# UNDERSTANDING THE ADSORPTIVE INTERACTIONS OF CARBON DIOXIDE WITH METAL-ORGANIC FRAMEWORK (IRMOF-1) USING A THEORETICAL APPROACH

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**Abstract.** Density Functional based Tight-binding method with dispersion corrections and Molecular Dynamics (MD) simulations were performed to study the carbon dioxide ($CO_2$) adsorption process on a metal-organic framework (IRMOF-1). The adsorption centers, adsorption energy, adsorption capacity, diffusion coefficient, and the effect of temperature on the adsorption process have been thoroughly examined and elucidated. The calculated results reveal that the favorable $CO_2$ adsorption site on IRMOF-1 is the position where the $CO_2$ molecule is located in the cavity formed by the metal cluster and oxygen atoms of the three – COO groups of the organic ligand. The $CO_2$ molecules were instantly adsorbed on the IRMOF-1 structure as "anchors" to hold the next molecules in place. The Monte Carlo simulation results demonstrate that when the concentration of $CO_2$ molecules is low, they preferentially adsorb onto the surface of IRMOF-1. As the number of $CO_2$ molecules increases, they will gradually occupy the free space inside the crystal. The MD simulations with constant volume and temperature have shown that up to 350 K, $CO_2$ was still dynamically adsorbed on IRMOF-1, without being desorbed. The calculated diffusion coefficients imply that $CO_2$ would diffuse into IRMOF-1 slower than methane, but quicker than oxygen and nitrogen. Therefore, it is feasible to separate $CO_2$ from its mixture with oxygen and nitrogen using IRMOF-1.

*Keywords:* DFTB, molecular dynamics, $CO_2$, MOFs, adsorption.

*Classification numbers*: 2.6.2, 2.8.2, 3.5.1.

## 1. INTRODUCTION

Recently, the rapid increase in the concentration of carbon dioxide ($CO_2$) in the atmosphere has led to global climate change, causing serious impacts on the environment and human health. The issue of reducing emissions and $CO_2$ concentrations in the atmosphere is one of the urgent and topical challenges. Currently, carbon capture and storage (CCS) technology has been applied directly at emission sources such as thermal power plants using fossil fuels. However, the main limitation of this technology is that it requires high energy consumption, involving separation, filtration, compression, transport and storage processes, and therefore does not completely solve the problem [1, 2]. Another promising and potential direction is to capture and

convert $CO_2$ into other useful products, creating a "green" artificial carbon cycle. Several types of materials, including ionic liquids [3], zeolites [4], porous carbon materials [5], porous organic polymers [6], covalent organic framework materials [7], and metal-organic framework materials (MOFs) [8] have been studied for this purpose. Among them, MOFs are considered as a promising adsorbent and catalytic material due to their unique advantages such as high specific surface area; easy to modification; highly hybrid and compatible with other materials; high catalytic efficiency, high reusability, and stability. In addition, MOFs also have the high ability to selectively adsorb $CO_2$ from a mixture of other gases such as $N_2O$, $CH_4$, etc. [9, 10].

The mechanism of $CO_2$ adsorption on MOFs has been intensively studied both theoretically and experimentally to determine the nature of the adsorption process, adsorption centers, adsorption capacity, etc. Many studies have shown that the $CO_2$ adsorption process on MOFs has a physical nature, in which van der Waals (vdW) interactions play an important role [11 - 13]. In the work of Neaton *et al*. [13], the authors used the DFT method with vdW correction to study the role of dispersion interactions for $CO_2$ adsorption in Mg -MOF74 and Ca-BTT. The results show that the vdW interaction can contribute up to 50 % of the interaction energy between $CO_2$ and MOF. Correcting the vdW interaction allows to predict the adsorption enthalpy with chemical accuracy compared with the experimental value.

When adsorbed on MOFs, due to the nature of physical adsorption, $CO_2$ is preferably adsorbed near the metal clusters, where the vdW interaction is strongest. Nachtigall *et al*., using density functional theory (DFT) combined with microtherometric measurements, has shown that at low concentrations, $CO_2$ molecules are preferentially adsorbed on the valence unsaturated metal cluster sites of MOF (CuBTC) [14]. As the concentration increases, $CO_2$ is gradually adsorbed at the outer edges, then in the center of the crystal.

