Detection of Carbon, Sulfur, and Nitrogen Dioxide Pollutants with a 2D Ca$_{12}$O$_{12}$ Nanostructured Material

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ABSTRACT: In recent times, nanomaterials have been applied for the detection and sensing of toxic gases in the environment owing to their large surface-to-volume ratio and efficiency. CO$_2$ is a toxic gas that is associated with causing global warming, while SO$_2$ and NO$_2$ are also characterized as nonbenign gases in the sense that when inhaled, they increase the rate of respiratory infections. Therefore, there is an explicit reason to develop efficient nanosensors for monitoring and sensing of these gases in the environment. Herein, we performed quantum chemical simulation on a Ca$_{12}$O$_{12}$ nanocage as an efficient nanosensor for sensing and monitoring of these gases (CO$_2$, SO$_2$, NO$_2$) by employing high-level density functional theory modeling at the B3LYP-GD3(BJ)/6-311+G-(d,p) level of theory. The results obtained from our studies revealed that the adsorption of CO$_2$ and SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage with adsorption energies of $-2.01$ and $-5.85$ eV, respectively, is chemisorption in nature, while that of NO$_2$ possessing an adsorption energy of $-0.69$ eV is related to physisorption. Moreover, frontier molecular orbital (FMO), global reactivity descriptors, and noncovalent interaction (NCI) analysis revealed that the adsorption of CO$_2$ and SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage is stable adsorption, while that of NO$_2$ is unstable adsorption. Thus, we can infer that the Ca$_{12}$O$_{12}$ nanocage is more efficient as a nanosensor in sensing CO$_2$ and SO$_2$ gases than in sensing NO$_2$ gas.

1. INTRODUCTION

Two-dimensional (2D) nanostructured materials are materials with sizes between 0.1 and 100 nm diameter and are used in the fabrication of nanodevices due to their high surface-to-volume ratio and good compatibility with the device architecture. Nanostructured materials are composed of in-plane bonds interwoven by weak van der Waals forces in a layered fashion. The uniqueness of these materials lies in the ability of modification through the rehybridization of orbitals and chemical bonds compared to their three-dimensional counterparts. 2D nanomaterials such as graphene hexagonal boron nitride and metal dichalcogenides have attracted lots of attention due to their satisfactory properties and widespread use in electronics, optoelectronics, catalysis, energy storage facilities, sensors, solar cells, lithium batteries, composites, etc. 2D nanomaterials can also be uniformly dispersed in water-based lubricants with successful modification. Due to their excellent properties, these materials find considerable applications. Several interesting properties have been reported for these materials. Recently, the magnetic homonuclear bonds in boron nitride nanosheets were reported in ref 11 using density functional theory (DFT) methods to examine the structural diversity of the considered nanostructured material. Their results demonstrated excellent stability and polarity, which was attributed to the magnetic moments of the homonuclear boron/nitrogen bond. The utilization of 2D boron nitride and its Ga- and Al-functionalized nanostructured composites as effective sensors of dichlorosilane was recently studied in ref 12. Their results revealed considerably stable adsorption of the studied gas onto the surface and show that functionalization with the metal atoms enhances the sensing attribute of the studied nanostructured materials. Also, the effectiveness of boron nitride nanostructured material has been investigated as a possible drug carrier for acetylsalicylic acid. The molecular electronic and structural properties of the complexes were considered by DFT methods. The surface was observed to bind effectively with the drug molecule via chemisorption and physisorption mechanisms and, as such, could deliver the considered drug molecule effectively. DFT studies were...
equally employed for the investigation of monolayer MoS\(_2\) and WSe\(_2\) as well as few-layered transition-metal adsorptions of CO, NH\(_3\), NO, and NO\(_2\). Only minimal changes in adsorption characteristics were observed for the different studied gases regardless of significant changes in the electronic structure and properties orchestrated by band gap variations. Overall, the studied surfaces adsorbed NO\(_2\) preferentially when compared to other counterparts.\(^\text{15}\)

NO\(_3\), SO\(_2\), and CO\(_2\) are important ambient air pollutants and are highly intense in confined spaces, causing global challenges, which contribute to global warming, and they are toxic pollutant gases with pungent smell. Exposure to them might likely cause severe injury and perhaps result in death, depending on the degree of exposure. Nitrogen oxide (NO\(_2\)) and CO\(_2\) constitute the main air pollutants, which result from combustion from power plants, vehicles, and several industrial processes. The presence of these gases in the atmosphere increases the risk of respiratory tract infections.\(^\text{15}\) SO\(_2\) is the main air pollutant released mostly as a result of the industrial operation as well as coal and oil burning.\(^\text{18}\) However, it is an indirect greenhouse gas because it is coupled with elemental carbon to form aerosols. Eliminating these gases completely from the environment has been difficult for scientists and researchers for some decades, which is why an insight into the adsorption mechanism and potential of various efficient surfaces is still required; computational screening helps immensely in this regard. Recently, layered materials of different dimensions have attracted considerable attention due to their demonstrated potential as sensors,\(^\text{17}\) supercapacitors,\(^\text{18}\) catalyst,\(^\text{19}\) and nanovehicles.\(^\text{20}\) These materials continuously appear in scientific publications and conferences due to their high surface-to-volume ratio and high mechanical and chemical stability.

Therefore, motivated by these reports, an attempt is put forward herein to investigate the efficacy of calcium oxide (Ca\(_{12}\)O\(_{12}\)) nanostructured material as an efficient nanosensor of selected atmospheric gases (NO\(_2\), SO\(_2\), and CO\(_2\)). Appropriate quantum chemical calculations have been employed herein to arrive at various conclusions on the subject matter. The famous B3LYP with D3 dispersion of Grimme’s has been utilized together with the split valence basis set 6-311+G(d,p) of John Popple. Molecular properties such as the frontier molecular orbital (FMO) method, which reveal molecular stability and electronic interactions with the external environment, are also considered; the adsorption behavior of the surface toward the studied gases has been considered appropriately. The susceptibility of intermolecular interactions of the adsorbate gases and the adsorbent surface is revealed by the natural bond orbital analysis, quantum theory of atoms in molecule (QTAIM), and noncovalent interaction based on the reduced density gradient model. These objectives have carefully been considered to address the formulated research questions, which are as follows: (1) Do Ca\(_{12}\)O\(_{12}\) nanocages possess the required surface-to-volume ratio to adsorb the studied gases? (2) If yes, what is the extent or affinity of Ca\(_{12}\)O\(_{12}\) toward the considered gases? (3) Which among the studied gases is preferentially (selectively) adsorbed by the studied surface? (4) What type of adsorption mechanism is exhibited by the adsorbent surface and how does the energy gap of the surface change upon the preferential adsorption of the considered gases? To address these questions, several adsorption configurations of Ca\(_{12}\)O\(_{12}\) nanocages with the respective gases have been investigated to evaluate the efficacy and potency of the surface to detect these pollutants.

2. COMPUTATIONAL DETAILS

Geometry optimization of all of the investigated gases and nanocages was conducted using the density functional theory (DFT) method at the B3LYP-GD3(BJ)/6-311+G(d,p) level of theory and was accomplished with the aid of the Gaussian 16 software program.\(^\text{21}\) B3LYP-GD3(BJ), which is an exchange–correlation functional with the D3 version of Grimme’s dispersion correction encompassing the famous Becke–Johnson damping was utilized for this study as it serves best for accurately predicting weak interactions and also mostly applied for adsorption studies as seen in reported works of several authors.\(^\text{22,23}\) We also ensured that the optimized structures attained local minima on the potential energy surface by taking into consideration frequency calculations at the same level of theory, and this was confirmed by the absence of imaginary frequencies. The Frontier molecular orbital (FMO) analysis was carried out to verify the stability of the isolated nanocage and gas-adsorbed nanocages. Natural bond orbital (NBO) analysis was also performed on the studied systems with the aid of the NBO 7.0 module\(^\text{24}\) embedded in Gaussian 16 software code. The density of states (DOS) was established using Multiwfn 3.7 dev\(^\text{25}\) and GaussSum\(^\text{26}\) software. Molecular electrostatic potential (ESP) was performed using Multiwfn 3.7 dev, and the generated files were exported to VMD 1.9.3\(^\text{27}\) software for visualization. Quantum theory of atoms in the molecule (QTAIM) topological analysis was also evaluated with the help of Multiwfn software package. Furthermore, the weak interaction involved during the adsorption studies was characterized by the noncovalent interaction (NCI) method using Multiwfn 3.7 dev and Gnuplot\(^\text{28}\) software program.

