Combined DFT and MD simulation approach for the study of SO_2 and CO_2 adsorption on graphite (111) surface in aqueous medium

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ABSTRACT

In this study, density functional theory (DFT) calculations combined with molecular dynamics (MD) simulation have been used to understand the adsorption mechanism of sulfur dioxide (SO_2) and carbon dioxide (CO_2) on the graphite surface in aqueous medium, in view of analytical and environmental application. The global reactivity descriptors, such as the frontier molecular orbital energies (E_{HOMO} and E_{LUMO}), gap energy (ΔE_{gap}), absolute hardness (η) and softens (σ), fraction of electrons transferred (ΔN) and electronegativity (χ) were evaluated. The dynamic descriptors calculated by the MD simulation such as the adsorption energy (E_{ads}), total energy (E_{tot}), deformation energy (E_{def}), rigid adsorption energy (RAE) and dE_{ads}/dNi were also calculated and discussed. The obtained results indicated strong electron acceptor ability and high adsorption energy, which can suggest good adsorption ability. The interaction energies ($\Delta E_{interaction}$) were negative for both gases indicating strong attractive force between the molecules and the graphite surface. The highest values of the binding energy ($\Delta E_{binding}$) indicate that the adsorption of each molecule is strong and stable, which is in agreement with the interaction energies. The values of E_{HOMO} and E_{ads} were negative, indicating that the complete chemical processes occur spontaneously. Furthermore, MD simulation was applied to investigate the most stable configuration of the molecules on the graphite (111) surface. The larger E_{ads} and the smaller bond distances indicate that graphite exhibited higher sensitivity to interact with SO_2 and CO_2 molecules in an aqueous medium.

1. Introduction

Atmospheric pollution stands as one of the more important environmental issues, conducting to great social impact problems, such as depletion of the ozone layer, acid rain, photochemical smog or greenhouse effect [1]. The change observed during the last decades in the natural greenhouse is due to the release in the atmosphere by the human activities of certain gases, so-called as greenhouse gases. Among these atmospheric pollutants, CO_2 and SO_2 are critical ones, being majors responsible for acid rain, in addition to their inherent toxicity [2]. In many industrial processes, coal and oil burning will generate a large volume of these gases.

The emissions from the combustion of fossil fuels are contributing to an increase in the concentration of CO_2 in the atmosphere, resulting in serious environmental problems [3–5]. This gas is usually accepted as the most contributing specie in the global climate change [6,7]. Moreover, it

is the most important greenhouse gas, accounting for 78% of the global anthropogenic emission in 2011 [8]. In addition, SO_2 is a well-known local pollutant and one of the primary waste gases released from a number of industrial activities, such as combustion processes, like refining of sulfur-rich minerals or production of sulfuric acid. The average emission factor of SO_2 for gas-turbine, steam and combined-cycle power plants is equal to 3.842, 15.276 and 2.325 g kWh^{-1} respectively [9]. In view of the environmental and health problems [10,11], the detection and the removal of SO_2 and CO_2 are highly encouraged. There are extremely toxic and harmful for both human health and the environment [12]. Many studies have been devoted to the development of gas molecules sensors as a safety precaution device [13]. Researchers attach the importance to continuous on-site surveillance of air pollutants to protect the human body from damage.

Among the different techniques used to trap gases, the adsorption on mineral-based absorbents appears as a method of choice for the chemical

industry because of its easy operation, flexibility, simplicity in design and insensitivity [14]. In addition, the adsorption process is the most important process contributing in the development of gas molecule sensors. To the best of our knowledge there is no research in literatures on the study of interaction of SO_2 and CO_2 molecules on the graphite surface. Because of important roles of abovementioned species in atmosphere, developing straightforward methods and introducing new adsorbent materials seems to be essential. Many adsorbents such as activated carbon, carbon nanotubes, Pt-doped and Au-doped single--walled carbon nanotube, zeolite, titan dioxide, graphene, magnesium oxide and graphite that is, have been applied for the adsorption of gas [15–21]. In this study, we choose graphite as an adsorbent because it is the most promising, owing to soft, non-flammable, non-toxic, low cost, does not emit fumes, and has a low coefficient of friction. Moreover, this adsorbent respect the environment. The studies of the adsorption behaviors based on the analysis of the geometric structure, adsorption energy, charge transfer, and electronic property of SO_2 and CO_2 gaseous species on the Bernal phase of graphite. This hexagonal crystal phase, more abundant in nature, is characterized by purely covalent in-plane bonding and a weak Van der Waals interaction in the inter-planar bonding [22].

