

Adsorption Performance of Pristine and Functionalized C₁₈ towards Hazardous Gases

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Introduction

The world is experiencing a pollution problem as a result of the rapid industrial growth and increase in the global population. Fossil fuels are one of the main sources of energy used worldwide, and when they are burned improperly in factories and automobiles, extremely dangerous petrol pollutants like carbon monoxide (CO) and nitrogen monoxide (NO) are released into the atmosphere^[1]. Both gases are invisible "silent killers" since they have no colour, smell, or taste^[2]. While the NO gas molecule irritates the skin, eyes, and mucous membranes, it quickly interacts with ozone or atmospheric radicals to produce NO₂, the prolonged exposure to CO causes loss of consciousness along with cardiac irregularities and deadly respiratory problems^[3].

Ammonia (NH₃) another toxic gas which is also colorless but most abundant nitrogen containing compounds in the environment. It is building block for the synthesis of many pharmaceuticals. It is used in many cleaning products but its high concentrated form is very hazardous to human body which causes diseases of the lower airways and interstitial lung^[4]. Acute exposure to high level of NH₃ in our environment may be irritating to human skin, throat, eyes, and lungs and cause coughing and burns. Lung damage and death are also possible after exposure to very high concentration of NH₃^[5]. HCN, often known as hydrogen cyanide, is one more toxic chemical that is frequently employed in mining, chemical synthesis, electroplating, fumigation, and the manufacture of synthetic fibres, plastics, dyes, and insecticides^[6]. HCN is most frequently encountered in the gaseous state at room temperature due to its volatility and low boiling point (25.6 °C) and employees from the aforementioned locations run the risk of inhaling this deadly gas^[7]. As it interferes with cellular respiration, such exposure to HCN can have devastating effects on the brain, heart, blood vessels, and lungs^[8]. Due to the contamination of our environment and human life, tracing these hazardous gases is a very serious topic, and therefore solid-state gas sensing technology is being needed in daily life and various commercial

businesses.

On account of its allotropy, carbon has grabbed the interest of many researchers. Allotropes range from diamond to graphite, with properties that differ from each other^[9]. Due to their distinctive structural, electronic, chemical, optical, and sensing properties, the most famous sp^2 hybridized allotrope of the carbon family—two-dimensional (2D) structured graphene^[10] and graphene oxide, one-dimensional (1D) materials like carbon nanotubes^[11], and zero-dimensional (0D) structures like fullerene nanocages^{[12][13]} have been used in a variety of diverse fields, including hazardous gas sensing. For a variety of uses, other carbon allotropes including carbon rings with hybridization (sp or sp^2) and graphdiyne with mixed hybridization (sp^2 - sp) are also being researched^[14]. C_n nanoclusters are notable for their role in the synthesis of conducting polymers, thin solid diamond sheets, nanotubes, fullerenes, and carbon clusters; depending on their configuration and dimensions^[15].

However, there is still a lack of an in-depth understanding of complex cluster formations and their essential features in comparison to smaller ones. Carbon cluster properties vary depending on their topologies and dimensions, ranging from carbon atom chains to ring-like formations, nano-cages to tubes^[16]. Following that, the synthesis of different carbon clusters and isomers emerges as a promising low-cost application sector. The newest carbon allotrope, an 18 carbon sp -hybridized ring, was added in 2019. In the year 2019, Kaiser et al.^[17] successfully synthesised cyclo[18]carbon, or C_{18} . Unlike the other allotropes, it is sp -hybridized with two-fold coordination. Since its synthesis, it has gotten a lot of attention. The C_{18} nanocluster is believed to have outstanding sensing properties because it is the smallest all-carbon electron acceptor^[14]. The present thesis explores the application of pristine and functionalized C_{18} nanocluster as a potential candidate in hazardous gas sensing or removal devices.