Here, the relationship between electrical conductivity and \(E_g\) can be seen in eq 1.\(^\text{29–51}\)

\[
sigma = \sigma_0 \exp(-E_g/2kT)
\] (1)

where \(\sigma\) is electrical conductivity, \(k\) signifies the Boltzmann constant, and \(E_g\) is the energy gap.

Global reactivity descriptors were estimated based on Koopmans approximation using the following equations\(^\text{32–34}\)

\[
\begin{align*}
\text{IP} & = -E_{\text{HOMO}} \\
\text{EA} & = -E_{\text{LUMO}} \\
\eta & = \frac{I - A}{2} \\
S & = \frac{I}{2}\eta \\
\chi & = -\mu = \frac{I + A}{2} \\
\omega & = \mu \eta
\end{align*}
\] (2)–(7)

where \(\eta\), \(S\), \(\chi\), and \(\omega\) are chemical hardness, softness, electrophilicity, and nucleophilicity, respectively. Adsorption energies of the studied gases adsorbed on the respective nanocages were also computed using eq 8.\(^\text{35,36}\)

\[
E_{\text{ads}} = E_{\text{cage/gas}} - E_{\text{cage}} - E_{\text{gas}} + \Delta E_{\text{BSSE}} + \Delta E_{\text{ZPE}}
\] (8)
Energy adsorption is presented in eq 10

\[ \Delta E = \Delta E_{\text{cluster}} - \Delta E_{\text{gas}} - \Delta E_{\text{cage}} \] (9)

The transition between the recovery time of a sensor and adsorption energy is presented in eq 10

\[ \tau = \nu_0 \exp \left( \frac{-E_{\text{ads}}}{kT} \right) \] (10)

where \( \tau \) is the recovery time, \( \nu_0 \) is the attempt frequency and its value is taken as \( 10^{-12} \) s\(^{-1} \) as reported by several authors, \( E_{\text{ads}} \) denotes adsorption energy, \( k \) and \( T \) represent Boltzmann’s constant \( (8.62 \times 10^{-5} \text{ eV/K}) \) and temperature \( (30 \text{ s 0 K}) \), respectively. The optimized geometry of the studied gases is presented (Figure 1).

### 3. RESULTS AND DISCUSSION

#### 3.1. Geometric and Structural Analysis

Geometry optimization of Ca\(_{12}\)O\(_{12}\) nanocages was evaluated using the DFT/B3LYP-GD3(BJ)/6-311+G(d,p) method. The studied Ca\(_{12}\)O\(_{12}\) nanocage comprises eight hexagonal rings and six tetragonal rings, as shown in Figure 2. The Ca–O bond consists of two bonds, namely, a Ca–O bond between a hexagonal ring and a tetragonal ring, and a Ca–O bond between two hexagonal rings. The Ca–O bond length existing between the two hexagonal rings was found to be 2.158 Å, while the Ca–O bond length exhibited between a hexagonal and a tetragonal was 2.197 Å. Initially, the adsorption of the studied gases (CO\(_2\), SO\(_2\), NO\(_2\)) on the Ca\(_{12}\)O\(_{12}\) nanocage was evaluated at different positions on the studied nanocage. The considered positions are as follows: on the center of the tetragon, on the center of the hexagon, on the and bonds, and on top of Ca and O atoms. However, after optimization of the adsorbed gases at different positions, the results show that the adsorbed gases preferred to be adsorbed on top of the Ca and O atoms as a result of the high electropositive and electronegative nature of the Ca and O atoms, respectively. Thus, the highly electronegative oxygen atoms present in the gases bind on top of the highly electropositive Ca atom, while the less electronegative atoms like sulfur and carbon atoms find its route on top of the O atom of the nanocage with the only exception of the nitrogen atom of the NO\(_2\) gas, which preferred to bind to the Ca atom as a result of its high electronegativity close to that of the O atom present in the cage. Moreover, after adsorption of the gases (CO\(_2\), SO\(_2\), NO\(_2\)) on the Ca\(_{12}\)O\(_{12}\) nanocage, Ca–O bond lengths were found to increase. This elongation of the Ca–O bond length is a result of charge transfer from the adsorbed gas to the Ca\(_{12}\)O\(_{12}\) nanocage, which is confirmed by their transferred charge having a negative value as also reported in the literature. For the CO\(_2@\text{Ca}_{12}\text{O}_{12}\) nanocage, the bond existing between the Ca\(_{23}\)–O bond increased from 2.197 to 2.457 Å, while the bond between Ca\(_{14}\)–O was observed to increase from 2.158 to 2.211 Å with a \( Q_{\text{NBO}} \) charge of −0.722 e being transferred from the CO\(_2\) gas to the Ca\(_{12}\)O\(_{12}\) nanocage. Similarly, for the SO\(_2@\text{Ca}_{12}\text{O}_{12}\) nanocage, the bond between Ca\(_{15}\)–O was seen to increase from 2.197 to 2.477 Å, while the bond between Ca\(_{33}\)–O\(_2\) elongated from 2.158 to 2.159 Å as a result of a \( Q_{\text{NBO}} \) charge of −0.532 e transferred from SO\(_2\) gas to the Ca\(_{12}\)O\(_{12}\) nanocage. Lastly, for NO\(_2@\text{Ca}_{12}\text{O}_{12}\) the bond between Ca\(_{23}\)–O was elongated from 2.158 to 2.159 Å with a \( Q_{\text{NBO}} \) charge of −0.521 e transferred from NO\(_2\) gas to the Ca\(_{12}\)O\(_{12}\) nanocage.

Figure 1. Optimized geometry of the studied gases at the B3LYP-D3 GD3(BJ)/6-31G(d) theory level.

Figure 2. Relaxed geometry of the studied nanocages with atomic labeling and selected bond distances.
O₂ depicted an increase from 2.197 to 2.477 Å, while that of the bond occurring in Ca₁₂₋₃O₆ manifested an increase from 2.158 to 2.171 Å, with −0.125 e charge being transferred from NO₂ gas to the Ca₁₂O₁₂ nanocage. In all cases, the studied nanocages maintained singlet multiplicity and zero net charge, thus maintaining structural stability (Table 1).

Table 1. Structural Properties of the Studied Systems; Bond Length of Adsorption (d_ads), Bond Length between Hexagonal and Tetragonal Rings (r₆₄), Bond Length between Two Hexagonal (r₆₆)

| structure | d_ads Å | r₆₄ Å | r₆₆ Å |
|-----------|---------|-------|-------|
| Ca₁₂O₁₂   |         |       |       |
| CO₂@Ca₁₂O₁₂ | 2.197 | 2.158 |
| SO₂@Ca₁₂O₁₂ | 2.282 | 2.171 |

The Fermi level of −4.5888 eV. At this end, the large energy gap of CO₂@Ca₁₂O₁₂ and SO₂@Ca₁₂O₁₂ nanocages compared to that of the isolated Ca₁₂O₁₂ nanocage reflects the stable adsorption of CO₂ and SO₂ gas on the Ca₁₂O₁₂ nanocage, while the low energy gap value of the NO₂@Ca₁₂O₁₂ nanocage compared to the isolated Ca₁₂O₁₂ nanocage indicates unstable adsorption of the NO₂ on the Ca₁₂O₁₂ nanocage with Eₕ value less than 4 eV. From this line of reasoning and variations in the energy gap among the preferential adsorption of the respective gases, we can infer that the Ca₁₂O₁₂ nanocage is a better nanosensor for sensing CO₂ and SO₂ gases than NO₂ gas. This can be further confirmed based on the relationship of energy gap with electrical conductivity and the notion that potentiometric and voltammetric sensors are designed in line with either an increase or decrease in the energy gap upon adsorption.⁵⁴ The increase/decrease in the energy gap prior to adsorption could also suggest a possible transition of the Ca₁₂O₁₂ nanocage from an insulator to a semiconductor and therefore could also facilitate the better sensing attributes exhibited in the case of CO₂ and SO₂ adsorption. However, NO₂ could also be sensed by the studied nanocage; nonetheless, the unfavorable nature of the adsorption by virtue of the dramatic decrease in energy gap, which is directly related to a decrease in conductivity, makes the adsorption process unfavorable and thus hinders the stability of the nanocage during the adsorption process. The exact reduction in energy gap was observed to be 2.1% for NO₂@Ca₁₂O₁₂, which is dramatic in comparison with CO₂ (0.0615%) and SO₂ (0.0632%) adsorption and therefore further validates the unfavorable adsorption nature of this system. To confirm that charge was transferred from the adsorbed atmospheric pollutants (CO₂, SO₂, NO₂) to the Ca₁₂O₁₂ nanocage, as reported in Section 3.1, we visualized their HOMO–LUMO plots, as seen in Figure 3. As evident from the plot, the HOMO of the isolated Ca₁₂O₁₂ nanocage is concentrated only on the oxygen atoms of the nanocage, while the LUMO is evenly distributed on the oxygen and calcium atoms of the isolated Ca₁₂O₁₂ nanocage. The HOMOs of the gas-adsorbed nanocages are localized only on the adsorbed gases (CO₂, SO₂, NO₂), while the LUMOs are majorly distributed on the Ca₁₂O₁₂ nanocage. Thus, validating that charge was transferred from the adsorbed gases to the Ca₁₂O₁₂ nanocage. Moreover, as reported previously, energy gap (Eₕ) determines the electrical conductivity of a system in the sense that as the energy gap decreases, the electrical conductivity of the system increases, while as the energy gap increases, its electrical conductivity decreases. The relationship between these two terms is summarized in eq 1.