In this study, we combine the density functional theory calculations with molecular dynamics to investigate the electrical properties and adsorption capacity of graphite monolayer, exploring the feasibility of graphite monolayer for SO_2 and CO_2 sensor applications. The more favorable adsorption configurations are determined through the calculation of adsorption energy, charge transfer and adsorption distance. Electron localization function and electronic structures (molecular electrostatic potential and Mulliken charge) have also been calculated to further explain the adsorption mechanism. Furthermore, we consider adsorption capacity as a normative parameter to explore suitable gas molecule sensor.

2. Computational details

2.1. Density functional theory detail

Gaussian 09 W program package was used for the calculations [23]. The first task of the computing study was to determine the optimized geometry of the considered molecules using the M06 [24] with LanL2DZ basis set. Theoretical parameters, such as energy of the LUMO (E_{LUMO}), energy of the HOMO (E_{HOMO}), electronic affinity ($A = -E_{LUMO}$), ionization potential ($I = -E_{HOMO}$), energy gap ($\Delta E_{gap} = E_{HOMO} - E_{LUMO}$), dipole moment ($\mu$), hardness ($\eta$), absolute electronegativity (χ) and the number of transferred electrons (ΔN) have been used to understand the favorable adsorption sites for the molecules. Absolute electronegativity (χ), hardness (η), softness (S) and $\Delta E_{back-donation}$ were calculated from the energies of the frontier molecular orbitals using Eqs. (1)–(4), respectively [25]:

$$\chi = -\frac{I + A}{2} = \frac{-(E_{HOMO} + E_{LUMO})}{2} \tag{1}$$

$$\eta = \frac{-(E_{HOMO} - E_{LUMO})}{2} \tag{2}$$

$$S = \frac{1}{\eta} = \frac{-2}{E_{HOMO} - E_{LUMO}} \tag{3}$$

$$\Delta E_{back-donation} = \frac{-\eta}{4} \tag{4}$$

The fraction of electrons transferred from the gaseous molecule to carbon graphite surface, ΔN_{max}, was calculated according to Eq. (5) [26]:

$$\Delta N_{max} = \frac{\chi}{2\eta} \tag{5}$$

2.2. Molecular dynamic simulation procedure

The molecular dynamic (MD) simulations were used to calculate the low-configuration adsorption energy of the interaction between the adsorbates and the graphite surface in an aqueous medium. Chemical descriptors calculated using the adsorption locator module (Accelrys, San Diego, CA, USA) implemented in Material Studio 8.0, distributed by BIOVIA society [27] were used to build substrate/molecule/solvent system. The simulation of the interaction between the single molecule (SO_2 or CO_2) and the graphite (111) surface was carried out in a simulation box $(35\ Å)^3$. A vacuum plate of 35 Å thickness was introduced on the graphite (111) surface and was then enlarged to a supercell ($7 \times 7 \times 7$) as shown in Fig. 1. MD calculation was realized by applying five cycles (2000 steps in each cycle) of simulated annealing. The lowest potential energy configurations were sampled at the steps of low temperatures. MD simulations were obtained using an NVT canonical ensemble at 298 K and simulation time of 300 ps (1 fs time step). The long-range electrostatic interactions were treated using the Ewald summation method. Interactions with Van der Waals have been treated by a cutoff distance of 12.5 Å and a spline width of 1 Å. For the whole simulation procedure, COMPASS force field [28] was used to optimize the structures of all components of the system (graphite surface/gas molecule/400 water molecules). The adsorption study of the molecule, or molecules set, is based on the preliminary determination of the potential interaction energy of the adsorbate-substrate system. This energy is generally written as the sum of three contributions:

- The total interaction energy between the molecule and the equilibrium surface denoted $E_{molecule+surface}$.
- The total internal energy of the surface, after possible relaxation, without the presence of the molecule, noted $E_{surface}$.
- The total energy of the molecule relaxed without the surface, noted $E_{molecule}$. Thus, the adsorption energy of the surface molecule system is in the form:

$$E_{ads} = E_{molecule+surface} - E_{surface} - E_{molecule} \tag{6}$$

wherein E_{ads} denotes as the interaction energy between the single gas molecules and graphite (111) surface.

