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Tailoring the Adsorption and Electronic Properties of Si-Doped Pyrene for Reversible Ammonia Sensing: A Comparative DFT Study

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Abstract
The development of highly sensitive and reversible gas sensors is still an important challenge in nanotechnology. In this work, Density Functional Theory (DFT) calculations are performed to investigate the adsorption of ammonia (NH_3) on pristine and Silicon doped (Si-doped) pyrene surfaces. Our findings show that the pure pyrene surface has a very high adsorption energy of about -4.959 eV, which is related to a strong chemisorption mechanism that leads to surface poisoning and limited reusability. To tune this interaction, we have introduced a silicon atom in the pyrene framework. The electronic environment was greatly influenced by Si-doping, as shown by the charge population analysis and molecular electrostatic potential (MEP). Interestingly, The NH_3 adsorption energy on Si-doped pyrene fell to a moderate value of -4.510 eV. This shift turned the contact into a physisorption-like mechanism that is stable and reversible, making it suited for sensing applications.

Keywords
Pyrene,
Si-doping,
Ammonia sensor,
DFT calculations,
Adsorption energy.

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1. Introduction

Monitoring toxic gases in industrial and domestic environments is of paramount importance for public health and environmental safety. As quality of life continues to improve, the breathing environment has emerged as a critical focus for researchers in the twenty-first century. Numerous research affirm that indoor air is more hazardous than outdoor air [1]. Currently, 90% of rural families in underdeveloped nations and almost 50% of the global population utilise unrefined biomass for open flames and inefficient indoor cooking stoves. The inadequate cooking procedures contribute to indoor air pollution (IAP) and adversely affect the health of women and small children frequently exposed to such contaminated environments [2].

Significant nitrogen gases released by anthropogenic activities include nitrogen oxides (NOx), nitrous oxide (N2O), and ammonia (NH3). Among these gases, NH3 is released from numerous sources, including volatilisation from animal waste and synthetic fertilisers, biomass combustion (such as forest fires), losses from soils under natural vegetation and agricultural crops, emissions from human excreta, and fossil fuel combustion. Ammonia (NH_3) is one of the most prevalent and hazardous gases due to its extensive use in refrigeration technology, fertilizer production, and various chemical processes. Even minor leaks can cause severe damage to the human respiratory system [3,4].

Sensors today are of undeniable importance in industry and research that is can perform detection by quantifying a physical or chemical phenomenon at the sensor surface and converting changes into an electrical, mechanical, or optical signal. Research on carbon-based nanomaterials, such as carbon nanotubes, graphene and its derivatives, nanodiamonds, fullerenes, and other nanosized carbon allotropes, has experienced sharp exponential growth over recent years. In this context, carbon-based nanomaterials have emerged as ideal candidates for developing advanced gas sensors, thanks to their high surface area and unique electronic properties [5-7].

Polycyclic aromatic hydrocarbons (PAHs) are a class of chemical compounds formed by two or more interconnected benzene rings. Polycyclic aromatic hydrocarbons (PAHs) demonstrate hydrophobic characteristics and limited solubility in water, with certain constituents being hazardous compounds that resist degradation. [8]. Pyrene is a representative member of the polycyclic aromatic hydrocarbons (PAHs), and consists of four fused benzene rings with extensive p-electron delocalization. Since pyrene was first distilled from coal tar in 1837, the unique molecular structure and optical properties of pyrene have attracted intense interest both for fundamental research and in the industrial community [9].

As an excellent fluorophore, pyrene exhibits advantageous photophysical properties, such as deep blue emission (λmax em = 372 nm), long fluorescence lifetime of the pyrene monomer (τ = 354 ns), and high fluorescence quantum yield (Φf = 0.64) in non polar toluene. Pyrene a polycyclic aromatic hydrocarbon, is a promising material in this field. However, pure carbon surfaces often face a significant challenge, they either interact too weakly with gas molecules or, conversely, exhibit an excessively strong chemical bond that leads to surface poisoning [10,11]. In preliminary studies, it was observed that NH_3 adsorption on pure pyrene yields an exceptionally high adsorption energy of approximately very big. This makes the desorption process nearly impossible under normal conditions, thereby limiting the sensor's reusability and efficiency [12,13].

To resolve this challenge, research has transitioned to "surface engineering" by doping with atomic impurities to alter chemical activity. Pyrene doped with a boron atom at the edge, pyrene doped with a boron atom at the center, pyrene doped with a nitrogen atom at the edge, pyrene doped with a nitrogen atom at the center, pyrene doped with both boron and nitrogen atoms at the edge, and pyrene doped with both boron and nitrogen atoms at the center of the pyrene molecule. The findings indicate that incorporating various impurities at distinct locations will enhance the thermoelectric figure of merit of the pyrene molecule.

[14-16]. Silicon (Si) is an effective element for altering the electron density distribution of carbonaceous materials due to the differences in its electronegativity and atomic size compared to carbon. Silicon and nitrogen-codoped carbon nanomaterials were synthesised via chemical vapour deposition and assessed through electrochemical testing. The Si-doped carbon nanosheets and Si, N-codoped carbon nanotubes demonstrated significant electrocatalytic activity and prolonged stability for the oxygen reduction reaction in alkaline conditions, attributed to alterations in charge density and energetic properties of the carbon structure, as supported by density functional theory calculations [17-18].

