

Article

Transition-Metal-Doped Graphene for Volatile Sulfur Compound Detection: A DFT Study

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Abstract

The adsorption behavior of selected volatile sulfur compounds on graphene was examined using density functional theory. The analytes of interest are hydrogen sulfide, methyl mercaptan and dimethyl sulfide, which are found in the exhaled breath of halitosis patients. The human breath contains several volatile compounds that act as chemical fingerprints of what is happening inside the body. This study employs first-principles calculations to investigate the structural, electronic, and adsorption properties of pristine and transition-metal-doped graphene (Fe, Ru, and Os) for the detection of key volatile sulfur compounds relevant to breath analysis and halitosis screening. According to our findings, when a single carbon atom is substituted with an iron, ruthenium or osmium atom in the optimized graphene sheet, which is equivalent to a dopant concentration of 2 mol% in experiments, the adsorption behavior of the system is altered significantly. Based on the resultant adsorption behavior and electronic structure alterations, important sensor properties were examined. This work presents a non-invasive approach for halitosis detection, therapeutic monitoring, and metabolic status observation by analyzing the volatile sulfur compounds present in exhaled breath. Additionally, this study demonstrates how computational modeling can be used as a decision support tool.

Keywords: volatile sulfur compounds (VSCs); halitosis; graphene; density functional theory; adsorption profile; electronic structure

1. Introduction

Graphene is a one-atom-thick material that introduces a new paradigm in materials science, enabling direct access to low-dimensional physics. For many years, chemical sensors have been created to identify different concentrations of gases and vapors for use in a variety of fields, including industry, space exploration, environmental monitoring, military, and medical diagnostics [1]. The foundation of clinical breath analysis is the detection of numerous significant metabolites and biomarker molecules in an exhaled breath, many of which are associated with human disease or physiological conditions that may result in deterioration in health [2]. Representing a fast-developing field in diagnosis science, breathomics (breath analysis) is widely utilized to diagnose patients with a range of illnesses, including cancer [3,4].

The birth of modern breath analysis can be traced to 1971, when Pauling et al. [5] used gas–liquid partition chromatography to identify more than 200 volatile chemical



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constituents in human breath and urine vapor. The role of volatile sulfur compounds in producing bacteria that colonize the dorsal surface of the tongue was recently understood as a primary cause of halitosis (bad breath). Oral production of malodorous substances is most commonly associated with by-products of bacterial metabolic degradation and occurs on oral surfaces, in periodontal pockets, particularly on the dorsal tongue surface [6].

Humans produce sulfur-containing molecules as a result of inadequate methionine metabolism in the transamination pathway [7]. Recently, Rahimi and Solimannejad investigated the adsorption behavior of a newly synthesized 2D polyaramid monolayer [8] and pentagonal BCP nanosheet [9] with respect to the hazardous gases SO_2 and H_2S . First-principles investigations have demonstrated that DFT-based approaches provide atomistic insights into how defects and dopants regulate the electronic transport properties of two-dimensional materials [10].

Hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH) and dimethyl sulfide [$(\text{CH}_3)_2\text{S}$] account for approximately 90% of volatile sulfur compounds [11]. The concentration of volatile sulfide compounds in exhaled breath is being assessed as possible biomarkers for various diseases. The vast majority of pathologies causing halitosis lies within the oropharynx [12]. Wang et al. [13] fabricated an all-solid-state mixed potential type H_2S gas sensor with yttria-stabilized zirconia solid electrolyte and cobaltous stannate (Co_2SnO_4) sensing electrode for monitoring halitosis disease, whereby the sensor displayed good reproducibility, selectivity, humidity resistance and stability.

One of the main causes of halitosis has been identified as VSC-producing bacteria colonizing the tongue. These bacteria can cause foul breath and can thrive in an oxygen-depleted environment [14]. Besides halitosis, exhaled levels of sulphur-containing compounds are often elevated in patients with liver failure and allograft rejection [15]. Characteristic breath odor in cirrhotic patients is largely driven by sulphur-containing volatile organic compounds, notably ethyl mercaptan, dimethyl sulfide, and dimethyl disulfide [16]. The development of an electronic nose to accurately quantify all volatile compounds is part of the future of oral malodor detection and treatment. Recent studies have employed density functional theory to model the interactions of volatile organic compounds, many of which are biomarkers in human breath, with nanostructured sensor materials, revealing adsorption energies, charge transfer, and changes in electronic properties that correlate with sensor response [17–19].

In human breath, volatile sulfur compounds are typically measured using gas chromatography (GC) as the research gold standard, often paired with sulfur-specific detectors or mass spectrometry; GC separates compounds by retention time, allowing precise identification and quantification at very low concentrations in breath samples [20,21]. For routine clinical or point-of-care use, portable instruments are widely used: the Halimeter is a sulfide monitor that detects total VSC levels, especially H_2S and, to a lesser degree, CH_3SH , but cannot reliably distinguish between individual VSCs and is largely insensitive to dimethyl sulfide [22,23]. Thus, there is a need to explore other novel sensor materials and gas sensor arrays aimed at improving sensitivity and selectivity for VSC biomarkers.

Distinct volatile sulfur compounds are associated with different etiologies and severities of halitosis, ranging from hygiene-related intra-oral conditions (H_2S) to periodontal pathology (CH_3SH) and systemic disease indicators [$(\text{CH}_3)_2\text{S}$], underscoring the diagnostic value of selective breath-based VSC detection as summarized in Table 1. These compounds are typically present in human breath at trace-level concentrations, with reported halitosis threshold values of approximately 93.6 ppb for H_2S , 12 ppb for CH_3SH , and 24 ppb for [$(\text{CH}_3)_2\text{S}$] [23,24].

Table 1. Major volatile sulfur compounds investigated in this work and their characteristic odors, common biological sources, associated clinical significance, and recommended management strategies.

VSC	Characteristic Odor	Primary Source	Clinical Significance	Typical Management
H ₂ S	Rotten eggs	- Tongue coating - Poor oral hygiene	Mild intra-oral halitosis	- Tongue scraping - Improved oral hygiene - Zinc-based mouth rinses
CH ₃ SH	Cabbage	Periodontal disease	Severe/pathological halitosis	- Periodontal therapy - Treatment of gum inflammation - Antibacterial intervention
(CH ₃) ₂ S	Sweet/putrid	Systemic conditions (liver, blood)	Extra-oral halitosis	- Liver function assessment - Gastrointestinal or metabolic evaluation

Such low detection limits necessitate highly sensitive sensing technologies. Gas chromatography remains the research gold standard for VSC detection; however, the development of cost-effective and highly sensitive sensing materials capable of detecting VSCs at low ppb levels is essential for real-time breath analysis [25]. In this regard, transition-metal-doped graphene, exhibiting strong adsorption energies and notable electronic structure modulation, represents a promising candidate for trace-level VSC detection.

2. Methodology

The first-principles calculations were undertaken based on density functional theory formalism [26] as implemented in Vienna Ab-initio Simulation Package (VASP) [27], with the aid of high-performance computing [28]. During relaxations, the positions of all atoms were allowed to fully relax until the force on each atom was less than 0.01 eV/Å between two ionic steps, and the convergence of the electronic self-consistent energy is less than 10^{−6} eV.