Objectives

Our aim is to provide the better understanding of physical and chemical properties of the C₁₈ nanocluster and detailed study of the transition metal and other impurity atom doping induced characteristic of the C₁₈. The main focus of this work is to investigate the effect of the functionalization on electronic and optical properties to analyse the change in adsorption performance of hazardous gas on the C₁₈. The primary objective of this thesis is to provide the understanding of enhancement of adsorption performance of hazardous gas before and after tuning properties of the C₁₈ nanocluster.

However, the specific objectives are:

1. To determine the ground state and stable geometric structure of the C₁₈ nanocluster.
2. To study the electronic structure of C₁₈ and to tune the electronic properties by functionalization.
3. To study the stabilization of the C₁₈ specific sites with hazardous gases.
4. To understand the surface chemistry of C₁₈ with various hazardous gases.
5. To investigate the work function for better understanding of sensing behaviour.
6. Also, to calculate adsorption energy, work-function, recovery time, conductivity and so on.

Summary of Research Work

The present thesis is organized in the following manner.

Chapter 1: Introduction

The chapter explains the need for hazardous gas sensing. In addition, various examples of carbon based nanomaterials and allotropes as gas sensors have been explored. The techniques for synthesis of C₁₈ and its significant properties are addressed^{[17][18]}. Chapter 1 also introduces the properties of carbon allotropes and explains why the quest for novel carbon nanomaterials is always

coveted. It also briefly explores the need of impurity doping (substitution and decoration) in carbon nanomaterials for enhancing the adsorption performance. The current technological progresses in the properties of C₁₈ on theoretical aspects are highlighted as well.

Chapter 2: Theoretical Framework

Theoretical description of computational methodology used throughout the work is presented in this chapter. Formalism of DFT by discussing Kohn-Sham equation^[19] to its implementation in Gaussian 09 package^[20] is discussed. Exchange-correlation along with basis sets is discussed. Time-dependent density functional theory^[21] (TD-DFT) is briefly described. Finally, applications of quantum chemical methods like geometry optimization, frequency, molecular orbitals, dipole moment, and UV spectra calculations are given in present chapter.

Chapter 3: Prediction of Pristine C₁₈ Nanocluster as a Hazardous Gas Sensor

In this chapter, the adsorption performance of the gases CO, NO and NH₃ with C₁₈ nanocluster has been investigated using DFT calculation. We have analyzed structural, electronic and sensing properties of C₁₈ along with Raman spectra to understand the sensing behaviour. We observed the CO and NO molecules show chemisorption whereas NH₃ molecule shows physisorption towards C₁₈ nanocluster. The decrement of HOMO-LUMO gap after adsorption shows increment in conductivity, which is good gesture for sensor application^[22]. The fast recovery time of C₁₈ (nanosecond to femtosecond) for CO and NO adsorption, make it portable and its abundance in nature as low-cost gas sensors^[23]. In nutshell, the analysis of adsorption and electronic properties suggest that the C₁₈ nanocluster can be used as the ultra-fast hazardous gas sensor. Figure 1 graphically represents adsorption performance of pristine C₁₈ nanocluster towards CO, NO, and NH₃ gas molecules.

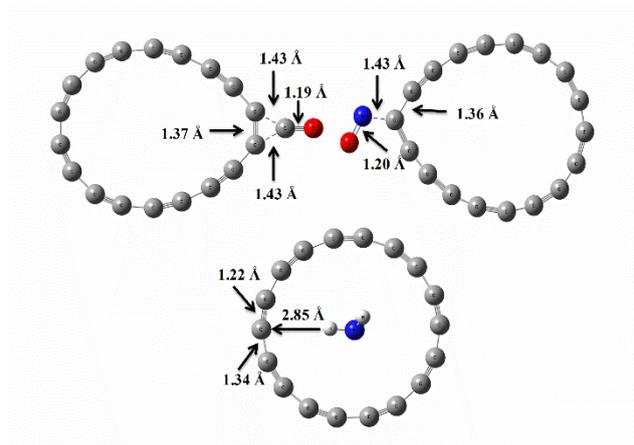


Figure 1: Minimum energetic optimized geometry of the carbon monoxide (CO) and nitrogen monoxide (NO) and ammonia (NH₃) gas molecules adsorbed C₁₈ nanocluster along with structural changes, respectively.

