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Sensing of Environmental Hazardous Gases Using Nitrogen-Containing Macrocyclic Compounds: Quantum Chemical Approach

A Thesis Submitted in Partial Fulfilment of the Requirements for the
Master Degree in Environment and Sustainable Development

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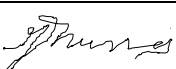
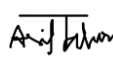
discussing the student whose details are stated above in public. The discussion committee recommends the following:

The student is awarded the grade PASS in the thesis course ESD548.

☐ Without making any changes to the thesis.

☒ After making the modifications attached with this decision.

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Abstract

Surging public demands for safety due to toxic industrial emissions and pollutants have come to the attention of the World Health Organization (WHO). These industrial emissions (e.g., CO₂, CO, and CH₄) cause serious complications for human health and all living organisms. The need to sense these gases has attracted much attention due to increasing environmental issues (e.g., climate change). Therefore, the importance of developing gas sensors that can better discern and, hence more easily detect industrial gases is growing daily. Recent studies found that industrial emissions have risen drastically in the atmosphere compared to the past century. Because of the ongoing growth in both automobiles and industries. The present study demonstrates the sensitivity and adsorption capacity of three macrocyclic compounds (Kekulene, Naphthyridine and Calixarene) as sensor materials for the detection of greenhouse gases including CO₂, CO, and CH₄. by using density functional theory (DFT) calculations. As a result, the most stable analyt@macrocycle among investigated macrocycles (Kekulene, Naphthyridine and Calixarene) was CH₄@Kekulene, CO₂@Naphthyridine and CO₂@Calixarene, respectively, with interaction energy values measuring -3.87, -9.09, and -2.99, respectively. QTAIM and NCI analysis confirmed the presence of NCIs and weak van der Waals interactions in all analyt@macrocycle complexes. FMO analysis showed negligible changes in the HOMO–LUMO energy gap (E_{gap}) across the studied complexes. This research contributes to establishing links between academia, regulatory agencies and research institutes to minimize industrial toxic emissions and have low-cost-efficient sensor materials for sensing the most common environmental pollutants. Publications

Dedication

I sincerely thank my parents for their constant support and encouragement throughout my education. I am also thankful to my little angel “Shaikha” (born during this thesis's writing). I look forward to sharing experiences in life with my daughter and having fantastic and illuminating times ahead with her.

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List of Content

Defense Committee’s Approval	B
Abstract	C
Dedication	D
Acknowledgments.....	E
List of Content	F
List of Tables.....	J
List of Figures.....	L
List of Abbreviation.....	P
CHAPTER ONE: INTRODUCTION	ERROR! BOOKMARK NOT DEFINED.
1. Introduction.....	2
1.1 RESEARCH PROBLEM	ERROR! BOOKMARK NOT DEFINED.
1.2 RESEARCH QUESTIONS	ERROR! BOOKMARK NOT DEFINED.
1.3 RESEARCH OBJECTIVES	ERROR! BOOKMARK NOT DEFINED.
1.4 RESEARCH SIGNIFICANCE ...	ERROR! BOOKMARK NOT DEFINED.
1.5 THE STUDY’S SETTING	ERROR! BOOKMARK NOT DEFINED.
1.6 RESEARCH TERMINOLOGY ..	ERROR! BOOKMARK NOT DEFINED.
CHAPTER TWO: LITERATURE REVIEW	ERROR! BOOKMARK NOT DEFINED.
2. LITERATURE REVIEW	ERROR! BOOKMARK NOT DEFINED.
2.1 AIR POLLUTION HISTORY: ..	ERROR! BOOKMARK NOT DEFINED.
2.2 SENSING OF CH ₄ , CO ₂ , AND CO	ERROR! BOOKMARK NOT DEFINED.
2.3 SENSING OF GASES USING “MACROCYCLES” AS A SENSOR.....	ERROR! BOOKMARK NOT DEFINED.
CHAPTER THREE: METHODS AND PROCEDURES	ERROR! BOOKMARK NOT DEFINED.
3. CHAPTER THREE: METHODS AND PROCEDURES	ERROR! BOOKMARK NOT DEFINED.
3.1 COMPUTATIONAL METHODS:	ERROR! BOOKMARK NOT DEFINED.
CHAPTER FOUR: RESULTS, DISCUSSION, ANDRECOMMENDATIONS.....	ERROR! BOOKMARK NOT DEFINED.

4.	RESULTS, DISCUSSION, AND RECOMMENDATION	ERROR! BOOKMARK NOT DEFINED.
4.1	HEXAAZAKEKULENE (KEKULENE) MACROCYCLE:.....	ERROR! BOOKMARK NOT DEFINED.
4.1.1	Geometry Optimization of CH ₄ , CO and CO ₂ @Kekulene	Error! Bookmark not defined.
4.1.2	Interaction Energies of Kekulene Macrocycle	Error! Bookmark not defined.
4.1.3	QTAIM Analysis of CH ₄ , CO and CO ₂ @Kekulene:	Error! Bookmark not defined.
4.1.4	NCI Anslsysis of CH ₄ , CO and CO ₂ @Kekulene.....	Error! Bookmark not defined.
4.1.5	Electronic Properties of CH ₄ , CO and CO ₂ @ Kekulene .	Error! Bookmark not defined.
4.2	OXACALIX[2]NAPHTHALENE[2]NAPHTHYRIDINE (NAPHTHYRIDINE)	ERROR! BOOKMARK NOT DEFINED.
4.2.1	Geometry Optimiz. of CH ₄ , CO and CO ₂ @Naphthyridine.....	Error! Bookmark not defined.
4.2.2	Interaction Energies of Naphthyridine Macrocycle	Error! Bookmark not defined.
4.2.3	QTAIM Analysis of Naphthyridine macrocycle	Error! Bookmark not defined.
4.2.4	NCI Anslsysis of CH ₄ , CO and CO ₂ @Naphthyridine	Error! Bookmark not defined.
4.2.5	Electronic Properties of CH ₄ , CO & CO ₂ @Naphthyridine.....	Error! Bookmark not defined.
4.3	OXACALIX[2]ARENE[2]PYRAZINE (CALIXARENE) MACROCYCLE	ERROR! BOOKMARK NOT DEFINED.
4.3.1	Geometry Optimization of CH ₄ , CO and CO ₂ @Calixarene	Error! Bookmark not defined.
4.3.2	Interaction Energies of Calixarene Macrocycle	Error! Bookmark not defined.
4.3.3	QTAIM Analysis of CH ₄ , CO and CO ₂ @Calixarene	Error! Bookmark not defined.
4.3.4	NCI Analysis of CH ₄ , CO and CO ₂ @Calixarene	Error! Bookmark not defined.

4.3.5	Electronic Properties of CH ₄ , CO and CO ₂ @Calixarene . Error! Bookmark not defined.
4.4	CONCLUSION AND RECOMMENDATIONS: Error! BOOKMARK NOT DEFINED.
REFERENCES	ERROR! BOOKMARK NOT DEFINED.
REFERENCES	ERROR! BOOKMARK NOT DEFINED.
الملخص	ERROR! BOOKMARK NOT DEFINED.

List of Tables

Table 1: Interaction energy for each interaction possibility (P) of Kekulene macrocycle.....	27
Table 2: bond critical point (BCP), Interacting atoms (Aint), interaction distances (D), interaction energies (Eint), electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), and total energy density (H) of analyte@Kekulene complex.	30
Table 3: Energy of HOMOs, LUMOs, HOMO-LUMO energy gaps (in eV) and charge transfer of analyte@ Kekulene.	37
Table 4: interaction energy for each interaction possibility (P) of Naphthyridine macrocycle.	41
Table 5: bond critical point (BCP), Interacting atoms (Aint), interaction distances (D), interaction energies (Eint), electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), and total energy density (H) of analyte@ Naphthyridine complexes.....	44
Table 6: Energy of HOMOs, LUMOs, HOMO-LUMO energy gaps (in eV) and charge transfer of analyte@Naphthyridine.	50
Table 7: bond critical point (BCP), Interacting atoms (Aint), interaction distances (D), interaction energies (Eint), electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), and total energy density (H) of analyte@ Calixarene complexes.	58
Table 8: Energy of HOMOs, LUMOs, HOMO-LUMO energy gaps (in eV) and charge transfer of analyte@ Calixarene.	61

List of Figures

Figure 1: Kekulene, Naphthyridine and Calixarene macrocycles (multi-nitrogen functional groups).....	4
Figure 2: 3,9,15,19,21,23-hexaazakekulene (Kekulene)	25
Figure 3: Front and side views of optimized geometry of Kekulene macrocycle.....	26
Figure 4: possible conformations (before optimization) of Kekulene macrocycle with each analyte.	28
Figure 5: Optimized (stable) geometries of anslyte@ kekulene complexes.....	28
Figure 6: Molecular electrostatic potential (MESP) isosurface of Kekulene macrocycle.	29
Figure 7: QTAIM representations of the bond paths (the orange lines) and the BCPs (the numbered orange spheres).	33
Figure 8: 3D isosurfaces of analyte@Kekulene complexes.	35
Figure 9: graphical depiction of the HOMO and LUMO isosurfaces to illustrate how adsorbing the analytes (CH ₄ , CO & CO) affects the sensor's (Kekulene) electrical environment.....	39
Figure 10: Oxacalix[2]naphthalene[2]naphthyridine (Naphthyridine) Macrocycle. ..	40
Figure 11: Front and side views of optimized geometry of Naphthyridine macrocycle.	41
Figure 12: possible conformations (before optimization) of Naphthyridine macrocycle with each analyte.	42
Figure 13: Optimized (stable) geometries of the anslyte@Naphthyridine complexes.	43

Figure 14: Molecular electrostatic potential (MESP) isosurface of Naphthyridine macrocycle.	44
Figure 15: QTAIM representations of the bond paths (the orange lines) and the BCPs (the numbered orange spheres) of Naphthyridine complexes.....	47
Figure 16: 3D isosurfaces of analyte@Naphthyridine complexes.	48
Figure 17: A graphical depiction of the HOMO and LUMO isosurfaces to illustrate how adsorbing the analytes (CH_4 , CO & CO_2) affects the sensor's (Naphthyridine) electrical environment.	51
Figure 18: Oxacalix[2]arene[2]pyrazine (Calixarene) Macrocycle.	52
Figure 19: Front and side views of optimized geometry of Calixarene macrocycle...	53
Figure 20: possible conformations (before optimization) of Calixarene macrocycle with each analyte.	54
Figure 21: Optimized (stable) geometries of the anslyte@Calixarene complexes.	55
Figure 22: Molecular electrostatic potential (MESP) isosurface of Calixarene macrocycle.	56
Figure 23: QTAIM representations of the bond paths (the orange lines) and the BCPs (the numbered orange spheres) of Naphthyridine complexes.....	60
Figure 24: 3D isosurfaces of analyte@Naphthyridine complexes.	60
Figure 25: a graphical depiction of the HOMO and LUMO isosurfaces to illustrate how adsorbing the analytes (CH_4 , CO & CO_2) affects the sensor's (Calixarene) electrical environment.	63

List of Abbreviation

Abbreviation	Full name
$\nabla^2\rho$	The Laplacian of the electron density
BCP	Bond critical point
D	Bond distance
E _{gap}	Highest occupied molecular orbital-Lowest unoccupied molecular orbital energy gap
EHOMO	Energy of the highest occupied molecular orbital
E _{int}	The interaction energy
ELUMO	Energy of the lowest unoccupied molecular orbital
FMO	Frontier molecular orbital
H	The total energy density
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
NBO	Natural bond orbital
QTAIM	Quantum theory of atom in molecules
Q	Charge transferred
SDG	Sustainable development goals
ρ	The electron density

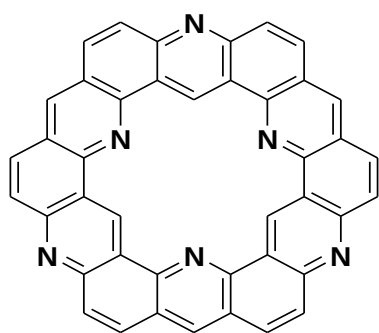
Chapter One:

Introduction

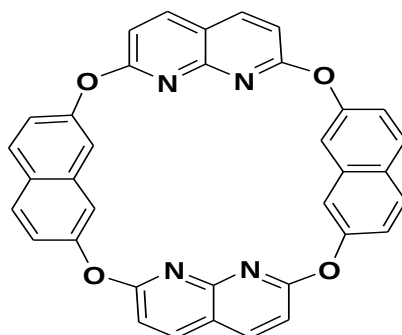
1. Chapter One: Introduction

The sensing of industrial gas molecules has gained major interest due to increasing environmental issues because of their ability to adversely affect human health and contribute to a range of environmental concerns (*e.g.*, climate change) (Chermahini, 2018; Mofidi & Reisi-Vanani, 2020). Notably, gases like methane (CH_4), carbon dioxide (CO_2), and carbon monoxide (CO) are widely recognized due to the serious threats they pose to the environment. These gases are mainly produced by agricultural practices, waste disposal sites, chemical factories, and incomplete burning of fuels (Kuzuyakov, 2006; Weaver, 2009a). As a result, the need for highly accurate and sensitive gas sensors continues to grow, driven by the importance of identifying toxic gases in industrial settings (Liu et al., 2012a). Carbon monoxide (CO) is colourless, has no smell, and cannot be tasted. It is produced after incomplete fossil fuels burning. Its poisonous nature mainly comes from how it combines with haemoglobin to form carboxyhemoglobin (COHb) in the blood, causing a lack of oxygen (hypoxia) (World Health Organization, 1999). The harmful impacts of carbon monoxide (CO) on health are widely known, especially in relation to the cardiovascular and central nervous systems, at CO exposure levels of 10–15 ppm (S. Zhang et al., 2013). Regarding environmental protection, one of the toughest tasks is tackling the reduction of toxic gases in environment , particularly the greenhouse gas CO_2 . The growing concentration of CO_2 in the atmosphere represents a critical warning sign for global climate stability. Ocean acidification, melting ice caps, and acid rain are urgent environmental issues caused by CO_2 emissions (Kurihara, 2008a; White et al., 2005). Methane (CH_4) is a colorless, odorless, and highly flammable gas, known for its explosive nature and its substantial

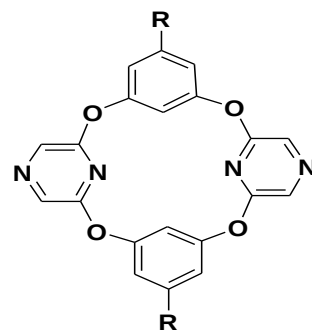
role in accelerating global warming. In terms of heat retention in the atmosphere, methane has a global warming potential nearly 25 times higher than that of carbon dioxide. The release of 1 kg of methane has the same impact as emitting 25 kg of CO₂. Human activities, such as landfills, contribute to at least 25% of the current global warming caused by methane (Nasresfahani et al., 2021). Various methods such as absorption, adsorption, membranes, and others have been widely used to tackle the issue of capturing and separating these gases (Rao & Rubin, 2002). Several types of solid materials are used to detect toxic gases by adsorbing or sensing them. These materials can be made of activated carbon (Feng et al., 2005), zeolites (Cosoli et al., 2008), metal–organic frameworks (Hamon et al., 2009), graphene (Chen et al., 2012), and covalent organic frameworks (Broom & Thomas, 2013). In recent years, attention has been increasingly paid to carbon nanostructures because of their powerful adsorption and high sensing abilities (Bieri et al., 2009). In nature, different forms of carbon can be found including carbon black, graphite, and diamond. In addition, due to continuous research and studies, the synthesis of new carbon forms such as fullerene, nanotube, and graphene has been discovered (Iijima, 1991; Novoselov et al., 2004). Modelling in general, and the density functional theory (DFT) approach in particular, provides researchers with significant advantages by reducing development time and material selection costs before conducting lab experiments. It also helps minimize the use of expensive and potentially hazardous chemicals, which may threaten both human health and environmental integrity (Bagayoko, 2014). The study anticipates that nitrogen-rich macrocyclic compounds (Figure 1) will serve as highly effective sensors for industrial gas detection (Siddique et al., 2022).



Kekulene Macrocycle



Naphthyridine Macrocycle



Calixarene Macrocycle

Fig. 1: Kekulene, Naphthyridine and Calixarene macrocycles (multi-nitrogen functional groups).

1.1 Research Problem

Industrial gases have the potential to adversely affect human health and make substantial contributions to a range of environmental concerns, including climate change, acid rain and many other environmental issues (Chermahini, 2018; Mofidi & Reisi-Vanani, 2020). Little is known regarding the theoretical investigation of Macrocyclic compounds as a sensor material for industrial gases (CH_4 , CO_2 and CO). Therefore, the demand for precise and sensitive advanced gas sensors has been increasing steadily, driven by the need to detect industrial toxic gas molecules (Liu et al., 2012).

1.2 Research Questions

This study seeks to answer the following questions:

1. How does the complexation of nitrogen-rich macrocycles with industrial gases (CH_4 , CO_2 and CO) affect the compounds' sensitivity and selectivity?
2. How do nitrogen-rich macrocyclic compounds' geometric and electronic properties change upon complexation with CH_4 , CO_2 , and CO ?
3. How do thermodynamic parameters, such as interaction energy, vary upon complexation of nitrogen-rich macrocyclic compounds with CH_4 , CO_2 , and CO , and what insights do these variations provide into their interaction behaviours?

1.3 Research Objectives

The current study has the following objectives:

1. To investigate the sensitivity and selectivity of Nitrogen-rich macrocyclic compounds toward industrial gases (CH_4 , CO_2 and CO) using the density functional theory (DFT) approach.
2. To analyse the changes in geometries and electronic properties of Nitrogen-rich macrocyclic compounds before and after complexation with analytes (industrial gases), analysts will also be investigated.
3. To explore the interaction behaviour and thermodynamic stabilities of Nitrogen-rich macrocyclic compounds toward industrial gases (CH_4 , CO_2 and CO).

