown in Fig. 23 for the case of CO$_2$ adsorption at 0.04 V bias. We calculated the contribution of two phonon modes on transmission, which are shown in Fig 24 (a,b). We present the transmission coefficients of the nano-sensor system with CO$_2$ adsorbed at temperatures 300 K, at bias of 0.04 V and for the lowest and highest phonon frequency modes in Fig. 24 (a,b). Similarly, coherent transport transmission for the case of CO adsorbed is shown in Fig. 25 at same temperature and voltage bias. Similar to the case of CO$_2$, we calculated the contribution of two phonon modes on transmission, which are shown in Fig 26 (a,b). In the end, we also included the effect of lattice vibration to electron transmission under same bias and room temperature. The results are shown in Fig. 27.

**Figure 23:** Coherent electron transmission coefficient (on Y-axis) as a function of charge carrier energy (on X-axis) for CO$_2$ adsorbed on the AGNR lattice at a bias voltage of 0.04 V. Fermi energy is set to zero.
Figure 24: Non-coherent electron transmission coefficient (on Y-axis) as a function of charge carrier energy (on X-axis) for CO₂ adsorbed on the AGNR lattice at a bias voltage of 0.04 V at temperature of 300 K. (a) Contribution from phonon with frequency 19.95 cm⁻¹. (b) Contribution from phonon with frequency 63.88 cm⁻¹. Fermi energy is set to zero.

We see that the electron transmission coefficient are on the order of 10⁻¹ for coherent case [e.g. for CO₂ adsorbed case, at Fermi energy (E=0): $t = 7.5767 \times 10^{-1}$], but for phonons with frequencies of 19.95 and 63.88 cm⁻¹ (corresponding lowest and highest vibration modes of the molecule with respect to the fixed nanoribbon) the non-coherent contributions to transmission coefficient are on the order of 10⁻⁶ and 10⁻⁸, for CO₂ and for phonons with frequencies of 12.14 and 80.68 cm⁻¹ (corresponding lowest and highest vibration modes of the molecule with respect to the fixed nanoribbon).
vibration modes of the molecule with respect to the fixed nanoribbon) transmission coefficient are on the order of $10^{-4}$ and $10^{-7}$ for CO, respectively. There are two key points we can deduce from this analysis: (i) For physisorption of gaseous molecules the contribution of molecular vibrations to electron transmission is not significant (in the case of CO$_2$, $10^{-5}$ to $10^{-7}$ times smaller for individual frequencies) (ii) phonon modes with lower frequencies have a greater effect on non-coherent transmission as compared to higher frequencies (two orders of magnitude smaller in case of CO$_2$ at T= 300 K). Also, we observed that non-coherent contributions from CO adsorption are generally more than the contributions from CO$_2$, as is evident by comparing Fig. 26 and 24. One possible reason might be the non-zero dipole moment of CO compared to the net zero dipole moment of CO$_2$. When we include the effect of lattice vibrations (Fig. 27), the effect of phonons to non-coherent transport in this case is seen to be much more significant than the effects of phonons from the adsorbed molecules vibrations (comparing Figs. 25, 26 and 27). This was expected as the atoms in the lattice are strongly bound to each other and their motion will lead to significant change in transmission coefficient, as for we consider one molecule (either CO or CO$_2$) adsorption on the whole length of the nanoribbon for non-coherent transport calculations, the electronic transport mainly occur through the nanoribbon lattice (and not through a chain of adsorbed molecules that could be the case for higher molecule concentrations). Therefore, any direct disruption in the nanoribbon lattice order causes larger non-coherent contribution compared to adsorbed molecule vibration.
Figure 25: Coherent electron transmission coefficient (on Y-axis) as a function of charge carrier energy (on X-axis) for CO adsorbed on the AGNR lattice at a bias voltage of 0.04 V. Fermi energy is set to zero.
**Figure 26:** Non-coherent electron transmission coefficient (on Y-axis) as a function of charge carrier energy (on X-axis) for CO adsorbed on the AGNR lattice at a bias voltage of 0.04 V at temperature of 300 K. (a) Contribution from phonon with frequency 12.14 cm\(^{-1}\). (b) Contribution from phonon with frequency 80.68 cm\(^{-1}\).

