CHAPTER 1
INTRODUCTION

1.1. Hazardous Gas Sensing

Millions of people around the world suffer from the imperative environmental issue of air pollution. It is triggered by the emission of hazardous gases into the atmosphere, which poses serious risks to ecosystems, human health, and the global climate. The causes of air pollution include industrial emissions, modes of transportation such as cars, buses, and trucks, agricultural activities such as the use of fertilizers, pesticides, and burning of crop residues, household activities such as cooking with fossil fuels and using heating appliances, as well as the presence of indoor pollutants like tobacco smoke. Additionally, natural events such as volcanic eruptions, wildfires, and dust storms release natural pollutants into the air [1]. As mentioned earlier, the air pollution causes the release of multiple hazardous gases. Some of the hazardous gases are described below.

Carbon monoxide (CO) is a colorless, odorless, and highly toxic gas. It is produced by incomplete combustion of carbon-containing fuels, such as gasoline, natural gas, and coal. CO is a major concern in indoor environments with poor ventilation, as it can accumulate and pose significant health risks [2]. Inhalation of CO can lead to symptoms ranging from mild headache, dizziness, and nausea to severe poisoning, coma, and even death. Due to its toxic nature and potential for accidental exposure, the accurate detection and monitoring of CO are crucial for ensuring safety in various settings [3]. Nitrogen monoxide (NO), also known as nitric oxide, is a colorless gas with a pungent odor. It is produced by combustion processes and is an important component of air pollution [4]. NO plays a role in atmospheric chemistry, contributing to the formation of pollutants such as nitrogen dioxide (NO_2) and ozone (O_3). In high concentrations, NO can have detrimental effects on human health, particularly on the respiratory system. It can cause respiratory irritation, lung damage, and exacerbate existing respiratory conditions. Monitoring and controlling NO emissions are essential for minimizing air pollution and protecting human health.

Ammonia (NH_3) is another toxic and colorless gas with a strong, pungent odor. It is produced naturally by decomposition processes and is also widely used in industrial applications, agriculture, and cleaning products [5]. NH_3 is commonly encountered in agricultural settings, such as livestock farms, where it is released from animal waste and fertilizers. It is highly soluble in water and can pose risks to aquatic life in case of water pollution. Exposure to high concentrations of NH_3 can cause eye, nose, and throat irritation, as well as respiratory problems. Effective monitoring and control of NH_3 emissions are important for minimizing its impact on human health and the environment. Hydrogen cyanide (HCN) is a highly toxic and volatile gas with a bitter almond-like odor. It is primarily produced by certain industrial processes, such as the burning of plastics and the extraction of precious metals. HCN is extremely hazardous and poses significant health risks even at low concentrations. Inhalation of HCN can lead to symptoms ranging from headache, dizziness, and confusion to respiratory distress, seizures, and cardiac arrest. Due to its high toxicity and potential for exposure in industrial settings, accurate detection and monitoring of HCN are critical for ensuring worker safety and preventing accidental poisoning [6].

In a nutshell, hazardous gas sensing is a crucial tool for protecting human health and the environment by detecting potential risks. Utilizing sensors, helps identify potential risks, enabling timely interventions, and promoting a safer living environment. By providing real-time data, it helps prevent accidents and minimize toxic exposure, ensuring a sustainable future.