1.4 Research Significance

The ultimate aim of this study is to take part to have precise and sensitive gas sensors that fulfil the need to detect industrial toxic gas molecules. Recently, there has been an increasing need for highly accurate and sensitive advanced gas sensors to detect industrial gases that pose risks to human health and the environment. In addition, there has been limited research on the sensing behaviour of Macrocyclic compounds toward industrial gases in theoretical studies. This study assists experimentalists in creating new macrocyclic sensors and lays the groundwork for the development of sensing capabilities.

1.5 The Study's Setting

This study was conducted computationally using quantum chemistry-based software (**Gaussian, GaussView, VMD, and Multiwfn**). The density functional theory (DFT) has been primarily adapted to produce the data in this research. The computations have been conducted mainly on my personal computer. After the availability of the high-performance computer within the facilities of the Benefit Advanced AI and Computing Lab at the University of Bahrain, part of this study was conducted using it.

1.6 Research Terminology

Most of the terminology used in the thesis is commonly known to all chemists. However, some terminology may be only known to computational chemists and are therefore explained in the following list:

- DFT; a strongly developed computational quantum mechanical theory used to simplify the electron-electron interactions within the Schrödinger equation. Thus, providing an accurate approximation to the solution of the Schrödinger equation with reasonable computational time (Teale et al., 2022).
- Functional; within the DFT, many methods can be used to describe the electron-electron interactions, each with its pros and cons. These methods are called the functionals (Liao et al., 2022).
- Basis-set; is the set of functions used to describe the position of the electrons within the subspace of the molecule (Morgante & Peverati, 2020).
- Optimization; the first step in any computational chemistry study in which the geometric parameters of the designed structure are optimized to the lowest possible energy to yield the optimized geometries (Szabo & Ostlund, 2012).

Chapter Two:

Literature Review

2. Chapter Two: Literature Review

2.1 Air Pollution History:

ince the onset of the Industrial Revolution around 1760, the Earth's atmosphere has undergone significant changes, leading to a rapid increase in pollutant emissions (Ashton, 1998). There are now cities and urban regions on every continent, and these places are home to about half of the world's population. As a result, this population is being subjected to ever increasing levels of air pollution. The concept of "air pollution" lacks a straightforward definition. It can be posited that the onset of air pollution coincided with the advent of fuel combustion. Essentially, any human-generated emissions that alter the atmosphere's chemical makeup can be classified as air pollution (Arbex et al., 2012). Daly & Zannetti (2007) defines "air pollutant" as any substance released into the atmosphere—whether from human activity, natural biological processes, or geological sources—that is either not typically present in the air or found in unusually high concentrations, potentially leading to harmful effects over time or immediately. According to Vallero (2008), the term "air pollution" refers to the negative consequences that are caused by any and all causes that contribute to the pollution of the atmosphere that leads to the deterioration of the ecosystem. During the early 20th century, laws aimed at controlling air pollution were generally limited in scope and lacked real effectiveness. This was a direct result of the importance of coal-fueled steam power to the progression of the economy (Mosley, 2014). Midway through the 20th century, instances of air pollution in urban areas across Europe and the United States, such as the London Fog of 1952 and the Donora Smog of 1948, resulted in a notable rise in mortality and hospitalizations. These events highlighted the serious risks associated with prolonged exposure to

elevated levels of air pollution (Keating, 2001). As many governments look at solutions for pollution reduction, the effect of air pollution on public health has gradually grown in importance during policy deliberations (Kurihara, 2008b). Historically, air pollution, also known as outdoor pollution, has been shown to be responsible for 1.15 million deaths worldwide, which accounts for about 2% of all deaths (Arbex et al., 2012). According to the World Health Organization, indoor air pollution in Brazil is currently linked to around 10,700 deaths each year—and that number could rise to as many as 20,000 annually in the coming years; this is five times as many deaths as are considered to be caused by passive or ambient smoking. The majority of human cancers are believed to be caused by external variables such as smoking, medicines, nutrition, viruses, air pollutants, and water pollutants. When compared to rural locations, urban areas have been found to have higher rates of developing all types of cancer, especially cancers of the lung, nasopharynx, larynx, esophagus, mouth, and throat cancer (Brunekreef & Holgate, 2002). Children, the elderly, and those with pre-existing health conditions are especially at risk from the harmful effects of air pollution. Although most of the pollution produced by the burning of fossil fuel is released into the outdoors, human exposure happens both indoors and outside (Lee et al., 2011). Methane (CH_4), carbon dioxide (CO_2), and carbon monoxide (CO) are a few of the pollutants produced when fossil fuels are used for transportation, energy production, and other purposes as a considerable percentage of the global energy demand is increasing steadily. Out of these demanded, 85% of total energy is met by nonrenewable energy, mainly due to vehicular traffic and power generation (Akinyele & Rayudu, 2014). In addition, agriculture, industrial operations, and incomplete combustion of fossil fuel are the major sources of these toxic gases (Weaver, 2009). Recently, air pollution has gained significant research attention due to its role in various

environmental problems, including acid rain, global warming, ozone layer depletion, and climate change (Al-Thani et al., 2018).

2.2 Sensing of CH₄, CO₂, and CO using Different Methods:

Because of the growing concerns that we have about the environment and health, The area of gas sensor research has seen increasing attention in recent years (Rocha et al., 2008). However, accurate sensing of air pollutants is of great significance to control and limit air pollution, and for better human health and environmental management. Specifically, development of advanced gas sensors that offer improved sensitivity and selectivity for monitoring industrial gases (Zheng et al., 2017). In previous research, various solid materials, including activated carbon, have been utilized as gas sensors (Feng et al., 2005), zeolites (Cosoli et al., 2008), metal–organic frameworks (Hamon et al., 2009), graphene (Chen et al., 2012), and covalent organic frameworks (Broom & Thomas, 2013). The growing levels of air pollution have led to a rising need for the creation of gas sensors that are highly selective and sensitive (Liu et al., 2012). The twenty-first century has seen increased efforts to enhance the performance of gas sensing materials by setting specific criteria. These include high operating temperatures, elevated sensitivity, rapid response times, easy recovery, and precise target recognition (Nagarajan et al., 2021). Gas sensors are able to perform their function by measuring the electrical conductivity as well as other physical characteristics as a result of changes in electrical and chemical states that are formed between the sensing material and the analyte that is being measured. According to Sohail et al. (2022), there was a clear indication that the Olympocene surface had weak interactions with CH₄, CO₂, and CO. On the other hand, Sattar et al. (2022) demonstrated that the sensitivity and interaction energies of twisted

nanographene analogues ($C_{32}H_{16}$ and $C_{64}H_{32}$) with CH_4 were notably elevated. A previous study done by Mofidi & Reisi-Vanani (2020) studied the adsorption of CO and CO_2 molecules on oxidised graphyne structures using DFT-D calculations. Results indicated that the introduction of oxygen atoms leads to the formation of highly stable oxides in the presence of CO and CO_2 molecules. Espinal (2004) conducted an investigation into how carbon monoxide interacts with carbon-based materials through DFT calculations. The results showed that CO adsorption on carbon-based models is thermodynamically favorable, mainly due to the highly exothermic nature of the reactions. Zhao et al. (2012) utilized oxygen plasma-treated carbon nanotubes for carbon monoxide detection, demonstrating significant selectivity and the ability to detect low levels of CO, reaching as low as 5 ppm at ambient temperature. Ao et al. (2008) conducted DFT calculations and discovered that aluminum-doped graphene exhibits significant CO adsorption due to the formation of Al–CO bonds. Furthermore, A significant amount of research on the adsorption of CO_2 onto carbon materials has been conducted over the past few decades (Cinke et al., 2003; K. J. Lee & Kim, 2013). CO_2 adsorption on the single-walled carbon nanotubes was investigated by Cinke et al. (2003), theoretically and experimentally. They discovered that a physisorption process occurs, with nanotubes capable of adsorbing almost double the amount of CO_2 in comparison to activated carbon; both experimental and computational findings were similar. Moreover, in a study done by F. Eftaiha et al. (2016), The uptake of CO_2 by oligomeric chitin-acetate dissolved in Dimethyl Sulfoxide, a sustainable solvent, presents an innovative environmentally friendly method for capturing CO_2 . El-Hendawy et al. (2011) Investigated the thermodynamic feasibility of gas-phase CO sequestration as carbonate or monomethylcarbonate using density functional theory (DFT) calculations. The findings indicate that the

interaction between the dinuclear cryptate and the carbonate anion is thermodynamically more advantageous compared to its reaction with the monomethylcarbonate anion. Nikmanesh et al. (2021) Examined how methane adsorption influences the electronic properties of titanium (Ti)-decorated γ -graphyne. The findings indicate that γ -graphyne modified with titanium exhibits outstanding sensitivity to CH_4 gas, characterized by strong selectivity and rapid recovery times. Consequently, Nikmanesh's research promotes the increasing application of titanium-decorated γ -graphyne in the creation of methane sensors. Using DFT calculations, Osouleddini & Rastegar, (2019) investigated how CO_2 and CH_4 molecules interact with both pristine graphene and graphene modified with tetracyanoethylene. Their study found that the modified graphene exhibits stronger interactions with CO_2 and CH_4 than the unmodified graphene. However, the changes in the electronic properties were minimal, making both types of graphene unsuitable for use as practical sensors for these gases. Hu et al. (2024) explored the potential of transition metal-doped C_9N_4 for use in gas sensing applications. Their findings showed that $\text{Cr-C}_9\text{N}_4$ and $\text{Fe}_2\text{-C}_9\text{N}_4$ exhibit strong gas adsorption capabilities, offering valuable theoretical insights that could help in the development of more advanced sensor materials.

2.3 Sensing of Gases using “Macrocycles” as a Sensor:

“Macrocycle” refer to organic molecules that contain at least one sizable ring composed of 12 or more atoms (Dai et al., 2021). Sajid et al. (2020) compared cyclic oligofuran and their straight-chain analogues in terms of sensitivity and selectivity toward gaseous analytes (CO , CO_2 ,

N_2H_4 , HCN , H_2O_2 , H_2S , and CH_4) via DFT calculation. The results of the research unequivocally showed that the cyclic structure improves not only the sensitivity but also the selectivity and stability of the complexes, as validated by DFT calculations. Sajid et al. (2022) were the first to demonstrate the use of monocyclic C_{18} and B_9N_9 as effective materials for detecting and removing chemical warfare agents. Their results indicated that these agents exhibit stronger adsorption on the B_9N_9 structure compared to C_{18} . In another study done by Dai et al. (2021), the conjugated macrocycle was identified as the optimal material, exhibiting excellent selectivity for CO_2 adsorption while showing no sensitivity toward N_2 . Eftaiha et al. (2021) conducted a study on a series of diamine-tetraamido macrocyclic molecules using DFT calculations; the results indicated that the diamine-tetraamido macrocyclic compound can effectively capture CO_2 . Ashirov et al. (2023) synthesized three-dimensional (3D) porous organic polymers (POPs) by polycondensing an octaketone-based macrocycle with phenazine-2,3,7,8-tetraamine hydrochloride. These newly developed 3D-mm POPs showed impressive CO_2 adsorption performance, including a high binding enthalpy of 40.6 kJ/mol and a strong capacity for capturing CO_2 . Siddique et al. (2022) conducted a study on the adsorption of nitrogen- and sulfur-containing gases—specifically N_2O , NO_2 , H_2S , SO_2 , and SO_3 —on the organic aza-macrocyclic compound hexaazabipyH₂ (HA) using DFT simulations. The findings indicated that HA can detect these gases, with interaction energies of -4.80 , -4.86 , -7.09 , -7.42 , and -11.64 kcal/mol for NO_2 , N_2O , H_2S , SO_2 , and SO_3 , respectively, demonstrating less sensitivity to nitrogen-based gases. Sadia et al. (2023) proposed the use of cyclic tetrapyrrole as a promising sensor for identifying harmful sulfur gases, employing the DFT framework in their research. Their findings indicated that cyclic tetrapyrrole exhibits considerable sensitivity to sulfur irritants. The interaction energies for these sulfur gases

in relation to cyclic tetrapyrrole varied between -25.6 and -89.2 kJ mol $^{-1}$. Another study performed by Sajid, Khan, et al. (2020) employed DFT calculations to explore the interaction behavior of cyclic tetrapyrrole and tetrapyrrole in detecting harmful gases such as phosgene, thiophosgene, and formaldehyde. The findings indicated that cyclic tetrapyrrole displayed the greatest sensitivity to these analytes, in the following sequence: formaldehyde > phosgene > thiophosgene. Furthermore, a strong hydrogen bond was observed between cyclic tetrapyrrole and the analytes. In summary, the high sensitivity of cyclic tetrapyrrole makes it a promising material for gas sensing (Sajid et al., 2020). Furthermore, the results concerning cyclic tetrapyrrole and their predictions offer valuable recommendations for researchers aiming to develop highly sensitive sensors for detecting toxic substances (S. Ullah et al., 2022). To identify hazardous chemical warfare agents, researchers have used density functional theory (DFT) to study how the nerve agent cyclosarin interacts with Cucurbit[n]uril (CB[n])—a host molecule where n ranges from 5 to 8. The binding of cyclosarin to CB $_{[6]}$ is thermodynamically more favorable than its interactions with other CB $_{[n]}$ variants, as suggested by van der Waals forces (Bhat et al., 2023). Sajid et al. (2019) using DFT calculations, explore the sensing properties of cyclic oligothiophenes for various analytes, such as NH $_3$, CO, CO $_2$, N $_2$ H $_4$, HCN, H $_2$ O $_2$, H $_2$ S, CH $_4$, CH $_3$ OH, SO $_2$, SO $_3$, and H $_2$ O, were examined. Geometries and interaction energies were optimized using the B3LYP method combined with Grimme's dispersion correction (B3LYP-D3), along with the 6-31++G(d,p) basis set. The findings highlight the potential of cyclic oligothiophenes for designing advanced atmospheric sensors, which could outperform conventional sensor technologies. DFT calculations were used to investigate the formation of complexes between β -cyclodextrin, acting as the host molecule, and various gaseous substances such as N $_2$ O, CO $_2$, NO $_2$, SO $_2$,

HCN, CH₄, and CH₃CH₂CH₃. (Dudev & Spassov, 2024). The findings indicate that the host macrocycle demonstrates significant efficiency in capturing polar compounds like N₂O, HCN, NO₂, and SO₂, as well as non-polar molecules with strong electronegative centers, such as CO₂. Typically, the efficacy of gas encapsulation improves as the polarity of the guest molecule increases. On the other hand, β-cyclodextrin appears to be ineffective at binding non-polar hydrocarbons—specifically methane and propane in this case. The purpose of this section was to evaluate the existing literature by highlighting the history of greenhouse gas sensing using macrocyclic materials. Different sensing methods were discussed in this section. It is to be noted that, various sensing methods discussed in the literature have led to the recognition of gaps in knowledge since there are no comparative DFT studies have been conducted related to greenhouse gas sensing using macrocyclic materials as a sensor.

Chapter Three:

Methods and Procedures

3. Chapter Three: Methods and Procedures

All primary data presented in the thesis have been obtained via computational quantum chemical calculations.

3.1 Computational Methods:

All DFT calculations were carried out using the Gaussian 09 software package (Frisch et al., 2009), the results have been visualized using GaussView 6.0.16 (Roy D. Dennington et al., 2009). Stability analysis and geometry optimisation was conducted by using ω B97XD /def2SVP method of DFT. With the Grimme D2 dispersion correction included, the hybrid ω B97XD functional was selected since it is designed to take long-range interactions into consideration (Chai & Head-Gordon, 2008a). To accurately estimate non-covalent interaction energies, the ω B97XD functional known for its long-range dispersion corrections was employed (strongly suggested) (Azofra et al., 2014; Chai & Head-Gordon, 2008c). It has been seen in the literature that the B3LYP functional provides electronic characteristics that are equivalent to experimental data (Ayub, 2014; Sajid et al., 2018; H. Ullah et al., 2013), whereas the ω B97XD functional poorly shows the electronic properties (Asif et al., 2022; Ayub, 2016). For this reason, all electronic analyses executed using B3LYP functional. Each optimised geometry has had its frequency calculated to make sure it is a local minimum (Ira N. Levine, 2014). The interaction energies were calculated using Equation 1.

$$E_{\text{int}} = E_{\text{complex}} - (E_{\text{surface}} + E_{\text{analyte}}) + \text{BSSE} \quad (\text{Eq.1})$$

Where E_{complex} , E_{surface} and E_{analyte} represent the energies of analytes@surfaces, energy of surfaces (adsorbents/macrocycle) and energy of analysts ($\text{CH}_4, \text{CO}_2, \text{CO}$), respectively.

For evaluation of the effect of greenhouse gases on the conductivity of the macrocycles, the E_{gap} has been calculated according to Equation 2:

$$E_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (\text{Eq. 2})$$

E_{LUMO} and E_{HOMO} refer to the energies of the Lowest Unoccupied Molecular Orbital (LUMO) and the Highest Occupied Molecular Orbital (HOMO), respectively. Single-point energy calculations using the B3LYP functional were performed on the previously optimized structures to determine the energy gap (E_{gap}). The B3LYP functional was chosen for E_{gap} calculations due to its proven effectiveness in accurately predicting experimental data for these properties (Allangawi et al., 2024). Additionally, the isosurfaces corresponding to the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) were rendered utilizing GaussView version 6.0.16 (Akhter et al., 2023). Furthermore, the charges corresponding to natural bond orbitals (NBO) were calculated with Gaussian 09 (Glendening et al., 2012).