The electron–ion interactions were described using the projector augmented-wave (PAW) method [29]. The use of an extended basis set is advisable when the adopted basis functions are strictly localized for systems like those with two dimensions, surfaces, and those prone to long-range interactions in order to obtain a concrete description of their electronic properties [30]. Upon convergence, a vacuum padding of 15 Å was included to avoid spurious interactions between periodic replicas. Dipole correction was enforced so as to cancel the artificial electric field generated by the periodic boundary conditions imposed on the electrostatic potential inherent to asymmetric slabs, as recommended by Bengtsson [31]. A 3 × 3 × 1 Gamma-centered k-point mesh was used to integrate the Brillouin zone.

The cut-off energy of the plane wave was set to 350 eV, providing a good balance between computational efficiency and accuracy. In order to account for the nonlocal van der Waals interactions to the estimation of adsorption energies, the optB88-vdW functional [32] was taken into consideration. Spin polarization was explicitly included in all calculations to account for possible magnetic effects arising from the presence of transition-metal dopants (Fe, Ru, and Os). It should be noted that Fe, Ru, and Os possess partially filled d orbitals that may induce localized magnetic moments when incorporated into the graphene

lattice. However, the present work focuses primarily on adsorption energetics and sensing characteristics at a dilute dopant concentration of approximately 2 mol%.

A 5×5 graphene sheet comprising 50 carbon atoms was constructed, and a vacuum layer of adequate thickness was introduced along the z-direction to suppress artificial interlayer interactions arising from periodic boundary conditions. To investigate their interaction with VSCs, the modified graphene models were built with particular functionalization so as to ascertain the impact of each graphene modification on VSC detection sensitivity and specificity, and thus find potential materials for targeted design that have promising volatile sulfur compound sensing applications.

Initial adsorption geometries were constructed using the Ripper software [33], by placing analyte molecules above the graphene surface with the center of mass (COM) oriented along the surface normal. The initial vertical separation between the substrate surface and the analyte COM was systematically varied from 2.5 to 6.5 Å to sample a broad range of interaction distances. All generated structures were fully relaxed to obtain the energetically preferred adsorption configurations. Charge-related calculations were carried out using the Bader approach [34] and post-processed using VASPKIT [35].

3. Results and Discussion

3.1. Geometrical Structure

Figure 1a shows a 5×5 supercell of an optimized geometric structure of pristine graphene (no dopant), a two-dimensional (2D) material that is structured as a honeycomb lattice of carbon atoms with periodic boundary conditions along x and y axes. The pristine graphene structure was initially optimized before the creation of the supercell. After the geometry optimization, the lattice constant of pristine graphene was calculated to be 2.47 Å, which is in accordance with previous theoretical and experimental values [36–39].

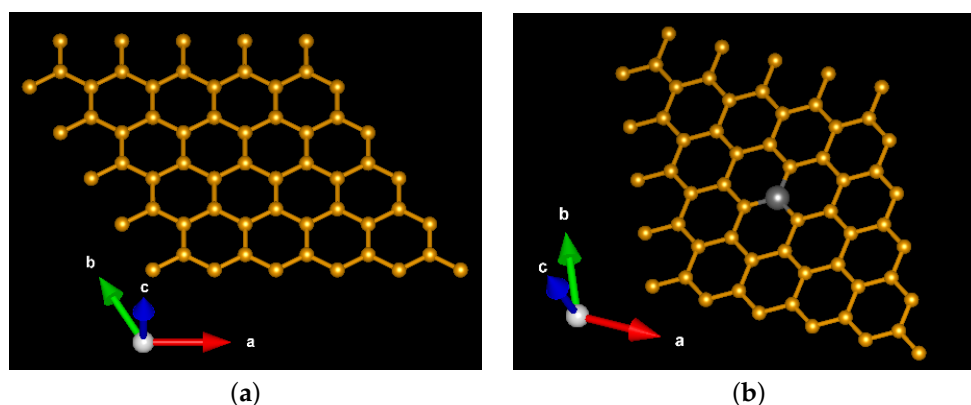


Figure 1. (a) Pristine graphene visualized using VESTA [40]. (b) Single-atom-doped graphene.

The gray atom in Figure 1b represents the single-atom dopant of either iron (Fe), ruthenium (Ru) or osmium (Os) that carbon has been substituted with in the graphene sheet so as to check its effect on the adsorption capability of graphene. Note that substitution of one C atom in a 5×5 graphene supercell results in a system containing 50 atoms (given that the primitive cell of graphene consists of two carbon atoms), corresponding to a dopant concentration of 2 mol% under experimental conditions. Figure 2 shows the isolated molecular structures of the volatile sulfur compounds of interest. Figures 3 and 4 give the visual presentation of a model of volatile sulfur compounds adsorbed on pristine and iron-doped graphene, respectively.

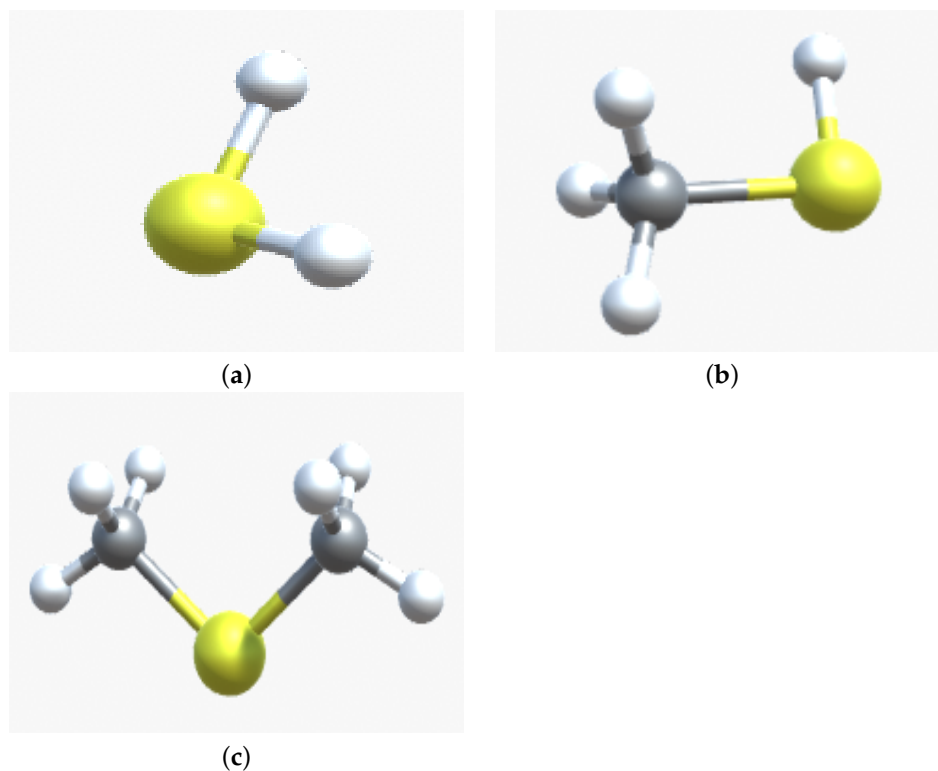


Figure 2. Molecular structures of hydrogen sulfide (a), methyl mercaptan (b), and dimethyl sulfide (c). The yellow, white and gray spheres denote sulfur, hydrogen and carbon atoms, respectively.