1.2. Carbon Allotropes as Gas Sensors

Researchers have been focused on the manufacturing and development of environmental hazardous gas sensors and adsorbents for the past few years. It has been investigated how several carbon allotropes, including fullerene (C_{60}), graphene, graphene nanoribbons, graphene quantum dots, and carbon nanotubes, can be used to detect dangerous chemicals like CO, NO, and NH_3 [7-9]. Wang et al. investigated graphene's capacity to detect CO gas molecules and discovered that the CO gas molecules interact physically with graphene at adsorption energies and distances of 0.01 eV and 3.85, respectively [10]. However, aluminium (Al) doping modifies the adsorption energy and adsorption distance (-2.69 eV and 2.06 Å) to alter the interaction type from physisorption to chemisorption [11]. According to Zhang et al., the physisorption and chemisorption of NO gas on pristine and Ti or N-doped graphene sheets, respectively, is observed [12]. Research using density functional theory (DFT) also shows that NH_3 gas adsorption performance on pure graphene surfaces is relatively subpar, similar to that of CO and NO gases [5]. The CO, NO, and NH_3 adsorption capabilities on the un-doped (Sc, Ti, V, Cr, and Al) carbon nanotubes exhibit physisorption interaction with low adsorption energy and high adsorption distance. Apart from to graphene and carbon nanotubes, other carbon allotropes such as armchair graphene nanoribbons, zigzag graphene nanoribbons, graphene quantum dots, and graphene sheets exhibit a similar trend of gas adsorption [13-15]. However, novel materials remain sought after, even if the majority of allotropes have been employed for hazardous gas sensing.

1.3. Novel Carbon Allotropes and Cyclo[n]carbons

Carbon allotropes are a diverse and fascinating group of materials that have captured the interest of researchers across various fields. While graphene, carbon nanotubes (CNTs), and fullerenes (such as C_{60}) are well-known carbon allotropes, there are indeed many other intriguing structures that have been experimentally synthesized and studied, including C_{70} and C_{36} fullerenes [16]. Additionally, cyclo[n]carbons have also been attracting researchers due to their distinct properties and potential applications. Cyclo[n]carbons, represented by the formula C_n, are intriguing structures composed of rings of 2-coordinate carbon atoms [17]. These molecular carbon allotropes have attracted significant interest as a potential alternative family of carbon materials. However, their existence and properties have been a subject of debate and exploration due to their highly reactive and elusive nature.

