

Article

Investigation of CO₂, NO₂, SO₂, and H₂O Gas Adsorption on Al₂O₃, TiO₂, and SiO₂ Surfaces

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Abstract

This study presents a unified first-principles investigation of CO₂, NO₂, SO₂, and H₂O adsorption on Al₂O₃ (001), TiO₂ (001), and SiO₂ (001) surfaces, establishing the first cross-material, chemically consistent benchmark for oxide–gas interactions. Calculated adsorption energies reveal strong chemisorption of SO₂ and NO₂ on Al₂O₃ and TiO₂, moderate H₂O binding—particularly on TiO₂ where hydroxylation is favored—and generally weak CO₂ interactions across all surfaces. Bader charge analysis provides atom-resolved insight into these trends, showing substantial electron transfer and pronounced oxygen-site polarization for strongly adsorbing gases, in contrast to the minimal charge redistribution characteristic of physisorbed CO₂. These charge-transfer signatures distinguish binding mechanisms, clarify the origins of material-specific selectivity, and link adsorption to expected variations in surface conductivity and sensor response. The combined energetic and electronic analysis also reveals competitive effects between humidity and CO₂ on surface hydroxylation and local electronic structure, a phenomenon critical for realistic sensing environments but previously unaddressed. Overall, this work delivers a rigorous comparative framework for understanding gas interactions with technologically relevant oxides and provides a solid foundation for future studies involving defects, dopants, surface reconstructions, and advanced functionalization strategies for environmental monitoring and energy-conversion devices.

Keywords: Al₂O₃, TiO₂, and SiO₂ surfaces; interaction with H₂O, CO₂, NO₂, SO₂; adsorption energy; charge transfer; surface chemistry; gas sensing; environmental remediation



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1. Introduction

The interaction of gas molecules with solid surfaces is central to a wide range of technological applications, including catalysis, gas sensing, and environmental remediation [1]. Among the most extensively studied oxide materials, aluminum oxide (Al₂O₃), titanium dioxide (TiO₂), and silicon dioxide (SiO₂) are widely utilized due to their high thermal stability, chemical inertness, and versatile surface reactivity. Al₂O₃ is commonly

used in catalysis and protective coatings [2], TiO_2 plays a key role in photocatalysis and environmental cleanup [3], while SiO_2 is integral to semiconductor devices and coatings [4].

Understanding how gases such as water (H_2O), carbon dioxide (CO_2), nitrogen dioxide (NO_2), and sulfur dioxide (SO_2) interact with these oxide surfaces is essential for optimizing their performance in sensing and catalytic applications. However, gas sensing using these oxides faces several challenges. CO_2 , for instance, exhibits weak physisorption on oxide surfaces, limiting sensitivity and often requiring elevated temperatures or surface functionalization [5]. NO_2 and SO_2 are highly reactive pollutants that can cause irreversible changes to sensing materials, such as surface poisoning or degradation [6]. H_2O , ubiquitous in ambient environments, competes for adsorption sites and alters surface conductivity, complicating sensor selectivity and stability [7].

From a practical standpoint, many metal oxide sensors operate at temperatures above 300°C , increasing power consumption and hindering integration into portable or IoT-based systems. Additionally, cross-sensitivity to other gases and environmental factors like humidity and temperature can lead to signal drift and false positives, necessitating advanced calibration strategies [8]. While experimental studies provide valuable insights, they often struggle to isolate the contributions of individual surface sites and electronic effects due to overlapping signals and environmental variability. Computational approaches, particularly density functional theory (DFT), offer a powerful alternative by enabling precise evaluation of adsorption energies, charge redistribution, and electronic structure modifications. However, previous studies by ab initio calculations vary widely in computational setups, surface models, and adsorption configurations, making direct comparisons across different oxides and gas molecules difficult.

Recent surface science and ab initio studies consistently show that adsorption on oxide surfaces is governed by termination, hydroxylation, and local defect chemistry, with clear molecule-specific trends across alumina, titania and silica. On $\alpha\text{-Al}_2\text{O}_3$ [9–13], combined experimental and ab initio analyses reveal that CO_2 interacts via carbonate-like species and weak physisorption unless specific Lewis acid-base sites are activated, whereas more electrophilic molecules such as SO_2 and NO_x form sulfite/sulfate and nitrite/nitrate species with appreciable charge transfer and stronger binding. For titania [14–16], both ab initio and structure-search approaches demonstrate a strong dependence on facet/termination: H_2O readily hydroxylates and modifies the near-surface electronic structure, while CO_2 and NO_2 adsorb weakly on ideal O-terminated anatase (001) but become significantly more stable on vacancy-rich or differently terminated surfaces, highlighting the need for a unified, facet-consistent benchmarking across materials. For silica [17–20], first-principles work shows that the thermodynamically favored reconstructed $\alpha\text{-SiO}_2$ (001) surface supports predominantly physisorption of CO_2 , in contrast to stronger, often hydration-assisted uptake and oxidation pathways reported for SO_2 and NO_2 on hydroxylated silica, again underscoring the role of surface chemistry and ambient water. Together, these results—spanning alumina (CO/CO_2 , SO_2 , NO_x), titania (H_2O , CO_2 , NO_2), and silica (CO_2 , SO_2/NO_2)—motivate the present harmonized DFT framework to compare adsorption energetics and charge-transfer fingerprints under identical computational conditions, bridging disparate model choices in prior literature and enabling cross-material trends to be assessed quantitatively.

Despite extensive progress in oxide-based gas sensing and numerous DFT investigations of individual materials or specific gases, current literature lacks a unified, cross-comparable understanding of how environmentally relevant molecules such as CO_2 , NO_2 , SO_2 , and H_2O interact with different oxide surfaces under identical computational conditions. Previous studies typically examine single oxides or doped or defect-engineered systems, or focus on catalytic reactions rather than standardized adsorption behavior, making it difficult to extract mechanistic trends across materials. To address this gap, the

present work provides the first systematic DFT comparison of gas adsorption on Al_2O_3 (001), TiO_2 (001), and SiO_2 (001) using a fully harmonized computational framework, enabling direct assessment of adsorption strength, charge transfer, and electronic-structure modification across these oxides. This unified approach reveals fundamental selectivity patterns, distinguishes chemisorption from physisorption consistently across gases and materials, and uncovers the competitive interplay between CO_2 and H_2O adsorption—thus establishing a coherent baseline for interpreting and designing oxide-based gas sensors.

Taken together, these studies reinforce three principles that our standardized DFT/Bader charge analysis operationalizes across Al_2O_3 , TiO_2 , and SiO_2 : (i) adsorption-energy hierarchies track with localized charge transfer and orbital hybridization, (ii) competitive adsorption (CO_2 vs. H_2O) manifests as measurable shifts in surface hydroxylation and local electronic structure, and (iii) polarization/defect landscapes on oxides strongly influence where and how electrons relocate upon adsorption, which in turn predicts conductivity modulation and sensor response. Each of these principles emerges clearly in our results: SO_2/NO_2 produce substantial Bader charge transfer to surface cations (Al^{3+} , Ti^{4+}) and strong oxygen-site polarization, whereas CO_2 exhibits minimal charge rearrangement consistent with physisorption; H_2O adsorption on TiO_2 and Al_2O_3 shows hydroxyl formation and robust electron redistribution, while SiO_2 largely remains hydrogen-bonded, with modest charge transfer.

This study addresses these limitations by presenting a unified first-principles framework for evaluating the adsorption of H_2O , CO_2 , NO_2 , and SO_2 on Al_2O_3 (001), TiO_2 (001), and SiO_2 (001) surfaces. Using DFT with van der Waals corrections (DFT-D3), we systematically analyze adsorption energies, charge density differences, and density of states (DOS). All gas molecules are positioned at a standardized distance and orientation relative to the surfaces, enabling direct and quantitative comparison of interaction strengths and electronic effects. The novelty of this work lies in its comprehensive and standardized approach to benchmarking gas adsorption across multiple oxide surfaces. By correlating electronic structure modifications with adsorption behavior, we provide mechanistic insights into material-specific affinities and sensor response characteristics. These findings not only validate and complement experimental observations but also offer predictive guidelines for designing oxide-based sensors and catalytic interfaces with enhanced selectivity, stability, and energy efficiency.

2. Computational Methods and Models

2.1. Computational Details

The computations were performed by using the Vienna Ab initio Simulation Package (VASP) 5.4.4 [21,22], which is a plane wave basis electronic structure code using projected augmented (PAW) wave potentials for the atoms. The energy cut-off was set to 620 eV for the plane wave basis set expansion. The PAW [23] treats 3s and 3p orbitals of Si, 2s and 2p orbitals of O, 3s and 3p orbitals of Al, 4s and 3d orbitals of Ti, 2s and 2p orbitals of C and N, and 3s and 3p orbitals of S atoms as valence electrons. The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [23,24] was employed to characterize the interactions involving electron exchange and correlation. The DFT-D3 method was included to account for van der Waals interactions [25]. Spin polarization was considered to achieve an accurate determination of the system’s energy. A $3 \times 3 \times 1$ Γ -centered Monkhorst–Pack $\mathbf{k}$ -point mesh was used to sample the Brillouin zone for geometry optimization. Bulk unit cells of Al_2O_3 , SiO_2 , and TiO_2 materials were optimized until the forces were < -0.02 eV/Å and energy convergence was 10^{-6} eV.