Despite being a common approach for studying the structure and electronic properties of solids, utilizing the traditional DFT method to research $CO_2$ adsorption on MOFs is problematic due to the enormous scale of the system, which can range from hundreds to thousands of atoms. Recently, several other computational approaches, such as the QM/MM hybrid method [15, 16] or the enhanced simulation method employing force fields [17] have recently been used to investigate the $CO_2$ adsorption process on MOFs. These approaches have been shown to be efficient in calculation costs as well as accuracy.

In this paper, we present the results of a theoretical study on the $CO_2$ adsorption on IRMOF-1 using a combination of tight-binding density functional theory (DFTB) with vdW interaction and molecular dynamic (MD) simulations. The adsorption centers, adsorption capacity, $CO_2$ diffusion coefficient, and the effect of temperature on the adsorption process will be thoroughly examined and elucidated.

## 2. COMPUTATIONAL DETAILS

This study focuses on IRMOF-1, commonly known as MOF-5, which is one of the most widely used MOF materials. IRMOF-1 is formed by binding 1,4-benzenedicarboxylate (BDC) to $Zn_4O$ clusters. The unit cell of IRMOF-1 has a cubic structure, belongs to the space group Fm3□m and contains 424 atoms, with the molecular formula $Zn_{32}C_{192}H_{96}O_{104}$. The periodic boundary conditions were applied in all calculations.

Because of the large system size, the density functional based tight-binding (DFTB) method implemented in the CP2K open-source code was used for structure optimization and energy determination [18]. The Slater-Koster parameter set from the DFTB source [19] was

used. The vdW interactions were taken into account through the D3 model proposed by Grimme [20]. For IRMOF-1, the structure optimization was performed for the entire crystal structure, including the optimization of the atom positions and the lattice parameters taking into account the stress tensors in periodic boundary conditions. In these calculations, the external pressure acting on the crystal was chosen to be 1.0 bar.

The adsorption energy ($E_{ads}$), a thermodynamic parameter describing the extent of the adsorption process, is calculated as follows:

$$E_{ads} = E(MOF+CO_2) - E(MOF) - E(CO_2) \tag{1}$$

where $E(MOF+CO_2)$, $E(MOF)$, $E(CO_2)$ are the energy of the adsorbed $CO_2$ on MOF, the isolated MOF and $CO_2$ structures, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Structure optimization

First, the suitability of the DFTB method for the investigated system was verified by optimizing the structures of some typical MO (IRMOF-1, IRMOF-2, IRMOF-3, ZIF-3) and some gas molecules ($CO_2$, $CH_4$, $N_2$, $O_2$). The calculation results along with the experimental values are presented in Table 1 and Table 2.

The lattice parameters obtained from the DFTB optimization procedure are in good agreement with the experimental data. The largest error in the structure optimization for the lattice cells was found to be approximately 3.9 % in IRMOF-3 and ZIP-3. These findings clearly illustrate the suitability and the high accuracy of the DFTB method for the investigated periodic systems with large crystal sizes (nearly 500 atoms).

*Table 1.* Lattice parameters (lattice constants - a, b, c (Å), angles - α, β, γ (°)) of the optimized structures of IRMOF-1, IRMOF-2, IRMOF-3, ZIP-3 by DFTB method with dispersion correction.

| Parameter | *A* | *B* | *c* | *α* | *β* | *γ* |
|---|---|---|---|---|---|---|
| **IRMOF-1** | | | | | | |
| Calc. | 26.689 | 26.689 | 26.689 | 90.0 | 90.0 | 90.0 |
| Exp. [22] | 25.832 | 25.832 | 25.832 | 90.0 | 90.0 | 90.0 |
| Error, % | 3.3 | 3.3 | 3.3 | 0.0 | 0.0 | 0.0 |
| **IRMOF-2** | | | | | | |
| Calc. | 26.488 | 26.488 | 26.488 | 90.0 | 90.0 | 90.0 |
| Exp. [22] | 25.772 | 25.772 | 25.772 | 90.0 | 90.0 | 90.0 |
| Error, % | 2.8 | 2.8 | 2.8 | 0.0 | 0.0 | 0.0 |
| **IRMOF-3** | | | | | | |
| Calc. | 26.768 | 26.768 | 26.768 | 90.0 | 90.0 | 90.0 |
| Exp. [22] | 25.747 | 25.747 | 25.747 | 90.0 | 90.0 | 90.0 |
| Error, % | 3.9 | 3.9 | 3.9 | 0.0 | 0.0 | 0.0 |
| **ZIP-3** | | | | | | |
| Calc. | 19.522 | 19.522 | 16.630 | 90.0 | 90.0 | 90.0 |
| Exp. [23] | 18.970 | 18.970 | 16.740 | 90.0 | 90.0 | 90.0 |
| Error, % | 3.9 | 3.9 | 0.7 | 0.0 | 0.0 | 0.0 |