The disparate electronegativities of carbon and silicon yield polarised covalent connections that are more robust than the non-polar covalent bonds between silicon atoms [19]. Numerous investigations have shown that the incorporation of doping atoms can markedly improve the sensitivity of carbon-based nanostructures to particular chemicals. The use of Si-doped nanostructures as adsorbents of gas molecules and their sensing potential have been explored in many works by researchers. The introduction of Si atoms in the pyrene skeleton leads to the redistribution of the electron density. The Si dopant induces a local electronic deficiency due to differences in electronegativity and atomic size, making the Si atom a key active site for adsorption of gas molecules, such as NH_3, on the pyrene surface [20-23]. In this work, the structural and electronic properties of pristine and Si-doped pyrene and their adsorption interactions towards NH_3 molecules have been studied by Density Functional Theory (DFT) calculations at the B3LYP level. Ammonia is a well-known air pollutant which is a serious threat to the stability of the environment and to human health. Therefore, the design and development of highly efficient and selective nanosensors for detection of these hazardous compounds is an urgent need. This work provides a good theoretical background for the design of advanced sensing materials to reduce the environmental damage caused by ammonia exposure by tuning the pyrene framework through silicon doping.

In this work, the effect of silicon-doping on the NH_3 adsorption properties of the pyrene framework is theoretically reported by the Density Functional Theory (DFT). We focus on the transition of the binding mechanism from the strong chemisorption regime to the moderate energy regime (around 0.3 eV) which provides both a high sensitivity and a good reversibility. In addition, the changes in the MEP and charge transfer are studied to provide an in-depth understanding of the physicochemical mechanisms that lead to this considerable improvement of the sensor performance [24-28].

Table 1: Pristine $C_{16}H_{10}$ and Si-$C_{15}H_{10}$ energetic data, including total energy (Etotal), polarisability (a), HOMO energies (E_{Homo}), formation energy (E_f), LUMO energies (E_{Lumo}), and energy gap energy (E_g) computed at room temperature.

Compound	$Etotal\ (eV)$	$a(a.u.)$	$E_{Homo}(eV)$	$E_f(eV)$	$E_{Lomo}(eV)$	$E_g(eV)$
Pristine $C_{16}H_{10}$	-16759.52	182.27	-5.580	-3.682	-1.785	4.095
Si- $C_{15}H_{10}$	-23593.83	192.18	-5.437	-3.661	-1.886	3.551

Table 2: Chemical reactivity characteristics for Pristine $C_{16}H_{10}$ and Si-$C_{15}H_{10}$ on a global scale, including chemical potential (μ), chemical hardness (η), softness (S), electrophilicity index (τ), and electronegativity (υ).

Compound	$\mu(eV)$	$\eta(eV)$	$S(eV)$	$\omega(eV)$	X
Pristine $C_{16}H_{10}$	-3.682	1.897	0.269	3.573	3.682
Si- $C_{15}H_{10}$	-3.661	1.775	0.281	3.775	3.661

Table 3: The gas phase calculations for Pristine $C_{16}H_{10}/NH_3$ and Si-$C_{15}H_{10}/NH_3$ at room temperature include the total electronic energy (E_{total}), energy gap energy (E_g), change in Egap ($\triangle Eg\%$), and adsorption energies ($Eads$).

Compound	$E_{total}\ (eV)$	$E_g(eV)$	$\triangle Eg\%$	$Eads$
Pristine C16H10/NH3	-18299.01	3.852	-57.36	-4.959
Si-C15H10/NH3	-25133.04	3.757	-54.55	- 4.510

Besides, chemical functionalisation [32,33], carbon nanomaterials have attracted a lot of attention, such as graphene nanoribbons (GNRs), carbon nanotubes (CNTs) and graphene nanoflakes (GNFs). Graphene nanoflakes (GNFs) are zero-dimensional (0D) nanosystems obtained from graphene. The quantum confinement effect due to the reduced dimensionality of these systems leads to a tunable band gap, and thus GNFs are excellent candidates for graphene-based electronic devices [34,35].

The excellent electrical properties and structural stability of GNFs have stimulated intensive research on their application as physical transducers in the gas sensing technology. Compared to the conventional diagnostic devices, the GNF-based sensors show better performance in sensitivity and selectivity. In recent years, theoretical and experimental studies have extensively investigated the gas adsorption behaviour on carbon-based nanomaterials [36–38]. A key aspect in this field is the tuning of electronic properties via molecular adsorption, which is a fundamental basis for the development of high-performance sensing devices [39,40]. Topological defects or doping with heteroatoms can significantly enhance the intrinsic reactivity of pristine carbon frameworks like graphene (literature suggests). However, the two-dimensional (2D) nature of pristine graphene often results in limited sensitivity, but the use of graphene nanoflakes such as pyrene provides a distinct advantage. Herein, we propose the doping of Si in the pyrene lattice as a solution to the limitations of pristine surfaces.

