Adsorption Performance of Pristine and Functionalized C_{18} towards Hazardous Gases

EXECUTIVE SUMMARY OF THE THESIS

SUBMITTED TO

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

In

PHYSICS

BY

Vadalkar Shardul Ram

Under the supervision of

Dr. Keyur N. Vyas

Department of Physics, Faculty of Science

The Maharaja Sayajirao University of Baroda

Vadodara - 390002, Gujarat, India.

August – 2024

INDEX

Table of Contents of the Thesis

1. INTRODUCTION

The urgency of effective gas sensing mechanisms is underscored by the rising global air pollution levels and their detrimental impact on ecosystems and human health. Air pollution, primarily caused by industrial emissions, vehicular exhaust, and chemical processes, has become a critical global issue[1]. The presence of hazardous gases such as carbon monoxide (CO), nitrogen oxides (NOx), ammonia (NH_3), and hydrogen cyanide (HCN) poses severe risks to both the environment and human health[2][3]. These pollutants can lead to respiratory diseases, cardiovascular problems, and even mortality in humans, while also causing significant harm to flora and fauna, contributing to climate change and the degradation of natural habitats.

The thesis begins by highlighting the significance of gas sensing technologies in mitigating these adverse effects. Gas sensors play a crucial role in detecting and monitoring harmful gases, enabling timely intervention and control measures to reduce exposure and prevent potential health hazards. The development of efficient and reliable gas sensors is therefore essential for ensuring air quality and safeguarding public health. In this context, the thesis emphasizes the role of carbon-based materials in enhancing the efficiency of gas adsorption and detection. Carbon materials, such as graphene[4], carbon nanotubes[5], and fullerene[6] derivatives, have been extensively studied for their unique properties, including high surface area, chemical stability, and exceptional electrical conductivity, making them ideal candidates for gas sensing applications. Among these, cyclo[18]carbon (C_{18}), a novel carbon allotrope synthesized in 2019, has garnered significant attention due to its distinct structural and electronic properties[7][8].

Cyclo[18]carbon (C_{18}), a novel carbon allotrope, consists of 18 carbon atoms arranged in a ring structure with alternating single and triple bonds, giving it a unique electronic configuration[7][9]. This configuration imparts remarkable reactivity and the potential for strong interactions with gas molecules. The thesis explores how the distinct characteristics of C_{18} can be harnessed to develop advanced gas sensors with enhanced sensitivity and selectivity. The research caves into the synthesis techniques for C_{18} and its functionalization with various dopants to improve its adsorption properties[10][11]. By doping C_{18} with elements such as boron, nitrogen, aluminum, silicon, and phosphorus, the electronic structure and surface reactivity can be tailored to enhance the interaction with specific gas molecules. This functionalization aims to optimize the adsorption energies, charge transfer,

and recovery times, making C_{18}-based nanoclusters highly effective for gas sensing applications.

2. THEORETICAL FRAMEWORK

Theoretical framework behind the computational methodology employed in this thesis centers around Density Functional Theory (DFT)[12] to study the interactions between toxic gases and C_{18} nanoclusters. Gaussian 09 was used for simulations[13], employing the wB97XD functional, a hybrid functional with dispersion correction[7]. This functional was chosen for its ability to accurately capture the dispersion interactions critical for adsorption studies.

The 6-311G++(d,p) basis set was utilized for geometry optimizations and frequency calculations. This basis set strikes a balance between computational efficiency and accuracy, ensuring reliable predictions of molecular geometries and vibrational properties for pristine and functionalized C_{18} nanoclusters. For the nanoclusters decorated with transition metals (Ni, Pd, Pt), the LanL2DZ basis set was chosen[14]. This basis set includes effective core potentials (ECPs) for the metal atoms and a large basis set for the remaining atoms, optimizing the computational resources while maintaining accuracy in describing the electronic structure of the nanocluster-metal complexes.

Initial geometries of pristine and functionalized C_{18} nanoclusters as well as gas molecules were optimized to obtain stable structures with minimized energy. The optimization process involved adjusting the atomic positions to achieve the lowest possible total energy, ensuring that the structures were at their most stable configurations. The adsorption energies of gas molecules on the nanoclusters were calculated by optimizing the geometries of the adsorbed complexes and comparing the total energies before and after adsorption. Raman and IR spectra were calculated to validate the stability of the pristine and functionalized nanoclusters hence to study the vibrational characteristics associated with gas adsorption.

