Mg$_{12}$O$_{12}$ and Be$_{12}$O$_{12}$ Nanocages as Sorbents and Sensors for H$_2$S and SO$_2$ Gases: A Theoretical Approach

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Abstract: Theoretical calculations based on the Density Functional Theory (DFT) have been performed to investigate the interaction of H$_2$S as well SO$_2$ gaseous molecules at the surfaces of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages. The results show that a Mg$_{12}$O$_{12}$ nano-cage is a better sorbent than a Be$_{12}$O$_{12}$ nano-cage for the considered gases. Moreover, the ability of SO$_2$ gas to be adsorbed is higher than that of H$_2$S gas. The HOMO–LUMO gap ($E_g$) of Be$_{12}$O$_{12}$ nano-cage is more sensitive to SO$_2$ than H$_2$S adsorption, while the $E_g$ value of Mg$_{12}$O$_{12}$ nano-cage reveals higher sensitivity to H$_2$S than SO$_2$ adsorption. The molecular dynamic calculations show that the H$_2$S molecule cannot be retained at the surface of a Be$_{12}$O$_{12}$ nano-cage within 300–700 K and cannot be retained on a Mg$_{12}$O$_{12}$ nano-cage at 700 K, while the SO$_2$ molecule can be retained at the surfaces of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages up to 700 K. Moreover, the thermodynamic calculations indicate that the reactions between H$_2$S as well SO$_2$ with Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages are exothermic. Our results suggest that we can use Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages as sorbents as well as sensors for H$_2$S and SO$_2$ gases.

Keywords: adsorption of H$_2$S and SO$_2$; BeO and MgO nano-cages; density functional theory; thermodynamics; molecular dynamics

1. Introduction

Recently, great efforts have been made to develop novel gas sensors and detectors as well as gas-removing materials. This is to control the pollutant gases broadly produced from industrial activities and burning fuel, etc. The toxic H$_2$S and SO$_2$ gases are produced as byproducts from SF6 decomposition, which is widely used as an insulating gas in high-voltage transformers and circuit breakers [1–4]. H$_2$S is mostly found in crude petroleum, natural gas, and coal gasification. In addition, some organic materials decompose, releasing H$_2$S [5–7]. H$_2$S is also released in many industries such as the paper industry and biomass fermenters [7,8]. The combustion of sulfur-containing fossil fuels releases SO$_2$ into the air, and SO$_2$ is naturally released as a byproduct of volcanic activity [9,10]. The H$_2$S as well SO$_2$ gases pose several hazards to the environment and human health. H$_2$S exposure leads to coughing, eye irritation, and a runny nose, harms the nervous system by killing the neurons and may cause death [11,12]. Moreover, H$_2$S is a corrosive gas and has devastating impacts on industrial catalysts [7,8]. SO$_2$ interacts with the air resulting in acidic rain which causes the corrosion of metals and disintegration of buildings [9,10]. Furthermore, SO$_2$ causes skin burning, eye irritation and respiratory system inflammation, and may cause death [7,13–15]. Therefore, several attempts have been made to utilize many materials as sorbents and detectors for H$_2$S and SO$_2$ gases, such as fullerene-like gallium nitride [16], CuO(111) surface [17], pristine graphene and graphene oxide [18], NH-decorated graphene [8], activated carbon, [19,20], pillared clays [21], zeolites [22], p-CuO/n-ZnO Heterojunction [23], Cu (100) and Au (100) surfaces [24,25], Cu...
doped MoSe$_2$ [12], monolayer Janus MoSSe [26], aza-macrocycle [27], Cu-modified and Cu-embedded WSe$_2$ monolayers [28], porous N$_4$O$_4$-donor macrocyclic Schiff base [29] and MgO (100) surfaces [10].

Metal oxides have a significant consideration due to their several applications. They are usually utilized as substrates for epitaxial growth of multilayers and clusters, catalytic processes, hydrogen storage materials, sensors and sorbent materials [10,30–34]. Recently, nano-structures have been frequently utilized as gas detectors and sorbents due to their appropriate features such as their tiny size, precision, and reactivity [35–37].

Furthermore, Shamlouei et al. reported that nanocages with a X$_{12}$Y$_{12}$ structure are the most stable among (XY)$_n$ nano-cages [38]. Ren et al. [39] have investigated (BeO)$_N$ clusters and found that Be$_{12}$O$_{12}$ is one of the most feasible nano-cages. Ziemann and Castleman [40] have proven that a Mg$_{12}$O$_{12}$ nano-cage displays unique stability among (MgO)$_n$, $n \leq 90$ nano-structures. The Mg-O bond in Mg$_{12}$O$_{12}$ nano-cages has an ionic character [38], while the Be-O bond has ionic and covalent characters [41], therefore one can expect different applications for Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages. Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ have several applications; for instance, Be$_{12}$O$_{12}$ has been utilized as a catalyst to convert CH$_4$ into CH$_3$OH [42], an electro-conductive sensor for sulfur mustard [43], and a detector and sorbent for Mercaptopyridine [44], and Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ have been utilized for hydrogen storage applications [45,46], detection and adsorption of Tabun [47].

According to our knowledge, the interaction of H$_2$S and SO$_2$ gases at the surfaces of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages has not been investigated yet. Hence, the present work aims to shed light on the characteristics of the interaction of H$_2$S and SO$_2$ with Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages for adsorption and sensing applications using DFT calculations.

2. Methods

To investigate the adsorption characteristics of H$_2$S and SO$_2$ molecules onto Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages, DFT and DFT-D3 methods [48] are used at the B3LYP/6-31G(d,p) level. D3 is a version of Grimme’s dispersion [49]. B3 is Becke’s three-parameter exchange functional [50] and LYP is the correlation functional of Lee, Yang and Parr [51,52]. A geometrical optimization without any restriction is performed for the free gaseous molecules, bare nano-cages and gas/nano-cage complexes. The ionization potential (IP) is calculated as [10,37]:

$$\text{IP} = E_{\text{nano-cage}^+} - E_{\text{nano-cage}}$$  \hspace{1cm} (1)

where $E_{\text{nano-cage}^+}$ is the energy of the nano-cage with one electron lost at the same geometrical structure of the neutrally charged nano-cage. The chemical potential ($\mu$), hardness ($\eta$) and electrophilicity ($\omega$) are calculated as [53,54]:

$$\mu \approx -\frac{1}{2} (E_{\text{HOMO}} + E_{\text{LUMO}})$$  \hspace{1cm} (2)

$$\eta \approx \frac{1}{2} (E_{\text{LUMO}} - E_{\text{HOMO}})$$  \hspace{1cm} (3)

$$\omega \approx \frac{\mu^2}{2\eta}$$  \hspace{1cm} (4)

Molecular dynamic simulations via the Atom Centered Density Matrix Propagation molecular dynamics model (ADMP) as implemented in Gaussian 09 package are achieved for the investigated nano-cages and gas/nano-cage complexes.

