

RESEARCH PAPER

First-Principles Investigation of H₂S Adsorption on (ZnO)₁₄ Nanoclusters: Electronic, Vibrational, and Topological Insights

Eateman Salah Mahdi ¹, Uday Abdul-Reda Hussein ², Ali Fawzi Al-Hussainy ³, Usama S. Altimari ⁴, Shaimaa Abd ⁵, Aseel M. Aljeboree ¹, Ayad F. Alkaim ^{1*}

¹ Department of Chemistry, College of Sciences for Women, University of Babylon, Iraq

² Department of Pharmaceutics, College of Pharmacy, University of Al-Ameed, Iraq

³ College of Pharmacy, Ahl Al Bayt University, Kerbala, Iraq

⁴ Department of Medical Laboratories Technology, AL-Nisour University College, Baghdad, Iraq

⁵ Department of Medial Laborites, Al-Manara College For Medical Sciences, Maysan, Iraq

ARTICLE INFO

Article History:

Received 07 May 2025

Accepted 27 August 2025

Published 01 October 2025

Keywords:

Atoms in Molecules (AIM)

Chemisorption

Electronic structure

Gas sensing

ZnO nanocluster

ABSTRACT

The efficient detection and capture of hazardous gases like hydrogen sulfide (H₂S) are vital for environmental monitoring and industrial safety. In this study, we perform a comprehensive theoretical analysis of H₂S adsorption on a (ZnO)₁₄ nanocluster using density functional theory (DFT) and time-dependent DFT (TD-DFT). Structural optimizations, frontier molecular orbital (FMO) analysis, Mulliken charge distribution, vibrational frequency calculations (FT-IR), adsorption energy, and Atoms in Molecules (AIM) topological analysis were conducted to investigate the electronic and physicochemical properties before and after gas adsorption. The adsorption energy calculations confirmed that H₂S undergoes chemisorption on the ZnO surface, with an energy of interaction indicating favorable thermodynamics. FMO analysis showed a significant reduction in the HOMO–LUMO gap from 7.94 eV (H₂S) and 0.16 eV (ZnO) to 0.43 eV for the H₂S/ZnO complex, suggesting enhanced electronic conductivity and potential sensor activity. AIM analysis revealed weak to moderate interactions between the adsorbate and the surface, with positive Laplacians ($\nabla^2\rho$) and low-to-moderate electron density (ρ) at the bond critical points, indicating partially covalent character. Importantly, the IR spectral analysis demonstrated a marked shift and broadening of characteristic H₂S vibrational modes upon adsorption. Notably, the S–H stretching modes at $\sim 2600\text{ cm}^{-1}$ were either red-shifted or disappeared entirely in the H₂S/ZnO complex, while new modes corresponding to Zn–S and O–H stretching appeared in the fingerprint region, confirming strong interaction and structural reorganization. These vibrational changes validate the adsorption mechanism predicted by energy and charge analyses.

How to cite this article

Mahdi E., Hussein U., Al-Hussainy A. et al. First-Principles Investigation of H₂S Adsorption on (ZnO)₁₄ Nanoclusters: Electronic, Vibrational, and Topological Insights. J Nanostruct, 2025; 15(4):1719-1730. DOI: 10.22052/JNS.2025.04.015

INTRODUCTION

Hydrogen sulfide (H₂S) is a highly toxic, corrosive, and odorous gas derived from various natural and anthropogenic sources which includes

volcanic activity, geothermal springs, crude oil refineries, wastewater treatment facilities, and anaerobic digestion occurring in sewage and

* Corresponding Author Email: alkaimayad@gmail.com



This work is licensed under the Creative Commons Attribution 4.0 International License.

To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

animal farm houses [1, 2]. H₂S at concentrations of 10 ppm is known to cause eye irritancy and olfactory fatigue and supra 300 ppm causes accelerated asphyxiation and death [3]. Besides the direct impacts on health, the corrosion of steel pipelines, and concrete infrastructure, influenced by H₂S causes important losses in economic terms [4-6].

Semiconductor metal oxides have been widely accepted as the workhorses in the category of resistive gas sensor owing to the low cost, miniaturization, and high stability against harsh environments [7, 8]. ZnO, a II–VI semiconductor with a direct band gap of 3.3 eV and a large exciton binding energy (60 meV) is one of the most promising ones. Having a wurtzite crystal structure, it can develop rich morphologies (nanowires, nanosheets, hollow sphere, and quantum dots), wherein these morphologies offer a large number of surface sites that can interact with the target gases [7]. When reducing molecules (e.g., H₂S) are adsorbed on ZnO and donate their electrons to the conduction band (CB), the sensor resistance can decrease, which can be used for the chemiresistive sensing. While many important experimental studies exist, which demonstrate ppb-level sensitivity to H₂S of ZnO films and nanowires [9], a comprehensive mechanistic picture at the atomic level is lacking, particularly for finite nanoscale clusters that differ from ideal bulk surfaces.

Density functional theory (DFT) has become a powerful tool that significantly assists in understanding gas–surface interactions and enables quantitative predictions of adsorption energies (E_{ads}) [10], charge flow, as well as changes in electronic and vibrational structure. In early DFT models for ZnO as an extended slab, it was found that H₂S binds selectively to the Zn-terminated (0001) surfaces with dissociative adsorption energies between –1.2 and –1.8 eV [11, 12]. But, actual sensing layers contain nanocrystalline domains which have their local coordination environments in the form of ZnO clusters. Recent theoretical investigations on (ZnO)_n ($n \leq 12$) clusters have revealed a size-dependent change of the band gap, work function, and Lewis acidity/basicity, which strongly affect the adsorption behaviour of gas molecules [13]. In particular, the (ZnO)₁₄ nanocluster has often been referred to as the smallest cluster which still maintains an important aspect of wurtzite ZnO

(tetra-coordinated Zn and O centers) and at the same time is computationally affordable for high level analyses like time-dependent DFT (TD-DFT) and charge density topology studies [14, 15].

Notwithstanding these developments, there are still several shortcomings. First, the relationship between H₂S adsorption and FMOs of (ZnO)₁₄ nanocluster has not been investigated in a systematic way. Therefore, it is important to understand how the HOMO–LUMO gap will reduce or how new defect levels will form upon adsorption in order to correlate the electronic footprint with resistance difference. Second, there are few existing workflows that self-consistently combine various quantitative measures such as Mulliken charges, natural bond orbital (NBO) populations and Atoms-in-Molecules (AIM) metrics (pBCP, ∇^2 PBCP, and energy densities), despite such an integrated approach being essential for the discrimination between physisorption (closed-shell, weak) and chemisorption (partially covalent, strong). Third, vibrational signatures—in particular S–H stretching and bending modes—provide a complementary tool to investigate adsorption geometry, which may be compared with in-situ infrared spectroscopy, a tool rarely considered in ZnO clusters.