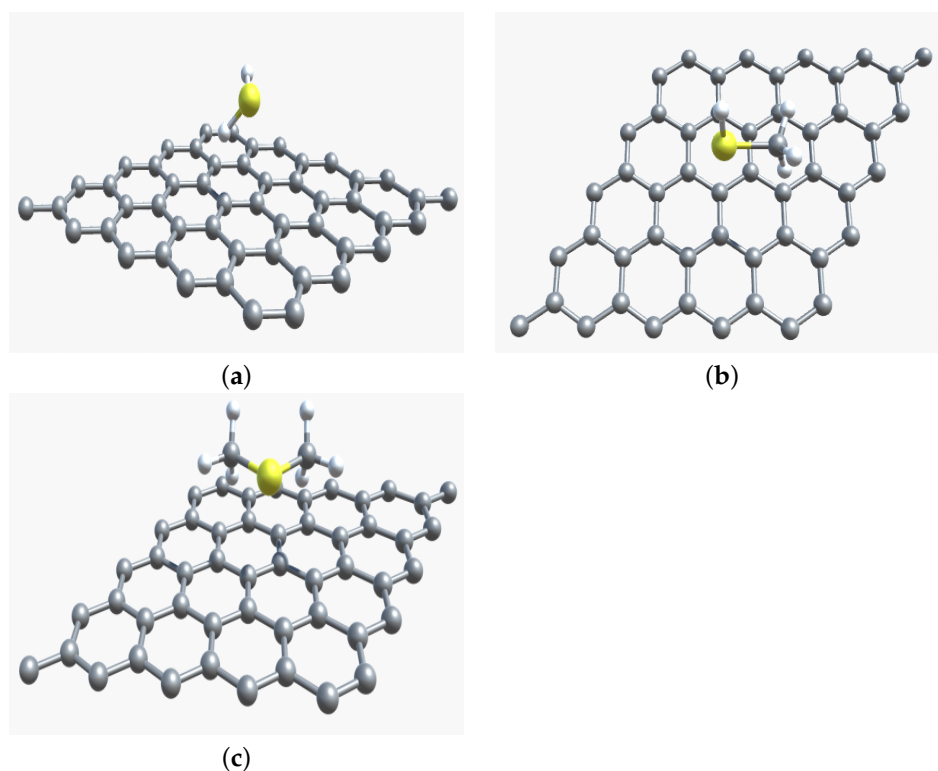


Figure 3. (a) Hydrogen sulfide, (b) methyl mercaptan, and (c) dimethyl sulfide adsorbed on pristine graphene, visualized using CrysX [41].

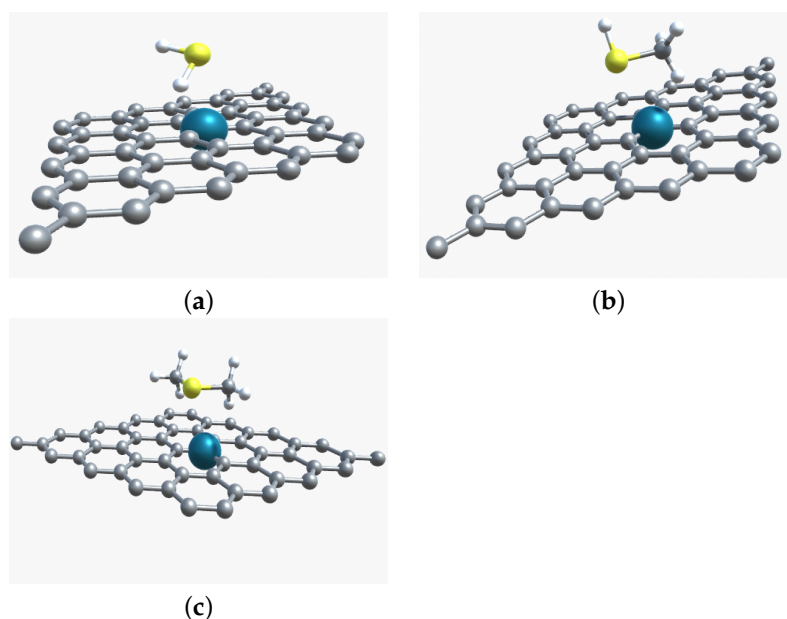


Figure 4. (a) Hydrogen sulfide, (b) methyl mercaptan, and (c) dimethyl sulfide adsorbed on iron-doped graphene.

3.2. Dopant Formation Energy

Since the adsorption characteristics of gas molecules are intrinsically governed by the nature and stability of the active adsorption sites, evaluating the dopant formation energy constitutes a fundamental prerequisite in first-principles adsorption studies. The formation energy provides a thermodynamic measure of the feasibility of incorporating a foreign atom into the host lattice and, consequently, determines whether the proposed doped configuration is experimentally attainable and sufficiently stable.

Establishing the stability of the doped substrate ensures that the subsequently calculated adsorption energies, charge-transfer characteristics, and electronic responses are physically meaningful and relevant for practical sensing applications. Therefore, the dopant formation energy serves as an important descriptor linking material stability with adsorption performance and sensor functionality, in accordance with the defect thermodynamics framework developed by Zhang and Northrup [42] and comprehensively reviewed by Freysoldt et al. [43].

Accordingly, the thermodynamic stability of the substitutionally doped graphene systems was assessed by calculating the formation energy (E_f) using

$$E_f = E_{M-Gr} - E_{Gr} - \mu_M + \mu_C; \quad (1)$$

where E_{M-Gr} and E_{Gr} denote the total energies of the metal-doped graphene and pristine graphene supercells, respectively, while μ_M and μ_C represent the chemical potentials of the dopant metal atom ($M = \text{Fe, Ru, Os}$) and carbon atom, respectively. This expression corresponds to the substitution of one carbon atom in the pristine graphene lattice by a single metal atom. The total energies E_{M-Gr} and E_{Gr} were obtained from fully optimized structures using spin-polarized density functional theory calculations.

The chemical potential of the dopant atom, μ_M , was determined from the energy per atom of the corresponding bulk metallic phase, namely body-centered cubic Fe, hexagonal close-packed Ru, and hexagonal close-packed Os, whereas the carbon chemical potential, μ_C , was evaluated from the energy per atom of pristine graphene. Negative values of E_f indicate that the substitutional incorporation of the dopant atom is thermodynamically favorable, whereas positive values imply that the doping process is energetically unfavorable.

For all substitutional doping calculations, the total energy of pristine graphene remained constant at $E_{Gr} = -442.48$ eV, while the corresponding carbon chemical potential was $\mu_C = -8.69$ eV/atom. Table 2 summarizes the calculated dopant formation energies for substitutional Fe-, Ru-, and Os-doped graphene. All three dopants exhibit negative formation energies, confirming that substitution of a carbon atom by the transition metal is thermodynamically favorable according to Equation (1). This indicates that the doped graphene configurations are energetically stable and can be regarded as feasible model systems for subsequent adsorption investigations.

Table 2. Calculated chemical potentials and substitutional formation energies of transition-metal-doped graphene. Negative formation energies indicate thermodynamically favorable incorporation of the dopant into the graphene lattice.