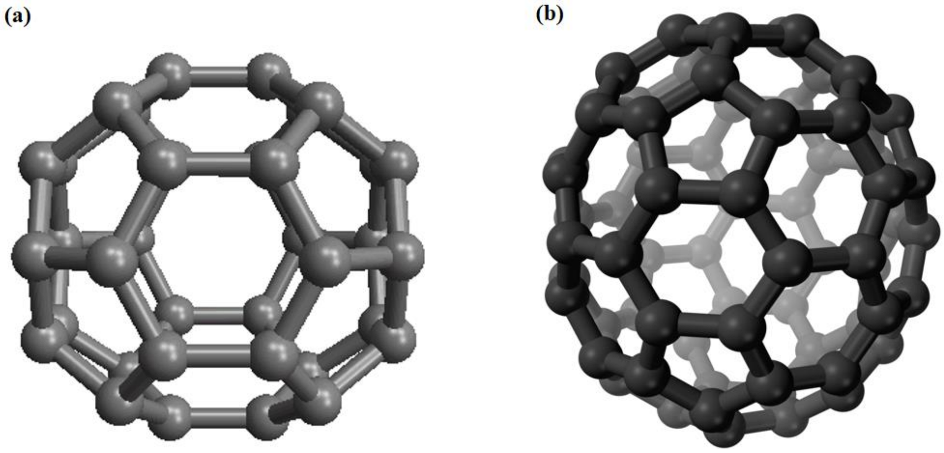

Figure 1.1: Structural Models of (a) C_{36} (b) C_{70} fullerene

In the gas phase, there are evidences that suggest the presence of cyclocarbons, but these species had not been structurally characterized or extensively studied in condensed phases. The challenges lie in their high reactivity and instability, which make their synthesis and isolation difficult. One of the fundamental and controversial questions surrounding cyclo[n]carbons is their structural arrangement. It remains uncertain whether these carbon rings are polyynic, featuring alternating single and triple bonds of varying lengths, or cumulenic, where consecutive double bonds are present. This structural ambiguity arises due to the highly strained nature of the carbon rings and the potential for different bonding patterns. Resolving the debate between polyynic and cumulenic structures is crucial for understanding the electronic and mechanical properties of cyclo[n]carbons and their potential applications [17]. However, due to the challenges in experimental characterization, theoretical studies using computational methods like density functional theory (DFT) have provided valuable insights into the structural and electronic properties of these carbon allotropes. However, researchers continued exploring novel synthesis methods and innovative techniques to stabilize and study cyclo[n]carbons in condensed phases. Such advancements paved the way for deeper investigations into their properties and potential applications in nanotechnology and materials science. In one such advancement, researchers managed to successfully synthesize an 18 atom C_n ring [18].

1.4. New Addition in the Family of Carbon Allotropes: C_{18}

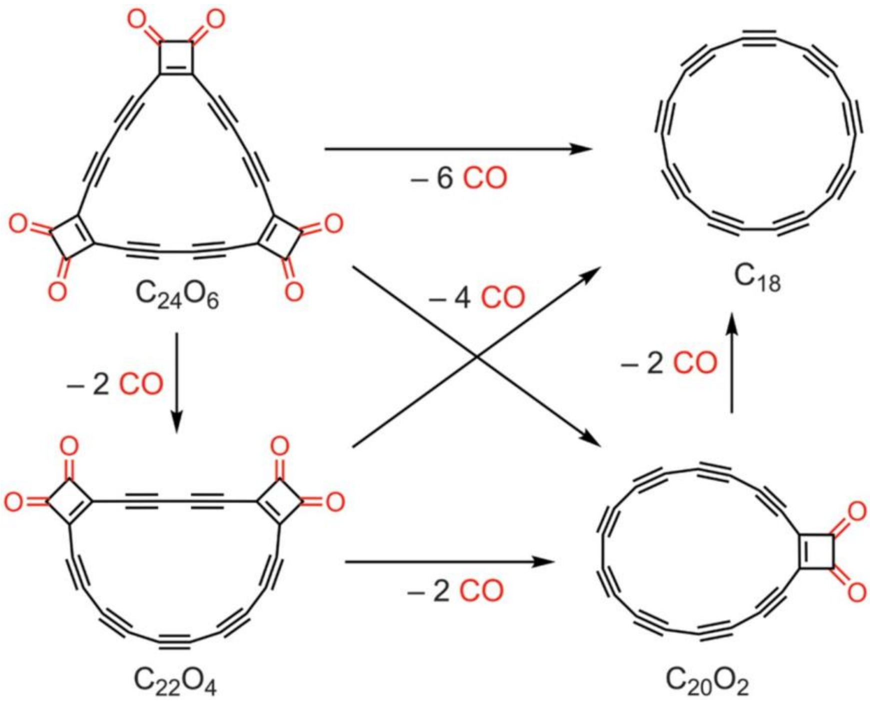

Figure 1.2: Reaction Scheme for the Formation of C_{18}

In a remarkable breakthrough, Kaiser et al. successfully synthesized and isolated cyclo[18]carbon (C_{18}) in 2019, marking a significant milestone in the field of carbon allotropes. Cyclo[n]carbons, which are composed of rings of two-coordinate atoms, have long fascinated chemists due to their unique structural properties [18]. However, their high reactivity and instability have posed significant challenges in their isolation and structural characterization [19]. The successful synthesis of C_{18} involved a pioneering approach utilizing atom manipulation on a bilayer of sodium chloride (NaCl) on a copper (Cu) substrate at an ultra-low temperature of 5 Kelvin. By carefully manipulating the arrangement of atoms on the surface, the researchers were able to eliminate carbon monoxide (CO) molecules from a precursor known as cyclocarbon oxide ($C_{24}O_6$), resulting in the formation and isolation of C_{18} ring [20].

The reaction scheme of the synthesis can be seen in figure 1.2. This groundbreaking achievement showcased the potential of atom manipulation techniques in controlling the formation and stability of highly reactive carbon allotropes.