**Figure 27:** Coherent and total (non-coherent plus coherent) electron transmission coefficient (on Y-axis) as a function of charge carrier energy (on X-axis) for CO adsorbed on the AGNR lattice at a bias voltage of 0.04 V at temperature of 300 K, including the vibration of the hexagon underneath it. Blue curve shows coherent contribution. Red curve represents the total (non-coherent plus coherent) contribution from phonon with frequency (FRQ-6) 274.40 cm\(^{-1}\). Green curve represents the total (non-coherent plus coherent) contribution from phonon with frequency (FRQ-11) 726.58 cm\(^{-1}\). Fermi energy is set to zero.

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It should be mentioned that, the non-coherent results presented above are based on first order Born approximation.

3.5. Raman spectra before and after NO$_2$ adsorption

Figure 28: Calculated and normalized (to the highest value of each system) Raman spectra of NO$_2$, pristine five unit cell AGNR7 cluster (PRS), NO$_2$ adsorbed via oxygen atom on the edge of the five unit cell AGNR7 cluster (ODE), NO$_2$ adsorbed via oxygen
atom at center location of the five unit cell AGNR7 cluster (ODC), NO$_2$ adsorbed via nitrogen atom on the edge of the five unit cell AGNR7 cluster (NDE). The vibrational frequency and corresponding motion, which result in Raman spectra peaks for pristine 5AGNR7 system, are shown in the inset.

Raman intensities are calculated for five unit cell AGNR7 cluster system and are shown in Fig. 28. Weakly bonded cases (PHY, HB) are excluded and chemisorbed cases (ODE, NDE, ODC) are shown with Raman spectra of pristine 5AGNR7 and pure NO$_2$ gas. As discussed earlier, the calculation of Raman spectra is sensitive to method and basis. Due to a relatively large system size and computational time required, we couldn’t use polarized basis and perturbative method (like MP2), which would have been apt for calculating accurate Raman spectra of the weakly bonded systems. Instead, we focus our attention on chemisorbed cases, and show origins of marker bands and relative shifts in Raman spectra upon NO$_2$ adsorption at different locations. Moreover due to anharmonic vibrations of edge C-H bonds which are concentrated below 1000 cm$^{-1}$ (mostly containing out of plane vibrations of edge H and some C atoms) and above 3000 cm$^{-1}$ (mostly C-H stretching modes), we show Raman spectra in the range of 1000-1700 cm$^{-1}$. In this range we can expect to see marker bands of graphene. Comparing experimentally obtained vibrational spectra of pure NO$_2$ gas$^{187}$, we observed that our calculated frequencies were down shifted by 6%. This level of accuracy should give us qualitative results, since we are concerned with shifts and not the absolute values.

One of the main marker bands/peaks of graphitic material is called the G-band. The G-band originates due to degeneracy of in-plane transverse optic and in-plane longitudinal optic modes at the Γ point, in the range$^{188}$ 1580 cm$^{-1}$ and 1600 cm$^{-1}$. This
belongs to the 2-D $E_{2g}$ transition\textsuperscript{189} and thus called the G-band. Also defect induced D-band is observed on defected graphitic materials around the frequency of 1350 cm$^{-1}$. The origin of this marker band is the phonon mode around K point which leads to $A_{1g}$ symmetry\textsuperscript{86,129,189}.