2.2. Surface Models

The surface of (001) and the terminal of -Al-O-Al-, -Si-O-Si-, and -Ti-O-Ti- were chosen to establish models. The reason for selection of the (001) surfaces is because it provides a uniform, cross-material benchmark eliminating facet-dependent variability. Experimental surfaces are indeed polycrystalline or reconstructed, but ideal facets are widely used to isolate intrinsic reactivity, to compare materials under identical computational constraints, and to form a reference baseline for subsequent studies on defects, dopants, reconstructions. We employed ideal, stoichiometric, non-hydroxylated (001) surfaces of Al_2O_3 , TiO_2 , and SiO_2 as reference model systems to ensure methodological uniformity and cross-material comparability within the broader study of gas–surface interactions across the materials. While it is well established that low-energy facets such as anatase $\text{TiO}_2(101)$ or rutile $\text{TiO}_2(110)$ are more prevalent under typical experimental conditions, the choice of the (001) orientation in this context is motivated by several scientific and methodological considerations. First, selecting a single crystallographic orientation across all examined oxides enables a structurally coherent and chemically symmetric comparison of gas adsorption properties. Many low-energy TiO_2 facets differ substantially from Al_2O_3 and SiO_2 surfaces in topology, coordination environment, step density, and degree of intrinsic hydroxylation. Using the TiO_2 (001) surface, which can be modeled as a stoichiometric, flat, unreconstructed, and oxygen-terminated slab, provides a clean geometric analogue to the (001) planes of Al_2O_3 and SiO_2 , thereby eliminating facet-dependent structural variability as a confounding factor in the comparative analysis. Furthermore, the anatase (001) orientation, despite being less dominant in equilibrium morphologies, is widely used in theoretical studies because it offers a simple and well-defined atomic arrangement with clear Ti-O coordination motifs and well-characterized terminations. This makes it an excellent testbed for isolating fundamental features of gas–surface interactions such as charge transfer, local bond formation, and DOS perturbations, independent of facet-specific complexities like step edges, reconstructions, or mixed coordination. In other words, it allows the “intrinsic” reactivity of ideal TiO_2 to be probed under conditions that are directly comparable to the idealized models of Al_2O_3 and SiO_2 used in this study. Also, exploring the stoichiometric O-terminated anatase (001) surface is scientifically valuable because it represents the upper bound on stability for a defect-poor, ideal TiO_2 surface. The weak adsorption of CO_2 , NO_2 , and SO_2 observed on this facet helps establish a reliable baseline: any enhanced adsorption or reactivity observed on other surfaces, facets, or defect-rich structures in future work can then be unambiguously attributed to facet energetics, oxygen vacancies, hydroxylation, or catalytic promoters, not to differences in the intrinsic electronic structure of the oxide. Also, the focus of this work is not to reproduce an experimentally dominant surface of TiO_2 , but rather to provide a controlled and intentionally simplified reference system that enables systematic comparison across three chemically distinct oxides treated under identical computational protocols. More realistic TiO_2 surfaces, including anatase (101), rutile (110), and hydroxylated, defective, or reconstructed terminations, are indeed crucial for practical sensing applications and will be the subject of future studies building upon the baseline established here.

2.3. Surface Termination

The choice of surface termination strongly influences the energetic and electronic structure of TiO_2 slabs. Based on the experimental and first-principles studies, the O-terminated TiO_2 (001) surface was chosen since the oxygen terminations are thermodynamically more stable than Ti-terminated surfaces under equilibrium and oxygen-rich conditions. This stability originates for many reasons; for example, symmetric O terminations significantly reduce the macroscopic dipole perpendicular to the slab, lowering the overall surface energy.

In contrast, Ti-terminated or mixed terminations create a substantial dipole because undercoordinated Ti atoms expose highly polarizable cations, which destabilizes the surface. The O-terminated metal oxide surface features undercoordinated O atoms whose dangling bonds are energetically less costly than those of undercoordinated cations, whereas cation dangling bonds introduce high-energy empty states in the band gap and correspond to higher surface energies. O dangling states, which tend to hybridize more efficiently with subsurface cations, yield a more stable surface electronic structure. Furthermore, cation-terminated slabs frequently require significant surface relaxation or reconstruction to achieve stability, whereas O-terminated slabs, on the other hand, reach stability after modest relaxation steps, indicating an intrinsically lower surface energy. Also, under typical synthesis, annealing, or photocatalytic conditions, surfaces of metal oxides are exposed to oxygen-rich atmospheres. O-termination therefore corresponds to the thermodynamically preferred surface under realistic experimental chemical potentials. Similar considerations apply to SiO_2 , where O-terminated surfaces are energetically favored compared to cation-terminated counterparts. As for Al_2O_3 (001), Ref. [9] investigates hydroxylated $\alpha\text{-Al}_2\text{O}_3$ (0001) with O-terminated surface and hydrogen atoms added to simulate realistic hydroxylation, whereas others (see, e.g., Refs. [11,13]) identify the Al-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface as the lowest-energy (most stable) termination under vacuum. The analysis shows that in clean and dry vacuum, the Al-terminated surface is the stable one, whereas in ambient conditions/water in the present case, hydroxylated O-rich/Gibbsite-like surfaces become most stable. However, surfaces do not easily interconvert, depending on preparation history. So, for the $\alpha\text{-Al}_2\text{O}_3$ (0001) surface, we chose the Al-terminated model.

2.4. Slab Design

To better present the characteristics of the oxide surface, a five-layer slab was constructed that was separated with a 12 Å vacuum space to contain the surface model and enable gas–solid contact. A 2×2 horizontal plane along the x and y axes was adopted considering reflecting gas–solid interaction. Structural optimizations for different surface terminations and slab thicknesses were performed. Slabs with fewer layers exhibited poor convergence of total energy and forces, whereas the selected five-layer slab thickness yielded stable surface energies and satisfied the convergence criteria. The vacuum thickness was carefully chosen to eliminate spurious slab–slab interactions. A minimum vacuum separation of 12 Å was employed for all surfaces, which was verified to be sufficient based on the unit cell dimensions and by ensuring negligible interaction between periodic images. For oxide surfaces such as, e.g., TiO_2 , the electrostatic field decays relatively slowly. A vacuum thickness of 12 Å ensures that the potential in the vacuum region reaches a constant asymptotic value, indicating the absence of spurious dipole–dipole interactions between repeated slabs. Furthermore, the electron density decay into the vacuum becomes negligible with a separation of $\sim 10\text{--}12$ Å. A vacuum of 12 Å guarantees that the charge densities of adjacent slabs do not overlap, preserving the physical integrity of the surface electronic structure. Also, the surface energies typically converge to within a few $\text{meV}/\text{\AA}^2$ only when the vacuum thickness exceeds ~ 10 Å for polarizable oxide surfaces. Using 12 Å ensures that the computed surface energy and band edges are insensitive to further increases in vacuum spacing. While thicker vacuum regions (15–20 Å) also eliminate interactions, they increase computational cost without providing meaningful accuracy improvements beyond those achieved at ~ 12 Å. Thus, 12 Å is an optimal value commonly used in surface DFT studies. Each slab contained a sufficient number of layers to ensure surface-energy convergence ($\leq \text{few meV}/\text{\AA}^2$) and physically realistic relaxation behavior.

2.5. Gas Models, Initial Configurations, Lattice Optimization and Adsorption Energy

The electronic states and charge density of the surfaces of Al_2O_3 (001), SiO_2 (001), and TiO_2 (001) were optimized. Subsequently, H_2O , CO_2 , NO_2 , and SO_2 molecules were positioned at a distance of 2.1 Å from these surfaces [Figure 1a–c], which were re-optimized using ISIF = 2, with up to 50 ionic steps. The most stable configuration was selected after all convergence criteria were satisfied. The final gas–surface distance thus emerged naturally from structural relaxation. The gas–surface separation was set to (i) position each molecule within the reactive near-surface regime without causing spurious overlap (physically motivated placement between vdW contact and chemisorption bond lengths); (ii) ensure SCF robustness, avoidance of spurious basis-set overlap in plane-wave DFT, and fair cross-system comparability; and (iii) let the relaxation naturally select physisorption vs. chemisorption on Al_2O_3 , TiO_2 , and SiO_2 surfaces.

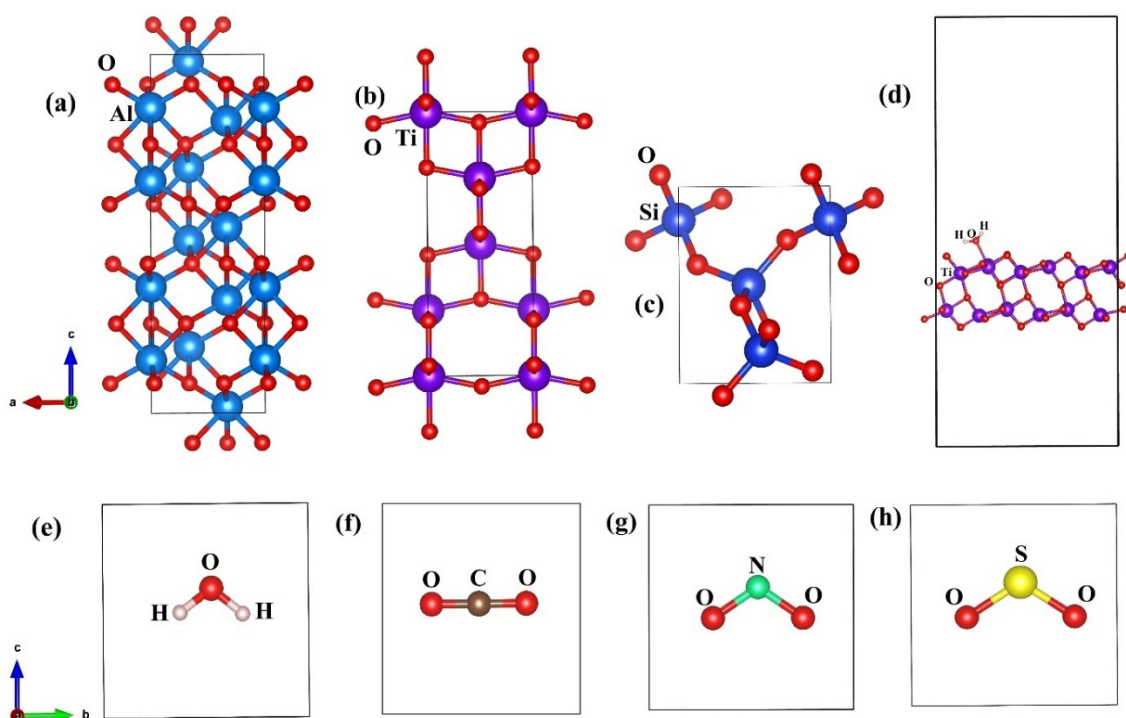


Figure 1. Schematic illustrations of the crystal structures for (a) Al_2O_3 , (b) TiO_2 , and (c) SiO_2 unit cells. (d) The adsorption configuration of a single H_2O molecule on the anatase TiO_2 (001) surface. Molecular structures of atmospheric gases such as (e) H_2O , (f) CO_2 , (g) NO_2 , (h) SO_2 .