3.3. Global Reactivity Descriptors. Global reactivity descriptor was also considered in this study to confirm the chemical reactivity and natural stability of the studied isolated and gas-adsorbed nanocages. According to Koopmans’
theorem, global reactivity descriptor parameters such as ionization potential (IP), electron affinity (EA), global hardness ($\eta$), global softness ($S$), chemical potential ($\mu$), electronegativity ($\chi$), and electrophilicity ($\omega$) are essential for characterizing the reactivity and stability of a compound. Global reactivity descriptors of the studied systems estimated at the DFT/B3LYP-GD3(BJ)/6-311+G(d,p) level are presented in Table 3. Here, the ionization potential is related to the negative of the HOMO energy, while electron affinity is tagged to the negative of the LUMO energy. From the table, the ionization potential of Ca$_{12}$O$_{12}$, CO$_2$@Ca$_{12}$O$_{12}$, SO$_2$@Ca$_{12}$O$_{12}$, and NO$_2$@Ca$_{12}$O$_{12}$ nanocages were 5.1114, 5.3900, 5.4012, and 5.6023 eV with corresponding electron affinity values of 0.9938, 1.2109, 1.2204, and 3.5753 eV, respectively. As clearly seen from the result, the gas-adsorbed nanocages were observed to demonstrate higher IP and EA values compared to the isolated Ca$_{12}$O$_{12}$ nanocage. This implies that proper charge transfer took place within the gas-adsorbed nanocages than within the isolated Ca$_{12}$O$_{12}$ nanocage. In addition, the NO$_2$@Ca$_{12}$O$_{12}$ nanocage exhibited the highest ionization and electron affinity among the studied systems as a result of its highest HOMO and LUMO energy values, respectively. Global hardness and global softness aid in explicitly explaining the nature of chemical reactivity and the natural stability of a compound. The higher the value of global hardness, the less reactive and more stable a compound is, while a high value of global softness represents a greater reactivity and less stability for the compound. From our study, the SO$_2$@Ca$_{12}$O$_{12}$ nanocage demonstrated the highest global hardness (2.0904 eV) and the least global softness (0.2392 eV$^{-1}$) values, followed by the CO$_2$@Ca$_{12}$O$_{12}$ nanocage with respective global hardness and softness values of 2.0896 eV and 0.2393 eV$^{-1}$, respectively, while the NO$_2$@Ca$_{12}$O$_{12}$ nanocage exhibited the least and highest global hardness (1.0135 eV) and softness values (0.4933 eV$^{-1}$), respectively. From this result, we can infer that the adsorption of SO$_2$ and CO$_2$ gases on the Ca$_{12}$O$_{12}$ nanocage is stable adsorption, while the adsorption of NO$_2$ gas is unstable adsorption. Thus, the Ca$_{12}$O$_{12}$ nanocage is a better nanosensor for sensing SO$_2$ and CO$_2$ gases than for sensing NO$_2$ gas. This clear observation is also in tandem with the results of the frontier molecular orbital analysis. Chemical potential also gives important information on the reactivity of a particular compound with respect to polarizability. A high value of chemical potential for a compound indicates that the compound can easily be polarized in the presence of an external electric field or chemical reagent, while a low value in chemical potential suggests a lower effect of the external electric field or chemical reagent on polarizing the compound. In this lane, the NO$_2$@Ca$_{12}$O$_{12}$ nanocage also showed the highest value of chemical potential ($-4.5888$ eV) than all of the studied nanocages, indicating that it is the most reactive and unstable system compared to other studied nanocages.

Table 3. Global Reactivity Descriptors of the Examined Nanocages

| structure       | IP  | EA  | $\eta$ (eV) | $S$ (eV$^{-1}$) | $\mu$ (eV) | $\chi$ (eV) | $\omega$ (eV) |
|-----------------|-----|-----|-------------|----------------|------------|-------------|---------------|
| Ca$_{12}$O$_{12}$ | 5.1114 | 0.9938 | 2.0588 | 0.2429 | -3.0526 | 3.0526 | 2.2631 |
| CO$_2$@Ca$_{12}$O$_{12}$ | 5.3900 | 1.2109 | 2.0896 | 0.2393 | -3.3005 | 3.3005 | 2.6066 |
| SO$_2$@Ca$_{12}$O$_{12}$ | 5.4012 | 1.2204 | 2.0904 | 0.2392 | -3.3108 | 3.3108 | 2.6218 |
| NO$_2$@Ca$_{12}$O$_{12}$ | 5.6023 | 3.5753 | 1.0135 | 0.4933 | -4.5888 | 4.5888 | 10.3883 |

Figure 3. HOMO–LUMO plot of the studied systems.
systems. This result also is in total agreement with the FMO and global softness and hardness results. Next, electronegativity and electrophilicity can also be utilized to characterize the reactivity of a compound. More specifically, electronegativity is the tendency of a particular compound to give out electrons. The studied Ca$_{12}$O$_{12}$, CO$_2$@Ca$_{12}$O$_{12}$, SO$_2$@Ca$_{12}$O$_{12}$, and NO$_2$@Ca$_{12}$O$_{12}$ nanocages adopted electronegativity values of 3.0526, 3.3005, 3.3108, and 4.5888 eV, respectively. This result obtained reflects that the NO$_2$@Ca$_{12}$O$_{12}$ nanocage brilliantly exhibited the highest value of electronegativity, indicating that it can give out electrons easily, and this can be attributed to the high electronegativity value of the N atom present on the sensed NO$_2$ gas, while the isolated Ca$_{12}$O$_{12}$ nanocage exhibited the least value of electronegativity. Electrophilicity, which is another global reactivity descriptor, is related to how prone a compound is to electrophilic attack. The investigated Ca$_{12}$O$_{12}$, CO$_2$@Ca$_{12}$O$_{12}$, SO$_2$@Ca$_{12}$O$_{12}$, and NO$_2$@Ca$_{12}$O$_{12}$ systems unveiled electrophilicity values of 2.2631, 2.6066, 2.6218, and 10.3883 eV, respectively. As observed from the result, it is explicitly seen that the NO$_2$@Ca$_{12}$O$_{12}$ nanocage exhibited the highest electrophilicity value, which highlights that it is the most prone system toward electrophilic attack, while CO$_2$@Ca$_{12}$O$_{12}$ and SO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocages that exhibited low electrophilicity values are less susceptible to electrophilic attack compared to the NO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocage. Thus, the result from global reactivity descriptors also classified the adsorption of CO$_2$ and SO$_2$ on Ca$_{12}$O$_{12}$ as stable adsorption, while adsorption of NO$_2$ as unstable adsorption.