Dopant	Bulk Reference Phase	μ_M (eV/atom)	E_{M-Gr} (eV)	E_f (eV)	Stability
Fe	bcc	−8.36	−445.62	−3.47	Highest thermodynamic stability
Ru	hcp	−9.25	−445.56	−2.52	Thermodynamically stable
Os	hcp	−11.24	−445.97	−0.94	Thermodynamically stable (least favorable among the three)

Among the three dopants, Fe-doped graphene exhibits the most negative formation energy (−3.47 eV), followed by Ru (−2.52 eV) and Os (−0.94 eV). The larger negative formation energy of Fe indicates that its incorporation into the graphene lattice is energetically the most favorable option, suggesting the strongest dopant–graphene interaction and the greatest structural stability. Although Os-doped graphene possesses the least negative formation energy, its value remains below zero, demonstrating that substitutional Os incorporation is still thermodynamically favorable, albeit with comparatively lower stability than Fe- and Ru-doped graphene. These results establish that all three transition-metal-doped graphene systems are intrinsically stable and therefore constitute reliable substrates for evaluating the adsorption behavior and sensing performance toward volatile sulfur compounds.

3.3. Adsorption Energy Profile

Different distances (at times referred to as height) from the center of mass (COM) of the gas molecule to the substrate surface were considered during simulation so as to determine the most stable adsorption configuration that has the lowest total energy and the highest magnitude of the resultant adsorption energy. The strength of interaction between gas molecules and the adsorption sheet surface was evaluated through calculation of the adsorption energy. Equation (2) was applied when computing the approximate adsorption energies after carrying out density functional theory simulations.

$$E_{ads} = E_{graphene+gas} - [E_{graphene} + E_{gas}] \quad (2)$$

The physical meaning of each term is as follows: E_{ads} is the adsorption energy, $E_{graphene+gas}$ is the total energy of the combined system after the gas molecule is adsorbed on graphene and the structure is fully relaxed, $E_{graphene}$ is the total energy of the clean (isolated) graphene surface, calculated in the same supercell and with the same computational parameters, and E_{gas} is the total energy of the isolated gas molecule, usually calculated in a

large vacuum box to avoid interactions with periodic images. According to Equation (2), a negative adsorption energy indicates a stable and energetically favorable adsorption process, with larger negative values corresponding to stronger interactions between the gas molecule and the graphene surface.

The convergence of total energy with respect to vacuum thickness was examined to eliminate spurious interactions between periodically repeated graphene layers. As shown in Figure 5a, the total energy decreases rapidly at small vacuum sizes and gradually converges as the vacuum thickness increases. Beyond 12 Å, the variation in total energy becomes negligible, indicating sufficient decoupling between periodic images. Consequently, a vacuum thickness of 15 Å was adopted for all subsequent calculations.

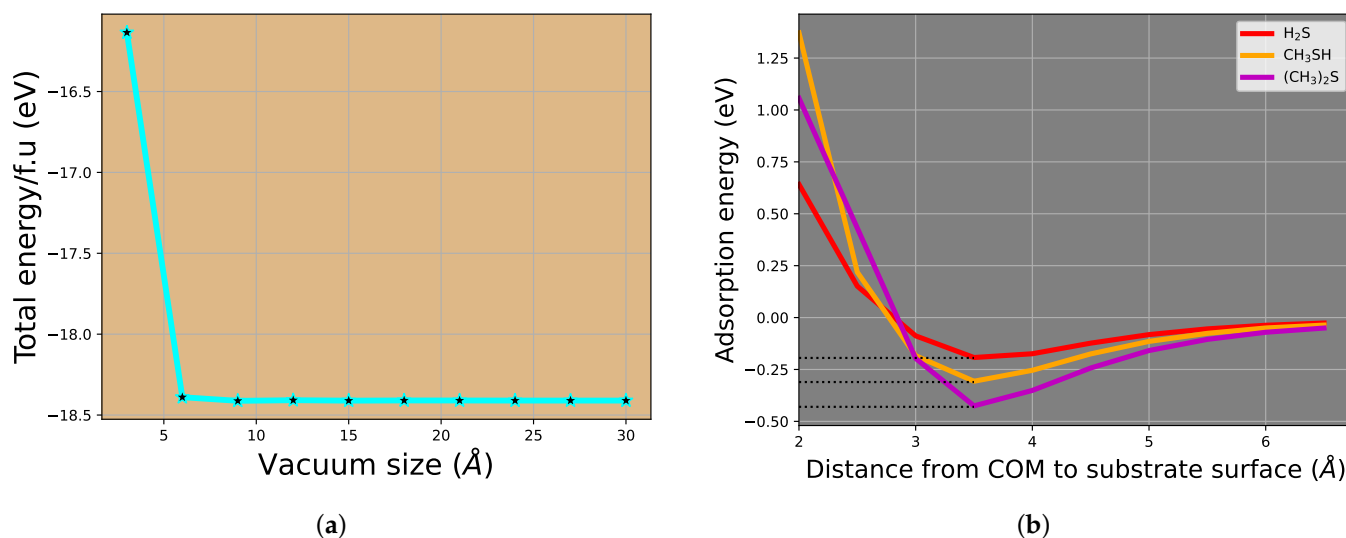


Figure 5. (a) Vacuum size convergence. (b) Adsorption energy profiles.

Our DFT results suggest that the volatile sulfur compounds of interest are physically adsorbed (physisorbed) on the pristine graphene because of the weak interactions, as shown in Figure 5b, where values less than -0.5 eV were obtained, as indicated by the dotted lines on the y-axis. At large separations (>6 Å), the adsorption energy approaches zero, indicating negligible interaction between the adsorbate and the adsorbent. As the molecule approaches the surface, the adsorption energy decreases and reaches a minimum, corresponding to the equilibrium adsorption configuration. At shorter distances, the adsorption energy increases sharply due to strong repulsive interactions [44].

Upon doping graphene with a single atom of iron or ruthenium, the interactions between the gas molecules and doped graphene substrate increased greatly with values between -1.2 eV and -2.73 eV, demonstrating strong chemisorption. On the other hand, osmium-doped graphene portrayed weak adsorption within the physisorption window when both methyl mercaptan and dimethyl sulfide were adsorbed, as shown in Figures 5b, 6a,b and 7.