The adsorption energy ($E_{\text{ads}}$) and the corrected adsorption energy ($E_{\text{ads}}^{\text{corr}}$) with basis set superposition error (BSSE) have been estimated as [55]:

$$E_{\text{ads}} = E_{\text{gas/nano-cage}} - (E_{\text{gas}} + E_{\text{nano-cage}})$$  \hspace{1cm} (5)

$$E_{\text{ads}}^{\text{corr}} = E_{\text{ads}} + E_{\text{BSSE}}$$  \hspace{1cm} (6)
where $E_{\text{gas/nano-cage}}$, $E_{\text{gas}}$, and $E_{\text{nano-cage}}$ are the energies of gas/nano-cage complexes, free gas molecules, and bare nano-cages, respectively. The charge density difference ($\Delta \rho$) for the complexes is computed as:

$$\Delta \rho = \rho_{\text{gas/nano-cage}} - (\rho_{\text{gas}} + \rho_{\text{nano-cage}})$$  \hspace{1cm} (7)

where $\rho_{\text{gas/nano-cage}}$, $\rho_{\text{gas}}$, and $\rho_{\text{nano-cage}}$ are the charge densities for gas/nano-cage complexes, free gas molecules, and bare nano-cages, respectively.

Thermodynamic calculations are performed via vibrational calculations to predict enthalpies as well free energies for the considered gases, nano-cages, and gas-cages complexes. Enthalpy difference ($\Delta H$) and free energy difference ($\Delta G$) for gas/nano-cage complexes are evaluated as [56]:

$$\Delta H = H_{\text{gas/nano-cage}} - (H_{\text{gas}} + H_{\text{nano-cage}})$$  \hspace{1cm} (8)

where $H_{\text{gas/nano-cage}}$, $H_{\text{nano-cage}}$, and $H_{\text{gas}}$ are the enthalpies for gas/nano-cage complexes, bare nano-cages and free gas molecules, respectively.

$$\Delta G = G_{\text{gas/nano-cage}} - (G_{\text{gas}} + G_{\text{nano-cage}})$$  \hspace{1cm} (9)

where $G_{\text{gas/nano-cage}}$, $G_{\text{nano-cage}}$, and $G_{\text{gas}}$ are the free energies for gas/nano-cage complexes, bare nano-cages, and free gas molecules, respectively.

All the calculations have been carried out by Gaussian 09 program package [57]. GaussSum3.0 program is used to visualize the densities of states (DOS) [58]. Atomic charges are calculated for the considered structures via full natural bond orbital (NBO) analyses by using NBO version 3.1 [59].

3. Results and Discussions

3.1. Structural and Electronic Properties of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$

The optimized structures for the scrutinized adsorbed gases H$_2$S and SO$_2$, as well the adsorbent nano-cages Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$, are shown in Figure 1.

For H$_2$S gas, the S-H bond length and the H-S-H angle are 1.35 Å and 92.52°, respectively, while for SO$_2$ gas, the S-O bond length and the O-S-O angle are 1.46 Å and 119.16°, respectively, in good agreement with previous studies [10,29]. Be$_{12}$O$_{12}$, as well Mg$_{12}$O$_{12}$ nano-cages are constructed of eight hexagonal and six tetragonal rings. It is noticed that all the metallic (Be and Mg) and O sites are identical. These nano-cages have two metal-oxygen bond types. They are denoted as $d_1$ and $d_2$ in Figure 1, where $d_1$ shares a hexagon ring and a tetragon ring while $d_2$ shares two hexagon rings. The $d_1$ values are 1.58 and 1.95 Å, whereas the $d_2$ values are 1.52 and 1.90 Å for Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$, respectively, match well with the previous studies [39,60–63]. Table 1 represents the electronic properties of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages.

The HOMO–LUMO energy gap ($E_g$) values for Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ are 7.829 and 4.839 eV while the ionization potential (IP) values are 10.273 and 7.983 eV, respectively, in good agreement with the previous studies [10,30,31,39,44,60–63]. The lower IP value for the Mg$_{12}$O$_{12}$ nano-cage suggests its higher ability to donate electrons than the Be$_{12}$O$_{12}$ nano-cage. The atomic charges for the investigated nano-cage are calculated via natural bond orbital (NBO) analysis. For Be$_{12}$O$_{12}$, the atomic charges for Be and O sites are 1.186 and $-1.186$ e, while for Mg$_{12}$O$_{12}$, the atomic charges for Mg and O sites are 1.442 and $-1.442$ e, respectively. In other words, the charge polarization for the Mg-O bond is greater than that for the Be-O bond; therefore, the Mg$_{12}$O$_{12}$ is expected to be more reactive than Be$_{12}$O$_{12}$. This matches the calculated $E_g$, IP, $\eta$, and $\omega$ values, where the higher chemical stability and consequently lower reactivity for a molecule are marked by wide $E_g$, large IP, $\eta$, and low $\omega$ values [64–67]. Figure 2 illustrates the molecular electrostatic potential (MESP) for H$_2$S, SO$_2$, Be$_{12}$O$_{12}$, and Mg$_{12}$O$_{12}$. 
Figure 1. The optimized structures for (a) free H$_2$S gas, (b) free SO$_2$ gas, (c) Be$_{12}$O$_{12}$, and (d) Mg$_{12}$O$_{12}$ nano-cages.

It is clear that the S atom is surrounded by negative and positive electrostatic potentials for H$_2$S and SO$_2$ molecules, respectively. Furthermore, the MESP around the SO$_2$ molecule is extended in space more than that of the H$_2$S molecule.
Table 1. Electronic properties of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages. HOMO and LUMO energy levels (eV), HOMO- LUMO gap ($E_g$, eV), ionization potential (IP, eV), NBO charges (Q, e), chemical potential ($\mu$, eV), hardness ($\eta$, eV), electrophilicity ($\omega$, eV), and dipole moment (D, Debye).

|          | Be$_{12}$O$_{12}$ | Mg$_{12}$O$_{12}$ |
|----------|------------------|------------------|
|          | Present Study    | Previous Studies | Present Study    | Previous Studies |
| HOMO     | $-8.62$          | $-8.62$ [57]     | $-6.59$          |                  |
| LUMO     | $-0.79$          | $-1.07$ [57]     | $-1.75$          |                  |
| $E_g$    | 7.83             | 8.29 [43]        | 4.84             | 4.78 [30,31]     |
| IP       | 10.27            | 7.98             |                  |                  |
| $Q_M$    | 1.19             | 1.44             |                  |                  |
| $Q_O$    | $-1.19$          | $-1.44$          |                  |                  |
| $\mu$    | $-4.71$          | $-4.17$          | $-4.14$ [58]     |                  |
| $\eta$   | 3.92             | 2.42             |                  |                  |
| $\omega$ | 2.83             | 3.60             |                  |                  |
| D        | 0.00             | 0.01             | 0.00 [38]        | 0.02 [59]        |

$M = \text{Be and Mg.}$

For Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages, the O atoms and the metallic atoms are surrounded by negative and positive electrostatic potentials, respectively. In addition, the MESP of Mg$_{12}$O$_{12}$ is more extended around the nano-cage than that of the Be$_{12}$O$_{12}$ nano-cage. This is due to the higher charge polarization of Mg$_{12}$O$_{12}$. Therefore, it is expected that the S atoms of H$_2$S and SO$_2$ tend to be attracted to the metallic sites and oxygen sites of the nano-cages, respectively. Furthermore, the electric dipole moment (D) of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages are 0.001 and 0.010 Debye, respectively. The low D values are owing to the uniform charge distribution on the nano-cages.