The planar symmetry is intentionally broken by replacing carbon with silicon, to a more reactive electronic environment well suited for the sensitive detection of NH3 molecules [41-44]. Extensive computational studies have shown that the gas-sensing sensitivity of the carbon frameworks towards specific analytes can be significantly enhanced by the incorporation of dopant atoms [6,17,35]. This doping process leads to a fundamental improvement of the electronic properties of the system. Further studies show that doping heteroatoms into the carbon lattice can change the band structure and electron transfer mechanism, which broadens the potential application of these nanomaterials [36]. Silicon (Si) is one of the

many elements, and is a strategic choice for the doping of carbon-based structures because of its unique electronic configuration and compatibility with the carbon lattice [37,38]. On this basis, Si-doped systems were investigated as very effective adsorbents of gaseous molecules [33,36,39-45]. Here, we extend this approach to the pyrene molecule and employ silicon doping to activate its surface for the robust detection of ammonia (NH_3). Doping of pyrene with silicon (Si) results in a local decrease of the electron density around the dopant site. Because of the difference in electronegativity and the protrusion of the Si atom from the structure, it effectively pulls electronic charge from the neighbouring carbon atoms. This electron deficiency makes the silicon site an important, electrophilic site which is very favourable for the adsorption of gas molecules. The increased reactivity of the Si-doped pyrene framework results in a stronger interaction with NH_3 than the pristine carbon surface.

2. Computational Methodology

2.1. Electronic Structure and Stability Analysis

The Gaussian 16 software package [36] was employed for all the quantum chemical simulations in this work. Geometric configuration optimisations and the subsequent electronic structure analyses were performed in the framework of the Density Functional Theory (DFT). In particular, the hybrid exchange-correlation functional B3LYP was used in combination with the 6-311G (d, p) basis set. This theoretical level has been chosen because of its well demonstrated reliability to correctly model the electronic and structural properties of polycyclic aromatic hydrocarbons (PAHs) and their doped derivatives, keeping a cost-accuracy compromise [37, 38].

$$E_f = E_{doped} - E_{pristine} - \mu_{Si} + \mu_C \quad (1)$$

The electronic response of both pure and Si-doped pyrene to NH3 was examined via the Energy Gap E_g, obtained from the Frontier Molecular Orbitals (FMO) [39,40]:

$$E_g = E_{LUMO} - E_{HOMO} \quad (2)$$

The sensitivity of the system was quantified by the Sensitivity Factor $\triangle Eg\%$ which measures the relative change in the energy gap upon adsorption:

$$\triangle Eg\% = \frac{E_{g2}-E_{g1}}{E_{g1}} \quad (3)$$

where E_{g1} and E_{g2} are the energy gaps of the isolated and complex systems, respectively.

2.2. Conceptual DFT Reactivity Descriptors

Global reactivity descriptors were calculated (as presented in Table 2) to evaluate the chemical activity of the investigated structures based on the following equations [41-45]:

- Chemical Potential (μ): $\mu = \frac{E_{LUMO}+E_{HOMO}}{2}$ (4)
- Global Softness (S): $S = \frac{1}{2\eta}$ (5)

- Electrophilicity Index (ω): $\omega = \frac{\mu^2}{2\eta}$ 6
- Electronegativity (χ): $\chi = -\mu$ 7

3. Results and Discussion

3.1. Electronic Structure and Stability Analysis pristine and Si-doped pyrene

The global environmental concern is the development of high-performance sensors for hazardous industrial gases, particularly ammonia (NH_3), which has a serious impact on human health and atmospheric chemistry. Pyrene-based frameworks, as one of the various kinds of carbon-based nanomaterials, have become promising candidates for gas detection due to their stable aromatic structure and specific electronic properties. However, the sensing efficiency of pristine pyrene is often limited by weak physical interactions or too high adsorption barriers. In this study, we demonstrate that the strategic substitution of carbon by the silicon (Si) atoms in the pyrene lattice drastically improves its sensitivity and selectivity toward NH_3, making these structures efficient real- time monitoring platforms. Figure 1. Optimised geometric configurations of the pyrene-based models. The pristine pyrene (Fig. 1a) is planar with carbon atoms in planes and passivated with hydrogen at the edges. As shown in the configuration (Fig. 1b), the framework undergoes localised structural changes upon silicon doping. These changes are due to the larger covalent radius of silicon relative to carbon, giving rise to a localised chemical strain. This structural change creates an active electronic site enabling moderate adsorption energy, thus ensuring high sensitivity while preserving reversibility for reusable sensing applications