3. PREDICTION OF PRSITINE C_{18} NANOCLUSTER AS A HAZARDOUS GAS SENSOR

The adsorption performance of the gases CO, NO, and NH_3 with the C_{18} nanocluster has been examined using DFT calculations in this chapter. To understand the sensing behavior, we analyzed the structural, electrical, and sensing properties of C_{18}, as well as its

Raman spectra. The findings revealed that CO and NO molecules undergo chemisorption, while NH_3 molecules exhibit physisorption on the C_{18} nanocluster. The decrease in the HOMO-LUMO gap following adsorption leads to an increase in conductivity, indicating the potential of C_{18} for sensor applications. Additionally, the quick recovery time (ranging from nanoseconds to femtoseconds) for CO and NO adsorption enhances its portability, and its natural abundance makes it suitable for low-cost gas sensors. In summary, the adsorption and electrical properties of the C_{18} nanocluster suggest that it can be employed as an ultra-fast sensor for hazardous gases[15].

4. EFFECT OF BORON AND NITROGEN DOPING ON MOLECULAR ADSORPTION

One of the most effective methods for enhancing the molecular adsorption performance of bulk and nanostructures is doping. In this chapter, we investigated the adsorption performance of Boron and Nitrogen doped C_{18} nanoclusters, denoted as $C_{17}X$ (X = B, N), towards the gases CO, NO, and NH_3 using first-principles calculations. The structural, electronic, and sensing properties of the $C_{17}X$ nanoclusters were studied to understand their sensing behavior, employing the Gaussian 09 package. For the $C_{17}B$ nanocluster, interactions with CO, NO, and NH_3 molecules resulted in chemisorption. The order of adsorption energies was: CO (-1.41 eV) > NH_3 (-1.81 eV) > NO (-2 eV). Conversely, for the $C_{17}N$ nanocluster, interactions with CO and NH_3 resulted in physisorption, with chemisorption observed only for NO gas. The adsorption energy order for $C_{17}N$ was: CO (-0.15 eV) > NH_3 (-0.25 eV) > NO (-1.32 eV). The long recovery time observed for the $C_{17}B$ nanocluster after adsorption makes it suitable for gas removal applications, whereas the shorter recovery time for the $C_{17}N$ nanocluster, particularly for CO and NH_3 adsorption, indicates its potential for sensor applications. The molecular adsorption of CO, NO, and NH_3 gases on $C_{17}B$ and $C_{17}N$ nanoclusters also leads to changes in the structural properties of the nanoclusters[16].

5. TRANSITION METAL-DECORATED C_{18} AS CO, NO & NH_3 SCAVENGER

The adsorption performance of CO, NO, and NH3 gases on transition metal (Ni, Pd, and Pt) decorated C_{18} nanoclusters was investigated again. Transition metals were chosen as impurity atoms because their presence enhances adsorption due to orbital interactions 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 the nitrogen atom in NH_3. The dispersion-

corrected hybrid wB97XD functional with the LanL2DZ basis set, as implemented in Gaussian 09, was used for the calculations. Besides evaluating sensing properties, the study also examined the structural, electronic, topological, and spectroscopic properties of these nanoclusters. Significant adsorption energies and long computed recovery times suggest chemisorption, indicating that transition metal-decorated C_{18} nanoclusters are suitable for removing CO, NO, and NH_3 gases from specific environments[17].

6. ADSORPTION OF HCN ON Al, Si, P-DECORATED C_{18} NANOCLUSTER

Hydrogen cyanide (HCN) is a hazardous chemical, typically found in gaseous form due to its high volatility, necessitating effective detection methods. In this study, we investigated the adsorption characteristics of C_{18} nanoclusters towards HCN molecules. The adsorption of pure C_{18} towards HCN showed minimal adsorption energy and a substantial adsorption distance. To enhance the interaction between HCN and C_{18}, we coated the nanocluster with Al, Si, and P atoms. Among these, the $C_{18}Al$ nanocluster emerged as the most effective HCN sensor, exhibiting optimal adsorption energy (-0.61 eV), a favorable adsorption distance (2.11 Å), and a recovery time of 17.7 ms[18].

7. SUMMARY AND FUTURE PROSPECTS

The findings of the present thesis highlight the unique strengths of various nanoclusters in gas sensing and removal applications. Unmodified C_{18} shows significant promise as a rapid-response sensor, capable of quickly detecting gases. In contrast, $C_{17}B$ proves highly effective in removing CO, NO, and NH_3 gases, while $C_{17}N$ excels specifically in eliminating NO gas. Furthermore, $C_{18}Ni$, $C_{18}Pd$, and $C_{18}Pt$ demonstrate substantial potential for gas removal. Among these, the $C_{18}Al$ nanocluster stands out, exhibiting significant promise as a sensor for detecting HCN gas. These observations indicate that each nanocluster offers specialized applications with tailored strengths that can be utilized in diverse gas sensing and removal scenarios.