To examine the interactions between the surfaces and the analytes, the analyses of the Quantum Theory of Atoms in Molecules (QTAIM) and Non-Covalent Interactions (NCI) were conducted, using Multiwfn 8.0 software with wavefunction data derived from the B3LYP/def2SVP level (Axel Becke, 2007; Lu & Chen, 2012). The visualisation of QTAIM and NCI analysis was performed using Visual Molecular Dynamics version 1.9 (VMD) (Humphrey et al., 1996).

Chapter Four:

Results, Discussion, and Recommendations

4. Chapter Four: Results, Discussion, and Recommendation

DFT calculations have been used by applying ω B97XD/def2svp level of theory in order to study three different macrocycles (kekulene, Naphthyridine and pyrazine) potentials as a sensing material toward greenhouse gases (CH_4 , CO, and CO_2). This function is the most reliable one due to its ability to precisely measure the non-covalent interactions, including dispersion, van der Waals forces, and hydrogen bonding (Chai & Head-Gordon, 2008b). Furthermore, analytes may interact with ring surfaces in a variety of ways. Therefore, it is necessary to consider all ways during the testing of analyte@macrocycle at different positions.

4.1 Hexaazakekulene (Kekulene) Macrocycle:

Recently, the attention of people has been diverted toward nitrogen-containing macrocycles (Newkome et al., 1989) those appear as a promising candidates in the field of sensing. 3,9,15,19,21,23-Hexaazakekulene (kekulene) macrocycle contains six hydrogens along with three nitrogens in its internal cavity (Figure 2). (Newkome & Lee, 1983).

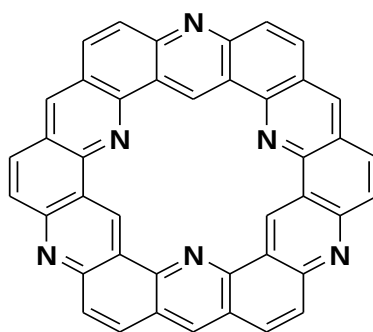


Fig. 2: 3,9,15,19,21,23-hexaazakekulene (Kekulene)

Kekulene was synthesized by reacting Monoprotected proflavine with 0.5 equivalent of paraformaldehyde to give tripyridinyl diamine. This is followed by getting rid of ethoxycarbonyl under basic conditions, which leads to producing of Kekulene (Tatibouet et al., 1997).

The nitrogen atom in pyridine displays nucleophilic properties because of its lone pair of electrons, which cannot be extensively delocalized across the aromatic ring. As a result, pyridine shows a heightened sensitivity to cations and electrophilic agents (Abdolmaleki et al., 2020). However, Pyridine is a weak base (the electrons are not very available for donation). In addition, Pyridine is polar and capable of forming hydrogen bonds (Ochiai, 1953; Ortega et al., 2018). In order to test the sensitivity of Kekulene macrocycle, physical and chemical characteristics were identified.

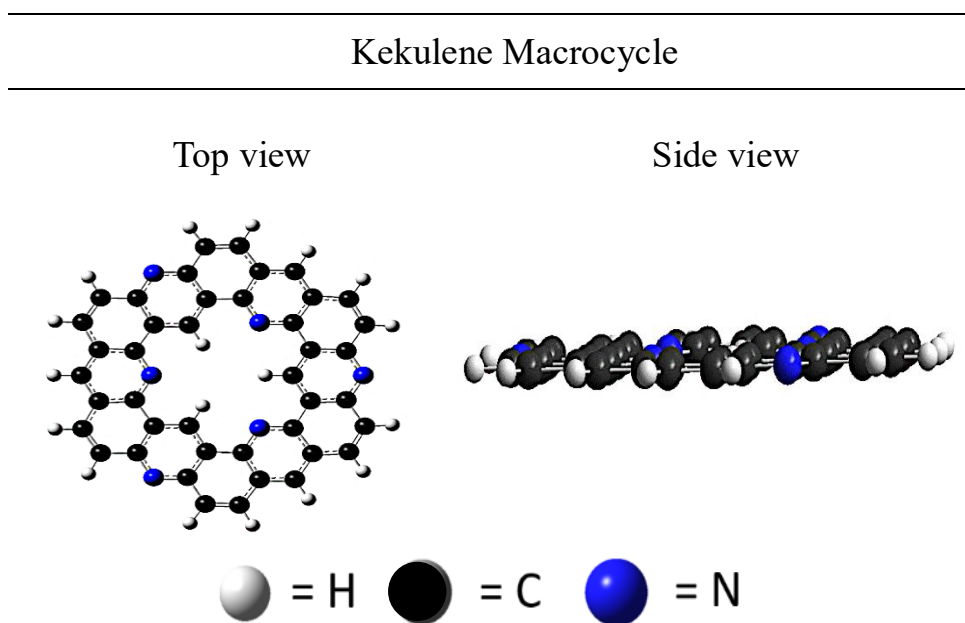


Fig. 3: Front and side views of optimized geometry of Kekulene macrocycle.

4.1.1 Geometry Optimization of CH₄, CO and CO₂@Kekulene Complexes:

Kekulene has been evaluated as a sensor toward greenhouse gases, including CH₄, CO, and CO₂ and optimised using ω B97XD/def2svp level of theory. The optimized geometry of the considered sensor is shown in Figure 2. Kekulene is a 2D, hexameric macrocycle having six hetero-ring subunits (pyridin), each subunit possessing one heteroatom (Nitrogen) that are alternately located at the inner and outer loci of the macrocycle (Figure 2).

Table 1: Interaction energy for each interaction possibility (P) of Kekulene macrocycle.

System	Most stable	2 nd stable	3 rd stable	4 rd stable
CH ₄ @Kekulene	P3 (-4.93)	P2 (-4.89)	P4 (-3.30)	P1 (-2.61)
CO@Kekulene	P3 (-3.18)	P2 (-3.05)	P1 (-3.05)	P4(-3.06)
CO ₂ @Kekulene	P1 (-5.74)	P4 (-5.73)	P3 (-5.47)	P2(-5.47)

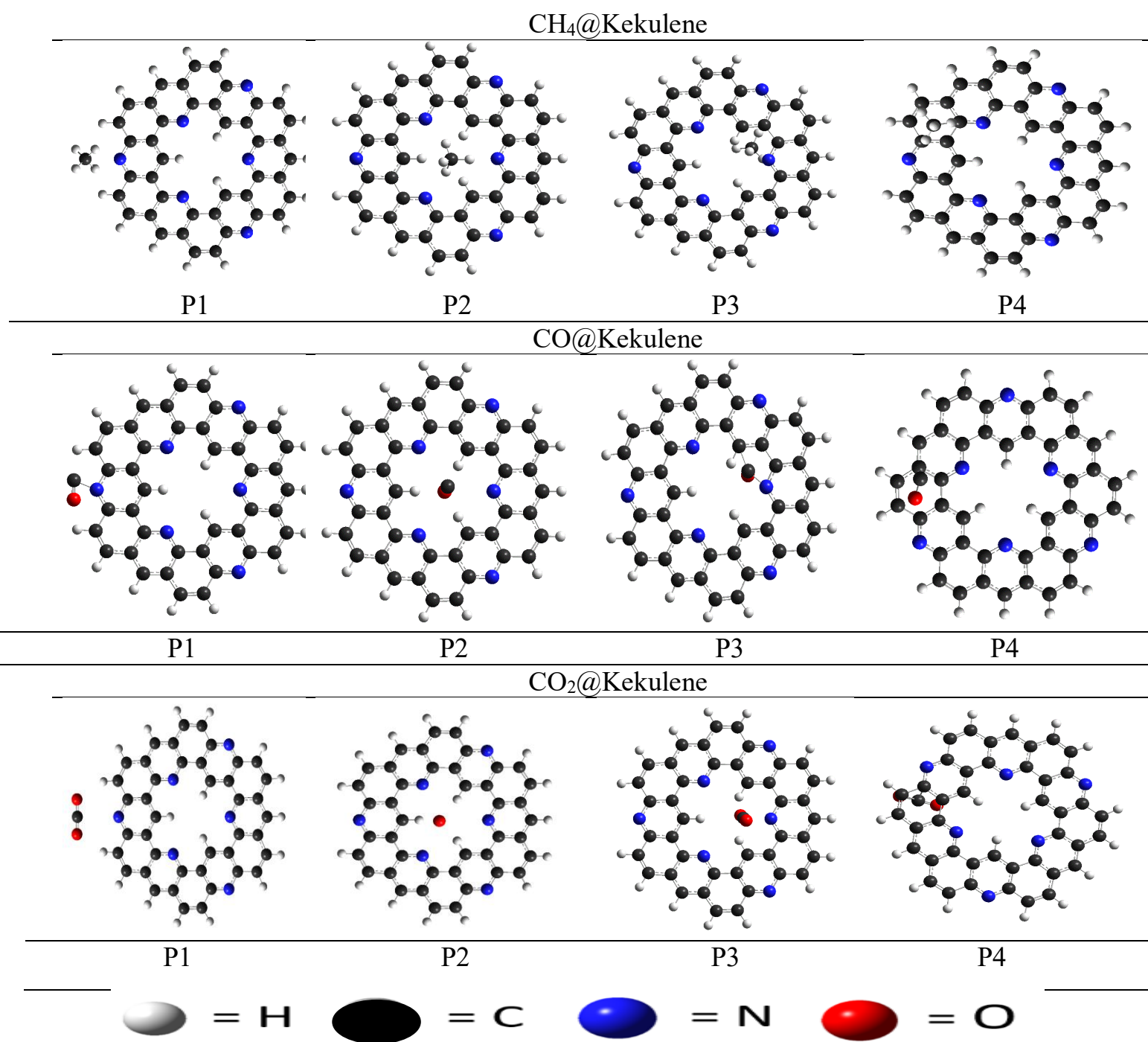


Fig. 4: Possible conformations (before optimization) of Kekulene macrocycle with analytes (CH_4 , CO , and CO_2).

Four different interaction possibilities between Kekulene and each analyte (CH_4 , CO , and CO_2) are optimized and shown in Figure 4. Among them, only the most stable complex with lower interaction energy is selected for further analysis (Table 1). The most stable structures of macrocycles onto each analyte (analyte@macrocycle) are shown in Figure 5. To facilitate comprehension, the complexes are named as CH_4 @Kekulene, CO @Kekulene and CO_2 @Kekulene. The nitrogen atom in pyridine subunits in the Kekulene macrocycle is expected to interact with the analytes (CH_4 , CO , and CO_2) because of the lone pair of electrons on the nitrogen atom.

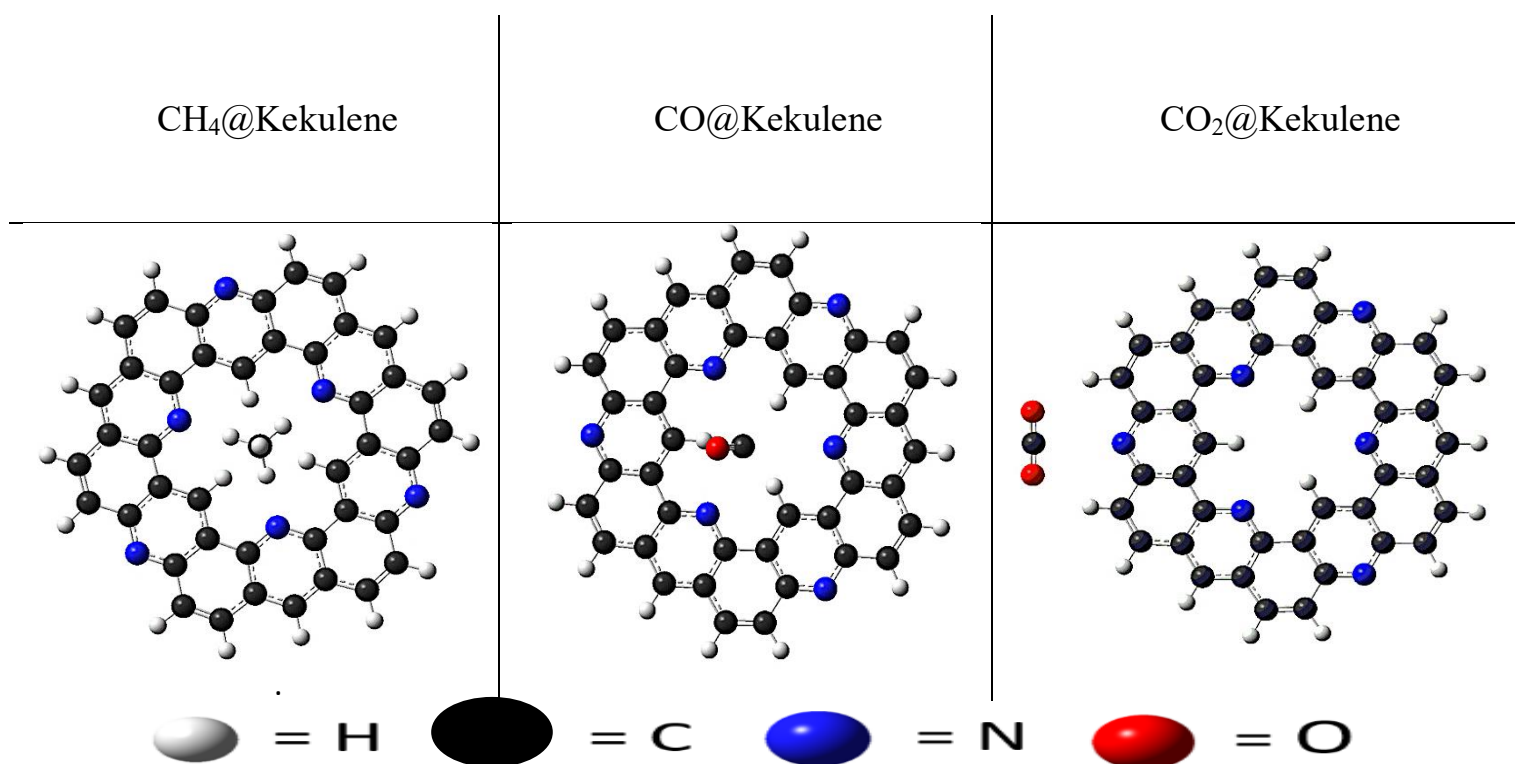


Fig. 5: Optimized (stable) geometries of anslyte@ kekulene complexes

In the analysis of Molecular Electrostatic Potential (MESP), the blue areas indicate regions that are deficient in electrons (electrophilic), whereas the red areas signify regions that are abundant in electrons (nucleophilic).

In this study, Molecular electrostatic potential (MESP) isosurfaces reveal that the cavity of Kekulene is nucleophilic (electron-rich). CO_2 acts as an electrophile, which explains its presence outside the cavity (Figure 5). The chemistry of CO is slightly ambivalent. CO has a small dipole moment, with the C atom. As a reason, it can act as both a nucleophile and an electrophile. with Kekulene macrocycle, CO acts as an electrophile (inside the macrocycle cavity). However, methane does not have a lone pair of electrons on the central atom. In other words, methane is not nucleophile, such that it binds more tightly to the nucleophilic site as in Kekulene cavity.

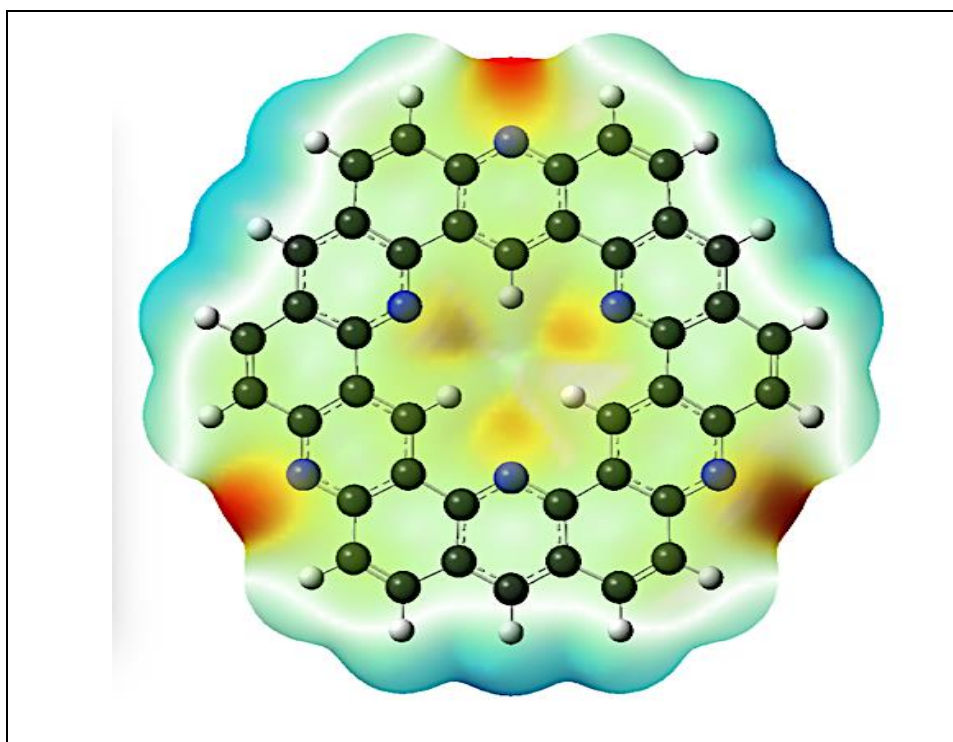


Fig. 6: Molecular electrostatic potential (MESP) isosurface of Kekulene macrocycle.

Table 2: bond critical point (BCP), Interacting atoms (A_{int}), interaction distances (D), interaction energies (E_{int}), electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), and total energy density (H) of analyte@Kekulene complexes.