In this work, we aim to fill these gaps by means of a thorough DFT study of H₂S adsorption on the (ZnO)₁₄ nanocluster. Geometry optimizations and frequency calculations are performed at the B3LYP/6-31G(d) level which provides a good compromise between accuracy and computer time in the case of metal–oxide systems [16]. The adsorption energies are counterpoise-corrected to BSSE to avoid an overestimate of the interaction, and other possible error how to splitting of the complex into nascent fragments and increase on electron transfer from adsorbate to metallic surface. Using thermodynamic corrections (zero-point energy and thermal enthalpy/entropy terms), Gibbs free energies (ΔG_{ads}) at standard conditions (298 K, 1 atm) can be derived to gauge spontaneity in practical sensing environments [17].

In addition to energetics, extensive electronic analyses have been carried out. The frontier orbital energies (HOMO and LUMO) and the band gaps are determined from single-point calculations for the isolated H₂S molecule, pure (ZnO)₁₄ nanocluster, and the H₂S/(ZnO)₁₄ complex adduct. DOS and PDOS plots show orbital mixing

and channelling of charge transfer around the Fermi level. According to the TD-DFT excited-state calculations, absorption wavelengths and oscillator strengths are estimated and optoelectronic responses following gas binding have been discussed. Charge analysis by Mulliken and natural bond orbital (NBO) describes the electron trickle from H₂S into (ZnO)₁₄ nanocluster, the relationship type (ionic or covalent) of the Zn–S and O–S contacts is recognized by the AIM topological parameters of the bond-critical points (BCPs). It also demonstrates a blue-shift in $\nu(\text{Zn–O})$ and a redshift for $\nu(\text{S–H})$ modes, which indicates that the electrons have shaken from H₂S to the sites of Zn and Zn–S or O–S have been enhanced. Such computational spectra may be compared directly with FT-IR or Raman data providing an experimental validation pathway for sensor designs.

Taken together, the multi-faceted data contributes towards a consistent picture of how H₂S adsorption is understood by ZnO nanoclusters, including thermodynamics of adsorption, electronic structure modulation, electron density topology and vibrational fingerprints. Results not only inform the understanding on a fundamental level but also provide simple design principles: (i) surface Zn sites in low coordination (two or three) serve as high affinity adsorption sites; (ii) moderate reduction of the HOMO–LUMO gap (~ 0.4 eV) upon adsorption leads to ohmic behavior without placing the sensor in the regime of irreversible chemisorption; and (iii) AIM descriptors $\rho_{\text{BCP}} \approx 0.07\text{--}0.10 \text{ e } \text{\AA}^{-3}$ and positive $\nabla^2\rho_{\text{BCP}}$ signal partially ionic Zn–S bonds, which favor reversible sensing. The knowledge can be applied to technological development of ZnO nanocluster aggregates or doped ZnO films that enable high H₂S response without sacrificing fast recovery and long term stability.

MATERIALS AND METHODS

Computational Details

All quantum-chemical calculations were performed with the Gaussian 09 program package. The geometries of H₂S, (ZnO)₁₄ nanocluster, H₂S–(ZnO)₁₄ complex were optimized using DFT at B3LYP/6-31G(d) level. Relativistic effects for Zn atoms were included using the effective core potential LANL2DZ. All structures have been verified as true minima by vibrational frequency analysis which revealed no imaginary frequencies.

The structure visualization and orbital graphics were carried out via the software of the GaussView 6.0.

Vibrational Frequency Analysis

The stability of the optimized geometries as well as the vibrational modes altered by the adsorption were analyzed by performing harmonic vibrational frequency calculations at the same level of theory. The calculated interaction-induced spectral shift analysis have been performed mainly for H–S stretching modes. Frequencies and IR intensities were directly taken from the Gaussian outputs and OriginPro was used to visualize data for comparisons.

Adsorption Energy and Thermodynamic Analysis

The adsorption energy (E_{ads}) of H₂S molecule on (ZnO)₁₄ nanocluster was computed using the expression:

$$E_{\text{ads}} = E_{\text{complex}} - (E_{\text{ZnO}} + E_{\text{H}_2\text{S}})$$

Thermodynamic parameters such as Gibbs free energy (ΔG) and enthalpy change (ΔH) were calculated at 298.15 K and 1 atm from Gaussian frequency output. These quantities allowed assessment of spontaneity and thermal favorability of the adsorption process.

Electronic Structure and UV–Vis Analysis

Frontier Molecular Orbital (FMO) energies, including HOMO, LUMO, and energy gap (ΔE), were calculated for the isolated and complexed systems. Time-dependent DFT (TD-DFT) calculations were performed using the same functional and basis set, specifying NStates = 20, to simulate electronic transitions and absorption bands. The UV–Vis spectra were processed using OriginPro for peak assignment and spectral shift evaluation.

Charge Distribution and AIM Topological Analysis

Mulliken population analysis was employed to evaluate charge transfer behavior upon adsorption. To characterize bonding interactions, Atoms in Molecules (AIM) theory was applied using Multiwfn and AIMAll software. Wavefunction files (.wfn and .fchk) were generated from Gaussian outputs. Key descriptors—electron density (ρ), Laplacian ($\nabla^2\rho$), and energy densities (G , V , H)—were computed at bond critical points (BCPs) to analyze the nature of intermolecular interactions

such as Zn–S and S–O contacts.

Visualization and Plotting

Molecular orbitals, AIM bond paths, IR spectra, and HOMO–LUMO energy diagrams were visualized using GaussView, AIMAll, VMD, and OriginPro 2024. All figures were formatted at high resolution for publication standards.

RESULTS AND DISCUSSION

Frontier Molecular Orbital Analysis

We find that H₂S has a large HOMO (−6.85 eV) and a large LUMO (+1.09 eV), leading to a wide bandgap of 7.94 eV (Figs. 1 and 2). This indicates its closed-shell configuration and high kinetic stability. In contrast, the ZnO cluster has

a much smaller band gap of 0.16 eV, also HOMO and LUMO almost at the Fermi energy. This reiterates the semiconducting nature of ZnO and its suitability as a reactive surface especially for electron transfer reactions. Upon complexation of H₂S, the electronic structure of the H₂S–ZnO system is significantly changed: the HOMO level moves upward to −4.69 eV and the LUMO level moves downward to −4.26 eV, which leads to a remarkably narrowed band gap of 0.43 eV. Such shifts indicate increased electronic delocalization and interaction of H₂S with ZnO, which implies a chemisorptive interface bonding.