3. Results and discussion

3.1. Density functional theory and molecular dynamics simulations

3.1.1. Electronic distribution

The frontier molecular orbitals HOMO and LUMO and the molecular electrostatic potential of the chemical species are very important in defining their reactivity and determining the electrophilic and nucleophilic sites [29]. To study the effect of the electronic properties and the molecular structure towards the adsorption of the SO_2 and CO_2 on the graphite surface, a quantum chemical calculation has been applied. The optimized structure, the frontier molecular orbital density distributions (HOMO and LUMO) and molecular electrostatic potential (MEP) of the molecules obtained by the M06/LanL2DZ method are shown in Fig. 1. The nucleophilic ones are colored in light blue and blue and the red and yellow colors in MEP map indicate the electrophilic active region. The initial and promoted molecules give chelated species on the surface by exchanging electrons between atoms of molecules and p-orbital of carbon of graphite surface to from covalent coordinate through the chemical adsorption process. Fig. 2 shows clearly that the more electron-rich regions are mainly localized around the oxygen atoms. The electrophilic sites are localized at the oxygen atoms of both SO_2 and CO_2. The more negatively charged heteroatom can interacts with surface, through an electron donor-acceptor reaction type [21,30].
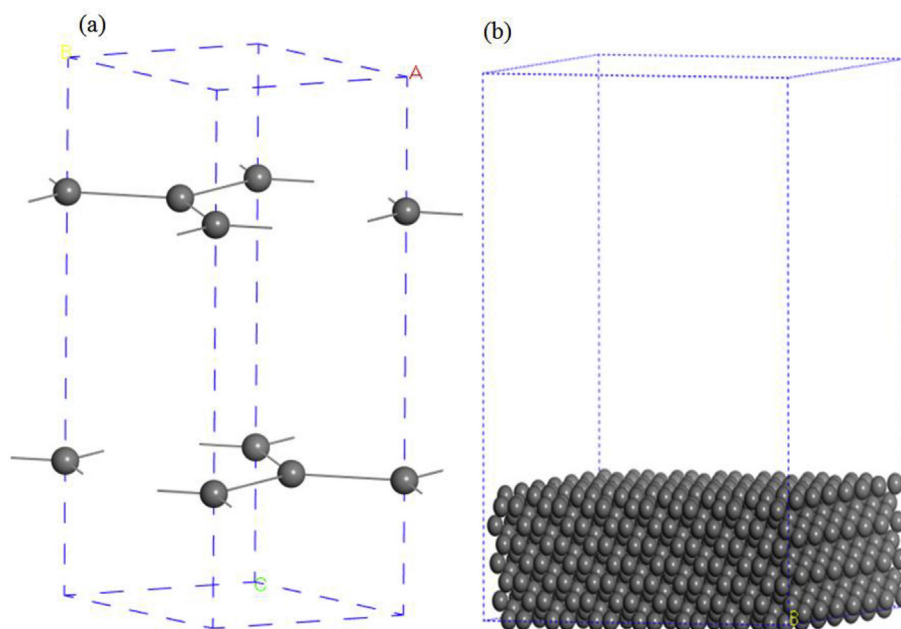
Fig. 1. Supercell of graphite after the optimization (a) and graphite (111) surface models (b).
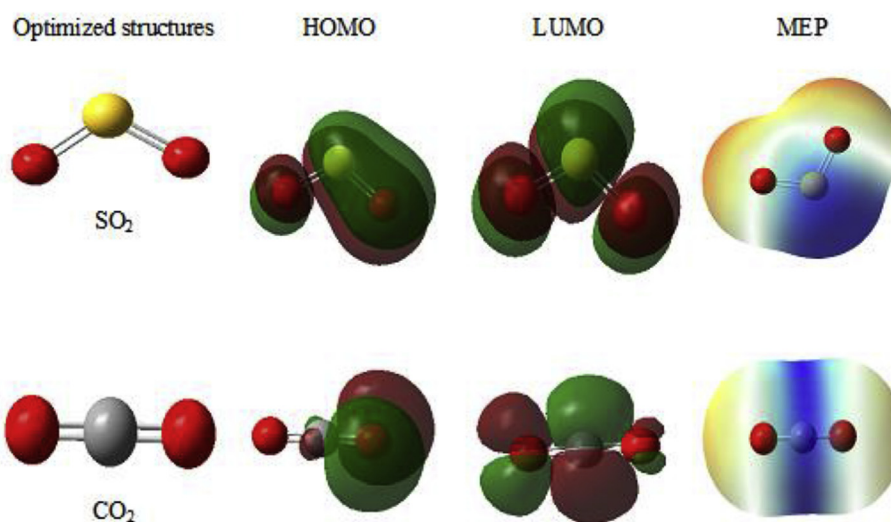