The future scope of this research involves exploring advanced functionalization techniques beyond traditional doping and decoration to enhance nanocluster properties. Promising avenues include forming C_{18} dimers[19], which stack nanoclusters to study combined interactions, potentially improving gas adsorption efficacy. Another approach is decorating C_{18} nanoclusters on 2D monolayers like graphene, significantly altering surface chemistry to create interfaces with tunable adsorption properties[20]. Additionally, carbon-based cyclic clusters, such as cyclo[16]carbon (C_{16}), show promise for gas adsorption due

to their unique properties[21][22]. By investigating these strategies, researchers can develop highly efficient, selective, and versatile materials for gas adsorption, addressing critical environmental and safety challenges across various industries.

BIBLIOGRAPHY:

[1] D. Upadhyay, B. Roondhe, A. Pratap, P. K. Jha, *Appl. Surf. Sci.* **2019**, *476*, 198–204.

[2] A. Lorente, K. F. Boersma, H. J. Eskes, J. P. Veefkind, J. H. G. M. van Geffen, M. B. de Zeeuw, H. A. C. Denier van der Gon, S. Beirle, M. C. Krol, *Sci. Rep.* **2019**, *9*, 1–10.

[3] M. T. Ahmed, S. Islam, F. Ahmed, *R. Soc. Open Sci.* **2022**, *9*, DOI 10.1098/rsos.220778.

[4] G. AK, *Science (80-.).* **2009**, *324*, 1530–1534.

[5] T. Zhang, S. Mubeen, N. V. Myung, M. A. Deshusses, *Nanotechnology* **2008**, *19*, 1–2.

[6] D. Paul, A. Vaidyanathan, U. Sarkar, B. Chakraborty, *Struct. Chem.* **2021**, *32*, 2259–2270.

[7] K. Kaiser, L. M. Scriven, F. Schulz, P. Gawel, L. Gross, H. L. Anderson, *Science (80-.).* **2019**, *365*, 1299–1301.

[8] L. M. Scriven, K. Kaiser, F. Schulz, A. J. Sterling, **2020**, 1–19.

[9] Z. Liu, T. Lu, Q. Chen, *Carbon N. Y.* **2020**, *165*, 461–467.

[10] A. Kanzariya, S. Vadalkar, S. K. Jana, L. K. Saini, P. K. Jha, *J. Phys. Chem. Solids* **2024**, *186*, 111799.

[11] H. Mistry, D. Chodvadiya, S. Vadalkar, K. N. Vyas, P. K. Jha, *Surfaces and Interfaces* **2024**, *46*, DOI 10.1016/j.surfin.2024.103958.

[12] W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974–12980.

[13] et al. M. J. Frisch, Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., *Gaussian 09, Revis. A.02, Gaussian, Inc.* **2016**, 1–2.

[14] Y. Yang, M. N. Weaver, K. M. Merz, *J. Phys. Chem. A* **2009**, *113*, 9843–9851.

[15] S. Vadalkar, D. Chodvadiya, N. N. Som, K. N. Vyas, P. K. Jha, B. Chakraborty, *ChemistrySelect* **2022**, *7*, e202103874.

[16] S. Vadalkar, D. Chodvadiya, N. N. Som, K. N. Vyas, P. K. Jha, *ChemistrySelect* **2023**, *8*, e202204862.

[17] S. Vadalkar, D. Chodvadiya, H. Mistry, N. N. Som, K. N. Vyas, P. K. Jha, *Comput. Theor. Chem.* **2024**, *1238*, 114724.

[18] S. Vadalkar, D. Chodvadiya, K. N. Vyas, P. K. Jha, *Mater. Today Proc.* **2022**, *67*, 229–237.

[19] Z. Liu, T. Lu, Q. Chen, *Carbon N. Y.* **2021**, *171*, 514–523.

[20] M. V. Nikolic, V. Milovanovic, Z. Z. Vasiljevic, Z. Stamenkovic, *Sensors (Switzerland)* **2020**, *20*, 1–31.

[21] A. Kanzariya, S. Vadalkar, L. K. Saini, P. K. Jha, *Int. J. Hydrogen Energy* **2024**, *71*, 400–410.

[22] Y. Gao, F. Albrecht, I. Rončević, I. Ettedgui, P. Kumar, L. M. Scriven, K. E. Christensen, S. Mishra, L. Righetti, M. Rossmannek, I. Tavernelli, H. L. Anderson, L. Gross, **2023**, 23–28.