3.4. NBO Analysis. To validate the nature of the donor–acceptor orbital interaction persisting between the adsorbed gases on the selected nanocage, we employed the natural bond orbital (NBO) analysis to this effect. The NBO method serves as an approach for narrowing down the complex Schrödinger equation to a simple chemical bonding concept for its users to assimilate. In addition, NBO analysis also gives a good highlight on the intermolecular charge transfer and electron delocalization taking place between the adsorbed gases and the studied nanocage. In this study, NBO analysis was established using the DFT/B3LYP-GD3 (Bj)/6-311+G(d,p) method. The strength of interaction occurring between the donor and acceptor orbital is characterized by stabilization energy ($E^i$). The more intense the donor–acceptor orbital interaction, the higher the value of stabilization energy. The stabilization energy experienced by the donor–acceptor orbitals of the studied systems was calculated in line with our previous work. The stabilization energy constituting the most interacting donor–acceptor orbitals of the studied systems is shown in Table 4. From the result, the isolated Ca$_{12}$O$_{12}$ nanocage was found to exhibit the bonding donor–acceptor interaction of $\sigma^*$ to $\sigma^*$ and the nonbonding interaction of LP $\rightarrow$ LP*. Systematically, the $\sigma$ to $\sigma^*$ bonding interaction was observed between the donor and acceptor orbitals of $\sigma$O$_1$→Ca$_{12}$, $\sigma$O$_3$→Ca$_{12}$, and $\sigma$O$_{15}$→Ca$_{12}$ with respective stabilization energies of 2.73 and 1.49 kcal/mol, while the LP $\rightarrow$ LP* donor–acceptor orbital interaction was seen in LP(2) O$_1$ $\rightarrow$ $\sigma$O$_{15}$→Ca$_{12}$ LP(1) O$_1$ $\rightarrow$ $\sigma$O$_{15}$→Ca$_{12}$ and LP(3) O$_1$ $\rightarrow$ $\sigma$O$_{15}$→Ca$_{12}$ with an individual stabilization energy value of 2.35, 1.88, and 1.06 kcal/mol, respectively. Thus, LP $\rightarrow$ LP* constitutes most of the stabilization energy values that aid in stabilizing the isolated Ca$_{12}$O$_{12}$ nanocage.

However, for the CO$_2$@Ca$_{12}$O$_{12}$ nanocage, the most persisting interactions were obvious from the donor–acceptor orbitals of LP $\rightarrow$ LP*, $\pi^*$ $\rightarrow$ LP, $\pi^*$ $\rightarrow$ $\sigma^*$, and $\pi^*$ $\rightarrow$ LP*. The LP $\rightarrow$ LP* nonbonding interaction was visible in LP(3) O$_{15}$ $\rightarrow$ LP(1) C$_{27}$ and LP(4) O$_2$ $\rightarrow$ LP(1) C$_{27}$ donor–acceptor orbitals with specific stabilization energies of 379.03 and 21.40 kcal/mol, respectively. The $\pi^*$ $\rightarrow$ LP interaction was demonstrated by $\sigma$O$_{25}$→C$_{27}$ $\rightarrow$ LP(3) O$_{26}$ having a stabilization energy of 39.84 kcal/mol. The $\pi^*$ $\rightarrow$ LP* antibonding interaction was observed between the donor and acceptor orbital of $\pi^*$O$_{25}$→C$_{27}$ $\rightarrow$ $\sigma$O$_{25}$→C$_{27}$ with a stabilization energy of 19.65 kcal/mol. The LP $\rightarrow$ LP* interaction is depicted between the donor and acceptor orbitals of $\pi^*$O$_{25}$→C$_{27}$ $\rightarrow$ LP(1) C$_{23}$ possessing a stabilization energy value of 13.57 kcal/mol. From this result, it can be seen that the nonbonding interaction of LP $\rightarrow$ LP* donor–acceptor orbitals contributed to the most in stabilizing the CO$_2$@Ca$_{12}$O$_{12}$ nanocage.

Similarly, for the SO$_2$@Ca$_{12}$O$_{12}$ nanocage, the most probable interaction was observed in LP $\rightarrow$ $\sigma^*$, LP $\rightarrow$ LP*, $\sigma^*$ $\rightarrow$ $\sigma^*$, and $\sigma^*$ $\rightarrow$ LP* donor–acceptor orbitals. The nonbonding interaction was noticed between the donor–acceptor orbitals of LP(3) O$_{27}$ $\rightarrow$ $\sigma$O$_{25}$→S$_{25}$ LP(3) O$_{26}$ $\rightarrow$ $\sigma$O$_{25}$→S$_{25}$, LP(2) O$_8$ $\rightarrow$ LP(1) C$_{15}$ and $\sigma$S$_{25}$→O$_{26}$ $\rightarrow$ LP(1) C$_{33}$ adopting individual stabilization energies of 72.94, 27.59, 7.44, and 0.74 kcal/mol, respectively, while the antibonding interaction was seen in the $\sigma^*$O$_{25}$→S$_{25}$ $\rightarrow$ $\sigma^*$O$_{25}$→S$_{25}$ donor–acceptor orbital exhibiting a stabilization energy of 9.00 kcal/mol.

### Table 4. Second-Order Perturbation Theory Analysis of the Most Interacting Donor–Acceptor NBO of the Studied Nanocages

| Ca$_{12}$O$_{12}$ | $\sigma_1$ (a.u.) | $\sigma_1$ (a.u.) | $\sigma_1$ (a.u.) |
|------------------|-------------------|-------------------|-------------------|
| donor (i) acceptor (j) | $E^{(1)}$ (kcal/mol) | $E^{(2)}$ (kcal/mol) | $E^{(3)}$ (kcal/mol) |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 2.73 | 2.35 | 1.06 |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 1.88 | 1.49 | 1.06 |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 1.49 | 1.06 | 1.06 |

| CO$_2$@Ca$_{12}$O$_{12}$ | $\sigma_1$ (a.u.) | $\sigma_1$ (a.u.) | $\sigma_1$ (a.u.) |
|------------------|-------------------|-------------------|-------------------|
| donor (i) acceptor (j) | $E^{(1)}$ (kcal/mol) | $E^{(2)}$ (kcal/mol) | $E^{(3)}$ (kcal/mol) |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 379.03 | 72.94 | 16.11 |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 27.59 | 6.09 | 0.74 |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 7.44 | 0.22 | 0.03 |

| SO$_2$@Ca$_{12}$O$_{12}$ | $\sigma_1$ (a.u.) | $\sigma_1$ (a.u.) | $\sigma_1$ (a.u.) |
|------------------|-------------------|-------------------|-------------------|
| donor (i) acceptor (j) | $E^{(1)}$ (kcal/mol) | $E^{(2)}$ (kcal/mol) | $E^{(3)}$ (kcal/mol) |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 9.00 | 0.74 | 0.03 |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 0.74 | 0.03 | 0.03 |
| $\sigma_1$ $\rightarrow$ $\sigma_1$ | 0.03 | 0.03 | 0.03 |
6.09 kcal/mol. As evident from this result, we can infer that the LP → σ* donor–acceptor interaction contributed the most to the stabilization of the SO₃@Ca₁₂O₁₂ gas-adsorbed nanocage. Moreover, for the NO₃@Ca₁₂O₁₂ gas-adsorbed nanocage, the strongest interactions were exhibited by LP → LP*, LP → σ, σ → σ, and σ → LP* transitions. The nonbonding type of interaction was obvious between the donor–acceptor orbitals of LP(3) O₂₅ → LP*(1) Ca₂₃, LP(2) O₂₆ → σO₂₅–N₇₂, LP(1) N₇₂ → LP*(1) Ca₂₃ and σO₂₅–N₇₂ → LP*(1) Ca₂₃ with stabilization energies of 16.11, 6.52, 0.22, and 0.03 kcal/mol, respectively, whereas the bonding interaction was observed between the donor–acceptor orbital of σO₂₅–N₇₂ → σO₂₅–N₇₂ with a stabilization energy of 1.69 kcal/mol. At this end, we can draw an inference that the LP → LP* transition contributed mostly to stabilizing the NO₃@Ca₁₂O₁₂ nanocage.

3.5. Density of States (DOS). The density of states plots have been utilized to further give insight into the charge density transfer arising from intermolecular interactions of the gases with the nanostructured surface. Partial density of states (PDOS) explicates the contributions of individual atomic and molecular orbitals to distinct quantum states in the studied nanostructured materials. The conductivities of the surfaces are also revealed from the DOS plots more explicitly. The PDOS of the surface along with the adsorbed gases is shown in Figure 4, while the energy gap and total DOS are shown in Figure 5. The s, p, and d orbitals are observed to contribute the maximum to the HOMO energies in the PDOS plots of the nanosurface, while the LUMO has its maximum contributions from the s- and p-hybridized orbitals. In the three different adsorption configurations of the adsorbed gases on the nanosurfaces, the electronic hybridization from the atomic orbitals was observed to change considerably with major contributions from the d and s atomic orbitals to the LUMO, while the HOMO was observed to be dominant in the adsorbed gases and to be absent in the surface of the adsorbed cases, signifying significant charge density delocalization from the surface to the gas fragments and vice versa. Prior to adsorption of the gases (CO₂, NO₂, SO₃) on the Ca₁₂O₁₂ nanocage, negative LUMO density was observed to be dominant in the ring cage, whereas after the adsorption of the gases, the LUMO density was observed to change considerably, and the LUMO at the nanocage centers changed to positive density, thus confirming the electron density transfer from the surface to the gases. The HOMO in all cases for the adsorbed nanocages is localized majorly in the CO₂, NO₂, and SO₃ fragments. This result clearly shows that the delocalization of charge density occurs upon the adsorption of CO₂, NO₂, and SO₃, and considerable changes in energy gap, as shown in Figure 4b, were observed in both the PDOS and total DOS plots, thus affirming the sensitivity of the surface to the adsorbed gases.