*Table 2.* Optimized parameters (bond lengths – d, Å; bond angles - <, degree) of $CO_2$, $CH_4$, $N_2$, $O_2$ by DFTB method with dispersion correction.

| Molecule | Parameters | | Molecule | Parameters |
|----------|-----------|-----------|----------|-----------|
| $CO_2$ | d(C-O), Å | <OCO, degree | $N_2$ | d(N-N), Å |
| Calc. | 1.180 | 180.0 | Calc. | 1.092 |
| Exp. [24] | 1.162 | 180.0 | Exp. [26] | 1.098 |
| Error, % | 1.5 | 0.0 | Error, % | 0.5 |
| $CH_4$ | d(C-H), Å | <HCH, degree | $O_2$ | d(O-O), Å |
| Calc. | 1.084 | 109.5 | Calc. | 1.211 |
| Exp. [25] | 1.087 | 109.5 | Exp. [26] | 1.208 |
| Error, % | 0.3 | 0.0 | Error, % | 0.3 |

The results obtained are also completely consistent with the previous publications. For instance, using the DFTB method to study the structures and electronic properties of some MOFs, Heine *et al.* showed an error of 3.6 % for the lattice parameters of Cu-BTC [21]. It should be noted that an accurate optimization procedure for the lattice parameters is extremely important because an error of only 1 Å will increase the internal pressure up to thousands of bars in the crystal.

The results of structure optimization for gas molecules by the DFTB method show very high accuracy. The highest deviation from the experimental value is 1.5 % for the C-O bond in the $CO_2$ molecule. Thus, the DFTB method is a suitable and accurate method for the investigated systems.

## 3.2. Adsorption of $CO_2$ on IRMOF-1

*3.2.1. Adsorption centers, adsorption energy and adsorption capacity*

Since the IRMOF-1 system is periodic, two possible adsorption regions are studied: region (1) corresponds to the cavity of the metal cluster and region (2) corresponds to the adsorption region on the organic ligand (see Figure 1). Initial adsorption configurations were constructed by randomly placing $CO_2$ molecules in regions (1) and (2). After optimization, three adsorption configurations were obtained: two configurations P1a, P1b corresponding to the $CO_2$ adsorption into region (1) and P2 configuration corresponding to the $CO_2$ adsorption into region (2). Figure 2 illustrates the adsorption configurations along with the respective adsorption energies.

Among the three adsorption configurations obtained, P1a corresponds to the most negative adsorption energy value. That is, the favorable $CO_2$ adsorption site on IRMOF-1 is the position where the $CO_2$ molecule is located in the cavity formed by the cluster $[Zn_4O]^{6+}$ and 6 O atoms of the three –COO groups of the BDC ligand. The distance between the $CO_2$ molecule and IRMOF-1 (O=C=O⋯X, where X is Zn, O of IRMOF-1) is about 3 Å. Obviously, with the adsorption energy smaller than 20 kJ mol$^{-1}$ and the interaction distance larger than any covalent bond length, it can be confirmed that $CO_2$ is physically adsorbed on the IRMOF-1 structure. The $E_{ads}$ calculated by the DFTB method is consistent with the experimental adsorption energy value of $CO_2$/IRMOF-1 (-15.1±0.4 kJ mol$^{-1}$) obtained by Farruseng *et al.* [27]. Especially if compared with the average value of -15.94 kJ mol$^{-1}$ corresponding to the two configurations P1a and P1b, the DFTB method with dispersion corrections showed a high accuracy for determination of $E_{ads}$.

In addition, the energy difference between P1a and P1b configurations is not large, so the $CO_2$ molecule can be adsorbed at both sites.
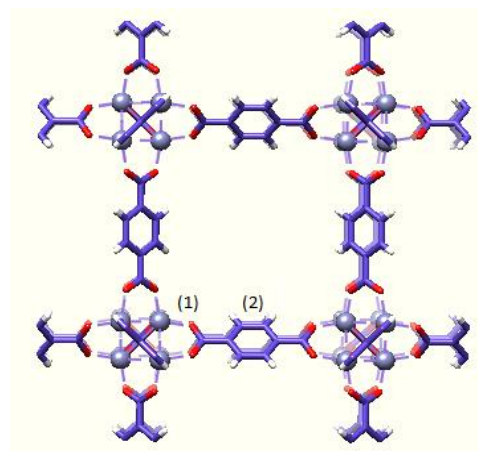


