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Adsorption Performance and Sensing ability of Heteroatom-Functionalized Si-doped Single-Walled Carbon Nanotubes: A Computational Study of Caffeine adsorption

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Abstract

This study examined the sensing performance of caffeine on pristine and heteroatom modified silicon decorated carbon nanotubes (CNTs) for the purpose of determining which modified CNT surface provides the most promising combination of adsorption and electronic response. The study was carried out using density functional theory (DFT) calculations at the PBE0-D3/def2SVP level, to obtain stable molecular structures. Adsorption energy calculations resulted in negative values ranging from -1.12 to -0.46 eV, confirming favourable caffeine adsorption. The CFN-SiS@CNT system showcased the strongest adsorption energy with the value of -1.12 e V. NBO analysis supported this result by revealing significant donor-acceptor interactions, with CFN-SiS@CNT exhibiting the highest stabilization energies of 86.93 and 57.97 kcal/mol, indicating strong orbital interaction and electron delocalization between caffeine and SiS@CNT surface. NCI analysis showed that adsorption was predominantly associated with van der Waals interactions, while localized attractive and steric interactions also contributed to the overall adsorption process as seen in CFN-SiP@CNT and CFN-SiS@CNT. The findings of this study demonstrate that heteroatom functionalization alters and improves the electronic response and adsorption characteristics of Si-doped CNTs, identifying CFN-SiS@CNT as the most promising for caffeine adsorption and sensing applications.

Keywords: DFT, Sensing, Heteroatom, Silicon, Carbon-nanotubes, Caffeine.

1.0 Introduction

Caffeine (1,3,7-trimethylxanthine) is the most widely used psychoactive chemical substance in the world, naturally found in coffee beans, tea leaves, cocoa and kola nuts. Caffeine is a stimulant, with a beneficial effect on the central nervous system, and is widely used to increase alertness and decrease fatigue, and is therefore extensively incorporated into drinks, energy drinks, dietary supplements, pharmaceuticals and many processed food products [1-3]. Caffeine, within the recommended limits, is generally safe, but there is some evidence that long-term use can lead to sleep disturbances, anxiety, high blood pressure, cardiovascular problems, altered neurological reactions, and other negative physiological effects, especially in sensitive individuals [4,5]. Therefore, the routine determination of caffeine has become a crucial part in product standardization and regulatory compliance [6]. Several analytical techniques have been investigated for the determination of caffeine in food systems and the chromatographic, spectroscopic and electrochemical approaches have been widely used due to their method reliability [7-11]. Despite these developments, the ability to achieve routine testing of food continues to be limited by the high cost of equipment, complicated sample preparation procedures and difficulties in delivering timely, consistent analysis. Such constraints have driven the development of molecular recognition materials that exhibit measurable electronic responses to target analytes. Carbon-based nanomaterials have been widely investigated for molecular detection and contaminant removal, owing to their tunable surface chemistry and electronic properties that can be engineered for selective interaction with target molecules. Among these, carbon nanotubes (CNTs) remain particularly attractive due to their high surface area, structural stability, rapid charge transport, and accessible adsorption sites. Surface composition and local electronic environment are the dominant factors governing CNT-based system performance. Wang et al. (2020) demonstrated that controlled modification of carbon structure redistributes interfacial electron density, improving both adsorption capacity and functional performance [12]. Hayat et al. (2024) further showed that heteroatom incorporation creates adsorption-active defect sites and redistributes local charge density, strengthening interaction with target molecules [13]. In particular, nitrogen (N), phosphorus (P), sulfur (S), and silicon (Si) doping has emerged as an effective route for enhancing charge transfer and interaction strength in carbon networks. Alongside experimental development, computational studies have become essential for understanding the molecular factors governing adsorption and sensing behavior prior to

fabrication. Among these approaches, density functional theory (DFT) has been widely adopted for its ability to evaluate adsorption energies, charge transfer, intermolecular interactions, and adsorption-induced electronic property changes in detail. Panahi et al. (2021) investigated caffeine adsorption on hybrid hBN/graphene hexagonal nanoflakes and established that adsorption stability depends strongly on configuration and the local electronic characteristics of the surface [14]. Lee et al. (2012) examined caffeine adsorption on single-walled carbon nanotubes using first-principles calculations and reported that interaction occurs predominantly through π - π stacking, accompanied by measurable electronic property changes, confirming CNT potential for both molecular adsorption and sensing [15]. El Fatimy et al. (2024) extended this understanding by demonstrating that nanotube geometry governs molecular accommodation and interaction characteristics during caffeine confinement within single-walled CNT cavities, underscoring the role of structural control in regulating adsorption at the molecular level [16]. In another theoretical investigation, Rajkamal et al. (2023) evaluated caffeine adsorption on heteroatom-modified carbon-based materials and showed that surface modification enhances adsorption affinity through changes in electronic interaction and charge-transfer characteristics between caffeine and the adsorption surface [17]. Existing studies on caffeine monitoring have largely focused on experimental detection systems or conventional adsorption materials, while computational investigations of CNT-based caffeine sensing remain limited and are often restricted to adsorption energetics and structural analysis. In this study, heteroatom-functionalized Si-doped single-walled carbon nanotubes were computationally engineered and systematically evaluated using integrated energetic, electronic, and topological descriptors to identify multifunctional materials for simultaneous caffeine adsorption and sensing in food-related applications. The PBE0-GD3/def2-SVP level of theory was therefore adopted in this study because hybrid functionals provide improved treatment of charge-transfer interaction and frontier orbital behavior, while Grimme's D3 dispersion correction enhances the description of intermolecular adsorption interactions. The def2-SVP basis set further provides balanced computational efficiency and reliable electronic density for structural, energetic, and wavefunction-based analyses. To achieve the objective of this study, geometry optimization, adsorption energy calculations, molecular electrostatic surface potential (MESP), solvation analysis, frontier molecular orbital (FMO), quantum descriptor evaluation, natural bond orbital (NBO), quantum theory of atoms in molecules (QTAIM), and non-covalent interaction (NCI) analyses were performed. These analyses jointly provide in-depth

understanding of the adsorption behavior, sensing response, charge-transfer mechanisms, and intermolecular interactions governing caffeine detection on modified CNT systems.