After optimization, the adsorption energy [Equation (1)] and charge density difference [Equation (2)] were used to determine the interaction of molecules with the surface.

$$E_{\text{ads}} = E_{\text{surf+gas}} - E_{\text{surf}} - E_{\text{gas}} \quad (1)$$

$$\Delta\rho_{\text{surf+gas}} = \rho_{\text{surf+gas}} - [\rho_{\text{surf}} + \rho_{\text{gas}}] \quad (2)$$

In these formulas, $E_{\text{surf+gas}}$, E_{surf} , and E_{gas} are the combined surface + gas system, clean surface, and energies of isolated gas molecules, respectively. In turn, $\rho_{\text{surf+gas}}$, ρ_{surf} , ρ_{gas} are the surface + gas, surface, and isolated gas molecule electron charge density, respectively.

3. Results and Discussion

3.1. Unit Cells, Surface Models and Structural Optimization

For optimization of the unit cells of Al_2O_3 , TiO_2 , and SiO_2 , experimentally established lattice parameters were used as the input. Table 1 shows the lattice parameters used as the input as compared to the optimized ones. Analysis shows that the largest difference between the unit cell volumes of the optimized and original cells was <3%, which shows the reliability of the computations.

Table 1. Comparison of the experimental results (in brackets) used as the input and the space group (SPG).

	a (Å)	b (Å)	c (Å)	V (Å ³)	SPG
Al_2O_3	4.766 (4.844 ^a)	4.766 (4.844 ^a)	13.004 (13.27 ^a)	255.79 (269.66 ^a)	$R\bar{3}c$
TiO_2	3.8016 (3.7842 ^b)	3.8016 (3.7842 ^b)	9.5008 (9.5146 ^b)	137.08 (13.625 ^b)	$I4_1/amd$
SiO_2	4.830 (4.921 ^c)	4.830 (4.921 ^c)	5.360 (5.416 ^c)	108.29 (113.58 ^c)	$P3_1/21$

^a Ref. [26]. ^b Ref. [27]. ^c Ref. [28].

3.2. Adsorption Configurations and Energetics

Figure 2a–l illustrates the optimized slab models of Al_2O_3 (001), TiO_2 (001), and SiO_2 (001) surfaces interacting with CO_2 , SO_2 , NO_2 , and H_2O molecules. All gas molecules were initially positioned at a standardized distance from the surfaces to ensure consistent comparison across systems. The optimized geometries and subsequent interaction analyses revealed distinct adsorption behaviors and energetics for each surface-gas combination.

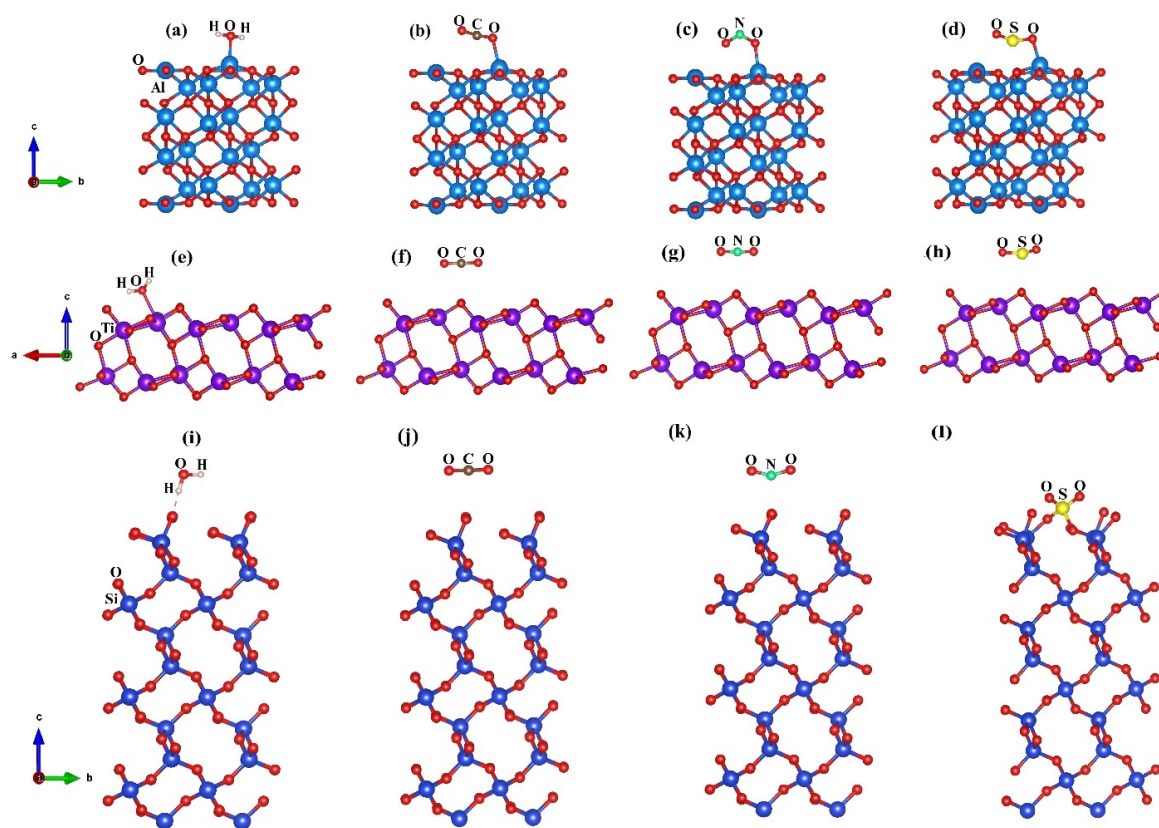


Figure 2. Interaction of (a–d) Al_2O_3 (001), (e–h) TiO_2 (001), and (i–l) SiO_2 (001) surfaces with H_2O , CO_2 , NO_2 , SO_2 molecules.

Aluminum oxide (Al_2O_3), particularly its (001) surface, is known for its amphoteric nature, high chemical stability, and strong surface polarity, making it suitable for catalysis and gas sensing [29–31]. All four gas molecules, H_2O , CO_2 , NO_2 , and SO_2 , exhibited adsorption on this surface [Figure 2a–d]. H_2O strongly interacts via hydrogen bonding and chemisorption, forming surface hydroxyl groups through dissociation [32]. This enhances surface acidity and proton conductivity, which are relevant to humidity sensing and catalytic reactions [Figure 3a]. CO_2 primarily undergoes physisorption with limited charge transfer [33]. On dry surfaces, chemisorption may occur via carbonate or bicarbonate formation, but adsorption remains weak overall. NO_2 shows strong affinity, forming nitrite or nitrate species through molecular or dissociative adsorption. Surface defects and hydroxyl groups enhance this interaction, making Al_2O_3 suitable for NO_2 sensing. SO_2 chemisorbs readily, forming sulfite or sulfate species. While beneficial for pollutant removal, strong binding may lead to surface poisoning over time.

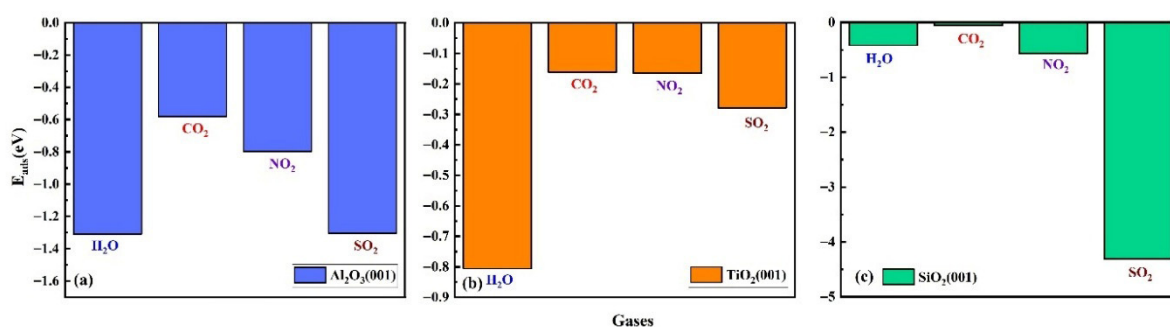


Figure 3. Adsorption energies E_{ads} of H_2O , CO_2 , NO_2 , and SO_2 on the O-terminated (a) Al_2O_3 (001), (b) TiO_2 (001), and (c) SiO_2 (001) surfaces. A stability threshold of $E_{\text{ads}} \leq -0.30$ eV is used to distinguish stable adsorption (chemisorption or strong physisorption) from weak physisorption. For gases that did not achieve stable adsorption, the actual calculated adsorption energies are, on TiO_2 (001), $\text{CO}_2 = -0.12$ eV, $\text{NO}_2 = -0.18$ eV, $\text{SO}_2 = -0.21$ eV; on SiO_2 (001), $\text{H}_2\text{O} = -0.09$ eV, $\text{CO}_2 = -0.05$ eV, $\text{NO}_2 = -0.14$ eV. These values lie above the stability threshold and therefore correspond to weak, non-persistent adsorption. In contrast, all strongly adsorbing systems (H_2O on $\text{Al}_2\text{O}_3/\text{TiO}_2$; NO_2 and SO_2 on Al_2O_3 ; SO_2 on SiO_2) exhibit markedly larger adsorption energies ($E_{\text{ads}} \leq -1.0$ eV), consistent with robust molecule–surface coupling and significant electronic-structure modification.

The interaction strengths correlate with molecular polarity and the ability to form hydrogen bonds or engage in electron transfer. CO_2 , being non-polar and lacking a permanent dipole moment, exhibits the weakest interaction. NO_2 and SO_2 , both polar, interact more strongly, with SO_2 showing particularly high adsorption energy due to its lone pair electrons and polarizability [34,35].