3.6. Molecular Electrostatic Potential Analysis. The visualization of molecular electrostatic potential surfaces is highly essential for the wholistic comprehension of electron density localization, biointeraction, hydrogen bonding interactions, and the detection of potential reactive sites in molecules. Regions of high electron densities are explicated by low values of electrostatic potential, and high ESP values often express the relative absence of electron density. To understand and predict the most susceptible regions of both nucleophilic and electrophilic adsorption sites, the ESP isosurface plot was obtained from the B3LYP/6-311+G(d,p) optimized geometry. The molecular electrostatic potential (MEP) isosurface is shown in Figure 6. It clearly shows that the negative electrostatic density regions are localized on the oxygen atoms of the clusters, sulfate, carbonate, and nitrate...
anions adsorbed on the nanocages, while the electropositive zones are located on the metal centers of the nanoclusters, in accordance with the Mulliken population distribution. The regions of low electrostatic potential density are marked in blue, while the negative ESP regions are marked in red. The ESP isosurface clearly shows that regions of high electron density, which could act as potential adsorption sites, are localized on the oxygen atoms of the nanoclusters, whereas the region with the strongest attraction potential is the red-colored surface on the nanocluster and exhibits a high propensity for electrophilic adsorption. Positive ESP regions marked in white are minimally dispersed in between the metal centers and oxygen atoms of the adsorbed gases.

Figure 5. DOS of (a) the isolated Ca\textsubscript{12}O\textsubscript{12} nanocage, (b) the CO\textsubscript{2}@Ca\textsubscript{12}O\textsubscript{12} gas-adsorbed nanocage, (c) the SO\textsubscript{2}@Ca\textsubscript{12}O\textsubscript{12} gas-adsorbed nanocage, (d) the NO\textsubscript{2}@Ca\textsubscript{12}O\textsubscript{12} gas-adsorbed nanocage revealing their energy gap and contributions in the HOMO and LUMO orbital.

Figure 6. Molecular electrostatic potential isosurfaces of (a) the CO\textsubscript{2}@Ca\textsubscript{12}O\textsubscript{12} gas-adsorbed nanocage, (b) the SO\textsubscript{2}@Ca\textsubscript{12}O\textsubscript{12} gas-adsorbed nanocage, and (c) the NO\textsubscript{2}@Ca\textsubscript{12}O\textsubscript{12} gas-adsorbed nanocage.
3.7. Adsorption of CO₂, SO₂, and NO₂ on the Ca$_{12}$O$_{12}$ Nanocage. Adsorption energy ($E_{ads}$) and thermodynamic parameters were also evaluated to confirm the type of adsorption and the feasibility of adsorption of the studied gases on the Ca$_{12}$O$_{12}$ nanocage during the adsorption process. In this present study, adsorption energy and thermodynamics parameters of the investigated gas-adsorbed nanocages were evaluated using the DFT/B3LYP-GD3(BJ)/6-31+G(d,p) theory level. As obvious from our result presented in Table 5, it is clearly observed that all of the gas-adsorbed nanocages exhibited negative values of adsorption energy, signifying a favorable adsorption process. Also, taking into consideration the calculated thermodynamics parameters such as enthalpy of adsorption ($\Delta H$), Gibb's free energy of adsorption ($\Delta G$), and entropy of adsorption ($\Delta S$) of the gas-adsorbed nanocages, the adsorption of all of the studied gases presented negative values of $\Delta H$ and $\Delta G$, while the $\Delta S$ value was positive. This result revealed that the adsorption process of the studied gases on the Ca$_{12}$O$_{12}$ nanocage is favorable and spontaneous. Here, the $E_{ads}$ of CO$_2$@Ca$_{12}$O$_{12}$ was $-2.01$ eV with $\Delta H$, $\Delta G$, and $\Delta S$ values of $-55.44$, $-41.20$ kcal/mol, and 457.84 kcal/mol K$^{-1}$, respectively. Next, the adsorption of SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage exhibited an $E_{ads}$ value of $-5.85$ eV, possessing individual $\Delta H$, $\Delta G$, and $\Delta S$ values of $-132.02$, $-123.04$ kcal/mol, and 463.11 cal/mol K$^{-1}$, respectively. Moreover, the adsorption of NO$_2$ on the Ca$_{12}$O$_{12}$ nanocage exhibited an $E_{ads}$ value of $-0.69$ eV having $\Delta H$, $\Delta G$, and $\Delta S$ values of $-24.63$, $-15.82$ kcal/mol, and 465.14 cal/mol K$^{-1}$, respectively. To sum up, we can infer that the high adsorption energy of CO$_2$@Ca$_{12}$O$_{12}$ and SO$_2$@Ca$_{12}$O$_{12}$ can be related to chemisorption, while low adsorption energy of NO$_2$@Ca$_{12}$O$_{12}$ corresponds to physisorption; this is consistent with other studies. Thus, this result is also in tandem that the adsorption of CO$_2$ and SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage is stable adsorption, while that of NO$_2$ adsorption is unstable adsorption.

3.8. Quantum Theory of Atoms in Molecule (QTAIM). Quantum theory of atoms in molecule is a paramount quantum mechanics tool used for analyzing the type of chemical interaction and strength of the interaction occurring between two bonded atoms. QTAIM provides adequate information on the type of inter- and intramolecular interactions such as covalent (shared) interaction and noncovalent (closed shell) interactions, e.g., electrostatic interaction, van der Waals interaction, and hydrogen bond interaction that is evident between two bonded atoms. Also, QTAIM depends fully on the electron density or charge distribution present in the chemical bond interaction in the sense that a decrease in in the electron density corresponds to a closed-shell interaction, while an increase in electron density is in relation to a covalent (shared) interaction. Herein, Bader's topological analysis was utilized for characterization of the nature and strength of chemical bond interaction and electron density distribution between the sensed gases and the Ca$_{12}$O$_{12}$ nanocage at the DFT/B3LYP-GD3(BJ)/6-31+G(d,p) level of theory using the Multifunc software package. The B3LYP-GD3(BJ) hybrid exchange–correlation functional with D3 version of Grimme’s dispersion correction incorporated with Becke–Johnson damping correction was employed for the characterization of these interactions due to the fact that it can accurately predict weak interactions. As proposed by Bader, two or more atoms involved in an intra- and intermolecular interaction are linked by a bond path. In the same line, a saddle point along the bond path, which indicates an area of maximum distribution of electron density, is associated with the bond critical point (BCP). Several parameters can be obtained from a bond critical point between two or more interacting atoms, which is crucial for characterizing the nature and strength of a chemical bond interaction. A few among those parameters are electron density $\rho(r)$, Laplacian of electron density $\nabla^2 \rho(r)$, Lagrangian kinetic energy $G(r)$, potential energy density $\nabla \cdot V(r)$, total energy density $H(r)$, electron localization function (ELF), localized orbital locator (LOL), bond ellipticity ($\varepsilon$), and eigenvalues of the diagonalized Hessian matrix ($\lambda_1$, $\lambda_2$, $\lambda_3$). More importantly, from the abovementioned parameters, when $\nabla^2 \rho(r) < 0$ and $H(r) < 0$, it indicates covalent (shared) interaction, while a noncovalent (closed shell) interaction originating from weak hydrogen bond, van der Waals interaction, and electrostatic interaction exist when $\nabla^2 \rho(r) > 0$ and $H(r) > 0$. However, a partially covalent interaction is prompt to occur when $\nabla^2 \rho(r) > 0$ and $H(r) < 0$. In addition, $G(r)/V(r) > 1$ confirms that

### Table 5. $E_{ads}$ (Adsorption Energy in eV), $\Delta H$ (Enthalpy in kcal/mol), $\Delta G$ (Gibb’s Free Energy in kcal/mol), and $\Delta S$ (Entropy in cal/mol K$^{-1}$)

| structure       | $E_{ads}$ | $\Delta H$ | $\Delta G$ | $\Delta S$ |
|-----------------|-----------|------------|------------|------------|
| CO$_2$@Ca$_{12}$O$_{12}$ | -2.01     | -55.44     | -41.20     | 457.84     |
| SO$_2$@Ca$_{12}$O$_{12}$ | -5.85     | -132.02    | -123.04    | 463.11     |
| NO$_2$@Ca$_{12}$O$_{12}$ | -0.69     | -24.63     | -15.82     | 465.14     |