Table 3 summarizes the optimal adsorption height and adsorption energy of H₂S, CH₃SH, and (CH₃)₂S on pristine and transition-metal-doped graphene surfaces. Clear trends emerge regarding the role of metal dopants in tuning gas–surface interactions. For pristine graphene, all three gas molecules adsorb at a relatively large distance of ≈ 3.5 Å, with weakly negative adsorption energies ranging from -0.19 to -0.42 eV. These characteristics indicate physisorption, dominated by weak van der Waals interactions. Among the volatile sulfur compounds, the comparative adsorption strength is provided in Equation (3).

$$(\text{CH}_3)_2\text{S} > \text{CH}_3\text{SH} > \text{H}_2\text{S} \quad (3)$$

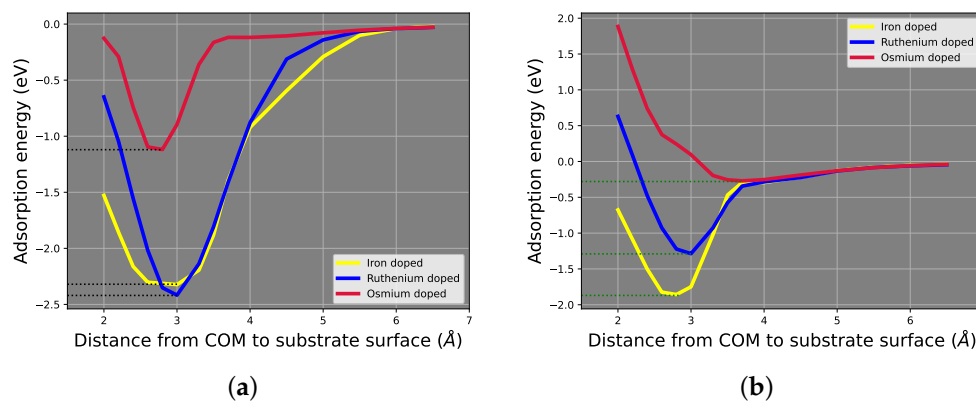


Figure 6. (a) Effect of various dopants on graphene towards hydrogen sulfide adsorption. (b) Effect of various dopants on graphene towards methyl mercaptan adsorption.

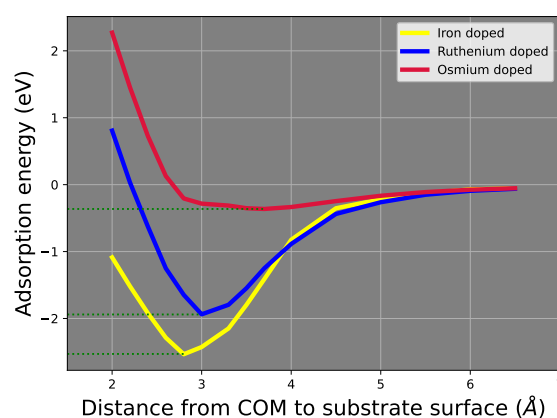


Figure 7. Effect of various dopants on graphene towards dimethyl sulfide adsorption.

Table 3. Calculated adsorption characteristics of volatile sulfur compounds on pristine and transition-metal-doped graphene. The adsorption height (h), adsorption energy (E_{ads}), and estimated recovery time (τ) are reported at 298 and 398 K.

Dopant	Gas	h (Å)	E_{ads} (eV)	τ (298 K)	τ (398 K)
Pristine	H ₂ S	3.5	−0.19	1.63×10^{-9}	2.54×10^{-10}
	CH ₃ SH	3.5	−0.31	1.74×10^{-7}	8.40×10^{-9}
	(CH ₃) ₂ S	3.5	−0.42	1.26×10^{-5}	2.07×10^{-7}
Fe	H ₂ S	3.0	−2.32	1.65×10^{27}	2.33×10^{17}
	CH ₃ SH	2.8	−1.86	2.77×10^{19}	3.51×10^{11}
	(CH ₃) ₂ S	2.8	−2.53	5.86×10^{30}	1.06×10^{20}
Ru	H ₂ S	3.0	−2.42	8.09×10^{28}	4.30×10^{18}
	CH ₃ SH	3.0	−1.29	6.40×10^9	2.14×10^4
	(CH ₃) ₂ S	3.0	−1.94	6.22×10^{20}	3.61×10^{12}
Os	H ₂ S	2.8	−1.11	5.80×10^6	1.12×10^2
	CH ₃ SH	3.7	−0.27	3.67×10^{-8}	2.62×10^{-9}
	(CH ₃) ₂ S	3.7	−0.36	1.22×10^{-6}	3.61×10^{-8}

This suggests that increasing molecular size and polarizability enhances interaction with graphene. However, the overall weak adsorption implies limited sensitivity of pristine graphene toward sulfur-containing gases.

Iron doping dramatically enhances adsorption. The equilibrium adsorption heights decrease to 2.8–3.0 Å, accompanied by strongly negative adsorption energies (−1.86 to −2.53 eV). This indicates a transition from physisorption to chemisorption, driven by

strong hybridization between Fe-3d states and sulfur orbitals. Notably, $(\text{CH}_3)_2\text{S}$ exhibits the strongest adsorption (-2.53 eV), followed closely by H_2S (-2.32 eV). Ruthenium doping also significantly strengthens adsorption compared to pristine graphene, with adsorption energies between -1.29 and -2.42 eV and a uniform adsorption height of 3.0 Å. The strongest interaction is observed for H_2S (-2.42 eV), indicating that Ru-doped graphene may exhibit selectivity toward H_2S over larger sulfur compounds. Compared to Fe doping, Ru shows slightly weaker binding for $(\text{CH}_3)_2\text{S}$, suggesting a more balanced interaction strength that may favor sensor reversibility.

In contrast, Os-doped graphene exhibits weaker adsorption, particularly for CH_3SH and $(\text{CH}_3)_2\text{S}$, with adsorption energies of only -0.27 and -0.36 eV, respectively, and a larger adsorption height (3.7 Å). These values are comparable to pristine graphene and indicate physisorption. H_2S shows moderately stronger interaction (-1.11 eV) at a shorter distance (2.8 Å), suggesting limited chemisorptive character. Os doping appears less effective in enhancing sulfur-gas adsorption. Collectively, these results demonstrate that transition-metal doping effectively tailors the adsorption behavior of graphene toward sulfur-containing gases, with Fe and Ru dopants inducing strong chemisorption, while Os doping results in comparatively weak interactions.

The comparatively weak adsorption exhibited by Os-doped graphene, particularly for CH_3SH and $(\text{CH}_3)_2\text{S}$, may be attributed to the distinct electronic characteristics of Os. Although Fe, Ru, and Os are all Group 8 transition metals, their d-orbitals differ significantly in spatial extent and energetic position. Fe-3d and Ru-4d states remain sufficiently available near the Fermi level to hybridize strongly with the S-3p orbitals of the adsorbed molecules, resulting in pronounced chemisorption. In contrast, the more contracted and lower-lying Os-5d states, together with stronger Os-C bonding, reduce the extent of d-p orbital overlap with sulfur orbitals.

Consequently, CH_3SH and $(\text{CH}_3)_2\text{S}$ interact only weakly with Os-doped graphene, exhibiting adsorption energies comparable to those of pristine graphene, while H_2S still exhibits moderate chemisorptive character owing to its smaller molecular size and lower steric hindrance. Similar differences among Group 8 transition metals have been reported by Zhou et al. [45] for Fe-, Ru-, and Os-modified WTe_2 , where distinct adsorption strengths toward sulfur-containing gases were attributed to variations in orbital hybridization and electronic structures despite their common group affiliation.

The recovery time (τ) is an essential parameter for evaluating the reusability and practical applicability of gas sensors, as it represents the time required for adsorbed gas molecules to desorb from the sensing surface and restore the sensor to its initial state [46]. An optimal gas sensing material should exhibit a balance between sufficient adsorption strength for effective detection and reasonably short recovery times for repeated operation. This can be estimated using the Arrhenius equation [47,48]:

$$\tau = A^{-1} \exp\left(\frac{-E_{\text{ads}}}{k_B T}\right) \quad (4)$$

where A is the apparent frequency coefficient (10^{-12} s^{-1}) from reference [49], E_{ads} is the adsorption energy, k_B is the Boltzmann constant, and T is the working temperature, set to 298 K.