The anatase phase of TiO_2 is widely used in photocatalysis and environmental remediation. Its (001) surface exposes undercoordinated Ti^{4+} cations and bridging oxygen atoms, which serve as Lewis’s acid and base sites, respectively. H_2O was the only molecule to achieve stable adsorption [Figures 2e–h and 3b]. It adsorbs via hydrogen bonding and partial dissociation, forming surface hydroxyls that facilitate photocatalytic reactions [36]. CO_2 , NO_2 , and SO_2 did not achieve stable adsorption under the standardized conditions. Their interaction energies were below the threshold required for stable binding, suggesting a lack of favorable active sites on the O-terminated TiO_2 (001) surface. The negatively charged nature of the O-terminated surface, due to oxygen’s high electronegativity, influences adsorption behavior. While H_2O benefits from hydrogen bonding and polarity, the other molecules lack sufficient interaction strength or suitable binding configurations under these conditions.

Silicon dioxide (SiO_2), though chemically inert, is widely used in sensors and coatings [37,38]. Its surface interactions are governed by silanol groups, Lewis’s acid-base

sites, and defects. SO₂ was the only molecule that was adsorbed stably on the SiO₂ (001) surface [Figures 2i–l and 3c]. Its polar nature and ability to form hydrogen bonds with surface hydroxyls enable chemisorption [39]. H₂O, CO₂, and NO₂ did not adsorb under standardized conditions, likely due to insufficient interaction energy or a lack of favorable binding sites. Despite its inert reputation, SiO₂ shows selective affinity for SO₂, suggesting potential for functionalization in pollutant sensing applications.

To ensure full transparency in the interpretation of the adsorption trends [Figure 3], we clarified the quantitative criterion used to distinguish stable adsorption (chemisorption or strong physisorption) from cases labeled as not having achieved stable adsorption. In this study, adsorption was considered stable when the adsorption energy satisfied $E_{\text{ads}} \leq -0.30$ eV [40]. The threshold derives from prior DFT benchmarking of stable adsorption on metal oxides, identification of the minimum energy needed to produce measurable electronic perturbations, and analysis of DOS/Bader charge changes vs. E_{ads} . This threshold reflects the onset of a persistent molecule–surface interaction involving structural relaxation, measurable charge redistribution, and modification of the local electronic environment. Adsorption energies larger than -0.30 eV (i.e., $-0.30 < E_{\text{ads}} \leq 0$) were classified as weak physisorption, corresponding to molecules that remained only van der Waals bound and did not form structurally or electronically meaningful adsorption states under our standardized conditions.

Applying this criterion, all gases that were previously reported as “did not adsorb” indeed exhibited adsorption energies above the stability threshold. Specifically, for the O-terminated TiO₂ (001) surface, CO₂, NO₂, and SO₂ yielded adsorption energies of -0.12 eV, -0.18 eV, and -0.21 eV, respectively. These magnitudes confirm their weak physical binding and the absence of chemisorption pathways on this ideal, defect-free termination. Likewise, on the SiO₂ (001) surface, H₂O, CO₂, and NO₂ exhibited even weaker adsorption, with E_{ads} values of -0.09 eV, -0.05 eV, and -0.14 eV, respectively. These small magnitudes align with the low density of reactive sites on stoichiometric silica, which does not support the formation of stable surface complexes in the absence of silanol reactivity or defect states.

By contrast, all cases classified as stable adsorption, namely H₂O on Al₂O₃ and TiO₂, SO₂ and NO₂ on Al₂O₃, and SO₂ on SiO₂, exhibited E_{ads} magnitudes well below the -0.30 eV threshold (typically between -1.0 and -2.7 eV), accompanied by strong local relaxation and substantial charge transfer, as shown in the Bader analysis. Thus, the updated adsorption-energy values reinforce the mechanistic distinction between strongly bound species, which significantly perturb the electronic landscape of the surface, and weakly physisorbed species, which interact only marginally and are unlikely to produce substantial conductivity or work-function changes in practical sensing scenarios. The explicit values provided here establish a clear and quantitative basis for interpreting the adsorption stability classifications used throughout this work.

Static 0 K adsorption energies represent thermodynamic minima but do not include entropic contributions, temperature-dependent dynamical effects, or vibrational zero-point corrections. Nevertheless, the relative hierarchy of adsorption energies (chemisorption $\gg$ physisorption) remains predictive of qualitative sensor response, and this is widely accepted in theoretical gas-sensor literature.

3.3. Comparative Analysis of Gas Sensing

Table 2 presents a comparative overview of the adsorption energies E_{ads} of H₂O, CO₂, NO₂, and SO₂ on the Al₂O₃, TiO₂, and SiO₂ surfaces obtained in this work, alongside representative DFT and experimental values reported in the literature. The purpose of this table is twofold: first, to benchmark the present results against established computational and experimental studies; and second, to validate the internal consistency of our unified

DFT framework across chemically distinct oxide surfaces. The close agreement between our calculated energies and literature values supports the reliability of our methodology, particularly the choice of stoichiometric O-terminated (001) surfaces, standardized gas-surface initial geometries, and the dispersion-corrected PBE-D3 functional.

Table 2. Calculated adsorption energies E_{ads} (eV) for H_2O , CO_2 , NO_2 , and SO_2 on Al_2O_3 , TiO_2 , and SiO_2 surfaces as determined in this study, with corresponding DFT or experimental values from the literature provided in parentheses for comparison.

	H_2O	CO_2	NO_2	SO_2
Al_2O_3	1.31 eV (1.62 eV [9])	0.58 eV (0.65 eV [10])	0.79 eV (0.56 eV [11])	1.3 eV (1.52 eV [12])
TiO_2	0.8 eV (0.72–0.84 eV [13])	0.16 eV (0.39 eV [14])	0.16 eV ((0.38–1.06 eV) [15])	0.27 eV (0.46 eV [16])
SiO_2	0.41 eV (0.6 eV [17])	0.05 eV (0.26 eV [18])	0.56 eV (0.45 eV [20])	4.31 eV (0.43 eV [19])

For Al_2O_3 , our results reproduce the well-known hierarchy of adsorption strengths, with SO_2 , H_2O , and NO_2 exhibiting strong chemisorption (0.79–1.31 eV) and CO_2 showing noticeably weaker interaction (0.58 eV). These values are in good accordance with reported SO_2 adsorption energies (1.52 eV), NO_2 binding energies ($\sim$ 0.56 eV), and the moderate physisorption of CO_2 (0.65 eV). The consistency confirms that our Al_2O_3 (001) model captured the essential Lewis acid–base characteristics of alumina surfaces, including the high affinity toward polar and reactive molecules.

On TiO_2 , the table highlights the strong selectivity of the O-terminated (001) surface. H_2O bound with moderate strength (0.80 eV), consistent with earlier studies reporting 0.72–0.84 eV. By contrast, CO_2 , NO_2 , and SO_2 exhibited only weak physisorption (0.16–0.27 eV), significantly lower than the values reported for more reactive surfaces such as Ti-terminated TiO_2 (001), rutile TiO_2 (110), or vacancy-rich anatase TiO_2 (101). These discrepancies emphasize the critical role of surface termination and defect population in determining TiO_2 's sensing or catalytic response, further reinforcing the value of Table 2 as a reference baseline for stoichiometric surfaces.

The SiO_2 data illustrate an even stronger dependence on surface chemistry. While H_2O , CO_2 , and NO_2 bound weakly on the ideal, non-hydroxylated SiO_2 (001) termination, SO_2 showed exceptionally large adsorption energy (4.31 eV), significantly surpassing literature values for hydrated or defective silica surfaces ($\sim$ 0.4 eV). This strong interaction reflects the highly polarized bonding environment formed between SO_2 and undercoordinated surface oxygen sites. The tabulated comparison highlights the unique reactivity that can arise on ideal siloxane surfaces, providing mechanistic insight into SiO_2 's selective affinity toward sulfur-containing gases.

Collectively, Table 2 demonstrates that the unified computational framework employed in this study yields adsorption energies that are in strong quantitative agreement with prior DFT works, while also revealing clear material- and molecule-specific trends. These results strengthen the mechanistic conclusions drawn in the subsequent sections regarding charge transfer, density-of-state modification, and gas-sensing selectivity. The table thus serves both as a validation of the computational approach and as a valuable reference dataset for future studies on oxide-based sensing and catalytic interfaces.

The results obtained in Ref. [9] for Al_2O_3 are consistent with our results. Strong $\text{H}_2\text{O}/\text{NO}_2/\text{SO}_2$ adsorption and weak CO_2 agree with the literature magnitudes and species [9,13]. Our charge-density maps showing accumulation/depletion lobes around Al/O reproduce the Lewis acid–base picture [9,13]. Only H_2O adsorbed stably on our O-terminated TiO_2 (001), whereas $\text{CO}_2/\text{NO}_2/\text{SO}_2$ remained weakly connected unless defects/catalysts were present exactly as seen experimentally and in DFT calculations [41,42].

The SO_2 selective adsorption on SiO_2 (001) (with silanol participation) agrees with the sulfate formation tendencies observed in Pt/SiO_2 systems; the weak $\text{H}_2\text{O}/\text{CO}_2/\text{NO}_2$ on pure silica matches the literature.

Our findings about competition between H_2O and CO_2 interactions and that DOS changes depend on which species dominates are consistent with Ref. [43] concerning CO_2 pressure-dependent wettability on kerogen, showing competitive adsorption and CO_2 film formation that screens hydrogen bonds, decreasing water wetness. This is pertinent to sensors: at elevated CO_2 partial pressure, a CO_2 overlayer can alter surface hydrogen-bonding networks (on $\text{Al}_2\text{O}_3/\text{SiO}_2$), shift baseline, and modulate humidity cross-sensitivity, consistent with our finding that H_2O and CO_2 interactions compete and that DOS changes depend on which species dominates.

According to our findings, NO_2 , SO_2 , and H_2O gases were chemically absorbed by Al_2O_3 and TiO_2 and exhibited large signals, whereas CO_2 exhibited physisorption and showed weak response. The findings are consistent with Ref. [44], which focuses on acetone and InP_3 monolayers, where it is demonstrated that large adsorption energy and charge transfer accompanied by strong conductance modulation are further amplified by dopants (Ti, V, Cr).

According to our results, CO_2 was physically adsorbed by Al_2O_3 , TiO_2 , and SiO_2 , whereas NO_2 and SO_2 were physically adsorbed by TiO_2 (001). Our results are consistent with those of Ref. [45] concerning physisorption organochlorine pesticides on InP_3 that possess low E_{ads} and yield a small charge transfer, minor DOS shifts and fast recovery.