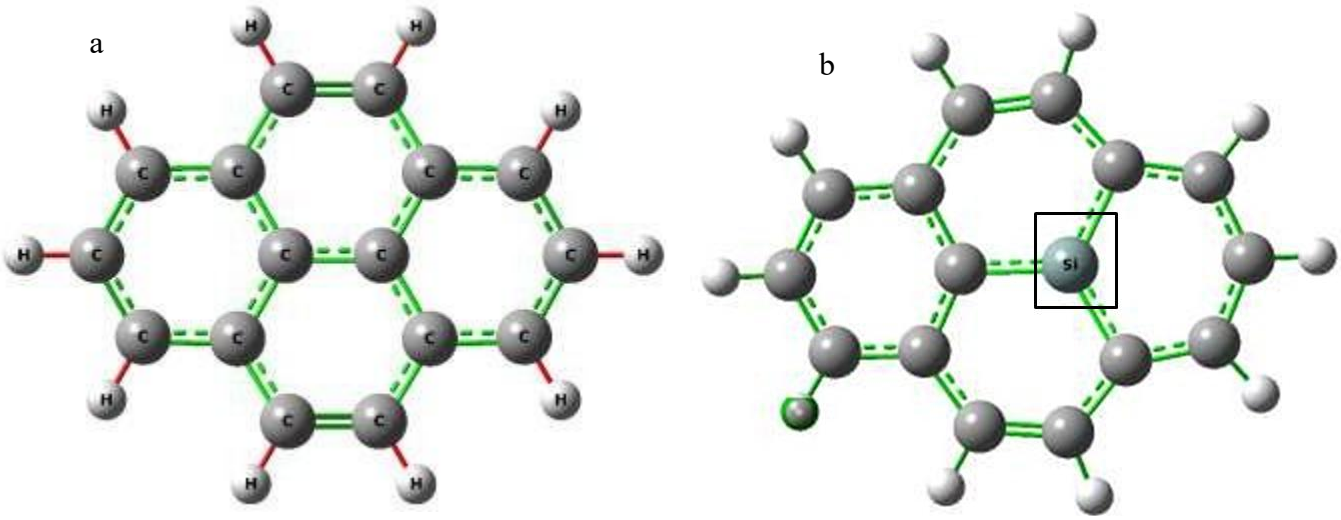

Fig .1. Optimized geometric structures of: (a) pristine pyrene ($C_{16}H_{10}$) (b) Si-doped pyrene dot ($C_{15}H_{10}$ Si).

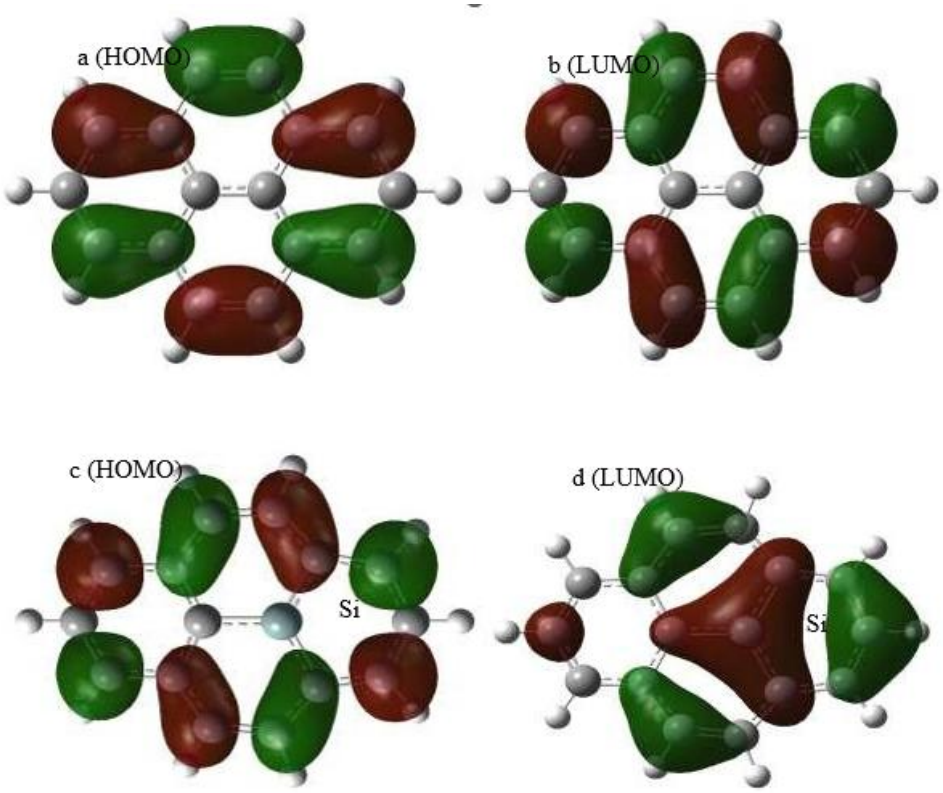

Fig .2. Spatial distribution of the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) for pristine (a, b) and silicon-doped pyrene-based QDs (c, d).

Figure 1, spatial distributions of the HOMO-LUMO orbitals for pristine pyrene and Si- doped configurations, which can explain the large reduction of the energy gap. In the perfect pyrene structure, the orbitals are spread evenly and uniformly across the carbon rings, resulting in a large gap of 4.095 eV, which implies high electronic stability and low conductivity. However, an interesting hybridisation and localisation of orbitals is found when pyrene is doped with silicon atoms. The energy gap decreases to 3.551 eV in this transition, and the orbitals are strongly localised in the Si-C bond regions.

Such an orbital localisation means that the Si atoms have created new energy states (donor or acceptor levels) in the original band gap of pyrene, acting as 'electronic bridges' to promote charge transfer. The overlap between the frontier orbitals of the sensor and the incoming ammonia molecule (NH_3) will be essentially limited to these 'frontier zones' which are highly reactive and produced by the silicon. These spatial characteristics confirm that silicon-doping converts pyrene into an ideal electronic platform for gas detection, with improved sensitivity compared to the pristine structure.

3.2 Gas Sensing Performance and Adsorption Mechanism of NH3 on Si-doped Pyrene

This section evaluates the potential of the studied structures as gas sensors. To distinguish between the different systems, the configurations following the adsorption of ammonia (NH3). We investigate the interaction between NH3 molecules and these configurations to determine how silicon doping influences the adsorption energy and the subsequent electronic response. These parameters serve as the fundamental indicators for assessing both the sensing sensitivity and selectivity of the proposed sensor.