2.0 Computational details

PBE0-D3/def2SVP level of theory was employed as it provides accuracy in optimization [18]. The def2svp basis set reduces computational cost, and the D3 correction accounts for dispersion forces making the combination suitable for adsorption studies [19]. Sketching of compounds was carried out with GaussView 6.0.16 software package and visualized using Chemcraft, HOMO-LUMO studies were also carried out using Chemcraft and energy gap values of the studied compounds were calculated using the Gaussian 09W calculation setup [20]. Quantum descriptors were also calculated alongside energy gap. NBO analysis was carried out with the help of Gaussian 09W which has an in-built algorithm, to understand donor-receptor interactions. Multiwfn was employed for NCI and QTAIM analysis, which are generally the study of weak interactions. MESP was done using GaussView 6.0 to map out the electrophilic and nucleophilic region of the studied compounds. Adsorption and Solvation studies were carried out using Gaussian 09W calculation summary setup [21]. Equations used included; $IP = -(E_{HOMO})$ (1), $EA = -(E_{LUMO})$ (2), $-\mu = (E_{HOMO} + E_{LUMO})/2$ (3), $\chi = \eta = (E_{HOMO} + E_{LUMO})/2$, (4), $S = \left(\frac{1}{2\eta}\right)$, (5), $\omega = \frac{(-\mu^2)}{2\eta}$, (6), $E_{ads} = E_{complex} - (E_{surface} + E_{adsorbate})$ (7), and , $E_{sol} = E_{water} - E_{gas}$ (8), as Equations (1) – (8) respectively. The continuum solvation method on the 5;5 CNT employed was the SMD, with the solvent being [22,23].

3.0 Geometry optimization

3.0.1 Bond properties of CFN and CNT surfaces

Geometry optimization enables determination of the stability of structures, and it was done to ensure the bond lengths of the studied structures remained in normal ranges. **Table S1** presents the optimized bond lengths of CFN and the pristine and heteroatom-doped CNT surfaces. The obtained geometrical parameters generally fall within the standard ranges, indicating that the geometry optimization process preserved the structural integrity and stability of the molecular systems. The C=O bond length of CFN was recorded as 1.212 Å, which agrees well with the normal carbonyl bond range of approximately 1.20 Å to 1.23 Å [24]. The C-N bond also maintained the expected bond length range of partially conjugated C-N bonds 1.35 Å to 1.47 Å with a bond length of 1.408 Å, while the C-H bond length corresponds closely to the standard value of 1.09 Å [25]. Looking

at the CNT surfaces, we see C₉=C₁₀ bond lengths ranging from 1.366 Å to 1.378 Å which are characteristic of sp² hybridized carbon to carbon double bonds commonly observed in graphitic systems and carbon nanotubes, where values of 1.34 Å to 1.40 Å are expected. Also, C₁₁-C₁₂ single bond lengths that ranged from 1.451 Å to 1.479 Å are consistent with normal carbon to carbon single bond lengths [26]. The slight elongation observed in certain surfaces, particularly SiN@CNT, could be attributed to electronic redistribution which is caused by heteroatom incorporation into the nanotube framework [27]. Silicon possessing a larger atomic radius than carbon alongside lower electronegativity causes adjacent carbon-carbon bonds to weaken which increases the bond distances slightly. The Si-C bond lengths that ranged from 1.764 Å to 1.831 Å also correspond to the standard Si-C covalent bond values reported to be around 1.75 Å to 1.90 Å [28]. Looking at the Si-N bond, compared to the Si-C, slight elongation is noticed and this can be attributed to lone pair repulsion and orbital mismatch between nitrogen and silicon atoms [28]. Lastly, the Si-P and Si-S bonds of 1.868 Å and 1.845 Å respectively reflect the larger atomic sizes of phosphorus and sulfur, which naturally produce longer bond distances.

3.0.2 Bond properties of CNT surfaces post adsorption

Bond lengths of the modified CNT surfaces after adsorption alongside the newly formed interaction bonds between the adsorbent and adsorbate are displayed in **Table S2**. The comparison with the surfaces before adsorption shows slight variations in a series of bond lengths, indicating electronic interactions and charge redistribution during adsorption. Reduction was noticed in most complexes post adsorption especially in CFN-SiN@CNT and CFN-SiP@CNT and this reduction points out partial strengthening of π -conjugated framework due to electron delocalization between CFN and the nanotube surface [29]. Electron density around conjugated carbon atoms is usually enhanced by adsorption and this increases the bond order and causes minor bond contraction [30]. These changes are also observed in the C₁₁-C₁₂ bonds indicating structural adjustment of the CNT framework in response to adsorbate interaction. In most cases, the bond lengths decrease relative to the isolated surfaces, implying stabilization of the nanotube backbone after adsorption. C-H bond lengths which displayed non-significant changes, indicates that hydrogen atoms were not directly involved in the adsorption process and therefore retained their normal bonding environment. There were more significant changes observed in the heteroatom-containing bonds, as the Si-C bond in CFN-SiN@CNT shortened considerably from 1.831 Å to 1.763 Å, suggesting stronger orbital overlap and enhanced electron transfer after adsorption [31]. Also, Si-C bond in

CFN-SiS@CNT increased slightly to 1.792 Å, indicating mild bond weakening due to steric effects and redistribution of electron density toward the adsorbed CFN molecule while P-C bond decreased from 1.868 Å to 1.775 Å after adsorption, which may be due to improved electronic stabilization of the phosphorus-doped system upon interaction with CFN. The newly formed bonds post adsorption showcased successful interaction between CFN and the modified CNT surfaces. Bond lengths of 2.133 Å to 2.171 Å are longer than conventional covalent bonds but shorter than weak van der Waals, this is an indication of moderate intermolecular interactions dominated by physisorption with partial orbital overlap [32].

