CHAPTER 7
SUMMARY AND FUTURE PROSPECTS

7.1. THESIS IN A NUTSHELL

The present thesis investigated the adsorption capabilities of both pristine and modified C_{18} nanoclusters concerning hazardous gases. It began with an exploration of needs for other gas sensing and has introduced the significance of carbon allotropes focusing on C_{18} synthesis techniques and impurity doping for enhanced adsorption. Theoretical frameworks utilising Density Functional Theory (DFT) methods have been established laying the groundwork for subsequent analysis. The study evaluated adsorption performance of pristine C_{18} towards CO, NO, NH_3, and HCN gases showcasing option and physics option behaviour suggesting its potential as a hazardous gas sensor.

The sections that follow, describe briefly the outcome of all investigations presented in different chapters of the thesis starts with an extensive overview of the necessity for hazardous gas sensing, emphasizing the pressing issue of air pollution worldwide. The first chapter underscored the detrimental effects of gases like carbon monoxide (CO), nitrogen monoxide (NO), ammonia (NH_3), and hydrogen cyanide (HCN) on environmental ecosystems and human health. Furthermore, it explored the utilization of diverse carbon allotropes, including graphene, carbon nanotubes, and fullerene derivatives, in detecting and analyzing hazardous gases. Investigations utilizing Density Functional Theory (DFT) demonstrated the interaction between these carbon allotropes and gas molecules such as CO, NO, and NH_3, highlighting their potential applications in gas sensing technology. The chapter also delved into the fascinating world of novel carbon allotropes, particularly focusing on cyclo[n]carbons. It discussed their structural arrangements, remarkable reactivity, and the challenges involved in their experimental characterization. Theoretical studies, employing computational methods like DFT, offered valuable insights into their properties, while advancements in synthesis methods paved the way for further exploration and potential applications in nanotechnology. Shifting focus to the pioneering synthesis and structural characterization of cyclo[18]carbon (C_{18}) in 2019, this chapter highlighted a significant milestone in carbon allotrope research. This set the stage for exploring the application of pristine and functionalized C_{18} nanoclusters in hazardous gas sensing or removal devices, presenting a promising avenue for future research and development.

Our investigations using DFT, explored the structural, electronic, vibrational, and adsorption properties of toxic gas molecules on the C_{18} nanocluster. The study aimed to understand how these molecules interacted with the nanocluster, foreshadowing its potential

applications in gas sensing. The stability of C_{18}, confirmed by its negative formation energy and the absence of imaginary frequencies in Raman and IR plots. Adsorption studies revealed intriguing behaviours: CO and NO gas molecules exhibited short adsorption distances and low energies, indicating a chemisorption process with the nanocluster. On the other hand, NH_3 gas showed notably longer adsorption distances, suggesting a physisorption behaviour on the C_{18} nanocluster surface. Examining charge transfer during adsorption uncovered interesting insights. The transfer of charges from the C_{18} to CO and NH_3 gas molecules, and vice versa with the NO gas molecule, led to the variation in dipole moments. Additionally, the reduction in the HOMO-LUMO gap post-adsorption pointed to an increase in electrical conductivity, hinting at the potential of the C_{18} nanocluster as a conductivity based gas sensor. The analysis of electron densities surrounding the adsorbed gas molecules further supported the distinction between chemisorption and physisorption. The concentration of electron densities near CO and NO gas molecules aligned with their chemisorption behaviour, while their absence near NH_3 gas molecules supported the idea of physisorption. A significant finding was the calculated short recovery time for CO and NO gas molecules, suggesting the potential use of the C_{18} nanocluster as a 'rapid-response gas sensor.'

The present work also examined the geometric, electrical, and sensing properties of both doped and pure polyynic cyclo[18]carbons. On the pristine C_{18}, the gases (CO, NO, and NH_3) were found to undergo physisorption. Introducing boron and nitrogen doping led to reductions in the HOMO-LUMO gap by 8.75% and 29.9%, respectively. Nitrogen doping resulted in only NO (-1.32 eV) exhibiting chemisorption, while the other gases displayed physisorption. Conversely, all three gases (CO, NO, and NH_3) exhibited chemisorption upon boron doping, with adsorption energies ranking as follows: CO (-1.41 eV) > NH_3 (-1.81 eV) > NO (-2 eV). The $C_{17}B$ nanocluster demonstrates potential as a conductivity-based (σ-type) sensor for CO and NO gases, given that a material's sensing response relies on the relative change in electrical conductivity. However, the calculated recovery time for $C_{17}B$ appears relatively lengthy, potentially suggesting its utilization as a gas molecule remover or molecular adsorbent for reservoir applications. On the contrary, for $C_{17}N$, the adsorption energy sequence is CO (-0.15 eV) > NH_3 (-0.25 eV) > NO (-1.32 eV). This implies a quick recovery period for CO and NH_3 adsorption, hinting at the potential utility of the $C_{17}N$ nanocluster in CO and NH_3 gas sensor applications.