An elevated temperature of 398 K was additionally considered to emulate practical operating conditions of gas sensors, which are often thermally activated to enhance desorption and recovery kinetics. This temperature also enables physically meaningful Arrhenius-based estimation of recovery times, where room-temperature calculations may otherwise overestimate adsorption stability and lead to unrealistically slow desorption.

The calculated recovery times depicted in Table 3 indicate that pristine graphene enables rapid desorption of all volatile sulfur compounds, with recovery occurring within the nanosecond–microsecond range at room temperature, consistent with physisorption-dominated interactions. Elevating the operating temperature from 298 to 398 K significantly reduces the recovery times due to enhanced thermal activation [45,50].

In contrast, Fe- and Ru-doped graphene exhibit extremely long recovery times for H₂S and dimethyl sulfide, suggesting limited suitability for reusable room-temperature sensing applications. Conversely, Os-doped graphene shows more balanced sensing behavior, with CH₃SH and dimethyl sulfide desorbing rapidly, while H₂S desorbs within approximately 112 s at 398 K. These results indicate that Os-doped graphene provides an improved compromise between adsorption strength and sensor regenerability compared with Fe- and Ru-doped systems.

3.4. Selectivity Probe

The selectivity of a gas sensor is a critical performance metric because human breath contains numerous background gases in concentrations much higher than the target volatile sulfur compounds. Since Fe-doped graphene exhibited the strongest adsorption toward all investigated VSCs, its response toward the major interfering breath constituents, namely N₂, O₂, and H₂O, was further evaluated. As illustrated in Figure 8, all three interfering gases interact only weakly with the Fe-doped graphene surface, exhibiting adsorption energies below approximately −0.44 eV over the entire range of adsorption distances. Such weak interactions are characteristic of physisorption, where van der Waals forces dominate and negligible orbital hybridization occurs.

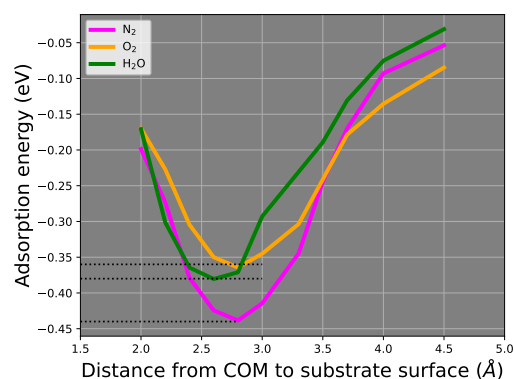


Figure 8. Adsorption of interfering gases in iron-doped graphene.

In contrast, the adsorption energies of the target sulfur-containing molecules are substantially more negative, reaching −2.32 eV for H₂S, −1.86 eV for CH₃SH, and −2.53 eV for (CH₃)₂S₂ on Fe-doped graphene, indicating strong chemisorption arising from hybridization between the Fe 3d orbitals and the sulfur 3p orbitals. The pronounced difference between the adsorption strengths of the target analytes and the interfering gases demonstrates that sulfur-containing molecules bind preferentially to the active Fe site, whereas N₂, O₂, and H₂O are unlikely to occupy or block these adsorption sites under normal operating conditions.

These results indicate that Fe-doped graphene possesses excellent intrinsic selectivity toward volatile sulfur compounds. The weak adsorption of the common breath constituents implies that they can readily desorb from the sensing surface without producing significant changes in the electronic properties of the material, while the VSCs induce strong adsorption and substantial electronic perturbations. Consequently, the sensing response is expected to originate predominantly from sulfur-containing biomarkers rather than background gases,

highlighting the suitability of Fe-doped graphene for selective breath-based detection of halitosis biomarkers.

3.5. Charge Density Analysis

The charge density difference map presented in Figure 9, where yellow and cyan isosurfaces denote electron accumulation and electron depletion, respectively, reveals a pronounced redistribution of electron density following H₂S adsorption on Fe-doped graphene. Significant electron accumulation and depletion are localized primarily at the Fe–S interface, while only minimal charge redistribution is observed around the hydrogen atoms and the surrounding graphene lattice.

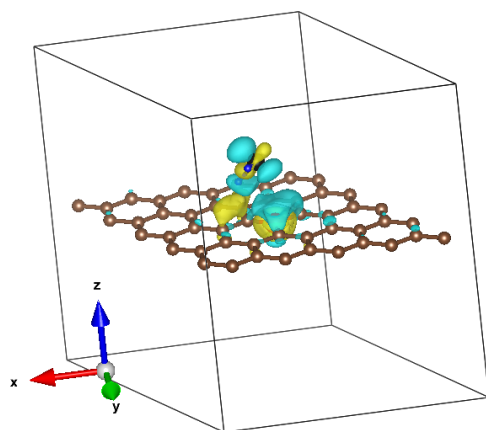


Figure 9. Charge density difference of H₂S adsorbed on iron-doped graphene.

The charge density difference was obtained by subtracting the electron densities of the isolated adsorbate molecule and the clean substrate from the total electron density of the relaxed adsorption system. The calculation was performed using Equation (5).

$$\Delta\rho(\mathbf{r}) = \rho_{\text{Fe-graphene}+\text{H}_2\text{S}}(\mathbf{r}) - \rho_{\text{Fe-graphene}}(\mathbf{r}) - \rho_{\text{H}_2\text{S}}(\mathbf{r}) \quad (5)$$

This localized redistribution demonstrates that the Fe dopant serves as the primary active adsorption site, facilitating charge transfer between the substrate and the H₂S molecule through Fe–S orbital hybridization. The coexistence of electron accumulation and depletion at the adsorption interface confirms the formation of a chemical interaction between H₂S and Fe-doped graphene. These findings are consistent with the Bader charge analysis, which quantitatively confirms charge transfer between the adsorbate and the substrate, and explain the observed modulation of the electronic properties that underpins the enhanced gas-sensing performance of the Fe-doped graphene system.

3.6. Work Function

The work function (Φ) is a fundamental surface electronic property that represents the minimum energy required to remove an electron from the Fermi level to the vacuum level [51]. It is highly sensitive to adsorption-induced charge redistribution and is therefore an important descriptor for evaluating the sensing performance of gas-sensitive materials. The work function was determined from the planar-averaged electrostatic potential according to Equation (6), where (E_{vac}) denotes the vacuum potential obtained from the plateau region of the electrostatic potential profile and (E_F) is the Fermi energy.

$$\Phi = E_{vac} - E_F \quad (6)$$

The calculated work-function values for Fe-doped graphene before and after H₂S adsorption are summarized in Table 4. A reduction of approximately 0.56 eV is observed following adsorption, indicating significant modification of the surface electronic structure induced by H₂S.

Table 4. Calculated work function of Fe-doped graphene before and after H₂S adsorption.