System	BCP	A_{int}	D	E_{int}	ρ	$\nabla^2\rho$	H
CH ₄ @Kekulene	1	NH	2.79	-3.87	0.0062	0.0189	0.0006
	2	NH	2.78		0.0062	0.0191	0.0006
	3	HH	2.98		0.0042	0.0042	0.0014
	4	HH	2.98		0.0042	0.0042	0.0014
	5	NH	2.79		0.0062	0.0062	0.0006
CO@Kekulene	1	NC	3.51	-2.27	0.0036	0.0118	0.0007
	2	HC	2.92		0.0044	0.0160	0.0011
	3	HC	2.79		0.0051	0.0204	0.0014
	4	HC	3.01		0.0037	0.0131	0.0009
	5	NC	3.67		0.0028	0.0092	0.0006
CO ₂ @Kekulene	1	HO	2.33	-3.55	0.0117	0.0359	0.0003
	2	NC	3.12		0.0074	0.0267	0.0013
	3	HO	2.33		0.0117	0.0359	0.0003

4.1.2 Interaction Energies of Kekulene Macrocycle Toward Greenhouse Gases (CH₄, CO and CO₂):

The interaction of analytes with the Kekulene macrocycle leads to changes in several geometric characteristics. The two main factors to test the interaction strength (sensitivity) include interaction energy (E_{int}) and interaction distances (D) (Sajid et al., 2017a). As illustrated in Table 2, the negative interaction energies of Kekulene complexes suggest that the interactions are significantly exothermic, making them thermodynamically advantageous. In addition, the more negative values the more stable the systems, and vice versa (F. Ullah et al., 2020). The interaction energy values of CH₄@Kekulene, CO@Kekulene, and CO₂@Kekulene complexes are -3.87 kcal mol⁻¹, -2.27 kcal mol⁻¹, and -3.55 kcal mol⁻¹, respectively (Table 2). In the case of CH₄@Kekulene, the measured

interaction energy for the complex was $-3.87 \text{ kcal mol}^{-1}$, and the closest distance between the interacting atoms of the analyte and the Kekulene macrocycle (N...H) was found to be $2.78 \text{ \AA}$. The primary mode of interaction between CH_4 and Kekulene is through hydrogen bonding, supplemented by weak van der Waals forces. Likewise, the engagement of CO with the Kekulene macrocycle yields an interaction energy of $-2.27 \text{ kcal mol}^{-1}$, accompanied by a distance of $2.79 \text{ \AA}$ between the nearest interacting atoms of the analyte and the macrocycle. However, The E_{int} of CO_2 with Kekulene is $-3.55 \text{ kcal mol}^{-1}$ with $2.33 \text{ \AA}$ (H...O) interaction distance. CO_2 @Kekulene interaction is Primarily via hydrogen bonding in conjunction with weak van der Waals forces. As a result, the E_{int} value of CH_4 @Kekulene complex is the greatest, and the interaction distance is the shortest among all the investigated complexes. The highest E_{int} and shortest bond length observed in CH_4 @Kekulene result from effective hydrogen bonding and van der Waals forces within the complex. According to Sajid et al. (2017) the interaction trend between pyrrole (a nitrogen-containing surface) and analytes follows the order of $\text{CH}_4 > \text{CO}_2 > \text{CO}$. A similar pattern was also observed in the interaction between Kekulene (a pyridine subunit) and analytes. In this study, the results show that the sensitivity of Kekulene macrocycle is higher towards CH_4 as compared to CO and CO_2 . Kekulene macrocycle has a big nucleophilic cavity, which is a favourable place for the interaction of electrophiles such as CH_4 .

4.1.3 Quantum Theory of Atoms in Molecules (QTAIM) Analysis of CH₄, CO and CO₂@ Kekulene Complexes:

QTAIM is a widely accepted analysis (Alver et al., 2019), it is used to thoroughly characterize the strength of interaction between Kekulene and the analytes. In QTAIM, the electron density analysis focuses on identifying and highlighting the trajectories of maximum electron density between pairs of interacting atoms, called bond paths. Each bond path includes a specific point known as the bond critical point (BCP), which represents the peak electron density. The characteristics of atomic interactions can be assessed by examining different parameters at the bond critical point (BCP), such as electron density (ρ), the Laplacian of electron density ($\nabla^2\rho$), and total energy density (H). The intensity of these interactions is related to the level of electron density, while the signs of both the Laplacian and total energy densities indicate the nature of the interaction: specifically, when both $\nabla^2\rho$ and H are positive, this implies purely noncovalent interactions. Covalent characteristics are indicated when $\nabla^2\rho$ is positive and H is negative, whereas absolute covalent interactions are present when both $\nabla^2\rho$ and H are negative (Cortés-Guzmán & Bader, 2005). In this study, both $\nabla^2\rho$ and H have exhibited positive values (Table 2), indicating the presence of noncovalent interactions in analyte@Kekulene complexes. An electronic density (ρ) value above 0.1 typically indicates electrostatic interactions or hydrogen bonding, whereas values below 0.1 suggest weak van der Waals forces. In this study, the ρ values for all examined Kekulene complexes were found to be below 0.1 atomic units, highlighting the crucial role of weak van der Waals interactions in stabilizing these complexes. As shown in Table 2, the values of ρ range from 0.0028 to 0.0117 au in analyte@Kekulene complexes. All complexes of analyte@Kekulene feature multiple BCPs.

The bond with the shortest distance corresponds to the highest bond strength, indicated by the greatest electron density, which aligns with the expectation of stronger chemical bonds (Sanderson, 1976). These results are aligned with NCI analysis. (section 4.1.4). $\text{CH}_4@$ Kekulene and $\text{CO}@$ Kekulene have five BCPs. However, the binding orientations vary because of the distinct characteristics of the analytes. While $\text{CO}_2@$ Kekulene has three BCPs. All bond critical points (BCPs) discovered within the analyte@Kekulene systems are associated with weak noncovalent interactions, as evidenced by bond lengths greater than 2.5 Å. In contrast, the $\text{CO}_2@$ Kekulene scenario reveals a notably stronger interaction between a hydrogen atom from Kekulene and one of the oxygen atoms in the CO_2 molecule.

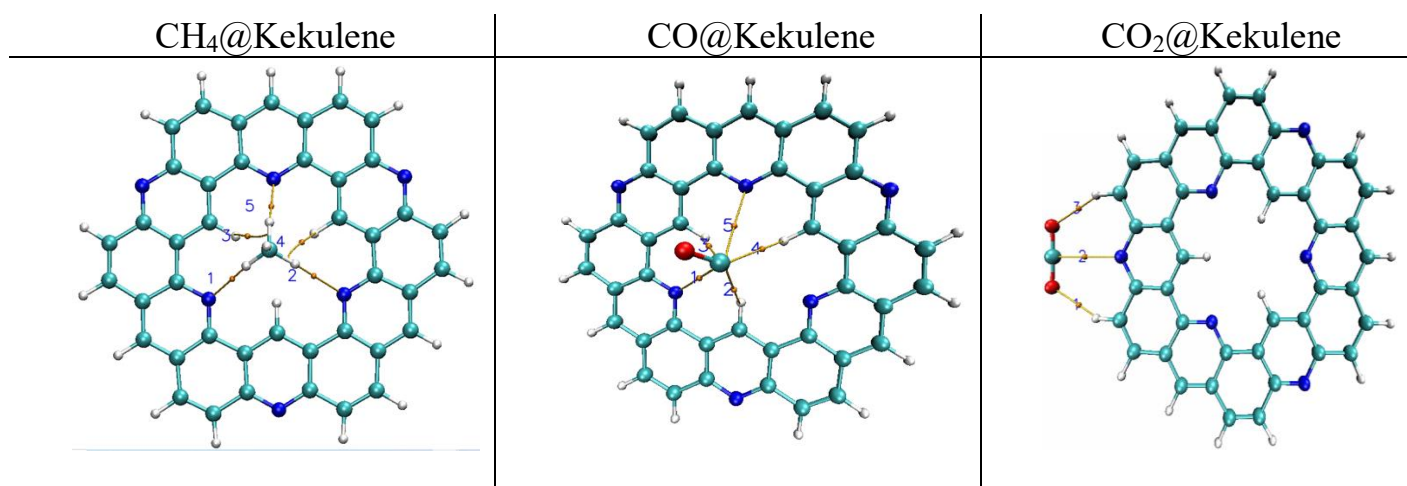


Fig. 7: QTAIM representations of CH_4 , CO and $\text{CO}_2@$ Kekulene complexes, respectively. The yellow lines represent bond paths, while the numbered orange spheres represent BCPs.

4.1.4 Non-Covalent Interactions (NCI) Analysis of CH₄, CO and CO₂@Kekulene Complexes:

The analysis of non-covalent interactions (NCI) is a contemporary theoretical approach aimed at visualizing these interactions through topological examination of electron density and its reduced gradient. This method utilizes three distinct color codes: green, red, and blue. The green hue signifies weak interactions, including dispersion forces or dipole–dipole interactions. In contrast, strong electrostatic interactions are depicted in blue, while the presence of steric repulsions is indicated by the red color (Sajid et al., 2021). The 3D isosurfaces of the analyte@Kekulene complexes are shown in Figure 8. Examination of these surfaces for all analytes (CH₄, CO, and CO₂) revealed that the green regions between the Kekulene macrocycle and the corresponding analytes, indicating the existence of weak interactions. Additionally, the absence of blue hues around the analytes and Kekulene signifies that there are no hydrogen bonds or strong interactions present. In the case of CH₄@Kekulene, the green coloration appears more extensive and denser, signifying stronger interactions between CH₄ atoms and Kekulene compared to other analyte@Kekulene complexes. Additionally, the NCI results for CH₄@Kekulene corroborate earlier findings by confirming both the strongest interaction energy and the shortest distance between interacting components.

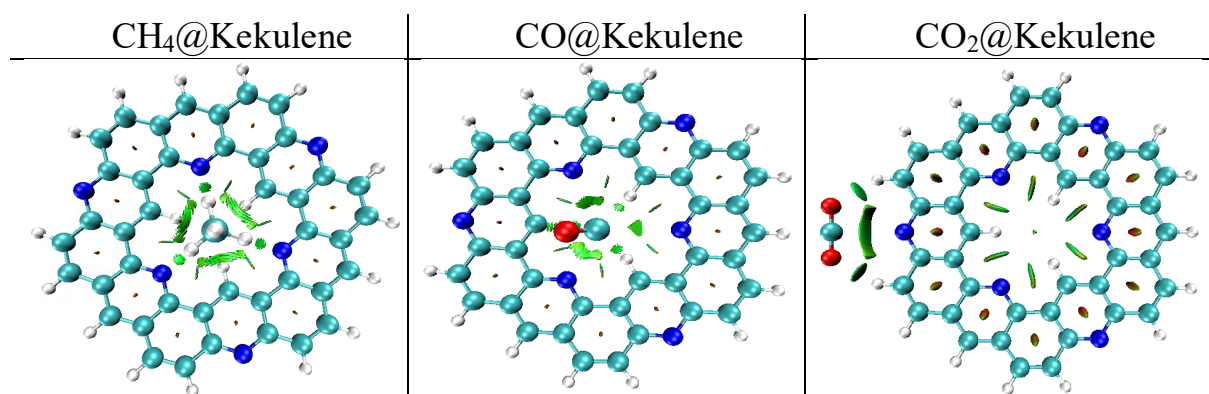


Fig. 8: 3D isosurfaces of analyte@Kekulene complexes.

4.1.5 Electronic Properties Analysis of CH₄, CO and CO₂@Kekulene Complexes:

Following the interaction with analytes, the changes in the electronic properties of Kekulene are evaluated, including the HOMO and LUMO energy levels, the HOMO–LUMO energy gap, and the extent of charge transfer. Electronic properties are tested upon the orbitals' capacities to donate and receive electrons. B3LYP/def2SVP method has been used for the electronic properties analysis. The method was selected based on literature evidence indicating that the B3LYP functional provides results closely matching experimental observations (Ayub, 2014; Sajid et al., 2018; H. Ullah et al., 2013), whereas the ω B97XD functional poorly estimates the electronic properties (Asif et al., 2022; Ayub, 2016). Natural Bond Orbital (NBO) and Frontier Molecular Orbital (FMO) analyses are utilized to explore the electronic characteristics of the systems being studied. These methods are essential for evaluating how sensitive the sensor, Kekulene, is to different analytes (Beheshtian et al., 2012a). When two species engage in interaction, it leads to a specific exchange process. This allows the highest-energy molecular orbital (HOMO) to transfer

electrons to the lowest-energy molecular orbital (LUMO). The energy difference (E_{gap}) between the electron-donating highest occupied molecular orbital (HOMO) and the electron-accepting lowest unoccupied molecular orbital (LUMO) has been employed to evaluate the stability of complexes such as analyt@Kekulene . This measure also aids in defining the nature of interactions and gauging electrical conductivity. Importantly, there is an inverse relationship between the conductivity of the macrocycle and the E_{gap} separating HOMO from LUMO; thus, even minor variations in E_{gap} can significantly impact conductivity (Beheshtian et al., 2012). The reduction of E_{gap} signifies an increasing in the system's conductivity, a crucial factor in sensing research. The variation in conductivity indicates the sensor's capability to identify the targeted analytes (Azam et al., 2017). The results in Table 3 show that the HOMO orbitals of bare Kekulene macrocycle is -6.08 eV. whereas LUMO was -2.37eV. However, it is notable that the E_{gap} has decreased from 3.72 eV in the pristine surface to 3.71, 3.70, and 3.71 eV for $\text{CH}_4\text{@Kekulene}$, CO@Kekulene , and $\text{CO}_2\text{@Kekulene}$, respectively. The insignificant reduction due to the weak interaction between Kekulene macrocycle and the analysts (CH_4 , CO , and CO_2). To investigate the impact of analyte adsorption on the electronic characteristics of the sensor, Figure 9 presents graphical illustrations of the HOMO and LUMO isosurfaces. These illustrations indicate that the electron densities associated with both HOMO and LUMO orbitals are spread across the surface of Kekulene (pristin), which is a consequence of resonance throughout the entire macrocycle. The electron density in the LUMO experiences minor shifts due to additional nodes (regions deficient in electrons), stemming from its relatively lower stability compared to the HOMO. Furthermore, there is no overlap between the Kekulene macrocycle and the absorbed analytes since covalent interactions are absent. Additionally, following complexation with analytes, there are no

significant alterations in electron density for either HOMO or LUMO, as strong distortions do not occur (indicating weak van der Waals interactions).

Table 3: Energy of HOMOs, LUMOs, HOMO-LUMO energy gaps (in eV) and charge transfer of analyte@ Kekulene.

System	E_{HOMO}	E_{LUMO}	E_{gap}	Charge transfer (Q)
Kekulene	-6.09	-2.37	3.72	
CH ₄ @Kekulene	-6.10	-2.39	3.71	-0.007
CO@Kekulene	-6.09	-2.39	3.70	0.003
CO ₂ @Kekulene	-6.10	-2.39	3.71	0.002

Natural Bond Orbital (NBO) analysis was utilized to evaluate the charge transfer (Q) occurring between the analytes and the surface. Positive NBO charge values represent analytes that donate electrons to the sensing material, while negative NBO charges signify the reverse process. As shown in Table 3, CO@Kekulene and CO₂@ Kekulene complexes had positive NPO charge values of 0.003 |e| , and 0.002 |e|, respectively. Indicating that the charges transfer from the analyst (CO and CO₂) to the Kekulene macrocycle. In Kekulene macrocycle, the electron cloud is moved by the oxygen of analyts (in CO and CO₂) that are rich in electrons toward Kekulene macrocycle. While CH₄@Kekulene had negative NBO charge (-0.007 |e|), indicating that the electron cloud is moved from Kekulene (nitrogen in pyridin) surface to CH₄ analyst. Results indicate that CH₄ exhibits superior sensing capabilities for Kekulene compared to CO₂ and CO, as evidenced by interaction energy and charge transfer assessments. Furthermore, the NBO charge analysis findings align with the interaction energy results; specifically, a significant level of charge transfer is noted for the CH₄@Kekulene complex, which also registers the highest interaction energy. In contrast, the CO₂@Kekulene complex demonstrates

the lowest charge transfer (0.002 |e|), attributed to its interaction involving two electron-rich oxygen atoms present in CO₂.