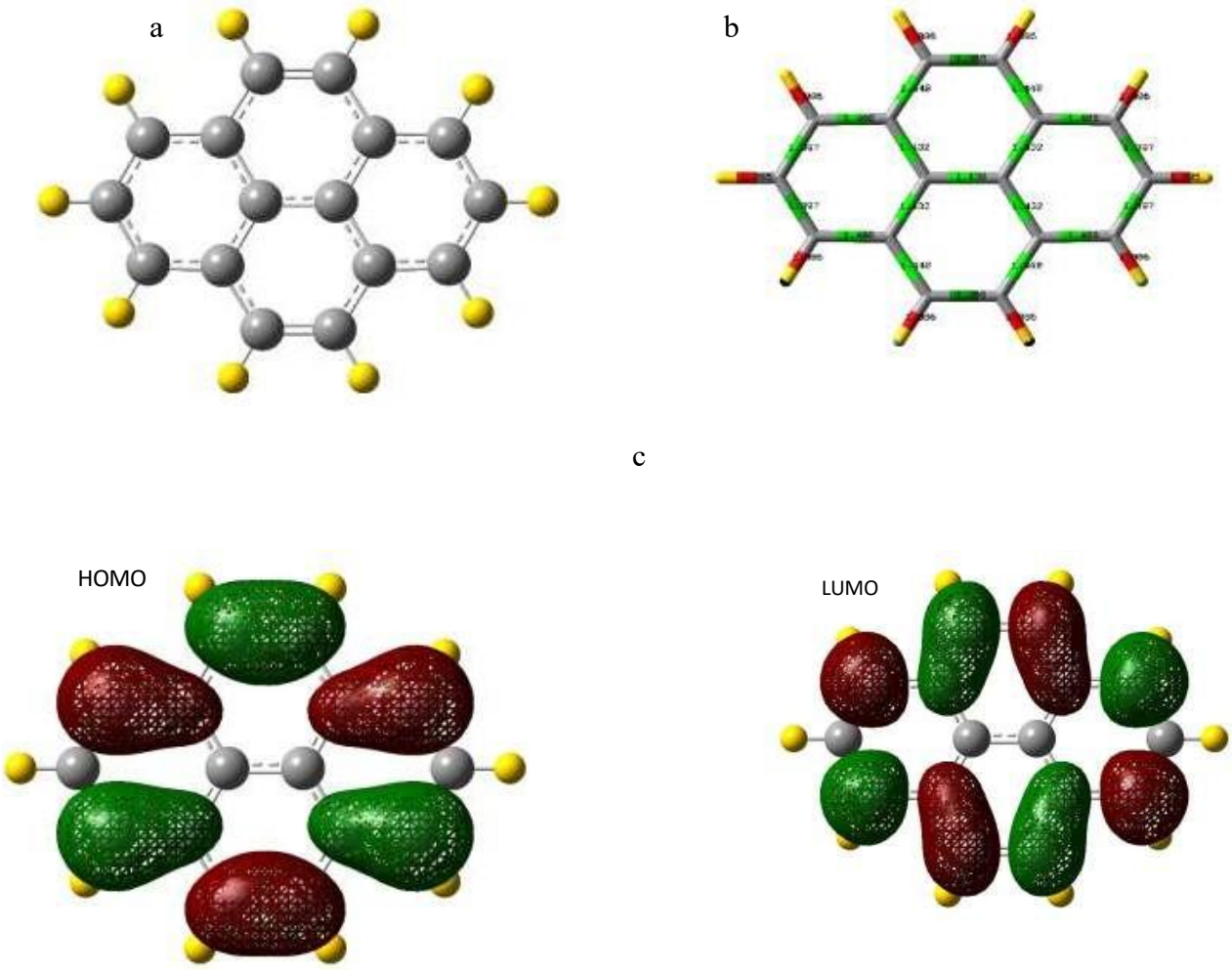

Fig. 3. The molecular blueprint (a), the lengths of the bonds (in Å units) (b), and the HOMO-LUMO plots (c) of pure pyrene