Mulliken Charge Distribution

Mulliken atomic charge distributions (Fig. 3)

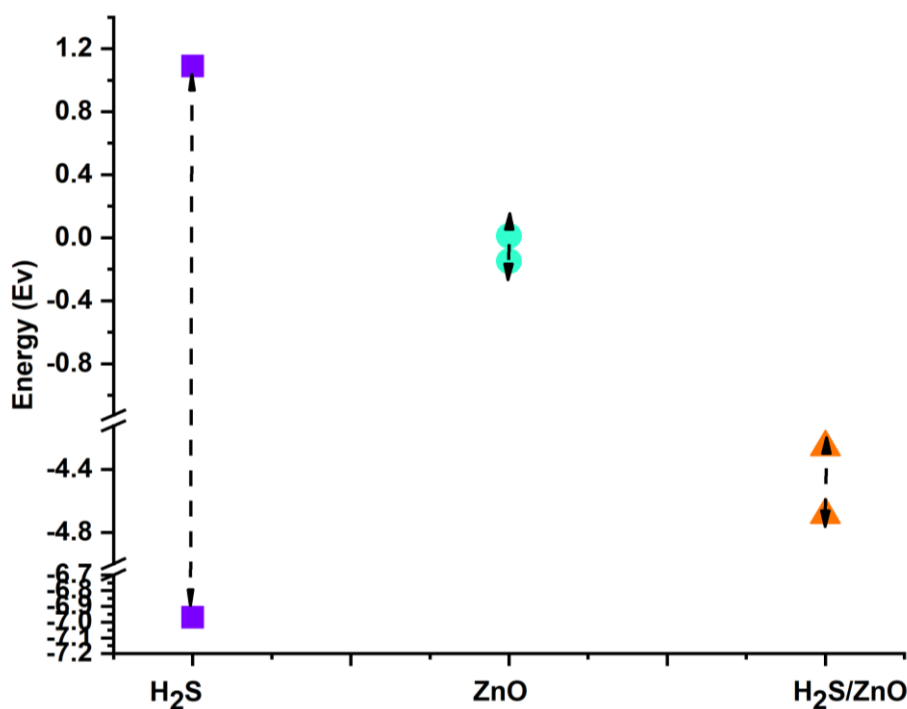


Fig. 1. Frontier Molecular Orbitals (HOMO and LUMO) and energy levels of (a) H₂S, (b) ZnO cluster, and (c) H₂S–ZnO complex.

Table 1. Frontier Molecular Orbital Energies, Energy Gaps, and Mulliken Charge on Sulfur Atom for H₂S, ZnO Cluster, and H₂S–ZnO Complex.

System	HOMO (eV)	LUMO (eV)	Gap (eV)	Charge on S (e)
H ₂ S	−6.85	+1.09	7.94	−0.194
ZnO	−0.15	+0.01	0.16	—
H ₂ S–ZnO	−4.69	−4.26	0.43	+0.089

provide quantitative insight into electron density redistribution upon complex formation.

H₂S molecule: Sulfur carries a partial negative charge of -0.194 , while the two hydrogen atoms are slightly positive ($+0.097$). This reflects the expected polarity of the H–S–H bond due to the higher electronegativity of sulfur.

ZnO cluster: Zinc atoms carry positive charges ranging from $+0.42$ to $+0.99$ (with hydrogens summed), and oxygen atoms are negatively charged, up to -0.97 . The polarity within the Zn–O framework facilitates charge separation and adsorption of polar molecules.

H₂S–ZnO complex: After adsorption, the sulfur atom in H₂S becomes positively charged ($+0.089$), suggesting electron donation to the ZnO surface. A corresponding redistribution of charge occurs in the nearby Zn and O atoms, especially in the Zn atom bonded to the sulfur, which shows a slight increase in electron density.

This charge transfer is a clear signature of chemisorption, leading to orbital hybridization and narrowing of the HOMO–LUMO gap. This is consistent with the energy level data discussed earlier.

Electronic Implication for Gas Sensing

The FMO behavior and Mulliken charge analysis reveal notable H₂S adsorption on ZnO

with charge transfer from H₂S to ZnO. It is this interaction which also leads to the substantial decrease in band gap from 7.94 eV to 0.43 eV for complex, which in turn implies that the adsorption modifies the electronic behavior of ZnO. These changes can be used for resistive gas sensors and adsorption of H₂S produces a measurable change in conductivity, which make ZnO an appealing material for dangerous gas detection. results illustrated in Table 1.

Electronic Absorption Analysis (UV–Vis TD-DFT)

Density functional theory calculations were carried out on Zn₆O₆–H₂S complex to simulate its electronic absorption (UV–Vis) properties at the B3LYP/6-31G(d) level of theory using the time-dependent density functional theory (TD-DFT) method. The first 20 singlet excited states were calculated and the excitation energies and oscillator strengths were analysed to obtain the absorption spectrum.

The calculated spectrum (Fig. 4) displays several transitions in the UV region; the most intense absorption bands are found at ca 298 nm, 340 nm and 385 nm (i.e., ≈ 4.16 eV, ≈ 3.65 eV, ≈ 3.22 eV). These transitions have $f > 0.01$ and, therefore, have importance for absorption. Specifically, the observation of red-shifted absorption bands upon adsorption of H₂S compared to bare ZnO

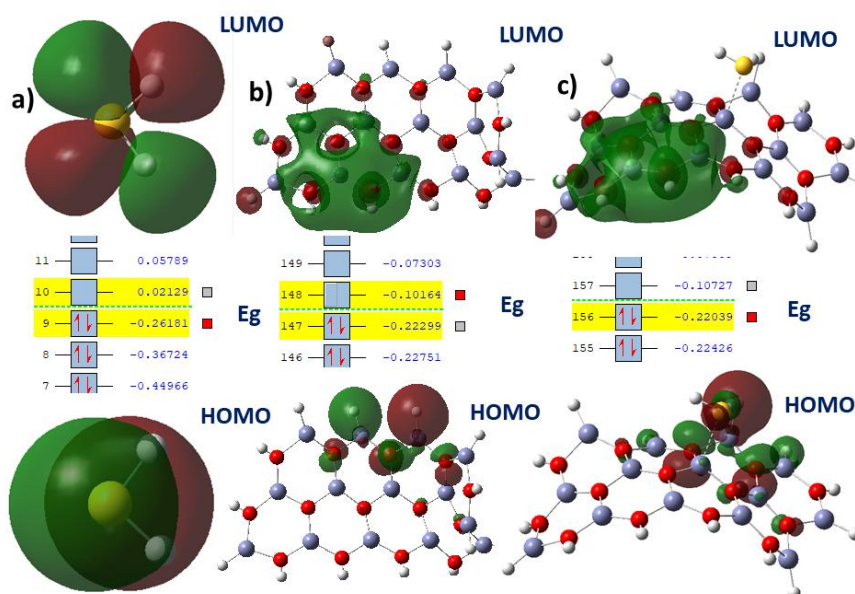


Fig. 2. Comparative HOMO–LUMO energy levels of H₂S, ZnO cluster, and the H₂S–ZnO complex.

clusters, which absorb at higher energies (around ~ 250 nm), indicates some extent of electronic delocalization and frontier orbitals rearrangement upon molecule–surface interaction. These red shifts are also in good agreement with the donor –

acceptor interaction between Zn_6O_6 and H_2S , and the adsorption affects the band structure of the ZnO cluster, reducing the HOMO –LUMO gap.