Fig. 2. Optimized structures, frontier molecular orbitals density distribution (HOMO, LUMO) and molecular electrostatic potential (MEP) for SO_2 and CO_2 species.

3.1.2. Quantum chemical parameters

Theoretical studies at the molecular level have been reported to gain insight on the molecules chemical activity taking into account their structural and electronic properties. The energy of the lowest unoccupied molecular orbital (E_{LUMO}) is related to the ability of a molecule to accept electrons, a low value of the E_{LUMO} means that the molecule is favorable to accept electrons. On the other hand, the energy of the highest occupied molecular orbital (E_{HOMO}) generally describes the ability of a molecule to give electrons. For this reason, the E_{LUMO} and E_{HOMO} are very beneficial parameters that can be utilized to understand the chemical reactivity of the gas molecule. These molecular orbitals have a crucial role in the understanding of the chemical reactivity at the atomic level. Furthermore, they are other important descriptors for the explanation of various chemical reactions. The calculated global descriptors responsible for the reactivity of SO_2 and CO_2, such as E_{HOMO}, E_{LUMO}, energy gap (ΔE_{gap}), softness (S), hardness (η), electronegativity (χ), number of transferred electrons (ΔN) and energy change ($\Delta E_{back-donation}$), are shown in Table 1.

A high value of the E_{HOMO} facilitates the tendency of gas molecules to yield electrons to acceptable compounds of electrons having unoccupied molecular orbitals with low energy levels. Consequently, this elevated value designates the affinity of electrons transfer to a suitable acceptor molecule which hence favors the adsorption of the gas molecules onto

Table 1

Quantum chemical parameters of CO_2 and SO_2 calculated by DFT at M06/LANL2DZ level (in eV).

Molecule	E_{HOMO}	E_{LUMO}	ΔE_{gap}	S	H	χ	ΔN_{max}	$\Delta E_{back-donation}$
CO_2	−9.671	−1.508	8.162	0.245	4.081	5.590	0.685	0.393
SO_2	−9.406	−6.256	3.149	0.635	1.575	7.831	2.486	1.020

the graphite surface [31]. Moreover, the ΔE_{gap} is an important parameter that indicates the reactivity tendency of molecule towards the graphite surface [32]. When, ΔE_{gap} decreases, the adsorption performance of the coating molecule on the graphite surface increases. The examination of the data presented in Table 2, shows that the high values of E_{HOMO} (−9.671eV for CO_2 and -9.406 for SO_2) reveal the elevated adsorbed capacity, which does not correlate well with other quantum parameters and adsorption energy. The results obtained indicated that the trend in the E_{LUMO} is as follows: $SO_2 < CO_2$, which implies that SO_2 molecule, is more suitable to accept electrons from the p-orbital of the graphite leading to the formation of a covalent bond. Therefore, the formation of this last depends on the low value of the gap energy (3.149 eV). So, the absorption effectiveness increases with the increase in the electron transfer ability to the graphite surface. Moreover, the relationship between quantum chemical properties and adsorption is often based on the Lewis theory of acids-bases. The Hardness (η) and softness (S) are also two features to measure the molecular stability and reactivity [33–35]. The carbon graphite would preferentially interact with molecules that have low η and high S values, as the soft molecule with the lower value of ΔE_{gap} exchange easily electrons with their environment.