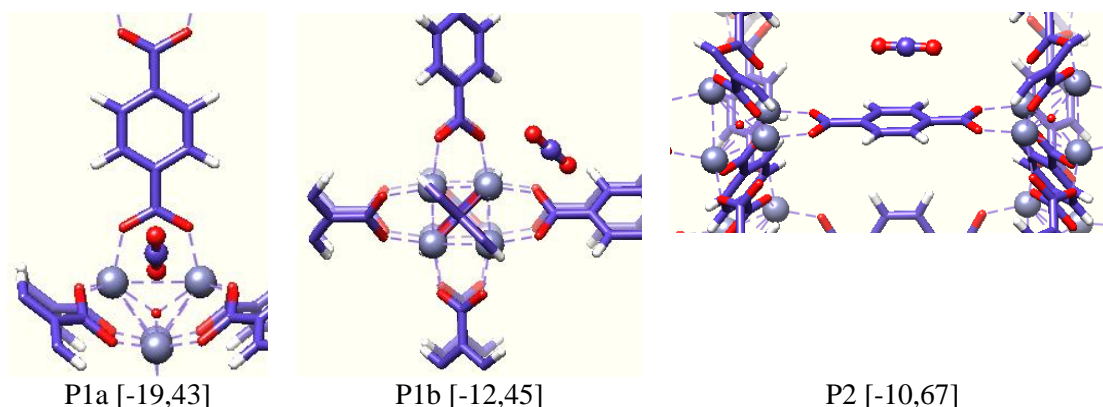*Figure 1.* Possible adsorption sites for $CO_2$.



P1a [-19,43]       P1b [-12,45]                    P2 [-10,67]

*Figure 2.* Optimized adsorption configurations of $CO_2$ on IRMOF-1 and respective adsorption energy (in brackets, kJ mol$^{-1}$).

Monte Carlo simulation (MC) was also utilized to find the preferred adsorption site and compare it to the DFTB method. The results obtained are extremely consistent. The most preferred adsorption sites and second preferred sites determined by MC simulation are quite similar to those obtained from the DFTB method. It should be noted that the MC approach has the advantage of not requiring the initial position of the $CO_2$ molecule on the IRMOF-1 structure to be assumed. However, this method cannot be used for structure optimization, and thus, it is not feasible to determine the adsorption energy with high precision.

**Adsorption capacity of $CO_2$ on IRMOF-1**

If only considering the situation of a $CO_2$ molecule being adsorbed at P1a position, then there will be four comparable P1a locations for one cluster $[Zn_4O]^{6+}$. Therefore, the maximal theoretical adsorption capacity (q) (corresponding to the P1a configuration) can be determined using the mole ratio of $CO_2$/Zn = 4/4. That is, the $CO_2$ adsorption capacity (q) is about $1.6.10^{-3}$ g $CO_2$/g IRMOF-1 or 0.16 % (m/m). This value is significantly lower than the experimental result of 8.5 % (m/m) [28] at a pressure of 1 bar. Therefore, $CO_2$ is also adsorbed at positions other

than P1a. For instance, there are four sites 1a and four sites 1b in a cluster $[Zn_4O]^{6+}$. If $CO_2$ is adsorbed at all of these sites, the $CO_2$ adsorption capacity, in this case, is q(1a, 1b) = 0.32 % (m/m). Similarly, if the P2 position is included, one benzene ring will have two P2 positions, then q(1a, 1b, 2) = 0.40 % (m/m). However, this calculated adsorption capacity is still much lower than the experimental value of 8.5 % (m/m). This finding demonstrates that $CO_2$ is adsorbed in IRMOF-1 at several more positions, albeit the adsorption energy is not as negative as at the three positions described above. Therefore, we hypothesize that $CO_2$ molecules can still be "trapped" in the empty space of IRMOF-1 with high density through vdW interactions with atoms of IRMOF-1, as well as between $CO_2$ molecules, especially at high pressure. It has been shown that the $CO_2$ adsorption capacity can reach 95.5 % (m/m) at a pressure of 35 bar [29], providing evidence to support the aforementioned hypothesis. We further postulated that the $CO_2$ molecules immediately adsorbed on the IRMOF-1 structure as "anchors" to hold other $CO_2$ molecules (which do not interact directly with the MOF) in place. Therefore, it is of great importance to study the adsorption and interaction of the "anchor" $CO_2$ molecules with IRMOF-1.