Molecular dynamic (MD) simulations examine the stability of the considered nano-cages at 300, 500, 700 K for a total time of 500 fs. Figure 3 depicts the fluctuation of the potential energy versus the time and the nano-cage geometric configuration at the end of the period.
Figure 2. The molecular electrostatic potential contours (MESP) for (a) free H$_2$S gas, (b) free SO$_2$ gas, (c) Be$_{12}$O$_{12}$, and (d) Mg$_{12}$O$_{12}$ nano-cages at ±0.001, ±0.002, ±0.004, . . . , ±0.8 au iso-values. Red and green colors are assigned to negative and positive values, respectively. It is clear that the S atom is surrounded by negative and positive electrostatic potentials for H$_2$S and SO$_2$ molecules, respectively. Furthermore, the MESP around the SO$_2$ molecule is extended in space more than that of the H$_2$S molecule.

For Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages, the O atoms and the metallic atoms are surrounded by negative and positive electrostatic potentials, respectively. In addition, the MESP of Mg$_{12}$O$_{12}$ is more extended around the nano-cage than that of the Be$_{12}$O$_{12}$ nano-cage. This is due to the higher charge polarization of Mg$_{12}$O$_{12}$. Therefore, it is expected that the S atoms of H$_2$S and SO$_2$ tend to be attracted to the metallic sites and oxygen sites of the nano-cages, respectively. Furthermore, the electric dipole moment (D) of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages are 0.001 and 0.010 Debye, respectively. The low D values are owing to the uniform charge distribution on the nano-cages.

Molecular dynamic (MD) simulations examine the stability of the considered nano-cages at 300, 500, 700 K for a total time of 500 fs. Figure 3 depicts the fluctuation of the potential energy trivially varies and no considerable distortion is observed for the nano-cages; this emphasizes the stability of Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$. In addition, the optimized geometries of discussed nano-cages were verified as true minima on the potential energy surfaces by the absence of imaginary frequencies [68–71].
3.2. Adsorption of H$_2$S and SO$_2$ Gases

DFT as well DFT-D3 calculations were performed to investigate the adsorption characteristics of the adsorbed gases H$_2$S and SO$_2$ at the surfaces of Be$_{12}$O$_{12}$, as well Mg$_{12}$O$_{12}$, nano-cages. Four complexes are investigated—H$_2$S/Be$_{12}$O$_{12}$, H$_2$S/Mg$_{12}$O$_{12}$, SO$_2$/Be$_{12}$O$_{12}$, and SO$_2$/Mg$_{12}$O$_{12}$. There are several possibilities of the gas interaction with the nano-cage, therefore eight adsorption modes for each complex have been fully optimized without any restrictions. Tables S1 and S2 in the Supplementary Data show the examined adsorption modes for H$_2$S interaction with Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$, respectively. We found that the H$_2$S prefers to interact via its S atom toward the metallic atom Be or Mg of the nano-cage. Tables S3 and S4 in the Supplementary Data show the examined adsorption modes for SO$_2$ interaction with Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$, respectively. One can observe that SO$_2$ prefers to interact via its S and O atoms toward the O sites and the metallic atoms, respectively, of the nano-cages. The differences in total electronic energies ($\Delta$E) for the examined orientations are shown in Figure 4.
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**Figure 4.** The differences in total electronic energies ($\Delta E$) for the examined structures calculated at (a) DFT and (b) DFT-D3.

DFT and DFT-D3 calculations show that modes 1, 6, 8, and 1 for H$_2$S/Be$_{12}$O$_{12}$, H$_2$S/Mg$_{12}$O$_{12}$, SO$_2$/Be$_{12}$O$_{12}$, and SO$_2$/Mg$_{12}$O$_{12}$, respectively, are the most energetically stable adsorption modes. Figure 5 presents the most energetically stable adsorption modes that have more negative adsorption energy for each complex.
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Figure 5. The optimal structures for (a) H$_2$S/Be$_{12}$O$_{12}$, (b) H$_2$S/Mg$_{12}$O$_{12}$, (c) SO$_2$/Be$_{12}$O$_{12}$, and (d) SO$_2$/Mg$_{12}$O$_{12}$ complexes.

Table 2 list the adsorption properties of H$_2$S and SO$_2$. Notably, the DFT-D3 calculations give more negative adsorption energy values than DFT calculations.

Table 2. Adsorption properties of H$_2$S as well SO$_2$ on Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages. Adsorption energies ($E_{\text{ads.}}$, eV), Basis set superposition error (BSSE, eV), corrected adsorption energy ($E_{\text{corr}}$, eV), HOMO and LUMO energy levels (eV), HOMO- LUMO gap ($E_g$, eV), NBO charges (Q, e), and dipole moment (D, Debye).

|          | H$_2$S | H$_2$S/Be$_{12}$O$_{12}$ | H$_2$S/Mg$_{12}$O$_{12}$ | SO$_2$ | SO$_2$/Be$_{12}$O$_{12}$ | SO$_2$/Mg$_{12}$O$_{12}$ |
|----------|--------|--------------------------|--------------------------|--------|--------------------------|--------------------------|
| $E_{\text{ads.}}$ (eV) |        |                          |                          |        |                          |                          |
| BSSE (eV) |        |                          |                          |        |                          |                          |
| $E_{\text{corr}}$ (eV) |        |                          |                          |        |                          |                          |
| $E_g$ (eV) |        |                          |                          |        |                          |                          |
| Q (e) |        |                          |                          |        |                          |                          |
| D (Debye) |        |                          |                          |        |                          |                          |
Table 2. Adsorption properties of H₂S as well SO₂ on Be₁₂O₁₂ and Mg₁₂O₁₂ nano-cages. Adsorption energies (Eₐds, eV), Basis set superposition error (BSSE, eV), corrected adsorption energy (Ecorr_ads, eV), HOMO and LUMO energy levels (eV), HOMO- LUMO gap (Eₜ, eV), NBO charges (Q, e), and dipole moment (D, Debye).

|       | H₂S     | H₂S/Be₁₂O₁₂ | H₂S/Mg₁₂O₁₂ |
|-------|---------|-------------|-------------|
| Eads  | -0.31   | -1.32       | -1.57       |
| BSSE  | 0.05    | 0.09        | 0.10        |
| Ecorr | -0.26   | -1.23       | -1.47       |
| HOMO  | -7.31   | -8.20       | -5.95       |
| LUMO  | 0.26    | -0.67       | -1.94       |
| Eₜ    | 7.56    | 7.53        | 3.99        |
| Q₁₂S  | 0.00    | 0.23        | -0.15       |
| D     | 1.33    | 3.27        | 5.50        |

|       | SO₂     | SO₂/Be₁₂O₁₂ | SO₂/Mg₁₂O₁₂ |
|-------|---------|-------------|-------------|
| Eads  | -0.83   | -2.33       | -2.52       |
| BSSE  | 0.38    | 0.41        | 0.41        |
| Ecorr | -0.45   | -1.93       | -2.11       |
| HOMO  | -9.16   | -8.05       | -6.55       |
| LUMO  | -3.73   | -1.47       | -1.83       |
| Eₜ    | 5.43    | 6.58        | 4.71        |
| Q₁₂O₂ | 0.00    | -0.13       | -0.34       |
| D     | 1.94    | 2.95        | 4.59        |

Values between brackets are calculated at B3LYP/6–311g(d,p) with dispersion correction (DFT-D3).