3.1 Adsorption Studies

The interaction strength between caffeine (CFN) and the doped CNT surfaces was assessed through adsorption energy (E_{ads}) calculations. As shown in **Table 1**, all calculated adsorption energies are negative, indicating that caffeine adsorption is thermodynamically favorable. E_{ads} was calculated according to **Equation (7)**, where $E_{complex}$ is the total energy of the CFN-CNT complex, $E_{surface}$ is the energy of the doped CNT surface, and $E_{adsorbate}$ is the energy of the caffeine molecule. Among the four systems, CFN-SiS@CNT had the most negative E_{ads} (-1.12 eV), indicating the strongest interaction with caffeine, whereas CFN-SiN@CNT exhibited the weakest interaction. Similar enhancement of adsorption following heteroatom modification has been reported for carbon-based nanomaterials. Shahabi and Tavakol (2017) reported that sulfur heteroatoms in single-walled CNTs shift electron density outward and generate low-lying virtual orbitals accessible to polar ring structures [33]. Likewise, Ma et al. (2021) demonstrated that sulfur-modified carbonaceous materials achieve higher efficiency for organic contaminant removal through non-radical electron-transfer mechanisms that reduce structural mismatch during adsorption [34]. Consistent with these findings, the results obtained imply that the dopant's nature plays an important role in regulating the adsorption performance of the modified nanotubes. To further elucidate the origin of the observed adsorption trend, complementary electronic and topological analyses, including MESP, FMO, NBO, QTAIM, and NCI, were performed.

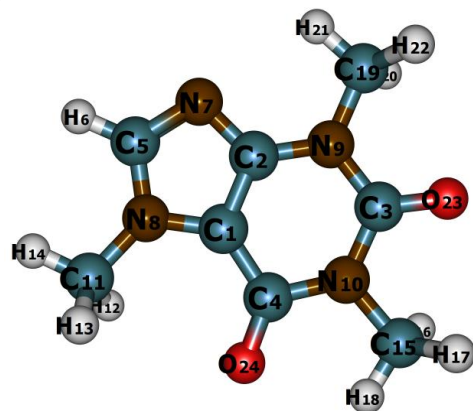
Table 1: Adsorption energies and adsorption characteristics of caffeine on pristine and doped CNT systems calculated at the PBE0-D3/def2SVP level

System	E _{complex} eV	E _{adsorbate} eV	E _{surface} eV	E _{ads} eV
CFN-Si@CNT	-129156.66	-18480.65	-110674.98	-1.02
CFN-SiN@CNT	-129607.59	-18480.65	-111126.48	-0.46
CFN-SiP@CNT	-137402.69	-18480.65	-118921.13	-0.91
CFN-SiS@CNT	-138947.58	-18480.65	-120465.81	-1.12

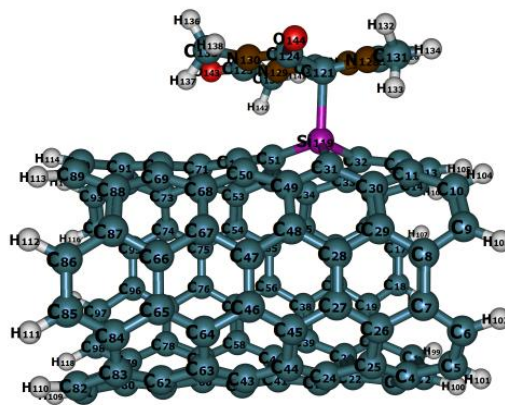
3.2 Electronic properties

3.2.1 Frontier Molecular Orbital (FMO) Analysis

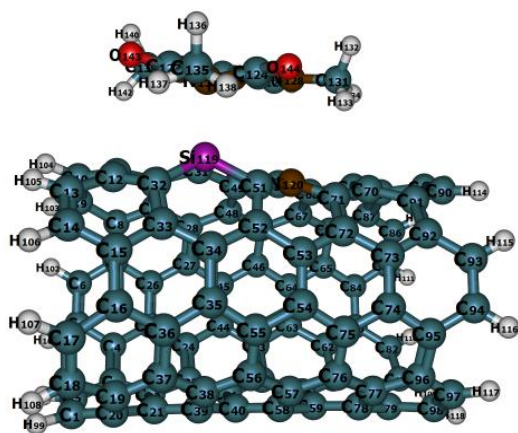
The Frontier Molecular Orbital (FMO) analysis was carried out to evaluate the effect of caffeine adsorption on the electronic properties of the modified CNT systems [35]. The iso-surface plots of CNT doped and co-doped surfaces and CNT surfaces post adsorption are represented in **Figure S1** and **Figure S2**. Energy gap values were calculated for CFN, CNT surfaces and CNT surfaces post adsorption and are represented in **Table 2**. The energy gap values for the studied compounds ranged from 1.380 eV to 5.564 eV, with CFN being the highest and SiN@CNT being the lowest. Energy gap values of CNT modified surfaces ranged from 1.380 eV to 1.891 eV in the order of SiP@CNT (1.891 eV) > SiS@CNT (1.828 eV) > Si@CNT (1.811 eV) > SiN@CNT (1.380 eV). Following caffeine adsorption, modest changes in the HOMO-LUMO gap were observed. The energy gap increased for CFN-SiN@CNT, CFN-SiS@CNT, CFN-SiP@CNT, while it decreased for CFN-Si@CNT. The increase in energy gap after adsorption suggests increase in electronic stability [36], while the slight reduction observed for CFN-Si@CNT indicates enhanced electronic conductivity and charge transfer capability [37]. Although CFN-SiS@CNT exhibited the strongest adsorption energy, the reduced HOMO-LUMO gap observed in CFN-Si@CNT indicates that adsorption strength and electronic response are not necessarily governed by the same factors. To further interpret these electronic changes, the quantum descriptors were calculated using **Equations (1-6)** with chemical softness and chemical hardness giving insight to the reactivity and stability status of the surfaces post adsorption. Their values are recorded in **Table 2** below.