The present thesis conducted a thorough examination of the structural, electronic, topological, spectroscopic, and sensing attributes of $C_{18}TM$ nanoclusters in their interactions

with the toxic gases CO, NO, and NH_3. The calculated adsorption energies consistently exhibited a strong attraction, consistently displaying notably negative values across all scenarios. Notably, we observed a significant sensing reaction, especially regarding NO over $C_{18}Ni$ and CO over $C_{18}Pd$ nanoclusters, indicating their potential usefulness in conductivity-based sensors. The Quantum Theory of Atoms in Molecules (QTAIM) revealed the strength of each interaction, offering valuable insights into the bonding nature within these systems. Similarly, our analysis of Raman spectra illuminated the vibrational characteristics linked to these interactions. Moreover, the Non-Covalent Interaction (NCI) analysis effectively outlined the mechanisms governing van der Waals interactions. An intriguing outcome concerns the prolonged recovery times identified in our calculations, attributable to the highly negative adsorption energies. This extended desorption duration implies that $C_{18}TM$ nanoclusters might be more suited for removing CO, NO, and NH_3 gases rather than serving as quick-response sensors.

The Density Functional Theory was finally utilized to explore the structural, electronic, and molecular adsorption attributes of HCN on C_{18}, $C_{18}Al$, $C_{18}Si$, and $C_{18}P$ nanoclusters. The pristine C_{18} nanocluster revealed physisorption behaviour when interacting with the HCN molecule, characterized by a considerable adsorption distance of 3.01 Å and a minimal adsorption energy of -0.24 eV. To enhance adsorption efficiency, dopants (decorative atoms) in the form of Al, Si, and P were introduced. The adorned nanoclusters displayed negative binding energy and negative formation energy, indicating a robust interaction between the dopants and the C_{18} nanocluster, ensuring structural stability. However, it's important to note that $C_{18}Al$, $C_{18}Si$, and $C_{18}P$ nanoclusters also exhibited physisorption behaviour when interacting with the HCN molecule. Among these, the adsorption energy of the HCN molecule on $C_{18}Al$ was notable (-0.61 eV), with a short adsorption distance of 2.11 Å. Particularly noteworthy is recovery time for $C_{18}Al$ being 17.7 ms, making it the most promising candidate for an HCN sensor among the discussed nanoclusters.

Figure 7.1 illustrates the objectives achieved in this thesis with a flowchart. Table 7.1 highlights the crucial adsorption properties of the C_{18} nanocluster both before and after the process of doping and decoration.
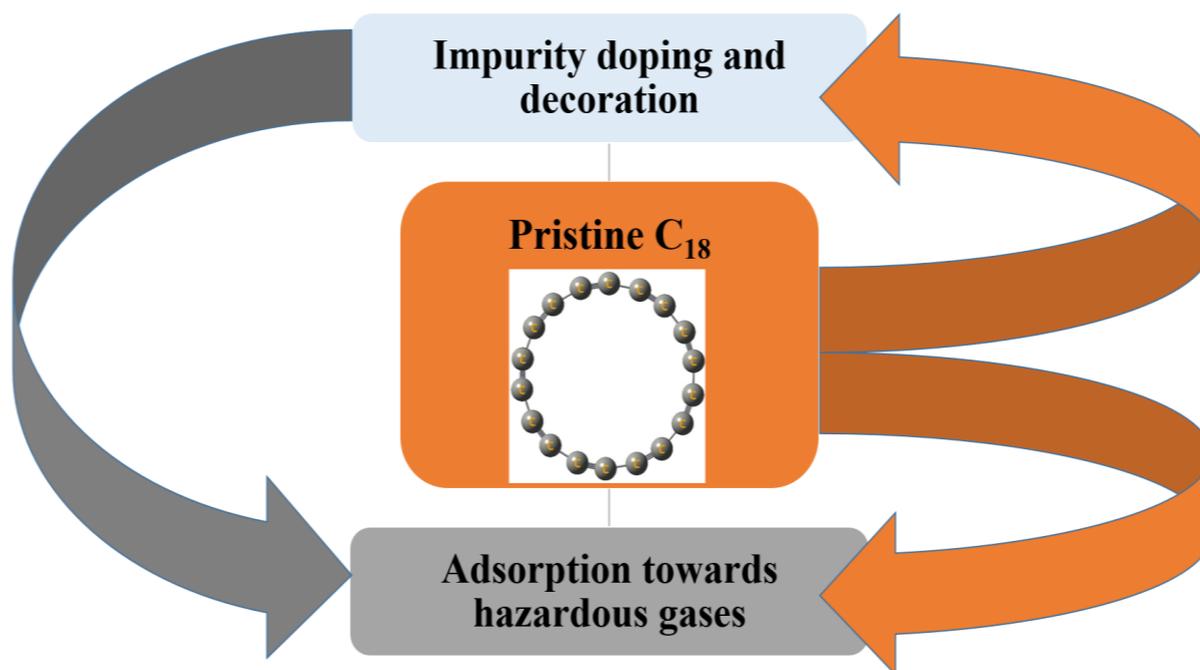
Figure 7.1: Objectives Achieved in the Thesis