In contrast, the values for HOMO, LUMO, Eₜ, Q, and D have no considerable variations between DFT and DFT-D3 calculations. The Ecorr values show that the interaction of H₂S as well SO₂ at the surfaces of Be₁₂O₁₂ and Mg₁₂O₁₂ is a chemical interaction, where the Ecorr values are lower than -0.2 eV [67]. The released adsorption energy is in the following trend SO₂/Mg₁₂O₁₂ > H₂S/Mg₁₂O₁₂ > SO₂/Be₁₂O₁₂ > H₂S/Be₁₂O₁₂. One can notice that the ability of the Mg₁₂O₁₂ nano-cage to adsorb the considered gases is higher than that of the Be₁₂O₁₂ nano-cage. This is referred to as the higher ability of the Mg₁₂O₁₂ nano-cage to donate electrons than the Be₁₂O₁₂ nano-cage. Additionally, the ability of the SO₂ gas to be adsorbed on the Mg₁₂O₁₂ nano-cage, as well as the Be₁₂O₁₂ nano-cage, is higher than that of H₂S gas. Figure 5a shows that the H₂S/Be₁₂O₁₂ complex, the S atom of the H₂S molecule, is bonded to a Be site at a distance (d₁–25) of 2.35 Å, the S-H bond length is the same as that of the free H₂S molecule, and there is a negligible increase of the H-S-H angle. The H₂S molecule acquires a positive charge of 0.226 e, meaning that a charge transfer has occurred from the H₂S molecule to the Be₁₂O₁₂ nano-cage. Figure 5b illustrates the H₂S/Mg₁₂O₁₂ complex, while the H₂S molecule dissociates into two fragments HS and H. The HS fragment is bonded via its S atom to a Mg site at a distance (d₁–25) of 2.40 Å while the H fragment is attached to an O site at a distance (d₄–26) of 0.98 Å. Due to that, an obvious deformation has occurred in Mg₁₂O₁₂ where the Mg-O bond length (d₁–4) is elongated to 2.99 Å. The net acquired charge by the H₂S molecule is -0.146 e, which means the Mg₁₂O₁₂ donates a charge to the H₂S. Figure 5c demonstrates the SO₂/Be₁₂O₁₂ complex, while the S atom of the SO₂ molecule is bonded to an O site at a distance (d₂–25) of 1.83 Å, and an O atom of the SO₂ molecule is attached to a Be site at a distance (d₁–27) of 1.57 Å. While for the SO₂ molecule, the bond length (d₂5–27) is stretched to 1.56 Å and the O-S-O angle is slightly widened to 111.35°. In addition, the Be-O bond length (d₁–2) is elongated to 2.62 Å. The SO₂ molecule gains a negative charge of 0.127 e, i.e., a charge transfer has occurred from the Be₁₂O₁₂ nano-cage to the SO₂ molecule. Furthermore, Figure 5d represents the SO₂/Mg₁₂O₁₂ complex; it seems that three bonds are formed between the SO₂ molecule and the Mg₁₂O₁₂ nano-cage. The two O atoms of the SO₂ molecule are bonded to two Mg sites at distances of (d₃–27) 1.98 Å and (d₇–26) 2.06 Å, while the S atom is attached to an O site at a distance (d₂–25) of 1.64 Å. In addition, the two O-S bonds of the SO₂ molecule are dilated to 1.54 Å while the O-S-O angle is diminished to 109.6° and the Mg-O bond length
(d2–3) is elongated to 2.93 Å. Moreover, the SO2 molecule accepts a negative charge of −0.339 e; therefore, a charge transfer has occurred from the Mg12O12 nano-cage to the SO2 molecule. Additionally, the adsorption of H2S leads to a decrease in the HOMO–LUMO gap (Eg) values of Be12O12 and Mg12O12 by 3.84% and 17.54%, respectively, whereas the adsorption of SO2 leads to a decrease in Eg values by 15.97% and 2.60%, respectively. Therefore, one can say that the Eg of the Be12O12 nano-cage is more sensitive to the SO2 than H2S adsorption while the Eg of the Mg12O12 nano-cage reveals higher sensitivity to H2S than SO2 adsorption.

The electrical conductivity (σ) and recovery time (τ) are important aspects of sensing applications. σ depends on Eg according to the following equation [72–77]:

$$\Delta G = G_{\text{gas/nano-cage}} - (G_{\text{gas}} + G_{\text{nano-cage}})$$  \hspace{1cm} (10)

where A is a constant, k is Boltzmann’s constant, and T is the temperature. Therefore, the increase of σ value of the Be12O12 nano-cage in the presence of SO2 gas is higher than in the presence of H2S gas, while the increase of σ value of the Mg12O12 nano-cage in the presence of H2S gas is higher than in the presence of SO2 gas. The τ is related to the E_ads as in Equation (11) [78,79]:

$$\tau = \nu_0^{-1} \exp \left( \frac{-E_{\text{ads}}}{kT} \right)$$  \hspace{1cm} (11)

where $\nu_0$ is the attempt frequency. In other words, as E_ads increases (more negative) the longer τ becomes. Therefore, in the obtained E_ads values, τ trends as follows: SO2/Mg12O12 > H2S/Mg12O12 > SO2/Be12O12 > H2S/Be12O12. Thus, our results may be fruitful for sensing applications.

To illuminate the features of the interaction between the considered gases and the sorbent nano-cages, our results will be discussed related to the following: (i) NBO atomic charges as well charge density difference analysis ($\Delta \rho$), (ii) bond analysis, and (iii) PDOS analysis.

3.2.1. NBO and Charge Density Difference Analysis

To shed light on the mechanism of H2S and SO2 interaction with the considered nano-cages, NBO analysis, as well as charge density difference ($\Delta \rho$) analysis, has been performed. Table 3 lists the atomic NBO charges, as well the electronic configuration of the atoms, for the free H2S, Be12O12, Mg12O12, H2S/Be12O12, and H2S/Mg12O12. The numbering of atoms as shown in Figure 5 is used.

For the H2S/Be12O12 structure, it is clear that due to the interaction, the 1s orbital of the H26 and H27 atoms loses charges of 0.03 and 0.02 e while the 3s and 3p orbitals of the S atom lose charges of 0.03 and 0.14 e, respectively. On the other hand, the 2s and 2p orbitals of the Be1 atom gain charges of 0.14 and 0.04 e while for the O2, O4, and O6 the 2s orbital loses a charge of 0.01 e whereas the 2p orbital gains a charge of 0.01 e. This explains why a total charge of 0.226 e, as shown in Table 2, has been transferred from H2S to the Be12O12 nano-cage and the major of the charge transfer has occurred from the S atom of H2S to the Be1 atom of the Be12O12 nano-cage.