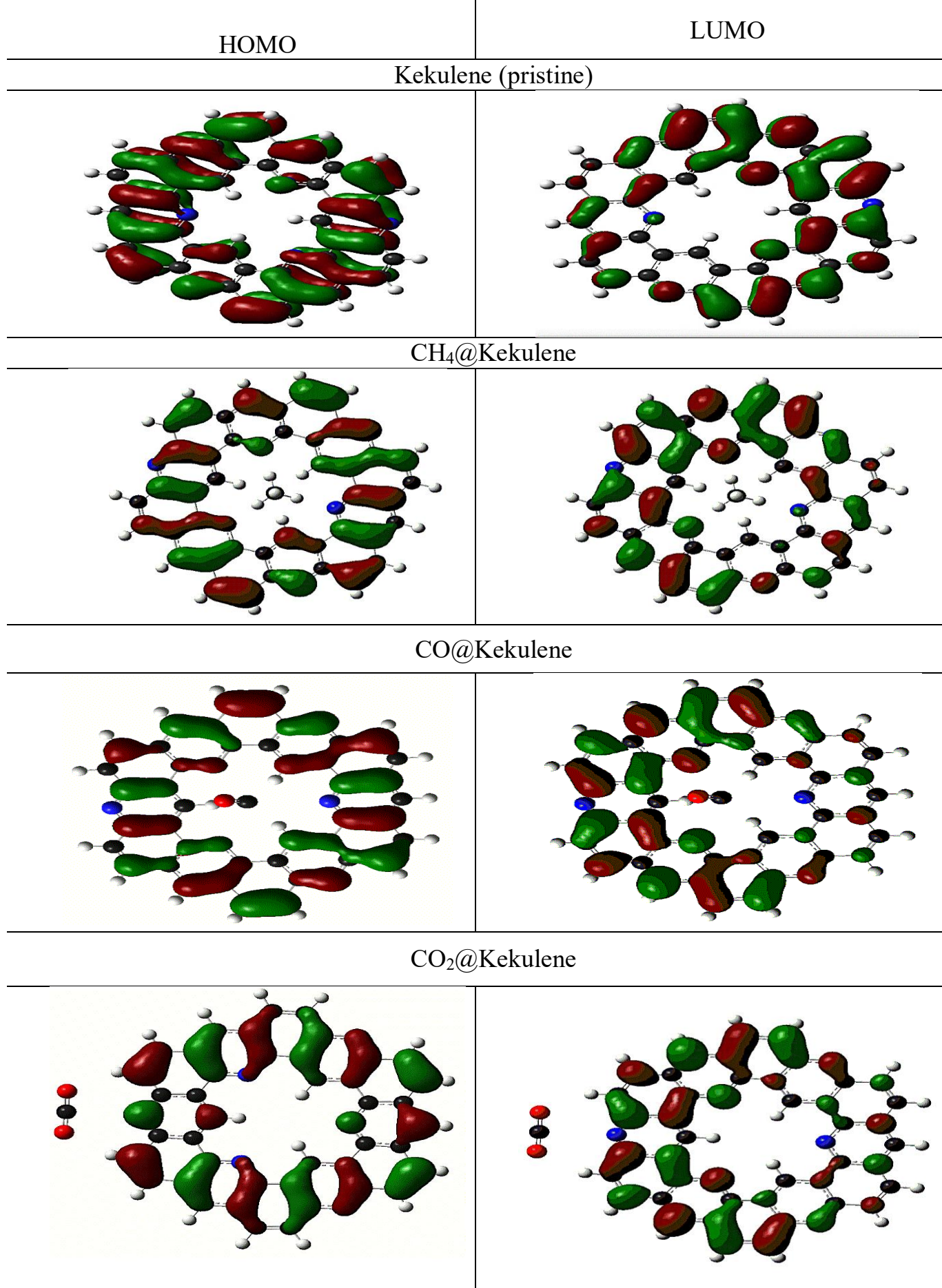


Fig. 9: Graphical depiction of the HOMO and LUMO isosurfaces to illustrate how adsorbing the analytes (CH₄, CO & CO₂) affects the sensor's (Kekulene) electrical environment.

4.2 Oxacalix[2]naphthalene[2]naphthyridine (Naphthyridine) Macrocycle:

Naphthalene is a well-known aromatic compound composed of two fused benzene rings. Diazanaphthalenes retain the core structure of naphthalene but incorporate two nitrogen atoms in place of two CH groups. These compounds, with the molecular formula $C_8H_6N_2$, are classified into two primary types: benzodiazines, where both nitrogen atoms are situated within the same ring, and naphthyridines, where each ring contains one nitrogen atom. Naphthyridines exist in six possible isomeric forms, defined by the positions of the nitrogen atoms—specifically at 1,5-, 1,6-, 1,7-, 1,8-, 2,6-, and 2,7-positions. Among these, the 1,8-naphthyridine derivatives have attracted notable scientific interest due to their distinct structural and electronic properties (Leshner et al., 1962). Naphthyridine functions as a structural subunit within the naphthyridine-based macrocycle. This macrocycle is characterized by an internal cavity that incorporates four nitrogen atoms and four hydrogen atoms. The compound oxacalix[2]naphthalene[2]naphthyridine was synthesized via a condensation reaction involving 2,7-dichloro-1,8-naphthyridine and 2,7-dihydroxy naphthalene (Katz et al., 2007). Furthermore, the electronic properties of naphthyridines follow the "pyridine" pattern (Paudler & Sheets, 1983).

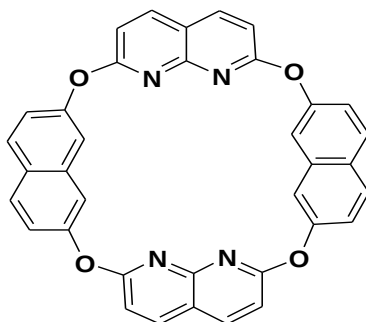


Fig. 10: Oxacalix[2]naphthalene[2]naphthyridine (Naphthyridine) Macrocycle.

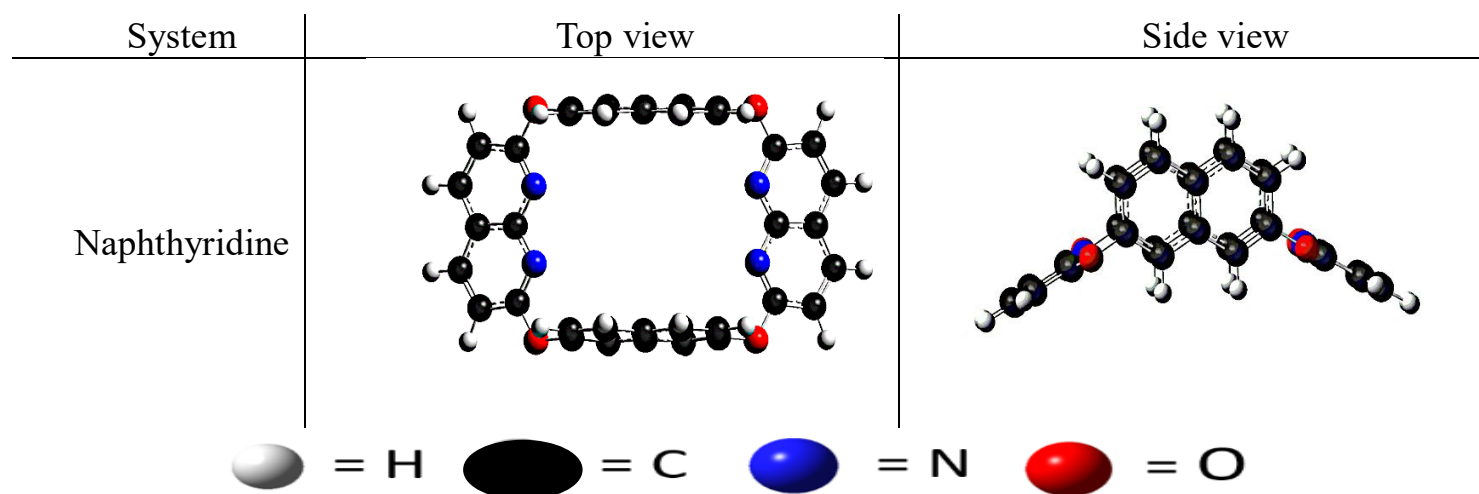


Fig. 11: Front and side views of optimized geometry of Naphthyridine macrocycle.

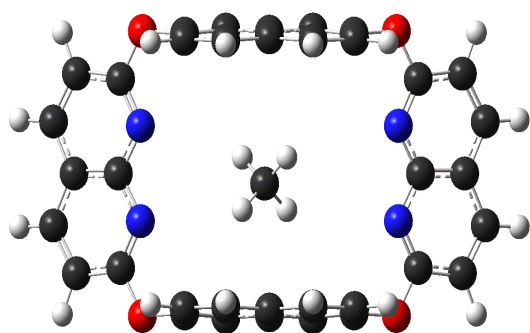
4.2.1 Geometry Optimization of CH₄, CO and CO₂@Naphthyridine Complexes:

The naphthyridine-based macrocycle has been evaluated for its sensing capabilities toward various gases, including CH₄, CO, and CO₂ and optimized using ω B97XD/def2svp level of theory. The optimized geometry of the considered sensor is shown in Figure 11. Naphthyridine is a 3D macrocycle having eight six-membered rings, four of them are hetero-rings. The subunit possesses one heteroatom (Nitrogen), all Nitrogens are located at the inner loci of the macrocycle.

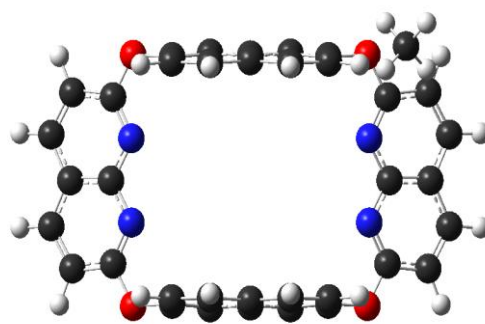
Table 4: interaction energy for each interaction possibility (P) of Naphthyridine macrocycle.

System	Most stable	2 nd stable
CH ₄ @Naphthyridine	P1 (-7.74)	P2 (-3.92)
CO@Naphthyridine	P1 (-7.57)	P2 (-2.26)
CO ₂ @Naphthyridine	P1 (-12.39)	P2 (-4.29)

CH₄@Naphthyridine

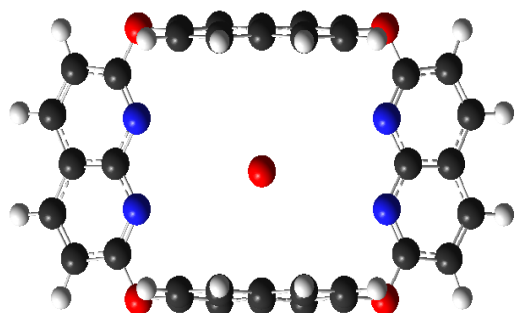


P1

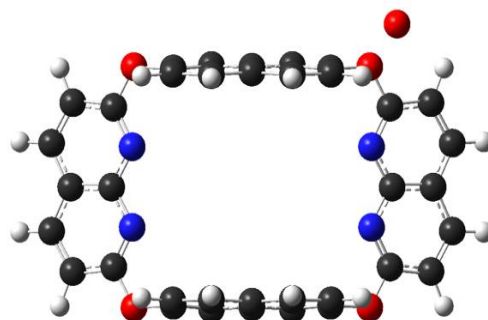


P2

CO@Naphthyridine

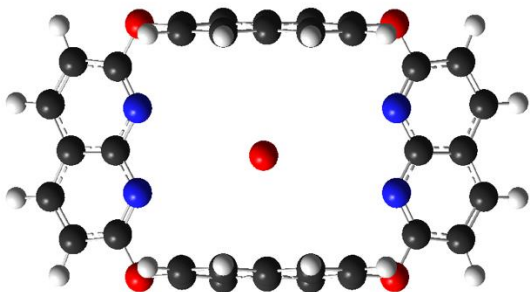


P1

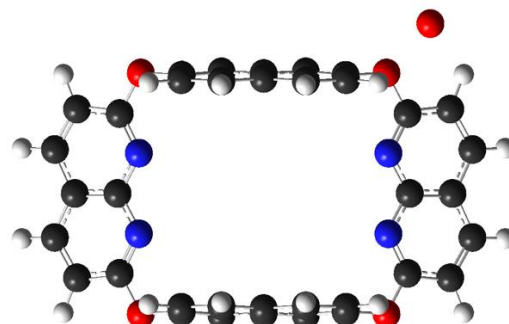


P2

CO₂@Naphthyridine



P1



P2



Fig. 12: possible conformations (before optimization) of anslyt@Naphthyridine complexes.

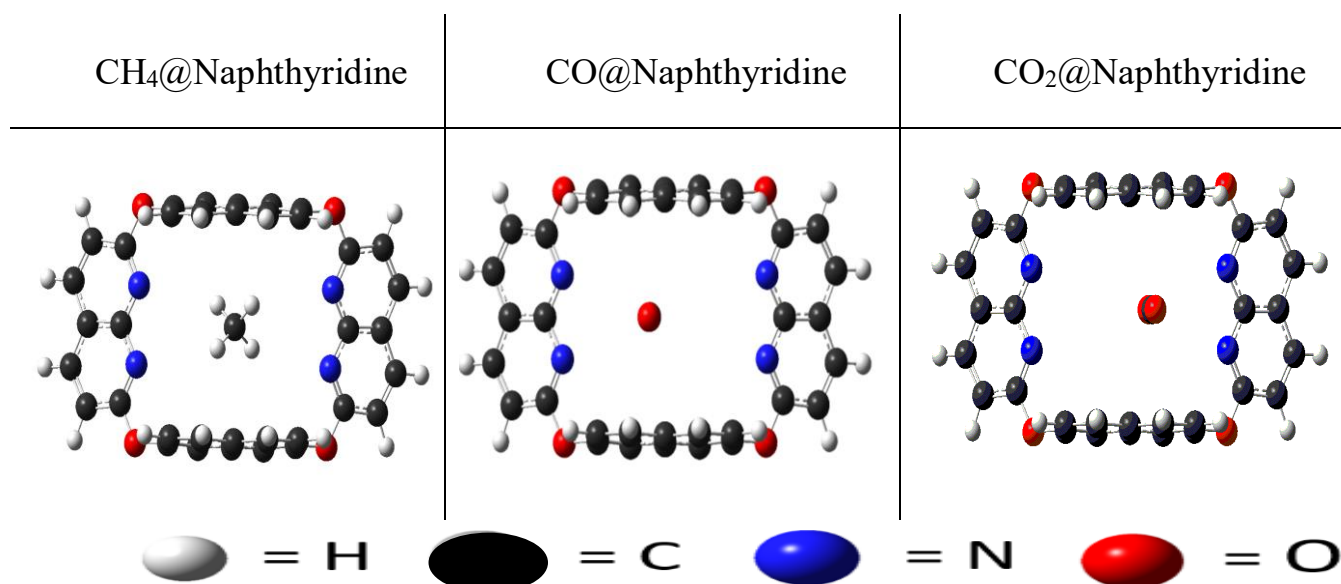


Fig. 13: Optimized (stable) geometries of analyt@Naphthyridine complexes.

Two possible interaction modes between Naphthyridine and each analyte (CH₄, CO, and CO₂) are depicted in Figure 12. The interaction energies (E_{int}) for each mode are presented in Table 4. Among them, only the most stable complex with lower interaction energy is selected for further analysis. The most stable macrocycle for each analyt (analyt@Naphthyridine) is shown in Figure 13. For ease of understanding, the complexes are named as CH₄@Naphthyridine, CO@Naphthyridine and CO₂@Naphthyridine. The nitrogen in the Naphthyridine macrocycle is expected to interact with the analyts (CH₄, CO, and CO₂) because of the lone pair of electrons.

In the MEP analysis, the areas depicted in blue indicate regions that are deficient in electrons (electrophilic), whereas the area shown in red signifies regions that are abundant in electrons (nucleophilic). The molecular electrostatic potential (MESP) isosurfaces (Figure 14) reveal that the cavity of the naphthyridine macrocycle is nucleophilic in nature, indicating a region of high electron density. CO₂ acts as an electrophile because the oxygen atoms withdraw electron density, giving the carbon a

partial positive charge. This characteristic explains why CO₂ was present inside the cavity. In contrast, CO has a small dipole moment, with the carbon atom carrying a partial positive charge. As a result, CO can act as both a nucleophile and an electrophile. In the case of Naphthyridine, CO acts as an electrophile within the macrocyclic cavity. However, methane (CH₄) lacks a lone pair of electrons on its central atom, meaning it is not a nucleophile. As a result, it does not bind as strongly to the nucleophilic site within the Naphthyridine cavity.

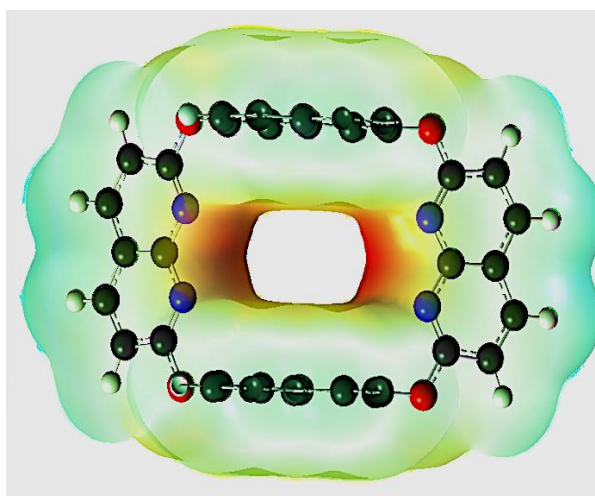


Fig. 14: Molecular electrostatic potential (MESP) isosurface of Naphthyridine macrocycle.

Table 5: bond critical point (BCP), Interacting atoms (A_{int}), interaction distances (D), interaction energies (E_{int}), electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), and total energy density (H) of analyte@Naphthyridine complexes.