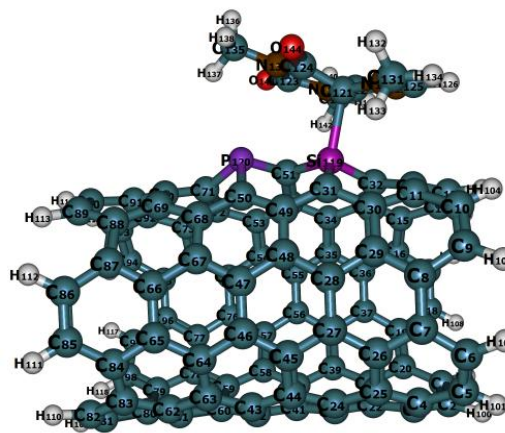
CFN



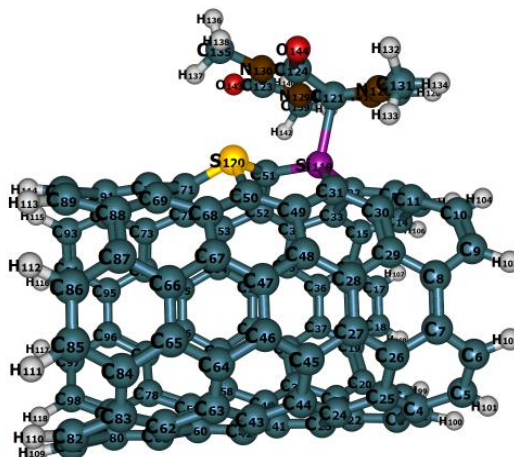
CFN-Si@CNT



CFN-SiN@CNT

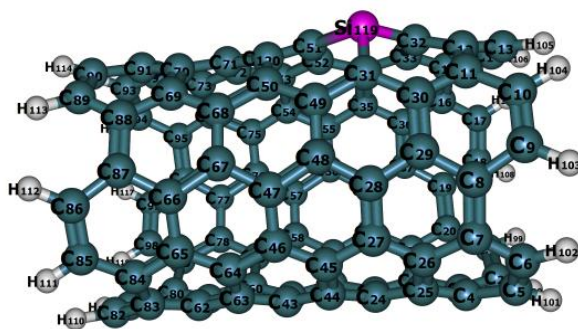


CFN-SiP@CNT

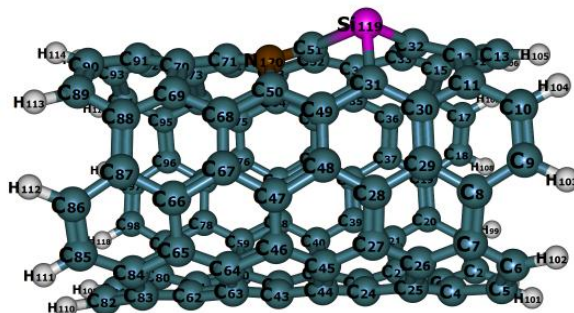
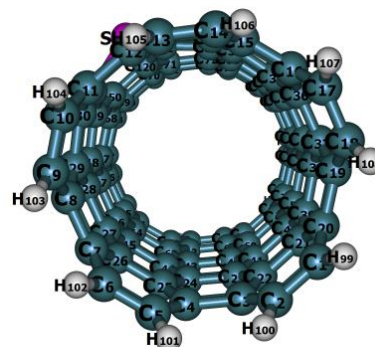


CFN-SiS@CNT

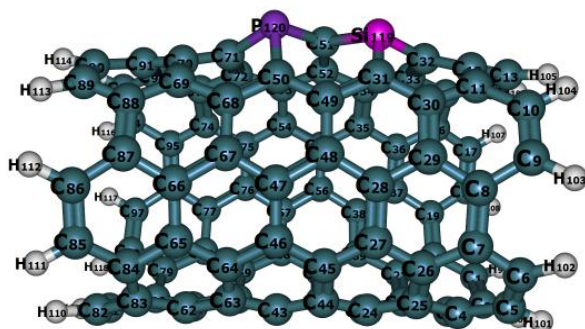
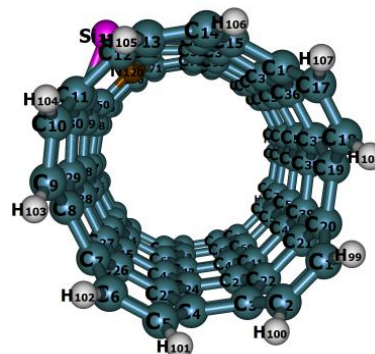
Figure 1: Visualization of post adsorption of CFN with modified CNT surfaces



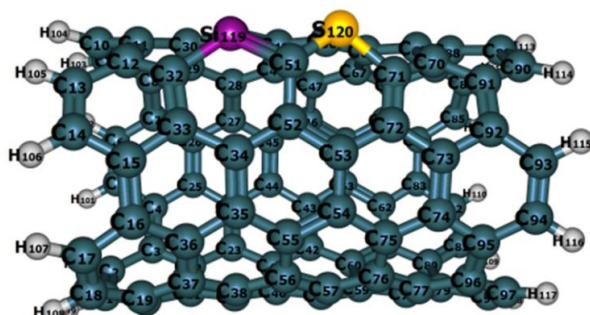
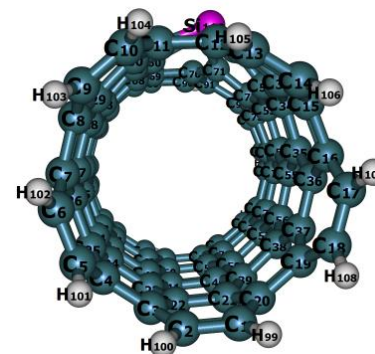
Si@CNT