System	E_F (eV)	Φ (eV)	$\Delta\Phi$ (eV)
Fe-doped graphene	−2.94	5.26	—
H ₂ S/Fe-doped graphene	−2.38	4.70	−0.56

The planar-averaged electrostatic potentials for Fe-doped graphene before and after H₂S adsorption are presented in Figure 10a,b. Prior to adsorption, the work function of Fe-doped graphene is calculated to be approximately 5.26 eV, whereas adsorption of H₂S reduces the work function to approximately 4.70 eV, corresponding to a decrease of about 0.56 eV. This reduction indicates that H₂S adsorption substantially modifies the surface electrostatic potential through adsorption-induced charge redistribution at the Fe–S interface. Consequently, the surface dipole moment is altered, shifting the Fermi level closer to the vacuum level, thereby lowering the energy required for electron emission.

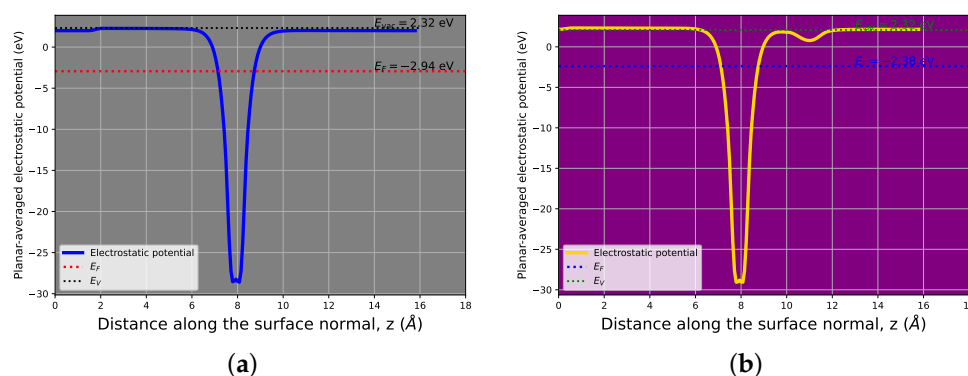


Figure 10. (a) Work function of iron-doped graphene without gas molecule. (b) Work function of iron-doped graphene after H₂S adsorption.

The observed decrease in work function is consistent with the strong chemisorption predicted from the adsorption energy (−2.32 eV), as well as the charge density difference and density-of-states analyses, which reveal significant electronic coupling between the Fe (3d) orbitals and the S (3p) states of the adsorbed H₂S molecule. The sizeable work-function modulation therefore confirms that H₂S adsorption induces substantial changes in the surface electronic structure of Fe-doped graphene. Such a pronounced variation in work function is advantageous for resistive and Kelvin probe-based gas sensing because the adsorption event can be directly translated into an experimentally measurable electrical signal. These findings further demonstrate that Fe-doped graphene possesses excellent potential as a highly sensitive sensing material for hydrogen sulfide detection.

3.7. Electronic Structure

To elucidate the effect of dopants on the electronic properties of graphene upon gas adsorption, detailed electronic-structure analyses were performed only for pristine and Fe-doped graphene. This selection was motivated by the adsorption results, which showed that Fe-doped graphene exhibited the strongest interaction with all three VSC molecules and the largest adsorption energies for CH₃SH and (CH₃)₂S, whereas Ru- and Os-doped graphene displayed comparatively weaker adsorption characteristics. The pure graphene

is a zero-bandgap semiconductor. The lack of an intrinsic bandgap in pristine graphene restricts its electronic applications, making doping a viable strategy for engineering its semiconducting behavior [52]. As seen in Figure 11a, the total density of states of pristine graphene exhibits the characteristic semimetallic behavior with a pronounced depletion of states at the Fermi level (EF), corresponding to the Dirac point.

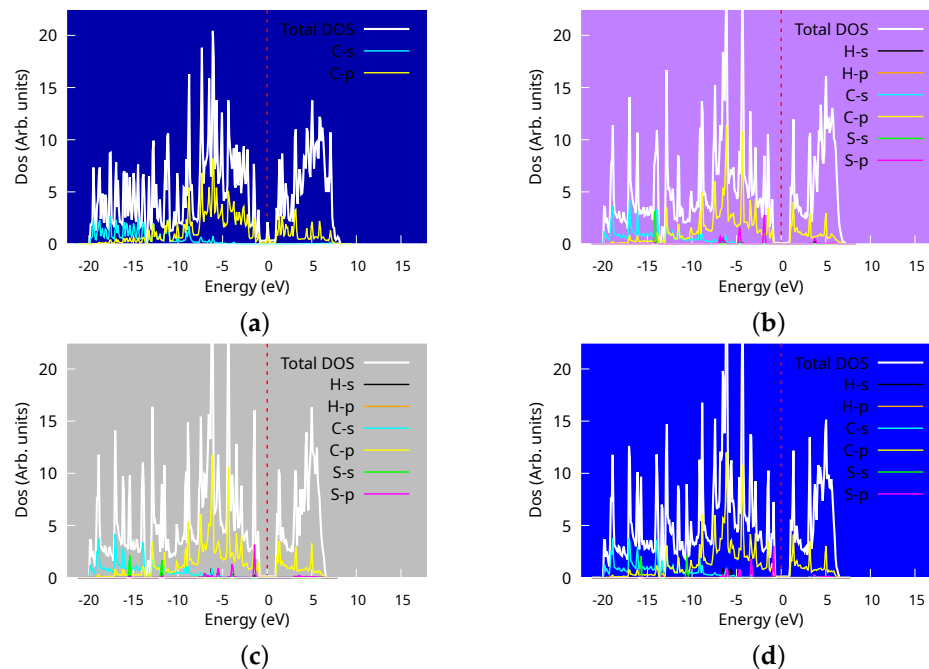


Figure 11. (a) shows the total density of states of pristine graphene, (b) H₂S-adsorbed, (c) CH₃SH-adsorbed, and (d) (CH₃)₂S-adsorbed systems. The Fermi level is set to 0 eV.

The valence region between -8 and 0 eV is dominated by Π bonding states originating from C 2p orbitals, while deeper valence states arise from σ bonding contributions of sp^2 -hybridized carbon atoms [53,54]. Prominent peaks around -6 eV and -3 eV correspond to van Hove singularities inherent to the two-dimensional hexagonal lattice [55]. Above the Fermi level, the conduction region is primarily composed of Π^* antibonding states, symmetrically distributed with respect to the valence Π states [56]. The absence of mid-gap states confirms that the graphene sheet retains its intrinsic electronic structure and provides a reliable reference for subsequent adsorption analysis.

According to Figure 11b, upon adsorption of H₂S, the semimetallic nature of graphene is preserved, as evidenced by the near-zero DOS at the Fermi level. Additional localized states appear in the -8 to -4 eV region, primarily originating from S 3p and H-S bonding orbitals. However, the absence of new states near the Fermi level indicates weak orbital hybridization between sulfur lone-pair electrons and graphene Π states. The negligible Fermi-level shift suggests minimal charge transfer, confirming physisorption-dominated interaction.

As shown in Figure 11c, adsorption of methyl mercaptan induces a moderate modification of the graphene electronic structure. While the Dirac-point feature is largely retained, a slight enhancement in DOS near the Fermi level suggests weak donor interaction. New states observed between -9 and -4 eV originate from CH₃ and S 3p orbitals, with subtle hybridization effects in the Π bonding region. These results indicate stronger electronic coupling compared to H₂S, though the semimetallic nature remains intact.