Table 7.1: adsorption properties of the C_{18} nanocluster both before and after the process of doping and decoration

System	CO adsorption		NO adsorption		NH₃ adsorption		HCN adsorption	
	E_{ad} (eV)	d (Å)	E_{ad} (eV)	d (Å)	E_{ad} (eV)	d (Å)	E_{ad} (eV)	d (Å)
Pristine C_{18}	-0.31	1.43	-0.29	1.43	-0.23	2.85	-	-
$C_{17}B$	-1.41	1.51	-2.00	1.42	-1.81	1.59	-	-
$C_{17}N$	-0.15	4.28	-1.32	1.49	-0.25	3.41	-	-
$C_{18}Ni$	-1.98	1.78	-1.96	1.72	-1.89	1.98	-	-
$C_{18}Pd$	-1.55	1.72	-1.09	1.95	-1.41	2.20	-	
$C_{18}Pt$	-2.31	1.89	-1.87	1.87	-1.99	2.14	-	-
$C_{18}Al$	-	-	-	-	-	-	-0.61	2.11
$C_{18}Si$	-	-	-	-	-	-	-0.20	2.83
$C_{18}P$	-	-	-	-	-	-	-0.24	3.42

The pristine C_{18} nanocluster shows moderate to weak adsorption for CO, NO, and NH₃ with relatively low adsorption energies and moderately short distances. $C_{17}B$ and $C_{17}N$ display significantly stronger adsorption for all gases compared to the pristine C_{18}. $C_{18}Ni$, $C_{18}Pd$, and $C_{18}Pt$ nanoclusters exhibit strong adsorption tendencies similar to $C_{17}B$ and $C_{17}N$ for CO, NO, and NH₃. $C_{18}Al$, $C_{18}Si$, and $C_{18}P$ for HCN adsorption, show relatively moderate adsorption energies and distances.

From this interpretation, one can conclude that:

- Pristine C_{18} poses candidature for rapid-response sensors.
- $C_{17}B$ is suitable for the removal applications of CO, NO, and NH_3 gas molecules. $C_{17}N$ only good for NO gas removal.
- Similarly, $C_{18}Ni$, $C_{18}Pd$, and $C_{18}Pd$ offer better candidature for the removal applications.
- $C_{18}Al$ nanocluster is potentially good candidate for HCN sensing.

7.2. FUNCTIONALIZATION BEYOND DOPING AND DECORATION

Functionalization of materials goes beyond doping (substituting impurity atoms) and decoration (adding surface modifiers). It involves altering or enhancing properties.

7.2.1. C_{18} Dimer:

By stacking one C_{18} nanocluster atop another to form dimers, researchers gain insight into combined interactions and behaviours between these individual units. This unique arrangement allows for the investigation of potential synergistic effects or modified adsorption behaviours that differ from those observed in individual clusters. Such dimerization could lead to the emergence of novel structural and electronic properties, potentially bolstering efficacy of the nanoclusters in adsorbing hazardous gases. A recent comprehensive study by Liu et al.[1], delves deeply into the C_{18} nanocluster, meticulously exploring its interactions with the external environment, understanding its interactions with small molecules, and offering insights into its behaviour in a condensed phase, particularly examining the distinctive characteristics within the C_{18} dimer

7.2.2. Decoration of C_{18} on 2D Monolayers:

The process of attaching or depositing C_{18} nanoclusters onto 2D monolayers, such as graphene or alternative 2D materials, holds the potential to induce significant alterations in the surface chemistry and structural composition of these monolayers. Delving into the intricacies of the interactions between C_{18} nanoclusters and the 2D substrate presents an opportunity to engineer precisely tailored interfaces. These interfaces could offer a spectrum of tunable adsorption properties specifically designed for various gas molecules, thereby opening avenues for creating surfaces optimized for targeted gas adsorption applications.

7.3. OTHER CARBON RINGS

Numerous carbon-based cyclic clusters have shown promise in their ability to adsorb hazardous gases owing to their distinctive properties. An example lies in the recent work by Gao et al., who achieved the synthesis of cyclo[16]carbon (referred to as C_{16}) through tip-induced on-surface chemistry. This innovative method involved the precise manipulation of atoms on a surface to create and stabilize the C_{16} structure [2].

Therefore, the multidisciplinary nature of gas adsorption research offers numerous opportunities for innovation and advancement. By exploring these avenues, researchers can pave the way for the development of highly efficient, selective, and versatile materials tailored for gas adsorption, contributing to various industries and addressing pressing environmental and safety challenges.

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"The worthwhile problems are the ones you can really solve or help solve, the ones you can really contribute something to. No problem is too small or too trivial if we can really do something about it."

-Richard P. Feynman