The calculations indicate also that SO_2 has the highest electronegativity value compared to CO_2. The fraction of electrons transferred for both gases is negative so the studied gases were the acceptor of electrons, and the carbon surface was the donor of electrons. The higher ΔN_{max} was obtained for SO_2, confirming that this molecule can donate electrons to the vacant orbital of graphite surface favoring the formation of adsorptive bonds. This result confirms the good chemical adsorption of SO_2 compared to CO_2. Finally, $\Delta E_{back-donation}$ was negative in both cases, indicating an energetically favored back-donation from the molecule to graphite. The electron donating ability follows the order $SO_2 > CO_2$ in good agreement with the molecular dynamic studies.

Some quantum chemical parameters obtained from the DFT/M06/LAN2DZ using Gaussian-09 program package were compared with the previous records of various methods as listed in Table 2. Excitation of CO_2 and SO_2 molecules becomes easier when their ΔE_{gap} converges or becomes smaller. Generally, DFT/M06 method used in calculating the ΔE_{gap} of CO_2 and SO_2 gave values that are low and are quite smaller than the band gap of other methods. Moreover, it can be observed that the theoretical data of the present study were found to be better than those of some corresponding quantum chemical study in the literature.

3.1.3. Mulliken charge distribution

Mulliken population analysis provides information about the active sites of a molecule. The Mulliken charge calculated for the oxygen, sulfur and carbon atoms in the SO_2 and CO_2 molecules are gathered in Table 3. The table indicates that the oxygen atoms carry negative charges in both molecules, while carbon and sulfur atoms carry more positive charges. This result means that oxygen atoms can offer electrons to the graphite atoms to form coordinate bond. We can also emphasize that the highest negative charges were found for the oxygen atoms of SO_2, which therefore imply that SO_2 bind strongly to the surface of graphite than CO_2.

3.1.4. Binding energy

Interaction energy, which results from the binding of gas molecules to

Table 2

Comparison of quantum chemical parameters calculated by DFT/M06/LANL2DZ of CO_2 and SO_2 should be compared with other studies in the literature (in eV).

Gas	Method	E_{HOMO}	E_{LUMO}	ΔE_{gap}	References
CO_2	TD-SCF B3LYP/6-31G (d)	−10.067	0.814	10.881	[36]
	DFT/B3PW91/LANL2DZ	−10.377	−0.346	10.031	[37]
	DFT/M06/LANL2DZ	−9.671	−1.508	8.162	This study
SO_2	TD-SCF B3LYP/6-31G (d)	−8.984	−3.617	5.367	[36]
	DFT/B3LYP/6-31G (d,p)	−8.98	−3.62	5.36	[38]
	DFT/M06/LANL2DZ	−9.406	−6.256	3.149	This study

Table 3

Calculated Mulliken atomic charges for atoms of SO_2 and CO_2 using DFT at the M06/LANL2DZ basis set.

	C	O2	O3	S
SO_2		−0.577	−0.577	1.153
CO_2	0.474	−0.237	−0.237	

graphite surface, was calculated to measure the stability of gas-graphite (111) surface complexes. A more negative value of differential interaction energy indicates that the adsorption system is stronger and stable [39,40]. There are many gas molecule interaction modes with carbon graphite and a better description can be obtained by calculating the difference between the total bond energy of $C_{graphite}$-gas ($C_{graphite}$-SO_2 or $C_{graphite}$-CO_2) complexes (E_{total}) and energy isolated from gas molecule (E_{gas}) and energy isolated from carbon (E_C) using DFT method. However, the interaction or binding energies were estimated according to Eq. (7) [41]:

$$\Delta E_{binding} = -\Delta E_{int} = (E_{gas} + E_C) - E_{system} \tag{7}$$

where E_{system} is the total energy of the full system carbon and adsorbed gas molecule, E_{gas} is the energy of the molecule without the surface, E_C is the energy of graphite (111) surface without the gas molecule.

The values of the interaction energy of the molecules on graphite (111) surface are regrouped in Table 4. The Table indicates that SO_2 systems has higher negative interaction energy compared to the CO_2 systems. Therefore, the adsorption of sulfur dioxide on the graphite surface in aqueous solution is easier than carbon dioxide. Thus, the adsorption of SO_2 and CO_2 onto a graphite surface occurs at the part of the molecule which has the greatest softness, lowest hardness, large binding energy and higher negative interaction energy.