SiN@CNT



SiP@CNT



SiS@CNT

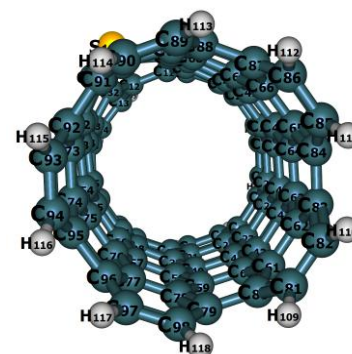


Figure 1: Visualization of doped and co-doped systems of CNT surfaces

Table 2: Energy gap and quantum descriptor values of the studied molecules

Surfaces										
	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g (eV)	IP (eV)	EA (eV)	$-\mu$ (eV)	η (eV)	σ (eV)	χ (eV)	ω (eV)
CFN	-0.808	-6.372	5.564	6.372	0.808	-3.590	2.782	0.180	3.590	2.317
Si@CNT	-2.996	-4.806	1.811	4.806	2.996	-3.901	0.905	0.552	3.901	8.405
SiN@CNT	-3.152	-4.532	1.380	4.532	3.152	-3.842	0.690	0.724	3.842	10.702
SiP@CNT	-2.846	-4.737	1.891	4.737	2.846	-3.792	0.945	0.528	3.792	7.605
SiS@CNT	-2.893	-4.721	1.828	4.721	2.893	-3.807	0.914	0.546	3.807	7.928
Interactions										
	E_{LUMO} (eV)	E_{HOMO} (eV)	E_g (eV)	IP (eV)	EA (eV)	μ (eV)	η (eV)	σ (eV ⁻¹)	χ (eV)	ω (eV)
CFN-Si@CNT	-2.790	-4.581	1.791	4.581	2.790	-3.685	0.895	0.558	3.685	7.583
CFN-SiN@CNT	-2.480	-4.041	1.562	4.041	2.480	-3.260	0.781	0.640	3.260	6.805
CFN-SiP@CNT	-2.620	-4.552	1.932	4.552	2.620	-3.586	0.966	0.517	3.586	6.656
CFN-SiS@CNT	-2.636	-4.522	1.885	4.521	2.636	-3.580	0.942	0.530	3.580	6.796

3.2.2 NBO

The adsorption energy calculations identified CFN-SiS@CNT as the most stable interaction. To determine whether this energetic preference is supported by the orbital interactions, Natural Bond Orbital (NBO) analysis was conducted to assess the donor-acceptor interaction, charge transfer, and electronic stabilization of caffeine adsorption onto the investigated CNT systems. The second-order perturbation stabilization energy $E^{(2)}$ is useful as an indicator of the degree of electron delocalization between the donor and the acceptor orbital. The greater the $E^{(2)}$ value, the more significant the orbital interaction and the more stable the adsorption complex [38]. Among the studied systems, CFN-SiS@CNT showed the largest stabilization energies. The $LP(1)C_{122} \rightarrow$

LP*(2)Si₁₁₉ and LP(1)N₁₂₈ → LP*(3)Si₁₁₉ interactions produced E⁽²⁾ values of 86.93 and 57.97 kcal/mol, respectively, together with comparatively high F(i,j) values of 0.165 and 0.146 a.u as shown in **Table 3** below. The interaction pattern that was observed for CFN-SiS@CNT agrees with adsorption energy results, suggesting that S incorporation changed the local electronic environment around the Si adsorption center, making it more likely to have stronger interaction with the adsorbate.

Table 3: Natural Bond Orbital (NBO) analysis of donor-acceptor interactions and electronic stabilization for caffeine adsorption on pristine and doped CNT systems at the PBE0-D3/def2SVP level

Systems	Donor(i)	Acceptor (j)	E ⁽²⁾ kcal/mol	E(j)-E(i) a.u	F(i,j) a.u
CFN-Si@CNT	$\pi C_{51} - C_{120}$	$\pi^* C_{123} - O_{143}$	1.64	0.27	0.020
	$\sigma C_{32} - Si_{119}$	$\pi^* C_{121} - C_{122}$	5.09	0.45	0.048
	LP(1)N ₁₂₉	$\sigma^* C_{31} - Si_{119}$	5.01	0.67	0.054
	LP(1)N ₁₃₀	$\pi^* C_{51} - C_{120}$	5.21	0.44	0.045
CFN-SiN@CNT	$\sigma C_{51} - Si_{119}$	LP*(1)C ₁₂₃	23.14	0.05	0.045
	$\sigma C_{51} - Si_{119}$	LP*(1)C ₁₂₄	4.04	0.12	0.032
	LP(1)N ₁₃₀	$\sigma^* C_{51} - Si_{119}$	13.29	0.50	0.103
	LP(1)N ₁₃₀	LP*(2)Si ₁₁₉	13.09	0.57	0.113
CFN-SiP@CNT	$\pi C_{31} - C_{49}$	$\pi^* C_{121} - C_{124}$	0.44	0.26	0.014
	LP(1)P ₁₂₀	LP*(1)C ₁₂₃	1.30	0.27	0.030
	LP(3)O ₁₄₃	$\sigma^* C_{71} - P_{120}$	0.03	0.52	0.006
	$\pi C_{121} - C_{124}$	LP*(1)Si ₁₁₉	7.39	0.08	0.032
CFN-SiS@CNT	$\pi C_{71} - C_{72}$	$\pi^* C_{123} - O_{143}$	2.39	0.38	0.027
	$\pi C_{50} - S_{120}$	$\pi^* C_{121} - C_{124}$	3.18	0.36	0.033
	LP(1)C ₁₂₂	LP*(2)Si ₁₁₉	86.93	0.30	0.165
	LP(1)N ₁₂₈	LP*(3)Si ₁₁₉	57.97	0.44	0.146

3.2.3 Molecular Electrostatic Potential (MEP) analysis

The purpose of MEP analysis is to determine the electrophilic and or nucleophilic regions of a complex, giving insight to the distribution of electron density using color codes that represent these regions [39]. The electrophilic region is the site for nucleophilic attack and the nucleophilic region the site for electrophilic attack represented by colors blue and red respectively, with blue indicating an electron poor region and red indicating an electron rich region [40]. As observed in **Figure 3**, the electrophilic region can be seen around the atoms of the adsorbent across all interactions describing where the electron poor regions are. The sky-blue color observed around the atoms of the adsorbate suggests moderate nucleophilic regions, which is slightly an electron poor region. An orange-like color is observed at the middle of the CNT across all interactions which is an indication of a moderate nucleophilic region, which is slightly an electron rich region. In CFN-Si@CNT a yellow like color can be observed around the atoms of the adsorbate mixed with the sky-blue, indicating a mildly electron rich region. This phenomenon of charge separation of electron deficient margin and electron rich core may suggest that adsorption is driven by electrostatic attraction between the positive electrostatic potential (blue) and negative electrostatic potential (red) [41]. The orange core provides secondary stabilization, and the complexes should preferentially interact with polar molecules and cations rather than non-polar species.