Chapter 4: Effect of Boron and Nitrogen Doping on Molecular Adsorption

Doping is one of the most important mechanisms used to enhance the molecular adsorption performance of bulk and nanostructures^[13]. In this chapter, we have investigated the adsorption performance of Boron and Nitrogen doped C₁₈ nanocluster or C₁₇X (X=B,N) towards the gases CO, NO and NH₃ by means of first principles calculations. The structural, electronic, and sensing properties of C₁₇X nanoclusters are studied to understand its sensing behavior, using Gaussian 09 package^[24]. The interaction of C₁₇B nanocluster with CO, NO and NH₃ molecules results into chemical adsorption. The order of adsorption energies is: CO (-1.41 eV) > NH₃ (-1.81 eV) > NO (-2 eV). However, in case of C₁₇N, the interaction with CO and NH₃ results into physisorption, and chemisorption is observed only for its interaction with NO gas molecule. The adsorption energy order goes as: CO (-0.15 eV) > NH₃ (-0.25 eV) > NO (-1.32 eV)^[25]. The long recovery time in case of C₁₇B nanocluster after the adsorption, makes it suitable for removal applications, whereas shorter recovery time (in case of C₁₇N nanocluster for CO and NH₃ adsorption), is suitable for sensor applications. The molecular adsorption of the gases CO, NO and NH₃ over C₁₇B and C₁₇N nanoclusters, yields changes in structural properties of the nanoclusters. As it is evident from the figure 2, the adsorptions of CO and NH₃ over C₁₇N

nanocluster are physisorption type, the rest are chemisorption.

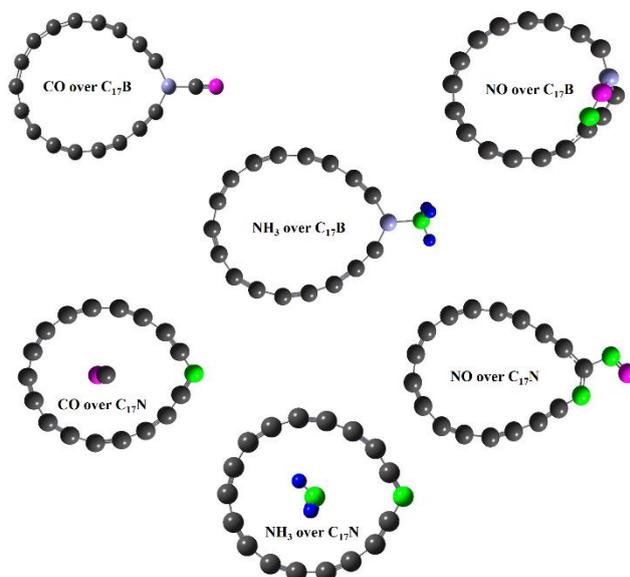


Figure 2: Minimum energetic optimized geometry of the carbon monoxide (CO) and nitrogen monoxide (NO) and ammonia (NH₃) gas molecules adsorbed C₁₇B and C₁₇N nanoclusters, respectively.

Chapter 5: Transition Metal-decorated C₁₈ as a CO, NO, and NH₃ Scavenger

In this chapter, again the CO, NO, and NH₃ gases have been considered to observe their adsorption performance over transition metal (Ni, Pd and Pt) decorated C₁₈ nanocluster. The reason for choosing transition metals as impurity atoms is: the impurity decoration of transition metal atom improves adsorption. Which is due to the orbital interaction and the charge transfer from the 3d orbitals of the transition metals to the 2p orbitals of oxygen atoms in CO and NO molecules, and 2p orbital of N-atom in NH₃ molecule^[26]. The dispersion corrected hybrid ω B97XD^[27] has been chosen with LanL2DZ^[28] basis set implemented by Gaussian 09 package. Apart from the sensing properties, the structural, electronic, and spectroscopic properties have also been explored. Appreciable adsorption energies and long computed recovery times indicate chemisorption and imply that the transition metal-decorated C₁₈ nanocluster can be used in removal application of CO, NO, and NH₃ gases, from specific environments^[29].