3.2. Molecular dynamic simulation study

Molecular dynamic simulation was performed to further study the adsorption behavior of gaseous molecules on the graphite (111) surface. Thus, MD simulation reasonably predicts the most favorable configuration of the adsorbed molecules on the low adsorption energy graphite surface. The Van der Waals, total, electrostatic, average total, and intermolecular energies for the systems under study; graphite (111)/(SO_2, CO_2) with solvent molecules (400 H_2O) are calculated and presented in Fig. 3.

The total energy of configuration E_m is calculated according to Eq. (8) [42]:

$$E_m = E_m^{AA} + E_m^{AS} + U_m^A \tag{8}$$

where E_m^{AA} is the intermolecular energy between the gaseous molecules, E_m^{AS} is the interaction energy between the gas molecule and the graphite surface, and U_m^{AS} is the total intramolecular energy of the gas.

The intramolecular energy of the gas is not included as its structure is fixed throughout the simulation. Therefore, this energy contribution is fixed and vanishes, since only energy differences play a role in adsorption locator calculations.

The total intramolecular energy is the sum of the intramolecular energy of all adsorbates of all components [42]:

Table 4

Total, gases and graphite interactions of the gas-graphite complexes calculated by DFT method at M06/LANL2DZ basis set (in kJ/mol).

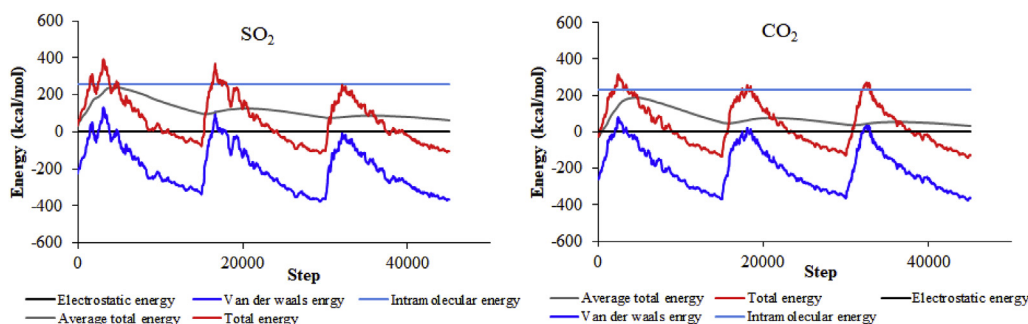| Gas	E_{total}	E_{gas}	E_C	$\Delta E_{interaction}$
CO_2	−594424.788	−494813.365	−99178.398	−433.025
SO_2	−520941.812	−420978.721	−99178.3981	−784.693

Fig. 3. Total, average total, Van der Waals, electrostatic and intramolecular energies distribution for SO_2 and CO_2/400 H_2O/graphite (111) obtained by adsorption locator module.

$$U^A = \sum_{\{N\}m} U_{intra} \qquad (9)$$

where {N} denotes the set of adsorbate loadings of all components in configuration *m*.

As the simulation starts with a clean graphite (111) surface, the first stage is to adsorb the specified number of water molecules and gas molecules. This is accomplished by a random series of insertion steps and equilibration moves (only moves that do not change the loading are permitted) until the specified loading has been reached. During this stage, only insertion steps that do not create structures with intermolecular close contacts and that pass all adsorbate location constraints are accepted [42].

For both CO_2 and SO_2 molecules adsorption in the presence of water molecules, it is noted that the electrostatic energy is equal zero, on the other hand, the intramolecular energy is different to 0, but admits a stable energy value for both molecules, which means that it has no electric charge with a point responsible for electrostatic interactions (electrostatic bonding). It was also observed that the total energy and the average total energy were positive, which do not exceed 400 kcal/mol. Moreover, the energy of Van der Waals admits negative and positive values that do not exceed the values of average total energy. The Van der Waals interaction has a dominant contribution to the molecule's adsorption on the graphite. From Fig. 3, it can be seen that the intermolecular energy is stable. Therefore, this energy causes covalent bonds between the gas molecules and the graphite atoms.