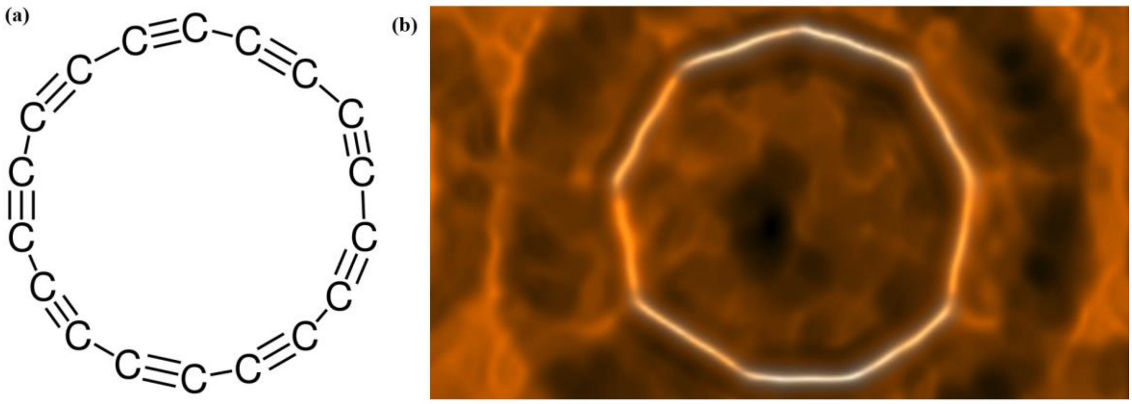

Figure 1.3: (a) Structural Formula (b) Experimentally Realized Structure through AFM for C_{18}

To characterize the structure of the synthesized C_{18}, high-resolution atomic force microscopy (AFM) was employed. The AFM analysis revealed a distinctive polyynic structure for C_{18} (see figure 3), with clearly defined positions of alternating triple and single bonds. This observation confirmed the long-standing theoretical predictions and provided experimental evidence for the existence of C_{18} as a stable cyclo[n]carbon [18]. The successful synthesis and structural characterization of C_{18} not only represent a significant advancement in the understanding of cyclo[n]carbons but also open up new possibilities for the synthesis of other carbon-based materials. The high reactivity of cyclocarbon and cyclocarbon oxide species [21] allows for induced covalent coupling between molecules through precise atom manipulation, paving the way for the synthesis of diverse carbon-rich materials with tailored structures and properties. The present thesis explores the application of pristine and functionalized C_{18} nanocluster as a potential candidate in hazardous gas sensing or removal devices.

1.5. Research Objectives

Our primary goal is to advance our comprehension of the physical and chemical properties of the C_{18} nanocluster and conduct an in-depth examination of the distinct characteristics brought about by the functionalization of transition metals and other impurity atoms within C_{18}. Our central emphasis in this research is to explore how functionalization impacts the electronic and optical properties, thereby influencing the adsorption performance of hazardous gases on C_{18}. The core objective of this thesis is to offer insights into the enhancement of gas adsorption capabilities in C_{18} nanoclusters through property modifications.

Outlined below are the specific objectives guiding our study:

1. To ascertain the ground state and identify the stable geometric structure of the C_{18} nanocluster.
2. To comprehensively analyze the electronic structure of C_{18} and investigate methods to tailor its electronic properties through functionalization.
3. To understand how the specific sites of C_{18} interact and stabilize when exposed to hazardous gases, shedding light on the adsorption mechanisms.
4. To elucidate the interaction mechanism between the surface of C_{18} and various hazardous gases.
5. To calculate the work function of C_{18} to gain deeper insights into its sensing behavior, particularly concerning gas adsorption.
6. Finally, to quantify various parameters such as adsorption energy, work function, recovery time, and conductivity, among others, to comprehensively evaluate the adsorption performance of C_{18} nanoclusters in different scenarios.