System	BCP	A_{int}	D	E_{int}	ρ	$\nabla^2\rho$	H
CH ₄ @Naphthyridine	1	CH	2.84	-5.39	0.0064	0.0209	0.0010
	2	CH	2.97		0.0055	0.0178	0.0010
	3	NH	3.43		0.0019	0.0077	0.0006
	4	NH	3.03		0.0038	0.0132	0.0007
	5	NH	3.03		0.0038	0.0133	0.0007
	6	CH	2.84		0.0064	0.0208	0.0010
	7	CH	2.96		0.0055	0.0178	0.0010
	8	NH	3.43		0.0019	0.0077	0.0006

CO@Naphthyridine	1	CO	3.37	-5.39	0.0044	0.0144	0.0006
	2	CC	3.48		0.0040	0.0008	0.0008
	3	NC	3.34		0.0046	0.0158	0.0009
	4	NC	3.34		0.0046	0.0158	0.0009
	5	CO	3.37		0.0044	0.0144	0.0006
	6	CC	3.49		0.0039	0.0129	0.0008
CO ₂ @Naphthyridine	1	CO	3.41	-9.09	0.0043	0.0145	0.0006
	2	CO	3.54		0.0038	0.0126	0.0007
	3	NC	3.08		0.0070	0.0288	0.0015
	4	NC	3.08		0.0070	0.0287	0.0015
	5	CO	3.41		0.0044	0.0144	0.0006
	6	CO	3.56		0.0037	0.0123	0.0007

4.2.2 Interaction Energies of Naphthyridine Macrocycle Toward Greenhouse Gases (CH₄, CO and CO₂):

The engagement of analysts with the Naphthyridine macrocycle leads to alterations in several geometric parameters. The two main factors to test the interaction strength (sensitivity) include interaction energy (E_{int}) and interaction distances (D) (Sajid et al., 2017a). As illustrated in Table 5, the unfavorable interaction energies of Naphthyridine complexes indicate that the interaction is significantly exothermic, making it thermodynamically advantageous. In addition, the more negative values the more stable the systems, and vice versa (F. Ullah et al., 2020). The interaction energy value of CH₄@ Naphthyridine, CO@ Naphthyridine, and CO₂@ Naphthyridine complexes are -5.39 kcal mol⁻¹, -5.39 kcal mol⁻¹, and -9.09 kcal mol⁻¹, respectively. As shown in Table 5, the E_{int} of CH₄@Naphthyridine complex was -5.39 kcal mol⁻¹. However, the distance between the closest interacting atoms of the analyte and the naphthyridine macrocycle (C⋯H) was found to be 2.84 Å. The interaction of CH₄ with the macrocycle is primarily governed by weak van der Waals forces. Similarly, the interaction of CO with Naphthyridine macrocycle results in E_{int} of -5.39

kcal mol⁻¹ with 3.35Å(N...C) interaction distance between the nearest interacting atoms of analyte and macrocycle. However, The E_{int} of CO₂ with Naphthyridine macrocycle is -9.09 kcal mol⁻¹ with 3.08Å (N...C) interaction distance. Furthermore, the interaction between CO₂ and naphthyridine primarily involved hydrogen bonding, supplemented by minor van der Waals forces. As a result, The E_{int} value of CO₂@Naphthyridine complex is higher, and the interaction distance is shorter than CO but more than CH₄. The highest E_{int} and relatively short bond length of CO₂@Naphthyridine is because of efficient hydrogen bonding and van der Waals interactions in the complex. The general trend of interaction (considering both interaction energy and interaction distances) between Naphthyridine and analytes was CO₂>CH₄>CO. In this study, the results show that the sensitivity of Naphthyridine macrocycle is higher towards CO₂ analytes than CO and CH₄. Naphthyridine macrocycle has a highly nucleophilic cavity, which is a favourable place for the interaction of electrophiles such as CO₂.

4.2.3 Quantum Theory of Atoms in Molecules (QTAIM) Analysis of Naphthyridine macrocycle complexes (CH₄, CO and CO₂@Naphthyridine):

In the examined systems, both the Laplacian of electron density ($\nabla^2\rho$) and the total energy density (H) show positive values (refer to Table 5), indicating that noncovalent interactions are present in the analyte@Naphthyridine complexes. These findings indicate that the primary factor in stabilizing the complexes is weak van der Waals forces, given that all related electron density (ρ) measurements fall below 0.1 atomic units (au). Specifically, ρ values for the analyte@Naphthyridine systems range from 0.0019 to 0.0070 au, as reported in Table 5. Additionally, each complex contains multiple bond critical points (BCPs),

further supporting the presence of weak intermolecular interactions. It is noteworthy that a shorter bond distance corresponds to a higher bond strength, characterized by increased electron density, which aligns with the general expectation of stronger chemical bonds (Sanderson, 1976). These results align with NCI analysis (refer to section 4.2.4). Both CO@Naphthyridine and CO₂@Naphthyridine exhibit six bond critical points (BCPs). However, there are variations in their binding orientations, which can be attributed to the differing properties of the analytes. In contrast, CH₄@Naphthyridine displays eight BCPs. Furthermore, all BCPs associated with analyte@Naphthyridine indicate weak noncovalent interactions characterized by extended bond distances ($D > 2.5 \text{ \AA}$).

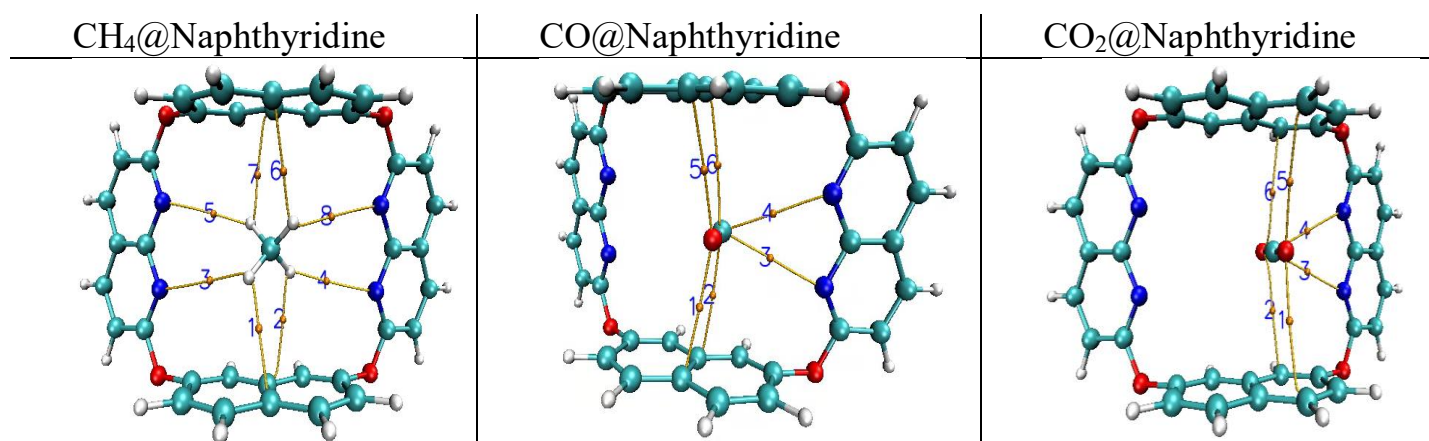


Fig. 15: QTAIM representations of CH₄, CO and CO₂@Naphthyridine complexes, respectively. The yellow lines represent bond paths, while the numbered orange spheres represent BCPs.

4.2.4 Non-Covalent Interactions (NCI) Analysis of CH₄, CO and CO₂@Naphthyridine Complexes:

The 3D isosurfaces representing the analyte@Naphthyridine complexes are shown in Figure 16. These isosurfaces for all the analytes (CH₄, CO, and CO₂) reveal green regions located between the Naphthyridine macrocycle and the analytes, indicating weak non-covalent

interactions. Conversely, the absence of blue color in the regions between the analytes and Naphthyridine indicates a lack of hydrogen bonds or significant interactions.

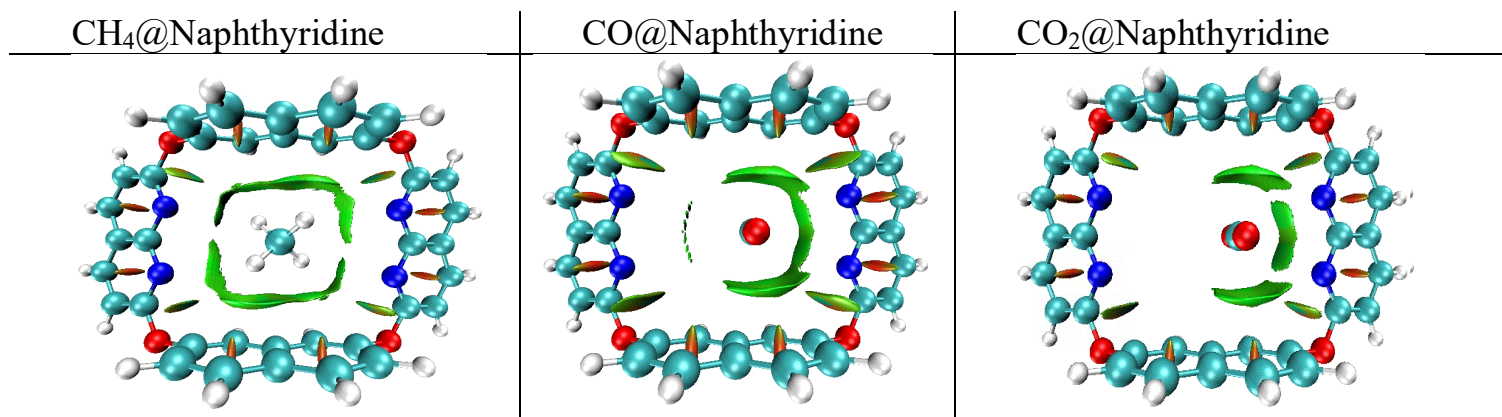


Fig. 16: 3D isosurfaces of analyte@Naphthyridine complexes.

4.2.5 Electronic Properties Analysis of CH₄, CO and CO₂@Naphthyridine Complexes:

Following the interaction with the analytes, an evaluation is conducted on the changes in the electronic characteristics of Naphthyridine. This includes examining the energies associated with its HOMO and LUMO orbitals, determining the energy gaps between these orbitals, and assessing the extent of charge transfer. Electronic properties are tested upon the orbitals' capacities to donate and receive electrons. B3LYP/def2SVP method has been used for the electronic properties analysis. The choice to adopt this method is supported by the literature, where the B3LYP functional has been shown to yield results consistent with experimental findings (Ayub, 2014; Sajid et al., 2018; H. Ullah et al., 2013), whereas the ω B97XD functional poorly estimates the electronic properties (Asif et al., 2022; Ayub, 2016). Natural Bond Orbital (NBO) and Frontier Molecular Orbital (FMO) analyses are utilized to examine the electronic properties of the systems being studied. These methods are

essential for evaluating the sensitivity of the Naphthyridine sensor to different analytes (Beheshtian et al., 2012a). The energy gap (E_{gap}) between the electron-donating HOMO and the electron-accepting LUMO is used to evaluate the stability of complexes, such as Analyte@Naphthyridine, and to characterize the nature of these interactions and their effects on electrical conductivity. Notably, the conductivity of the macrocycle is inversely related to the H-L E_{gap} , indicating that even minor variations in E_{gap} can significantly affect conductivity (Beheshtian et al., 2012). As shown in Table 6, the energy level of the HOMO for the bare Naphthyridine macrocycle is -5.92 eV, while its LUMO stands at -1.65 eV, leading to a HOMO-LUMO energy gap of 4.26 eV. After complexation with CH_4 , CO, and CO_2 , the measured EH-L energy gaps are 4.29 eV, 4.28 eV, and 4.16 eV respectively, as summarized in Table 6. After complexation, insignificant reduction in E_{gap} was these due to the weak interaction between Naphthyridine macrocycle and the analyts (CH_4 , CO, and CO_2). To examine the impact of analyte adsorption on the electronic environment of the sensor, Figure 17 presents graphical representations of the isosurfaces for both HOMO and LUMO. This depiction reveals that the electron densities of both HOMO and LUMO orbitals are spread across the surface of Naphthyridine, owing to resonance throughout the entire macrocycle. More nodes (Regions with no electron density) appear in LUMO due to the less stableity of LUMO compared to HOMO. In addition, no overlap between Naphthyridine macrocycle and the analysts because there is no covalent interaction. Moreover, No significant change in electron density of HOMO and LUMO after complexation with analysts because there is no strong distortion (weak Van der Waals interaction).

Table 6: Energy of HOMOs, LUMOs, HOMO-LUMO energy gaps (in eV) and charge transfer of analyte@Naphthyridine.

System	E _{HOMO}	E _{LUMO}	E _{gap}	Charge (Q)
Naphthyridine	-5.92	-1.65	4.26	
CH ₄ @Naphthyridine	-5.92	-1.62	4.29	-0.013
CO@Naphthyridine	-5.94	-1.65	4.28	-0.007
CO ₂ @Naphthyridine	-5.86	-1.70	4.16	-0.008

The charge transfer quantity (QNBO) occurring during the interactions between the analytes and surfaces was investigated through NBO charge analysis. Analytes transferring electrons to the sensing material are analogous to positive values of the NBO charge, whereas negative charges indicate the opposite. As shown in Table 6, CH₄@Naphthyridine, CO@Naphthyridine and CO₂@Naphthyridine complexes had negative Q_{NBO} values of -0.013 |e|, -0.007 |e|, and -0.008 |e|, respectively, indicating that the charges transfer from the Naphthyridine Macrocycle to the analyte (CH₄, CO and CO₂). In Naphthyridine macrocycle, the electron cloud is moved by the Nitrogen of Naphthyridine macrocycle toward the analytes (electron pair). Results indicate that CH₄ exhibits significant sensing capabilities for Naphthyridine through charge transfer mechanisms. Although, CO₂ shows higher sensitivity in term of interaction energy. The CO@Naphthyridine complex shows the least charge transfer (-0.007 |e|), corresponding to the interaction energy trend.

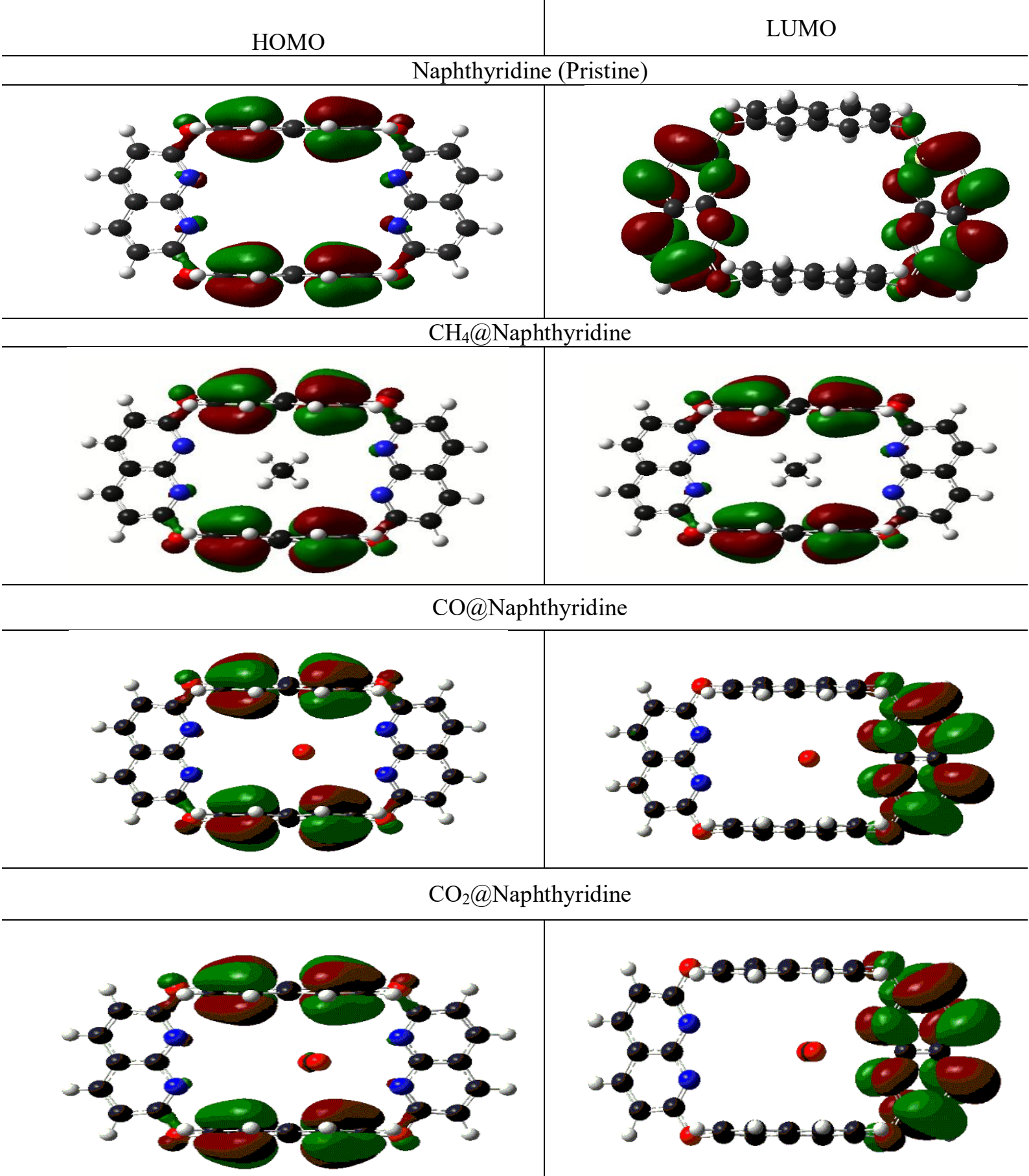


Fig. 17: A graphical depiction of the HOMO and LUMO isosurfaces to illustrate how adsorbing the analytes (CH₄, CO & CO₂) affects the sensor's (Naphthyridine) electrical environment.

4.3 Oxacalix[2]arene[2]pyrazine (Calixarene) Macrocycle:

The inaugural oxygen-bridged calixarene compound was created in 1966 by Sommer and Staab. This was achieved by reacting activated 2,6-dichloropyridine with 4,6-dichloropyrimidine, resulting in the formation of oxacalix[2]arene[2]pyrazine (C. Zhang & Chen, 2007). Calixarene is a macrocyclic structure made up of 4, 6, or 8 phenolic components connected by methylene linkages (Kermani et al., 2022). However, Replacing methylene in Calixarene macrocycle with sulfur, oxygen, or nitrogen to link the aromatic units has recently attracted much attention because of their synthetic availability and promising applications in the sensing field (Li et al., 2023). In addition, this macrocycle is a cage-like structure with high molecular symmetry. Moreover, Calixarene macrocycle contains two hydrogens in its internal cavity along with two nitrogens and four oxygens.