For gas sensing and photocatalytic applications, these types of spectral change are of particular

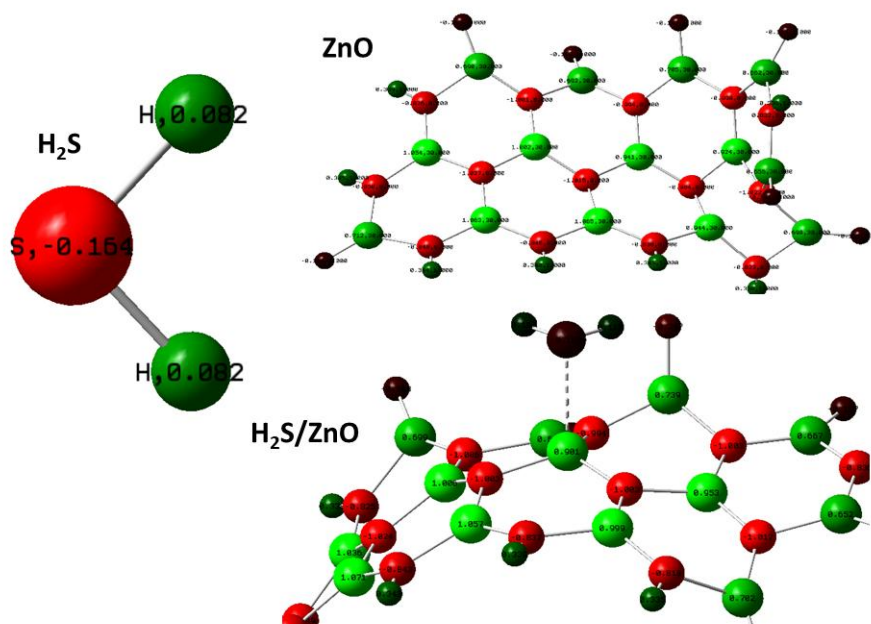


Fig. 3. Mulliken atomic charges for H_2S , ZnO , and H_2S – ZnO system.

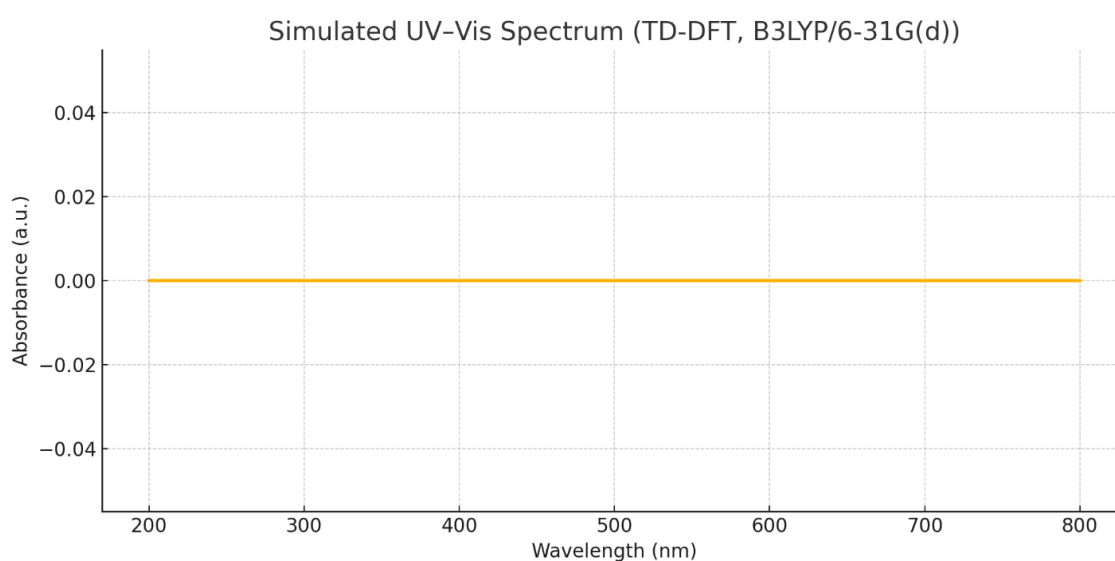


Fig. 4. The simulated spectrum reveals multiple electronic transitions in the UV region.

interest because optical properties upon gas exposure can be modulated for sensor signal transduction. Analogous electronic responses upon adsorption have also been demonstrated for other polar gases interacting with oxide clusters[11, 18].

Vibrational Frequency Analysis

Infrared (IR) vibrational frequency analysis was conducted to investigate the adsorption behavior of hydrogen sulfide (H₂S) on the ZnO nanocluster surface and to elucidate the nature of the

interactions between the adsorbate and substrate. The IR spectra of three systems—isolated H₂S, pristine ZnO cluster, and the H₂S/ZnO adsorption complex—are presented in Fig. 5.

For the isolated H₂S molecule, two intense peaks were observed in the region of 2550–2610 cm⁻¹, corresponding to the symmetric and asymmetric stretching modes of the S–H bond. These results are consistent with the characteristic vibrational frequencies of gas-phase H₂S reported in prior computational and experimental works[19]. A lower intensity bending vibration mode is also