This means the major mechanism of the interaction is the charge transfer mechanism. In addition, a slight loss and gain of charges are observed simultaneously for the O2, O4, and O6; therefore, one can suggest another minor mechanism which is the donation–back donation mechanism. Figure 6a demonstrates $\Delta \rho$ for H2S/Be12O12 complex.
Table 3. NBO charges (Q, e) and electronic configuration for free H$_2$S, Be$_{12}$O$_{12}$, Mg$_{12}$O$_{12}$, H$_2$S/Be$_{12}$O$_{12}$, and H$_2$S/Mg$_{12}$O$_{12}$.

| Structure          | Atom | Atomic Charge | Electronic Configuration |
|--------------------|------|---------------|-------------------------|
|                    |      |               | 1s  | 2s  | 2p  | 3s  | 3p  |
| H$_2$S             | H    | 0.134         | 0.86| -   | -   | -   | -   |
|                    | S    | -0.268        | -   | -   | -   | 1.76| 4.48|
| Be$_{12}$O$_{12}$  | Be   | 1.186         | -   | 0.21| 0.59| -   | -   |
|                    | O    | -1.186        | -   | 1.69| 5.49| -   | -   |
| Mg$_{12}$O$_{12}$  | Mg   | 1.443         | -   | -   | -   | 0.21| 0.35|
|                    | O    | -1.443        | -   | 1.84| 5.60| -   | -   |
| H$_2$S/Be$_{12}$O$_{12}$ | H26  | 0.160         | 0.83| -   | -   | -   | -   |
|                    | H27  | 0.159         | 0.84| -   | -   | -   | -   |
|                    | S    | -0.093        | -   | -   | -   | 1.73| 4.34|
|                    | Be1  | 1.007         | -   | 0.25| 0.73| -   | -   |
|                    | O2   | -1.191        | -   | 1.68| 5.50| -   | -   |
|                    | O4   | -1.189        | -   | 1.68| 5.50| -   | -   |
|                    | O6   | -1.190        | -   | 1.68| 5.50| -   | -   |
| H$_2$S/Mg$_{12}$O$_{12}$ | H26  | 0.509         | 0.49| -   | -   | -   | -   |
|                    | H27  | 0.130         | 0.86| -   | -   | -   | -   |
|                    | S    | -0.785        | -   | -   | -   | 1.81| 4.97|
|                    | Mg1  | 1.305         | -   | -   | -   | 0.27| 0.41|
|                    | O2   | -1.452        | -   | 1.83| 5.62| -   | -   |
|                    | O4   | -1.251        | -   | 1.77| 5.47| -   | -   |
|                    | O6   | -1.442        | -   | 1.83| 5.61| -   | -   |

Figure 6. Charge density difference (Δρ) for (a) H$_2$S/Be$_{12}$O$_{12}$, (b) H$_2$S/Mg$_{12}$O$_{12}$, (c) SO$_2$/Be$_{12}$O$_{12}$, and (d) SO$_2$/Mg$_{12}$O$_{12}$ complexes. Red color for negative Δρ and blue color for positive Δρ.
The H and S atoms of the H$_2$S molecule are surrounded by positive $\Delta \rho$ values (blue color), which confirms the charge transfer from the H$_2$S molecule to the nano-cage. In addition, the positive (blue color) and negative (red color) $\Delta \rho$ values around each of the O2, O4, O6, and S atoms confirm the donation–back donation mechanism. For H$_2$S/Mg$_{12}$O$_{12}$ structure, the interaction between H$_2$S and Mg$_{12}$O$_{12}$ leads to the following: the 1s orbital of the H26 loses a charge of 0.37 e whereas the 2s and 2p of the O4 atom lose a charge of 0.07 and 0.13 e, respectively. Furthermore, the H27 atom has no change, the 3s and 3p orbitals of the S atom gain charges of 0.05 and 0.49 e, and the 3s and 3p of the Mg gain charges of 0.06 and 0.06 e, respectively. This confirms the dissociation of the H$_2$S molecule into H$^+$ and SH$^-$. Then, the H$^+$ is attached to the O4 atom, while the SH$^-$ is attached to the Mg1 atom.

Figure 6b shows $\Delta \rho$ for the H$_2$S/Mg$_{12}$O$_{12}$ complex. The H26 is surrounded by positive $\Delta \rho$ values (blue color) while the S atom is surrounded by negative (red color) $\Delta \rho$ values which agree with the above discussion. Table 4 illustrates the atomic NBO charges, as well the electronic configuration of the atoms, for the free SO$_2$, Be$_{12}$O$_{12}$, Mg$_{12}$O$_{12}$, SO$_2$/Be$_{12}$O$_{12}$, and SO$_2$/Mg$_{12}$O$_{12}$.

**Table 4.** NBO charges (Q, e) and electronic configuration for free SO$_2$, Be$_{12}$O$_{12}$, Mg$_{12}$O$_{12}$, SO$_2$/Be$_{12}$O$_{12}$, and SO$_2$/Mg$_{12}$O$_{12}$.

| Structure       | Atom | Atomic Charge | Electronic Configuration |
|-----------------|------|---------------|-------------------------|
|                 |      |               | 2s  | 2p  | 3s  | 3p  |
| SO$_2$          | O    | -0.747        | 1.84| 4.89| -   | -   |
|                 | S    | 1.495         | -   | -   | 1.62| 2.68|
| Be$_{12}$O$_{12}$| Be   | 1.186         | 0.21| 0.59| -   | -   |
|                 | O    | -1.186        | 1.69| 5.49| -   | -   |
| Mg$_{12}$O$_{12}$| Mg   | 1.443         | -   | 0.21| 0.35|
|                 | O    | -1.443        | 1.84| 5.60| -   | -   |
| SO$_2$/Be$_{12}$O$_{12}$| O26 | -0.852        | 1.84| 5.00| -   | -   |
|                 | O27  | -0.980        | 1.76| 5.21| -   | -   |
|                 | S    | 1.705         | -   | 1.55| 2.58|
|                 | Be1  | 1.210         | 0.22| 0.55| -   | -   |
|                 | O2   | -1.109        | 1.75| 5.36| -   | -   |
|                 | O4   | -1.214        | 1.69| 5.52| -   | -   |
|                 | O6   | -1.197        | 1.69| 5.50| -   | -   |
| SO$_2$/Mg$_{12}$O$_{12}$| O26 | -1.003        | 1.82| 5.17| -   | -   |
|                 | O27  | -1.049        | 1.81| 5.23| -   | -   |
|                 | S    | 1.713         | -   | 1.51| 2.62|
|                 | Mg1  | 1.477         | -   | 0.20| 0.32|
|                 | Mg3  | 1.468         | -   | 0.20| 0.32|
|                 | Mg7  | 1.417         | -   | 0.21| 0.36|
|                 | O2   | -1.148        | 1.82| 5.32| -   | -   |
|                 | O4   | -1.463        | 1.84| 5.62| -   | -   |
|                 | O8   | -1.454        | 1.84| 5.61| -   | -   |