Chapter 6: Adsorption of HCN on Al, Si, and P-decorated C₁₈ Nanocluster

Hydrogen cyanide (HCN) is a poisonous compound that is likely to be found in a gaseous form due to its high volatility^[30]. Therefore, its tracing is necessary. In this chapter, we have studied adsorption properties of C₁₈ nanocluster towards HCN molecule. Pristine C₁₈ towards HCN yields negligible adsorption energy and large adsorption distance. For enhancement of interaction between HCN and C₁₈, we have decorated Al, Si, P atoms on C₁₈ nanocluster. After the decoration, we found that C₁₈Al nanocluster is most suitable candidate for HCN sensor due to optimal adsorption energy (-0.61 eV), adsorption distance (2.11 Å), and recovery time (17.7 ms).

Chapter 7: Summary and Future Scope

The last chapter of the thesis summarizes the entire work. It consists of a summary of results, conclusion, and future scope of the work.

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List of Publications related to Thesis

1. **Shardul Vadalkar**, Darshil Chodvadiya, Narayan N. Som, Keyur N. Vyas, Prafulla K. Jha, and Brahmananda Chakraborty. "An Ab-initio Study of the C₁₈ Nanocluster for Hazardous Gas Sensor Application." *ChemistrySelect* **7**, no. 3, e202103874 (2022).
2. **Shardul Vadalkar**, Darshil Chodvadiya, Narayan N. Som, Keyur N. Vyas, and Prafulla K. Jha. "Cyclo[18]carbon as a Hazardous Gas Scavenger: Effect of Boron and Nitrogen Doping on Molecular Adsorption." *ChemistrySelect* **8**, no. 23, e202204862 (2023).
3. **Shardul Vadalkar**, Darshil Chodvadiya, Heli Mistry, Narayan Som, Keyur N. Vyas, and Prafulla K. Jha. "A First Principles Prediction of Transition Metal-decorated C₁₈ Nanocluster as a Toxic Gas Scavenger: Study of Structural, Electronic, Spectroscopic, and Sensing Properties" (manuscript under preparation).
4. **Shardul Vadalkar**, Darshil Chodvadiya, Keyur N. Vyas, and Prafulla K. Jha. "Adsorption of HCN on Pristine and Al/Si/P Decorated C₁₈ Nanocluster: A First Principles Study." *Materials Today: Proceedings* **67**, 229-237 (2022). (conference paper)

List of Publications non-related to Thesis

1. Ashvin Kanzariya, **Shardul Vadalkar**, Sourav Jana, Keyur N. Vyas, L. K. Saini, and Prafulla K. Jha. "Adsorption of Hazardous Gas Molecules over Transition Metal-doped Graphene Quantum Dot: An Ab-initio Investigation for Sensing and Removal Applications" (submitted).

2. Heli Mistry, Darshil Chodvadiya, **Shardul Vadalkar**, Keyur N. Vyas, and Prafulla K. Jha. “Interaction Study of Pollutant CO and NO Gases with Pristine, Defected and Doped α -CX (X = N, P) Monolayers using Density Functional Theory” (submitted).
3. Akhilesh Gupta, **Shardul Vadalkar**, Keyur N. Vyas, and Prafulla K. Jha. “Medicinal Biomolecules Derived from Natural Autotrophs: A Quantum Chemical Study for Structural, Electronic and Reactivity Parameters” (manuscript under preparation).

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