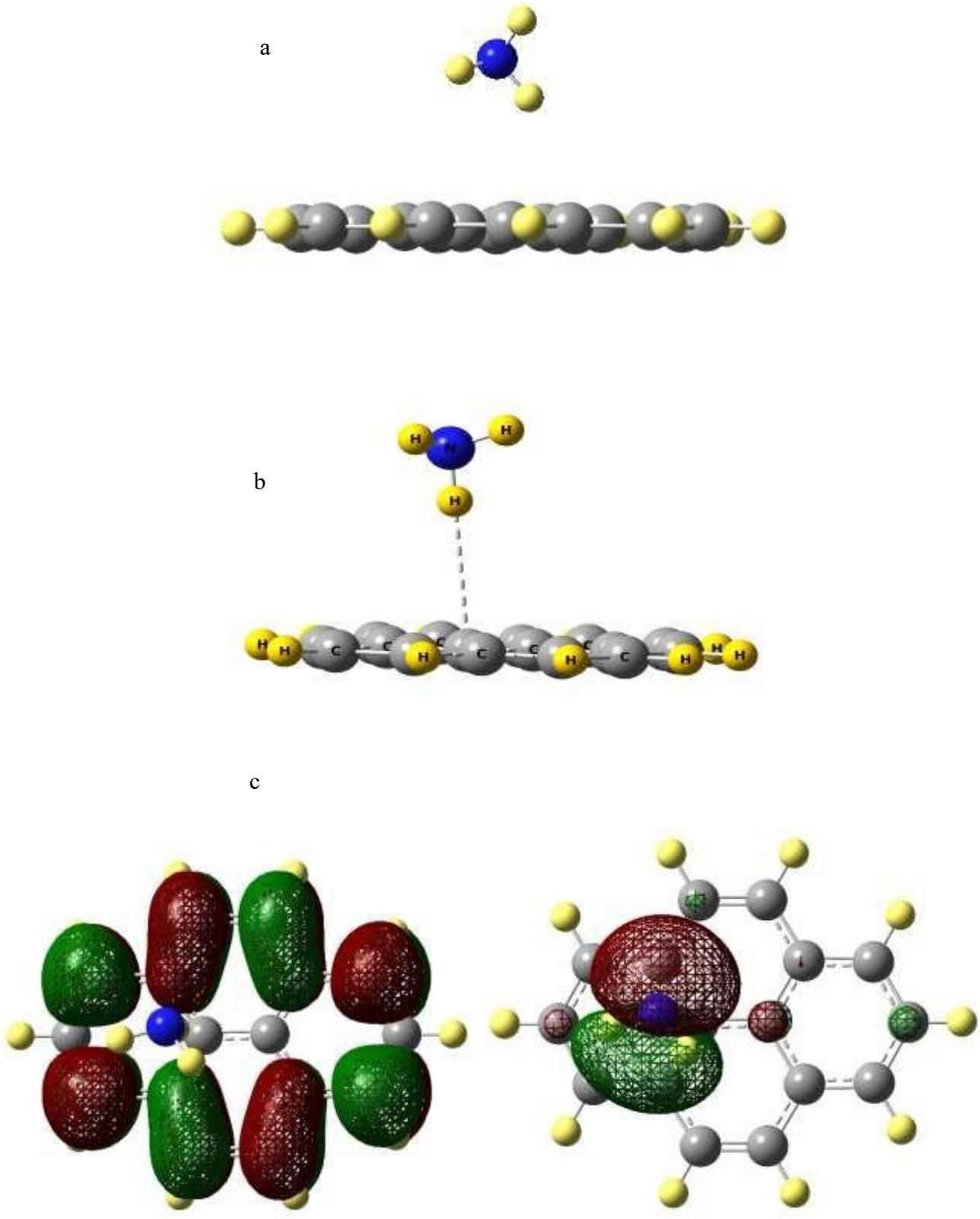

Fig. 4. The adsorption stability of the NH molecule on the surface of pyrene nanoflakes (a) is depicted alongside the Adsorbate-Substrate interaction of pyrene (b) and the corresponding HOMO-LUMO plots (c).