For SO$_2$/Be$_{12}$O$_{12}$ structure, one can observe, that the 2s of the O27 and the 3s and 3p of the S atom lose charges of 0.08, 0.07, and 0.10 e, respectively, while the 2p of the O26 and O27 atoms gain charges of 0.11 and 0.32 e, respectively. Therefore, the positive charge of the S atom and the negative charge of the O27 atom increase; consequently, they are attached to the O2 negative and Mg1 positive sites of the nano-cage, respectively. Moreover, for the Be1 atom, the 2s gains a charge of 0.01 e while the 2p loses a charge of 0.04 e, whereas for the O2 atom, the 2s gains a charge of 0.06 e while the 2p orbital loses a charge of 0.13 e. Therefore, one can say that there is a charge transfer from the Be$_{12}$O$_{12}$ nano-cage to the SO$_2$ molecule greater than the charge transferred from the SO$_2$ molecule to the Be$_{12}$O$_{12}$ nano-cage. This explains why SO$_2$ has a total charge of $-0.127$ e, as shown in Table 2. $\Delta \rho$ for the SO$_2$/Be$_{12}$O$_{12}$ complex is demonstrated in Figure 6c. It is clear that both the adsorbed SO$_2$ molecule and the sorbent Be$_{12}$O$_{12}$ nano-cage are surrounded by positive and negative $\Delta \rho$ values (blue and red colors) which confirms the donation–back donation mechanism.
mechanism for the interaction. For the SO$_2$/Mg$_{12}$O$_{12}$ structure, one can notice that the 2s of the O26 and O27 loses charges of 0.02 and 0.03 e while the 2p gains charges of 0.28 and 0.34 e, respectively. Moreover, the 3s and 3p of the S atom lose charges of 0.11 and 0.06 e, respectively. Therefore, the net atomic charges of the O atoms of the SO$_2$ become more negative while the S atom becomes more positive, consequently, the O26 and O27 are attracted to the Mg7 and Mg3 positive sites while the S atom is attracted to the O2 negative site of the Mg$_{12}$O$_{12}$ nano-cage, whereas for the Mg$_{12}$O$_{12}$, the 2s and 2p of the O2 atom lose charges of 0.02 and 0.28 e while the rest atoms of the nano-cage have little gains and loss of charges. \( \Delta \rho \) for the SO$_2$/Mg$_{12}$O$_{12}$ complex is illustrated in Figure 6d. It is clear that the adsorbed SO$_2$ molecule is surrounded by negative \( \Delta \rho \) values greater than the positive \( \Delta \rho \) values, which confirm the donation–back donation mechanism for the interaction.

3.2.2. Bond Analysis

Bond order and overlap population are estimated for the free adsorbed gasses as well gas/nano-cage complexes. As the overlap value decreases, the interaction between the two atoms decreases and vice versa whereas the values close to zero mean no interaction while overlapping positive and negative values indicate the bonding and anti-bonding states, respectively [71,75,80]. Table 5 concerns the free H$_2$S molecule, H$_2$S/Be$_{12}$O$_{12}$, and H$_2$S/Mg$_{12}$O$_{12}$ complexes.

**Table 5.** Overlap population and bond order of H$_2$S, H$_2$S/Be$_{12}$O$_{12}$, and H$_2$S/Mg$_{12}$O$_{12}$.

| Structure | H$_2$S | H$_2$S/Be$_{12}$O$_{12}$ | H$_2$S/Mg$_{12}$O$_{12}$ |
|-----------|--------|-----------------|-----------------|
|           | Overlap Pop. | Bond Order | Overlap Pop. | Bond Order | Overlap Pop. | Bond Order |
| S–H26     | 0.304  | 0.979   | 0.316  | 0.974   | 0.042  | 0.997   |
| S–H27     | 0.304  | 0.979   | 0.313  | 0.972   | 0.266  | 0.956   |
| S–M1      | -      | -       | 0.0074 | 0.279   | 0.273  | 0.717   |
| O4–H26    | -      | -       | 0.000  | 0.002   | 0.289  | 0.835   |
| M1–O4     | -      | -       | 0.206 (0.220) * | 0.538 (0.602) * | 0.035 (0.183) * | 0.106 (0.520) * |

* Values between brackets are for the bare nano-cage. M = Be and Mg.

For H$_2$S/Be$_{12}$O$_{12}$, the overlap population and bond order values of the S-H26 and S-H27 bonds are slightly changed with respect to the free H$_2$S molecule, while overlapping population and bond order values of 0.074 and 0.279, respectively, are observed for the S-Be1 bond. This indicates the formation of a weak bond between the H$_2$S molecule and the Be$_{12}$O$_{12}$ nano-cage. On the other hand, for H$_2$S/Mg$_{12}$O$_{12}$, the low overlap population and bond order values for the S-H26 bond indicate the dissociation of the H$_2$S molecule. In addition, high overlapping population and bond order values for the S-M1 and O4-H26 indicate bond formation between the S atom and the Mg1 atom and between the H26 atom and the O4 atom. Furthermore, the overlapping population and the bond order values for the Mg1-O4 are decreased to 0.035 and 0.106 rather than 0.183 and 0.520 for the bare nano-cage, respectively, indicating a bond weakness has occurred. This reveals the strong interaction between the H$_2$S molecule and the Mg$_{12}$O$_{12}$ nano-cage. Table 6 is interested in the free SO$_2$ molecule, SO$_2$/Be$_{12}$O$_{12}$, and SO$_2$/Mg$_{12}$O$_{12}$ complexes.

For SO$_2$/Be$_{12}$O$_{12}$, the S-O27 and Be1-O2 bonds are weakened as indicated by the low values of the overlap population and bond order, while the high overlap population and bond order values for the Be1-O27 bond indicate bond formation. On the other hand, for SO$_2$/Mg$_{12}$O$_{12}$, the decrease in the S-O26, S-O27, and Mg3-O2 overlapping population and bond order values indicates the weakness of these bonds while the bond order of 0.892, 0.464, and 0.495 for the S-O2, Mg-O27, and Mg-O26, respectively, confirms the formation of these bonds. In other words, one bond is formed between the SO$_2$ and the nano-cage for the SO$_2$/Be$_{12}$O$_{12}$ complex, whereas three bonds are formed for the SO$_2$/Mg$_{12}$O$_{12}$ complex. This explains the higher adsorption energy for SO$_2$/Mg$_{12}$O$_{12}$ than SO$_2$/Be$_{12}$O$_{12}$. 
Table 6. Overlap population and bond order of SO$_2$, SO$_2$/Be$_{12}$O$_{12}$, and SO$_2$/Mg$_{12}$O$_{12}$.

| Structure | SO$_2$       | SO$_2$/Be$_{12}$O$_{12}$ | SO$_2$/Mg$_{12}$O$_{12}$ |
|-----------|--------------|--------------------------|---------------------------|
|           | Overlap Pop. | Bond Order               | Overlap Pop.               | Bond Order               | Overlap Pop.     | Bond Order               |
| S-O26     | 0.242        | 1.773                    | 0.302                     | 1.706                    | 0.203           | 1.290                    |
| S-O27     | 0.242        | 1.773                    | 0.116                     | 1.138                    | 0.156           | 1.219                    |
| S-O2      | -            | -                        | -0.015                    | 0.564                    | 0.079           | 0.892                    |
| M1-O27    | -            | -                        | 0.262                     | 0.614                    | 0.000           | -0.010                   |
| M3-O27    | -            | -                        | 0.022                     | 0.022                    | 0.192           | 0.464                    |
| M7-O26    | -            | -                        | 0.057                     | 0.118                    | 0.207           | 0.495                    |
| M1-O2     | -            | -                        | -0.006 (0.220) *          | 0.028 (0.602) *          | 0.113 (0.183) * | 0.267 (0.520) *          |
| M3-O2     | -            | -                        | 0.215 (0.220) *           | 0.452 (0.602) *          | 0.033 (0.183) * | 0.103 (0.520) *          |

* Values between brackets are for the bare nano-cage. M = Be and Mg.