Theoretical description of computational methodology used throughout the work is presented in the **chapter 2**. Formalism of DFT by discussing Kohn-Sham equation to its implementation in Gaussian 09 package [22] is discussed. Exchange-correlation along with basis sets is discussed. Time-dependent density functional theory (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 this chapter.

The adsorption performance of the gases CO, NO, and NH_3 with C_{18} nanocluster has been examined using DFT calculations [23] in **chapter 3**. To understand the sensing behaviour, we examined the structural, electrical, and sensing properties of C_{18}, as well as Raman spectra. We discovered that CO and NO molecules chemisorb while NH_3 molecules physisorb towards the C_{18} nanocluster. The decrease in HOMO-LUMO gap following adsorption results in an increase in conductivity, which is a positive sign for sensor applications. The quick recovery time (nanosecond to femtosecond) of C_{18} for CO and NO adsorption makes it portable, and its abundance in nature makes it suitable for low-cost gas sensors. In a nutshell, the adsorption and electrical properties of the C_{18} nanocluster imply that it can be employed as an ultra-fast hazardous gas sensor.

One of the most significant methods of enhancing the molecular adsorption performance of bulk and nanostructures is doping. In the **chapter 4**, we have investigated the adsorption performance of Boron and Nitrogen doped C_{18} nanocluster or $C_{17}X$ (X=B,N) towards the gases CO, NO and NH_3 by means of first principles calculations [24]. The structural, electronic, and sensing properties of $C_{17}X$ nanoclusters are studied to understand its sensing behavior, using Gaussian 09 package. The interaction of $C_{17}B$ nanocluster with CO, NO and NH_3 molecules results into chemical adsorption. The order of adsorption energies is: CO (-1.41 eV) > NH_3 (-1.81 eV) > NO (-2 eV). However, in case of $C_{17}N$, the interaction with CO and NH_3 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) > NH_3 (-0.25 eV) > NO (-1.32 eV). The long recovery time in case of $C_{17}B$ nanocluster after the adsorption, makes it suitable for removal applications, whereas shorter recovery time (in case of $C_{17}N$ nanocluster for CO and NH_3 adsorption), is suitable for sensor applications. The molecular adsorption of the gases CO, NO and NH_3 over $C_{17}B$ and $C_{17}N$ nanoclusters, yields changes in structural properties of the nanoclusters.

In **chapter 5**, the adsorption performance of CO, NO, and NH_3 gases on transition metal (Ni, Pd, and Pt) decorated C_{18} nanoclusters was investigated once more. The reason for using transition metals as impurity atoms is that their impurity ornamentation increases adsorption. This is due to orbital contact and charge transfer from the transition metals' 3d orbitals to the 2p orbitals of oxygen atoms in CO and NO molecules, and the 2p orbital of N-atom in NH_3. The dispersion corrected hybrid ωB97XD with LanL2DZ basis set developed by Gaussian 09 package was used. In addition to sensing properties, structural, electronic, topological, and spectroscopic properties have been investigated. Appreciable adsorption energies and long computed recovery times indicate chemisorption and imply that the transition metal-decorated C_{18} nanocluster can be used in removal application of CO, NO, and NH_3 gases, from specific environments.

Hydrogen cyanide (HCN) is a hazardous chemical that is most frequently found in gaseous form due to its high volatility. As a result, tracing it is required. In **chapter 6**, we investigated the adsorption characteristics of C_{18} nanoclusters towards HCN molecule [25]. Adsorption of pure C_{18} towards HCN results in minimal adsorption energy and a considerable adsorption distance. We coated Al, Si, and P atoms on a C_{18} nanocluster to improve interaction between HCN and C_{18}. Following decorating, we discovered that $C_{18}Al$ nanocluster is the best choice for HCN sensor due to its optimum adsorption energy (-0.61 eV), adsorption distance (2.11), and recovery time (17.7 ms).

The final chapter of the thesis (**chapter 7**) summarises the entire work. It includes a summary of the results, the conclusion, and the future scope of the research.

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