### Table 6. QTAIM Result of the Studied Gas-Adsorbed Nanocages

| structure | bond | $\rho(r)$ | $\nabla^2 \rho(r)$ | $G(r)$ | $\nabla \cdot V(r)$ | $H(r)$ | ELF | LOL | $\varepsilon$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $\varepsilon / \lambda_1$ | $G(r)/V(r)$ |
|-----------|------|-----------|-------------------|-------|---------------------|-------|-----|-----|-------------|------------|------------|------------|-----------------|-------------|
| CO$_2$@Ca$_{12}$O$_{12}$ | C$_{27}$–O$_{3}$ | 0.2584 | -0.2723 | 0.2748 | -0.1678 | -0.3429 | 0.5454 | 0.5222 | 0.2133 | 0.0397 | 0.0349 | 0.0409 | 0.2211 | 0.0495 | 0.2642 | -0.0439 | -0.0418 | 6.3206 | 1.1375 |
|           | O$_{23}$–Ca$_{33}$ | 0.0362 | 0.1786 | 0.0397 | -0.0349 | 0.0049 | 0.0753 | 0.2221 | 0.0945 | 0.2642 | -0.0439 | -0.0418 | 6.3206 | 1.1375 |
|           | O$_{24}$–Ca$_{14}$ | 0.0343 | 0.1683 | 0.0372 | -0.0324 | 0.0048 | 0.0724 | 0.2183 | 0.0309 | 0.2480 | -0.0405 | -0.0393 | 6.3104 | 1.1481 |
| SO$_2$@Ca$_{12}$O$_{12}$ | S$_{27}$–O$_{3}$ | 0.1606 | 0.0118 | 0.1528 | -0.3026 | -0.1498 | 0.4428 | 0.4713 | 0.1756 | 0.4429 | -0.1981 | -0.2329 | 1.9017 | 0.5050 |
|           | O$_{36}$–Ca$_{33}$ | 0.0357 | 0.1748 | 0.0392 | -0.0348 | 0.0044 | 0.0742 | 0.2206 | 0.0734 | 0.2571 | -0.0426 | -0.0397 | 6.4761 | 1.1264 |
|           | O$_{37}$–Ca$_{15}$ | 0.0358 | 0.1553 | 0.0394 | -0.0349 | 0.0045 | 0.0743 | 0.2208 | 0.0733 | 0.2580 | -0.0399 | -0.0428 | 6.0280 | 1.1289 |
| NO$_2$@Ca$_{12}$O$_{12}$ | N$_{27}$–O$_{3}$ | 0.0261 | 0.1042 | 0.0235 | -0.0210 | 0.0025 | 0.0731 | 0.2193 | 0.3768 | 0.1467 | -0.0179 | -0.0246 | 5.9634 | 1.1190 |
|           | O$_{38}$–Ca$_{23}$ | 0.1080 | 0.5852 | 0.1572 | -0.1682 | -0.0109 | 0.1665 | 0.3089 | 0.1041 | 0.9260 | -0.1789 | -0.1620 | 5.7160 | 0.9346 |
the type of chemical bond interaction is noncovalent (closed shell) in nature, while covalent (shared) interaction is prominent when $G(r)/|\nabla| > 0.5$. Similarly, partially covalent interaction is prevalent when $G(r)/|\nabla| > 0.5$ and 1. Specifically, ELF occurs as a result of local excess kinetic energy density, which is attributed to Pauli repulsion. The ELF value is always observed in the range of 0–1, and when its value is between 0.5 and 1, it symbolizes the delocalization of electron density. ELF < 0.5 indicates the presence of noncovalent (closed shell) interactions, while ELF > 0.5 signifies that the type of chemical bond interaction is that of a covalent (shared) interaction. In the same light, when LOL > 0.5, it indicates that electron density is localized, while the delocalization of electron density appears when LOL < 0.5.

Furthermore, the strength of the bond formed during the intermolecular interaction between the adsorbed gas and the Ca$_{12}$O$_{12}$ nanocage can be characterized by the eigenvalues of the diagonalized Hessian matrix $(\lambda_1$ and $\lambda_2$). In characterizing the strength of the bond formed, a high value of $\lambda_1/\lambda_2$, obtained from the resulting bond formed indicates that the bond is strong. Another significant topological parameter is the bond ellipticity ($\epsilon$), which measures the extent of accumulation of charge based on the orbital of the electronic structure. Bond ellipticity also conveys useful information on the stability of a bond. A high bond ellipticity value ($\epsilon$ > 1) demonstrates that the bond formed during the chemical interaction is unstable.

The results obtained from the topological analysis of the studied gas-adsorbed nanocages are presented in Table 6 and Figure 7. As explicitly seen from the table, for the bond interactions occurring in the CO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocage, the C$_{2s}$–O$_7$ bond was observed to have $V^2 \rho(r) > 0$ and $H(r) < 0$, $G(r)/|\nabla| > 0.5$, and ELF > 0.5. This result implies that the type of chemical bond interaction formed is covalent (shared) in nature. O$_{3(1)}$–Ca$_{12}$ and O$_{3(2)}$–Ca$_{12}$ chemical bonds exhibiting values of $V^2 \rho(r) > 0$ and $H(r) > 0$, $G(r)/|\nabla| > 1$, and ELF < 0.5, indicating that they constitute noncovalent (closed shell) interaction, which can be related to the electrostatic character. In the case of the SO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocage, chemical bond interaction formed by S$_{2s}$–O$_7$, exhibited $V^2 \rho(r) > 0$ and $H(r) < 0$ and $G(r)/|\nabla| > 0.5$ and 1, indicating the interaction is partially covalent in nature. Also, interactions involved in O$_{3(2)}$–Ca$_{12}$ and O$_{27}$–Ca$_{12}$ bonds are seen to be noncovalent (close shell) in nature with values of $V^2 \rho(r) > 0$ and $H(r) > 0$, $G(r)/|\nabla| > 0.5$ and ELF < 0.5. Similarly, for the NO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocage, the N$_{2s}$–O$_7$ chemical bond interaction demonstrated values of $V^2 \rho(r) > 0$ and $H(r) > 0$, $G(r)/|\nabla| > 1$, and ELF < 0.5, which indicates noncovalent (closed shell) interactions. Likewise, the O$_{3(1)}$–Ca$_{23}$ interaction is between covalent and noncovalent interaction by exhibiting $V^2 \rho(r) > 0$ and $H(r) < 0$ and $G(r)/|\nabla| > 0.5$ and 1. Considering the LOL values of the interactions, the C$_{2s}$–O$_7$ chemical bond interaction possessed a value of LOL > 0.5, indicating the localization of electron density, while other interactions exhibited LOL < 0.5, which indicates delocalization of electron density. More interestingly, bond ellipticity ($\epsilon$) values of the studied gas-adsorbed nanocages are less than 1, indicating that bonds formed during the interaction are unstable. However, the $\epsilon$ value of the N$_{2s}$–O$_7$ interaction that arises from the adsorption of NO$_2$ gas on the Ca$_{12}$O$_{12}$ nanocage was found to be higher than that of other interactions, which implies that the bond formed during the interaction is more stable compared to those visualized on the adsorption of CO$_2$ and SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage. This result also supports the unstable adsorption of NO$_2$ gas on the Ca$_{12}$O$_{12}$ nanocage. Moreover, Ca–O interactions exhibited higher $\lambda_1/\lambda_2$ values, indicating that the strength of their bonds is very strong.