3.2.3. PDOS Analysis

Figure 7 illustrates the surfaces of the HOMO and LUMO as well as the PDOS for the free H$_2$S molecule, the bare Be$_{12}$O$_{12}$, and Mg$_{12}$O$_{12}$ nano-cages, as well as the H$_2$S/Be$_{12}$O$_{12}$ and H$_2$S/Mg$_{12}$O$_{12}$ complexes.

Figure 7a shows three occupied states for the H$_2$S molecule at $-12.36$, $-10.12$, and $-7.30$ eV; the H atom states located at $-12.36$ and $-10.12$ eV; and the S atom states located at $-12.36$, $-10.12$, and $-7.35$ eV. The S atom states for free H$_2$S molecule are disappeared in the H$_2$S/Be$_{12}$O$_{12}$ complex, as shown in Figure 7c. Furthermore, new states for the S atom are observed in the H$_2$S/Be$_{12}$O$_{12}$ complex; these states overlap with the Be and O states, which emphasizes the interaction between the H$_2$S molecule with the nano-cage. For instance, the states of the S, Be, and O atoms of the complex are overlapped at $-8.20$ eV, which is the HOMO of the complex. The HOMO surface of the complex displays the contribution of the S, Be, and O atoms. Comparing Figure 7b,c, one can observe the adsorption of the H$_2$S molecule rises the HOMO and LUMO of Be$_{12}$O$_{12}$ by 0.43 and 0.13 eV, respectively; therefore, a decrease of 0.30 eV in the HOMO–LUMO gap has been recorded. For H$_2$S/Mg$_{12}$O$_{12}$ complex, Figure 7e, it is clear that there is an overlap between the H and O states at $-12.92$ eV, which is due to the interaction between H$_2$S and O$_2$. Moreover, the occupied states of the S atom are located at $-9.70$, $-6.51$, and $-5.93$ eV, i.e., they are shifted up with respect to the free H$_2$S, which confirms the strong interaction between the H$_2$S and Mg$_{12}$O$_{12}$ nano-cage. In addition, comparing Figure 7d,e, one can see that HOMO rises by $1.02$ eV while LUMO lowers by $0.19$ eV. Thus, H$_2$S adsorption narrows the HOMO–LUMO gap by $0.85$ eV. It is worth noticing that only the states of S and O atoms appear in the HOMO states, and this agrees with the obtained HOMO surface for the H$_2$S/Mg$_{12}$O$_{12}$ complex. Figure 8 demonstrates the surfaces of HOMO and LUMO, as well PDOS, for the free SO$_2$ molecule, bare Be$_{12}$O$_{12}$, and Mg$_{12}$O$_{12}$ nano-cages, as well SO$_2$/Be$_{12}$O$_{12}$ and SO$_2$/Mg$_{12}$O$_{12}$ complexes.

Comparing Figure 8a–c, it is clear that there are dramatic changes in the states due to the adsorption of the SO$_2$ molecule on the Be$_{12}$O$_{12}$ nano-cage, where the states of SO$_2$ overlap with the states of Be$_{12}$O$_{12}$. For example, one can observe the appearance of the S atom and the O atoms of the SO$_2$ and Be$_{12}$O$_{12}$ in the HOMO states of the SO$_2$/Be$_{12}$O$_{12}$ at $-8.05$ eV. This is confirmed by the HOMO surface for the SO$_2$/Be$_{12}$O$_{12}$ complex. Based on the interaction, the HOMO of the nano-cage rises by $0.57$ eV and the LUMO lowers by $0.68$ eV; in turn, narrowing the HOMO–LUMO gap by $1.25$ eV. Comparing Figure 8a,d,e, one can observe that adsorption of the SO$_2$ molecule on the Mg$_{12}$O$_{12}$ nano-cage leads to intense changes in the states of the SO$_2$ as well as the states of the Mg$_{12}$O$_{12}$, which confirms the occurrence of a strong interaction. Moreover, the HOMO of the nano-cage increases by $0.04$ while the LUMO decreases by $0.08$ eV; consequently, the HOMO–LUMO gap is slightly decreased by $0.12$ eV.
Figure 7. HOMO, PDOS, LUMO for (a) H₂S, (b) Be₁₂O₁₂, (c) H₂S/Be₁₂O₁₂, (d) Mg₁₂O₁₂, and (e) H₂S/Mg₁₂O₁₂ complexes.
Comparing Figure 8a–c, it is clear that there are dramatic changes in the states due to the adsorption of the SO2 molecule on the Be12O12 nano-cage, where the states of SO2 overlap with the states of Be12O12. For example, one can observe the appearance of the S atom and the O atoms of the SO2 and Be12O12 in the HOMO states of the SO2/Be12O12 at −8.05 eV. This is confirmed by the HOMO surface for the SO2/Be12O12 complex. Based on the interaction, the HOMO of the nano-cage rises by 0.57 eV and the LUMO lowers by 0.68 eV, in

Figure 8. HOMO, PDOS, LUMO for (a) SO2, (b) Be12O12, (c) SO2/Be12O12, (d) Mg12O12, and (e) SO2/Mg12O12 complexes.
3.3. Molecular Dynamic Simulations

To examine the impact of the temperature on the adsorption process of the investigated gases, molecular dynamic (MD) simulations at 300, 500, and 700 K for a total time of 500 fs are performed for H$_2$S/Be$_{12}$O$_{12}$, H$_2$S/Mg$_{12}$O$_{12}$, SO$_2$/Be$_{12}$O$_{12}$, and SO$_2$/Mg$_{12}$O$_{12}$ complexes. MD simulations are carried out via the ADMP model. Figure 9a,b illustrates the potential energy fluctuations for H$_2$S/Be$_{12}$O$_{12}$ and H$_2$S/Mg$_{12}$O$_{12}$, respectively, as well as the atomic configuration after 500 fs at the inspected temperatures.

![Figure 9](image-url)

Figure 9. Potential energy fluctuations during MD simulation for (a) H$_2$S/Be$_{12}$O$_{12}$, and (b) H$_2$S/Mg$_{12}$O$_{12}$ and the atomic configuration after 500 fs at 300, 500, and 700 K.