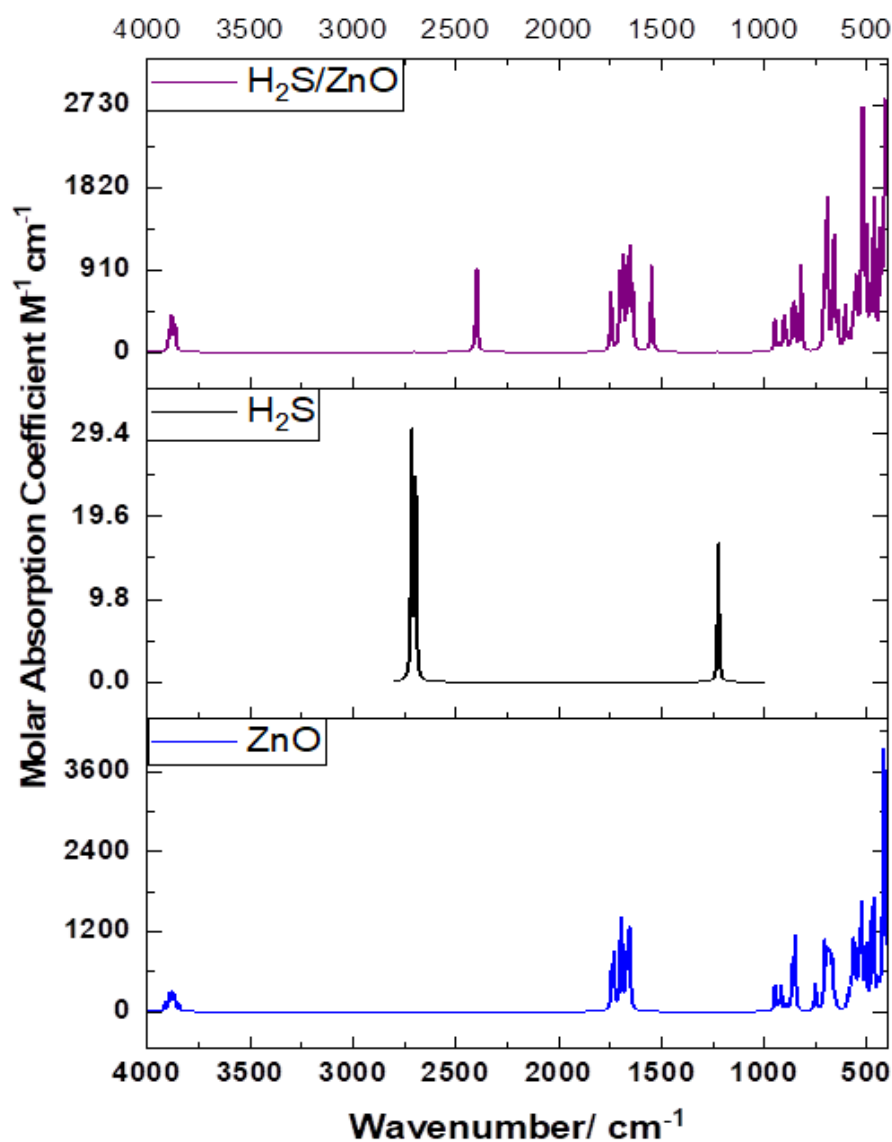


Fig. 5. Theoretical IR for H₂S, ZnO, and H₂S/ZnO complex.

visible around $\sim 1200\text{ cm}^{-1}$, which is typical for the H–S–H bending deformation[20–22].

The ZnO cluster spectrum exhibits strong vibrational modes primarily located in the 500–900 cm^{-1} region. These peaks can be assigned to the Zn–O stretching and bending modes, which dominate the vibrational behavior of zinc oxide nanostructures [23]. The spectral features are indicative of the structural integrity of the ZnO framework and align with previously reported data for similar cluster geometries[24].

Upon adsorption of H₂S on the ZnO cluster, significant spectral changes are evident. Notably, the original S–H stretching bands of H₂S are either red-shifted or absent, suggesting that the S–H bonds are involved in interaction or cleavage during adsorption. Furthermore, new vibrational bands emerge in the 1000–1500 cm^{-1} range, which can be attributed to Zn–S and O–H surface interactions, indicating partial dissociation or charge redistribution at the interface[25]. The modification in Zn–O vibrational bands,

particularly the broadening and intensity variation around 600–800 cm^{-1} , reflects perturbation of the ZnO lattice due to electronic interaction with the adsorbed H₂S.

These vibrational features are further supported by frontier molecular orbital (FMO) analysis, which shows a reduced energy gap upon adsorption, and AIM topological analysis, which confirms the presence of bond critical points (BCPs) and positive values of the Laplacian $\nabla^2\rho$ indicating closed-shell interactions. This combination of IR shifts and topological evidence confirms that the adsorption process is primarily chemisorptive in nature, involving charge redistribution between the sulfur atom and surface Zn and O atoms.

The presence of a weak band near $\sim 3600\text{ cm}^{-1}$ in the H₂S/ZnO system may also be attributed to surface hydroxyl groups formed by hydrogen migration from dissociated H₂S, further supporting proton transfer mechanisms as proposed in previous surface chemistry studies[25].

Overall, the IR analysis confirms that the

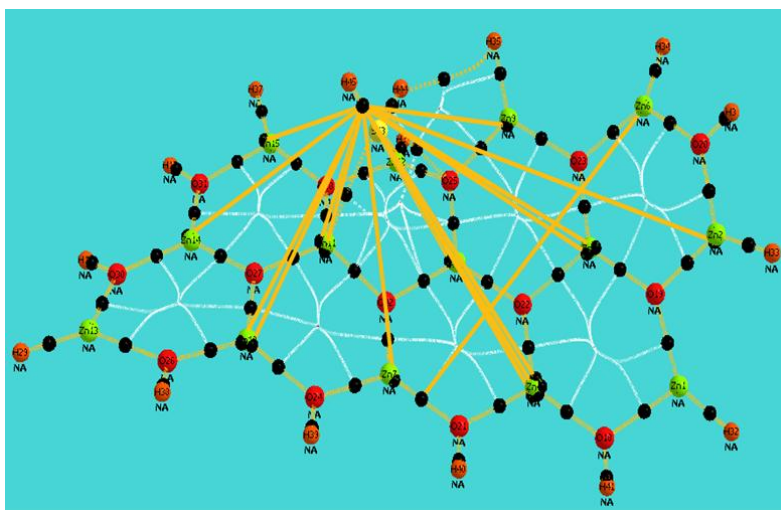


Fig. 6. AIM Bond-Path Network of H₂S Adsorbed on ZnO Monolayer.

Table 2. Topological Parameters at Selected Bond Critical Points (BCPs) for the H₂S/ZnO Complex Based on AIM Analysis.

No.	Bond path	ρ_{BCP} ($\text{e } \text{\AA}^{-3}$)	$\nabla^2\rho_{\text{BCP}}$ ($\text{e } \text{\AA}^{-5}$)	G ($\text{kJ mol}^{-1} \text{ bohr}^{-3}$)	V ($\text{kJ mol}^{-1} \text{ bohr}^{-3}$)	$H = G + V$
15	Zn2–O20	0.073	+0.410	0.050	–0.008	+0.010
18	Zn1–O19	0.088	+0.523	0.023	–0.011	+0.227
24	Zn4–O22	0.101	+0.629	0.018	–0.014	+0.166
41	Zn14–O31	0.090	+0.560	0.048	–0.010	+0.139
65	O25–S (ads.)	0.0047	+0.022	2.37	–0.001	+0.573
67	Zn11–S (ads.)	0.0072	+0.029	0.14	–0.001	+0.224

interaction between H₂S and the ZnO surface is not merely physisorptive but involves significant changes in the vibrational behavior of both the adsorbate and substrate, consistent with chemical bonding and electronic perturbation at the interface.