3.9. Noncovalent Interaction (NCI) Analysis. Even though QTAIM analysis can characterize noncovalent interactions, it lacks accuracy in predicting noncovalent interactions associated with weak interactions such as van der Waals interactions, hydrogen bond interactions, and π-stacking interactions, which are essential in the formation of chemical bonds.71–73 To tackle this bottleneck between our adsorbed gases and the Ca$_{12}$O$_{12}$ nanocage, we employed a real space method known as noncovalent interaction (NCI) analysis. The strength and type of noncovalent interaction present can be characterized using the product sign of the second eigenvalue of diagonalized Hessian matrix sign ($\lambda_2$) and electron density $\rho(r)$. Hence, the isosurface plot constituting the sign ($\lambda_2$)$\rho(r)$ real space function as the x-axis and reduced density gradient (RDG) on the vertical axis can brilliantly exhibit the strength and type of interaction that is consistent during adsorption of the studied gases and the Ca$_{12}$O$_{12}$ nanocage. In characterizing the weak interaction based on the RDG isosurface plot, the RDG isosurface value was set at 0.5 a.u. From the RDG isosurface plot as elucidated in Figure 8, when sign($\lambda_2$)$\rho(r) < 0$ reflects strong attraction (blue

Figure 7. Interaction of the gases on the Ca$_{12}$O$_{12}$ nanocage and their bond critical points (BCPs).
while van der Waals interaction is visible when \( \text{sign}(\lambda_2)\rho(r) \approx 0 \) (green region). However, a strong repulsive interaction is obvious when \( \text{sign}(\lambda_2)\rho(r) > 0 \) (red region). As evident from our RDG isosurface plots, it can be seen that for the gas-adsorbed nanocages, spike indicates strong attraction, and strong repulsion was prominent while it was absent for the isolated Ca\(_{12}\)O\(_{12}\) nanocage. Also, from the NCI plots, strong repulsive interaction was present in the gas-adsorbed nanocages. Interestingly, strong attraction and van der Waals interaction was found to exist in all of the gas-adsorbed nanocages, but the density of the spike characterizing the region of these interactions was seen to be higher in the CO\(_2\)@Ca\(_{12}\)O\(_{12}\) gas-adsorbed nanocage and the SO\(_2\)@Ca\(_{12}\)O\(_{12}\) gas-adsorbed nanocage than that in the NO\(_2\)@Ca\(_{12}\)O\(_{12}\) gas-adsorbed nanocage. This clear observation also confirms the classification of adsorption of CO\(_2\) and SO\(_2\) on the Ca\(_{12}\)O\(_{12}\) nanocage as stable adsorption, while the adsorption of NO\(_2\) on the Ca\(_{12}\)O\(_{12}\) nanocage is unstable.

3.10. Recovery Time. The recovery time of a sensor is very essential in the sensing mechanism. A sensor exhibiting long recovery time indicates strong adsorption, and thus the desorption of the adsorbate utilized would be difficult.\(^{38}\) The recovery time of a sensor is always determined experimentally by heating the sensor at a higher temperature or with the aid of vacuum ultraviolet (UV) light.\(^{39,40}\) In addition, during the adsorption of an adsorbate on a sensor, high adsorption energy will lead to a long recovery time of the sensor. Here, we considered the recovery time of our nanosensor after the adsorption of CO\(_2\), SO\(_2\), and NO\(_2\) gases using the relationship between the recovery time and the adsorption energy as used by several authors, and it is presented in eq 10 in Section 2. The computed result for the recovery time is presented in Table 7. As evident from the table, it is observed that the recovery of NO\(_2\) from the surface of Ca\(_{12}\)O\(_{12}\) is shorter (0.46 s) compared to the recovery of CO\(_2\) (9.607 s) and SO\(_2\) (8.028 s), and this correlates perfectly with the computed adsorption energies. This further validates the unfavorable adsorption nature of NO\(_2\), and thus, this gas will easily be desorbed from the surface. In fact, the sensitivity of the surface toward the NO\(_2\) gas is very small from this standpoint, and the gas relatively spends only limited time on the adsorbent surface before being desorbed. Moreover, among the sensed gases, the desorption of SO\(_2\) gas from the surface of the Ca\(_{12}\)O\(_{12}\) nanosensor is much more difficult due to its high adsorption energy (\(-5.85\) eV) and thus corresponds to a long recovery time of the simulated nanosensor.

**Table 7. Computed Recovery Time of the Proposed Nanosensor**

|         | CO\(_2\)@Ca\(_{12}\)O\(_{12}\) | SO\(_2\)@Ca\(_{12}\)O\(_{12}\) | NO\(_2\)@Ca\(_{12}\)O\(_{12}\) |
|---------|-------------------------------|-------------------------------|-------------------------------|
| Recovery Time (s) | 9.607 s                       | 8.028 s                       | 0.46 s                       |

Figure 8. NCI plot of (a) the isolated Ca\(_{12}\)O\(_{12}\) nanocage, (b) the CO\(_2\)@Ca\(_{12}\)O\(_{12}\) gas-adsorbed nanocage, (c) SO\(_2\)@Ca\(_{12}\)O\(_{12}\) gas-adsorbed nanocage, and (d) NO\(_2\)@Ca\(_{12}\)O\(_{12}\) gas-adsorbed nanocage.
4. CONCLUSIONS

Conclusively, we have meticulously executed quantum mechanical calculations on the Ca$_{12}$O$_{12}$ nanocage as a trustworthy nanosensor for sensing CO$_2$, SO$_2$, and NO$_2$ with the aid of high-level density functional theory at the B3LYP-GD3(BJ)/6-311+G(d,p) level of theory. Electronic properties such as frontier molecular orbital (FMO), natural bond order (NBO), density of states (DOS), and molecular electrostatic potential (MESP) were determined in this work. Similarly, interaction properties like adsorption energy, quantum theory of atoms in molecule (QTAIM), and noncovalent interaction (NCI) were explicitly evaluated. In addition, the recovery time of the Ca$_{12}$O$_{12}$ nanosensor was also estimated on desorption of the titled gases. The results from the adsorption energy of the studied systems revealed that CO$_2$@Ca$_{12}$O$_{12}$, SO$_2$@Ca$_{12}$O$_{12}$, and NO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocages exhibited remarkable adsorption energy values of −2.01, −5.85, and −0.69 eV, respectively. The high adsorption energy of CO$_2$@Ca$_{12}$O$_{12}$ and SO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocages is associated with chemisorption (stable adsorption), while the low adsorption energy of NO$_2$@Ca$_{12}$O$_{12}$ gas-adsorbed nanocage can be related to physisorption (unstable adsorption). Frontier molecular orbital (FMO) and global reactivity descriptor also confirmed the stable adsorption nature of CO$_2$ and SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage and the unstable adsorption of NO$_2$ on the Ca$_{12}$O$_{12}$ nanocage. This conclusion was further confirmed by carefully observing the variations in energy gap. Thus, the resultant increase in the energy gap of the Ca$_{12}$O$_{12}$ nanocage upon the preferential adsorption of CO$_2$ and SO$_2$, making the conductivity of the nanocage to tend toward that of semiconductors, was used to validate this observation. Several reports show that the increase or decrease in the energy gap of nanosensor materials affects the sensing attributes of the systems and is often used as a broader mark to assess the efficacy of sensor materials toward a specific adsorbent. The exact change in the energy gap for NO$_2$ adsorption was computed to be 2.1%, which shows a dramatic reduction in stability and conductivity in comparison with other studied gases and hence affirms the inability of the Ca$_{12}$O$_{12}$ nanosensor material to sense this gas effectively. In addition, the results from the topological analysis (QTAIM) were also in agreement with the abovementioned result in the sense that the bond ellipticity values originating from the adsorption of CO$_2$ and SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage were greater than that of NO$_2$ adsorption. Also, noncovalent interaction analysis revealed that the adsorption of CO$_2$ and SO$_2$ on the Ca$_{12}$O$_{12}$ nanocage is strong and stable adsorption by revealing denser colored spikes at the strong attraction region (blue region), while the adsorption of NO$_2$ was also verified to be weak and unstable with the appearance of less-dense colored spikes at the strong attraction region (blue region). The results obtained from the computations of desorption time revealed a shorter recovery time for the Ca$_{12}$O$_{12}$ nanosensor after the adsorption of NO$_2$ gas due to the weak and unstable adsorption nature and therefore suggest that NO$_2$ can easily desorb from the surface of the studied nanocage than being adsorbed. At this point, we can strongly infer that our simulated Ca$_{12}$O$_{12}$ nanocage is more efficient and sensitive in sensing CO$_2$ and SO$_2$ gas than NO$_2$. We gratefully acknowledge the support of the Centre for High-Performance Computing, South Africa, for providing computational resources for this project.
Study of Isoniazid Drug Delivery by MgO Nanocage.

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Azopbenzoquinolines: Experimental and Theoretical Investigations.

Excited State Dynamics, and the Photovoltaic Properties of Enalapril Spectroscopic, Conformational Analysis, Structural Benchmarking, and Molecular Modeling of Azo Dye Derivatives as Potential Candidate for Trypanosomiasis Treatment.

Chem. Phys. Impact 2022, 4, No. 100076.

Osigbemhe, I. G.; Louis, H.; Khan, E. M.; Etim, E. E.; Odey, D. O.; Oviawe, A. P.; Edet, H. O.; Obuye, F. Synthesis, Characterization, DFT Studies, and Molecular Modeling of 2-(2-hydroxy-5-methoxyphenyl)-methylidine)-amino Nicotinic Acid Against Some Selected Bacterial Receptors. J. Iran. Chem. Soc. 2022, 19, 3561–3576.