Upon comparison of Raman spectra of pristine 5AGNR\textsuperscript{7} (PRS) cluster to 2-D graphene\textsuperscript{80}, we see that G band (which is marker band) is degenerate for graphitic materials, but splits into two for 5AGNR\textsuperscript{7} cluster. Insets in Fig. 24 show motion of two central atoms of PRS-5GNR\textsuperscript{7} at 1600 cm$^{-1}$ and 1644 cm$^{-1}$. Their motion correspond to the in-plane transverse optic and in-plane longitudinal optic modes of graphene\textsuperscript{189}. This lifting of the degeneracy can be attributed to confinement effect, as the system we are considering is PAH and not 2-D infinite graphene sheet. Two more marker bands are identified at 1349 cm$^{-1}$ (D-band) and 1260 cm$^{-1}$ and their corresponding motions are shown in the insets of Fig. 28. These peaks also arise due to the confinement and edge effect which can be considered as a defect.

Upon chemisorption of NO\textsubscript{2} at the center and at the edge we see that the G peak at 1600 cm$^{-1}$ has increased intensity, whereas the G peak at 1640 cm$^{-1}$ is split into two smaller peaks of lesser intensity. We also observe that the peaks in the frequency range 1200-1300 cm$^{-1}$ have increased intensities upon NO\textsubscript{2} chemisorption. This effect was earlier reported in experiment on defected graphene systems. The crystallinity of graphene (extent of disorder or defect) sample can be determined by measuring the D/G peak intensity\textsuperscript{80,82,84,190}. We have earlier determined that the chemisorption of NO\textsubscript{2} results in formation of week $sp^2$ bonds, high energy barriers and less probability of formation of chemisorbed species. A recent experimental study found no trace of Raman
peaks arising due to adsorption of NO$_2$, even at high pressure, but found shifts in G peaks, attributed to charge transfer due to physisorption$^{185}$. By using confined structures like graphene nanoribbons, we show here that the edge can be an attribute to sensing, and can result in Raman spectra change.
4. Summary and Conclusions

We investigated two different classes of nano-sensors, one using bilayer graphenenanoribbons (BGNR’s) for electro-mechanical sensing, and the other using single layer armchair GNR (AGNR) for gas sensing. We show that bilayer armchair graphenenanoribbons (BAGNR) can have different energies and electronic structures, metallic or semiconducting, due to different types of stacking. Bilayer zigzag graphenenanoribbons (BZGNR) can have different edge magnetizations, in addition to various energies and band gaps, owing to inlayer and interlayer interactions for various stacking arrangements. In the case of BAGNR with a width of ~1 nm, the ground state corresponds to shifted graphite stacking with a planar shift between 1.65 and 2.25 Å. The band gap is in the range 0.13-0.04 eV and can be useful for practical applications such as nanoelectromechanical sensors. BZGNR has a non-magnetic ground state with inlayer and interlayer antiferromagnetic spin arrangement, with a planar shift of 0.71 Å corresponding to ground state, obtained by using local density approximation (LDA) to density functional theory (DFT) method.

The adsorption of CO and CO$_2$ on armchair graphenenanoribbons (AGNR) of ~1 nm width was investigated using MP2 relaxation combined with BLYP hybrid density functional formalism for different gas densities (surface coverages). All molecules are physisorbed on AGNR with little charge transfers (in the range -0.005 to+0.005 |e|). For CO, perpendicular orientations are metastable with binding energies higher than that of the parallel orientation. For CO$_2$ adsorption, only one minimum was found. CO$_2$ has a
binding energy of -350 meV as compared to CO with -252 meV for the most stable orientation of the molecule, i.e. parallel adsorption. Quantum conductance calculations on AGNR-based nanosensor reveal conductance shifts compared to pristine AGNR, on the order of few meV for one and two molecules per two unit cells of AGNR. Higher concentrations, possible at low temperatures, can result in significant change of band gap for perpendicular adsorption owing to creation of impurity states. Comparing our results with available experimental data indicate the possibility of mechanism besides direct molecular adsorption on graphene, such as substrate and carrier gas doping, as well as adsorption on defects and/or electrodes, contributing to gas detection. Because of the rather low binding energy of physisorbed carbon oxide molecules, achieving high surface coverage at room temperature is not feasible. As low surface coverage does not significantly alter electronic and transport characteristics of graphenenanoribbons, these systems, in their pristine/undoped/defect-free state, may not be suitable for electrochemical sensing of carbon oxides with low concentration at room temperature. Applying electric field perpendicular to the GNR surface can help orient the molecules perpendicular to the lattice and generate higher, more detectable, surface coverages. This approach, possibly combined with substrate and/or carrier gas doping, can also position the Fermi energy at a region of the band structure such that small energy shifts produced by adsorbed molecules can have detectable sensing outcome.