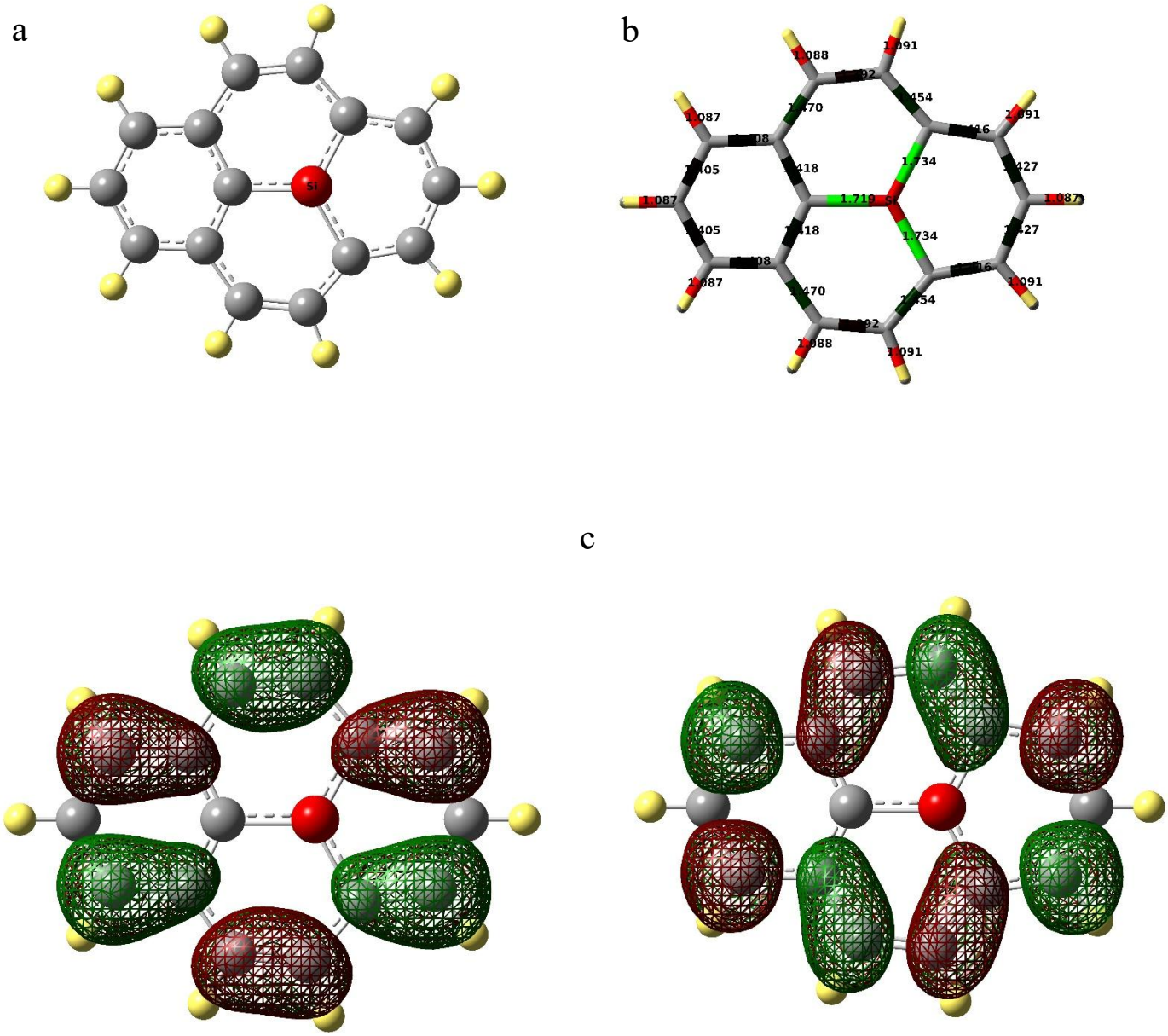

Fig. 5. Atomic structure: (a) bond lengths (in Å); (b) HOMO-LUMO plots of Si-pyrene.

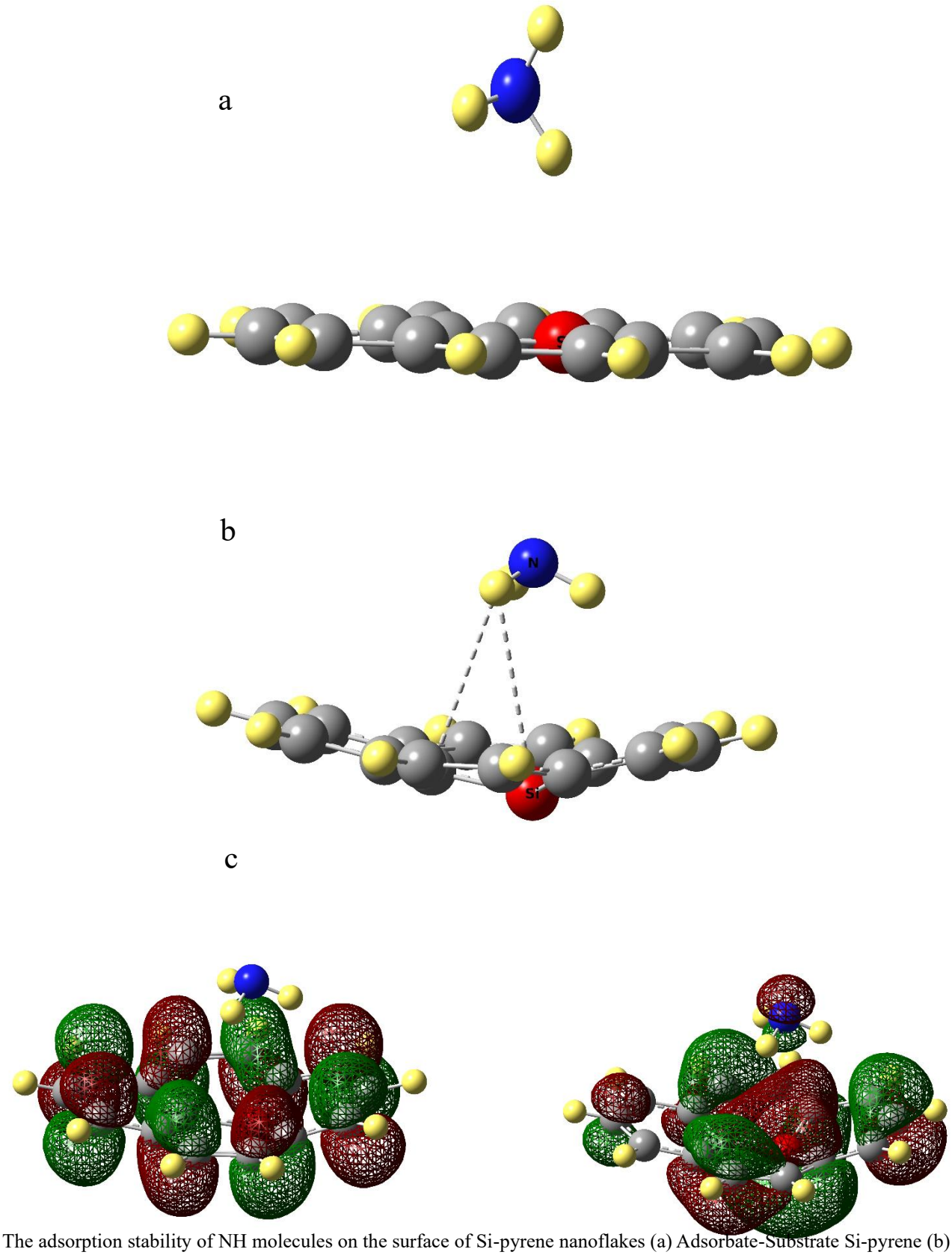

Fig. 6. The adsorption stability of NH molecules on the surface of Si-pyrene nanoflakes (a) Adsorbate-Substrate Si-pyrene (b) accompanied by HOMO-LUMO plots (c)

Initially, the atomic configuration of the optimised virgin GNFs in relation to ammonia is illustrated in Fig. 1(a). A graphene nanoflake represented by the chemical formula C24H12, comprising seven benzene rings, was examined. The terminal atoms of the nanoflake were saturated with hydrogen atoms to mitigate boundary effects. Figure 1(b) illustrates the optimised arrangement and bond lengths of pure graphene nanoflakes after comprehensive structural relaxing. The findings reveal a bond length of 1.42 Å between two carbon atoms, consistent with prior published studies [47,48].