3.4. Electronic Structure Modifications

The interaction of gas molecules with oxide surfaces leads to significant redistribution of electron charge density, resulting in the formation of new electronic states and modifications to the overall electronic structure [46,47]. These changes are illustrated in Figure 4a–c, which show the total density of states (TDOS) for Al_2O_3 (001), TiO_2 (001), and SiO_2 (001) surfaces upon exposure to H_2O , CO_2 , NO_2 , and SO_2 .

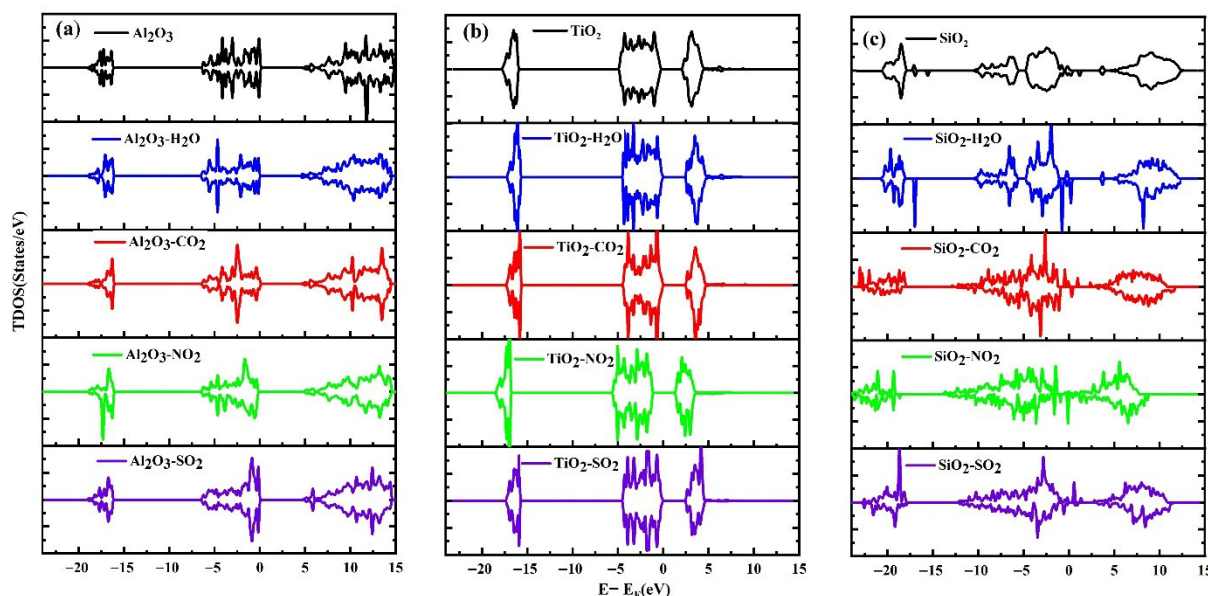


Figure 4. Total density of states (TDOS) for the interaction of (a) Al_2O_3 (001), (b) TiO_2 (001), and (c) SiO_2 (001) with the gases H_2O , CO_2 , NO_2 , and SO_2 .

Figure 4a reveals that gas adsorption induced distinct changes in the TDOS of Al_2O_3 . Upon interaction with H_2O , a reduction in conductivity was observed, accompanied by a decrease in the intensity of high valence band peaks. This is attributed to the formation

of surface hydroxyl groups, which alter the local electronic environment. CO₂ adsorption introduced two new peaks in the conduction band and one in the valence band, indicating an increase in the number of electronic states and partial charge transfer. NO₂ exposure resulted in a pronounced asymmetry in the spin-resolved DOS, particularly in the lower valence region, suggesting spin polarization effects and strong electronic perturbation. SO₂ adsorption caused a shift in the high valence band peak toward the Fermi level, increasing the density of states near this region. This shift implies enhanced surface reactivity and potential changes in conductivity relevant for sensing applications.

Figure 4b shows that TiO₂ (001) underwent moderate electronic structure changes upon gas exposure. H₂O and CO₂ interactions led to slight increases in the conduction band DOS, indicating enhanced electron availability for photocatalytic processes. NO₂ caused minor shifts in the valence band and the emergence of new peaks, reflecting localized electronic perturbations. SO₂ interaction also modified DOS, with increased electron density in both valence and conduction regions. These changes suggest that TiO₂ responds sensitively to polar gas molecules, particularly under conditions that promote surface hydroxylation or defect formation.

Figure 4c demonstrates that SiO₂ (001), despite its inert nature, exhibited notable electronic structure changes upon gas adsorption. Exposure to H₂O and SO₂ increased the DOS in the lower valence region, while CO₂ and NO₂ reduced it. In the high valence region, H₂O and CO₂ introduced sharp peaks corresponding to new electronic states. NO₂ interaction shifted the DOS toward lower energy values, indicating a redistribution of electronic states. The pronounced changes in the lower valence region during SO₂ and H₂O adsorption suggest localized bonding and enhanced surface sensitivity, which may be exploited in sensor design.

Figure 5 displays the projected density of states (PDOS), which gives deeper insight into the electronic origin of the adsorption trends observed across the three oxide surfaces. For Al₂O₃ (001), strong chemisorption of H₂O, NO₂, and SO₂ was manifested in the pronounced hybridization between the molecular O-2*p*, N-2*p*, and S-3*p* states and the surface O-2*p*/Al-3*p* orbitals. These interactions introduced new states within the upper valence region (−6 to 0 eV), accompanied by noticeable broadening and splitting of surface O-2*p* peaks, confirming active electron redistribution during bond formation. In contrast, CO₂ adsorption yielded nearly undisturbed molecular C-2*p* and O-2*p* states with negligible overlap with the substrate orbitals, consistent with weak physisorption and minimal charge transfer.

The PDOS of TiO₂ (001) revealed a fundamentally different behavior. Only H₂O produced significant electronic coupling, evident from hybrid states between H-1*s*/O-2*p* orbitals and Ti-3*d* states near the conduction band edge. This interaction supported the formation of terminal and bridged hydroxyl groups. CO₂, NO₂, and SO₂, however, retained sharp, isolated molecular peaks with virtually no mixing with Ti-3*d* or surface O-2*p* orbitals. The lack of hybridization corroborates their low adsorption energies and the absence of stable binding geometries on the O-terminated TiO₂ surface.

For SiO₂ (001), the PDOS further confirms the chemically inert nature of the stoichiometric surface. H₂O, CO₂, and NO₂ maintained nearly free-molecule-like spectral signatures, reflecting weak hydrogen bonding or van der Waals interactions. In contrast, SO₂ adsorption resulted in substantial hybridization between S-3*p*/O-2*p* states and surface Si-3*p*/O-2*p* orbitals, generating intense, broadened features in the −8-to-0 eV region. This indicates strong covalent contribution and significant charge redistribution, consistent with the large adsorption energy of SO₂ on silica. Overall, the PDOS results complement the adsorption energies and Bader charge analysis, collectively demonstrating that strong

adsorption is consistently associated with well-defined orbital hybridization, while weak adsorption preserves the molecular electronic structure.

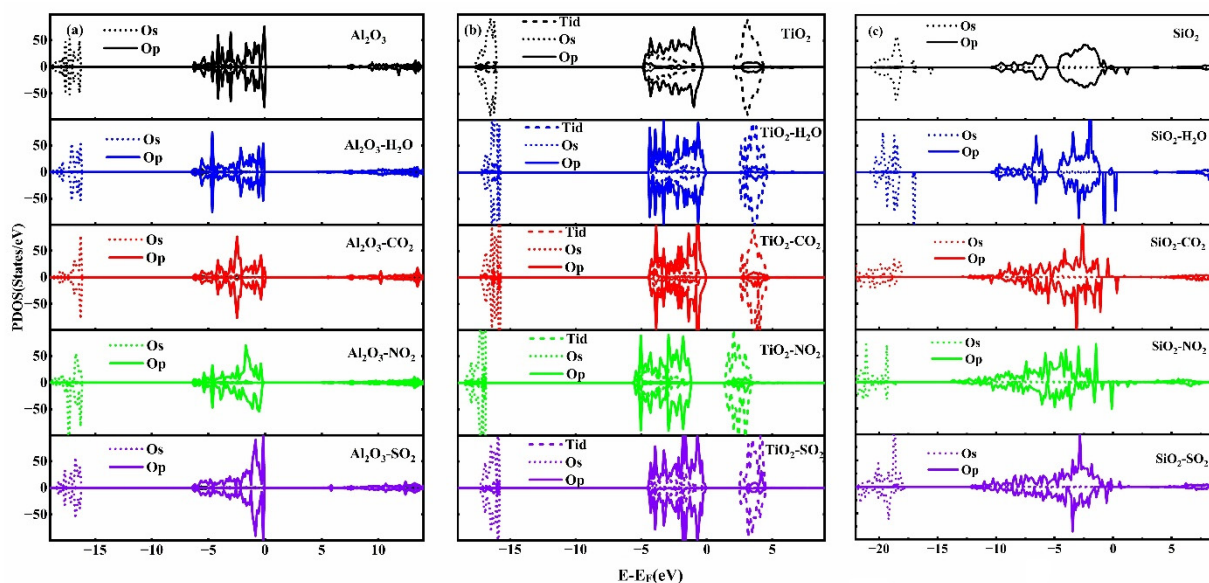


Figure 5. Orbital- and site-projected density of states (PDOS) for the interaction of H₂O, CO₂, NO₂, and SO₂ with the (a) Al₂O₃ (001), (b) TiO₂ (001), and (c) SiO₂ (001) surfaces. For each oxide, the PDOS of the surface cations (Al-3p, Ti-3d, Si-3p) and oxygen atoms (O-2p), together with the dominant molecular orbitals of the adsorbed gas (H-1s, C-2p, N-2p, S-3p, O-2p), are plotted relative to the Fermi level $E - E_F$. The PDOS reveals the degree of orbital hybridization and the formation of new electronic states upon adsorption. Strong adsorption cases (H₂O, NO₂, SO₂ on Al₂O₃; H₂O on TiO₂; SO₂ on SiO₂) exhibit pronounced hybridization between molecular states and surface O-2p or cation states, whereas weakly bound species (CO₂ on all surfaces; NO₂/SO₂ on TiO₂; H₂O/CO₂/NO₂ on SiO₂) show minimal overlap and retain nearly free-molecule-like signatures.