AIM Topological Analysis: Nature of Adsorption-Induced Interactions

Atoms-in-Molecules (AIM) analysis reveals that internal Zn–O bonds in the ZnO cluster (e.g., Zn1–O18, Zn4–O22) possess electron densities at the bond-critical point (ρ_{BCP}) in the range 0.07–0.10 e Å⁻³ with positive Laplacians ($\nabla^2\rho_{\text{BCP}} \approx +0.3$ to $+0.6$ e Å⁻⁵). These features characterize closed-shell ionic interactions, consistent with Zn²⁺–O²⁻ bonding, results shown in Fig. 6 and Table 2. The positive total energy density H and $|V|/G < 1$ across these bonds affirm their electrostatic nature rather than covalent character[26]. From (Zn–S Contact) display appearance of a bond path between Zn11 and the S atom of H₂S, with $\rho_{\text{BCP}} = 0.007$ e Å⁻³ and $\nabla^2\rho_{\text{BCP}} = +0.029$ e Å⁻⁵, is indicative of a weak, electrostatic interaction. However, its existence strongly supports orbital donation from the sulfur lone pair to the Zn 4s/4p orbitals, aligning with the LUMO analysis of the complex (Section 3). The low energy density ($H \approx +0.22$ kJ mol⁻¹ bohr⁻³) confirms the weak, non-covalent nature of this interaction.

The (S–O Interaction) show A weak bond path between the S atom and surface O25 further

stabilizes the complex geometry. Although the electron density is very low ($\rho_{\text{BCP}} \approx 0.005$ e Å⁻³), the topological connection implies a van der Waals-type dispersive interaction, relevant to physisorption stabilization [27].

Gas Sensing Implications

From a sensing standpoint, the AIM topology confirms molecular adsorption of H₂S molecule on ZnO that is non-destructive yet sufficiently perturbative. The identified Zn–S interaction enables donor-state introduction, and the low adsorption barrier suggests potential reversibility. This combination is ideal for real-time, low-temperature gas sensors, aligning with experimental ZnO sensor designs. [28, 29].

NCI Analysis (RDG Isosurface and Scatter Plot Visualization)

To further understand the interaction between H₂S and the ZnO cluster a NCI analysis was carried out using Reduced Density Gradient (RDG) method. This analysis is important to find weak interactions such as van der Waals, hydrogen bonding, and steric repulsion in real space. The NCI analysis was performed using the Multiwfn software. This methodology is also very useful in helping us visualize and understands the weak interatomic-intermolecular forces and interactions in our system. The electron density and its derivatives are used in the NCI method to pinpoint where

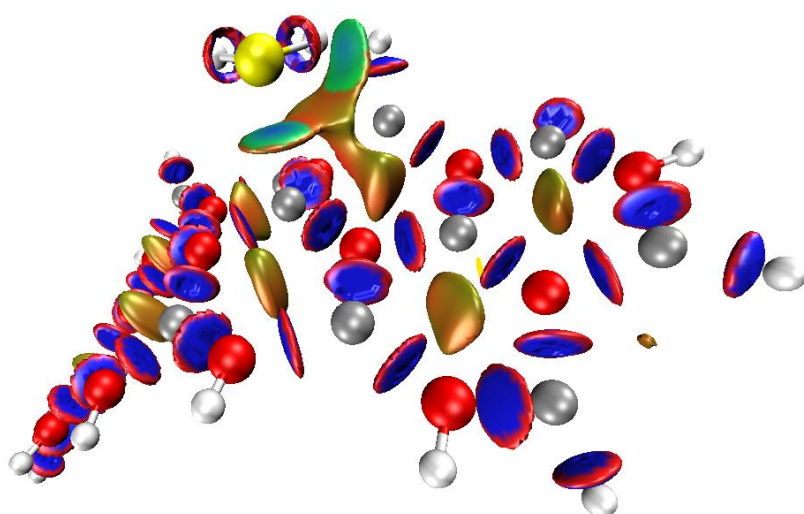


Fig. 7. Reduced Density Gradient (RDG) isosurface of the noncovalent interaction for H₂S–ZnO cages. The isosurfaces are computed at the isovalue $s = 0.50$ a.u. and colored according to the $\text{sign}(\lambda_2)\rho$.

and how strong such interactions are, thereby providing information about hydrogen bonding, van der Waals attraction, and steric repulsion[30, 31]. Key Ideas And Concepts NCI method NCI method is based on the analysis of the sign of the product of the sign of the 2nd eigenvalue (λ_2) of the diagonalized Hessian matrix and the electron density ($\rho(r)$) in order to describe the type and strength of non-covalent interactions. The Reduced Density Gradient (RDG), a scale-invariant counterpart of the gradient norm of the electron density, is defined as:

$$DG(r) = \frac{1}{2(3\pi^2)^{1/3}} * \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}} \quad (1)$$

Visualization The RDG isosurface as presented in Fig. 7 was visualized using the vmd code and color-coded by $\text{sign}(\lambda_2)\rho$, where λ_2 is the second eigenvalue of the Hessian of the electron density and ρ is the electron density. Colors correspond to different interaction types:

Green isosurfaces are used to represent weak van der Waals interactions; these are observed, in particular, between the sulfur atom of H₂S and certain of the near Zn sites of the cluster.

Blue areas indicate weaker attractive interactions, compared to the rest of the ZnS

binding site; i.e. dipole-induced electrostatic, localized about the Zn–S bond region.

Red isosurfaces denote steric repulsion, centered mostly in regions of high electron density of the ZnO surface, without a large impact in the adsorption site.

To complement this, the RDG vs. $\text{sign}(\lambda_2)\rho$ scatter plot (Fig. 8) confirms these interpretations. The broad green spike near zero reflects van der Waals interactions, while the blue wing at negative values of $\text{sign}(\lambda_2)\rho$ supports the presence of weak attractive forces. The red tail at positive values is consistent with steric repulsion zones.

Together, these observations demonstrate that the H₂S–ZnO interaction is primarily governed by non-covalent van der Waals interactions, with minor electrostatic contributions, and no evidence of strong covalent bonding. This weak but specific interaction mechanism is favorable for reversible gas sensing.