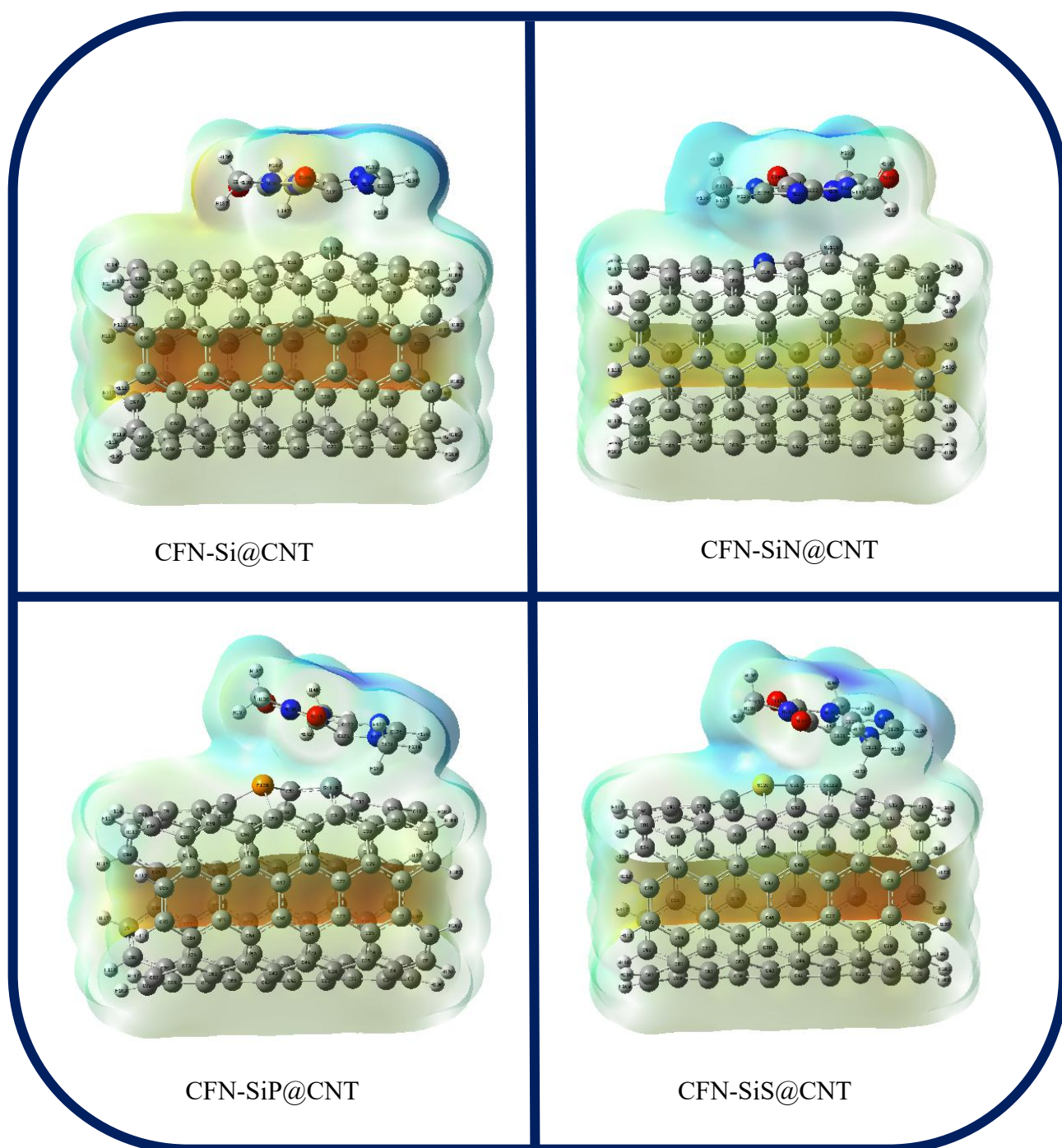


Figure 3: MEP plots of the studied surfaces post adsorption

3.3 Topological Analysis

3.3.1 QTAIM

The QTAIM analysis revealed that the nature of the interaction between caffeine and the CNT surfaces was predominantly closed-shell, as evidenced by the positive Laplacian values, $\nabla^2\rho(r) > 0$, at the bond critical points. However, the partially negative $H(r)$ values together with $|V(r)|/G(r)$ ratios ≥ 1 observed suggest that the adsorption process also possessed varying degrees of partial covalent character [42]. Across all systems, the $Si_{119} - C_{121}$ label of CFN-Si@CNT, CFN-SiS@CNT, CFN-SiP@CNT, and the $Si_{119} - N_{130}$ label of CFN-SiN@CNT showed partial covalent character and exhibited relatively the strongest topological interaction characteristics, including comparatively higher electron density ($\rho(r)$) and stronger potential energy density ($V(r)$) values at the bond critical points. The Electron Localization Function (ELF), which highlights regions where electron pairing is strong, had values less than 1 across all the systems, suggesting delocalization of electrons, typical of weak interactions. The values of the topological descriptors represented in **Table 4** revealed that the bond labels with high electron densities and negative $H(r)$ showed values tending to 0.5, indicating an increasing interaction strength [43]. Although the CFN-Si@CNT and CFN-SiP@CNT systems exhibited slightly greater electron localization according to ELF values, 2.81E-01 and 2.83E-01, respectively, while CFN-SiS@CNT maintained relatively the strongest interaction characteristics based on its higher electron density and more negative potential energy density, which is consistent with its highest adsorption energy and indicates stronger interfacial electronic stabilization following caffeine adsorption.

Table 4: QTAIM topological descriptors for caffeine adsorption on pristine and doped CNT systems at the PBE0-GD3/def2SVP level