The Monte Carlo simulation is performed to investigate the positions that $CO_2$ can occupy as the number of $CO_2$ molecules in the crystal increases. The lowest energy configurations obtained from MC simulations are shown in Figure 3 with 50, 100, and 200 $CO_2$ molecules in the IRMOF-1 cell, respectively.
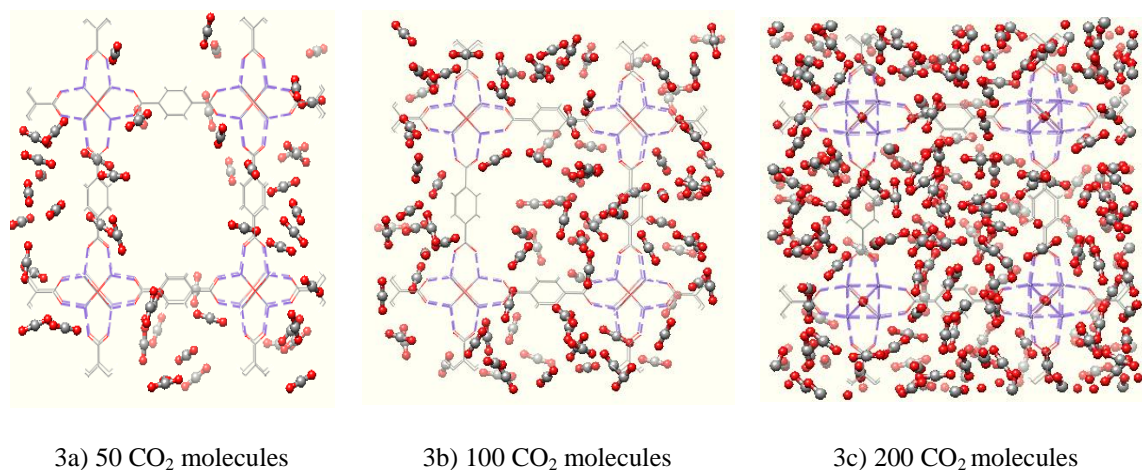


3a) 50 $CO_2$ molecules    3b) 100 $CO_2$ molecules    3c) 200 $CO_2$ molecules

*Figure3. The lowest energy configuration of 50, 100 and 200 $CO_2$ molecules in IRMOF-1.*

The results demonstrate that when the concentration of $CO_2$ molecules is low, they preferentially adsorb onto the surface of IRMOF-1 (Figure 3a). As the number of $CO_2$ molecules increases, they will gradually occupy the free space inside the crystal (Fig. 3b, 3c). Thus, the hollow porous structure of IRMOF-1 is very favorable for $CO_2$ storage and adsorption.

### 3.2.2. Influence of temperature on the $CO_2$ adsorption on IRMOF-1

The adsorption energy values obtained from the DFTB calculations include only the interaction potential at the energy minimum. In reality, because $CO_2$ molecules have thermal motion (kinetic energy), their total energy (potential and kinetic) increases with increasing temperature. When the kinetic energy exceeds the potential energy, the molecule moves away from the adsorption centers. In this study, molecular dynamics simulations with a fixed number

of atoms, N, a fixed volume, V, and a fixed temperature (NVT-MD) with a Nose thermostat were performed to investigate the influence of temperature on the adsorption process of $CO_2$ on IRMOF-1. The adsorption configurations were compared after 3760 fs of simulation. To evaluate the movement of the $CO_2$ molecule, we calculate the mean square deviation RMSD (Root-Mean-Square Deviation) for the $CO_2$ molecule according to the following formula:

$$RMSD(v,\ w) = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\|v_i - w_i\|^2} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}((v_{ix} - w_{ix})^2 + (v_{iy} - w_{iy})^2 + (v_{iz} - w_{iz})^2)} \quad (2)$$

This formula calculates the RMSD for two sets of **n-** points: **v** and **w**. Calculation results of RMSD values are presented in Table 3.

*Table 3.* RMSD of $CO_2$ molecule on IRMOF-1 at 300 K and 350 K.

| Temperature, K | 300 | 350 |
|---|---|---|
| RMSD, Å | 12.56 | 13.61 |

The RMSD value of $CO_2$ at 350 K is obviously greater than that at 300 K. As a result, the greater the temperature, the faster the $CO_2$ molecule moves on the adsorbent's surface. At 300 and 350 K, the $CO_2$ molecule has migrated away from the energy minimum on the potential surface, but it still "clings" on the IRMOF-1 and does not move into the crystal's center (if so, it is considered as desorption). That is, $CO_2$ is still dynamically adsorbed by IRMOF-1. This is another intriguing aspect of $CO_2$ adsorption by IRMOF-1.