System equilibrium state and the best adsorption configurations of the substrate-adsorbed gas, obtained by adsorption locator module

(COMPASS force field) [29] are depicted in Fig. 4. As can be seen from the figure, the interaction between the gas molecules and the graphite surface is in a parallel orientation from the surface. The molecules are adsorbed nearly plane on the graphite (111) surface in water solvent molecules with maximum surface coverage and contact, ensuring a strong interaction between adsorbate and substrate. In addition, the strong interaction of the system ensures that the adsorption process is chemical nature, which was confirmed by the high rigid adsorption energy (RAE.) values (in absolute values). Otherwise, the dipole moment (μ) of CO_2 is zero due to the lack of charge separation, on the other hand, the dipole moments of SO_2 (3.447D) are greater than zero. After adsorption, the values of the dipole moment increase significantly and become 3.115 D for CO_2–C and 7.639 D for the SO_2–C, due to the perturbation in the electron density at the interface of the graphite surface. Generally, molecules with high dipole moment tend to form strong dipole-dipole interactions with the adsorbate surface, resulting in strong adsorption on the surface [43]. Consequently, the numbers of electrons transferred are negatives, which imply that the graphite carbon becomes rich in electrons and the positive charges are accumulated on the gas molecules.

MD simulation was also applied to calculate the adsorption energies for the interaction of the molecules with graphite (111) surface. The calculated descriptors by the adsorption locator and the total energy, in kcal/mol, of the substrate-adsorbate configurations are presented in Table 5. The total energy is defined as the sum of the energy of the adsorbate components, the rigid adsorption energy and the deformation energy. While, adsorption energy (kcal/mol) reports energy released (or required) when the relaxed adsorbate components (molecule in H_2O) are
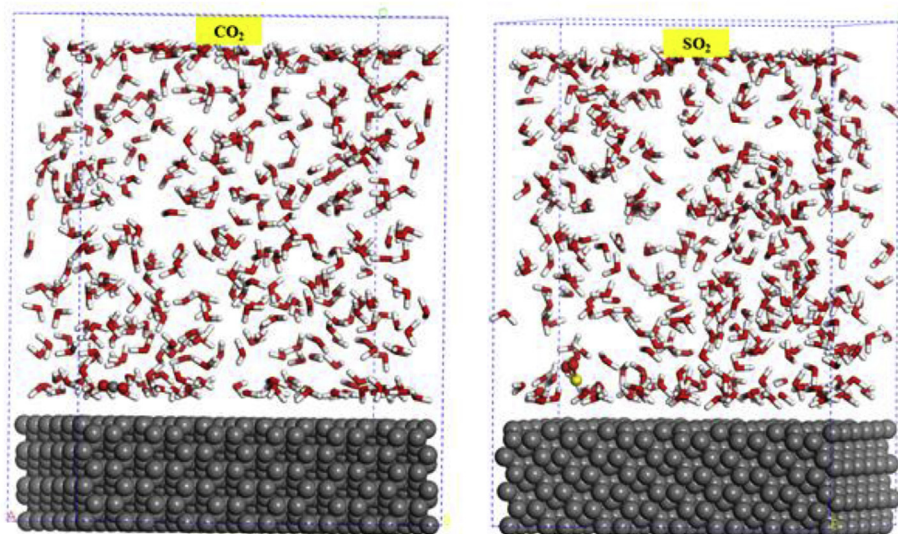

Fig. 4. Side views of the stable adsorption configurations for SO_2 and CO_2/400 H_2O/graphite (111) interface obtained by adsorption locator module.

Table 5
Outputs and descriptors calculated by the MD simulation for the adsorption of the SO_2 and CO_2 on the graphite (111) surface (kcal/mol).

Molecule	E_{tot}	E_{ads}	RAE	E_{def}	dE_{ads}/dNi_{gas}	dE_{ads}/dNi_{H2O}
SO_2	−633.93	−893.95	−634.02	−259.31	−33.30	−1.44
CO_2	−614.37	−846.20	−614.87	−231.34	−5.24	−1.32

adsorbed on the substrate. This energy is defined as the sum of the rigid adsorption energy and the deformation energy for the adsorbate components. Table 5 also shows (dE_{ads}/dNi), which reports the energies of SO_2, CO_2 and H_2O configurations, when one adsorbate component has been removed.