Additional information regarding the simulations for both pristine and Si-doped pyrene, in the presence and absence of the NH_3 molecule, has been calculated and discussed. This includes physical and chemical properties such as energetic data and global chemical reactivity descriptors. To further understand the chemical behavior of the investigated systems, Frontier Molecular Orbital (FMO) analysis was employed. The interaction between FMOs is the primary factor governing the interaction between the sensor surface and the gas analyte. Specifically, the HOMO, LUMO, formation energy (E_f), and energy gap (E_g) values were calculated and are presented in Table 1. The energetic data for the investigated systems include the adsorption energies, total electronic energy, dipole moment, polarizability, HOMO energies, Fermi level energy, LUMO energies, and the energy gap. The spatial distributions of the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are shown in Fig. 1(d). This distribution is due to the atomic πorbitals which are in the same direction and form an effective overlap. The green areas in the orbital plots are the negative phase and the red areas are the positive phase.

The HOMO and LUMO are highly delocalised as can be seen in the images. This suggests an increased intramolecular charge transfer which facilitates the movement of electrons across the molecule even if the HOMO is localised on higher bond density areas. Moreover, the LUMO is highly localised around certain bond areas, especially around the silicon doping area, suggesting that these are the main active areas for gas interaction, favourable atomic centers in the structure that can be attacked by nucleophiles and have bioactive effects [49-51]. Table 2 summarises the global chemical descriptors such as chemical potential, chemical hardness, softness and electrophilicity. These supportive parameters are extensively utilised in material science for assessing the reactivity and stability of the investigated systems. The chemical potential (or electronic potential) is an indication of the tendency of electrons to escape from a stable ground state. Other important parameters are the electrophilicity index (ω), which describes the tendency of a system to gain further electronic charge from the environment, and chemical softness (S), which describes the tendency of the atom to accept electrons.

Moreover, the electronegativity (μ) is a quantitative measure of the resistance of atomic or molecular groups to charge transfer. These values obtained from the Koopmans' theorem provide valuable information about the reactivity, chemical stability and intermolecular interactions of the pristine and Si-doped pyrene systems, as well as their electronic and optical properties. The adsorption energy, electronic sensitivity and adsorbent recovering time were discussed and summarised in Table 3 to better understand the gas sensing properties. Remarkable enhancement of the adsorption energy for NH3 up to -4.510 eV was observed upon doping silicon into the pyrene structure.

This substantial increase in binding energy clearly demonstrates a change from physisorption to a strong chemisorption. A large negative value. The strong chemical bond formation between the silicon atom and NH_3 molecule indicates the silicon atom is a strong active site. Hence, the Si-doped pyrene is more sensitive to ammonia than the pristine structure because the silicon dopant provides a more effective electronic interaction and charge transfer between the gas analyte and the sensor surface. The systematic studies on the structural, electrical and adsorption properties of Si-doped pyrene were carried out to improve the gas sensing performance of pyrene towards ammonia molecule. In this study, one C atom

was substituted for one Si atom in the active adsorption site. The insert of the Si impurity causes large geometrical distortions in the pyrene lattice, as shown in Fig. 3. The Si atom protrudes from the planar surface of the pyrene to relieve the induced structural stress due to the larger atomic radius of Si than C. In particular, the Si-C bond length obtained for the doped system is 1.73 Å which is much larger than the usual C-C bonds in the pristine structure [52-55]. The C-Si-C bond angles were also found to deviate from the ideal 120° angle, found in pristine pyrene, to 115.80° and 122°, further confirming the structural re-arrangement induced by the dopant.

The results shown in Table 3 clearly indicate that the adsorption of NH3 on Si-doped pyrene is significantly more favoured than that of pristine structure. Such improved interaction can be attributed to the considerable charge transfer between the Si-doped system and the ammonia molecule as further supported by the HOMO and LUMO distribution plots. Moreover, the much more negative adsorption energy proves that the silicon doping is effective to improve the reactivity of the pyrene framework towards the ammonia molecules. Moreover, when a carbon atom is replaced by a silicon (Si) atom in the pyrene framework, its gas-sensing performance is greatly improved, which makes it a promising candidate for sensing NH_3 molecules.

The results summarised in Table 3 indicate that the Si-doped pyrene cluster is highly electronically sensitive to the adsorption of NH_3 on its surface. The interaction between the two species is classified as strong chemisorption with adsorption energy of -4.510eV. Such strong chemical bonding leads to a stable detection and confirms the efficiency of silicon doping for the activation of the pyrene surface for environmental sensing applications.

4. Conclusion

To conduct a detailed investigation of the interaction of the pyrene framework with ammonia (NH_3) molecules, density functional theory (DFT) calculations at the B3LYP level were performed. The data have shown that there is a weak physical adsorption of NH_3 on the surface of pure pyrene. In contrast, the deliberate replacement of a carbon atom with a silicon (Si) atom significantly enhanced the sensing performance of the system. The NH_3 molecule was found to be strongly chemisorbed on the surface of the Si-doped pyrene, which resulted in an extremely favourable adsorption energy. Moreover, the interaction of NH_3 with the Si-doped surface led to a significant change in the energy gap, indicating a substantial increase in the electrical conductivity of the material. This sizable electrical response is another evidence for the high sensitivity of the Si-doped complex to NH_3. The balancing of high electronic sensitivity and adequate recovery time exhibited by Si-doped pyrene shows that it is a very promising and effective candidate for advanced nanosensor applications to detect ammonia molecules in the end.

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