### 3.2.3. Diffusion of $CO_2$ in IRMOF-1

The diffusion coefficient (D) can be calculated by the formula:

$$D = \frac{1}{6N_\alpha}\lim_{t\to\infty}\frac{d}{dt}\sum_{i=1}^{N_\alpha}\left\langle[r_i(t) - r_i(0)]^2\right\rangle \quad (3)$$

where, **r**(0) and **r**(t) are the position vectors of the molecule at time t = 0 and at time t, $N_\alpha$ is the number of molecules diffusing in the system.

The diffusion coefficient, which depends on temperature (and pressure), indicates the "mobility" of the adsorbed molecule in the adsorbent. Calculation of D will provide information for comparing the adsorption ability of different substances at different temperatures. The NVT molecular dynamics simulation was conducted with the initial structure P1a with the following parameters: The number of running steps is 100,000, the time of each step is 1 fs, the temperature is 300 K. The total simulation time was set up to 1000 ps (or 1 ns). The classical universal force field UFF (Universal Force Field) [30] was used.

From the MD simulation results, the diffusion coefficients for $CO_2$ and several other gases were calculated as shown in Table 4.

The experimental diffusion coefficient of $CO_2$ in IRMOF-1 was found to be between 8.1 - $11.5\times10^{-9}$ $cm^2s^{-1}$ at 295 - 331 K [31]. The substantial disparity between theoretical and experimental D values is owing to the fact that the computation time, while up to 1 ns (which is

very large for the MD calculations), is still too short in comparison to the experimental one. Furthermore, while the UFF potential is widely used for all elements in the periodic table, it is not optimized for the group of elements H, C, N, O, and Zn, resulting in restricted accuracy. However, when comparing D between different molecules and utilizing the same UFF potential in the computations, the absolute error is considered to be eliminated.

*Table 4.* Diffusion coefficient (D, $cm^2 s^{-1}$) of several gas molecules in IRMOF-1 at 300 K.

| Molecule | $CO_2$ | $CH_4$ | $O_2$ | $N_2$ |
|----------|--------|--------|-------|-------|
| D. $10^6$ | 1.636 | 2.483 | 0.9796 | 0.9807 |

The diffusion coefficients of the gases are as follows: $CH_4 > CO_2 > O_2 \approx N_2$, implying that $CO_2$ would diffuse into IRMOF-1 slower than $CH_4$, but quicker than $O_2$ and $N_2$. This finding allows for the prediction of the ability to separate $CO_2$ from a mixture with $O_2$ or $N_2$ gas. However, adsorbing and separating $CO_2$ from a $CO_2$/methane mixture using IRMOF-1 will be difficult. It should be emphasized that in order to examine the selective adsorption of $CO_2$ from a mixture of gases, thermodynamic (e.g., adsorption energy) and kinetic aspects of the adsorption process must be further evaluated.

## 4. CONCLUSIONS

In this work, we utilized the DFTB method with dispersion corrections and Molecular Dynamics simulations to investigate the $CO_2$ adsorption process on IRMOF-1. Our results indicate that the process involves physical adsorption. $CO_2$ is preferentially adsorbed around the metal cluster cavity. The adsorption capacity calculations suggested that, outside of the favored adsorption sites, $CO_2$ molecules may be "trapped" in the empty space of IRMOF-1 with high density via vdW interactions with IRMOF-1, as well as between $CO_2$ molecules. The $CO_2$ molecules were instantly adsorbed on the IRMOF- 1 structure as "anchors" to hold further molecules in place. The examination of the influence of temperature on the adsorption process revealed that, up to 350 K, $CO_2$ was still dynamically adsorbed on IRMOF-1, without being desorbed. Furthermore, because $CO_2$ diffuses in MOFs faster than $O_2$ and $N_2$, it is feasible to separate $CO_2$ from their mixture.

***CRediT authorship contribution statement.*** Ha Thi Thao: Investigation, formal analysis, data curation. Phung Thi Lan: Investigation, formal analysis, visualization. Nguyen Dinh Thoai: Investigation. Tran Thanh Hue: methodology, data curation. Nguyen Ngoc Ha: conceptualization, methodology, writing – original draft, writing – review & editing. Nguyen Thi Thu Ha: project administration, conceptualization, methodology, writing – review & editing.