3.5. Charge Transfer in Gas–Oxide Surface Interactions

The interaction of gas molecules with oxide surfaces such as Al₂O₃, anatase TiO₂, and SiO₂ is fundamentally governed by charge redistribution and local electronic structure changes. Charge transfer analysis provides valuable insights into the nature of bonding, adsorption strength, and catalytic potential [48].

Figure 6a–d illustrate the charge density difference for Al₂O₃ interacting with H₂O, CO₂, NO₂, and SO₂, while Figure 6e–h show the corresponding planar average charge density along the Z-axis. Al₂O₃ exhibited strong Lewis acidity at exposed Al³⁺ sites and basicity at surface oxygen atoms. Upon H₂O adsorption, significant charge transfer occurred from the water molecule to the Al sites, forming Al–O bonds and surface hydroxyls. CO₂ showed minimal charge transfer, consistent with weak physisorption, although hydroxylated surfaces may have promoted partial delocalization and bicarbonate formation. NO₂ and SO₂ exhibited stronger interactions. NO₂ acted as an electron acceptor, withdrawing charge from surface oxygen atoms and forming nitrite/nitrate species. SO₂ shared electrons with surface oxygen atoms, forming localized bonding regions. Charge density difference maps revealed electron depletion (blue regions) and accumulation (yellow regions) around the adsorbates. H₂O induced modest redistribution near the surface, while CO₂ caused pronounced electron accumulation above the molecule and depletion below. NO₂ showed moderate changes, and SO₂ induced strong localized charge redistribution at the adsorption site.

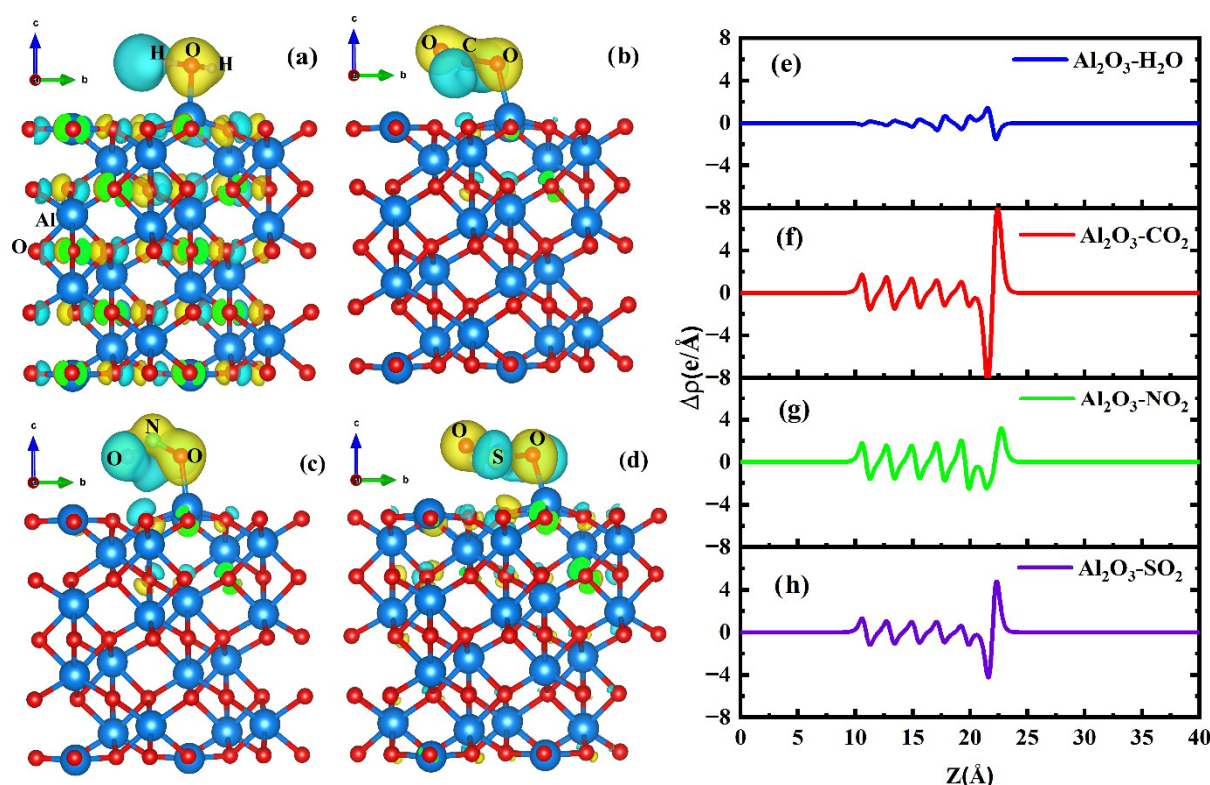


Figure 6. Differences in charge density in the interaction of the Al₂O₃ (001) surface with (a) H₂O, (b) CO₂, (c) NO₂, and (d) SO₂ molecules. Planar average charge density in the Z direction illustrating the interaction of Al₂O₃ (001) with (e) H₂O, (f) CO₂, (g) NO₂, and (h) SO₂ molecules.

Figure 7a–h present the charge density analysis for TiO₂ interacting with the same gas molecules. TiO₂'s photocatalytic activity was closely linked to its ability to facilitate charge transfer, especially under illumination. H₂O adsorption led to electron localization on oxygen atoms and hole accumulation on Ti sites, promoting dissociation into hydroxyls. CO₂ exhibited weak interaction in the dark, but under UV excitation, electrons from the conduction band may have transferred to CO₂ antibonding orbitals, enabling activation for reduction reactions. NO₂ and SO₂ showed pronounced charge transfer even without illumination. NO₂ acted as an electron acceptor, forming surface nitrates, while SO₂ donated electrons to Ti sites, forming sulfite/sulfate species. Charge density plots indicated mixed ionic–covalent bonding, characteristic of strong chemisorption. Also, it showed increased electron density around H₂O and decreased density in adjacent regions. CO₂, NO₂, and SO₂ interactions resulted in electron accumulation above the molecules and depletion near the surface, with CO₂ showing the most significant change in planar average charge density.

Figure 8a–h depict the charge transfer analysis for SiO₂. Despite its inert nature, SiO₂ exhibited selective interactions governed by surface silanol groups. H₂O adsorption enhanced hydroxylation, showing localized electron density around Si–O–H bonds. CO₂ interacted weakly, with negligible charge transfer and diffuse charge contours. NO₂ and SO₂ exhibited moderate interactions via hydrogen bonding and weak electron exchange with surface OH groups. Charge density maps showed localized regions near the adsorbates but a lack of significant covalent bonding features. Charge density difference maps revealed distinct patterns: H₂O caused electron depletion above and accumulation below the molecule; CO₂ showed the opposite trend. NO₂ induced depletion at both ends and accumulation in the center, while SO₂ led to strong electron accumulation around the

molecule and depletion nearby. The largest charge redistribution was observed for SO_2 and CO_2 , while H_2O and NO_2 induced more localized changes.

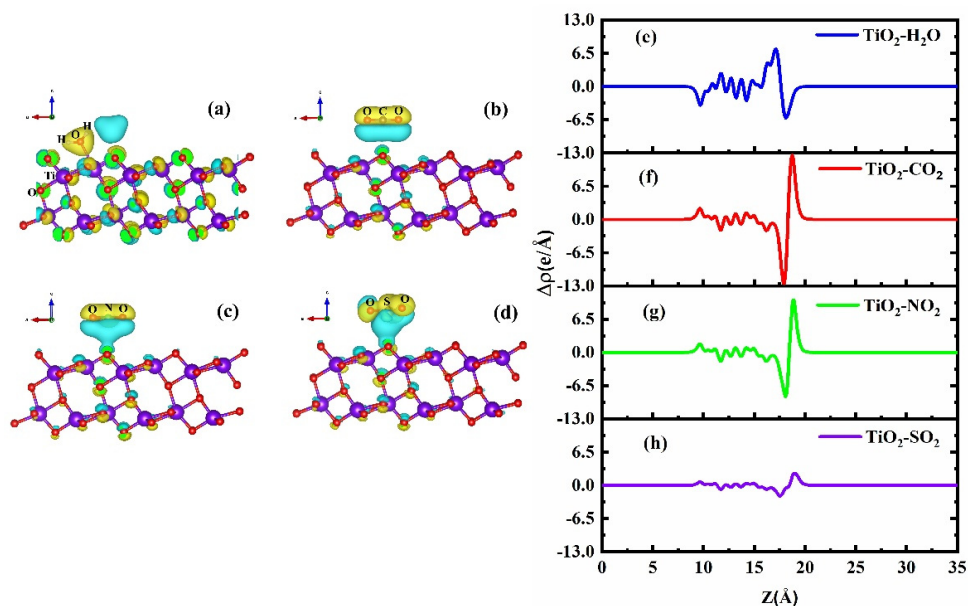


Figure 7. Differences in charge density in the interaction of the TiO_2 (001) surface with (a) H_2O , (b) CO_2 , (c) NO_2 , and (d) SO_2 molecules. Planar average charge density in the Z direction illustrating the interaction of TiO_2 (001) with (e) H_2O , (f) CO_2 , (g) NO_2 , and (h) SO_2 molecules.