Figure 11d shows that dimethyl sulfide adsorption results in the most pronounced modification of the graphene electronic structure. An increased DOS near the Fermi level indicates stronger electronic interaction and enhanced charge transfer compared to H₂S

and CH_3S . New states appearing between -10 and -4 eV are attributed to C-H bonding and S 3p orbitals, with significant hybridization effects observed in the graphene Π region around -3 eV. The partial suppression of the Dirac dip suggests symmetry perturbation, implying improved electronic sensitivity toward $(\text{CH}_3)_2\text{S}$ molecules.

As shown in Figure 12a, the inherent semimetallic nature of pure graphene is significantly altered by the density of states of Fe-doped graphene. Strong Fe 3d-derived states that cross the Fermi level take the place of the Dirac-point feature, suggesting metallic behavior. In the valence region, especially between -6 and -2 eV, there is strong hybridization between the Fe 3d and C 2p orbitals. Chemical reactivity toward sulfur-containing compounds is increased when partially filled Fe 3d states are present at the Fermi level, indicating advantageous d-p orbital interaction during adsorption. Since adsorption-induced perturbations around EF are anticipated to significantly affect the conductivity of the Fe-graphene system, this electronic arrangement is extremely beneficial for the detection of volatile sulfur compounds pertinent to halitosis screening.

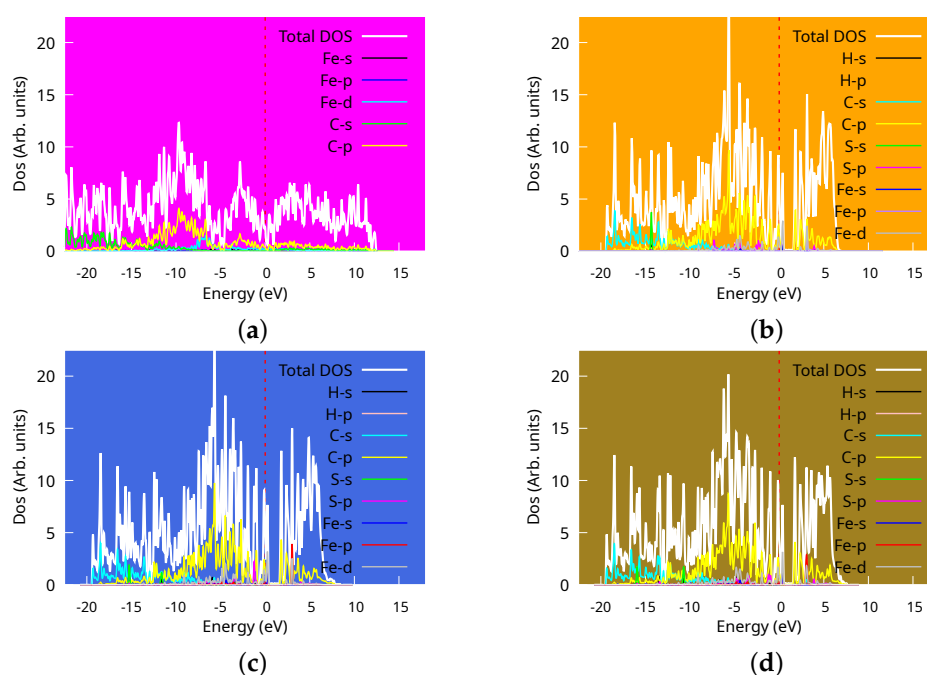


Figure 12. (a) shows the total density of states of iron-doped graphene, (b) H_2S -adsorbed, (c) CH_3SH -adsorbed, and (d) $(\text{CH}_3)_2\text{S}$ -adsorbed systems.

According to Figure 12b, the Fe-derived states close to the Fermi level exhibit observable redistribution and widening upon H_2S adsorption, suggesting d-p hybridization between Fe 3d and S 3p orbitals. The slight decrease in DOS at EF points to the donation of electrons from H_2S to the Fe core, which modifies metallic conductivity. Fe-S bonding interactions are evidenced by the emergence of new electronic states in the energy range of -7 to -4 eV. These modifications in the electronic structure suggest a detectable change in conductivity, suitable for volatile sulfur sensing, and confirms a chemisorption-driven interaction. As illustrated in Figure 12c, methyl mercaptan adsorption induces more pronounced electronic rearrangement than H_2S adsorption. Stronger d-p hybridization is indicated by the notable widening and intensity redistribution of the Fe 3d states close to the Fermi level. S 3p and methyl-derived orbitals interact with Fe 3d states to produce further hybrid states that are seen between -8 and -3 eV. Higher sensing sensitivity toward CH_3SH is implied by the significant change in DOS at the Fermi level, which points to improved charge transfer and better chemisorption.

Figure 12d shows the DOS of the $(\text{CH}_3)_2\text{S}$ -Fe-doped graphene system. Compared with H_2S and CH_3SH adsorption, $(\text{CH}_3)_2\text{S}$ induces a more substantial redistribution of Fe 3d states around the Fermi level, accompanied by the appearance of additional hybrid states between -8 and -3 eV arising from interactions between Fe 3d and S 3p orbitals. The enhanced DOS modulation near the Fermi level indicates stronger charge transfer and electronic coupling, consistent with the large adsorption energy obtained for this system. These features suggest that Fe-doped graphene exhibits high sensitivity toward dimethyl sulfide through a chemisorption-driven sensing mechanism.

4. Conclusions

This work contributes to identifying a portable, low-cost and low-power sensor that can be embedded into breath-test devices to analyze the major components of volatile sulfur compounds in patients suffering from tonsillitis. Furthermore, this computational work can provide a better understanding of the mechanisms of volatile sulfur compound adsorption on graphene. The influence of metal elements (iron, ruthenium and osmium) on the adsorption characteristics of graphene towards volatile sulfur compounds (hydrogen sulfide, methyl mercaptan and dimethyl sulfide) was explored. Our simulation results show that doping graphene with transition metals increases the interaction between graphene and volatile sulfur compounds. Additionally, doping results in changes in the electronic structure of the adsorbent after the adsorption process. Osmium-doped graphene can only chemisorb hydrogen sulfide gas. It displays weak adsorption strength towards methyl mercaptan and dimethyl sulfide molecules.

The combined adsorption energy, charge density difference, Bader charge, density-of-states, and work-function analyses provide comprehensive evidence that the sensing behavior of metal-doped graphene is primarily governed by strong interactions between the introduced metal active sites and sulfur-containing gas molecules. The incorporation of transition-metal dopants creates chemically active centers that facilitate effective analyte adsorption, charge transfer, and orbital hybridization between the metal d states and molecular orbitals of the adsorbed gases. Early detection of volatile sulfur compounds may facilitate timely diagnosis and monitoring of halitosis and related oral or systemic conditions, thereby supporting earlier clinical intervention and greatly aiding in disease management, especially in children below the age of five years.

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Abbreviations

The following abbreviations are used in this manuscript:

VSCs	Volatile sulfur compounds
DFT	Density functional theory
VASP	Vienna Ab-initio Simulation Package
CHPC	Centre for High-Performance Computing
ppb	Parts per billion

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