Eno, E. A.; Mbonu, J. I.; Louis, H.; Patrick-Ita, F. S.; Gber, T. E.; Unimke, T. O.; Okon, E. E. D.; Benjamin, I.; Offiong, O. E. Antimicrobial activities of 1-phenyl-3-methyl-4-trichloroacetetylpyrazolone: Experimental, DFT studies, and Molecular Docking Investigation. J. Iranian Chem. Soc. 2022, 99, No. 100524.

Mohammadi, M. D.; Abdullah, H. Y. Ab Initio Investigation for the Adsorption of Acrolein onto the Surface of C60, C59S1, and C59Ge: NBO, QTAIM, and NCI Analyses. Struct. Chem. 2022, 33, 365–378.

Farrokhpour, H.; Jouyapaezadeh, H.; Sohrroforouzani, S. V. Interaction of Different Types of Nanoclusters (Al12N12, Al12P12, B12N12, Be12O12, Mg12O12, Si12C12 and C24) with HCN and ClCN: DFT, TD-DFT, QTAIM, and NBO Calculations. Mol. Phys. 2020, 118, No. 1626506.

Mohammadi, M. D.; Abdullah, H. Y. Theoretical study of the Adsorption of Amantadine on Pristine, Al-, Ga-, and As-doped Boron Nitride Nanosheets: a PBC-DFT, NBO, and QTAIM Study. Theor. Chem. Acc. 2020, 139, No. 158.

Mohammadi, M. D.; Abdullah, H. Y. Adsorption of 1-chloro-1, 2, 2, 2-tetrafluoroethane onto pristine, Al, Ga-doped boron nitride nanosheet. Iran. J. Sci. Technol., Trans. A Sci. 2021, 45, 1267–1300.

Hoseinimehzad-Namin, M. S.; Rahimpour, E.; Ozkan, S. A.; Pargolghasemi, P.; Jouyban, A. Sensing of Carbamazepine by AlN and BN Nanoclusters in Gas and Solvent Phases: DFT and TD-DFT Calculation. J. Mol. Liq. 2022, 353, No. 118750.

Zhang, Y. H.; Li, Y. L.; Gong, F. L.; Xie, K. F.; Liu, M.; Zhang, H. L.; Fang, S. M. Al Doped cartilage-like ZnO for Enhanced NO Sensing Performance: An Experimental and DFT Investigation. Sens. Actuators, B 2020, 305, No. 127489.

Hadipour, N. L.; Peyghan, A. A.; Soleymanabadi, H. Theoretical Study on the Al-doped ZnO Nanoclusters for CO Chemical Sensors. J. Phys. Chem. C 2015, 119, 6398–6404.

Eslami, M.; Vahabi, V.; Peyghan, A. A. Sensing Properties of BN Nanotube toward Carcinogenic 4-chloroaniline: a Computational Study. Phys. E 2018, 97, 6–11.

Esfarji, A. D.; Nuraz, R. A Density Functional Theory Study on the Adsorption and Decomposition of Methanol on B12N12 Fullerene-like Nanocage. Superlattices Microstruct. 2014, 67, 54–60.

Rad, A. S.; Ayub, K. Detailed Surface Study of Adsorbed Nickel on Al12N12 Nano-cage. Thin Solid Films 2016, 612, 179–185.

Hossain, M. R.; Hasan, M. M.; Shamim, S. U. D.; Ferdous, T.; Hossain, M. A.; Ahmed, F. First-Principles Study of the Adsorption of Chloromethine Anticancer Drug on C24, B12N12 and B12C6N6 Nanocages. Comp. Theor. Chem. 2021, 1197, No. 113156.

Egemonye, T. C.; Louis, H.; Unimke, T. O.; Gber, T. E.; Edet, H. O.; Bassey, V. M.; Adeyinka, A. S. First principle density functional theory study on the electrochemical properties of cyclohexanol derivatives as organic carboxyl-based cathode material for lithium-ion batteries. Arabian J. Chem. 2022, 15, No. 104026.

Benjamin, I.; Udoidoko, A. D.; Louis, H.; Agwamba, E. C.; Unimke, T. O.; Owen, A. E.; Adeyinka, A. S. Antimalarial Potential of Naphthlene-sulfonic Acid Derivatives: Molecular Electronic Properties, Vibration Assignments, and in-silico Molecular Docking Studies. J. Mol. Struct. 2022, 1264, No. 133298.

Undiandeye, U. J.; Louis, H.; Gber, T. E.; Egemonye, T. C.; Agwamba, E. C.; Undiandeye, I. A.; Adeyinka, A. S.; Ita, B. I. Spectroscopic, Conformational Analysis, Structural Benchmarking, Excited State Dynamics, and the Photovoltic Properties of Enalapril and Lisinopril. J. Indian Chem. Soc. 2022, 99, No. 100500.

Ravaei, I.; Haghighat, M.; Azami, S. M. A DFT, AIM and NBO Study of Isoniazid Drug Delivery by MgO Nanocage. Appl. Surf. Sci. 2019, 469, 103–112.

Oishi, A. A.; Dhali, P.; Das, A.; Mondal, S.; Rad, A. S.; Hasan, M. M. Study of the Adsorption of Chloropirin on Pure and Ga and Al doped B12N12: A Comprehensive DFT and QTAIM Investigation. Mol. Simul. 2022, 48, 776–788.

Eno, E. A.; Louis, H.; Unimke, T. O.; Agwamba, E. C.; Etim, A. T.; Mbonu, J. I.; Edet, H. O.; Egemonye, T.; Adegoke, K. A.; Aumeur, U. S. Photovoltaic Properties of Novel Reactive Azobenzoquinolines: Experimental and Theoretical Investigations. Phys. Sci. Rev. 2022, DOI: 10.1515/psr-2021-0191.

Agwamba, E. C.; Udoidoko, A. D.; Louis, H.; Udoh, E. U.; Benjamin, I.; Igbalagh, A. T.; Edet, H. O.; Ejiofor, E. U.; Ushaka, U. B. Synthesis, Characterization, DFT Studies, and Molecular Modeling of Azo Dye Derivatives as Potential Candidate for Trypanosomiasis Treatment. Chem. Phys. Impact 2022, 4, No. 100076.
(66) Sajid, H.; Siddique, S. A.; Ahmed, E.; Arshad, M.; Gilani, M. A.; Rauf, A.; Imran, M.; Mahmood, T. DFT outcome for Comparative Analysis of Be12O12, Mg12O12 and Ca12O12 Nanocages toward Sensing of N2O, NO2, NO, H2S, SO2 and SO3 gases. Comput. Theor. Chem. 2022, 1211, No. 113694.

(67) Nemati-Kande, E.; Karimian, R.; Goodarzi, V.; Ghazizadeh, E. Feasibility of Pristine, Al-doped and Ga-doped Boron Nitride nanotubes for Detecting SF4 gas: A DFT, NBO and QTAIM Investigation. Appl. Surf. Sci. 2020, S10, No. 145490.

(68) Abdelmoulahi, H.; Ghalla, H.; Brandán, S. A.; Nasr, S. Structural Study and Vibrational Analyses of the Monomeric, Dimeric, Trimeric and tetrameric Species of Acetamide by using the FT-IR and Raman spectra, DFT Calculations and SQM Methodology. J. Mater. Environ. Sci. 2020, 6, 3094−3109.

(69) Mohammadi, M. D.; Salih, I. H.; Abdullah, H. Y. The Adsorption of Chlorofluoromethane on Pristine and Ge-doped silicon carbide Nanotube: a PBC-DFT, NBO, and QTAIM study. Mol. Simul. 2020, 46, 1405−1416.

(70) Nishat, M.; Hossain, M. R.; Hasan, M. M.; Hossain, M. K.; Hossain, M. A.; Ahmed, F. Interaction of Anagrelide Drug Molecule on pristine and doped boron Nitride Nanocages: A DFT, RDG, PCM and QTAIM Investigation. J. Biomol. Struct. Dyn. 2022, 1−17.

(71) Bader, R. F. W. Atoms in molecules. Acc. Chem. Res. 1985, 18, 9−15.

(72) Neal, R.; Samanta, P. N.; Leszczynski, J. First-Principles Modeling of Complexation of Anticancer Antibiotics with Fullerene (C60) Nanocage: Probing Non-covalent Interactions by Vibrational and Electronic Spectroscopy. J. Mol. Struct. 2022, 1255, No. 132449.

(73) Mohammadi, M. D.; Abdullah, H. Y.; Bhowmick, S.; Biskos, G. Theoretical investigation of X12O12 (X = Be, Mg, and Ca) in sensing CH2N2: A DFT study. Comput. Theor. Chem. 2022, 1198, No. 113168.