Systems	Interaction	BC Ps	$\rho(\mathbf{r})$ a.u	$\nabla^2 \rho(\mathbf{r})$ a.u	$H(\mathbf{r})$ a.u	$G(\mathbf{r})$ a.u	$V(\mathbf{r})$ a.u	$ V(\mathbf{r}) /G(\mathbf{r})$	λ_1 a.u	λ_2 a.u	λ_3 a.u	ε	ELF
CFN-Si@CNT	C ₇₁ – O ₁₄₃	165	3.99E-03	1.36E-02	6.74E-04	2.73E-03	-2.05E-03	7.51E-01	-2.24E-03	-1.17E-03	1.70E-02	9.12E-01	1.10E-02
	Si ₁₁₉ – C ₁₂₁	216	5.94E-02	7.34E-02	-2.32E-02	4.16E-02	-6.48E-02	1.56E+00	-5.97E-02	-5.71E-02	1.90E-01	4.68E-02	2.81E-01
	C ₁₁ – H ₁₃₃	260	6.72E-03	2.23E-02	1.10E-03	4.48E-03	-3.38E-03	7.54E-01	-5.42E-03	-4.15E-03	3.19E-02	3.06E-01	2.29E-02
	C ₅₁ – N ₁₂₉	186	8.33E-03	2.64E-02	1.26E-03	5.35E-03	-4.09E-03	7.64E-01	-4.23E-03	-1.77E-03	3.24E-02	1.39E+00	3.25E-02
CFN-SiN@CNT	C ₁₂ – O ₁₄₃	238	3.65E-03	1.22E-02	6.16E-04	2.42E-03	-1.81E-03	7.48E-01	-1.30E-03	-8.09E-04	1.43E-02	6.04E-01	1.03E-02
	Si ₁₁₉ – N ₁₃₀	210	5.13E-02	8.66E-02	-1.60E-02	3.77E-02	-5.38E-02	1.43E+00	-5.00E-02	-4.92E-02	1.86E-01	1.67E-02	2.25E-01
	C ₅₀ – C ₁₂₁	191	5.09E-03	1.70E-02	9.06E-04	3.33E-03	-2.43E-03	7.30E-01	-1.46E-03	-9.05E-04	1.93E-02	6.17E-01	1.64E-02
	C ₁₁ – H ₁₄₂	253	4.57E-03	1.48E-02	7.84E-04	2.91E-03	-2.12E-03	7.29E-01	-3.20E-03	-2.24E-03	2.02E-02	4.25E-01	1.51E-02
CFN-SiS@CNT	Si ₁₁₉ – C ₁₂₁	228	6.41E-02	1.00E-01	-2.53E-02	5.04E-02	-7.57E-02	1.50E+00	-6.69E-02	-6.54E-02	2.33E-01	2.35E-02	2.55E-01
	Si ₁₂₀ – N ₁₃₀	172	1.12E-02	3.06E-02	6.42E-04	7.02E-03	-6.38E-03	9.09E-01	-6.90E-03	-6.49E-03	4.40E-02	6.41E-02	5.01E-02
	C ₁₂ – C ₁₂₅	276	6.64E-03	2.23E-02	1.33E-03	4.25E-03	-2.92E-03	6.87E-01	-2.69E-03	-1.44E-03	2.65E-02	8.70E-02	2.43E-02
	C ₃₁ – H ₁₃₃	271	8.08E-03	2.59E-02	1.17E-03	5.32E-03	-4.15E-03	7.80E-01	-6.35E-03	-4.08E-03	3.64E-02	5.55E-01	2.98E-02
CFN-SiP@CNT	Si ₁₁₉ – C ₁₂₁	224	6.03E-02	7.37E-02	-2.39E-02	4.23E-02	-6.62E-02	1.57E+00	-6.09E-02	-5.79E-02	1.93E-01	5.23E-02	2.83E-01
	P ₁₂₀ – N ₁₃₀	171	9.49E-03	2.18E-02	4.58E-04	5.00E-03	-4.54E-03	9.08E-01	-5.52E-03	-5.02E-03	3.23E-02	1.00E-01	5.70E-02
	C ₃₁ – H ₁₃₃	271	7.03E-03	2.31E-02	1.12E-03	4.64E-03	-3.52E-03	7.59E-01	-5.14E-03	-2.64E-03	3.09E-02	9.46E-01	2.47E-02
	C ₁₂ – C ₁₂₅	275	7.58E-03	2.57E-02	1.54E-03	4.88E-03	-3.34E-03	6.84E-01	-3.29E-03	-2.22E-03	3.12E-02	4.79E-01	2.86E-02

3.3.2 Non-Covalent Interaction Analysis

The non-covalent interaction (NCI) analysis was carried out on CNT surfaces post-adsorption with CFN to visualize the intermolecular interactions. As shown in **Figure 3**, extensive green iso-surfaces are observed at the point of contact between the CNT surfaces and the caffeine molecule, indicating that weak dispersion (van der Waals) interactions contribute significantly to the adsorption process. The CFN-SiN@CNT system is predominantly characterized by these green isosurfaces, suggesting that the interaction is mainly governed by dispersion forces. In contrast, the CFN-Si@CNT, CFN-SiP@CNT and CFN-SiS@CNT systems exhibit localized blue and red isosurfaces in addition to the dominant green regions. The blue regions indicate localized attractive interactions, whereas the red regions correspond to steric repulsion arising from closed interatomic contacts. The coexistence of these features suggests that adsorption on these CNT surfaces is governed by a combination of dispersion interactions, localized attractive interactions and steric effects rather than by a single interaction mechanism [44].