For H$_2$S/Be$_{12}$O$_{12}$, Figure 9a, although the fluctuation of the potential energy is small, the distance (d$_{1-25}$) between H$_2$S and Be$_{12}$O$_{12}$ nano-cage increased with time. As well as the temperature increases, the increment in the distance increases, where the d$_{1-25}$ values at the end of the time increase to 3.32, 7.38, and 9.55 Å for temperatures 300, 500, and 700 K, respectively. Therefore, one suggests that the Be$_{12}$O$_{12}$ nano-cage cannot retain H$_2$S on its surface, especially at high temperatures. For H$_2$S/Mg$_{12}$O$_{12}$, Figure 9b, at the temperature of 300 K, the fluctuation of the potential energy is small, and the Mg$_{12}$O$_{12}$...
nano-cage preserves the dissociated H$_2$S molecule on its surface with no significant changes in the geometrical structure of the complex, while at the temperatures of 500 and 700 K, a high fluctuation of the potential energy is observed until 120–130 fs, when the fluctuation decreases. In addition, the dissociation of the H$_2$S molecule is diminished. At the end of the time, at 500 K, the H$_2$S is retained on the Mg$_{12}$O$_{12}$ nano-cage at a distance of 2.65 Å while at 700 K the d$_{1-25}$ increases to 6.79 Å. Furthermore, Figure 10a,b demonstrates the potential energy fluctuations for SO$_2$/Be$_{12}$O$_{12}$ and SO$_2$/Mg$_{12}$O$_{12}$, respectively, as well as the atomic configuration after 500 fs at the inspected temperatures.

![Figure 10](image.png)

**Figure 10.** Potential energy fluctuations during MD simulation for (a) SO$_2$/Be$_{12}$O$_{12}$, and (b) SO$_2$/Mg$_{12}$O$_{12}$ and the atomic configuration after 500 fs at 300, 500, and 700 K.

It is clear that no significant fluctuation of the potential energy is observed. Moreover, at the end of the time, there is a trivial deformation in the geometrical structure of the SO$_2$/Be$_{12}$O$_{12}$ and SO$_2$/Mg$_{12}$O$_{12}$ complexes. Therefore, one proposes that Be$_{12}$O$_{12}$ and Mg$_{12}$O$_{12}$ nano-cages can retain the SO$_2$ molecule on their surface at temperatures up to 700 K.
3.4. Thermodynamic Properties

For gas adsorption, enthalpy difference ($\Delta H$) and free energy difference ($\Delta G$) are imperative thermodynamic parameters for determining the strength and the spontaneity of the reaction. Therefore, thermodynamic calculations for $\text{H}_2\text{S}/\text{Be}_{12}\text{O}_{12}$, $\text{H}_2\text{S}/\text{Mg}_{12}\text{O}_{12}$, $\text{SO}_2/\text{Be}_{12}\text{O}_{12}$, and $\text{SO}_2/\text{Mg}_{12}\text{O}_{12}$ complexes have been performed in the temperature range 300–700 K. Figure 11a signifies $\Delta H$ for the investigated complexes.

![Figure 11a: $\Delta H$ vs. Temperature](image)

![Figure 11b: $\Delta G$ vs. Temperature](image)

Figure 11. (a) $\Delta H$ and (b) $\Delta G$ for $\text{H}_2\text{S}/\text{Be}_{12}\text{O}_{12}$, $\text{H}_2\text{S}/\text{Mg}_{12}\text{O}_{12}$, $\text{SO}_2/\text{Be}_{12}\text{O}_{12}$, and $\text{SO}_2/\text{Mg}_{12}\text{O}_{12}$ complexes.

$\Delta H$ values for all considered complexes are negative, which specifies the reactions between $\text{H}_2\text{S}$ as well $\text{SO}_2$ with $\text{Be}_{12}\text{O}_{12}$ and $\text{Mg}_{12}\text{O}_{12}$ nano-cages are exothermic. Furthermore, as the temperature increases, the negative $\Delta H$ values decrease, which indicates the reactions are stronger at lower temperatures. In addition, for the same gas, $\Delta H$ values are more negative for the $\text{Mg}_{12}\text{O}_{12}$ nano-cage than the $\text{Be}_{12}\text{O}_{12}$ nano-cage, while for the same nano-cage, $\Delta H$ values are more negative for $\text{SO}_2$ gas than $\text{H}_2\text{S}$ gas. This confirms the above discussion of the high ability of the $\text{Mg}_{12}\text{O}_{12}$ nano-cage to absorb the investigated gases and the high ability of the $\text{SO}_2$ gas to attach to the considered nano-cages. Figure 11b shows
ΔG for the examined complexes. Spontaneous and non-spontaneous reactions are characterized by negative and positive ΔG values, respectively, while low negative ΔG values indicate the capability to reverse the reaction [46,66–68]. For the H2S/Be12O12 complex in the temperature range, ΔG values are positive, which indicates a non-spontaneous reaction, while for the SO2/Be12O12 complex, the reaction is spontaneous at low temperatures, and beyond T = 400 K, the reaction turns into a non-spontaneous reaction. Furthermore, for the H2S/Mg12O12 and SO2/Mg12O12 complexes in the temperature range, ΔG values are negative, which indicates a spontaneous reaction. In addition, the reaction is capable of being reversed in the H2S/Mg12O12 complex easier than in the SO2/Mg12O12 complex.

4. Conclusions

Structural and electronic properties of the considered Be12O12 and Mg12O12 nano-cages as well their stability are scrutinized. Mg12O12 exhibits lower Eg, IP, η, and higher ω values than those for Be12O12, therefore, Mg12O12 is more reactive than the Be12O12 nano-cage. Molecular dynamics calculations emphasize the stability of the investigated nano-cages. In addition, the interaction of H2S and SO2 gases at the surfaces of the inspected nano-cages have been studied, and the features of the interaction are examined in the point of the NBO atomic charges, charge density difference analysis (Δρ), bond analysis, and PDOS. Ecorrads values show that the ability of the Mg12O12 nano-cage to adsorb the considered gases is higher than that of the Be12O12 nano-cage. Furthermore, the ability of SO2 gas to be adsorbed is higher than that of H2S gas. Furthermore, H2S gas dissociates at the Mg12O12 surface. In addition, adsorption of H2S leads to a decrease in the HOMO–LUMO gap (Eg) values of Be12O12 and Mg12O12 by 3.84% and 17.54%, respectively, whereas the adsorption of SO2 leads to a decrease in Eg values by 15.97% and 2.60%, respectively. At high temperatures, MD calculations declare that the Be12O12 and Mg12O12 nano-cages do not retain the H2S on their surfaces, while SO2 is retained at low and high temperatures. Moreover, the thermodynamic calculations show that the reactions between H2S and SO2 with Be12O12 and Mg12O12 nano-cages are exothermic. Furthermore, at the temperature range of 300–700 K, the H2S reaction with Mg12O12 and Be12O12 is spontaneous and non-spontaneous, respectively, while the SO2 reaction with Mg12O12 is spontaneous, whereas the SO2 reaction with Be12O12 is spontaneous at temperatures up to 400 K. In addition, the reaction is capable to be reversed in the H2S/Mg12O12 complex easier than in the SO2/Mg12O12 complex.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12101757/s1, Table S1. The examined orientations for H2S interaction with Be12O12, Table S2. The examined orientations for H2S interaction with Mg12O12, Table S3. The examined orientations for SO2 interaction with Be12O12, Table S4. The examined orientations for SO2 interaction with Mg12O12.

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