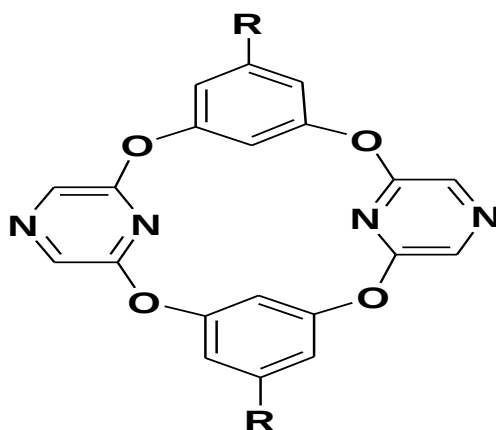


Fig. 18: The structure of Oxacalix[2]arene[2]pyrazine (Calixarene) macrocycle.

System		Top view		Side view
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Calixarene

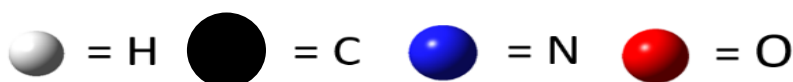
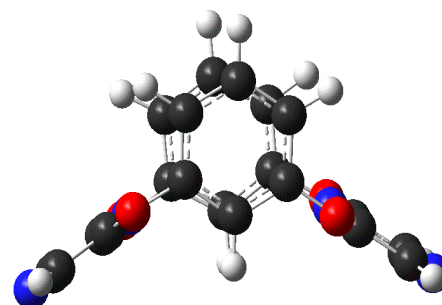
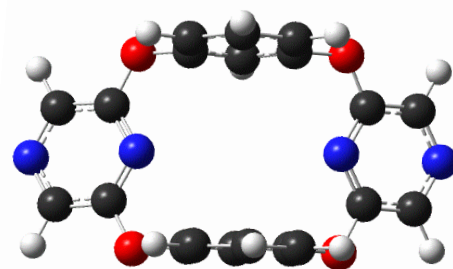


Fig. 19: Front and side views of optimized geometry of Calixarene macrocycle.

4.3.1 Geometry Optimization of CH₄, CO and CO₂@Calixarene Complexes:

Calixarene has been evaluated as a sensor for various gases, such as CH₄, CO, and CO₂, with optimizations carried out at the ω B97XD/def2svp theoretical level. The optimised structure of the sensor being examined is shown in Figure 19. Calixarene is a 3D macrocycle having four six-membered rings, two of them contain hetero-atoms. Each hetero-ring contains two nitrogens which are all located at the inner loci of the macrocycle.

Table 7: interaction energy for each interaction possibility (P) of Naphthyridine macrocycle.

System	Most stable	2 nd stable
CH ₄ @Calixarene	P1 (-3.93)	P2 (-1.88)
CO@Calixarene	P1 (-3.48)	P2 (-2.22)
CO ₂ @Calixarene	P1 (-6.12)	P2 (-5.27)

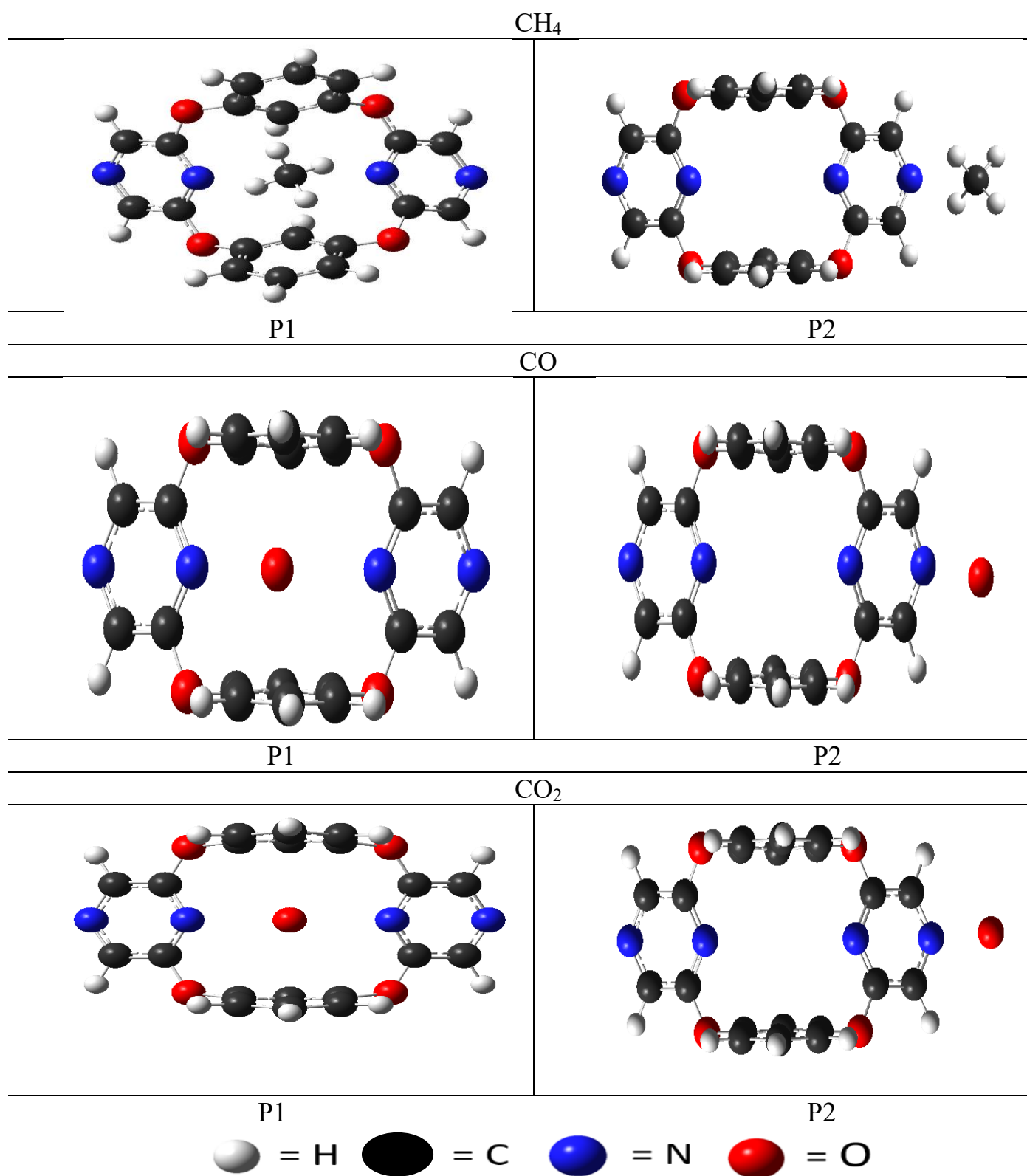


Fig. 20: possible conformations (before optimization) of Calixarene macrocycle with each analyte.

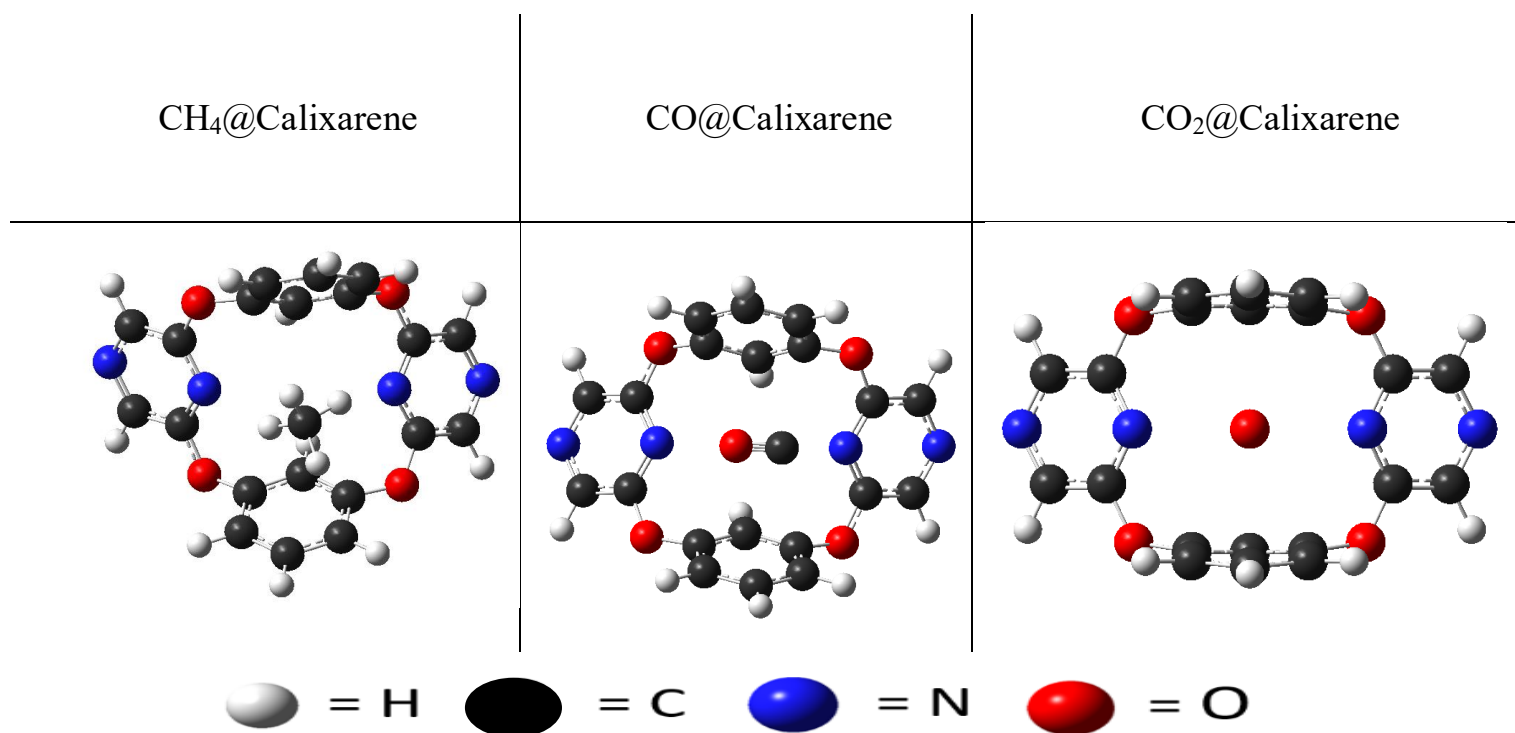


Fig. 21: Optimized (stable) geometries of the anslyte@Calixarene complexes.

Two interaction possibilities between Calixarene and each analyte (CH₄, CO, and CO₂) are shown in Figure 20. In addition E_{int} of each interaction possibility are listed in Table 7. Among these, only the complexes exhibiting the lowest interaction energy, indicating the highest stability, are selected for further analysis. The most stable complexes are shown in Figure 21. To facilitate understanding, these complexes are labeled as CH₄@Calixarene, CO@Calixarene, and CO₂@Calixarene. The nitrogens in the Calixarene macrocycle are expected to interact with the analytes (CH₄, CO, and CO₂) because of the lone pair of electrons.

Molecular electrostatic potential (MESP) isosurfaces (Figure 22) reveals that the electron density in Calixarene is condensed on the oxygen bridges between the aromatic. CO₂ is electrophile (Oxygen withdraws electron density from carbon, giving it a partial positive charge and rendering carbon dioxide an electrophile), this was the reason why CO₂ was inside the cavity (surrounded by electron clouds). CO has a small

dipole moment, with the C atom. As a reason, it can act as both a nucleophile and an electrophile. In Calixarene case, CO act as electrophile (inside the macrocycle cavity). However, the central atom in methane lacks a lone pair of electrons. In other words, methane is not nucleophile, such that it can binds more tightly to the nucleophilic site as in Calixarene cavity.

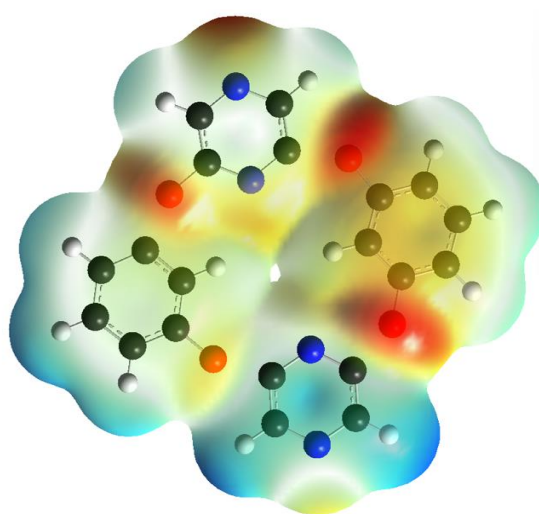


Fig. 22: Molecular electrostatic potential (MESP) isosurface of Calixarene macrocycle.

4.3.2 Interaction Energies of Calixarene Macrocycle Toward Greenhouse Gases (CH_4 , CO and CO_2):

The engagement of analytes with the Calixarene macrocycle results in alterations to various geometric properties. The two main factors to test the interaction strength (sensitivity) include interaction energy (E_{int}) and interaction distances (D) (Sajid et al., 2017a). As shown in Table 8, the negative interaction energies of Calixarene complexes indicate that the interaction is highly exothermic which is thermodynamically favourable. In addition, the more negative values the more stable the systems, and vice

versa (F. Ullah et al., 2020). The interaction energy values for the CH₄@Calixarene, CO@Calixarene, and CO₂@Calixarene complexes are -2.28, -1.45, and -2.99 kcal mol⁻¹, respectively, as presented in Table 8. Specifically, the CH₄@Calixarene complex exhibits an interaction energy of -2.28 kcal mol⁻¹. The shortest distance between the interacting atoms (C...H) within this complex is 2.89 Å, indicating weak non-covalent interaction. CH₄ interacts with Calixarene mainly through weak van der Waals interactions. Similarly, the interaction between CO and the Calixarene macrocycle yields an interaction energy (*E*_{int}) of -1.45 kcal mol⁻¹, with a distance of 3.26 Å (N...C) measured between the closest interacting atoms of the analyte and the macrocycle. However, The *E*_{int} of CO₂ with Calixarene is -2.99 kcal mol⁻¹ with 2.44Å (N...C) interaction distance. Additionally, the interaction between CO₂ and Calixarene was primarily mediated by hydrogen bonding, along with weaker van der Waals interactions. As a result, CO₂@Calixarene complex shows the greatest *E*_{int} value and the shortest interaction distance among other complexes. The general trend of interaction (considering both interaction energy and interaction distances) between Calixarene and analytes was CO₂ > CH₄ > CO (similar to Naphthyridine macrocycle). In this study, the results show that the sensitivity of Calixarene macrocycle is higher towards CO₂ analytes than CO and CH₄. Calixarene macrocycle has a highly nucleophilic cavity, which is a favourable place for the interaction of electrophiles such as CO₂.

Table 8: bond critical point (BCP), Interacting atoms (A_{int}), interaction distances (D), interaction energies (E_{int}), electron density (ρ), Laplacian of electron density ($\nabla^2\rho$), and total energy density (H) of analyte@Calixarene complexes.

System	BCP	A_{int}	D	E_{int}	ρ	$\nabla^2\rho$	H
CH ₄ @Calixarene	1	CH	2.97	-2.28	0.0058	0.0179	0.0010
	2	CH	2.89		0.0051	0.0165	0.0007
	3	NH	2.96		0.0044	0.0151	0.0007
	4	NH	2.97		0.0057	0.0178	0.0010
	5	NH	3.03		0.0047	0.0148	0.0007
CO@Calixarene	1	CH	3.27	-1.45	0.0062	0.0186	0.0011
	2	CH	3.41		0.0043	0.0142	0.0008
	3	NH	3.44		0.0031	0.0137	0.0007
	4	CO	3.37		0.0053	0.0154	0.0009
	5	CC	3.26		0.0058	0.0180	0.0006
CO ₂ @Calixarene	1	NC	2.58	-2.99	0.0208	0.0806	0.0022
	2	NC	2.44		0.0271	0.1071	0.0020
	3	CO	2.44		0.0271	0.1071	0.0021
	4	CC	2.58		0.0209	0.0806	0.0022

4.3.3 Quantum Theory of Atoms in Molecules (QTAIM) Analysis of CH₄, CO and CO₂@Calixarene Complexes:

In the systems we examined, both $\nabla^2\rho$ and H exhibit positive values (Table 8), which indicates that noncovalent interactions are present in analyte@Calixarene complexes. Regarding electronic density (ρ), a ρ value exceeding 0.1 signifies the presence of electrostatic interactions or hydrogen bonds, while a value below 0.1 indicates weak van der Waals forces. In this study, the weak van der Waals interactions dominate in stabilizing Calixarene complexes because the values of ρ for all the

complexes are less than 0.1 au. As illustrated in Table 8, the ρ values range from 0.0031 to 0.0271 au within analyte@Calixarene complexes. Each of these complexes comprises multiple bond critical points (BCPs). Furthermore, the bond distance that is shortest correlates with the highest bond strength (indicated by greater electron density), supporting the expectation of stronger chemical bonds (Sanderson, 1976). These results align with NCI analysis (refer to section 4.3.4). CO@Calixarene and CH₄@Calixarene exhibit five Binding Coordination Points (BCPs) each. Nevertheless, the binding orientations differ due to the distinct characteristics of the analytes. In contrast, CO₂@Calixarene contains four BCPs. Overall, all BCPs in analyte@Calixarene are indicative of weak noncovalent interactions characterized by extended bond distances ($D > 2.4$ Å).