Moreover, MD simulation can help to study the non-reactive, physical interactions between the adsorbed molecule and the surface. Once the chemical bond is formed during the realistic adsorption, the formation of bond can be studied by first-principle calculations with appropriate modeling and the formation energy along with other quantum descriptors is adopted to investigate the adsorption behavior. For surface adsorption with a periodic system, the formation energy per adsorbate molecule per unit cell is a negative quantity, which defined in Eq. (10) [44]:

$$E_{def} = E_{adsorbed-system} - (E_{molecule//molecule} + E_{surface//surface}) \qquad (10)$$

where $E_{adsorbed-system}$ is the energy of a fully relaxed unitary cell containing the slab in interaction with the adsorbed molecule, $E_{molecule//molecule}$ is the energy of the free and fully optimized adsorbed molecule and $E_{surface//surface}$ is the energy of a fully relaxed unitary cell containing the slab alone.

Table 5 shows that the values of adsorption energies are negative corresponding to an exothermic process, and the high absolute value of the adsorption energy reflects a strong adsorption behavior [44]. The large negative value for SO_2 indicates that its complex is more stable and strongly adsorbed on graphite surface compared to CO_2 [45]. This result is in agreement with the quantum descriptors obtained by DFT.

The larger E_{ads} and the smaller bond distances shown in Table 6 indicate that graphite exhibited higher sensitivity to interact with SO_2 and CO_2 molecules. The distances between molecules atoms (S, O or C) and the carbon atom of graphite show that both molecules have higher stability. The measured shortest bond distances between the active sites (=O) and the graphite (111) surface of the $C_{graphite}$-CO_2 or $C_{graphite}$-SO_2 complexes, in aqueous solution at equilibrium, were as follows: d_{C-O}: 3.456 Å and d_{C-S}: 3.345 Å, respectively. These distances are short and lower to the value of 3.5 Å, which indicates a strong chemical interaction [46]. This chemical interaction of the system was confirmed by the high energy value of RAE (in absolute values) and the high value of E_{HOMO}.

4. Conclusion

In this work, density functional theory and molecular dynamic simulation were employed to evaluate the adsorption behavior of SO_2 and CO_2 molecules on graphite surface at the molecular level. The quantum chemical parameters calculated by DFT/M06/LANL2DZ level for $C_{graphite}$-SO_2 and $C_{graphite}$-CO_2 complexes have provided information on the stability of interaction. It was found that the adsorption was chemical in nature and was spontaneous. SO_2 molecule was strongly adsorbed on the vacancy-defected graphite compared to CO_2. It can be seen from the results that the negative values of adsorption energies increase in the order of SO_2 > CO_2, which is in good agreement with the quantum parameters. The number of electron transfer was negative which implies that the graphite played the role of electron donor and the gas molecules are accepted electrons. The larger E_{ads} and the smaller bond distances indicate that graphite exhibited higher sensitivity to interact with SO_2 and CO_2 molecules in an aqueous medium.

Table 6
Bond length for $C_{graphite}$-molecule atoms (in Å).

Distance	d_{C-C}	d_{C-O}	d_{C-S}
SO_2		4.478	3.345
CO_2	3.891	3.456	

Data availability

The data used to support the findings of this study are available from the corresponding author upon request.

CRediT authorship contribution statement

M. Khnifira: Performed the calculations; Analyzed and interpreted the data, Formal analysis, Data curation, Writing – original draft. **A. Mahsoune:** Conceptualization, Conceived and designed the calculations; Analyzed and interpreted the data, Formal analysis, Data curation, Data curation, Writing – original draft, Writing – review & editing, Funding acquisition, Resources, Validation, Data curation, Writing – original draft, Writing – review & editing, Funding acquisition, Resources, Validation. **M.E. Belghiti:** Conceptualization, Conceived and designed the calculations; Analyzed and interpreted the data, Formal analysis, Data curation. **L. Khamar:** Conceptualization, Conceived and designed the calculations; Analyzed and interpreted the data, Formal analysis, Data curation. **M. Sadiq:** Conceptualization, Conceived and designed the calculations; Analyzed and interpreted the data, Formal analysis, Data curation. **M. Abdennouri:** Supervision, Conceptualization, Formal analysis, Conceived and designed the calculations; Analyzed and interpreted the data; Contributed reagents . **N. Barka:** Supervision, Conceptualization, Formal analysis, Conceived and designed the calculations; Analyzed and interpreted the data; Contributed reagents .

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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