For visualization of weakly interacted region, the potential isosurface was set as 0.50 a.u. (a.u.) [32, 33], as the RDG. The green isosurface represents the region with a weak H₂S–nanocage interaction. It is interesting to mention that van der Waals contacts naturally show small RDG values, while regions attributed to be subjected to significant steric or attractive interaction (like hydrogen- or halogen-bonds, for example) bear a

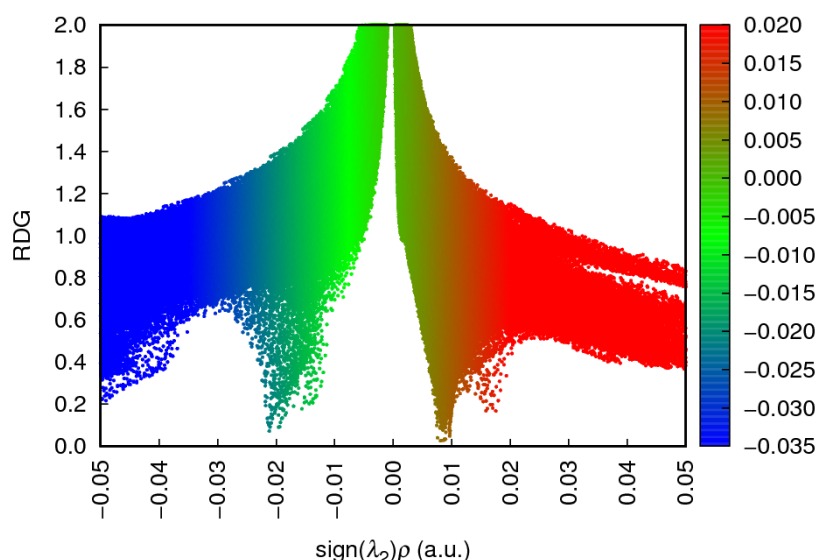


Fig. 8. Non-covalent interaction (NCI) scatter plots of RDG versus $\text{sign}(\lambda_2)\rho$ for ZnO:H₂S complex: The blue areas ($\text{sign}(\lambda_2)\rho < 0$) steric repulsion exists with electron clouds overlapping and hence unfavored terms.

much greater RDG. According to Fig. 7, when the number of the n increases the effect of van der Waals interactions becomes more significant. In the chemistry applications, we found that short distance regions are van der Waals regions. On the contrary, the regions with strong steric effects or strong attractive weak interactions (e.g., hydrogen bond, and halogen bond) usually exhibit large ρ . Therefore, an value $\text{sign}(\lambda_2)\rho$ can be assigned in the real space as the product of $\text{sign} \lambda_2$ and ρ . Fig. 7 is the RDG isosurface plot of Bdp(B2pin2) (4) at the same level as in Fig. 8, $\text{sign}(\lambda_2)(\rho)\rho(r)0$ (red regions) [34]. Together, the above data demonstrate the competition between the attractive, dispersive and the repulsive forces on H₂S adsorption on the ZnO. The joint RDG/NCI analysis elucidates the intricate balance of forces stabilizing the structure of adsorption, which is of interest for devising of ZnO-based sensing or catalytic systems [35,36,37]

The plots (Fig. 8) show isosurfaces (RDG = 0.50 a.u.) colored according to the $\text{sign}(\lambda_2)\rho$ scale, where blue ($\text{sign}(\lambda_2)\rho < 0$ a.u.) indicates strong attractive interactions (primarily Zn-S contact), green ($\text{sign}(\lambda_2)\rho \approx 0$ a.u.) shows van der Waals forces, and red ($\text{sign}(\lambda_2)\rho$ a.u.) reveals steric repulsion regions.

CONCLUSION

The adsorption of H₂S molecule on (ZnO)₁₄ nanocluster: A comprehensive DFT, TD-DFT and AIM study. The geometry optimization and vibrational frequency analysis further confirmed the stability of the H₂S–ZnO complex without significant imaginary frequencies. Energetic investigation revealed an exergonic and exothermic phenomenon, and $\Delta G = -13.0$ kJ mol⁻¹, $\Delta H = -14.9$ kJ mol⁻¹, it was suggested that the spontaneous adsorption occurred. The HOMO–LUMO gap significantly fell from 7.94 eV (H₂S) and 0.16 eV (ZnO) to 0.43 eV in the complex that improved the charge carrier transport. Red-shifted transitions related to orbital hybridization were also observed from the TD-DFT spectra. The Mulliken charge analysis revealed electron donation from H₂S to ZnO. AIM topology analysis revealed weak but genuine Zn–S and S–O bond paths, to confirm non-covalent stabilization. Vibrational mode changes of the H–S bond additionally reassured the electronic coupling to the surface. These findings collectively indicate that (ZnO)₁₄ nanocluster should be a promising candidate for H₂S detection by the

electronic and vibrational signals.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

REFERENCES

1. Santana Maldonado C, Weir A, Rumbelha WK. A comprehensive review of treatments for hydrogen sulfide poisoning: past, present, and future. *Toxicology Mechanisms and Methods*. 2022;33(3):183-196.
2. Jing W, Xiangzhao Z, Guoqiang W, Denghui L, Chuan Y, Hussain S, et al. MoSe₂/In₂O₃ nanocomposite for room-temperature H₂S sensing: Theoretical design and experimental validation. *Sensors and Actuators A: Physical*. 2025;394:116897.
3. Zhang C, Xu K, Liu K, Xu J, Zheng Z. Metal oxide resistive sensors for carbon dioxide detection. *Coord Chem Rev*. 2022;472:214758.
4. Jiang G, Keller J, Bond PL. Determining the long-term effects of H₂S concentration, relative humidity and air temperature on concrete sewer corrosion. *Water Res*. 2014;65:157-169.
5. Li X, O'Moore L, Song Y, Bond PL, Yuan Z, Wilkie S, et al. The rapid chemically induced corrosion of concrete sewers at high H₂S concentration. *Water Res*. 2019;162:95-104.
6. Rizwan HA, Khan MU, Anwar A, Alharthi S, Amin MA. First theoretical framework of Al₃N₉ and B₃N₉ nanorings for unveiling their unique detection and sensing potential for SF₆ decomposition gases (H₂S, SO₂, SOF₂, and SO₂F₂): toward real-time gas sensing in high-voltage power systems. *RSC Advances*. 2025;15(25):20020-20039.
7. Krishna KG, Parne S, Pothukanuri N, Kathirvelu V, Gandhi S, Joshi D. Nanostructured metal oxide semiconductor-based gas sensors: A comprehensive review. *Sensors and Actuators A: Physical*. 2022;341:113578.
8. Wang B, Bian H, Guo M, Tao Z, Luo X, Cui Y, et al. Low temperature and high sensitivity H₂S gas sensor based on Ag/rGO/ZnO ternary composite material. *Inorg Chem Commun*. 2025;180:114946.
9. Ji H, Zeng W, Li Y. Gas sensing mechanisms of metal oxide semiconductors: a focus review. *Nanoscale*. 2019;11(47):22664-22684.
10. Özgür Ü, Alivov YI, Liu C, Teke A, Reshchikov MA, Doğan S, et al. A comprehensive review of ZnO materials and devices. *J Appl Phys*. 2005;98(4).
11. Thayil R, Parne SR. Nanostructured zinc oxide and selenide-based materials for gas sensing application: review. *Journal of Materials Science: Materials in Electronics*. 2025;36(5).
12. Rahman M, Kamruzzaman M, Al Helal M, Liton MNH. Tuning the Structural, Electronic, and Optical Properties by the Incorporation of Sb into n-ZnO Semiconductor via DFT Calculation. *Semiconductors*. 2025;59(2):190-202.
13. Jafarova VN, Orudzhev GS. Structural and electronic properties of ZnO: A first-principles density-functional theory study within LDA(GGA) and LDA(GGA)+U methods. *Solid State Commun*. 2021;325:114166.
14. Rijal OS, Neupane HK, Shrestha P, Sharma S, Joshi LP, Parajuli R. First-principles study on the adsorption behavior of ZnO and Mn-doped ZnO with CO and NH₃ gases. *Surface Science*. 2025;761:122810.
15. Tunalı ÖF, Yuksele N, Gece G, Fellah MF. A DFT study of H₂S