***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.

## REFERENCES

1. Boot-Handford M. E., Abanades J. C., Anthony E. J., Blunt M. J., Brandani S., Mac Dowell N., Fernandez J. R., Ferrari M. C., Gross R., Hallett J. P., et al. - Carbon capture and storage update, Energy Environ. Sci. **7** (1) (2014) 130-189. https://doi.org/10.1039/c3ee42350f.

2. Raza A., Gholami R., Rezaee R., Rasouli V. and Rabiei M. - Significant aspects of carbon capture and storage – A review, Petroleum. **5** (4) (2019) 335-340. https://doi.org/10.1016/j.petlm.2018.12.007.

3. Babamohammadi S., Shamiri A. and Aroua M. K. - A review of $CO_2$ capture by absorption in ionic liquid-based solvents, Rev. Chem. Eng. **31** (4) (2015). https://doi.org/10.1515/revce-2014-0032.

4. Zagho M. M., Hassan M. K., Khraisheh M., Al-Maadeed M. A. A. and Nazarenko S. - A review on recent advances in CO2 separation using zeolite and zeolite-like materials as adsorbents and fillers in mixed matrix membranes (MMMs), CEJ Advances. **6** (2021) 100091. https://doi.org/https://doi.org/10.1016/j.ceja.2021.100091.

5. Sai Bhargava Reddy M., Ponnamma D., Sadasivuni K. K., Kumar B. and Abdullah A. M. - Carbon dioxide adsorption based on porous materials, RSC Advances. **11** (21) (2021) 12658-12681. https://doi.org/10.1039/D0RA10902A.

6. Mukhtar A., Saqib S., Mellon N. B., Rafiq S., Babar M., Ullah S., Muhammad N., Khan A. L., Ayoub M., Ibrahim M., et al. - A review on CO2 capture via nitrogen-doped porous polymers and catalytic conversion as a feedstock for fuels, J. Clean. Prod. **277** (2020) 123999. https://doi.org/https://doi.org/10.1016/j.jclepro.2020.123999.

7. Zeng Y., Zou R. and Zhao Y. - Covalent Organic Frameworks for CO2 Capture, Adv. Mater. **28** (2016) https://doi.org/10.1002/adma.201505004.

8. Lin Y., Kong C., Zhang Q. and Chen L. - Metal-Organic Frameworks for Carbon Dioxide Capture and Methane Storage, Adv. Energy Mater. **7** (4) (2017) 1601296. https://doi.org/https://doi.org/10.1002/aenm.201601296.

9. Kong L., Zou R., Bi W., Zhong R., Mu W., Liu J., Han R. P. S. and Zou R. - Selective adsorption of CO2/CH4 and CO2/N2 within a charged metal–organic framework, J. Mater. Chem. A. **2** (42) (2014) 17771-17778. https://doi.org/10.1039/C4TA01993H.

10. Qazvini O. T., Babarao R. and Telfer S. G. - Selective capture of carbon dioxide from hydrocarbons using a metal-organic framework, Nat. Commun. **12** (1) (2021) 197. https://doi.org/10.1038/s41467-020-20489-2.

11. Liu R.-S., Shi X.-D., Wang C.-T., Gao Y.-Z., Xu S., Hao G.-P., Chen S. and Lu A.-H. - Advances in Post-Combustion CO2 Capture by Physical Adsorption: From Materials Innovation to Separation Practice, ChemSusChem. **14** (6) (2021) 1428-1471. https://doi.org/https://doi.org/10.1002/cssc.202002677.

12. Elhenawy S. E. M., Khraisheh M., AlMomani F. and Walker G. - Metal-Organic Frameworks as a Platform for CO2 Capture and Chemical Processes: Adsorption, Membrane Separation, Catalytic-Conversion, and Electrochemical Reduction of CO2, Catalysts. 10 (11) (2020) https://doi.org/10.3390/catal10111293.

13. Poloni R., Smit B. and Neaton J. B. - CO2 capture by metal-organic frameworks with van der Waals density functionals, J. Phys. Chem. A. **116** (20) (2012) 4957-64. https://doi.org/10.1021/jp302190v.

14. Grajciar L., Wiersum A. D., Llewellyn P. L., Chang J. S. and Nachtigall P. - Understanding CO2 Adsorption in CuBTC MOF: Comparing Combined DFT–ab Initio Calculations with Microcalorimetry Experiments, J. Phys. Chem. C. **115** (36) (2011) 17925-17933. https://doi.org/10.1021/jp206002d.