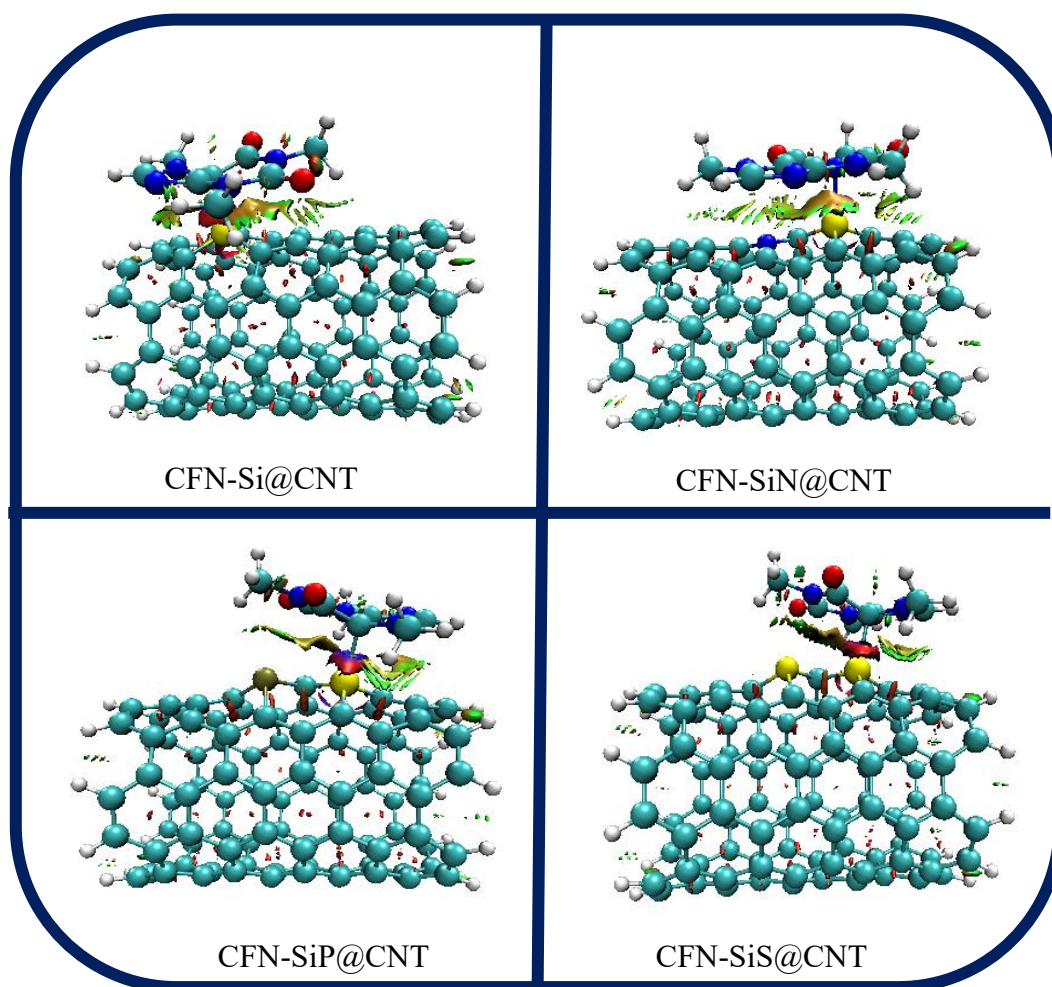


Figure 3: Visualization of weak interactions, NCI analysis

3.4 Solvation studies

Solvation studies were carried out on the surfaces post adsorption to determine their thermodynamic favorability and measure their stability in a solution. Solvation energy < 0 shows that the energy of the complex in solution is lower than in gas phase, indicating stabilization by the solvent [45]. The solvation energies were calculated using **Equation 8** and are represented in **Table 5**, and all being negative proves that their transition from gas phase into solution was favorable based on Gibbs free energy. As shown in **Table 5**, CFN-Si@CNT showcased the most negative solvation energy among the studied complexes with a value of -1.32 eV, indicating that it underwent the highest stabilization in the solvent medium. High negative solvation energies usually imply strong solute-solvent interactions and improved thermodynamic stability in solution phase and this behavior may be attributed to effective charge redistribution and stronger polarity within the complexes, which enhanced its interaction with the surrounding solvent molecules [46]. Negative solvation energies were also found of the rest of the interactions in the order of CFN-SiN@CNT < CFN-SiP@CNT < CFN-SiS@CNT < CFN-Si@CNT.

Table 5: Solvation energies of CNT surfaces post adsorption

Interactions	E solvent (a.u)	E gas (a.u)	E solvation (a.u)	E solvation (eV)
CFN-Si@CNT	-4746.46	-4746.41	-0.048857	1.32
CFN-SiN@CNT	-4763.03	-4762.98	-0.044993	1.22
CFN-SiP@CNT	-5049.50	-5049.45	-0.047519	1.29
CFN-SiS@CNT	-5106.27	-5106.22	-0.048252	1.31

4.0 Conclusions

The adsorption and sensing behavior of caffeine on pristine and heteroatom-modified silicon-decorated carbon nanotube systems was evaluated using DFT calculations. The results gotten from the various analysis provided good understanding of the structural stability, adsorption strength, electronic properties, intermolecular interactions, and sensing potential of the studied systems. Geometry optimization proved that all studied structures maintained stable bond lengths within standard ranges after optimization. Slight variations were observed in some bond lengths after heteroatom incorporation and adsorption which indicated localized electronic redistribution and structural adjustment without destabilizing the nanotube framework. This confirmed the reliability and stability of the computational models used in the study. Adsorption energy analysis revealed that all adsorption processes were thermodynamically favorable and spontaneous, as evidenced by the negative adsorption energy values obtained for all complexes. The adsorption energies followed the order $\text{CFN-SiN@CNT} < \text{CFN-SiP@CNT} < \text{CFN-Si@CNT} < \text{CFN-SiS@CNT}$, showing that the sulfur-doped system exhibited the strongest adsorption affinity toward caffeine. The highly negative adsorption energy of CFN-SiS@CNT indicated stronger interaction between the adsorbate and adsorbent surface, suggesting that sulfur incorporation enhanced the adsorption capability of the CNT system. The improved adsorption behavior was attributed to increased electronic polarization, defect formation, and enhanced donor-acceptor interaction created by sulfur doping. NCI analysis showed the presence of van der Waals, but does not mean the overall interaction was weak as the adsorption energies of the systems suggest otherwise, with adsorption being governed by multiple interaction mechanisms. The relatively low energy gap values of the modified CNT systems generally suggest that the materials possess good electronic sensitivity and may respond effectively to adsorption-induced electronic changes. Natural Bond Orbital analysis further supported the adsorption results by revealing donor-acceptor interactions and charge transfer between caffeine and the adsorption surfaces. CFN-SiS@CNT showed the highest stabilization energies and strongest orbital overlap among all systems, confirming stronger electronic interaction and improved adsorption activity in the sulfur-doped surface. These strong interactions suggest efficient electron delocalization between caffeine and the adsorption surface, which contributed significantly to the stability of the adsorption complex. The QTAIM and NCI analyses revealed that adsorption was mainly dominated by closed-shell interactions and weak van der Waals forces with partial covalent character. Adsorption did not occur through pure covalent

bonding, but through mixed interaction mechanism, hence, the coexistence of weak dispersive interactions and moderate attractive interactions. Solvation studies showed that all systems possessed highly negative energies showing thermodynamic favourability and stability in solution. While CFN-SiN@CNT displayed the most negative solvation energy, indicating stronger stabilization in solution phase, CFNSiS@CNT displayed the best adsorption performance due to its strong adsorption energy.

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