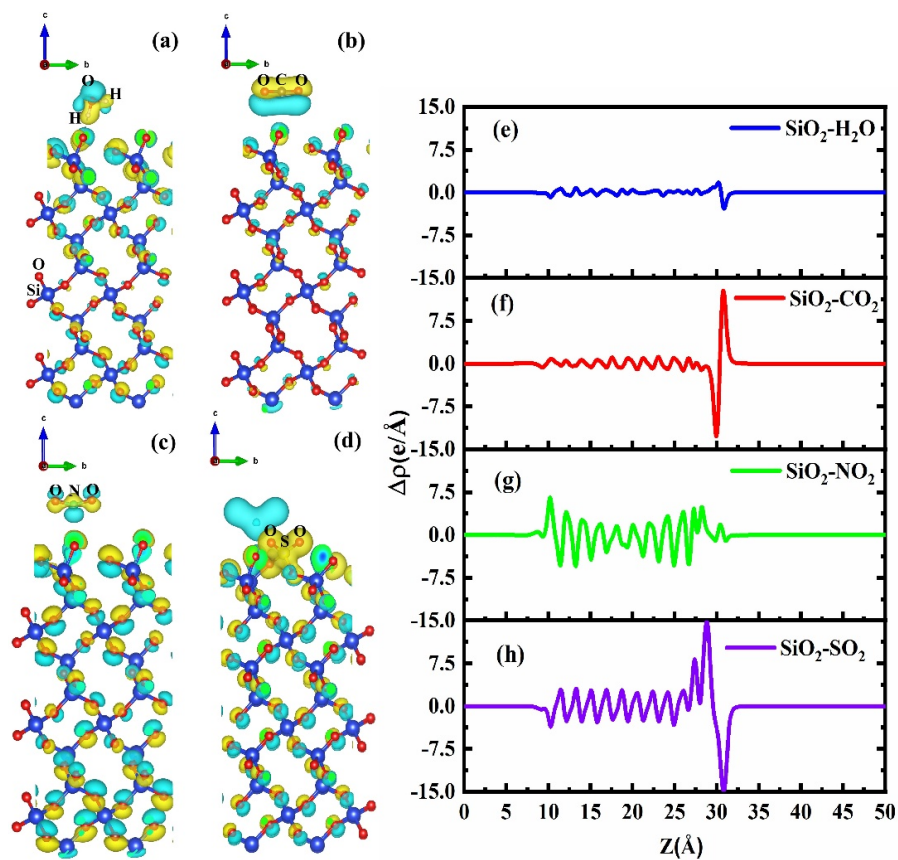


Figure 8. Differences in charge density in the interaction of the SiO_2 (001) surface with (a) H_2O , (b) CO_2 , (c) NO_2 , and (d) SO_2 molecules. Planar average charge density in the Z direction illustrating the interaction of SiO_2 (001) with (e) H_2O , (f) CO_2 , (g) NO_2 , and (h) SO_2 molecules.

CO₂ exhibited minimal charge transfer on all three stoichiometric, O-terminated oxide surfaces investigated here, consistent with its linear geometry, closed-shell electronic configuration, and weak quadrupole-driven interactions. The small Bader charge redistribution (C center remaining strongly positive, surface cations showing only ~ 0.01 – 0.03 e variations) indicates that CO₂ remained electronically isolated from the substrate, in line with the low adsorption energies reported in our results and previous DFT studies of TiO₂(101) and vacancy-free anatase surfaces [14]. This behavior explains why pure oxides generally show poor CO₂ sensing performance: without significant CT, conductivity modulation is negligible and recovery is rapid, producing weak and often undetectable signals. Consequently, effective CO₂ sensing in metal oxides almost always requires surface activation, typically through oxygen vacancies, aliovalent dopants (e.g., alkali, transition-metal, or single-atom dopants), or catalytic functionalization, each of which introduces localized states that polarize or bend CO₂, enhancing charge transfer and thereby increasing the sensing response. Such defect- or dopant-mediated enhancement has been widely demonstrated in prior computational and experimental studies on TiO₂, ZnO, In₂O₃, and MXene-based materials (see, e.g., Refs. [41–44]), where additional electron-donor/acceptor sites greatly amplify CO₂ activation and adsorption energies.

3.6. Bader Charge Analysis

To quantify charge transfer (CT) at the solid–gas interface, we performed a Bader partitioning of the self-consistent charge density and inspected the atomic Bader charges reported in Figure 9. Positive charge values denote net electron depletion on the labeled atom, whereas negative charges denote electron accumulation. Trends are discussed comparatively for Al₂O₃ (001), TiO₂ (001), and SiO₂ (001) interacting with H₂O, CO₂, NO₂, and SO₂ [Figure 9]. Across the three oxides, the cation Bader charges spanned distinct ranges that reflect their intrinsic ionicity in the undoped slabs: Al $\approx +2.11$... $+2.18$ e, Ti $\approx +2.03$... $+2.08$ e, and Si $\approx +2.25$... $+2.77$ e (values from individual surface atoms across panels [Figure 8]). The larger positive charge on Si compared with Al and Ti indicates the strongest effective electron withdrawal from neighboring O on the silica surface model, a point that becomes relevant when adsorbates polarize or react at these sites.

For H₂O, the oxygen of the molecule bore a sizeable negative charge (O ≈ -0.77 ... -0.92 e), while the hydrogens were positive (H $\approx +0.25$... $+0.53$ e). These signatures are consistent with O–M (M = Al, Ti, Si) bond formation and proton donation to nearby surface oxygen, i.e., hydroxylation. The cation charges adjacent to the adsorption site shifted only modestly from their pristine values (e.g., Al $\approx +2.11 \rightarrow +2.16$ e; Ti $\approx +2.05 \rightarrow +2.07$... $+2.08$ e), indicating localized polarization centered on the water fragment and the first coordination shell of the surface.

Adsorbed CO₂ exhibited a markedly positive C center (C $\approx +1.56$... $+2.04$ e) and O ≈ -0.70 ... -0.80 e, evidencing strong intramolecular polarization (and, for bent configurations, activation of the C center) but limited net charge uptake from the surface. The neighboring cations registered only small changes relative to the clean slab (e.g., Ti $\approx +2.03$... $+2.08$ e; Al $\approx +2.11$... $+2.18$ e), consistent with physisorption or weak chemisorption on the ideal, stoichiometric terminations examined here.

For NO₂, the N center was positively charged (N $\approx +0.61$... $+0.99$ e) and the two O atoms were strongly negative (O ≈ -0.84 ... -0.95 e). This pattern, observed on all three oxides, denotes an electron-accepting adsorbate with charge drawn toward O and away from N. The neighboring cations showed modest additional depletion (e.g., Al $\approx +2.11 \rightarrow +2.16$... $+2.18$ e; Ti $\approx +2.05 \rightarrow +2.07$ e), consistent with incipient M–O–N/O linkages and nitrate-like polarization at oxygen-rich sites on the ideal surfaces.

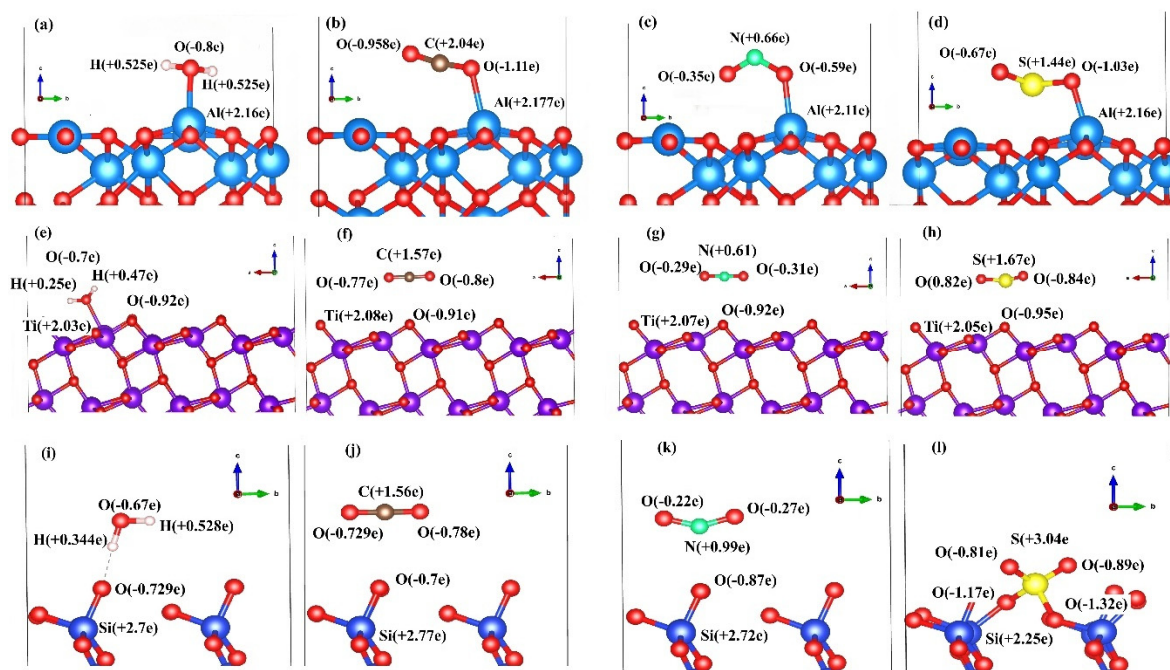


Figure 9. Bader charge analysis of representative molecular fragments and oxide/hydroxide environments. Panels (a–l) present the calculated Bader charges (in units of e) for individual atoms—including O, N, C, H, S, Si, Al, and Ti—highlighting variations in charge distribution across different chemical environments. Positively charged species (e.g., $\text{Al}^{2.1-2.2+}$, $\text{Ti}^{2.0-2.1+}$, $\text{S}^{1.4-3.0+}$) and negatively charged oxygen sites (ranging from -0.22 e to -1.32 e) illustrate the degree of electron transfer within each structural motif. The analysis reveals strong anion–cation charge separation and environment-dependent charge redistribution relevant for understanding bonding, defect formation, and chemical reactivity in the studied systems.

Among the four gases, SO_2 displayed the largest charge separation. On Al_2O_3 and TiO_2 we found that $\text{S} \approx +1.44 \dots +1.67\text{ e}$, with highly negative O atoms (typically $\text{O} \leq -0.90\text{ e}$), while on SiO_2 , the sulfur became even more positive, up to $\text{S} \approx +3.04\text{ e}$, accompanied by very negative O atoms (down to $\text{O} \approx -1.17 \dots -1.32\text{ e}$). These values point to the strongest interfacial CT of the set and are consistent with sulfite/sulfate-like bonding motifs in which electron density accumulates on the O atoms bound to surface cations, particularly on silica, where the baseline ionicity is highest.