15. Xu K., Moeljadi A. M. P., Mai B. K. and Hirao H. - How Does CO2 React with Styrene Oxide in Co-MOF-74 and Mg-MOF-74? Catalytic Mechanisms Proposed by QM/MM Calculations, J. Phys. Chem. C. **122** (1) (2017) 503-514. https://doi.org/10.1021/acs.jpcc.7b09790.

16. Moeljadi A. M. P., Schmid R. and Hirao H. - Dioxygen binding to Fe-MOF-74: microscopic insights from periodic QM/MM calculations, Can. J. Chem. **94** (12) (2016) 1144-1150. https://doi.org/10.1139/cjc-2016-0284.

17. Haldoupis E., Borycz J., Shi H., Vogiatzis K. D., Bai P., Queen W. L., Gagliardi L. and Siepmann J. I. - Ab Initio Derived Force Fields for Predicting CO2 Adsorption and Accessibility of Metal Sites in the Metal–Organic Frameworks M-MOF-74 (M = Mn, Co, Ni, Cu), J. Phys. Chem. C. **119** (28) (2015) 16058-16071. https://doi.org/10.1021/acs.jpcc.5b03700.

18. Kuhne T. D., Iannuzzi M., Del Ben M., Rybkin V. V., Seewald P., Stein F., Laino T., Khaliullin R. Z., Schutt O., Schiffmann F., et al. - CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations, J. Chem. Phys. **152** (19) (2020) 194103. https://doi.org/10.1063/5.0007045.

19. https://www.dftb.org/

20. Grimme S., Antony J., Ehrlich S. and Krieg H. - A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. **132** (15) (2010) 154104. https://doi.org/10.1063/1.3382344.

21. Lukose, B., Supronowicz, B., St. Petkov, P., Frenzel, J., Kuc, A.B., Seifert, G., Vayssilov, G.N. and Heine, T. - Structural properties of metal-organic frameworks within the density-functional based tight-binding method, Phys. Status Solidi B. 249 (2) (2012) 335-342. https://doi.org/10.1002/pssb.201100634.

22. Eddaoudi M., Kim J., Rosi N., Vodak D., Wachter J., Keeffe M. and Yaghi O. M. - Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage, Science. **295** (5554) (2002) 469. https://doi.org/10.1126/science.1067208.

23. Park K. S., Ni Z., Cote A. P., Choi J. Y., Huang R., Uribe-Romo F. J., Chae H. K., O'Keeffe M., Yaghi O. M. - Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, Proc. Natl. Acad. Sci. USA. **103**(27) (2006)10186-10191. doi: 10.1073/pnas.0602439103.

24. Herzberg G. - Electronic spectra and electronic structure of polyatomic molecules, Van Nostrand, New York, 1966, (in English).

25. Hirota E. - Anharmonic potential function and equilibrium structure of methane, J. Mol. Spectrosc. **77** (2) (1979) 213-221. https://doi.org/https://doi.org/10.1016/0022-2852(79)90103-6.

26. Huber K. P. and Herzberg G. - Molecular Spectra and Molecular Structure : IV. Constants of Diatomic Molecules, Van Nostrand, New York, 1979, (in English).

27. Farrusseng D., Daniel C., Gaudillere C., Ravon U., Schuurman Y., Mirodatos C., Dubbeldam D., Frost H. and Snurr R. Q. - Heats of adsorption for seven gases in three metal-organic frameworks: systematic comparison of experiment and simulation, Langmuir. **25** (13) (2009) 7383-8. https://doi.org/10.1021/la900283t.

28. Zhao Z., Li Z. and Lin Y. S. - Adsorption and Diffusion of Carbon Dioxide on Metal−Organic Framework (MOF-5), Ind. Eng. Chem. Res. **48** (22) (2009) 10015-10020. https://doi.org/10.1021/ie900665f.

29. Millward A. R. and Yaghi O. M. - Metal−Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature, J. Am. Chem. Soc. **127** (51) (2005) 17998-17999. https://doi.org/10.1021/ja0570032.

30. Rappe A. K., Casewit C. J., Colwell K. S., Goddard W. A. and Skiff W. M. - UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations, J. Am. Chem. Soc. **114** (25) (1992) 10024-10035. https://doi.org/10.1021/ja00051a040.

31. Zhao Z., Li Z. and Lin Y. S. - Adsorption and Diffusion of Carbon Dioxide on Metal−Organic Framework (MOF-5), Ind. Eng. Chem. Res. **48** (22) (2009) 10015-10020. https://doi.org/10.1021/ie900665f.