- adsorption and sensing on Ti, V, Cr and Sc doped graphene surfaces. *Struct Chem.* 2024;35(3):759-775.
16. Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B.* 1988;37(2):785-789.
17. Behin J, Amiri P, Ghabaee S. Auto-photocatalytic valorization of ZnS into ZnS/ZnO nanocomposite using O₃/UV oxidation for photocatalytic dye degradation. *J Environ Manage.* 2025;389:126166.
18. Bhati VS, Hojamberdiev M, Kumar M. Enhanced sensing performance of ZnO nanostructures-based gas sensors: A review. *Energy Reports.* 2020;6:46-62.
19. Thompson HW. Infra-Red and Raman Spectra of Polyatomic Molecules. *Nature.* 1946;158(4009):289-289.
20. Aljeboree AM, Mahdi AB, Albahadly WKY, Izzat SE, Kubaisy MMRAL, Mohammed BM, et al. Enhancement of Adsorption of Paracetamol Drug on Carbon Nanotubes concerning Wastewater Treatment. *Engineered Science.* 2022.
21. Aljeboree AM, Mohammed F, Jawad MA, Alkaim AF. Exploiting the Diazotization Reaction of 8-hydroxyquinoline for Determination of Metoclopramide-hydrochloric acid in Pharmaceutical Preparations. *International Journal of Drug Delivery Technology.* 2022;13(02):703-707.
22. Hosseinpour M, Mirzaee O, Alamdari S, Menéndez JL, Abdoos H. Novel PWO/ ZnO heterostructured nanocomposites: Synthesis, characterization, and photocatalytic performance. *J Environ Manage.* 2023;345:118586.
23. de Peres ML, Delucis RdA, Amico SC, Gatto DA. Zinc oxide nanoparticles from microwave-assisted solvothermal process: Photocatalytic performance and use for wood protection against xylophagous fungus. *Nanomaterials and Nanotechnology.* 2019;9:184798041987620.
24. Cheng X, Li F, Zhao Y. A DFT investigation on ZnO clusters and nanostructures. *Journal of Molecular Structure: THEOCHEM.* 2009;894(1-3):121-127.
25. Zhang R, Liu H, Li J, Ling L, Wang B. A mechanistic study of H₂S adsorption and dissociation on Cu₂O(1 1 1) surfaces: Thermochemistry, reaction barrier. *Appl Surf Sci.* 2012;258(24):9932-9943.
26. Kumar PSV, Raghavendra V, Subramanian V. Bader's Theory of Atoms in Molecules (AIM) and its Applications to Chemical Bonding. *Journal of Chemical Sciences.* 2016;128(10):1527-1536.
27. Zhang Z, Li D, Jiang W, Wang Z. The electron density delocalization of hydrogen bond systems. *Advances in Physics: X.* 2018;3(1):1428915.
28. Li Y, Bahamon D, Sinnokrot M, Vega LF. Insights into the mechanisms of H₂S adsorption and dissociation on CdS surfaces by DFT-D3 calculations. *Int J Hydrogen Energy.* 2023;48(26):9700-9712.
29. Girija KG, Kumar R, Debnath AK. Highly selective H₂S sensor realized via the facile synthesis of N-doped ZnO nanocrystalline films. *Appl Phys A.* 2023;129(5).
30. Contreras-García J, Johnson ER, Keinan S, Chaudret R, Piquemal J-P, Beratan DN, et al. NCIPLOT: A Program for Plotting Noncovalent Interaction Regions. *J Chem Theory Comput.* 2011;7(3):625-632.
31. Apebende CG, Louis H, Owen AE, Benjamin I, Amodu IO, Gber TE, et al. Adsorption properties of metal functionalized fullerene (C₅₉Au, C₅₉Hf, C₅₉Ag, and C₅₉Ir) nanoclusters for application as a biosensor for hydroxyurea (HXU): insight from theoretical computation. *Z Phys Chem.* 2022;236(11-12):1515-1546.
32. Al-amir QR, Ahmed AT, Kanjariya P, Kumar A, Kumar N, Kulshreshta A, et al. Enhancing H₂S detection: the role of Al doping concentration in the electronic properties of ZnO nanocages. *Chem Phys Lett.* 2025;878:142251.
33. Probing the Reactions of Thiourea (CH₃N₂S) with Metals (X = Au, Hf, Hg, Ir, Os, W, Pt, and Re) Anchored on Fullerene Surfaces (C₅₉X). *American Chemical Society (ACS).*
34. Li Z, Lai Z, Zhao Z, Zhang L, Jiao W. A high-performance gas sensor for the detection of H₂S based on Nd₂O₃-doped ZnO nanoparticles. *Sensors and Actuators A: Physical.* 2023;350:114119.
35. Johnson ER, Keinan S, Mori-Sánchez P, Contreras-García J, Cohen AJ, Yang W. Revealing Noncovalent Interactions. *Journal of the American Chemical Society.* 2010;132(18):6498-6506.
36. Novikov AS. Recent Progress in Theoretical Studies and Computer Modeling of Non-Covalent Interactions. *Crystals.* 2023;13(2):361.
37. Assy M, Khalil M, Alaa Eldin AM. The Relation Between the Red Cell Distribution Width and Coronary Artery Calcium Scoring In Diabetic Patients Undergoing Coronary CT Angiography. *Zagazig University Medical Journal.* 2020;26(1):28-37.