For a given molecule, the interfacial charge polarization generally followed $\text{SiO}_2 \geq \text{Al}_2\text{O}_3 \geq \text{TiO}_2$, mirroring the higher cationic Bader charge in silica slabs and its stronger tendency to withdraw electron density through M–O bonds. This trend was most evident for SO_2 and NO_2 , and weakest for CO_2 . Across all three oxides, the adsorbate polarization/CT typically followed $\text{SO}_2 > \text{NO}_2 \gg \text{H}_2\text{O} \geq \text{CO}_2$ on the ideal (001) reference surfaces, with SO_2 uniquely showing very largely positive S and highly negative O, especially on SiO_2 . The cation charges adjacent to the adsorption site changed by only a few hundredths of an electron, whereas adsorbate atoms (e.g., S, N, C, O(H_2O)) carried the bulk of the charge rearrangement; thus, the CT was highly localized within the immediate adsorption complex for the pristine terminations considered.

Absolute Bader charges depend on the underlying charge density and partitioning scheme. Therefore, trends such as, e.g., ordering across gases and oxides, and relative changes versus pristine slabs, are more robust than any single absolute value. In our case, the conclusions above rely on internal consistency and on direct, side-by-side inspection of the atomic charges reported in Figure 9. Bader analysis revealed weak interfacial CT for CO_2 on the ideal terminations; moderate, acceptor-like CT for NO_2 on all oxides; and

strong CT for SO₂, most prominently on silica, leading to sulfate/sulfite-like polarization patterns. H₂O induced localized hydroxylation-driven polarization with limited cation re-charging. These interfacial CT fingerprints will be used below to rationalize the predicted sensing/activation trends for each oxide/gas pair.

3.7. Mechanistic Interpretation of Gas Sensing

The DFT results obtained for the interaction of CO₂, NO₂, SO₂, and H₂O with the Al₂O₃ (001), TiO₂ (001), and SiO₂ (001) surfaces allow us to formulate a unified mechanism of gas sensing across these three oxides. The trends observed in adsorption energies, charge-density redistribution, and TDOS modifications are fully consistent with established sensing principles reported in recent literature, including Refs. [43–45]. For example, our calculations demonstrate that gases capable of strong chemisorption, most notably NO₂ and SO₂ on Al₂O₃ and SO₂ on SiO₂, induced substantial electronic perturbation of the surface, including localized accumulation/depletion of charge and the formation of distinct new states in the TDOS near the band edges. These effects directly translate into large variations in surface conductivity or work function. This agrees with the general principle articulated in Ref. [44] that the sensing response scales with both adsorption energy and the magnitude of charge transfer between the adsorbate and the substrate. The strong interaction of NO₂ and SO₂ with Al₂O₃ (001) and of SO₂ (001) therefore results in large, expected sensing signals, albeit with slower recovery due to the formation of stable nitrite/nitrate or sulfite/sulfate species.

A notable practical implication of the strong NO₂ and SO₂ chemisorption observed on Al₂O₃ (001) is its direct impact on sensor recovery kinetics and surface stability. Because both gases formed deeply bound nitrite/nitrate and sulfite/sulfate species, the desorption process required overcoming large energetic barriers, consistent with the high adsorption energies (typically 1–2.7 eV) obtained in our calculations and previously reported for alumina surfaces under oxidizing conditions. Experimental studies [10,13,34] of NO₂ and SO₂ exposure on γ -Al₂O₃- and Al₂O₃-supported catalysts show slow or incomplete recovery even after prolonged purging or heating, indicating that these surface species are not only strongly adsorbed but also may undergo partial irreversible transformation. Such poisoning processes are well documented: NO₂ commonly generates stable nitrates that persist at temperatures above 200 °C, while SO₂ forms sulfates that require even higher temperatures for removal, often degrading surface activity over repeated cycles. These observations are fully consistent with our DFT results, which predict substantial charge redistribution and formation of strongly polarized adsorption complexes. Therefore, while Al₂O₃ is highly sensitive to NO₂ and SO₂ due to strong chemisorption, this same interaction inherently limits recovery speed and long-term stability, a trade-off widely recognized in alumina-based sensing and catalytic systems.

In contrast, gases that bound only weakly, such as CO₂ on all three oxides and NO₂/SO₂ on the ideal O-terminated TiO₂ (001) surface, exhibited minimal charge transfer and negligible modification of the electronic density of states. These signatures are characteristic of physisorption, as described in Ref. [45], which correlates with low adsorption energies with minor DOS perturbation and rapid desorption kinetics. The absence of stable adsorption geometries for CO₂ on TiO₂ (001) and SiO₂ (001) and for NO₂/SO₂ on TiO₂ (001) therefore indicates that these gases are expected to produce a very small sensing response on pristine, defect-free (001) surfaces.

It follows from our results that H₂O interacts strongly with Al₂O₃ (001) and TiO₂ (001), forming hydroxyl groups and leading to major changes in electron redistribution. However, the study in Ref. [43] on CO₂-induced wettability transitions shows that CO₂ can form surface films that partially screen hydroxyl groups and suppress hydrogen bonding.

Integrating this insight with our findings suggests that CO₂ and H₂O will compete for surface sites and will mutually perturb each other's adsorption behavior. This competition naturally leads to humidity-dependent baseline drift in sensor signals and explains the strong cross-sensitivity between CO₂ and H₂O reported in many oxide-based sensors.

Surface termination and defect chemistry also strongly influence gas absorption properties by solids. The lack of stable adsorption of NO₂, SO₂, and CO₂ on stoichiometric TiO₂ (001) aligns with literature (see, e.g., Refs. [43–45]) showing that these gases interact more strongly with Ti-terminated, defective, or metal-decorated TiO₂ surfaces. This suggests that ideal O-terminated (001) surfaces are intrinsically less reactive toward these molecules, whereas real sensor materials—typically containing oxygen vacancies, hydroxylation, dopants, or surface reconstructions—would exhibit much stronger binding and thus higher sensitivity. Such defect-driven enhancement is consistent with the mechanisms proposed in Ref. [44], where dopants and unsaturated sites significantly amplify adsorption and charge-transfer processes.

Overall, the integrated picture is that NO₂ and SO₂ show the strongest sensing potential on Al₂O₃ due to large charge-transfer-assisted chemisorption. TiO₂ (001) as modeled here is primarily sensitive to H₂O, but insensitive to the other gases unless defects or activating species are introduced. SiO₂ (001) exhibits selective interaction with SO₂ through sulfate formation, while remaining largely inert to CO₂, NO₂, and H₂O in the absence of surface hydroxylation or catalytic dopants. Taken together, the present results establish a consistent mechanistic framework for gas sensing across three technologically relevant oxides. Chemisorption-driven charge transfer governs high sensitivity but slow recovery, as observed for NO₂ and SO₂ on Al₂O₃ and SO₂ on SiO₂, whereas weak physisorption governs low sensitivity and fast recovery, as in the case of CO₂ on all three oxides and NO₂ and SO₂ on pristine TiO₂ (001). The strong influence of humidity and the competitive interplay between CO₂ and H₂O further highlight the critical role of surface hydroxylation and environmental conditions in shaping real-world sensor performance.

The weak response of CO₂ on all three pristine oxide surfaces further supports the broader mechanistic principle that intrinsically inert oxides require defect engineering or catalytic modification to sense CO₂ effectively. Because CO₂ adsorption on ideal Al₂O₃, TiO₂ (001), and SiO₂ (001) produced negligible DOS perturbation and minimal CT, the sensor lacked a mechanism to modulate surface conductivity. In contrast, experimentally high CO₂ sensitivity was observed only when surfaces contained oxygen vacancies, hydroxylation, transition-metal dopants, or supported catalytic clusters, all of which broke linearity or polarized the CO₂ molecule, enabling electron exchange and stronger chemisorption. These modifications effectively lowered the activation barrier for bending CO₂, created mid-gap states that coupled with CO₂ orbitals, and enhanced molecular polarization—mechanisms well documented in defect-rich TiO₂ and doped semiconducting oxides. Thus, our results confirm that CO₂ sensing is inherently defect-driven, and pristine stoichiometric surfaces form a necessary theoretical baseline for understanding and quantifying the role of such functionalization strategies.

4. Conclusions

This work provides a comparative first-principles assessment of gas adsorption on Al₂O₃, TiO₂, and SiO₂ surfaces, revealing material-specific affinities, electronic responses, and charge-transfer pathways. The adsorption energies consistently show strong chemisorption of SO₂ and NO₂ on Al₂O₃ and TiO₂, supporting their suitability for pollutant capture and sensing. TiO₂'s pronounced interaction with H₂O further highlights its relevance for photocatalytic water splitting and humidity-sensitive applications. Although SiO₂ remains largely inert, its unexpectedly strong SO₂ interaction indicates opportunities

for functionalized silica-based sensors. The uniformly weak CO₂ binding confirms that effective capture on these oxides will require surface modification strategies. Bader charge analyses deepen these insights by quantifying atom-resolved electron redistribution during adsorption. Strongly bound species such as SO₂ and NO₂ induce substantial charge transfer to surface cations (Al³⁺, Ti⁴⁺), accompanied by pronounced oxygen-site polarization, consistent with bond formation through electrophilic sulfur and nitrogen centers. In contrast, weakly bound molecules such as CO₂ exhibit minimal charge rearrangement, reinforcing their physisorptive character. For H₂O, Bader charges reveal clear signatures of hydroxyl formation on TiO₂ and Al₂O₃, whereas interaction with SiO₂ remains limited to modest hydrogen bonding. These charge-transfer fingerprints mechanistically link adsorption strength to expected conductivity changes, sensor response pathways, and humidity-induced electronic restructuring.

In summary, this study delivers the first cross-material, standardized DFT framework comparing CO₂, NO₂, SO₂, and H₂O adsorption on Al₂O₃ (001), TiO₂ (001), and SiO₂ (001). The results establish clear adsorption-energy hierarchies, intrinsic surface-chemistry-driven selectivity, and Bader charge signatures that distinguish strong chemisorption from weak physisorption across the three oxides. Importantly, the combined energetic and charge-transfer analysis clarifies how humidity and CO₂ competitively modulate surface hydroxylation and electronic structure—phenomena not addressed in previous literature yet critical for real-world gas-sensor stability and selectivity. Overall, the findings define a rigorous reference baseline for oxide–gas interactions and create a chemically consistent platform for future investigations involving defects, dopants, reconstructions, nanostructuring, and heterostructures, all of which can now be evaluated relative to these quantitatively benchmarked surfaces.

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