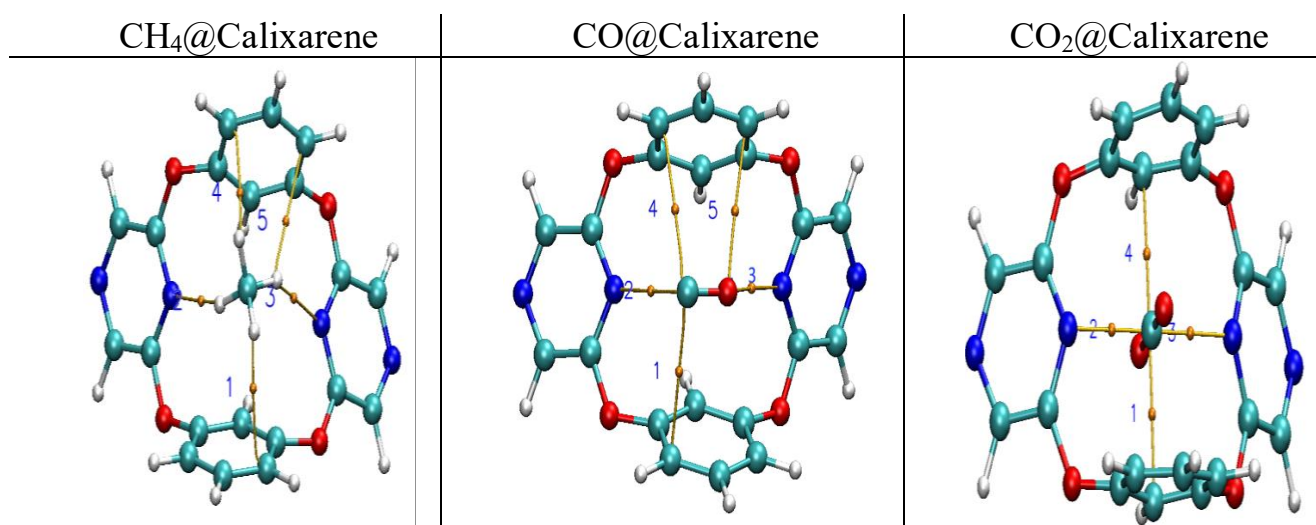


Fig. 23: QTAIM representations of CH₄, CO and CO₂@Calixarene complexes, respectively. The yellow lines represent bond paths, while the numbered orange spheres represent BCPs.

4.3.4 Non-Covalent Interactions (NCI) Analysis of CH₄, CO and CO₂@Calixarene Complexes:

Figure 24 shows the 3D isosurfaces for the complexes of the analytes with Calixarene. These isosurfaces, for different analytes (CH₄, CO, and CO₂), display green regions between the Calixarene macrocycle and the analytes, indicating weak non-covalent interactions. The lack of blue coloration observed between the analytes and Calixarene indicates the absence of hydrogen bonds or significant interactions.

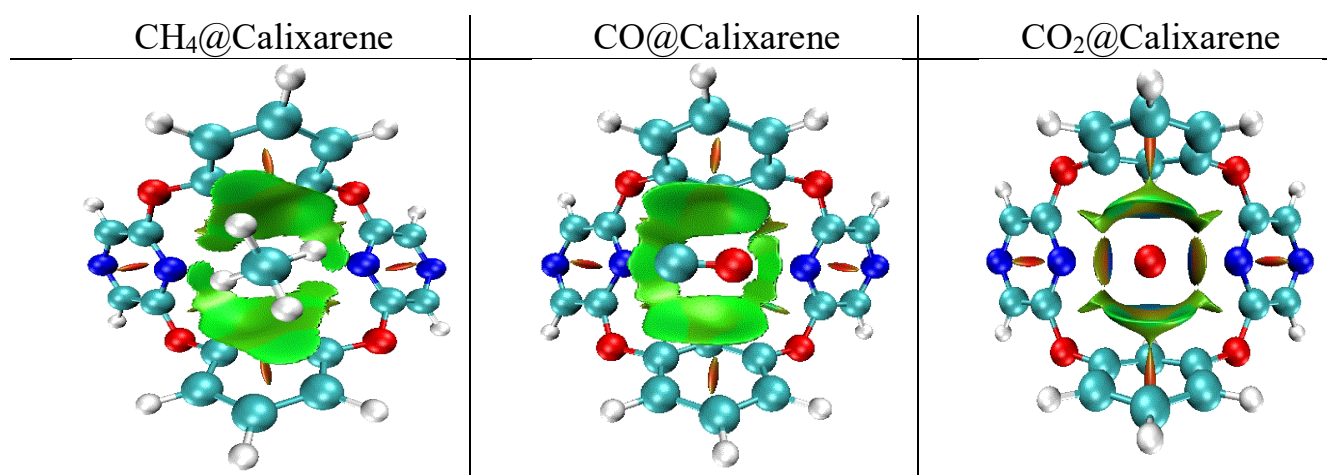


Fig. 24: 3D isosurfaces of analyte@Calixarene complexes.

4.3.5 Electronic Properties Analysis of CH₄, CO and CO₂@Calixarene Complexes:

The data presented in Table 8 indicates that the energy of the HOMO for the bare Calixarene macrocycle is -6.14 eV, and its LUMO energy registers at -4.53 eV., yielding a HOMO-LUMO energy gap of 2.9 eV. Following the complexation with CH₄, CO, and CO₂, the EH-L gaps measured were 2.00 eV, 1.99 eV, and 1.92 eV respectively (as shown in Table 8). This slight decrease in the EH-L gap can be attributed to the

minimal interaction between Calixarene and the analytes (CH_4 , CO , and CO_2). To explore the effect of these analytes on the sensor's electronic characteristics, Figure 25 provides graphical illustrations of the isosurfaces for both the HOMO and LUMO, showing that the electron densities for both orbitals are spread across the surface of Calixarene. No overlap between Calixarene macrocycle and the analysts because there is no covalent interaction. Moreover, no significant change in electron density of HOMO and LUMO after complexation with analysts due to the the weak interaction between Calixarene and analytes (CH_4 , CO and CO_2).

Table 9: Energy of HOMOs, LUMOs, HOMO-LUMO energy gaps (in eV) and charge transfer of analyte@ Calixarene.

System	E_{HOMO}	E_{LUMO}	E_{gap}	Charge transfer (Q)
Calixarene	-6.14	-4.53	2.90	
$\text{CH}_4@$ Calixarene	-6.55	-1.55	2.00	-0.008
$\text{CO}@$ Calixarene	-6.53	-4.55	1.99	-0.009
$\text{CO}_2@$ Calixarene	-6.52	-4.60	1.92	-0.064

The amount of charge (Q) exchanged during the interactions between the analyte and the surfaces was examined through NBO charge analysis. Analyte transferring electrons to the sensing material are analogous to positive values of the NBO charge, whereas negative charges indicate the opposite. As shown in Table 9, $\text{CH}_4@$ Calixarene, $\text{CO}@$ Calixarene and $\text{CO}_2@$ Calixarene complexes had negative QNBO values of -0.008 |e|, -0.009 |e|, and -0.064 |e|, respectively, indicating that the charges transfer from the Calixarene Macrocycle to the analyte (CH_4 , CO and CO_2). In Calixarene macrocycle, the electron cloud is moved by the Nitrogen of Calixarene macrocycle toward the analytes. Results demonstrate that CO_2 shows the highest sensing abilities for Calixarene based on charge transfer.

In addition, CO₂ shows the highest sensitivity in term of interaction energy. The CH₄@Calixarene complex exhibits the smallest level of charge transfer, measured at -0.008 |e|.

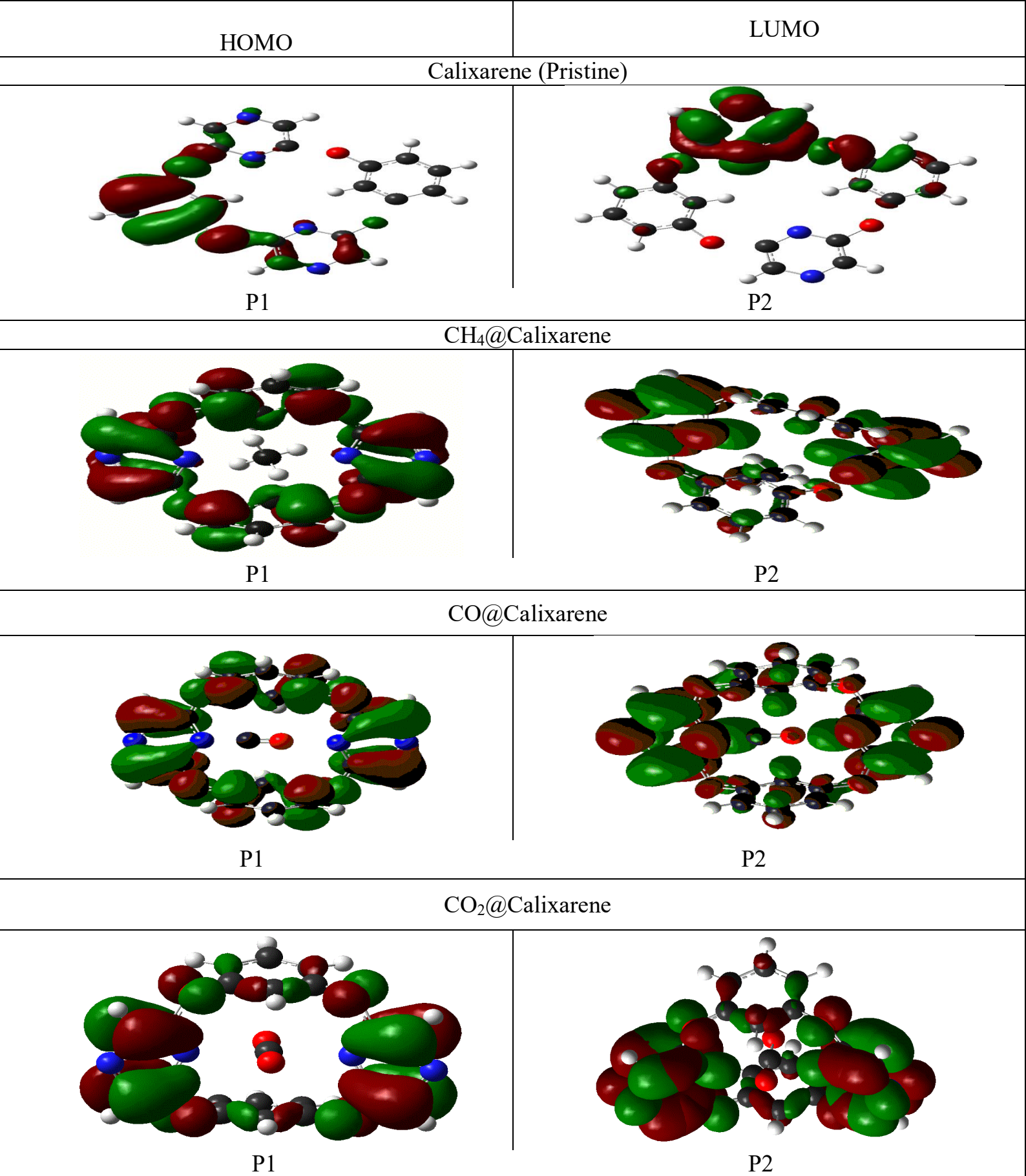


Fig. 25: a graphical depiction of the HOMO and LUMO isosurfaces to illustrate how adsorbing the analytes (CH₄, CO & CO) affects the sensor's (Calixarene) electrical environment.

4.4 Conclusion and Recommendations:

In this thesis, sensing of CH₄, CO, and CO₂ on the Kekulene, Naphthyridine and Calixarene macrocycles (nitrogen rich macrocycles) were assessed through DFT calculations by applying ω B97XD/def2svp level of theory. All possible orientations of the analytes on the surface were assessed to identify the configurations of analyte@macrocycle that are most stable.

Therefore, the stability of the complexes was assessed by calculating E_{int} , with more negative values indicating greater stability of the complex. Furthermore, QTAIM and NCI evaluations were conducted to define the interactions occurring between the analytes and the surfaces, classifying them as covalent, non-covalent, or covalent-like interactions. Another important parameter for the electrocatalysts is their conductivity, as they are expected to facilitate the flow of electrons from and to the electrode. As such, calculations of the E_{gap} have been conducted as decreased values of the E_{gap} indicate increasing electrical conductivities.

The findings indicate that Kekulene, Naphthyridine, and Calixarene macrocycles create stable adsorbed complexes with each of the analyzed substances (CH₄, CO, and CO₂). The interaction energies (E_{int}) suggest that these complexes possess thermodynamic stability, with the sensing process being exothermic in nature. The E_{int} values of CH₄@Kekulene, CO@Naphthyridine and CO₂@Calixarene complexes are the greatest, and the interaction distance is the shortest among the other investigated complexes. In addition, the Naphthyridine complexes exhibit the highest E_{int} values, with their interaction energies falling between -5.39 and -9.09 kcal/mol. In contrast, the interaction energies of Kekulene complexes vary from -3.87 to -2.27 kcal/mol, while Calixarene complexes show a range of

-1.45 to -2.99 kcal/mol. The findings from the QTAIM analysis of all examined complexes indicate that the interactions predominantly take place via weak non-covalent van der Waals forces. The electron density (ρ) measurements for each complex remain uniformly under 0.1 au, indicating that weak van der Waals interactions are likely present. Additionally, the green regions observed in the NCI isosurfaces for all the examined complexes emphasize the non-covalent interactions, particularly the van der Waals forces between the analytes and the macrocycles under investigation.

The FMO analysis indicated that there were slight variations in the HOMO-LUMO energy gap (E_{gap}) of the studied complexes, supporting the notion that weak non-covalent van der Waals interactions play a role. E_{gap} has decreased from 3.72 eV in the Kekulene (pristine) macrocycle to 3.71, 3.70, and 3.71 eV for CH_4 @Kekulene, CO @Kekulene, and CO_2 @Kekulene, respectively, and from 4.26 eV (pristine) to 4.29, 4.28 and 4.16 eV, for CH_4 @Naphthyridine, CO @Naphthyridine, and CO_2 @Naphthyridine, respectively. In the instance of Calixarene, the energy gap (E_{gap}) has been reduced from 2.9 eV in its pristine state to 2.00 eV, 1.99 eV, and 1.92 eV for the complexes CH_4 @Calixarene, CO @Calixarene, and CO_2 @Calixarene, respectively. Consequently, we propose that Naphthyridine is a viable candidate for detecting greenhouse gases such as CH_4 , CO , and CO_2 .

We hope that this thesis provides contribution towards the sensing of greenhouse gases. We aim to continue our work in this field and explore the possibility of synthesizing the proposed SACs for application on a lab scale and then hopefully on a larger scale.

For future research, it would be highly valuable to investigate the utility of the macrocycles that were analyzed toward other harmful gases (*e.g.*, H₂S, SO₂, NH₃, NO, and NO₂). In addition, the ω B97XD and the B3LYP functionals revealed high reliability for the stability investigation and electronic properties analysis, respectively. Thus, it is recommended that they are used for future work. If sufficient computational hardware is available, it is also recommended that these functionals may be benchmarked with the highly demanding state-of-the-art methods, such as the coupled cluster method. Regarding the Software, the Gaussian/GaussView package provided wide versatility, along with the Multiwfn code, and VMD visualisation program, high-quality research is attainable.

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الملخص

بسبب (WHO) إن الانبعاثات الصناعية السامة والملوثات البيئية تجتذب انتباه منظمة الصحة العالمية زيادة السلامة العامة. تسبب هذه الانبعاثات السامة مضاعفات خطيرة على صحة الإنسان وجميع الكائنات الحية. لقد جذبت طريقة امتصاص الغازات الصناعية الكثير من الاهتمام بسبب القضايا البيئية المتزايدة (على سبيل المثال، تغير المناخ). إن الحاجة إلى تطوير أجهزة استشعار غازية انتقائية وحساسة للغاية للكشف عن هذه الغازات الصناعية تتزايد باستمرار. وجدت الدراسات الحديثة أن انبعاثات الغازات الصناعية ارتفعت بشكل كبير في الغلاف الجوي مقارنة بالقرن الماضي بسبب النمو اللامتناهي للسيارات والصناعات. يمكن للغازات الصناعية حبس الحرارة في الغلاف الجوي والمساهمة بشكل كبير في ارتفاع درجات الحرارة والاحتباس الحراري العالمي.

لحماية البيئة والحد من المركبات الضارة بالصحة، فإن البحث عن أجهزة استشعار غازية فعالة للغاية للكشف عن الغازات السامة أمر حيوي للغاية لأغراض المراقبة والتحكم. تبحث الدراسة الحالية في حساسية وقدرة الامتصاص لثلاثة مركبات حلقة كبيرة (كيكولين، نفثيريدين، وكالكسارين) كمواد امتصاص فعالة للكشف عن غازات مختلفة بما في ذلك الميثان وثاني أكسيد الكربون وأول أكسيد الكربون. باستخدام حسابات نظرية الكثافة CH₄@Kekulene و CO₂@Naphthyridine أظهرت نتائج هذا البحث أن (DFT) الوظيفية وتحديث التفاعلات بشكل NCI وجود QAIM أكد تحليل Eint لها أعلى قيم CO₂@Calixarene و HOMO- بالتغيرات غير المحسوسة في فجوة الطاقة FMO أساسي عبر قوى فان دير فال الضعيفة. أفاد تحليل للمركبات المدروسة. يساهم هذا البحث في إقامة روابط بين الأوساط الأكاديمية والهيئات LUMO (Egap) التنظيمية ومعاهد البحث لتقليل الانبعاثات السامة الصناعية والحصول على مواد استشعار فعالة ومنخفضة التكلفة للاستشعار أكثر الملوثات البيئية شيوعاً.

جامعة البحرين

برنامج البيئة والتنمية
المستدامة



كلية العلوم

استشعار الغازات الخطرة على البيئة باستخدام المركبات الحلقية الكبيرة المحتوية على النيتروجين: النهج الكيميائي الكمي أطروحة مقدمة لاستيفاء جزء من درجة الماجستير في البيئة والتنمية المستدامة

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