For adsorption of one and two NO₂ molecules on graphenenanoribbons (GNRs), five geometries are found to be stable by first principles calculations: hydrogen bonded, physisorbed, chemisorption at edge through nitrogen atom, chemisorption at edge through oxygen atom, and chemisorption at center through oxygen atom. Formation of
hydrogen bonded and physisorbed cases have no energy barriers, whereas energy barriers ranging from 0.759 to 1.101 eV need to be overcome for chemisorption. Reaction rate calculations indicate that chemisorption at the edge through nitrogen is the most probable. Chemisorption of NO$_2$ results in weak $sp^3$ bonding and significant conductance modulations, while such modulations are detectable only at higher concentration for hydrogen bonded case. GNR edges provide hydrogen bonding sites and assist change of lattice hybridization, resulting in better sensor performance compared to two-dimensional graphene. A major part of the chemisorption energy barrier corresponds to transforming planar $sp^2$ lattice into deformed (weak) $sp^3$ state. Therefore chemisorption is more possible at folds and ripple, which can be externally induced, owing to reduced energy barrier because of pre-deformation. Strong quantum transport modulation, even for extremely low NO$_2$ concentrations, is predicted to improve detection characteristics of such GNR-based gas nanosensor.

We also address the issue of room-temperature effects on electronic transport modulations in AGNR used as a gas sensor. Coherent (excluding electron-phonon interactions) and non-coherent (including electron-phonon interactions) transports are calculated using nonequilibrium Green's function formalism and Born approximation. The non-coherent contributions arising from CO and CO$_2$ vibrations turn out to be a few orders of magnitudes less than the coherent transmission, with low-energy molecular vibrations having a larger effect than that of high-energy ones. We discuss the contribution of each phonon mode to electron transmission, and assess the thermal stability of sensor response for AGNR-based CO and CO$_2$ nanosensors at various temperatures.
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APPENDIX

Appendix A

PUBLICATIONS


• K. K. Paulla, C. Knick, A. H. Deer, A. A. Farajian, “Energetics, kinetics and transport features of NO2 sensing on graphene nanoribbons from First Principles” Submitted for publication. (June/2013)
Appendix B

PRESENTATIONS: Major International Conferences (abstract refereed and published)

1. K. K. Paulla, A. A. Farajian; Conduction modulation in Bilayer Graphene Nano-Ribbons; Materials Research Society (MRS), Boston, Massachusetts, USA, 2009 Fall meeting, Abstract # L6.4

2. K. K. Paulla, A. A. Farajian; Armchair Graphene Nano-Ribbon Nano-sensors for detection of individual gas molecules; Materials Research Society (MRS), Boston, Massachusetts, USA, 2010 Fall meeting. Abstract # B5.27

3. A. A. Farajian, K. K. Paulla; Electron-phonon interactions and room temperature transport in graphenenanoribbons with defects: An ab initio study; Materials Research Society (MRS), Boston, Massachusetts, USA, 2011 Fall meeting. Abstract # W8.3

4. K. K. Paulla, A. A. Farajian; Finite temperature quantum transport in nanosensors based on graphene nanoribbons;; American Physical Society (APS), Boston, Massachusetts, USA, 2012 March meeting. Abstract # H12 15